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Synthetic rutile preparation from Egyptian Ilmenite using hydrochloric acid in the presence of cellulose as reducing agent

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Abstract
The main objective of the present work is concerned with the usage of cellulose as a reductant in the precipitation of titanium as titanic acid $TiO(OH)_2$ from chloride leach liquor. For this aim, ilmenite concentrate sample is digested using HCl acid solution to prepare titanium and iron species. Several effective factors upon ilmenite dissolution were studied and optimized. The dissolution efficiencies of titanium and iron were 93 and 95% respectively by using 12M HCl, dissolution time of 1 h, 1/12 S/L ratio and dissolution temperature of 80 ^{o}C. The reduction of titaniferous solution was carried out by using 6 g/L cellulose for 2 h reaction time and 120 ^{o}C reaction temperature. The obtained data indicated that about 92.4% of Ti precipitation was achieved to produce higher quality synthetic rutile (99.4%).

Keywords: Titanium dioxide, Synthetic rutile, Ilmenite, Cellulose.

1. Introduction

Titanium dioxide (TiO_2) is extensively used in paints, paper, porcelain, plastics, fibers, photo- and bio-activity catalysts beside many other industries [1]. The main commercial processes for the production TiO_2 pigment from titanium minerals are the sulfate and chloride. The sulfate process is account for about 40% of the world TiO_2 production [2-4]. In this process, a feedstock finely ground ilmenite concentrate (≈ 44% TiO_2) or ilmenite slag (≈ 75% TiO_2) [5-6]. In response to increasing environmental pressures, numerous investigations have been carried out and innovative techniques developed to improve the process [7-9]. On the other hand, in the chloride process, a feedstock of high TiO_2 grade as rutile (94-98% TiO_2), anatase (90-95% TiO_2), leucoxene (67-69% TiO_2), or titanium slag (77- 90% TiO_2) is required. Currently about 60% of the global pigment production is produced by the chloride process [7]. The chloride process offers several advantages over the sulfate process such as the yield of high quality product, a more eco-friendly process and the generation of low amount of waste products. However it requires high capital investment and high quality feedstock [5]. Generally ilmenite is the main source of titanium and many processes have been commercially applied or proposed for its upgrading to synthetic rutile in order to become suitable as a feed for the chloride process. These processes include a combination of thermal oxidation and reduction by roasting, leaching and physical separation steps. Accordingly, iron converted to soluble ferrous or elemental form by reduction at high temperatures followed by its acid leaching to obtain rutile products. These processes include, Becher process [10], Murso process [11-12], Laporte process [13], Benelite process [14] and Austpac process [15]. Most of the previous processes involve high temperature pretreatment of ilmenite, which is an energy consuming and most of the subsequent acid leaching requires pressurized conditions, which make the process more complicated. Cellulosic materials, as cotton, wood fiber or pulp may be added to the produced acidic mixture after the titanium ores digestion with HCl acid for reduce iron species to ferrous ions [16].

1.1 Carrasco *et al*, (1994)

[17] Concluded that, acid steam explosion is a more efficient pretreatment for the fractionation of wood as cellulosic substrates with a low or moderate level of cellulose degradation. Hydrochloric acid solution is hydrolyzed the cellulose to produced hemi-cellulose then to glucose (see Figure 1).

The main component of cellulose is a biopolymer consisting of many glucose units connected through β-1, 4-glycosidic bonds. Breakage of the β-1, 4-glycosidic bonds by acids leads to the hydrolysis of cellulose polymers, resulting in the sugar molecule glucose or oligosaccharides. Mineral acids, such as HCl and H_2SO_4, have been used in the hydrolysis of cellulose [18].

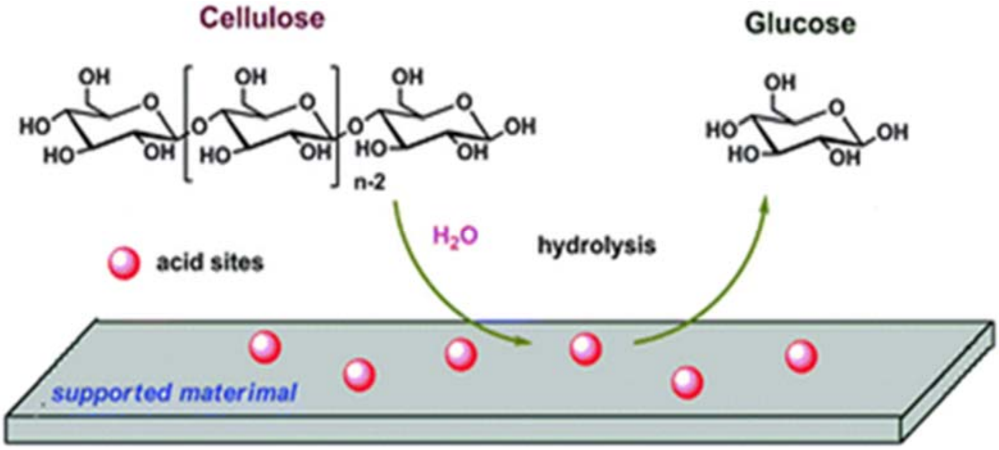


Fig 1: Cellulose degradation process using HCl acid

The present work proposed an easy process for the preparation of a synthetic rutile based on HCl acid leaching of ilmenite at ambient temperature. The leach liquor was then subjected to reduction step using cellulose as a reducing agent avoiding high temperature pretreatment or complicated pressure.

