

Preparation of pigment grade TiO_2 from Rosetta ilmenite via selective TOPO extraction of titanium from its hydrochloric acid solution

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ABSTRACT

Pigment grade TiO_2 has successfully been prepared from Rosetta ilmenite leach liquor. The latter has been prepared by reductive HCl leaching followed by selective Ti extraction using tri-octyl phosphine oxide (TOPO). This has been possible by partial reduction of the leached Ti values to its trivalent state. The relevant extraction and stripping factors have been optimized. For the former, these involved the aqueous phase acidity, the TOPO molarity, the time of extraction, the ratio of octanol as well as the A/O ratio. The optimized extraction conditions included: an aqueous phase acidity of 5M HCl, a 0.72M TOPO in kerosene together with an octanol volume ratio of 10% for 5 minutes at an A/O ratio of 1/1.

The optimized stripping factors have involved a 0.25M HCl for 10 minutes at an A/O ratio of 1/1.

The obtained strip liquor was then hydrolyzed to form the insoluble titanium hydroxide using the seed nuclei technique. After calcination the obtained product, it was found to be devoid of Fe, Mn, Cr and V.

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KEYWORDS

Ilmenite;
Titanium extraction;
HCl;
TOPO.

INTRODUCTION

Titanium occurs in nature in only two principal mineral forms that can be mined namely ilmenite ($\text{FeO} \cdot \text{TiO}_2$) and to a much less extent its weathered variety leucocoxene ($\text{Fe}_2\text{O}_3 \cdot \text{TiO}_2$) as well as rutile (TiO_2). Deposits of rutile are far more scarce than those of ilmenite which represent indeed 95% of the world production. Both ilmenite and rutile are used for the production of titanium metal and titanium dioxide white pigment which is the whitest of all white pigments. The titanium dioxide pigment is actually used in several industries e.g. paints, plastics, rubber, textile as well as ceramic and paper industries. On the other hand, titanium metal is involved in several

industries due to its inherent unique characteristics e.g. military aircrafts and missiles.

The increasing lack of rich rutile deposits has indeed resulted in increasing interest in the relatively lower grade ilmenite deposits to enrich its TiO_2 content. Several processes have been suggested to remove iron oxides and other impurities. Some of these processes have been industrially applied; namely conversion to synthetic rutile assaying 92–95% TiO_2 by roasting via the Becher process or by roasting and acid leaching (Benelite process) or else by smelting to a high titania slag plus low manganese iron product^[6].

Classically, manufacture of TiO_2 pigment from its minerals has been carried out via two main routes;

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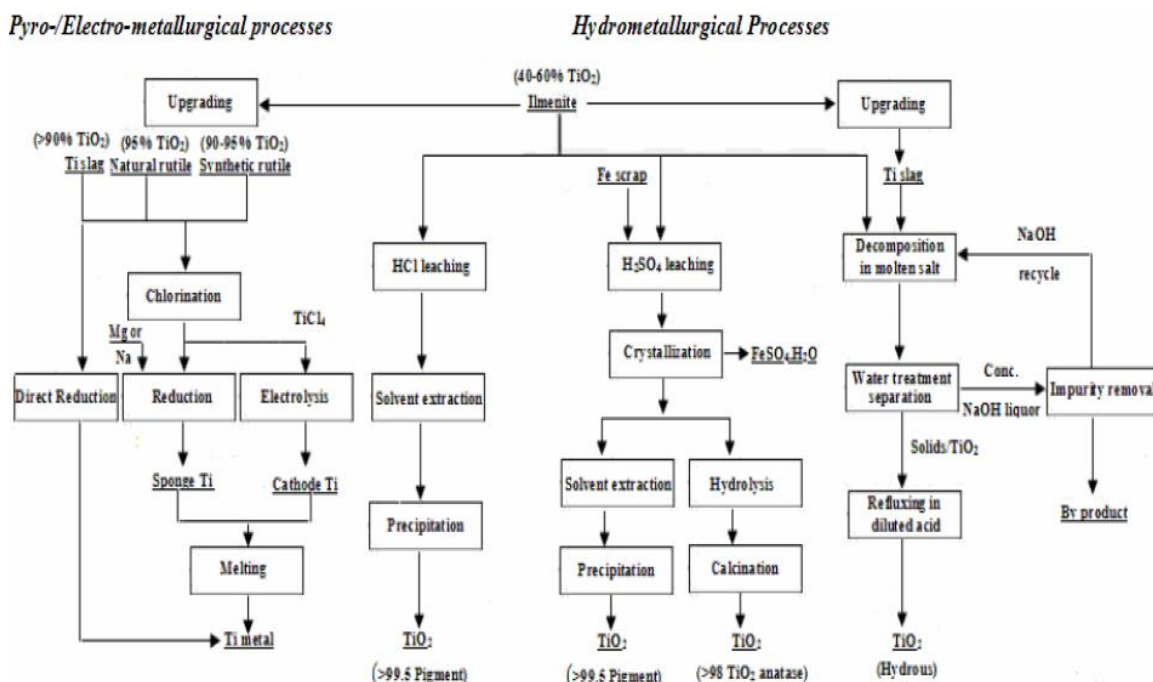
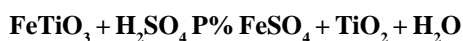
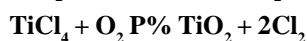
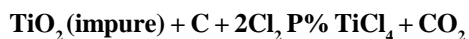


