Titanium Dioxide Recovery from Ilmenite Contained in Ferrotitaniferous Sands from Mompiche-Ecuador

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Abstract: Titanium dioxide (TiO_2) was recovered from ilmenite ($FeO \cdot TiO_2$) contained in ferrotitaniferous sands of Mompiche area, by the combination of the thermal treatments of oxidation and carbothermic reduction and the subsequent leaching with hydrochloric acid (HCl) of the thermally treated samples. This study was developed because of the large source of TiO_2 that Ecuador has, but has not developed enough research to place an industry to produce this compound. The oxidation at 900 °C for 3 h yielded a content of 11% of TiO_2, and the highest oxidation of ilmenite (82%) was achieved at 1,000 °C for 1 h. The carbothermic reduction with 15wt% carbon at 950 °C for 2 h achieved a content of 6% TiO_2 and 21% ilmenite. The combination of thermal treatments did not increase the content of TiO_2 but allowed to obtain more soluble minerals in HCl. The best results of leaching were obtained with 100 mL of 256 g/L HCl for 6 h at 70 °C and 10% solids of the sample oxidized at 900 °C for 3 h and subsequently reduced with 15wt% carbon at 950 °C for 2 h. The optimum leaching time was 4 h, giving a TiO_2 of 90% purity with a recovery of 43%.

Key words: Ferrotitaniferous sands, titanium dioxide, carbothermic reduction, acid leaching, ilmenite.
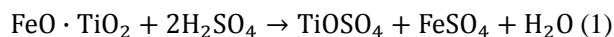
1. Introduction

On the north coast of Ecuador, mainly in Mompiche, Esmeraldas, there are potential ferrotitaniferous sands deposits with high contents of Fe and Ti, as was demonstrated by Diaz [1], who conducted geological and geophysical characterization of the Mompiche area, as well as, Chuquirima and Cortez [2] and Empresa Nacional Minera [3], who used the ferrotitaniferous sands to recover metallic iron. Ilmenite ($FeO \cdot TiO_2$) contained in ferrotitaniferous sands is one of the major sources of titanium dioxide (TiO_2) which is widely used as a white pigment in paints, cosmetics, coatings, plastics, rubbers, fibers, paper whitening, food additive, suncreen and also it is a source of titanium [4-6].

The TiO_2 recovery involves the conversion of ilmenite to TiO_2 by oxidation-reduction treatments and the removal of the iron minerals through acid leaching [7]. Due to the high chemical stability of ilmenite, TiO_2 extraction requires complicated processes that have not

been studied enough in Ecuador.

TiO_2 can be obtained through hydrometallurgy, by leaching with sulfuric acid (H_2SO_4) or hydrochloric acid (HCl). About 50% of the TiO_2 world production and more than 90% of the TiO_2 production in China are obtained using H_2SO_4 as leaching agent. However, this process requires large amounts of concentrated H_2SO_4, high temperature and generates a lot of waste, so leaching with HCl is increasing as an alternative technique [8]. Eqs. (1) and (2) simplified the leaching mechanism of ilmenite into H_2SO_4 and HCl respectively [8, 9].

$$FeO \cdot TiO_2 + 2H_2SO_4 \rightarrow TiOSO_4 + FeSO_4 + H_2O \quad (1)$$

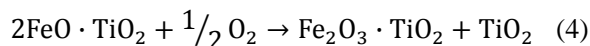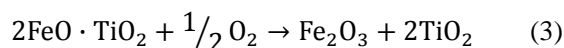$$FeO \cdot TiO_2 + 4HCl \rightarrow TiOCl_2 + FeCl_2 + 2H_2O \quad (2)$$

With the both acids the predominant leaching mechanism is the unreacted core model, which controlling steps are given by the chemical reaction or the diffusion of the leaching agent to reaction surface, depending on the leaching conditions [7, 8].