2. Experimental

2.1. Materials and reagents

A technological ilmenite sample is from Rosetta area and kindly provided from black sands project of the Nuclear Materials Authority, Egypt. The obtained sample is grounded and sized (-200 mesh) then subjected to X-ray diffraction (see Figure 2) and wet chemical analysis (see Table 1). All the chemicals employed, including hydrochloric, glucose and analytical reagents were of analytical reagent grade.

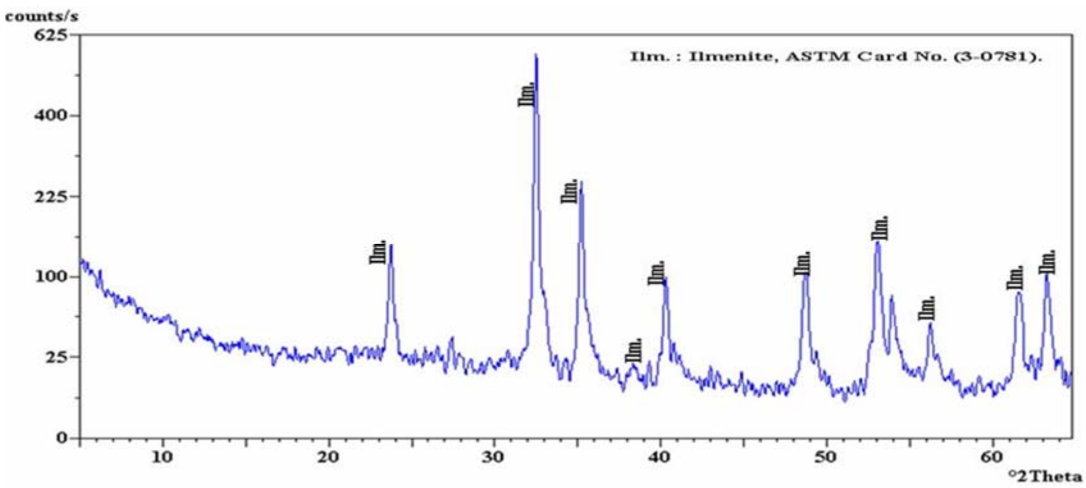


Fig 2: XRD pattern for the identification of Rosetta ilmenite sample

2.2. Experimental Procedures

The ilmenite dissolution experiments were performed in conical flasks fitted with a condenser and stirrer. The ilmenite sample was agitated with HCl acid at various conditions. At the end of each dissolution experiment the slurry was filtered, washed with distilled water and the obtained filtrate was subjected to titanium and iron analysis to calculate their dissolution efficiencies. The studied factors involved HCl acid concentration, S/L phase ratio, sample grain size, reaction time and refluxing temperature. Finally the obtained leach liquor under the optimum factors was then subjected to reduction step using cellulose. The reduction studied factors involved cellulose amount, reaction temperature and reaction time. Finally the treated solution was filtrated to separate titanium as titanic acid [TiO $(OH)_2$]. The precipitated after extensive washing with dilute HCl and warm water (60-70 ˚C) to separate any contaminated iron species was dried at 110 ˚C and calcinated at 850 ˚C then subjected to chemical analysis.

2.3. Analytical Procedures

The ilmenite sample (0.25 g) was first analyzed after preparing the solution through flame fusion with 2.0 g potassium pyro-sulfate ($K_2S_2O_7$). The fused mass then dissolved in 5 ml concentrated H_2SO_4 acid. Titanium was spectrophotometrically determined using tiron as a complexing agent at 430 nm. Total iron was titrimetrically determined against EDTA using sulfosalicylic acid indicator while the ferrous content was also titrimetrically analyzed against a standard potassium dichromate solution. Both calcium and magnesium have also been titrimetrically determined against EDTA using Eriochrome Black T and murexide indicators [19]. Sodium and potassium were analyzed using flame photometric method. Finally, ammonium molybdate has been used for the spectrophotometric determination of the silica at 640 nm. Analysis of the main three trace elements present (Mn, Cr and V) was performed by means of the atomic absorption at 279.5, 357.9 and 318.4 nm respectively. The chemical composition of the Rosetta ilmenite concentrate is given in (see Table 1). The ore contains 41.3% TiO_2, 27.9% FeO and 23.2% Fe_2O_3. This ore is considered as medium grade since it contains a relatively small amount of titanium.

