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Recovery of TiO_2 from Titaniferous Sand of Esmeraldas-Ecuador, using Ion Exchange Resins

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ABSTRACT.

The titanium oxide (TiO_2) was recovered from ilmenite ($FeO.TiO_2$) contained in the titaniferous sands of Esmeraldas Province through ion exchange resins in combination with methods of magnetic concentration, thermal treatment and chemical treatment. The magnetic separation allowed to reach ilmenite concentrations up to 57%. Thermal treatment was by smelting using NaOH as flux in 2: 1 ratio at 1100°C. The chemical treatment was by acid digestion with HCl in the presence and absence of metallic iron with subsequent separations of the formed precipitates at different pH ,using NH_4OH, Na_2S, concentrated HCl, etc. Finally, the effluent of the last acidic digestion with concentrated HCl is subjected to ion exchange resin using strongly anionic Amberlite IRA 400 applying optimum flow and column design conditions. After the ion exchange, the effluent is subjected to precipitation and calcinations, obtaining titanium oxide pigment with 97% purity and 19% recovery in the absence of metallic iron, and 90% purity with 40% recovery in the presence of metallic iron.

Keywords: Titaniferous sands, titanium dioxide, resin of ionic exchange, ilmenite, acid digestion, Magnetic concentration.

Introduction

The main natural resources of titanium present in the form of ilmenite ($FeTiO_3 = FeO.TiO_2$) are: rutile (TiO_2 Tetragonal - ditetragonal dipyramidal), brookite (TiO_2, orthorhombic crystal system), and anatase (TiO_2 tetragonal crystal system). The TiO_2 has wide range of applications: for instance, paint industry, pharmaceuticals production, cosmetics, food additives, photovoltaic cells, biomedical devices, rubber, fibers, air purification, and as antiseptic agent. TiO_2 constitutes the raw material to recover the metallic titanium (Ti) (Valderrama et al. 2005).

In 2009 the total world production of ilmenite was 5.3 million metric tonnes (Mt). The main producers were: South Africa (1.05 Mt), Australia (1.02 Mt), Canada (0. 75 Mt), China (0.7 Mt), India (0.6 Mt), Vietnam (0.6 Mt 12), Norway (0.30 Mt) and Ukraine (0.3 Mt). Today reserves of ilmenite and rutile are estimated to be around 650 and 42 million metric tons respectively (Gasques et al. 2014). The demand for titanium is strongly growing, mainly to cover the pigments manufacture needs in the Asiatic economies.

In international scale, the natural titanium oxide resources in form of Rutile, Anatase, Leucoxine, Perovskit, Sphene and Brookite are insufficient to meet the requirements of pigments manufacturers and other multiple industrial applications. Therefore, is of great interest to study the recovery of titanium oxide from ilmenite as another natural source by developing new, convenient and economic recovery processes or by improving existing recovery techniques.

The black sands are a common source of ilmenite, which represent a natural combination of iron oxides and titanium oxides. These oxides commonly found associated with other metals such as manganese, magnesium, aluminum, chromium, vanadium, calcium, zircon, monazite and certain varieties of silicates. (Dewan et al.2010, Chuquirima et al. 2014).

In Ecuador, several studies demonstrate that the beaches of the Pacific coast have huge quantities of titaniferous Sand (black sands), where ilmenite represents a potential source of titanium (Diaz 2013, Soledispa et al. 1990), nevertheless almost all TiO_2 consumed in Ecuador is imported. The statistics of the Central Bank of Ecuador reveals that in 2015 Ecuador imported 795.40 tons of TiO2 which cost 1,992,350 US $ (Trujillo et al. 2016).

The processes of TiO_2 recovery usually use one or a combination of the following methods: magnetic or gravimetric concentration (Diaz et al. 1995), thermal treatment (Mozammel et al. 2013), and chemical extraction (Fillipou et al. 2009).

Industrially, the chemical extraction is applied by several methods. The most communes are the followings:

1 Sulphate process is one of the oldest methods for the industrially production of TiO_2 pigment, but given the large quantity of acidic wastes and solid wastes generated by this process and the regeneration cost of H_2SO_4, other methods are become progressively more advantageous than the sulphate process (Fillipou et al. 2009).