When ilmenite is pre-treated by oxidation and carbothermic reduction, leaching in acids is enhanced [7]. The oxidation breaks the strong bond between iron

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oxides and titanium oxides inside ilmenite by oxidation of ferrous oxide (FeO) to ferric oxide (Fe_2O_3) producing TiO_2 and Fe_2O_3, if it is oxidized around 800 °C as shown in Eq. (3), when temperature arrives to 950 °C pseudobrookite ($Fe_2O_3 \cdot TiO_2$) is formed according to Eq. (4); the mechanism followed is the unreacted shrinking core model [10].

$$2FeO \cdot TiO_2 + {}^1\!/\!_2\, O_2 \rightarrow Fe_2O_3 + 2TiO_2 \qquad (3)$$

$$2FeO \cdot TiO_2 + {}^1\!/\!_2\, O_2 \rightarrow Fe_2O_3 \cdot TiO_2 + TiO_2 \quad (4)$$

Moreover, carbothermic reduction between 860 and 1,000 °C provides surface porosity to the mineral, produces more TiO_2 and reduces the iron oxide to more soluble species or to metallic iron, according to Eq. (5), converting almost whole ilmenite to TiO_2 [11, 12].

$$FeO \cdot TiO_2 + C \rightarrow Fe + TiO_2 + CO\ (g) \qquad (5)$$
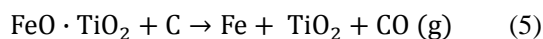
If carbothermic reduction is carried out above 1,000 °C, Boudouard reaction is produced as shown in Eq. (6), which is benefit to increase the ilmenite reduction according to Eq. (7) [11, 12].

$$C + CO_2\ (g) \rightarrow 2CO\ (g) \qquad (6)$$

$$FeO \cdot TiO_2 + CO\ (g) \rightarrow Fe + TiO_2 + CO_2(g) \quad (7)$$
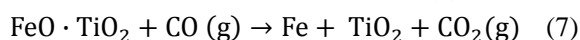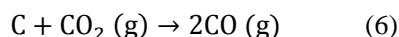
Finally, the iron impurities of pre-treated ferrotitaniferous sands must be removed by acid leaching, which depends on: temperature, acid concentration, particle size, leaching time and stirring speed [8, 9].

Due to almost all TiO_2 that Ecuador consumes is imported, according to the statistics from Banco Central del Ecuador, it is important to increase the investigation to recover TiO_2 from natural sources of this country. Current statistics show that Ecuador imported 795.40 t of TiO_2 with a total cost of US$1,992,350 (2015) [13]. This shows the great interest in this product and makes it imperative to develop a process to recover TiO_2 from Ecuadorian ores, which is precisely the aim of this study.

2. Experiment

2.1 Characterization of the Ferrotitaniferous Sands

Ferrotitaniferous sands collected from Playa del Suspiro in Mompiche area, Esmeraldas, Ecuador, were physically, chemically and mineralogically characterized. Physical characterization included: determination of bulk density, particle density and particle size (d_{80}). Chemical characterization was performed by XRF (X-ray fluorescence) in a Thermo Scientific Niton XL3t equipment. Mineralogical composition was determined by XRD (X-ray diffraction) in a Bruker AXS D8 Advance equipment, by semiquantitative analysis of crystalline phases.

2.2 Oxidation and Carbothermic Reduction of Ferrotitaniferous Sands

Thermal treatments were performed in a tube furnace Nabertherm P330, RT50-250/11, whose maximum temperature is 1,100 °C, and refractory combustion boats of 10 g capacity (for the ferrotitaniferous sands of this study) were used.

The oxidative treatment was performed in four steps, in order to analyze the influence of temperature, airflow, particle size and oxidation time on the decomposition of ilmenite and the subsequent conversion to TiO_2.

To analyze the effect of temperature during oxidation, experiments were performed with an airflow of 510 NL/h for 3 h at 650, 700, 750, 800, 900, 950 and 1,000 °C. Besides, experiments without airflow were executed and compared with the previous experiments. The effect of particle size was studied using the ferrotitaniferous sands pulverized to a particle size of 75 μm ($d_{100} = 75$ μm). To analyze the effect of oxidation time, 1, 2 and 3 h of oxidation were tested.

The carbothermic reduction was carried out with powdered activated carbon (80.2% fixed carbon) as the reductant, and the influence of the percentage of carbon, temperature, reduction time and the gaseous atmosphere were analyzed on the decomposition of ilmenite and their subsequent conversion to TiO_2.