Table 1: The chemical composition of the working ilmenite sample

Composition	TiO_2	Fe_2O_3	FeO	CaO	V_2O_5	Cr_2O_3	Na_2O	K_2O	MnO	SiO_2	MgO
Wt., %	41.30	23.20	27.9	0.9	0.52	0.71	0.3	0.1	1.7	1.2	1.1

3. Results and Discussions

3.1. Digestion using Hydrochloric Acid

The chosen ilmenite concentrate sample was first subjected to digestion using hydrochloric acid. For this purpose many digestion factors included acid concentration, ilmenite/acid ratio, ore grain size, reaction time and reaction temperature were studied and optimized. The expected chemical reactions of the Rosetta ilmenite concentrate with HCl are illustrated in the following equations:

$$FeOTiO_2 + 2HCl \longrightarrow Fe^{2+} + TiO^{2+} + 2Cl^- + 2OH^-$$

$$FeOTiO_2 + 4HCl \longrightarrow FeCl_2 + TiOCl_2 + 2H_2O$$

The predominant species of titanium at the used HCl concentration is $TiOCl_2$ [20].

3.1.1. Effect of Acid Concentration

To study the effect of HCl acid concentration upon titanium and iron dissolution from ilmenite, several experiments were performed using acid concentrations varying from 7 to 12 M. The other dissolution parameters were fixed at S/L ratio 1/15 at reaction temperature 80 °C for 2 h digestion time. From the obtained results plotted in Figure 3, it is obvious that, the dissolution efficiency of either Ti or Fe species is directly proportional to the acid concentration where at 12M HCl the dissolution efficiency is 93.2 and 95.1% respectively. The low dissolution of Ti at 7 M acid is due to the hydrolysis effect at low acidity.

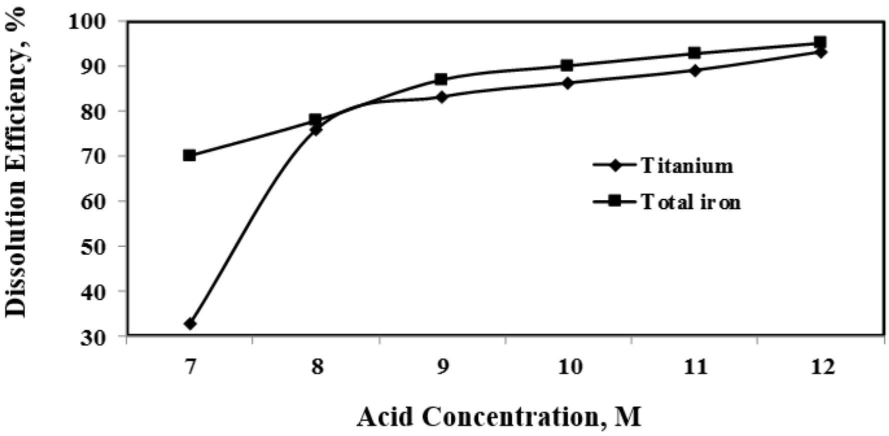


Fig 3: Effect of acid concentration on the dissolution efficiency of ilmenite (80 ºC, 2 hr, S/L ratio 1/15)

3.1.2. Effect of S/L Ratio

Working with 12 M HCl, the effect of S/L ratio was studied in the range of 1/5 to 1/20. The other leaching conditions were fixed at 80 °C reaction temperature for 2 h reaction time. The data in Figure 4 Indicated that, the dissolution efficiency of Ti is directly proportional to the decrease in the pulp density and in turn effective availability of acid solution to the ilmenite grain surface. Thus, as S/L ratio increased from 1/5 to 1/12 dissolution of Ti and Fe increased from 12% to 93.2 and from 77.2 to 95.1% respectively. Thereafter, slight increases in the Ti and Fe dissolution efficiencies have been realized. Therefore, S/L phase ratio of 1/12 is considered as the optimum value.

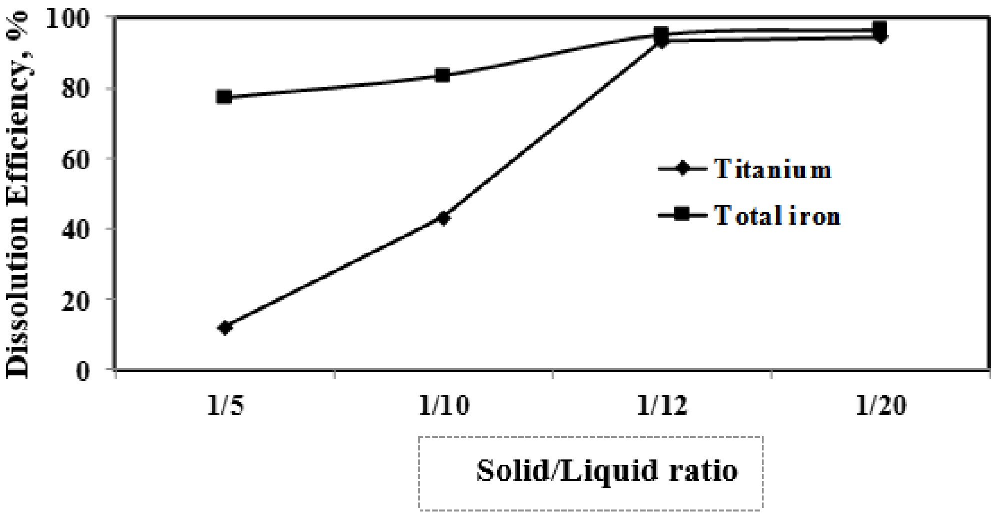


Fig 4: Effect of S/L ratio on the dissolution efficiency of ilmenite (12 M, 80 ºC, 2h)