Figure 1 : An overall schematic flowsheet for the processing of pigment grade TiO_2 and Ti metal (modified after Zhang et al, 2011)

namely the sulfate route and the chloride route and each of which requires different stocks. In the sulfate route, the feedstock is either finely ground ilmenite of minimum 44% TiO_2 or sulfatable titanium slag of 72% TiO_2 . In this route, the feedstock would be digested with strong sulfuric acid to solubilize titanium which is later hydrolyzed by precipitation to form the TiO_2 pigment after prior iron reduction and crystallization of ferrous sulfate.



In the chloride route, the feedstock includes mainly natural rutile (94–98% TiO_2), synthetic rutile (92–95% TiO_2) or chlorinatable titanium slag (80–90% TiO_2). In this route, a mixture of the feedstock with coke and chlorine is calcined to obtain gaseous TiCl_4 which is then condensed to a liquid while most of the impurities are separated as solids. The liquified TiCl_4 is then reheated to the gaseous state and mixed with hot oxygen to form very fine crystalline rutile:



In this regard, it has to be indicated that several works have also been achieved to prepare synthetic rutile by reductive acid leaching by essentially using HCl ^[5,7,8,13]. In acid leaching, the dissolved ferrous would

be crystallized while Ti is left for hydrolysis.

Recently, several research works have lately been conducted for the direct manufacture of pigment grade TiO_2 from different acid solutions of ilmenite concentrates using different organic solvents. This is due to their simplicity, versatility and easy recovery besides avoiding the disadvantages and/or requirements of the sulfate and chloride routes. The organophosphorus extractants whether the neutral or the acidic extractants have been extensively used for titanium extraction from its acidic leach liquors.

Zhang et al^[17] have presented a concise literature review of the developed titanium metallurgical processes whether those commercially applied or proposed for the production of pigment grade TiO_2 and titanium metal. These processes can actually be described in the frame of the two principal metallurgical categories; namely the conventional pyro- and electro metallurgical processes and the growing hydrometallurgical processes (Figure 1). While the former are only applied upon adequately rich titanium feed material (natural or synthetic rutile as well as titanium slag), the latter can generally be directly applied upon ilmenite. The hydrometallurgical processes indeed involve either an acid leaching step (HCl or H_2SO_4) or else using caustic leach processing by concentrated NaOH or KOH where an intermediate prod-

TABLE 1 : Chemical compositions of East Rosetta ilmenite concentrate

Oxide	TiO ₂	Fe ₂ O ₃	FeO	MnO	V ₂ O ₅	Cr ₂ O ₃	MgO	Al ₂ O ₃	CaO	SiO ₂
Wt. %	44.01	21.41	28.50	1.15	0.18	0.29	0.80	0.90	0.44	0.75

uct high in titanium and low in iron is obtained. Alternatively, ilmenite can be roasted with NaOH at 850°C and the product can be water leached, hydrolyzed and dissolved in mineral acid^[9].

The present work is concerned with the preparation of pigment grade TiO₂ from Rosetta ilmenite concentrate via selective solvent extraction of titanium using tri-octyl phosphine oxide (TOPO) after insurance of adequate reducing conditions of the Ti hydrochloric acid leach liquor. This is due to the fact that in a previous work by the author, it has not been possible to effect this selectivity since the reduced iron was oxidized during extraction and was thus co-extracted with titanium^[16]. Such a behavior would have necessitated working in a closed system or under an inert atmosphere i.e. in the absence of oxygen; a matter which would require additional costs. In that work, it was thus decided to subject the titanium solution to a prior Fe extraction using tri-octyl amine after its complete re-oxidation to the Fe³⁺ state by H₂O₂. In the meantime, to overcome this inconvenience, Duyvesteyn et al^[4] have applied two solvent extraction circuits where in the first TRPO was used and which resulted in a pregnant strip solution containing titanium and Fe³⁺ ions and a raffinate containing Fe²⁺ ions. The former – that might be subjected to an oxidation step – was then subjected to a second solvent extraction circuit using tri-octyl amine to form a second strip solution containing ferric iron and a raffinate containing pure titanium ions and has thus been subjected to hydrolysis.