The influence of the percentage of carbon was evaluated at 1,050 °C for 1 h with 10, 15, 20 and 40wt% of carbon. The effect of temperature was

studied at 900, 950 and 1,050 °C. To analyze the influence of reduction time, essays were performed for 1 and 2 h. Besides, the effect of inert gaseous atmosphere with 400 NL/h of carbon dioxide (CO_2) was evaluated.

To study the combination of the thermal treatments, essays were performed by combining the results that showed the lowest content of ilmenite or the highest percentage of TiO_2, obtained from the oxidation step, with the best results from the carbothermic reduction.

2.3 Hydrochloric Acid Leaching of Oxidized-Reduced Ferrotitaniferous Sands

Iron oxides and other impurities found in the thermally treated ferrotitaniferous sands were separated from TiO_2, which is slightly soluble in HCl, by leaching in 256 g/L HCl. Leaching essays were performed inside a fume hood over a heating plate at 70 °C with magnetic stirring.

Leaching process was studied by varying the pulp density (5, 10 and 20%) and leaching time (1, 2, 3, 4, 5 and 6 h). Additionally, the leaching of only reduced ferrotitaniferous sands was performed to evaluate the influence of pre-oxidation on the leaching efficiencies. The solid product obtained was washed with distilled water, dried at 100 °C for 5 h, calcined at 800 °C for 2 h and analyzed by XRD and XRF.

The leachates were analyzed by atomic absorption spectrophotometry (AA) in a Perkin Elmer Analyst 300 equipment to determine the concentrations of Fe and Ti. XRD analysis determined the purity of TiO_2. XRF analyses together with AA analyses were used for metallurgical balances.

3. Results

The studied ferrotitaniferous sands have a bulk density of 3.0 g/cm^3 and a particle density of 4.9 g/cm^3, demonstrating the presence of dense minerals, which is characteristic of ferrotitaniferous sands and agrees with the densities of the minerals that compose these sands, such as ilmenite (4.70 g/cm^3), magnetite (5.18 g/cm^3) and hematite (5.26 g/cm^3) [14]. The particle size (d_{80}) is 177 µm and corresponds to fine particles, so comminution was not necessary to prepare the samples for subsequent essays.

The chemical analysis shown in Table 1 indicates the ferrotitaniferous sands have a content of Fe and Ti of 52.1 and 15.4%, respectively.

The semiquantitative mineralogical analysis (XRD) showed the ferrotitaniferous sands contain 56% ilmenite, 25% hematite, 12% magnetite and 7% cummingtonite, the latter is a mineral that contains in its structure the impurities found in the chemical analysis.

3.1 Thermal Oxidative Treatment

Fig. 1 shows that between 650 and 750 °C, the percentage of ilmenite almost did not change, and the ferrotitaniferous sands were not altered; only a small amount of TiO_2 appeared. Hematite suffered changes from baseline and increased to a maximum of 42% at 900 °C, while at 950 °C and 1,000 °C decreased dramatically and reached a content of 21%. The pseudobrookite showed a drastic increase at 950 and 1,000 °C, reaching a maximum of 54%. Between 750 and 1,000 °C the percentage of ilmenite decreased while temperature increased, and a minimum ilmenite content of 9% at 1,000 °C was reached. The percentage of TiO_2 increased at higher temperatures, reaching a peak of 11% at 900 °C, while between 950 and 1,000 °C this percentage decreased.

The ferrotitaniferous sands suffer significant alterations from 900 °C; therefore, the influence of the airflow, particle size and time was further analyzed at 900, 950 and 1,000 °C. It was found that the airflow (510 NL/h) and smaller particle size (75 µm) are not

Table 1 Chemical characterization.