3.1.3. Effect of Grain Size

To study the effect of grain size upon Ti and Fe dissolution using 12M HCl, a dissolution experiments using ilmenite grain size ranging from -150 to -325 mesh were performed for a reaction time of 2 h at 80 ºC and using a S/L phase ratio of 1/12. The results in Figure 5 revealed that, the dissolution efficiency of Ti and Fe increased by increasing the ore grain size due to increase in the surface area of grains exposed to HCl solution. Therefore, 200 mesh would be considered an optimum grain size. More grinding to 325 mesh size resulted in only about 1% increase in the dissolution efficiency of titanium and iron respectively.

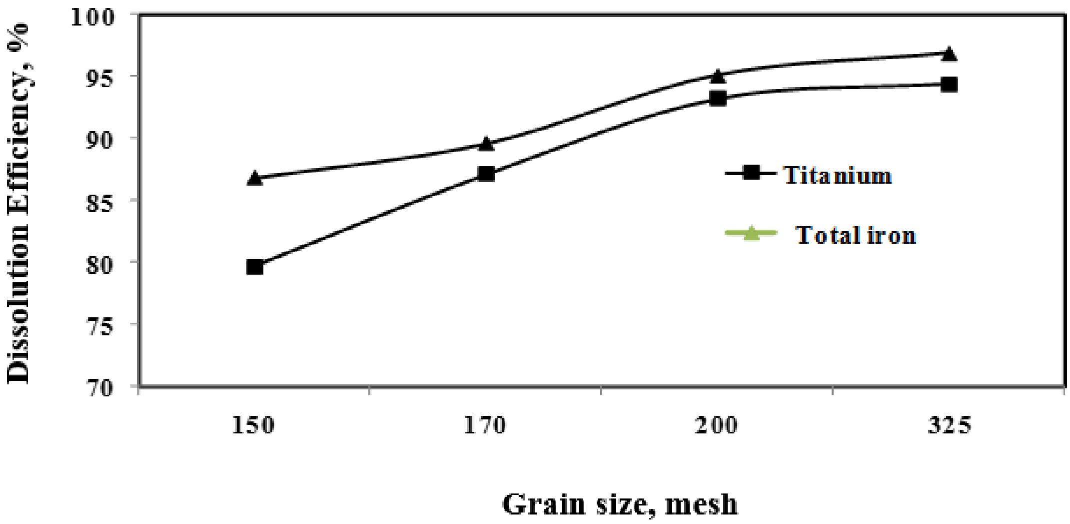


Fig 5: Effect of grain size on the dissolution efficiency of ilmenite
(12M HCl, 80 °C, 2 h, S/L ratio 1/20)

3.1.4. Effect of Time

To study the effect of reaction time upon ilmenite dissolution using 12M HCl, several experiments were performed at different time periods ranging from 1 to 4 h using a concentrate size of -200 mesh at 80 ºC and S/L ratio of 1/12. From the obtained results plotted in Figure 6 it is clear that, at 1 h reaction time the dissolution efficiency for Ti and Fe are about 93 and 95% increased to about 96 and 98% at 2.5 h respectively. Extending time to 4 h has an adverse effect upon the dissolution efficiency of both Ti and Fe to about 92% due to hydrolysis effects. Therefore, 1 h considered as optimum reaction time.

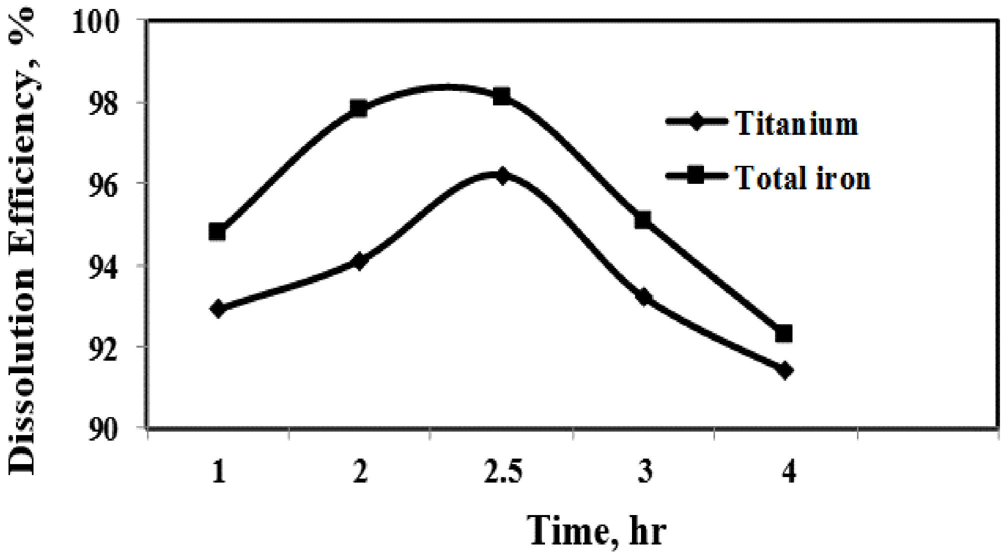


Fig 6: Effect of time on the dissolution efficiency of ilmenite
(12M HCl, 80 °C, S/L ratio 1/20)