In the present work, it was however found feasible to selectively extract the titanium value directly from its hydrochloric acid leach liquor through proper reduction of the latter by addition of extra iron powder until formation of adequate titanium ion species in its trivalent state (violet color). Presence of the latter would prevent Fe²⁺ oxidation during the direct selective TOPO extraction of titanium. In other words, co-extraction of iron with titanium into the working TOPO has been eliminated by applying two steps of reduction. These involved addition of 10 wt% metallic iron with respect to the input ilmenite during its leaching step as well as ad-

dition of an extra 10% to the obtained leach liquor.

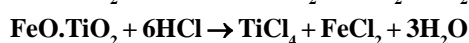
EXPERIMENTAL

Material

Preparation of the Ti leach liquor

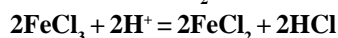
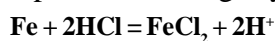
A sample of East Rosetta beach ilmenite concentrate (TABLE 1) was used in the present work to prepare the working Ti leach liquor by applying the optimum conditions previously determined and which have resulted in 95% leaching efficiency of the Ti^[16].

These conditions involved ilmenite leaching after grinding to -200 mesh size in concentrated HCl solution (12M) in 1/8 S/L ratio at 80°C for 1.5 hr and adding 10% Fe powder. The ilmenite dissolution reactions can be represented as follows:

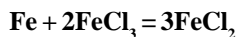


After filtration and washing, the assay of the obtained leach liquor was found to be attain 41.8 g TiO₂/l equivalent to 25 g Ti/l together with 48 g FeO/l and 6.7 g Fe₂O₃/l in about 5M HCl acid. To prevent the TOPO extraction of the present Fe³⁺ species or oxidation of the Fe²⁺ species to the extractable Fe³⁺ species prior to its extraction by TOPO, it was found necessary to add adequate Fe powder to reduce the former on one hand besides reducing some of the Ti⁴⁺ to Ti³⁺. Presence of the latter was found to be behind the direct reduction of any formed Fe³⁺ species and in turn prevented any co-extraction of iron species.

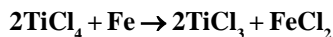
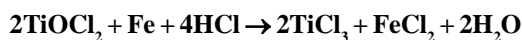
Accordingly, to ensure complete reduction of the Fe³⁺ species present in the obtained leach liquor besides having an excess Fe powder to reduce some Ti⁴⁺ to the violet Ti³⁺ species, 10% iron powder (with respect to the input ilmenite) was added. The latter would have thus first reduced the ferric iron equivalent to the present 6.7g Fe₂O₃/l which would be present as FeCl₃ after reaction with HCl and whose reduction can be represented through hydrogen as follows:



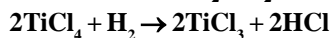
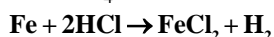
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On the other hand, the remaining metallic iron (4.4 g/l) would either directly react with the Ti^{4+} for its reduction to Ti^{3+} ; viz,

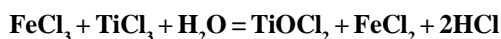


Or else through HCl and the evolved H_2 would reduce the TiCl_4 viz,



From these reactions, it is clearly evident that the excess iron could reduce about 7.5g Ti/l from the tetra- to trivalent state in a manner that the Ti^{4+} would assay about 17.5 g/l.

Preliminary experiments of selective Ti extraction from the prepared leach liquor by TOPO in kerosene have proved the non-extraction of any iron. In other words, it can be mentioned that any Fe^{3+} species formed during TOPO extraction, would be converted to the non-extractable Fe^{2+} species by Ti^{3+} as follows:



Analysis of the prepared working Ti leach liquor has been found to assay 25 g Ti/l (of which some is present in the trivalent state) and 66.7 g Fe^{2+} /l while no Fe^{3+} iron was detected.

Preparation of TOPO extractant

The TOPO extractant phase was prepared in this work by dissolving the required amount in kerosene. From the previous work of Zaki (op.cited), it was found that mixing the prepared TOPO phase with the Ti leach liquor has all the time resulted in the formation of a 3rd phase. Accordingly it was found necessary to add octanol in a 10% volume to the prepared TOPO phase.

Experimental procedures

Extraction procedure

The working titanium HCl leach liquor was then subjected to liquid/liquid extraction using TOPO to obtain a pregnant strip solution containing the titanium ions and a raffinate containing the ferrous ions. Kerosene was used as a suitable diluent for the extractant while octanol was used as a modifying agent to im-

prove the hydrodynamic properties of the system. The extraction experiments were performed in separating funnels where equal volumes of the aqueous and organic phases were mixed by a mechanical shaker at room temperature, until equilibrium was reached. The two phases were then separated and the concentration of titanium in the aqueous phase was determined. The studied relevant factors involved the aqueous phase acidity, the TOPO concentration, the contact time, the ratio of octanol in the organic phase and finally the A/O ratio.

