Preparation and Characterization of Nanosized Titania Prepared from Beach Black Sands Broad on the Mediterranean Sea Coast in Egypt via Reaction with Acids

Fouda, M.F.R., Amin, R.S., Saleh, H.I., Labib, A.A. and Mousa, H.A.

Inorganic Chemistry Department, National Research Center, Dokki, Cairo, Egypt

Abstract: In spite of the presence of huge quantities of black sands broaden along the beach of Mediterranean Sea, Egypt, which contain high reserves from ilmenite, only few studies were concerned with the extraction of titania with bearing titanium minerals. At the same time, the importation of titanium and titanium dioxide pigment costs, yearly, many millions of dollars. So that, the study in the article was directed to achieve the goal of production of such compounds at home. This achievement was verified through several steps. The first one was concerned with the characterization of ilmenite sample by means of suitable analytical and spectroscopic techniques. The second step was devoted to throw the light on different thermodynamic parameters of reaction of ilmenite with HCl and H₂SO₄ in order to suggest the kinetics and mechanism of the reaction, which help in addition to extraction experiments in determination of the optimum conditions which verify the optimum extraction of titania from ilmenite. The studies in the investigation was extended to include the preparation of nanosized titania from the reaction products. The dimensions of the later compound varied between 22 and 46 nm in case of using H₂SO₄ and varied between 29 and 59 nm in case of using HCl.

Key words: Black sands, nanosized titanium dioxide

INTRODUCTION

The black sands are found within Egypt with large reserves along the southern coast of Mediterranean Sea from Abu Kir (at the West) to Alarish (at the East), especially at the location of Rashid beach. Additional amounts of black sands were also found as sediments in the bottom of Nasser Lake (Naim, et al., 1994; El-Boke, et al., 1984; Abdel Monem, et al. 1989) at the southern part of Egypt. In that respect, few studies were devoted to separation of ferromagnetic materials (e.g. magnetite, hematite) and ilmenite from the other constituents of black sands depending on their magnetic properties (Dabbour, et al. 1989).

Ilmenite, separated from black sands, which is the mineral of choice in the present article, is used economically for production of titanium dioxide. The last compound is used in many fields of application such as manufacture of certain types of refractories (Goerenz, et al. 1997), catalysts (Aono, et al. 1997), cosmetics (Shio, et al. 1991), solar batteries (Vidal, et al. 1998) and ceramic materials (Siewert, et al. 1997). The extraction of titania from ilmenite (ore or mineral) was the subject of numerous studies ( Kataoka, 1973; Danuta, 1974; Burastero, 1977; Saucedo, 1977; Roehrborn, 1984; Girgin, 1990; Ahmed, et al. 1996; Chen, et al. 1999; Lakshmanan, et al. 2001, Ibrahim. Rt al. 2004; Li, et al. 2006; Sarker, et al. 2006.), but most of them appeared in the form of patents. Most of these studies were concerned with the extraction of titania from ilmenite by H₂SO₄ and HCl, whereas few ones were directed to extraction of titania by interaction with alkaline reagents (Hirano, et al. 1976; Kim, 1982; Amer, 1997 and Liu, 2006)

In spite of the presence of huge quantities of black sands broaden along the beach of Mediterranean Sea (Egypt), as mentioned before, and contain huge reserves from ilmenite, only few studies were concerned with the extraction of titania from bearing titanium minerals. At the same time the importation of titanium and titanium dioxide pigment grows yearly and associated with the increase in the expenses of foreign currency. Such situation makes it obligatory to search for methods and techniques suitable for production of titanium dioxide which is usually used as pigment, in order to save the foreign currency required for their importation.

Corresponding Author: Fouda, M.F.R., Inorganic Chemistry Department, National Research Center, Dokki, Cairo, Egypt
Email: mfrfouda@yahoo.com
Experimental:
Materials:
Chemicals:
The chemicals used in the present investigation were of analytical grade supplied from Merck (Darmstadt, Germany).

Ilmenite Concentrate Fraction:
The ilmenite concentrate separated from Egyptian black sands accumulated at Rosetta beach was obtained from the group of the black sands project in Nuclear Materials Authority (NMA) in Egypt. The quantity of ilmenite fraction (20 Kg) used throughout the investigation was ground to 75μm, followed by sampling according the usual manner followed in that respect (A.S.T.M., 1969).

Acid Leaching Procedure:
Acid leaching of ilmenite fraction was carried out using 250 cm$^3$ three necked glass reactor flask provided with a reflux condenser and a mechanical agitator with a teflon-coated stirring rod. The desired volume of HCl or H$_2$SO$_4$ with a specific molarity was poured in the reactor and heated using a thermostatically controlled heater. After reaching the desired temperature (70-110°C), ilmenite ore sample was added and after a certain time (30-300 min) the suspension of the reaction products was immediately filtered. Suitable volumes of the filtrate were taken for determination of titanium dioxide and iron according the method of analysis described (Jeffery, et al. 1989). The fraction extracted of iron oxide or titania from ilmenite was calculated by dividing the extracted amount of them by the amount found in the ilmenite fraction.