3.1.5. Effect of Temperature

Several experiments were performed to study the effect of the reaction temperature upon the dissolution efficiency of ilmenite using 12M HCl for 1 h reaction time in the S/L ratio of 1/12 at reaction temperatures ranging from 50 up to 100 ºC. Data represented in Figure 7 Indicated that both Ti and Fe dissolution increases as the temperature rises from 50 to 80 ºC. At 80 ºC, about 93 and 95% of Ti and Fe species are dissolved respectively. Increasing the temperature to 100 ºC, the dissolution efficiency of ilmenite has been seriously affected with respect to Ti (26.2%) and to a slight degree for Fe (90.1%). This serious decrease in Ti dissolution is due to its high polymerization and hydrolysis effects. Therefore, 80 ºC would be considered as the optimum temperature.

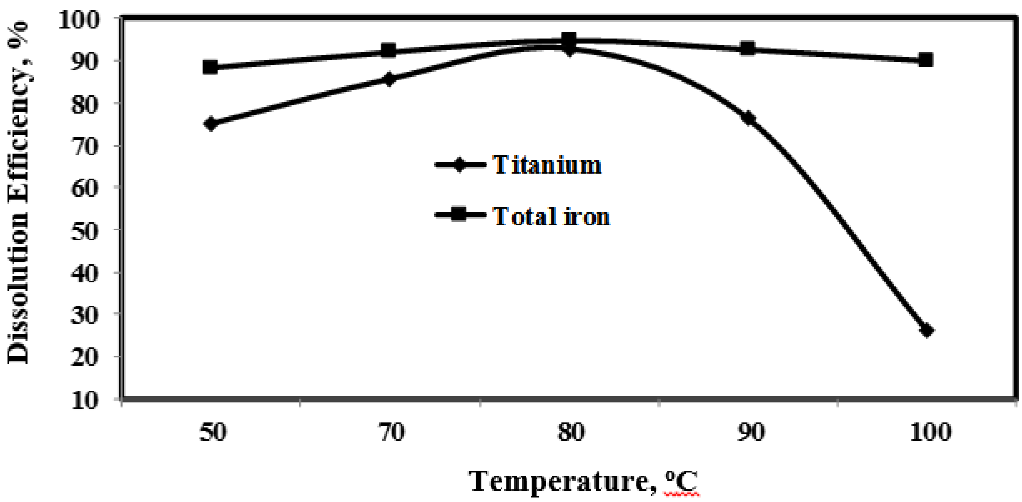


Fig 7: Effect of temperature on the dissolution efficiency of ilmenite
(12M HCl, 1 h, S/L ratio1/20)

Finally, it can be concluded from the foregoing dissolution study that, the optimum dissolution conditions effective to dissolve 93% of Ti and 95% of Fe from the present limonite sample are the following:

HCl concentration: 12M
Solid/Liquid ratio (S/L): 1/12
Dissolution time: 60 min
Dissolution temperature: 80 ˚C

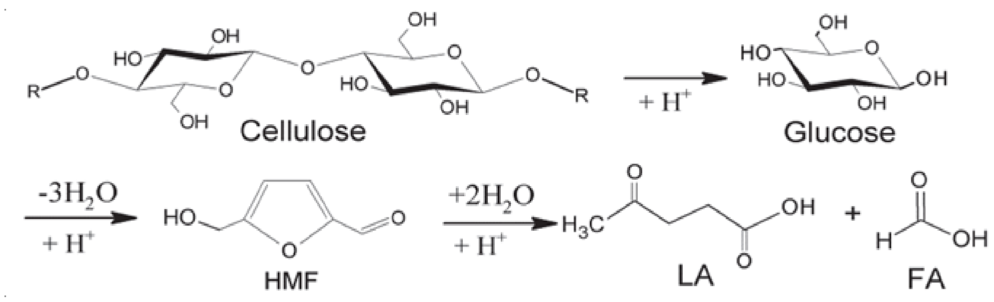
3.2. Preparation of chloride solution.

Applying the mentioned optimum dissolution conditions upon 25 g of the present ilmenite sample yields 1L of chloride solution. The elements of interest e.g. Ti, Fe, Cr, V and Mn were dissolved with dissolution efficiencies of 93%, 95%, 94.5%, 96.3% and 95.8% respectively. The complete chemical analysis of the prepared chloride solution revealed that it assays 9.6 g/L of Ti, 12.1 g/L of Fe, 0.11 g/L of Cr, 0.07 g/L of V and 0.31 g/L of Mn. There is also execs of Cl^- anions. The latter was adjusted to the reduction process of Fe species followed by precipitation of Ti.