Stripping procedure

Several experiments were performed to study the factors affecting titanium stripping from the loaded TOPO using HCl. Except otherwise cited, the stripping experiments were performed by shaking equal volumes of the aqueous and organic phases (A/O ratio 1/1) until equilibrium was reached. The two phases were then separated and the concentration of titanium in the aqueous phase was determined. The studied relevant factors involved HCl concentration, the contact time and the A/O ratio as well as the number of cycles.

Titanium hydrolysis and calcination procedures

The obtained strip liquor was hydrolyzed in the presence of seed nuclei to form the insoluble titanium hydroxide. For this process, proper seed nuclei have first been prepared by boiling a portion of the strip liquor to precipitate the soluble titanium in the form of the seed nuclei. The strip liquor was then added in two steps to the prepared seed nuclei and after a total stirring time of 2 hr under boiling the precipitated titanium hydroxide was filtered, properly washed and dried before calcination at a temperature of 850°C for 1 hr. By this procedure, it has been possible to obtain the pigment grade TiO_2 .

Analytical procedures

Analysis of iron and titanium were performed using the titrimetric and the spectrophotometric analytical methods respectively^[15]. Thus iron was titrimetrically determined against EDTA using sulfosalicylic acid indicator. While analysis of titanium was performed using tiron as the complexing agent and the absorbance was measured at 430 nm (Unicam UV2-100).

Concerning the final calcined TiO_2 pigment product was analyzed using atomic absorption technique (Unicam atomic absorption 969 Model) at 248.3, 357.9, 318.4 and 279.5 nm respectively. where it was found to be avoid of any Fe, Cr, V and Mn.

RESULTS AND DISCUSSION

Optimization of titanium extraction factors

Effect of HCl acid molarity

According to Sole^[12], the acidity of the titanium aqueous phase can affect phases miscibility, may provide a salting-out effect and may affect the chemical properties of the extractant. However, the main effect of the acidity is in determining the aqueous-phase speciation of titanium. It was concluded that most extractants are inefficient in regions where TiO^{2+} dominates (~ pH 0) apparently because of the high hydration energy of this species.

In order to study the effect of the hydrochloric acid molarity upon Ti extraction from the working solution (41.8 g TiO_2 /l equivalent to 25 g Ti/l), a series of extraction experiments was performed using an acidity varying from 5M to 10M HCl while the other extraction conditions were fixed at an A/O ratio of 1/1, an octanol volume ratio of 10% in the organic phase, a TOPO molarity of 0.72M and for a shaking contact time of 10 min. From the obtained results given in TABLE (2), it is obvious that the extraction efficiency of titanium at 5M HCl attained 64.5%. Increasing the acidity to 6, 7 and up to 10M did not bring any noticeable increase in the extraction efficiency of titanium. This is due to the input TOPO molarity of 0.72 that would be saturated with 17.3 g Ti/l according to stoichiometry of the extracted species in which Ti/TOPO molar ratio attains 1:2^[1,10,11]. Therefore, it could be inferred that 5M HCl is considered as the optimum value for the subsequent solvent extraction of Ti under the working conditions.

Effect of TOPO molarity

To study the effect of TOPO molarity on Ti extraction from the working Rosetta Ti solution in HCl acid, several extraction experiments were performed using a TOPO concentration varying from 0.54 to 0.90M. In

TABLE 2 : Effect of acidity upon the distribution coefficient and the extraction efficiency of Ti (TOPO molarity 0.72M, A/O ratio 1/1, octanol 10% and shaking time 10 min)

Acidity, M	Ti conc. at equilibrium, g/l		D_A^O	Extraction efficiency, %
	Organic phase	Aqueous phase		
5	16.1	8.9	1.8	64.5
6	16.3	8.7	1.9	65.1
7	16.5	8.5	1.9	65.9
9	16.8	8.2	2.1	67.0
10	17.1	7.9	2.2	68.3

TABLE 3 : Effect of TOPO molarity upon the distribution coefficient and the extraction efficiency of Ti (A/O ratio 1/1, octanol 10%, shaking time 10 min and 5M HCl)

TOPO, M	Ti conc. at equilibrium, g/l		D_A^O	Extraction efficiency, %
	Organic phase	Aqueous phase		
0.54	11.9	13.1	0.9	47.4
0.63	13.9	11.1	1.3	55.6
0.72	16.1	8.9	1.8	64.5
0.81	17.8	7.2	2.5	71.1
0.90	18.8	6.2	3.0	75.2

these experiments, the other extraction parameters were fixed at an A/O ratio of 1/1, an octanol volume ratio of 10% in the organic phase, a shaking contact time of 10 min and an aqueous phase acidity of 5M HCl.