The determination of titanium (Jeffery, et al. 1989) and iron in the leaching solutions was carried out according to two well known analytical methods followed in that respect.

Techniques and Measurements:
I- X-ray Diffraction Patterns (XRD):
X-ray diffractograms of ilmenite ore, different reaction products and titania were obtained by means of a chart recording Broker D$\alpha$ advance x-ray diffractometer using copper (K$\alpha$) target with a secondly monochromator. The instrument properly calibrated and adjusted with respect to the x-ray source, as the patterns were run at a scanning rate of 8° in 20/min at 40kv and 40mA.

II- X-ray Fluorescence Spectra (XRF):
The investigated sample was crushed then ground in a Herzog mill to obtain rich fine powder. The last one was mixed with 1.6g of binding wax in a small mill, on a speed 380 rpm for one minute. The sample was then put in an aluminum cup, after that it was pressed in an automatic pressed machine under 130 KN. The yielded disk specimen was measured by using AXIOS, WD-XRF Sequential Spectrometer (P Analytical, 2005), The Axios is a sequential instrument with a single goniometer based measuring channel, covering the complete measuring range. The instrument is microprocessed and controlled from an external computer, running an analytical software package (Super Q 4).

III- Electronic Absorption Spectra of Solutions:
The electronic absorption spectra of titanium solutions were measured in the matched 1cm fused silica cells with an automatic Shimadzu 240 graph spectrometer.

IV- Transmission Electron Microscope (TEM):
The samples used for transmission electron microscopy (TEM) observation were prepared by dispersing these samples in distilled water followed by ultrasonic vibration for half an hour. A drop of the depressed sample was placed onto a copper grid coated with a layer of amorphous carbon. A Jeol Transmission Electron Microscope, jel 1230, RV 120 KV was used to study the morphology of the sample.

RESULTS AND DISCUSSION

Before investigation of the different parameters of reaction kinetics and mechanism of interaction between ilmenite and HCl or H$_2$SO$_4$, it is reasonable to throw the light on the morphology as well as the composition of sample of ilmenite concentrate, separated from black sands.

The results of chemical analysis of the sample under investigation by means of x-ray fluorescence spectra are presented in Table 1, whereas x-ray diffractograms are illustrated in Fig. 1. The previous findings indicated that the ilmenite fraction was composed of four main phases. These phases namely are, FeTiO$_3$ (ilmenite), (Mg,Fe)(Ti,Fe)O$_3$ (substituted ilmenite), Fe$_3$O$_4$ (hematite), Fe$_7$O$_4$ (magnetite) and TiO$_2$ (rutile). On the other hand
the results of chemical analysis presented in Table 1 clarified that the ilmenite fraction may contain some other minerals which can be predicted from the presence of Al and Cr species in the ore. These minerals may be nominated as $\text{Fe}_0.65, \text{Fe}_{1.81}, \text{Mg}_{0.42}, \text{Al}_{0.1}, \text{Ti}_{0.0304}$, and $(\text{MgCr}_{0.4}, \text{Fe}_{1.6}, \text{O}_{4.0})$. The last two phases cannot be distinguished in the diffractograms due to that their percentages in the sample are lower than the limits of detection by means of X-ray diffractometer.

The values of the observed "d" spacings $d$ (Å) of the previous compounds coincide with those published in JCPDS-ICDD having the numbers: 75-0519, 83-2428, 24-0072, 76-1849 and 04-0551.

The petrography of the studied sample by means of reflected light microscope revealed that the sample is composed mainly of ilmenite (I) with some magnetite (M), hematite (H), and traces of rutile (R) and quartz (Q). Ilmenite occurs as sub angular to rounded, medium to coarse grains with a moderate reflectivity (Fig. 2). The majority of ilmenite grains were unaltered and free from inclusions and ex-solutions. Magnetite occurs as sub angular to rounded, medium to coarse grains with a high reflectivity compared to ilmenite and hematite (Fig. 3). The traces of rutile and quartz occur as isotropic (dark) sub angular to rounded fine grains (Fig. 4). They occur sometimes as fine inclusions inside ilmenite grains.