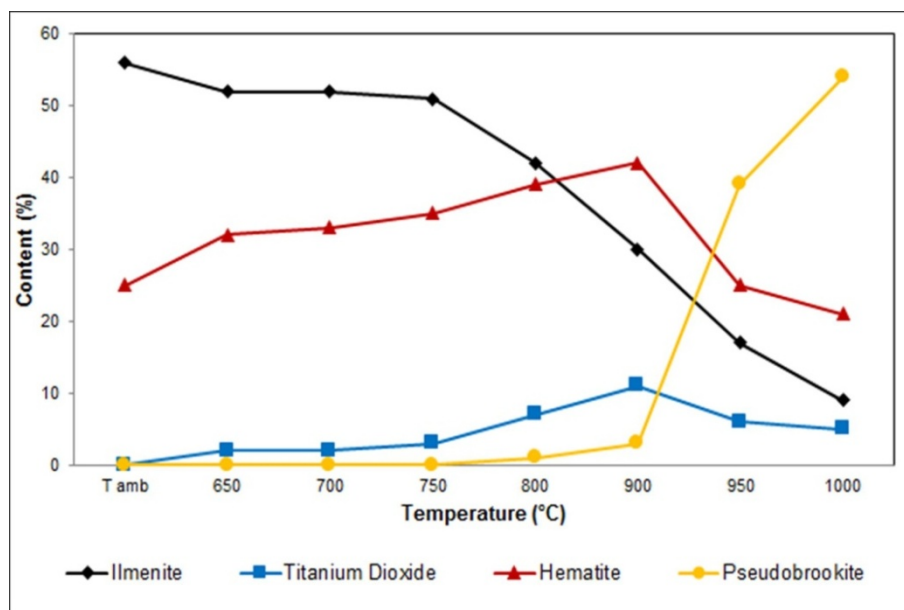| Element	Fe	Ti	Si	Mg	Ca	Al	Na	Mn
Content (%)	52.1	15.4	2.0	1.0	0.9	0.5	0.2	0.2

Fig. 1 Influence of temperature during the oxidation for 3 h with an airflow of 510 NL/h.

Table 2 Contents of ilmenite and TiO$_2$ obtained from samples oxidized without airflow and particle size of 177 µm.

Temperature (°C)	900			950			1,000		
Time (h)	1	2	3	1	2	3	1	2	3
Ilmenite (wt%)	49	42	33	31	28	19	10	10	9
Total TiO$_2$ (wt%) (brookite + rutile)	4	7	11	7	5	5	6	5	6

significantly influential during oxidation, so the influence of time was evaluated without airflow and with the original particle size of 177 µm.

Table 2 shows the results obtained from the oxidative treatment.

The best oxidation conditions that showed the lowest content of ilmenite or the highest percentage of TiO$_2$ were: no airflow at 900 °C for 3 h or no airflow at 1,000 °C for 1 h. At 900 °C for 3 h, a product with 33% of ilmenite and 11% of TiO$_2$ was obtained, which resulted in 42% of conversion of ilmenite to TiO$_2$, and at 1,000 °C for 1 h the product obtained consisted of 10% ilmenite and 6% of TiO$_2$, which implied 23% of conversion to TiO$_2$.

3.2 Thermal Reductive Treatment

The carbothermic reduction was performed at 1,050 °C for 1 h with 10, 15, 20 and 40wt% carbon to evaluate the influence of amount of carbon. These results are detailed in Fig. 2, which shows that as the percentage of carbon increased up to 20wt%, the titanomagnetite content increased. When the percentage of carbon increased to 40wt%, the contents of titanomagnetite and ilmenite remained constant.

The 10wt% carbon was insufficient because the sample was oxidized to form 43% of pseudobrookite. With 15wt% carbon, the sample was slightly oxidized forming 6% of pseudobrookite; however, residual carbon remained. Reduced samples with 20 and 40wt% carbon showed similar mineralogical composition, and also a large amount of residual carbon. Therefore, 15wt% carbon was enough to prevent the sample oxidation, so this condition was constant during the study of the influence of gaseous atmosphere, temperature and reduction time.

The evaluation of the influence of temperature, gaseous atmosphere and reduction time are shown in Table 3.