2. Chloride process. This process does not generate much waste as the sulfate, however the salts generated in this process are more harmful to the environment, cause more pollution and have to be handled more carefully. (Fillipou et al. 2009).

3. Becher process, Benelita process, Austpac process, and Altair process. All them are known processes but they are less employed due to the high cost of acid regeneration or because they are still investigated for industrial - scale development. (Fillipou et al. 2009).

The methods so far used for recovery of TiO_2 are ended with the chemical process. Therefore, the objective of this study is to obtain titanium dioxide from ilmenite titaniferous sands of Esmeraldas, proposing as methodology combining techniques of magnetic concentration, thermal treatment, chemical treatment by acid digestion and the use of ion exchange resins.

MATERIALS AND METHODS

Study area .A

The beaches of Esmeraldas province store large quantities of black sand which is the raw material for titanium dioxide. In this study the raw material of titaniferous sand obtained from the zone of Tola, Canton Eloy Alfaro (fig.1)

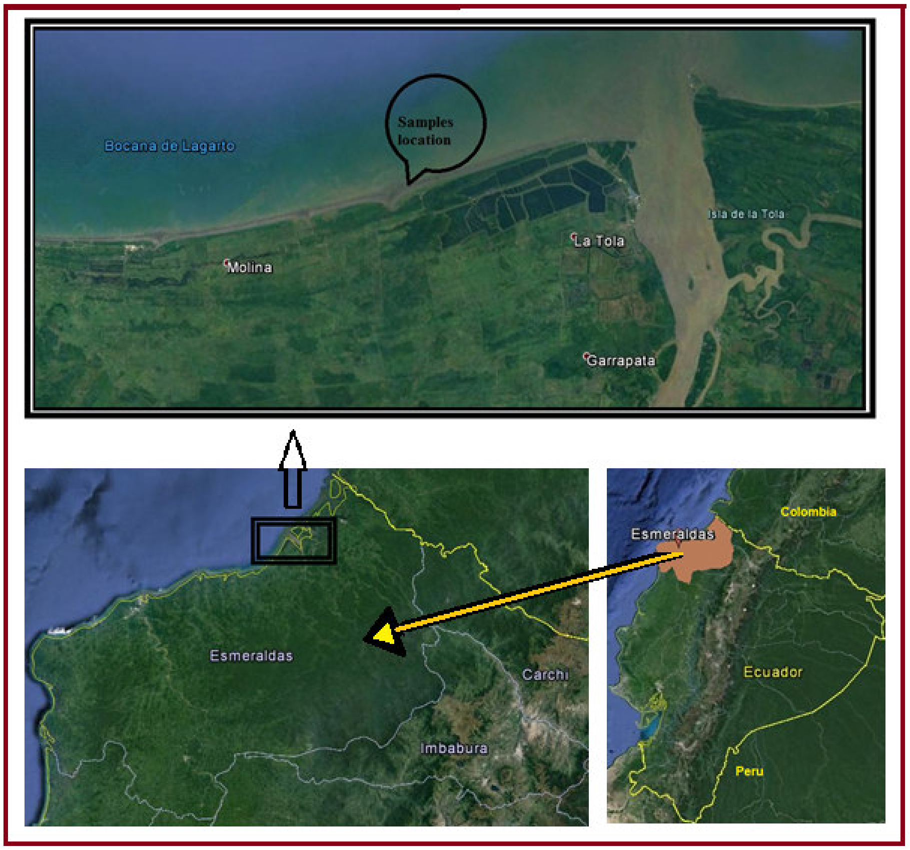

Fig. 1. Sample location in La Tola - Esmeraldas cantón

Recovery of TiO_2. .B

The recovery of Titanium Dioxide in the actual study involves magnetic concentration processes, thermal treatments, chemical treatments, and separation with ion exchange resins. The detailed application of these methods is explained as the following

1. **Magnetic Concentration:** Magnetic concentration of ilmenite from titaniferous sands was carried out using magnetic separator drum of Frantz type.

