

# A Study on the Recovery of Titanium Dioxide from Blast Furnace Slags via Roasting and Acid Leaching

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## Article History:

Received: 25 August 2018,

Revised: 05 October 2018

Accepted: 27 October 2018.

## ABSTRACT

In this research, parameters affecting the recovery of titanium dioxide from an iron slag sample from Esfahan Steel Company (located in Esfahan province, Iran) were studied. Roasting method with sodium carbonate followed by sulfuric acid leaching was utilized in this study. The best conditions for roasting with sodium carbonate were obtained at the temperature of 500°C with Na<sub>2</sub>CO<sub>3</sub>/slag ratio of 1/4, and in a period of 120 minutes. The optimum condition for titanium dioxide recovery from a -106µm-sized sample of iron blast furnace slag was achieved at temperature of 85°C, solid/liquid ratio of 1/15, sulfuric acid concentration of 2 M in 240 minutes. The maximum recovery was 53%. The kinetic study showed that the leaching process was controlled by the diffusion, in which the activation energy was 5.85kJ/Mol; it confirmed the diffusion control of the process.

**Keywords :** Iron slag, Roasting, Titanium dioxide, Leaching, Sulfuric acid

## 1. Introduction

Steelmaking industry produces significant quantities of byproducts, including slags, fly-ash, sludge, spent catalyst, ash, and alloyed scraps which contain a notable amount of heavy metals. Releasing such materials into the environment may lead to some significant problems [1, 2]. Moreover, considering the environmental laws in various countries as well as the problems of disposal and storage of the waste products, iron, and steel producing companies have encountered severe problems [1]. To name a few usages of iron-making slags, they can be utilized in the construction of railways and railroads, in glass-manufacturing, and as artificial stone and as a secondary source of vanadium [1, 3].

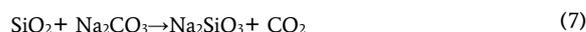
Titanium constitutes about 0.63 % of the earth crust, making it the ninth-ranked abundant element [4]. Titanium dioxide is one of the most commonly used ingredients for manufacturing pigments and chemicals [5]. Due to its thermal and chemical stability as well as its electrical, mechanical and optical properties, titanium and its compounds, particularly titanium dioxide, have found many applications in various essential industries including pigments, absorbents, porcelain, paper, rubber, and plastics [5-8].

The sulfate and the chloride processes are two widely used industrial processes for manufacturing titanium dioxide pigment [5- 13].

Many hydrometallurgical methods have been put forward to produce high-grade titanium dioxide. The hydrochloric and sulfuric acids have been used in the vast majority of direct leaching methods of titanium slag or ilmenite [14-17].

A new approach for producing TiO<sub>2</sub> pigment was also presented by the researchers [18-22]. In this method, the titanium-containing slag was roasted by sodium or potassium hydroxide, and then washed with water in order to improve the grade of titanium-bearing mineral. The resulting

product was then dissolved in acid, and through several additional processing steps, the titanium dioxide pigment was finally produced [6, 10, 18-22]. Some researchers used the roasting method in order to produce titanium dioxide pigment. They purified ilmenite, titanium slag, and low-grade waste products from various processes -such as Bayer's process- utilizing sodium and potassium roasting, particularly NaOH and Na<sub>2</sub>CO<sub>3</sub> [10, 21, 23-25]. By roasting the slag, Na<sub>2</sub>TiO<sub>3</sub> and Na<sub>2</sub>TiSiO<sub>5</sub> compounds were formed [24, 26]. After roasting, Si and Al which were considered as impurities could be converted to water-soluble materials. The insoluble sodium titanate products (NaFeTiO<sub>4</sub>, Na<sub>8</sub>Ti<sub>5</sub>O<sub>14</sub>, Na<sub>6</sub>Ti<sub>2</sub>O<sub>7</sub> and Na<sub>2</sub>TiO<sub>4</sub>) were then subjected to H<sub>2</sub>SO<sub>4</sub> acid dissolution [10, 27]. Via roasting, various compounds were generated from the slag according to stoichiometric reactions as described in Equations (1) to (7) [10, 18]. During the leaching with water, additional alkali and other water-soluble impurities such as sodium aluminate and silicate compounds were dissolved in water, with the pH of the aqueous solution set in the range of 12 to 14 [6, 22, 28]. Sodium ion in the Na<sub>2</sub>TiSiO<sub>5</sub> composition was difficult to dissolve in water, but this ion in Na<sub>2</sub>TiO<sub>3</sub> was readily replaced with hydrogen ion of water. This replacement is believed to be due to the inclusion of NaOH for reproduction [29].