3.3. Cellulose reduction and Ti Precipitation processes.

Cellulose was added to the prepared chloride solution to reduce Fe (III) to Fe (II) and avoid the formation of ferric-titanium containing compounds. Moreover to keep the Meta titanic acid [$TiO(OH)_2$] in the suspension phase during the distillation step and prevents its adherence to walls of the container [16]. Cellulose in the prepared chloride solution is converted to glucose which performs the reduction process of Fe ions.

Glucose (sugar) is classified as a reducing sugar only if it has an open-chain form with an aldehyde group or a free hemiacetal group. Monosaccharides such as glucose which contain an aldehyde group are known as aldoses, and those with a ketone group are known as ketoses. The aldehyde can be oxidized via a redox reaction in which Fe (III) is reduced to Fe (II). Sugars with ketone groups in their open chain form are capable of isomerizing via a series of tautomeric shifts to produce an aldehyde group in solution [21]. The overall reduction and hydrolysis processes were illustrated in the following equations. Acid-catalyzed cellulose hydrolysis to glucose. HMF (hydroxyl methyl furfural), LA (levulinic acid), FA (formic acid).



The hydrolysis reaction where HCl is released is given as follows:

$$TiOCl_2 + H_2O \longrightarrow TiO(OH)_2 + HCl$$

$$TiO(OH)_2 \xrightarrow{\text{Calcination}} TiO_2$$

Several factors were studied to optimize the reduction of Fe ions and hydrolysis of Ti ions (precipitation) processes.

3.3.1. Effect of Cellulose amount

To study the effect of cellulose amount on the reduction of ferric chloride and titanium precipitation after hydrolysis process several experiments were performed using different amounts from cellulose ranged from 0.1 g to 1 g added to 100 mL from chloride leach liquor at 90 ºC and the mixture was refluxed for 60 min. From the obtained results in Figure 8, it was obvious that, as the cellulose amount increased from 0.1 to 0.6, the iron precipitation on the synthetic rutile decreased from 53.5 to 10.5% and titanium precipitation increased from 36.1 to 89.2%. Thereafter, a slight increase in the titanium precipitation has been realized. So the optimum cellulose amount is 0.6 g/100 ml.

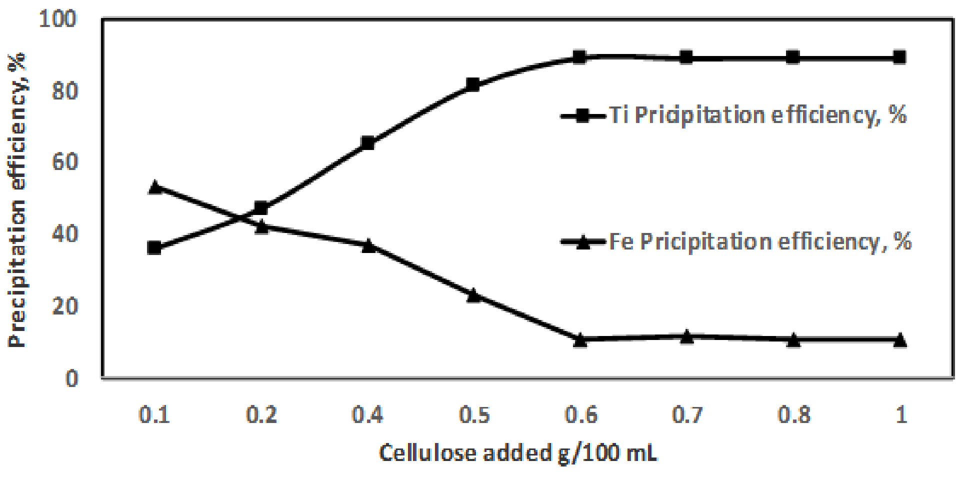


Figure 8. Effect of cellulose amount g/100mL on the reduction process and titanium precipitation at 90°C and 60 min.

3.3.2. Effect of Temperature

The action of heat is able HCl acid to convert cellulose into sugar which acts as a reluctant for Fe^{3+} species and aid the formation of insoluble Meta titanic acid [$TiO(OH)_2$]. For these purposes we study the effect of temperature in the range of 80 to 150 ºC on the reduction process and titanium precipitation using cellulose amount 0.6 g/100 mL for 60 min refluxing time with stirring. From the data illustrated in Figure 9 it was found that, as temperature increased from 80 to 120 ºC the iron precipitation on the synthetic rutile decreased from 12 to 0.7% and titanium precipitation increased from 88.5 to 91.5% and slightly increased as the temperature increased to 150 ºC so, the optimum refluxing temperature is 120 ºC.