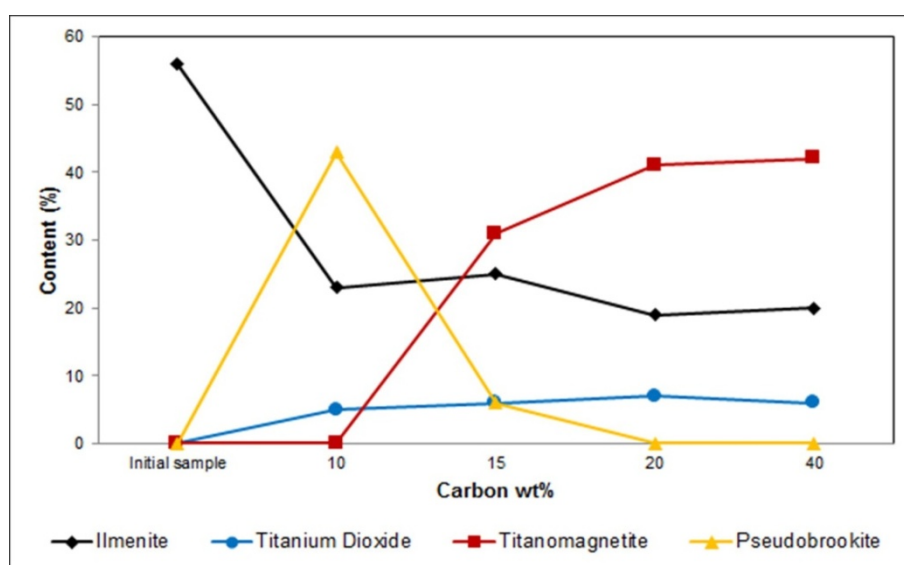The reductive condition that showed the highest decomposition of ilmenite and the highest content of

Fig. 2   Influence of the amount of carbon during the carbothermic reduction for 1 h.

Table 3   Contents of ilmenite and TiO$_2$ obtained from samples reduced with 15wt% of carbon.

Atmosphere	Without gaseous flow		With 400 NL/h of CO$_2$	
Temperature (°C)	950		1,050	
Time (h)	1	2	1	2
Ilmenite (wt%)	32	21	18	21
Total TiO$_2$ (wt%) (brookite + rutile)	4	6	5	5

Table 4   Contents of ilmenite and TiO$_2$ obtained from oxidized-reduced samples.

Thermal treatment	Oxidation at 900 °C (3 h) and reduction at 950 °C (2 h)	Oxidation at 1,000 °C (1 h) and reduction at 950 °C (2 h)
Ilmenite (wt%)	9	18
Total TiO$_2$ (wt%)	11	6

TiO$_2$ were 15wt% of carbon at 950 °C for 2 h without gaseous flow.

3.3 Thermal Oxidation-Reduction Treatment

The oxidized samples that showed the lowest percentage of ilmenite or the highest percentage of TiO$_2$ were selected and combined with the carbothermic reduction, in order to evaluate the influence of the combination of thermal treatments on the conversion of ilmenite to TiO$_2$, since this combination enhances the efficiency of subsequent leaching process [7]. These results are shown in Table 4.

The content of ilmenite was higher in the pre-oxidized samples than in the only-reduced samples,

and the TiO$_2$ content did not exceed the percentage in the pre-oxidized samples at 900 °C for 3 h. Therefore, the highest percentage of TiO$_2$ was obtained with the sample oxidized at 900 °C and subsequently reduced at 950 °C for 2 h without gaseous flow.

3.4 Titanium Dioxide Separation by Acid Leaching

The TiO$_2$ was separated from iron oxides and other impurities contained in the thermal treated ferrotitaniferous sands by leaching essays with 256 g/L HCl at 70 °C. The TiO$_2$ was obtained as a solid cake after filtration. Essays were performed with 100 mL of HCl and 10% solids for 6 h with two different samples: a sample only reduced at 950 °C for 2 h and another oxidized at 900 °C for 3 h and then reduced at 950 °C

for 2 h. The results of the acid leaching are shown in Fig. 3.

TiO$_2$ recovery was calculated based on the initial mass of TiO$_2$ found in the ilmenite and the amount of TiO$_2$ obtained as final product. TiO$_2$ recovery and purity percentages for only reduced sample were 19 and 78%, respectively, while for oxidized-reduced sample, these percentages were 43 and 90%, respectively.

Leaching essays were performed with 100 mL of 256 g/L HCl for 6 h at 70 °C with the sample oxidized at 900 °C for 3 h and then reduced at 950 °C for 2 h by varying the pulp density at 5, 10 and 20% solids. These results are shown in Fig. 4.