From the obtained results reported in TABLE (3), it is found that the extraction efficiency of Ti is directly proportional to the TOPO molarity. Thus, it was found that the Ti distribution coefficient varies from 0.9 to 3 corresponding to a Ti extraction efficiency varying from 47.4 to 75.2% at a TOPO concentration ranging from 0.54 to 0.90M respectively. As mentioned above, a 0.72M TOPO would be saturated with 17.3 g and which experimentally attained 16.1 g Ti/l; a value which is not far from the stoichiometric value. The almost complete depletion of titanium from the aqueous phase can indeed be realized in mixer settler under counter current operation in which the O/A ratio can be increased. This procedure can actually avoid the increased viscosity at higher TOPO molarity. Accordingly, 0.72M TOPO would therefore be considered as the optimum molarity for TOPO under the working conditions.

Effect of the shaking contact time

To study the effect of the shaking contact time upon Ti extraction from the working Rosetta Ti solution in

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HCl acid, several extraction experiments were performed under different time periods ranging from 1 to 20 minutes. The other experimental conditions were fixed at an A/O ratio of 1/1, a TOPO molarity of 0.72M, an octanol volume ratio of 10% of the organic phase and an aqueous phase acidity of 5M HCl.

From the obtained results summarized in TABLE (4), it is obvious that Ti extraction efficiency is directly proportional to the contact time where by its increase, the distribution coefficient and the extraction efficiency have increased reaching 1.7 and 62.7% respectively at 5 minutes. Extending the latter to 10 minutes did not bring a noticeable extraction efficiency and a contact time of 5 minutes would therefore considered as the optimum shaking time under the working conditions.

TABLE 4 : Effect of shaking time upon the distribution coefficient and the extraction efficiency of Ti (TOPO molarity 0.72M, A/O ratio 1/1, octanol 10% and 5M HCl)

Time, min.	Ti conc. at equilibrium, g/l		D_A^O	Extraction efficiency, %
	Organic phase	Aqueous phase		
1	5.8	19.2	0.3	23.0
2	12.1	12.9	0.9	48.3
3	13.5	11.5	1.2	53.9
5	15.7	9.3	1.7	62.7
10	16.1	8.9	1.8	64.5
20	16.3	8.7	1.9	65.2

TABLE 5 : Effect of octanol ratio upon the distribution coefficient and the extraction efficiency of Ti (TOPO molarity 0.72M, A/O ratio 1/1, shaking time 5 min and 5M HCl)

Octanol ratio, %	Ti conc. at equilibrium, g/l		D_A^O	Extraction efficiency, %
	Organic phase	Aqueous phase		
0	13.5	11.5	1.2	53.8
5	14.7	10.3	1.4	58.6
10	15.7	9.3	1.7	62.7
20	16.0	9.0	1.8	63.9
30	16.4	8.6	1.9	65.4

Effect of octanol/extractant volume ratio

Octanol is used as a modifier for the organic phase in a manner to prevent the formation of an undesirable titanium loaded phase that is not soluble in the diluent. To study its effect, a series of experiments was performed using an octanol volume ratio in the organic phase varying from 0 up to 30% keeping the other extraction parameters constant at an A/O ratio of 1/1, 0.72M

TOPO, an aqueous phase acidity of 5M HCl and a contact time of 5 min.

From the obtained results shown in TABLE (5), it is clear that as the ratio of octanol increases in the organic phase from 0 to 30%, the titanium extraction efficiency increased from about 54 to about 65%. At 10%, the extraction efficiency of Ti has attained about 63% which is not far from that (65%) at 30% ratio. Therefore, a 10% octanol in the organic phase is considered as an optimum value.

Effect of A/O ratio and construction of the McCabe Thiele

Extraction diagram

In order to study the effect of the A/O ratio upon Ti extraction, several extraction experiments were carried out using different ratios ranging from 1/4 to 4/1 at a TOPO molarity of 0.72M. In these experiments, the other working conditions involved an octanol ratio of 10% of the organic phase, an aqueous phase acidity of 5M HCl and an extraction time of 5 minutes.

From the obtained results summarized in TABLE (6), it is clearly evident that both the distribution coefficient and the extraction efficiency of titanium are directly proportional to the decrease in the A/O ratio. Decreasing the A/O to 1/4 where a distribution coefficient of 31 and an extraction efficiency of 98.8% have been obtained. This is due to the increased input [Extractant]/[Ti] ratio; a matter which would however be at the expense of a decrease in the titanium concentration in the organic phase that has decreased down to only 6.2 g/l. In the meantime, it would be possible at this A/O ratio of 1/4 to decrease the Ti concentration in the raffinate to only 0.2 g/l. On the contrary, at A/O ratios of 2/1, 3/1 and 4/1 the extraction efficiencies of titanium have decreased to 32.4, 22.5 and 17.3% respectively, however, the maximum titanium concentration would not exceed the stoichiometric ratio of Ti/TOPO of 1:2 (17.3g Ti/l). On the other hand, it has to be indicated herein that almost complete Ti extraction has been achieved at the A/O ratio of 1/4 i.e. both Ti^{4+} and Ti^{3+} have been extracted, however, after oxidation of the latter.