Subsequently, the titanium slag was roasted with Na<sub>2</sub>CO<sub>3</sub> at 850 °C, and then subjected to dissolution in sulfuric acid (concentration: 60%)

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and by using oxalic acid as a reducing agent. After some more stages, highly pure  $\text{TiO}_2$  (99.8%) was produced and ferrous sulfate ( $\text{FeSO}_4$ ) was removed as a by-product from the sulfate solution [10]. For the recovery of  $\text{TiO}_2$ ,  $\text{Al}_2\text{O}_3$  and pig iron from red mud, the Pyro-hydrometallurgy process was used. The molten pig iron was separated from the slag. The slag was later leached with sulfuric acid (30%) at a temperature of  $90^\circ\text{C}$ , and 84.7% of existing  $\text{TiO}_2$  in slag was recovered [27]. In order to enhance the recovery of poor titanium slag, it first roasted by sodium carbonate at different temperatures. The product was subsequently washed with water at  $50^\circ\text{C}$  for 30 minutes in order to remove the water-soluble impurities. It was observed that  $500^\circ\text{C}$  was the best agitation temperature [30].

The purpose of this research was to investigate the recovery of  $\text{TiO}_2$  from slag samples of an iron blast furnace. The supplied sample was roasted with sodium carbonate, and then it was leached by sulfuric acid. The effect of various parameters on the recovery of  $\text{TiO}_2$  was studied. The kinetic equation concurred with experimental data and the estimated value for activation energy.

## 2. Materials and methods

### 2.1. Materials

The iron making slag sample was collected from the mixer unit of Esfahan Steel Company. The plant is located in Esfahan province, Iran. X-Ray Diffraction (XRD) analysis of the sample is shown in Figure 1, which indicates that the main phases were iron, silicate, calcium, and alumino-silicate; and this was reasonably predictable due to the added materials during the melting process in the blast furnace. The chemical composition of the sample is shown in Table 1. Subsequently, pre-treatments, crushing, milling, gravity separation, and ultimately the roasting experiments with sodium carbonate were conducted on the sample.

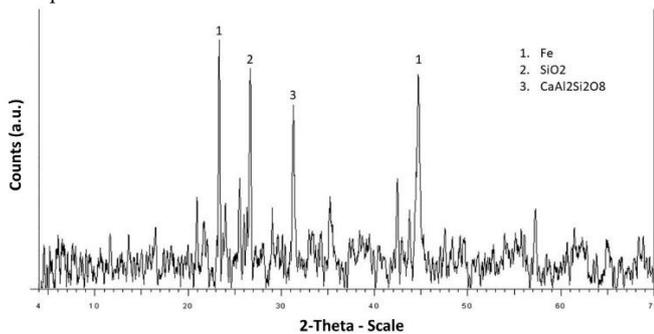


Figure 1. The XRD pattern of Iron Slag

Table1-The chemical composition of the iron slag (XRF)

|   | $\text{Fe}_2\text{O}_3$ | $\text{SiO}_2$ | $\text{CaO}$ | $\text{Al}_2\text{O}_3$ | $\text{MnO}$ | $\text{MgO}$ | $\text{TiO}_2$ | Other |
|---|-------------------------|----------------|--------------|-------------------------|--------------|--------------|----------------|-------|
| % | 35.6                    | 27.95          | 15.59        | 7.99                    | 5.63         | 2.96         | 2.63           | 1.64  |

### 2.2. Procedure

#### 2.2.1. Preparation of iron slag

A certain amount of slag with a specific particle size was thoroughly mixed with  $\text{Na}_2\text{CO}_3$  in a porcelain crucible, and roasted for two hours at various temperatures in a muffle furnace. The reaction product was subsequently washed with water at  $55^\circ\text{C}$  for 30 min. The sample was later filtered and washed with water. The cake was dried in an oven for twenty four hours at  $105^\circ\text{C}$ . The final product was added to a glass reactor containing sulfuric acid solution for chemical dissolution. Finally, the best roasting temperature was chosen according to the different recovery of titanium dioxide.

#### 2.2.2. Leaching procedures

A roasted sample was leached in a glass reactor by sulfuric acid under different experimental conditions. A certain amount of sulfuric acid and sample was then poured into the glass reactor, and the ratio of liquid to solid was controlled. The test temperature was adjusted using magnetic hotplates, according to the conditions of the experiments. Various factors affecting the recovery of titanium dioxide were investigated. Figure 2 demonstrates the flow diagram of the experimental procedure.