The flowchart (fig. 2) indicates the process steps and the applied magnetic field intensities.

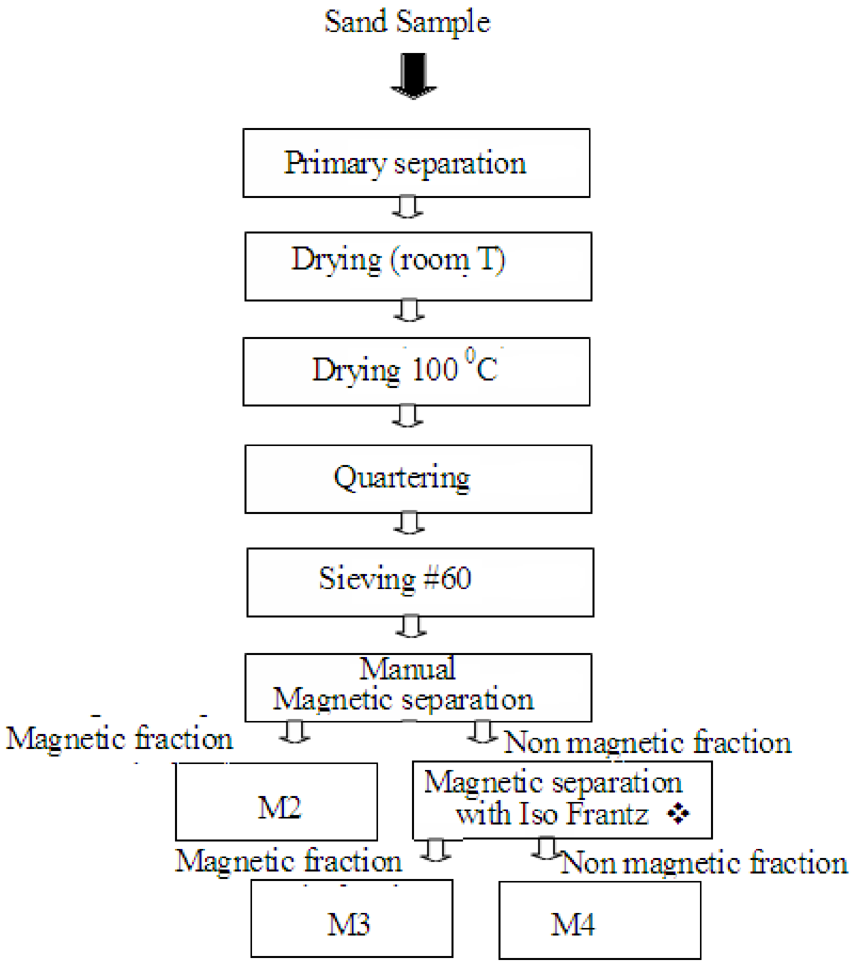

Fig. 2. Flow diagram of the magnetic concentration process for titaniferous sands. (❖Current 0.1 A, Vertical inclination 30^0,Lateral inclination 20^0,Vibration 7^0)

The sample M4 present higher content of TiO_2 after the magnetic concentration and therefore, it was selected for subsequent treatment.

2. Thermal Treatment.

The selected sample is smelted. A large scale potassium carbonate is used to act as flux. However it is more advantageous to use NaOH in proportions 4:1 to 1:2 between the raw material and flux, as shown in the diagram presented in figure 3.