<table>
<thead>
<tr>
<th>Constituent</th>
<th>Content (Wt %)</th>
<th>Constituent</th>
<th>Content (Wt %)</th>
<th>Constituent</th>
<th>Content (Wt %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{SiO}_2$</td>
<td>03.21</td>
<td>$\text{TiO}_2$</td>
<td>39.57</td>
<td>$\text{Al}_2\text{O}_3$</td>
<td>1.35</td>
</tr>
<tr>
<td>$\text{Fe}_2\text{O}_3(tot)$</td>
<td>51.66</td>
<td>$\text{MnO}$</td>
<td>0.43</td>
<td>$\text{MgO}$</td>
<td>1.07</td>
</tr>
<tr>
<td>$\text{CaO}$</td>
<td>00.45</td>
<td>$\text{Na}_2\text{O}$</td>
<td>0.025</td>
<td>$\text{K}_2\text{O}$</td>
<td>0.05</td>
</tr>
<tr>
<td>$\text{P}_2\text{O}_5$</td>
<td>00.07</td>
<td>$\text{SO}_3$</td>
<td>0.03</td>
<td>$\text{Cr}_2\text{O}_3$</td>
<td>0.53</td>
</tr>
<tr>
<td>$\text{ZrO}_2$</td>
<td>00.15</td>
<td>$\text{Cl}$</td>
<td>0.08</td>
<td>$\text{L.O.I}$</td>
<td>0.20</td>
</tr>
</tbody>
</table>

The petrography of the studied sample by means of reflected light microscope revealed that the sample is composed mainly of ilmenite (I) with some magnetite (M), hematite (H), and traces of rutile (R) and quartz (Q). Ilmenite occurs as sub angular to rounded, medium to coarse grains with a moderate reflectivity (Fig. 2). The majority of ilmenite grains were unaltered and free from inclusions and ex-solutions. Magnetite occurs as sub angular to rounded, medium to coarse grains with a high reflectivity compared to ilmenite and hematite (Fig. 3). The traces of rutile and quartz occur as isotropic (dark) sub angular to rounded fine grains (Fig. 4). They occur sometimes as fine inclusions inside ilmenite grains.
Factors Affecting the Acid Leaching of Beach Sand Ilmenite:

The leaching of the beach sand ilmenite by means of HCl or H\textsubscript{2}SO\textsubscript{4} can be described by the following reaction

\[ \text{FeTiO}_3 + 4 \text{HCl} \rightarrow \text{TiOCl}_2 + \text{FeCl}_2 + 2 \text{H}_2\text{O} \quad \ldots \ldots \quad (1) \]

\[ \text{FeTiO}_3 + 2 \text{H}_2\text{SO}_4 \rightarrow \text{TiOSO}_4 + \text{FeSO}_4 + 2 \text{H}_2\text{O} \quad \ldots \ldots \quad (2) \]

The main factors that can influence the rate of this reaction are: particle size, stirring, acid concentration, temperature and time of reaction as well as acid to ilmenite molar ratio. So that it is tried to study the influence of each of these parameters, in a systematic way.

Effect of Particle Size:

The effect of particle size on the dissolution of titanium and iron was investigated in 5.5 M HCl acid as well as 10 M H\textsubscript{2}SO\textsubscript{4} acid at 80°C, using particle size fractions amount to 40, 60 and 75 mm. It was found that the increase in the particle size of used ilmenite leads to a decrease in the dissolution of titanium and iron. Similar results have been reported by numerous authors (Olanipekun, 1999).

Effect of Stirring:

The effect of stirring speed (rpm) on the dissolution rate of ilmenite with 5.5 M HCl or 10 M H\textsubscript{2}SO\textsubscript{4} at 70°C with different stirring speeds (200, 400 and 600 rpm) showed that the leaching rate of titanium and iron was not increased with increasing the stirring speed in the range between 200 and 600 rpm. On the basis of these data, the subsequent experiments were carried out at a stirring speed amounted to 400 rpm to ensure that the contribution to mass transfer by natural convection was negligible. This finding was taking as an indication that the reaction is not a diffusion controlled reaction but it can be considered as a surface controlled one (Olanipekun, 1999). The same conclusion can also be gained from the values of activation energies as can we see latter.

Effect of Acid Concentration:

The effect of HCl or H\textsubscript{2}SO\textsubscript{4} concentration was investigated using acid concentrations laid in the range of 2.5-11 M at 80°C in case of HCl and laid in the range of 4-18 M at 90°C in case of H\textsubscript{2}SO\textsubscript{4}, respectively, for 3 h. The results illustrated in Figs. 5 and 6 showed that the dissolution rate of both titanium and iron was found to be increased, generally, by increasing acid concentration in case of HCl (Fig. 5). On the other hand in case of H\textsubscript{2}SO\textsubscript{4}, the dissolution rates of both titanium and iron were found to be increased by increasing H\textsubscript{2}SO\textsubscript{4} concentration up to 14 M, followed by a pronounced decrease in the percentage of extraction of both titanium and iron by increasing molarity of the acid. The last phenomenon may be explained on the basis that the solubility of sulfates, FeSO\textsubscript{4}, TiOSO\textsubscript{4} resulted from ilmenite species and Fe\textsubscript{2}(SO\textsubscript{4})\textsubscript{3} from trivalent iron species decreased by increasing H\textsubscript{2}SO\textsubscript{4} concentration due to the common ion effect. As a result, they covered the surface layer of ilmenite grains and prevented the dissolution of additional amounts of the inclosed ilmenite.
This phenomenon may also be ascribed to the formation of Ti$_2$O$_3$ which is less soluble in H$_2$SO$_4$ than tetravalent titanium species. The formation of Ti$_2$O$_3$ was confirmed from the appearance of its characteristic diffraction lines as revealed from x-ray diffraction patterns of the solid residue resulted from interaction of beach sand ilmenite with H$_2$SO$_4$ (Fig. 7). The values of the observed “d” spacings (Å) of Ti$_2$O$_3$, SiO$_2$, FeTiO$_3$, and TiO$_2$ coincide with those published in the corresponding to JCPDS-ICDD having the numbers: 71-1053, 05-0490, 75-0519 and 72-1148 and 72-1148 respectively.
The kinetic studies in the present investigation are confined to use 10 M H$_2$SO$_4$ which cause maximum leaching of both titanium and iron form the ilmenite concentrate after 5 hours. On the other hand 5.5 M HCl was used in such part of investigation irrespective of the finding which clarified that the percentage of extraction of titania as a result of using this acid molarity did not exceed 40% (Fig. 5). This choice was taken into consideration due to that the molarity of the acid does not change with heating since it possesses a constant boiling composition.

**Effect of Temperature on the Percentage of Extraction of Titania:**

The effect of temperature on the dissolution rates of both titanium and iron was investigated by reaction of ilmenite, fraction separated from beach sand with 5.5 M HCl or 10 M H$_2$SO$_4$ at temperatures fall in the range (70-110°C), where the molar ratios between HCl as well as H$_2$SO$_4$ and TiO$_2$ amounted to 1 : 208 and 1 : 378 respectively. From the results illustrated in Figs. 8-9, one can observe that the dissolution rates of titanium and iron were found to be increased rapidly by rising the leaching temperature. At 110°C the leaching of 100 % Ti and 100 % Fe was found to be achieved after 5 h, whereas less than 35% Ti and 41 % Fe were found to be leached at 70°C in case of H$_2$SO$_4$ (Fig.8). On the other hand 66 % Ti and 76 % Fe were found to be leached at 100°C after 5 h while less than 15 %Ti and 21 % Fe were extracted at 70°C in case of leaching in HCl as can be concluded from the results illustrated in (Fig.9).One can find that the values of extraction of iron were always higher than that of titanium in case of both acids. This finding may be attributed to that Fe$^{3+}$ as a hard acid is more compatible for reaction with hard bases Cl$^-$ and SO$_4^{2-}$ than Ti$^{4+}$.

**Effect of Time of Reaction on the Percentage of Extraction of Titania and Iron:**

The results illustrated in Fig.10 indicated that the dissolution rates of both titanium and iron increased, rapidly, by increasing the time of reaction. As the time progressed, a relatively small increase in titanium and iron was brought into the solution by increasing the leaching time from 3 to 5 h. The elongation of the time of reaction more than 5 h at high temperatures led to a decrease in the dissolution of ilmenite. This phenomenon may be ascribed to the probability of formation of polytitanates which are less soluble than ortho- or metatitanate. The formed polytitantes, probably, led to formation of a film surrounding the active sites of ilmenite molecule and thus made an adverse effect on the contact between reactants, hence a decrease in the reaction rate and percentage of extraction of titania and iron.
Fig. 8: Dissolution of iron and titanium in 10 M H$_2$SO$_4$ solution at different temperatures.

Fig. 9: Dissolution of iron and titanium in 5.5 M HCl solution at different temperatures.

Effect of the Molar Ratio Between, TiO$_2$ (In Ilmenite) and Acid on the Leaching of Titania and Iron:

The results presented in Table 2 showed that the dissolution rates of titanium and iron were increased with increasing molar ratio between reactants, as it was expected.

Analysis of Leaching Rates:

The dissolution rates of titanium and iron were analyzed according to the shrinking core model (Olanipekun, 1999). For reaction control provided that sand beach ilmenite is considered as a homogeneous spherical solid phase. For the titanium and iron dissolution kinetics, can be used and expressed by the following equation (Olanipekun, 1999):
Fig. 10: Variation of the percentage of extraction of titania and iron with 10 M \( \text{H}_2\text{SO}_4 \) and 5.5M \( \text{HCl} \) at 90°C.