The extraction data obtained at the applied A/O ratios ranging from 1/4 to 4/1 have been used to con-

TABLE 6 : Effect of A/O ratio upon the distribution coefficient and the extraction efficiency of Ti (TOPO molarity 0.72M, octanol 10%, shaking time 5 min and 5M HCl)

A/O ratio	Ti conc. at equilibrium, g/l		D_A^O	Extraction efficiency, %
	Organic phase	Aqueous phase		
1/4	6.2	0.2	31.0	98.8
1/3	8.0	0.9	8.9	96.4
1/2	11.5	2.0	5.8	92.2
1/1	15.7	9.3	1.7	62.7
2/1	16.2	16.9	1.0	32.4
3/1	16.9	19.4	0.9	22.5
4/1	17.3	20.7	0.8	17.3

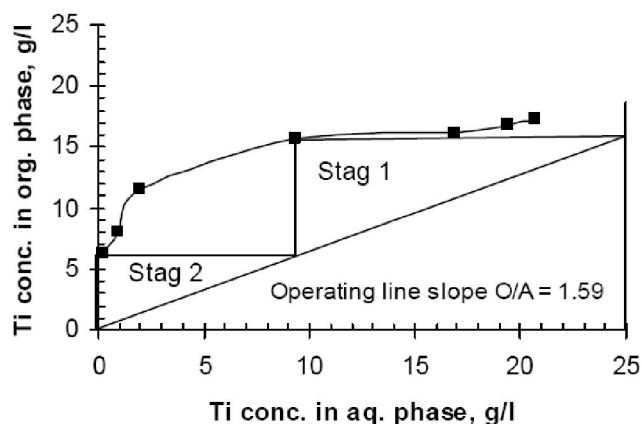


Figure 2 : McCabe-Thiele extraction diagram of Ti from solution (25 g Ti/l)

construct the corresponding McCabe-Thiele extraction diagram shown in Figure (2). From the latter, it was found that the slope of the operating line which is equivalent to the O/A flow rate in a counter current processing attained about 1.59. Using the latter flow rate, two extraction stages would be required for depleting the working solution assaying 25 g Ti/l and realizing saturation or maximum loading of the organic phase.

Optimization of titanium stripping factors

According to Duyvesteyn et al^[4], HCl was found a suitable stripping agent and therefore Ti in the present work was stripped from the loaded organic phase by this acid under different conditions. For this purpose, a Ti loaded organic phase was first prepared using the above determined optimum extraction conditions at which the working organic phase would be loaded with 15.7g Ti/l.

Effect of HCl acid molarity

In order to study the effect of HCl concentration

TABLE 7 : Effect of HCl molarity upon the stripping coefficient and the stripping efficiency of Ti (A/O ratio 1/1, shaking time 10 min)

HCl concentration, M	Ti conc. at equilibrium, g/l		S_O^A	Stripping efficiency, %
	Organic phase	Aqueous phase		
0.25	6.7	9.0	1.3	57.4
0.50	7.2	8.5	1.2	53.8
1	8.1	7.6	0.9	48.1
2	9.4	6.3	0.7	39.8

TABLE 8 : Effect of shaking time upon the stripping coefficient and the stripping efficiency of Ti (0.25M HCl, A/O ratio 1/1)

Time, min	Ti conc. at equilibrium, g/l		S_O^A	Stripping efficiency, %
	Organic phase	Aqueous phase		
5	7.8	7.9	1.0	50.6
10	6.7	9.0	1.3	57.4
20	6.1	9.6	1.6	61.0
30	5.5	10.2	1.9	64.8

upon the stripping efficiency of titanium, several experiments were performed using different acid concentrations ranging from 0.25 to 2M. The other stripping conditions were fixed at an A/O ratio of 1/1 and a stripping time of 10 minutes.

From the obtained results in TABLE (7), it was found that increasing the HCl concentration decreases the stripping efficiency of titanium. Thus while at 0.25M acid, the latter attained about 57%, it was found to gradually decrease by increasing the acid molarity to 2M down to only about 40%. This might be interpreted as due to the fact that increasing the acid molarity would help the formation of the extractable titanium species; namely $TiCl_4$. Therefore, 0.25M HCl would be considered as a practical optimum value.