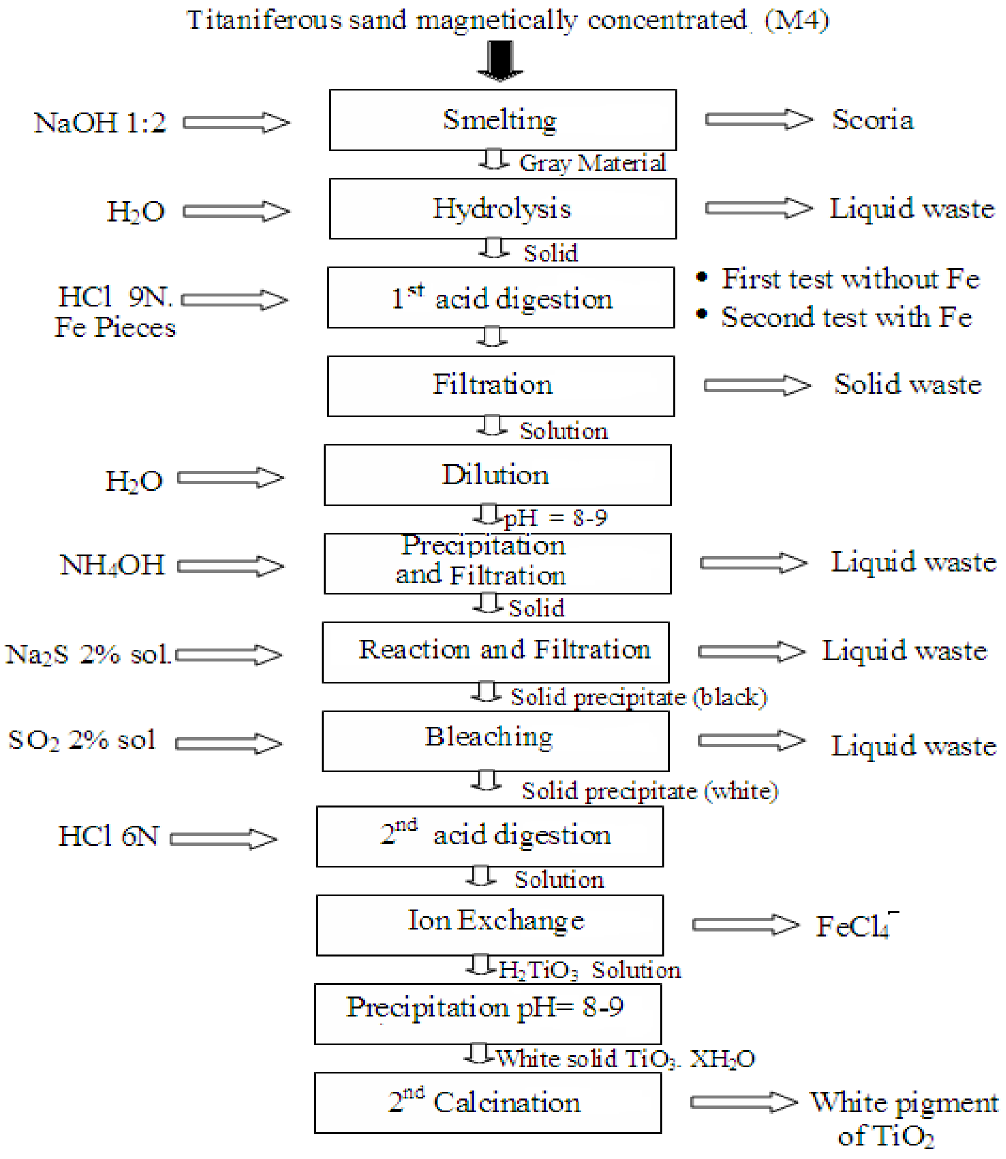

Fig.3. Flow chart of thermal treatment, chemical treatment, and ion exchange for magnetically concentrate titaniferous sand (M4 sample).

In this case NaOH was employed in the ratio 1: 2 . A high grade smelting furnace up to 1100°C, constantan thermocouple of iron and graphite crucible were used for this operation.

After the thermal treatment the sample differentiate en two zones: the nuclear pale gray part and the dark outer shell. For posterior treatments, the gray part which is richer in TiO_2 was chosen.

3. Chemical Treatment (Acid Digestion).

The gray sample which produced by the thermal treatment is mostly Na_2TiO_3 and Fe_2O_3. The oxides of iron are also presented but with smaller percentage. Those impurities are separated by acid digestion with HCl. The digestion have been carried out using two procedures; one in the absence of iron (test 1) and another with presence of small pieces of iron (test 2), obtaining significantly different results regarding the final yield of TiO2 pigments. figure 3 summarizes the applied chemical treatments .