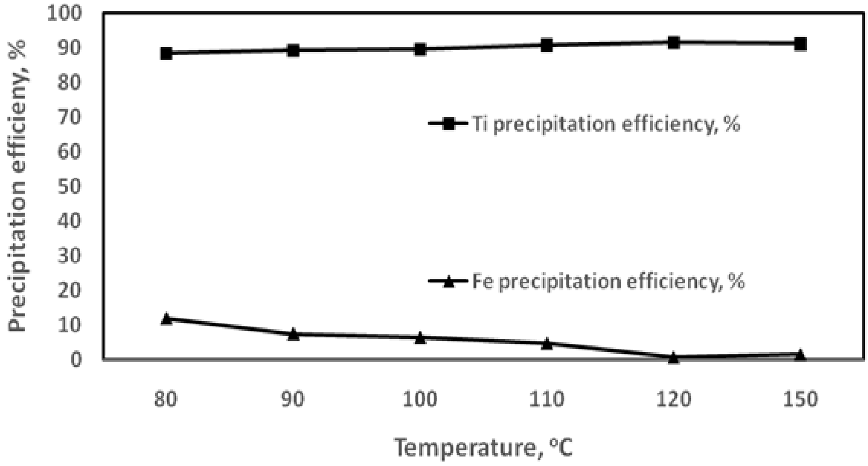


Figure 9. Effect of temperature on the reduction process and titanium precipitation at cellulose amount 0.6 g/100 mL and 60 min

3.3.3. Effect of Time

A series of experiments were performed to study the effect of refluxing time on the reduction process and titanium precipitation from chloride leach liquor solution. The refluxing time varied from 60 to 180 min at cellulose amount 0.6 g/100 mL and 120 ºC reaction temperature. Data in Figure 10 indicated that, as the reaction time increased from 60 to 120 min the iron precipitation on the synthetic rutile decreased from 0.8 to 0.03% and titanium precipitation increased from 91 to 92.4%. Extending the time beyond 120 min has no pronounced effect on the reduction process and titanium precipitation. Then the optimum refluxing time is 120 min. The produced titanic acid was subjected to drying at 110 ºC and calcination at 850 ºC.

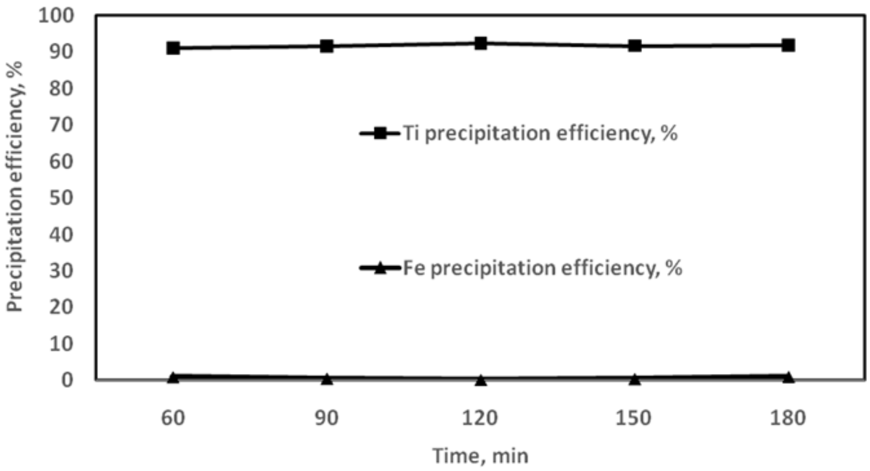


Figure 10. Effect of time on the reduction process and titanium precipitation at cellulose amount 0.6 g/100 mL and 120 ºC

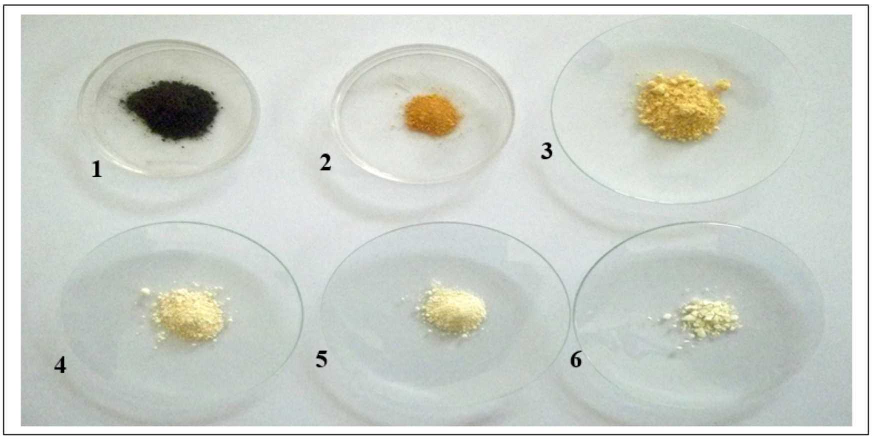


Figure 11. Effect of cellulose on the degree of whiteness of TiO_2

Increasing specimen whiteness (see Figure 11) indicates greater purity. Specimen No. 1 the original ilmenite sample, while samples from 2 to 6 were produced after cellulose treatment under various amount of cellulose added to the chloride leach liquor, the degree of white color increased with increasing amount of cellulose. Specimen no. 6 has the highest TiO_2 purity (99.4%). The final product then subjected to XRD (see Figure 12) and trace element analysis (see Table 2).