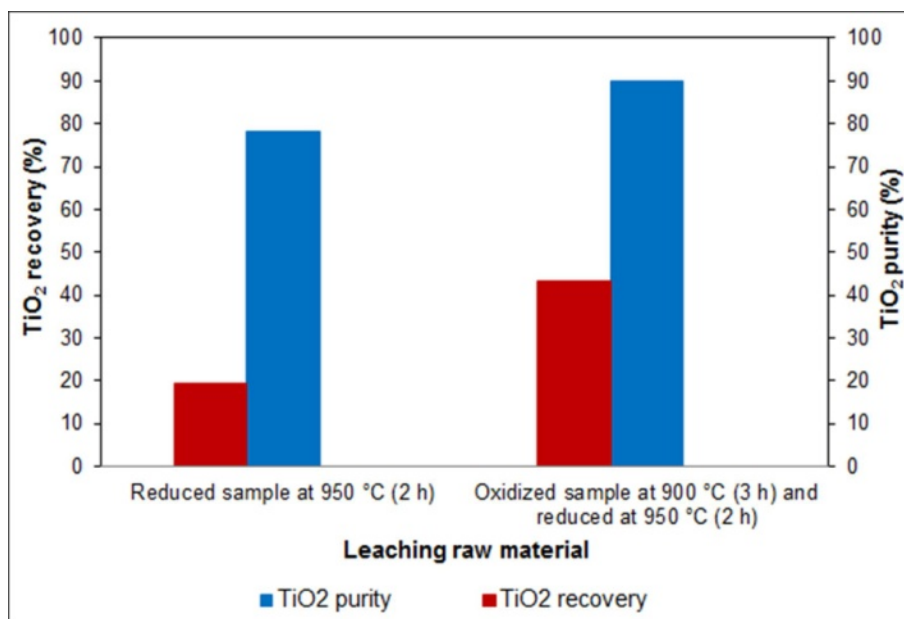The recovery percentage of TiO$_2$ with a pulp density of 5 and 10% solids was 43%, while with 20% solids

Fig. 3 **Recovery and purity of TiO$_2$ obtained from leaching essays of samples with different thermal treatments (10% solids; HCl = 256 g/L; time = 6 h; T = 70 °C).**
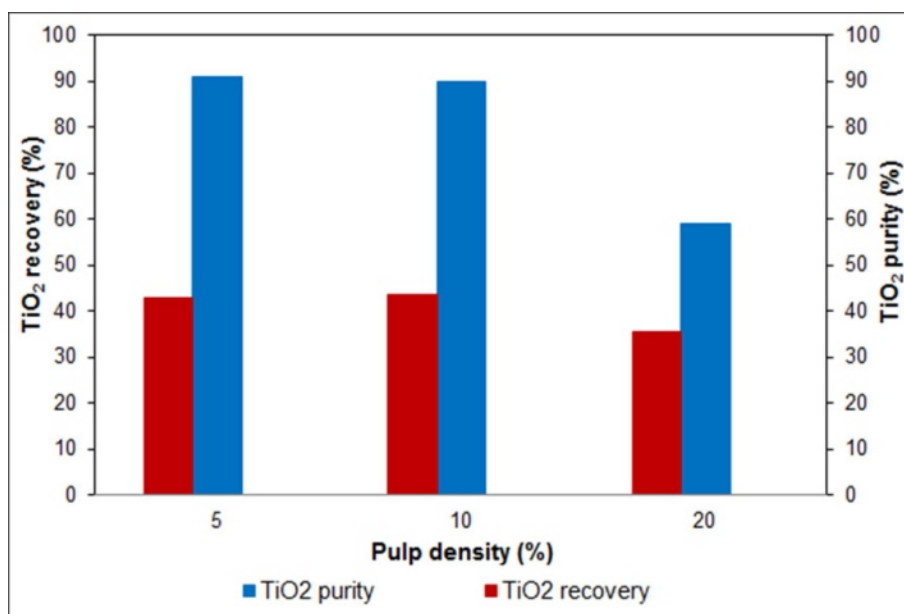