Table 2: Effect of molar ratio between acids (a) \( \text{H}_2\text{SO}_4 \) (10 M) and \( \text{TiO}_2 \) (in ilmenite) on the leaching efficiency at 90°C for 210 min (b) \( \text{HCl} \) (5.5 M) and \( \text{TiO}_2 \) (in ilmenite) on the leaching efficiency at 80°C for 210 min

<table>
<thead>
<tr>
<th>Molar ratio between Acid: ( \text{TiO}_2 )</th>
<th>(a) % Extraction</th>
<th>(b) % Extraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti Fe Ti Fe</td>
<td>Ti Fe Ti Fe</td>
<td></td>
</tr>
<tr>
<td>100 : 1</td>
<td>15 19</td>
<td>10 22</td>
</tr>
<tr>
<td>200 : 1</td>
<td>31 35</td>
<td>16 28</td>
</tr>
<tr>
<td>300 : 1</td>
<td>60 63</td>
<td>50 58</td>
</tr>
<tr>
<td>400 : 1</td>
<td>85 90</td>
<td>76 80</td>
</tr>
</tbody>
</table>

1- \((1 - x)^{1/3}\) = \(\frac{Mk_cC_A^3t}{dr} = k_it\), \( (3) \)

where \( k_i \) is the first-order rate constant (m min\(^{-1}\)), \( M \) is the molecular weight of the solid reactant (kg mol\(^{-1}\)), and \( C_A \) is the acid concentration (mole m\(^{-3}\)), \( x \) is the fraction reacted at time \( t \) (min) and \( k_l \) (m min\(^{-1}\)).

Examination of the plots of the above kinetic equation (3) clarified that the plots of the function \(1-(1-x)^{1/3}\) vs. time (t) gave straight lines up to different values of \( x \) as can be seen from Figs. 11-12. Eqn. 3 was found to be valid up to values of \( x \) amounted to 0.89 and 0.55 in case of leaching of titania with \( \text{H}_2\text{SO}_4 \) and \( \text{HCl} \), respectively. Whereas the corresponding values of \( x \) amounted to 0.93 and 0.59 in case of leaching of iron with the two acids mentioned before. When the values of \( x \) exceeded that mentioned before, eqn. 3 did not valid and a deviation from the straight lines was observed. This deviation may be ascribed to the formation of polymerized titanates which cover the surface of ilmenite particles and prevented the contact between acids and active sites on ilmenite particles, hence a decrease in the rate of reaction and percentage of extraction of both titanium and iron. The values of rate constants of the reaction of ilmenite with \( \text{H}_2\text{SO}_4 \) and \( \text{HCl} \) were presented in Table 3.

The values of activation energies of both titanium and iron in \( \text{HCl} \) and \( \text{H}_2\text{SO}_4 \) solutions were given in Table 4 and calculated according to Arrhenius eqn, which stated that:

\[ k = A \exp (- \frac{E_a}{RT}) \]

Where \( k \) is the overall rate constant (m\(^2\) min\(^{-1}\)), \( A \) is the frequency factor (min\(^{-1}\)), \( E_a \) is the activation energy (J mol\(^{-1}\)), \( R \) is the universal gas constant (8.314 J K\(^{-1}\) mol\(^{-1}\)), and \( T \) is the absolute reaction temperature (K).
Fig. 11: Plots of $1 - (1 - x)^{1/3}$ vs. time for titanium dissolution at various temperatures in 10M H$_2$SO$_4$ solution.

Fig. 12: Plots of $1 - (1 - x)^{1/3}$ vs. time for iron dissolution at various temperatures in 10 M H$_2$SO$_4$ solution.

Table 3: Rate constants for reaction of ilmenite with 10 M H$_2$SO$_4$ and 5.5 M HCl at different temperatures.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Rate constant ($k_r$) for reaction with 10 M H$_2$SO$_4$</th>
<th>Rate constant ($k_r$) for reaction with 5.5 M HCl (min$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$Ti$ ($x 10^{-5}$)</td>
<td>$Fe$ ($x 10^{4}$)</td>
</tr>
<tr>
<td>70</td>
<td>7.4</td>
<td>1.4</td>
</tr>
<tr>
<td>80</td>
<td>11.6</td>
<td>2.1</td>
</tr>
<tr>
<td>90</td>
<td>19.3</td>
<td>3.2</td>
</tr>
<tr>
<td>100</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>110</td>
<td>26.5</td>
<td>4.3</td>
</tr>
</tbody>
</table>

Molar ratio between H$_2$SO$_4$ and TiO$_2$ in the ore equals 378:1

Molar ratio between HCl and TiO$_2$ in the ore equals 208:1

Table 4: Values of activation energies for dissolution of titanium and iron, in case of reaction of 10 M H$_2$SO$_4$ and 5.5 M HCl with ilmenite fraction