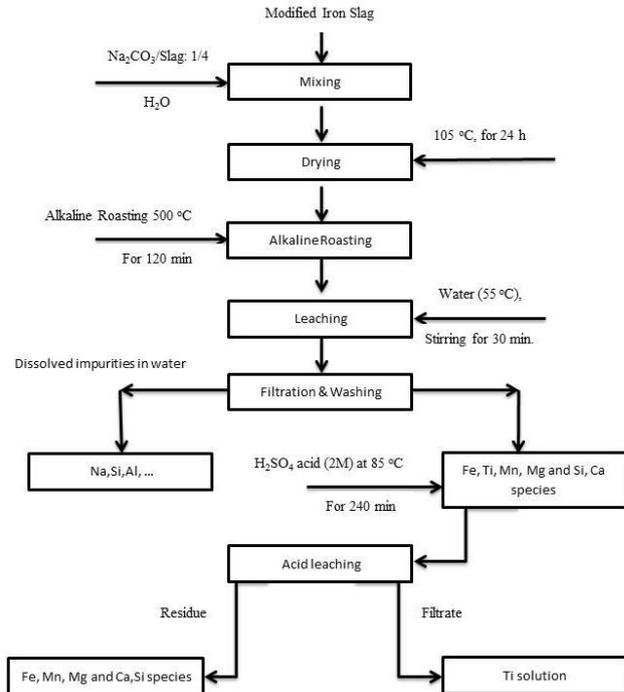


Figure 2. The flowchart of the experimental procedure

### 2.3. Analytical methods

The chemical compositions of the iron-making slag were examined via X-Ray Fluorescence (XRF). The structure and morphology of the samples were characterized employing a D8-Advance X-Ray Diffractometer (XRD) device which was equipped with copper  $\text{K}\alpha$  radiation ( $\lambda=1.540598\text{\AA}$ ) and a Philips SEM X130 (Scanning Electron Microscope), respectively. The elemental frequency in the sample was measured with a WDX-3PC XRF machine. The iron concentrations were examined via titration. The titanium dioxide concentration of the sample and the solution extracted from the leaching process were obtained by chromatography. A Unicam UV2-100 spectrophotometer was used to measure the absorbance of titanium at 430 nm, using iron as the complex agent.

## 3. Results and discussion

### 3.1. Effect of roasting temperature

Finely-ground slag sample was mixed with  $\text{Na}_2\text{CO}_3$  at the required ratio in a porcelain crucible. The mixture was roasted at temperatures of 300 to  $1000^\circ\text{C}$  for two hours in a muffle furnace under the desired conditions ( $\text{Na}_2\text{CO}_3/\text{slag}$  weight ratio: 1/4). The sample was then subjected to dissolution in water at  $55^\circ\text{C}$  for 30 minutes, during which the liquid to solid (slag) ratio was 10 to 1. The final product was then leached at  $50^\circ\text{C}$  for two hours under the following conditions: 250 rpm (rotational speed), the solid/liquid ratio: 10/1, 3 M sulfuric acid,  $d_{80} = 120\ \mu\text{m}$ . The recovery of titanium dioxide was found to be optimum at  $500^\circ\text{C}$ .

The XRD analysis of the roasted sample at  $500^\circ\text{C}$  with a  $\text{Na}_2\text{CO}_3$  to slag ratio of 1/4 is shown in Figure 3 (a). The results shown in Figure 3 indicate that the main phases in the product are  $\text{Na}_2\text{TiSiO}_5$ ,  $\text{Na}_2\text{TiO}_3$ ,

and other sodium and calcium compounds.  $\text{Na}_2\text{SiO}_3$  and  $\text{NaAlO}_2$  easily react with water [6]. The SEM image of the roasted product after rinsing is shown in Figure 3 (b). Compared with the primary slag, it had fewer impurities. The Wavelength Dispersive X-ray fluorescence (WDX) test was performed and showed that the sample mainly consisted of an approximately uniform distribution of calcium, silicon, iron, and titanium. The chemical composition of the roasted sample is shown in Table 2.

Table 2-The chemical composition of the roasted iron slag (XRF)

|   | $\text{SiO}_2$ | $\text{CaO}$ | $\text{Fe}_2\text{O}_3$ | $\text{MnO}$ | $\text{Al}_2\text{O}_3$ | $\text{TiO}_2$ | $\text{MgO}$ | Other |
|---|----------------|--------------|-------------------------|--------------|-------------------------|----------------|--------------|-------|
| % | 37.1           | 21.7         | 15.2                    | 8.1          | 6.6                     | 5.2            | 3.4          | 3.3   |