Effect of the shaking contact time

To study the effect of the shaking contact time upon titanium stripping efficiency, a series of stripping experiments were carried out for a shaking time periods ranging from 5 to 30 minutes using 0.25M HCl and an A/O ratio of 1/1. From the obtained data summarized in TABLE (8), it is obvious that a mixing time of 10 minutes was adequate to almost attain the equilibrium state at which a titanium stripping efficiency of about 57% has been obtained. Increasing the shaking time beyond 10 minutes has only brought a slight improvement.

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TABLE 9 : Effect of A/O ratio upon the stripping coefficient and the stripping efficiency of Ti (0.25M HCl, shaking time 10 min)

A/O ratio	Ti conc. at equilibrium, g/l		S_O^A	Stripping efficiency, %
	Organic phase	Aqueous phase		
4/1	4.9	2.7	0.6	68.3
3/1	5.2	3.5	0.7	67.1
2/1	5.5	5.1	0.9	65.2
1/1	6.7	9.0	1.3	57.4
1/2	8.7	14.1	1.6	44.9
1/3	10.1	16.8	1.7	35.6
1/4	11.0	18.7	1.7	29.7

Effect of A/O ratio

Using an acidity of 0.25M HCl, several stripping experiments were performed to study the effect of A/O ratio upon the stripping efficiency of titanium. These experiments were performed at a shaking time of 10 minutes. From the obtained results summarized in TABLE (9), it is indicated that by increasing the A/O ratio to 2/1 the stripping efficiency of titanium increased to 65.2%. However, further increase of the A/O ratio to 3/1 and even to 4/1 did not realize a perceptible improvement in the titanium stripping efficiency which has slightly increased to 67.1 and to only 68.3%. On the contrary, by decreasing the A/O ratio to 1/2, 1/3 and 1/4, the titanium stripping efficiency has progressively decreased to 44.9, 35.6 and to only 29.7% respectively.

Repeated stripping cycles

As mentioned above, failure to achieve effective stripping with 0.25M acid to practical levels in spite of increasing the volume of the stripping phase to 4/1, it was found convenient to study the effect of repeated stripping cycles. For this purpose, a loaded organic phase sample (15.7g Ti/l) was repeatedly stripped with a fresh stripping phase (0.25M HCl). In these experiments, a shaking time of 10 minutes and an A/O ratio of 1/1 have been used.

From the obtained data summarized in TABLE (10), it was found that accumulative stripping efficiency of up to 98.4% has been obtained by 5 successive stripping cycles and that titanium assay in the stripped organic phase has been decreased from 15.7 to only 0.3 g/l.

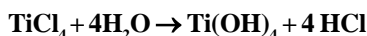
TABLE 10 : Effect of repeated stripping cycles upon titanium stripping efficiency (0.25M HCl, A/O ratio 1/1, and shaking time 10 min)

Stripping cycle no.	Ti conc. at equilibrium, g/l		Accumulative stripping efficiency, %
	Organic phase	Aqueous phase	
1	6.7	9.0	57.4
2	3.2	3.5	22.6
3	1.4	1.8	11.5
4	0.6	0.8	4.8
5	0.3	0.3	2.1

However, a stripping efficiency of 91.5% has been obtained by 3 cycles and at which the organic phase was depleted down to 1.4g Ti/l and which can be recycled to the extraction circuit.

Titanium hydrolysis, calcination and analysis

For product preparation, the titanium stripping solution was subjected to proper hydrolysis. For this purpose, some seed nuclei were first prepared as previously mentioned and upon which the Ti stripping solution was gradually added in two steps and for a total shaking time of 2 hr. Chemically, the hydrolysis reaction can be represented by the following reaction:



As a matter of fact, the seed nuclei would promote the hydrolysis reaction. i.e. the seed nuclei would provide the necessary site upon which the titanium hydrate would precipitate. The amount of seed nuclei used has attained approximately 1.5 to 2.0% w/w of the titanium to be hydrolyzed. Throughout the hydrolysis procedure, the seed suspension or the hydrolyzing mixture is stirred and maintained at boiling. The hydrolyzed precipitate of titanium hydrate was then filtered, washed and dried before calcination at 850°C in a muffle furnace for 1 hr to produce the pure titanium dioxide pigment. The latter was found to be of adequately high degree of brightness and friability. A representative portion of the product has been subjected to the analysis of some impurities; namely Fe, Cr, V and Mn using AAS technique and was actually found to be completely absent.

Finally, a generalized flowsheet has been designed showing the different unit operations that would be applied upon Rosetta ilmenite for the production of pigment grade TiO_2 (Figure 3). By this flowsheet, the TiO_2 recovery has attained about 93%.