4. Ion Exchange and calcination.

The effluent from the acid digestion contains anionic iron complex $FeCl^-_4$. To remove this complex, a strongly anionic exchange resin has been used. This resin is the synthetic AMBERLITE IRA-400 previously activated with HCl 9 N for 1 hour.

Different flows and assemblies of packed columns with resin were prepared. Through the analysis of the iron content of the effluent, before and after the ion exchange, the optimal conditions were defined. Finally the adopted arrangement was two columns in series with recirculation and optimal flow of 1.22ml/ min.
The volume of the recovered effluent which passed through the columns has been determined. Then 4% NH_4 OH has been added to precipitate the amorphous titanium.
The solid obtained was dried at 110 ° C for 12 hours then different samples have been calcinated at different intervals: 400 ° C to 650 ° C, 650 ° C to 800 °, 800 to 900° C. A purified titanium dioxide pigment has been obtained in different structures according to the temperature levels applied. The ion exchange and calcinations process is summarized in the Figure 3

RESULTS AND DISCUSSIONS

Magnetic concentration.

The results of magnetic concentration are presented in table 1. The results indicate that the raw material, M1, contains around 26% of TiO_2. By stoichiometry, assuming that all TiO_2 belongs to the ilmenite, the percentage of ilmenite ($FeO.TiO_2$) was around 50%. These datas are in agreement with previous studies carried out on titaniferous-sand in the Esmeraldas area (Martijena 1970, Diaz et al. 1995).

The high content of iron (quantified as Fe_2O_3 in the chemical analysis) and Titanium, confirms the presence of ilmenite and iron minerals such as magnetite (Fe_3O_4) and hematite (Fe_2O_3). The percentage of ilmenite ranges from 50% in the raw material to 55% in the magnetically separated fractions. This concentration is relatively high, however it can't be considered as a concentrate because a concentrate must have more than 75% of ilmenite(Xiong et al. 2011, Trujillo et al. 2014).

It is also observed that in the magnetically separated samples (M2, M3, M4), the TiO_2 content hardly increases, even in the sample M2 and M4 the change is limited, only a slight increase in levels of Ilmenite concentration ranging from 49.46% up to 55.25%, that’s only up to 6%. This shows that the magnetic concentration was not significant in the separation of ilmenite. These results are in agreement with those of Martijena, 1970.

Table 1 presents the magnetically separated samples with their respective chemical analysis.

Sample	MnO	CaO	TiO2	Fe2O3	MgO	Al2O3	SiO2
M1	0.25	0.87	25.72	51.42	1.57	-	20.17
M2	-	-	28.73	54.47	-	-	16.8
M3	-	-	24.53	51.69	-	-	23.78
M4	-	-	28.73	56.79	-	-	14.48

Where:

M1: Raw material (black sand).

M2: Strongly magnetic fraction (Separation with natural magnet)

M3: Magnetic fraction (separation with Iso Frantz)

M4: Non-magnetic fraction (separation with Iso Frantz)

It is clear that the most influential factor for the magnetic separation to have no effect is that the ilmenite, hematite and magnetite are intimately associated forming solid isomorphic solutions or incrustations of one mineral in another, with similar structures, atom distribution and dimensions in their molecules producing densities and molecular weights very close to each other and able to form a single crystalline lattice which complicates their separation by physical or mechanical means. However, other authors propose that in order to overcome the difficulty of concentrating the ilmenite by magnetic separation, an ultra fine grinding of the sample is necessary and conclude that finer granulometry allows an increase in the TiO_2 (Valderrama et al. 2005).

The TiO_2 recovery processes was followed by taking the M4 fraction for the next treatment process because it had the highest ilmenite content (55%).

Thermal treatment

Considering that the separation of the ilmenite was not relevant by magnetic means a flux was used that collects or drags the impurities. This method is applied when the removal of impurities can not be effected by physical or mechanical means.

The gray product of the thermal treatment of the sample M4 presented a composition of 37% Iron, 30% TiO_2, 26% SiO_2 and 7% of other compounds. While the composition of the slag (dark portion) was 80% Iron, 12% Titanium and 6% SiO_2.