Fig. 4 **Recovery and purity of TiO$_2$ obtained from leaching essays with pulp densities of 5, 10 and 20% (HCl = 256 g/L; time = 6 h; T = 70 °C).**
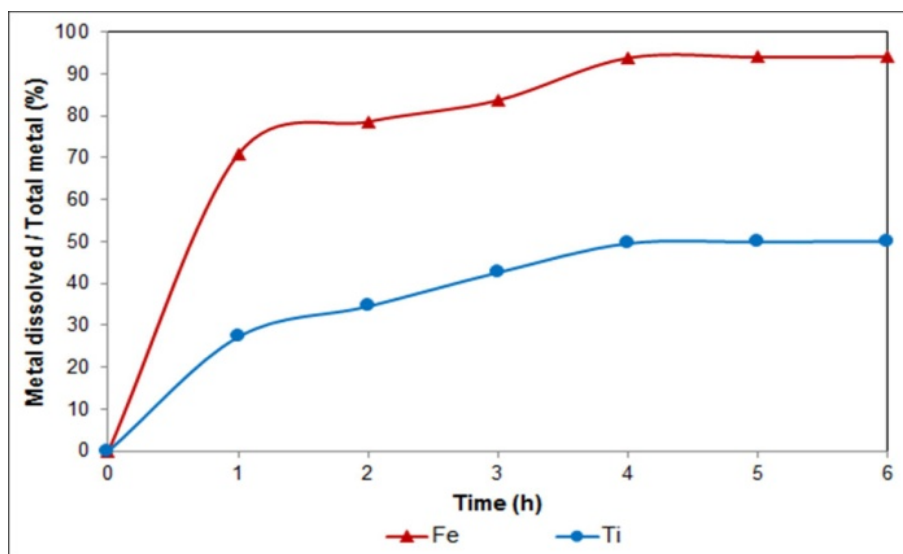
Fig. 5 Determination of the optimum leaching time with the dissolved Fe and Ti percentages (10% solids; HCl = 256 g/L; time = 6 h; T = 70 °C).

this percentage decreased to 35%. At 5 and 10% solids, the purity of TiO_2 was 90%, while at 20%, the purity decreased to 59%. When the pulp density was 20%, the TiO_2 recovery and purity percentages decreased.

To establish the best pulp density for leaching, the product recovery percentage was evaluated. With pulp densities of 5, 10 and 20%, the recoveries were 12, 13 and 16%, respectively. Although the product recovery was higher at a pulp density of 20%, the TiO_2 purity was lower (59%). Therefore, working at 10% solids was the best condition to achieve higher recovery, purity and production capacity.

Fig. 5 shows the results of dissolved Ti and dissolved Fe during acid leaching of the oxidized-reduced sample at different processing times.

At the first hour, 71% of Fe was dissolved, in the next two hours it increased to 84% and at the fourth hour, a plateau of 94% was reached. Dissolved Ti increased with time, and at the fourth hour, a plateau of 50% was attained. Therefore, a leaching time of 4 h was enough to reach the maximum removal of impurities.

4. Discussion

The density of the ferrotitaniferous sands is in according with the theoretical framework of the heavy

minerals that compose these sands (ilmenite, hematite and magnetite).

The FRX analysis showed the presence of titanium and iron minerals. The Ti content of 15.4% corresponds stoichiometrically to 46% ilmenite or 26% of TiO_2, which is the maximum amount of TiO_2 that can be recovered from Mompiche sands. The FRX results also showed the sands have some impurities such as silicon (Si), magnesium (Mg), calcium (Ca), aluminum (Al), sodium (Na) and manganese (Mn), which correspond to the cummingtonite. These ferrotitaniferous sands with 56% ilmenite, as shown in the XRD analysis, cannot be considered as an ilmenite concentrate because a concentrate must be composed of more than 75% ilmenite [15, 16]. Since the ilmenite content in these ferrotitaniferous sands is well below the minimum level required for industrial utilization, this work studied the leaching of oxidized-reduced ilmenite to improve the recovery process.

The behavior of the curves of Fig. 1 is almost consistent with Eqs. (3) and (4) because the stoichiometry of the reactions shows that with the first one, around 800 ℃, it obtains the double of TiO_2 than with the second one, around 950 ℃. This is one reason why the content of TiO_2 decrease at 950 ℃ and the pseudobrookite increase [10]. Hematite and TiO_2

diminishing were in agreement with the previous research of Zhang and Ostrovski [17] who also found that at temperatures near to 1,000 °C, these minerals react quickly to form pseudobrookite.

Comparing the oxidative results of this work with the results of Mozammel et al. [10], some differences were observed during oxidation, they reached the complete oxidation at 950 °C for 2 h, but in the present work even at 1,000 °C for 3 h the oxidation was incomplete. The reason of the larger oxidation percentages of Mozammel et al. [10] might be that they worked with ferrotitaniferous sands of 75.16% ilmenite and a minor content of impurities. Another difference was that Mozammel et al. found a metastable intermediate phase ($Fe_2O_3 \cdot 2TiO_2$) which forms during heating of ilmenite at 700-1,000 ℃ [10], the metastable phase was not detected by the present study at the same temperatures.