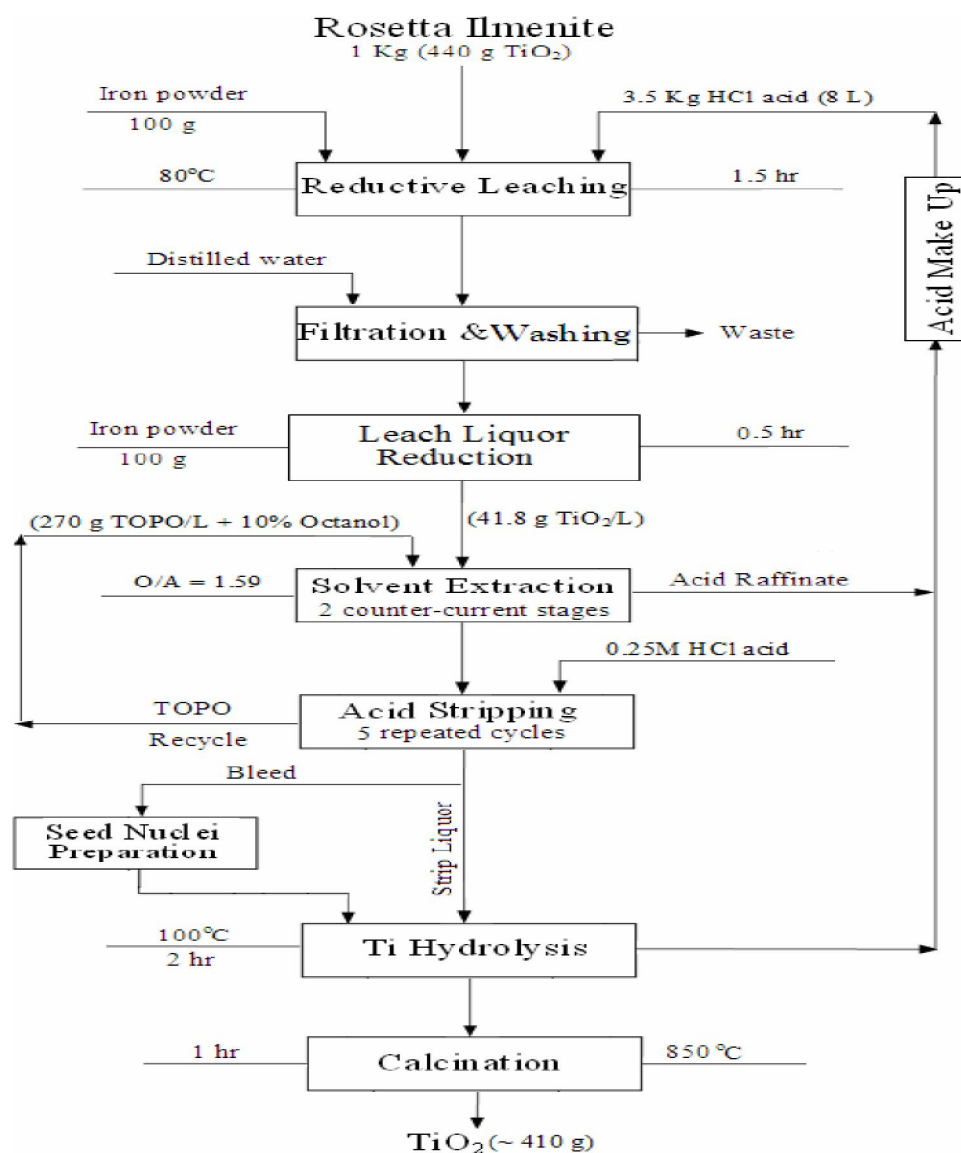


Figure 3 : An integrated flowsheet for the production of pigment grade titanium dioxide from Rosetta ilmenite concentrate

CONCLUSION

Selective solvent extraction of Ti from Rosetta ilmenite leach liquor by tri-octyl phosphine oxide (TOPO) has successfully been achieved via a prior partial reduction of Ti. To realize this objective it has been found necessary to apply two reductive steps where after the reductive leaching of Ti, the obtained leach liquor was further reduced by adding adequate metallic iron powder. The latter should be sufficient for reducing the leached Fe^{3+} iron besides partially reduce a fraction of the leached tetravalent Ti. The studied relevant extraction factors have been optimized; namely the aqueous phase acidity, the TOPO molarity, the contact time,

the volume ratio of octanol in the organic phase and the A/O ratio. Also, the relevant stripping factors of Ti from the loaded tri-octyl phosphine oxide extractant using HCl have been optimized. These factors have involved the HCl acid molarity, the contact time and the A/O ratio as well as the number of repeated cycles.

The stripped Ti solution was then subjected to hydrolysis to obtain the insoluble titanium hydroxide through the proper seeding technique. The precipitated TiO_2 hydrate was filtered, extensively washed and was then dried before calcination at 850°C for 1 hr where titanium dioxide TiO_2 pigment grade was obtained. The latter was found to be of adequately high degree of brightness and friability. By analysis of some of the harm-

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ful impurities, the Fe, Mn, Cr and V were found to be completely absent.

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