The formation of these compounds are justified by reaction 1 where the presence of TiO_2 in the form of titanate and the presence of oxides by products of oxidation are observed (Kirk 2007; Perez et al. 1996). The gray portion is taken to continue the process of recovery of TiO_2

$$2FeO.TiO_2 + 4NaOH + 1/2O_2 \xrightarrow{1100^oC} 2Na_2TiO_3 + Fe_2O_3 + 2H_2O \qquad (1)$$

Chemical treatment and ion exchange.

Hydrated titanium dioxide ($TiO_2.XH_2O$) (eq. 3) is the result of hydrolysis with water (eq. 2) of gray material which is the product of smelting. XH_2O water molecules give the character of acid (titanium oxides highly hydrated), and its gelatinous appearance corresponds to titanium as a hydrated compound whose structure, being similar to silicon (Si) because it belongs to the same family (Ayres G. 2017, Ullman F. 1999). Furthermore, the sample M4 carries a certain amount of Si, about 1 to 3%.

$$Na_2.TiO_3 + H_2O \rightarrow TiO_2(aq.) + 2NaOH \qquad (2)$$

$$TiO_2(aq.) \xrightarrow{H^+} TiO_2.xH_2O \rightarrow 2H_2TiO_3(gel) \qquad (3)$$

The two tests carried out in acid digestion in absence of iron (Test 1) and in the presence of iron pieces (Test 2) show coherent results in terms of yield: 19% of TiO_2 yield in test 1 and 40% of TiO_2 in the test 2. The results of the second test is around that reached by Trujillo et al. 2016 applying other methods of separation.
In the absence of metallic iron, only a substitution reaction occurs where Fe 3+ (III) forms the ferric chloride (eq.4). Therefore the reduction action in the presence of the metallic iron is favorable to increase the recovery of TiO_2, converting Fe (III) to Fe (II) in this stage of the process (eq. 5).

Test 1 (acid digestion in the absence of iron pieces)

$$\text{Test 1 :} \quad Fe_2O_3 + 6HCl \rightarrow 2FeCl_3 + 3H_2O \qquad (4)$$

Test 2 (acid digestion with presence of iron pieces)

$$\text{Test 2 :} \quad Fe_2O_3 + 6HCl + Fe^0 \rightarrow 3FeCl_2 + 3H_2O \qquad (5)$$

The result of the change of pH from acid to basic by the addition of Ammonium Hydroxide is the presence of $(NH4)_2TiO_3(s)$ salts and iron hydroxides confirmed by the presence of a yellowish solid precipitate through the following reactions:

$$H_2TiO_3 + 2NH_4(OH) \rightarrow (NH4)_2TiO_3(s) + 2H_2O \qquad (6)$$

$$FeCl_2 + 2NH_4(OH) \rightarrow Fe(OH)_2(s) + 2NH_4Cl \tag{7}$$

$$FeCl_3 + 3NH_4(OH) \rightarrow Fe(OH)_3(s) + 3NH_4Cl \tag{8}$$

The addition of sodium sulfide as a bleaching agent produced a color change from yellowish to black precipitate which indicated the formation of ferrous sulfide (eq.9). This precipitate is bleached with SO_2; (eq. 10) which, when reacted with Fe (II), forms the soluble ferrous sulphite (eq. 11) and is subsequently separated into the effluent.

$$Fe(OH)_2 + Na_2S \rightarrow FeS(s, black) + 2NaOH \tag{9}$$

$$SO_2 + H_2O \rightarrow H_2SO_3 \tag{10}$$

$$FeS + H_2SO_3 \rightarrow H_2S(g) + FeSO_3 \tag{11}$$

The result of the previous stage is a bleached precipitate, which corresponds to titanic acid H_2TiO_3, which is again digested in concentrated hydrochloric acid and the traces of iron (III) which may have remained in the $FeCl_4^-$ complex with the concentrated HCl. The formation of this complex is discussed in other works, such as that of Ponn 2006, who explains the formation of the complex through the following reactions:

$$FeCl_3 + H_2O \rightarrow Fe^{3+} + 3Cl^- \tag{12}$$

$$Fe^{3+} + 6H_2O \rightarrow [Fe(H_2O)_6]^{3+}(aq.) \tag{13}$$

$$[Fe(H_2O)_6]^{3+}(aq.) + 4HCl \rightarrow Fe(H_2O)_2Cl_4^- + 4H_3O^+ \tag{14}$$

$$Fe(H_2O)_2Cl_4^- + 2H^{2+} \rightarrow FeCl_4^-(aq.) + 2H_3O^+ \tag{15}$$

The anionic nature of the $FeCl_4^-$ (aq.) complex requires the use of an anionic resin to complete the purification process of TiO_2.

This was the criterion for selecting the strongly anionic resin AMBERLITA IRA 400. Studies on ferrous purification processes have been carried out successfully such as (Calvache 1989), also used this type of resin but in this study it was considered as variant the use of a double column series and recirculation to improve the operation of purification by ion exchange.

The chemical analyzes of the iron content in the effluent before the ion exchange (3485 ppm Fe_2O_3) and after the ion exchange (34 ppm Fe_2O_3) reflect a 99% Iron retention in the resin, being an excellent level of purification and high retention capacity of Resin Amberlite Ira 400.

As a qualitative result, it is evident the color change in the final effluent of the exchange column, as clear, transparent solution.

The purified solution of iron which is the ion exchange product was brought to pH 8-9 to recover the titanium oxide, $TiO_2.xH_2O$, which appeared as a white solid precipitate and was subsequently subjected to calcinations.The calcinations allows to reach the Rutile structure, which is the most stable phase and presents greater hardness. Its application is better for coatings and semiconductors (Pacheco et al. 2014)

The results of the XRD analysis for different samples of pigment obtained in test 1 (acid digestion in the absence of metal iron pieces) are summarized in table 2 where the percentage of the rutile, brookite and anatase phases formed in the final pigment after the calcination process together with the recovery percentage R and the concentration ratio pr are presented.

Tabla 2. Composition of the TiO_2 pigment obtained in the absence of iron (test 1)

Sample	°C	%TiO_2 as			∑%TiO_2	Hematite	R	K
		Rutile	Brookite	Anatase				
1	800-900	84,19	7,19	5,54	96,92	3,08	19,63	19,17
2	800-900	87.9	5,17	2,59	95,66	4,34	16,70	19,93
3	650-800	75,78	13,28	4,69	93,75	6,25	18,04	21,20
4	400-650	8,55	42,74	41,88	93,17	6,83	13,49	24.02

The percentage of total TiO_2 presented is the result of summation of the percentages as rutile, brookite and anatase structure.

In the first 2 samples treated from 800 to 900 ° C a high content of the rutile structure is observed whose presence is characteristic of this temperature, whereas in the sample 3 treated from 650 to 800 ° C the presence of a rutile / pseudo rutile (Mozzamel et al. 2013) is reduced by the incipient formation of a brookite structure, whose presence is possible in these ranges of temperature (Kirk 2007).

The sample 4 treated from 400 ° C to 650 ° C reflects the presence of the Anatase and Brookite structures in almost similar percentage of formation with a low percentage of rutile. Some studies confirm that in samples treated with HCl and calcinated at around 600 °C the formation of Rutille is possible (Mattews A. 1976) and even others authors conclude that samples treated with fluxes and subsequently calcined between 450 and 700 ° C present Mixtures of anatase and rutile (Ochoa et al. 2009).

The structures of obtained TiO2 are found around the temperature ranges reported in the literature (Kirk O. 2007; Gasques et al. 20014), however, a more sensitive control of time and temperature could better define the structures appearance percentages of of Rutile, anatase and brookite.

The results of Table 2 further demonstrate that at higher levels of TiO_2 there is a lower concentration of Fe as hematite, indicating that there has been a level of iron separation and purification of TiO_2 using ion exchange resins.