<table>
<thead>
<tr>
<th>Element</th>
<th>$E_a$ in H$_2$SO$_4$ (kJ mol$^{-1}$)</th>
<th>$E_a$ in HCl (kJ mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti</td>
<td>52.3</td>
<td>63.5</td>
</tr>
<tr>
<td>Fe</td>
<td>48.1</td>
<td>54.2</td>
</tr>
</tbody>
</table>

The values of activation energies were found to be different from the reported ones by other workers (Imahashi, 1976; Barton, 1979; Han, et al. 1986; Jablonski, 2001; Sasikumar, et al. 2004 and Liang, et al. 2005). This finding may be attributed to the difference between the mineralogy of ilmenite fraction under investigation and that for other ilmenite ores studied by other investigators (Imahashi, 1976; Barton, 1979; Han, et al. 1986; Jablonski, 2001; Sasikumar, et al. 2004 and Liang, et al. 2005). In other words, one can say that
this finding may be attributed to the difference between the molecular structure of ilmenite fraction under investigation and the structure of the ilmenite ore studied by other investigators. The x-ray diffraction patterns of the sample under investigation, illustrated in Fig.6, clarified that ilmenite fraction not only contains FeTiO$_3$ (ilmenite) but also contains some other species. The last ones are formed by isomorphous substitutions in the tetrahedral sites, instead of Fe$^{2+}$ as well as in octahedral sites instead of Ti$^{4+}$. These species namely are, (Mg, Fe) (Ti,Fe)$_3$O$_5$, Fe$_{0.65}$Fe$_{1.81}$Mg$_{0.42}$AlTiO$_3$O$_4$ and MgCr$_{0.4}$Fe$_{1.6}$O$_4$. This substitution may lead to an increase in the susceptibility of ilmenite molecules towards the acid attack due to the distortion which may be created in the crystalline structure of ilmenite network.

Although the values of energies of activation are higher in case of dissolution of iron than that for titanium, the rates of reactions in case of titanium leaching are higher than those corresponding to iron leaching in both acids. This finding may be attributed to the lower values of entropy of activation ($\Delta S^\circ$) of iron compared to that for titanium Table 5. The values of the last thermodynamic parameter were calculated according to eq. 7

$$\Delta S^\circ / 2.303R = \log K_r - 10.753 - \log T + E_a / 4.576 \ T$$

(7)

By inspection of the results presented in Tables 6 and 7, one can see that the values of entropy of activation for dissolution of titanium and iron by H$_2$SO$_4$ and HCl have high positive values. This finding indicated that the activated transition complexes are not significantly solvated by the reaction media. So that the transformation of the activated complexes to the end products do not suffer from retardation due to what is known as salvation effect. In case of one and the same acid one can notice that the degree of salvation of intermediate activated titanium complexes is always lower than that for iron intermediate complexes.

Table 5: Values of entropies of activation for interaction between (a) 10 M H$_2$SO$_4$ (b) 5.5 M HCl and ilmenite fraction at different temperatures

<table>
<thead>
<tr>
<th>Temperature(K)</th>
<th>(a) $\Delta S^\circ$(J)</th>
<th>(b) $\Delta S^\circ$(J)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ti</td>
<td>Fe</td>
</tr>
<tr>
<td>343</td>
<td>331.72</td>
<td>260.57</td>
</tr>
<tr>
<td>353</td>
<td>319.13</td>
<td>249.79</td>
</tr>
<tr>
<td>363</td>
<td>304.82</td>
<td>236.08</td>
</tr>
<tr>
<td>373</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>383</td>
<td>273.44</td>
<td>207.67</td>
</tr>
</tbody>
</table>

Based on the forgoing discussions, it is tried to explain the variation in the values of rate constants in the light of values of entropy of activation, as well as energy of activation. The values of reaction rate constants of titania and iron oxide with H$_2$SO$_4$ presented in Table 4 were found to be higher than that characteristic for leaching of both oxides with HCl. This finding may be attributed to the lower values of activation energy in case of H$_2$SO$_4$ in comparison to that characteristic for leaching with HCl. The values of rate of reactions not only depend on the value of activation energy but also depend on the value of entropy of activation in the frame of eqn. (6). In that respect one can say that the decrease in the value of energy of activation as well as the increase in the value of entropy of activation lead to an increase in the values of rate of reaction, and vice versa.