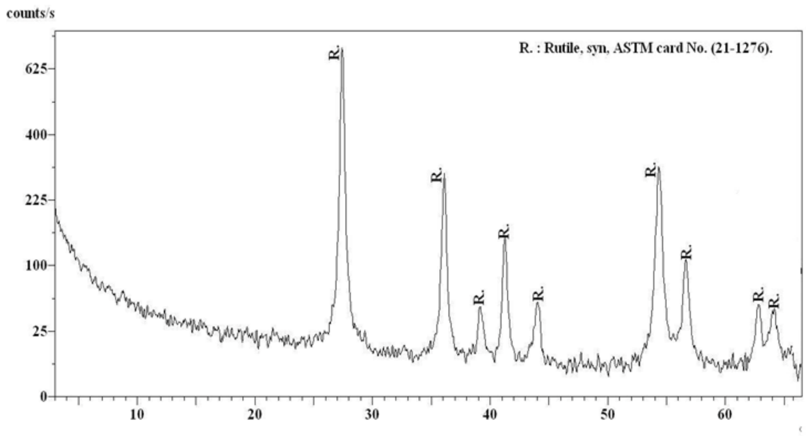


Figure 12. XRD pattern for the identification of pure synthetic rutile (TiO_2)

Table 2: The chemical analysis of the trace elements present in rutile product sample

Composition	Fe	Mn	Cr	V	Mg
ppm	125.2	6.1	24.4	18.3	4.5

The obtained data was used to design a flow-sheet in (see Figure 13) which describes the preparation of synthetic rutile TiO_2 with purity (99.4%) from Rosetta ilmenite concentrate.

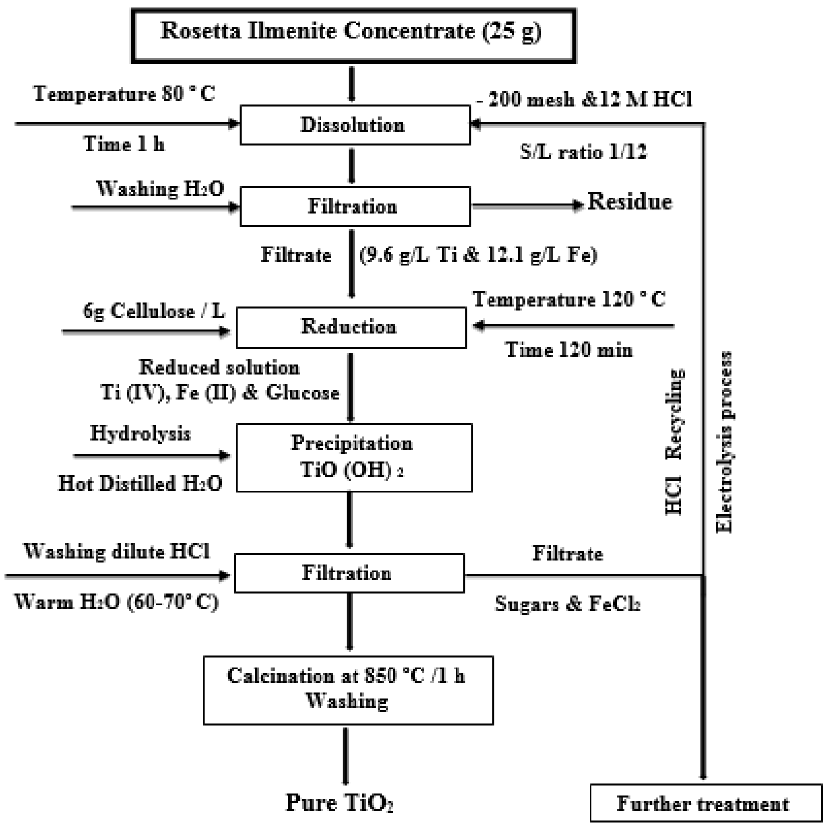


Figure 13. A generalized flow sheet for processing of Rosetta ilmenite concentrate via HCl acid digestion and reduction using cellulose for preparation pure synthetic rutile

Conclusion

The present work aims to produce an easy and economic process to prepare a high grade TiO_2 using cellulose as a reducing agent from chloride leach liquor obtained after limonite dissolution with HCl acid. Factors affecting the ilmenite dissolution were studied and optimized. The optimum dissolution results are 12M HCl for 1 h reaction time using S/L ratio of 1/12 at 80 ^oC. The leach liquor was then subjected to Ti precipitation using cellulose. Factors studied during this step were optimized. The resulted data indicated that about 92.4% of Ti precipitation yield was obtained as $TiO(OH)_2$ using 6 g/L cellulose after 2 h refluxing time at 120 ^oC.

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