However, these high percentages of TiO_2 purity reached between 93% and almost 97% in Test 1 gave low yields (approximately 14 to 20%) as observed in the table 2. These data are logical in relation to the ratio of concentration K. The high values of K between 19 and 24, reveal the difficulty in the recovery of TiO2 for test 1.

In test 2, however, when iron pieces were applied in the acid digestion step, purity levels TiO_2 of 90% and yields of around 40% were achieved. This indicates that the reduction power of the metallic iron applied in the acid digestion stage, favorably increases the yield (40%) with a slight decrease in the percentage of purity (90%). This work present 2 options to process TiO2 according to the requirements of purity or recovery yield. The purity and yield of the pigment in test 1 and 2 are compared in the figure 4.

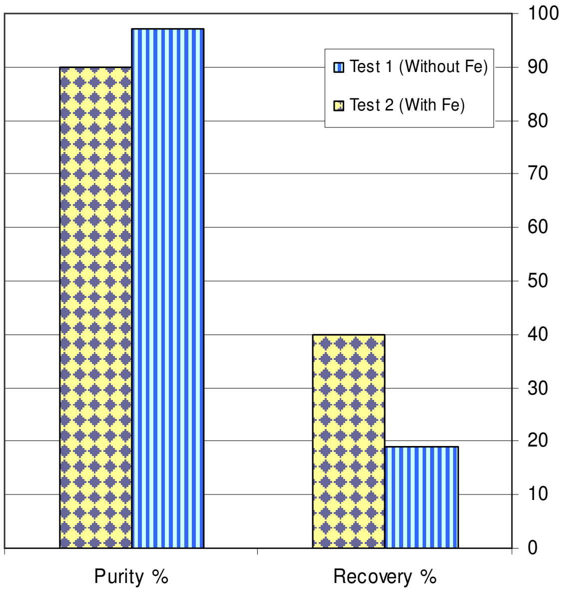

Fig. 4 Histogram of purity and recovery from test 1 and 2.

Figure 4 shows the percentages of recovery and purity of the TiO_2 pigment in test 1 and 2 obtained from the processing of titaniferous sands by applying ion exchange resin. The improvement in yield is clearly observed 40% with 90% purity in the presence of iron compared to 19% yield with purity 97% in the absence of iron. In general, it can be seen that while the purity of TiO2 increased, the recovery decreased.

CONCLUSIONS.

1. The iron sands of Esmeraldas, in the Olmedo zone, were found to contain: iron oxide, quartz and other silicates such as pyroxene, olivine, leucoxene, amphiboles, epidote, zircon and cinnabar.
2. The titaniferous sands studied have a real density of 4.84 g / cm3, an apparent density of 2.83 g / cm3, a particle size of 186 um and the chemical analysis reports a mineralogical content of 25.72% TiO2, quantified iron as Fe2O3 51.42%, SiO2 20.17%, MnO 0.25%, CaO 0.87% and MgO 1.57%
3. Thermal treatment using NaOH as a flux in a ratio of 2: 1 a temperature of 1100 Co was favorable to achieve a good level of TiO2 purity.
4. In the absence of metallic iron, the TiO2 purity level achieved was 97% with a recovery of 19%, which is generally the case in high purification processes: at higher levels of purity, lower levels of recovery occur.
5. The application of metallic iron to the acid digestion stage produced a high recovery of TiO2 of 40% with a slight decrease in the percentage of purity to 90%, presenting in this work two treatment options according to the requirements; high Purity or high yield, in the absence or presence of iron.
6. The magnetic separation and physical methods initially applied to the black sand do not increase significantly the TiO2 content, therefore it is not justified as an indispensable treatment prior to the recovery of TiO2.
7. The percentage of iron separated by the resin was 99%, highlighting the high retention capacity of the anionic resin Amberlita Ira 400.

8. The method presented in this work is acceptable to provide a contribution to the current works of recovery of TiO2, however this is likely to be improved considering that there is a large part of TiO2 lost in the solution leached, recommending a more sensitive control of time and temperature that it could better specify the percentages of appearance of the rutile, anatase and brookite structures of the samples in the calcination stage.

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