A Proposed Mechanism for Ilmenite Leaching:

The results of leaching of both titanium and iron proved that the reactions followed the shrinkage core model as it was mentioned before. This model assumes that the reaction rate is controlled by one of these three steps; diffusion of the acid through a film surrounding the particle, chemical reaction on the surface of the particle, and diffusion of the products back through the film. There is a good evidence that the last two steps compete in determining the rate of the ilmenite dissolution reaction. Thus the rate-determining step during the dissolution of ilmenite is dependent on the nature of titanium species in solution. When ilmenite comes into contact with hydrochloric or H$_2$SO$_4$ solutions, both iron and titanium go into solution. At this point, the rate is controlled by the rate of the chemical reaction. When low initial HCl -to- ilmenite mole ratio is used along with a high leach temperature once the Ti (IV) concentration in solution exceeds the value of $10^{-3}$ M, polymerization of titanium products will occur (Nabivanets, 1976). The diffusion of the resultant polymer chains away from the reaction interface will now become the rate-limiting step. The low ratio between H$_2$SO$_4$ and ilmenite causes the precipitation of TiOSO$_4$ at the surface of the ore. The rate-determining step in the leach reaction now changes to diffusion of the reacting species through the product layer.
Any additives that are added to the leach solution can influence the titanium species in solution and consequently the rate-determining step (Duncan, 1982). By stabilizing soluble species of iron and titanium, the rate of dissolution can be maintained. On the other hand, the rate of dissolution can be decreased significantly if the additives promote the formation of solid species of iron and titanium that precipitated from solution to form a product layer on the surfaces of the particles of ilmenite.

The information presented in the previous section led us to suggest that under certain conditions, the rate of the dissolution of ilmenite could be chemically surface controlled reaction. Under other conditions, it could be controlled by the diffusion of the reacting species and the resulting products to or away from the reaction interface or it can be controlled by the diffusion of these species through a product layer on the surface of the particles.

The tendency of Cl\(^-\) ions (Nabivanets, 1976) to promote polymerization of titanates makes HCl an inherently inferior dissolution medium by comparison with H\(_2\)SO\(_4\). The effectiveness of both acids can be improved by the addition of small amounts of fluoride, one of the few agents which form stable complexes with Ti\(^{4+}\) under the conditions of acidity and temperature employed in ilmenite dissolution.

Based on the values of different thermodynamic parameters of reactions between ilmenite and both acids (HCl, H\(_2\)SO\(_4\)), it is tried to throw the light on the kinetics and mechanism of these reactions. It is assumed that the first step is considered as the hydroxylation of the surface of ilmenite,

\[
\text{FeO}_\text{Ti}=O \quad + \quad \text{H}_2\text{O} \quad \underset{\text{fast}}{\underset{\text{reversible}}{\rightleftharpoons}} \quad \text{FeO}_\text{TiOH}
\]

The second step is concerned with the fast and reversible protonation process of the hydroxylated species of ilmenite,

\[
\text{FeO}_\text{TiOH} \quad + \quad 4\text{H}^+ \quad \overset{\text{fast}}{\underset{\text{reversible}}{\rightleftharpoons}} \quad \text{FeO}_\text{Ti(OH)}_2
\]

The third step is considered as the slow one (rate determining step) and concerned with the positively charged molecule resulted in the second step. This following step can be represented by the following eqn.

\[
\text{FeO}_\text{Ti(OH)}_2 \quad + \quad 4\text{L}^- \quad \overset{k_r}{\underset{\text{rate determining step}}{\rightarrow}} \quad \text{FeL}_2 + \text{Ti(OH)}_2\text{L}_2
\]

(L=Cl\(^-\) or 1/2SO\(_4\)^{2-}\)

The last step is considered as the rate determining step of desorption of metal cation-acid anion complex and leads to formation of FeL\(_2\) and Ti(OH)\(_2\)L\(_2\). The presence of hydroxyl groups in the formula of titanium product may be ascribed to that Ti\(^{4+}\) is more susceptible to react with OH\(^-\) cation than Fe\(^{2+}\) anion. This conclusion gained its importance from the fact that Ti(OH)\(_4\) can be precipitated at a lower pH value than the pH of precipitation of Fe\(^{3+}\) which amounted to ca. 3. Depending on these assumptions, one can observe that the values of the rate constant depend on the complexing affinity of anions towards Ti and Fe cations, and the degree of solvation of transient activated complex in the reaction media. So that the observed rate constants laid in the order 7.4 \times 10^{-5} - 2.65 \times 10^{-4} \text{ min}^{-1} in case of titanium and laid in the order 1.35 \times 10^{-4} - 4.3 \times 10^{-4} \text{ min}^{-1} in case of iron, using 10 M H\(_2\)SO\(_4\). On the other hand in case of leaching with 5.5 M HCl, the rate constants laid in the order 2.66 \times 10^{-5} - 1.5 \times 10^{-4} \text{ min}^{-1} in case of leaching titanium and laid in the order 7.83 \times 10^{-5} - 2.8 \times 10^{-4} \text{ min}^{-1} in case of leaching iron.
Preparation of Nanosized Titania from Egyptian Beach Sand Ilmenite:

The preparation of nanosized titania was achieved through several steps. The first step is concerned with the extraction of titania from ilmenite concentrate separated from black sands in Rosetta (Rashid) location (Egypt). The extraction process was carried out by means of reaction with 10 M H₂SO₄ and 5.5 M HCl, at 373-383K, for 5 h to achieve the highest percentage of extraction of titania (Figs.11 and 12). The reaction products were then filtered to remove the unreacted materials, whereas the filtrate contains sulfates or chlorides of titanium, aluminium, magnesium, chromium, di-, and trivalent iron species, beside the excess amounts of reacting acids. The species of Fe (III) which comes from magnetite (found in the ilmenite fraction) in the leach solution was reduced to Fe (II) by addition of metallic iron (in order to increase the difference in basicity between the resulted faintly basic Fe²⁺ and acidic Ti⁴⁺ species). The solution was then heated for 25 min followed by filtration to remove the excess amount of iron. The pH of the solution was adjusted to a pH value lower than 2 by sodium hydroxide, where the hydrolysis of titanyl salts was brought out by boiling. The hydrous oxide was filtered, washed dried, calcined at different temperatures and analyzed by XRF, which clarified that the sample of rutile produced by heating at 1000°C contains 98.6% TiO₂, 0.56% Fe₂O₃ and traces of silicon and aluminum. The resulted oxide was found to be almost free from the other colored ions of manganese, chromium which are found originally in the ilmenite fraction. The TEM image of titanium dioxide (produced by heating the hydrous acid of titanium at 700°C for 7h) at, in the form of anatase, resulted from ilmenite leaching with H₂SO₄ was illustrated in Fig.14. The image showed that most of the particles are spherical with a relatively narrow size distribution and others in the form of dusters which are conglomeration of smaller particles with a diameter varied between 22-46 nm On the other hand the TEM image (Fig.13) of titanium dioxide resulted from ilmenite leaching with HCl showed that the particles are irregular in their shapes. Some of these particles are spherical while some other, are elongated with a diameter ranged between 29 and 59 nm. The last value may be considered in harmony with the finding of (Nabivanets, 1976), who reported that chloride ion catalyzes the polymerization of TiOCl₂.  

Fig. 13: TEM image of TiO₂ particles prepared by leaching ilmenite with HCl. (the particle size ranged between 29 and 59 nm)

Fig. 14: TEM image of TiO₂ particles prepared by leaching ilmenite with H₂SO₄. (the particle size ranged between 22 and 46 nm)
The filtrate was considered a source of iron, and magnesium in addition to the excess amounts of unreacted acids. During the course of neutralization the traces of Fe\(^{3+}\) species was precipitated as Fe (OH) \(_{3}\) at a pH ca. 3 where it was separated by filtration. At a pH value amounted to ca. 7, ferrous hydroxide was precipitated and separated by filtration to use it in the preparation of red ferric oxide pigment. The processes of transformation of Fe (OH)\(_{3}\) to the red Fe\(_{2}O_{3}\) pigment is beyond the scope of the present investigation. The produced filtrate was then, contained a sufficient quantity of formed sodium sulfate and magnesium sulfate. The pH of this filtrate was then raised to a value ca. 12 where magnesium was precipitated as magnesium hydroxide which was separated by filtration. The pH of the last filtrate was then lowered to the neutrality (pH ca. 6-7) to convert the excess alkali to sodium sulfate. The solution was then cooled to 2°C to precipitate crystalline sodium sulfate decahydrate. The last compound was dehydrated by heating at 70-90°C. The anhydrous salt is economically useful since it is used in numerous industries. This proposed method is considered as a promising one since the consumption of the large quantity of energy used in the smelting process was avoided. In addition the excess amount of acid exploited in preparation of useful salt via sodium sulfate or sodium chloride in case of leaching with H\(_{2}SO_{4}\) or HCl, respectively.

**Conclusion:**

The economical exploitation of beach sand ilmenite which broaden along the coast of Mediterranean Sea, North Egypt, with huge reserves for production of nanosized titania can be achieved via acid leaching by means of H\(_{2}SO_{4}\) and HCl. The disadvantage of using a large excess of acids can be by converting these acids to the corresponding economically valuable salts such as NaCl or KCl and K\(_{2}SO_{4}\) or Na\(_{2}SO_{4}\). The higher percentage of iron in the beach sand ilmenite can be utilized for preparation of red iron oxide pigment, in order to increase the positive elements of economy of this process. It was found that the reactive nanosized titanium dioxide can be prepared from titanyl sulfate and titanyl chloride produced from the acid attack process. The ultrafine oxide was used in preparation of some metal titanates at relatively lower temperatures than the case of their preparation using micronized oxide, A large number of these oxides showed a remarkable ability for using them as pigments based on the results of their testing according the standard methods that followed in that respect.

**REFERENCES**