The carbothermic reduction of ferrotitaniferous sands was partial since metallic iron and complete conversion of ilmenite to TiO_2 were not obtained. Wang and Yuan [11] reported the formation of metallic iron during the carbothermic reduction with graphite (98% fixed carbon) at 900 °C for 2 h of a Bama ilmenite concentrate (49.78% TiO_2), but they did not detect the titanomagnetite phase. The partial reduction of ferrotitaniferous sands was achieved, but a productive conversion of ilmenite to TiO_2 was not obtained; however, more soluble minerals in HCl were obtaining, enhanced the subsequent leaching process.

The partial reduction obtained in the present work, even at 1,050 °C in CO_2 for 2 h, is not in agreement with the results found by Wang and Yuan [11], probably due to they used graphite that has more fixed carbon than the used in the present work or because of the higher content of impurities (including iron oxides, silicon, magnesium and manganese) and the lower content of ilmenite. Silicon, magnesium and manganese oxides inhibit the reduction of ilmenite and the iron oxides are reduced faster than ilmenite, which causes reduction competition between these minerals

and making difficult the reduction process to obtain TiO_2 [11, 18].

The results on Table 4 show that it is better carried out the pre-oxidation at 900 ℃ than at 1,000 ℃, these are in agreement with Zhang and Ostrovski [17], who concluded that the pre-oxidation increases the reduction of iron oxides, but if sintering occurs (around 1,000 °C), reduction is affected. However, Wang and Yuan [11] determined that performing the carbothermic reduction above 1,200 ℃ will enhance the ilmenite reduction because the effect of impurities and competition reactions becomes negligible.

Evidently, as shown in Fig. 3, applying the pre-oxidation at 900 °C for 3 h enhanced the leaching process by increasing the recovery and purity of TiO_2, as Sarker et al. [7] also demonstrated. The diminishing on the recovery and purity of TiO_2 in leaching process at 20% solids is probably due to the saturation of the solution; there is not enough HCl solution to dissolve all the iron oxides and other impurities. Additionally, when the solid percentage increases, there is less contact between the particles and the acid, diminishing the removal of Fe impurities, just as Van Dyk et al. [9] explained in their work.

5. Conclusions

Ferrotitaniferous sands from the north coast of Ecuador have a particle density of 4.9 g/cm^3, particle size of 177 μm, contents of Ti and Fe of 15.4 and 52.1% respectively, and a mineralogical content of 56% ilmenite, 12% magnetite, 25% hematite and 7% cummingtonite.

The best oxidation conditions obtained were: 900 °C for 3 h reaching 42% conversion of ilmenite to TiO_2, or oxidize at 1,000 °C for 1 h which was reached a conversion of 23%.

The most favorable condition to perform the carbothermic reduction was 15wt% carbon at 950 °C for 2 h, which yields 21% ilmenite and 6% TiO_2.

Applying the oxidative-reductive treatment achieved the highest ilmenite decomposition and formation of

TiO_2. The oxidation yielded the highest conversion of ilmenite to TiO_2, while the carbothermic reduction achieved the formation of titanomagnetite, which is a mineral more soluble in acids than ilmenite and completely soluble in HCl.

The highest recovery and purity of TiO_2 were 43 and 90% respectively, which were achieved by leaching a pulp of 10% solids with 100 mL of 256 g/L HCl at 70 °C for 4 h, after an oxidation-reduction treatment. The TiO_2 obtained of 90% purity corresponds, 87% to rutile phase and 3% to brookite phase.

The advantage of the HCl leaching was that we could obtain a TiO_2 with high purity in a few hours with a less amount of reactants, but the disadvantage was that almost a half of TiO_2 was lost in the leaching solution. However, it could increase the study to determine another process to recover the TiO_2 from leaching solution and probably with a higher purity.

Another way to improve the process could be to implement a method of ilmenite concentration before thermal treatments or increase the carbothermic reduction temperature above 1,200 ℃ in order to enhance the reduction process.

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