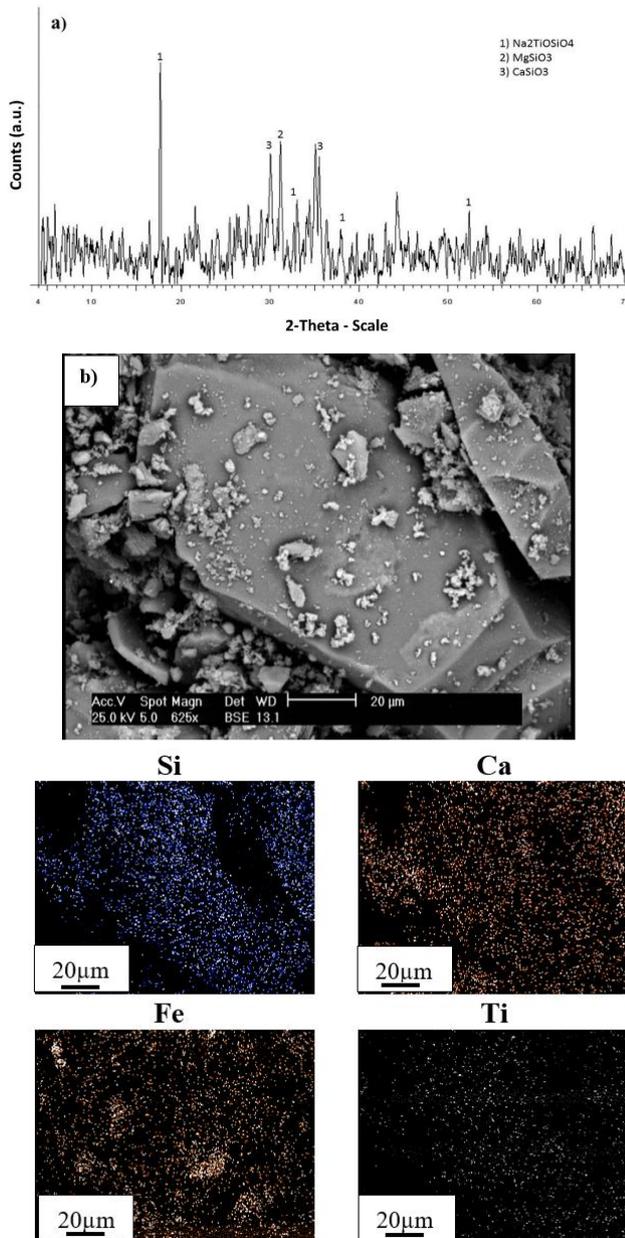


Figure 3. a) The XRD pattern of the roasted iron slag b) The SEM image and the WDX analysis of the roasted iron slag

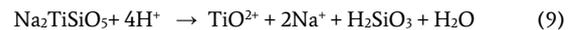
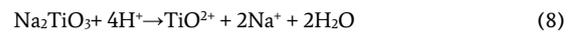
### 3.2. Effect of particle size

In order to investigate the effect of particle size on titanium dioxide recovery, experiments were carried out under the following conditions: temperature set at 50°C, sulfuric acid concentration of 3 M, stirring speed set at 250 rpm, solid to liquid ratio of 1/10, and time set two hours

with particle size dimensions of  $d_{80}=532, 160, 134, 114$  and  $106 \mu\text{m}$ . The results achieved are shown in Figure 4 (a). These results indicate that with a decrease in particle size, the recovery of titanium dioxide increased. By reducing the particle size, the number of liberated minerals and the specific surface area [29, 33] increases, therefore the recovery of titanium increases. By reducing the particle size from  $d_{80}=532$  to  $106 \mu\text{m}$ , the recovery of titanium dioxide increased significantly from about 30.6% to 40.4%. Therefore, the particle size of  $106 \mu\text{m}$  was selected as the optimum size for further experiments.

### 3.3. Effect of sulfuric acid concentration

When the roasted slag was digested by sulfuric acid and water-soluble sulfates (thiosulfate and ferro-sulfate) were formed, the titanium compounds were decomposed by acid, according to the Equations 8 and 9 [23, 24].



The concentration of acid was one of the factors affecting the recovery of materials in the leaching process. Therefore, to investigate the effect of sulfuric acid concentration on the recovery of titanium dioxide, concentrations of 0.5, 1, 1.5, 2, 3, 4, 5 and 6.5 M of acid were used. Experiments were carried out for different concentrations of acid concentration with following conditions: temperature 50 °C, a solid to liquid ratio of 1/10, a stirring speed of 250 rpm, particle size of  $106 \mu\text{m}$ , and two h of reaction time. The results obtained are presented in Figure 4 (b).

With increasing sulfuric acid concentration from 0.5 M to 2 M, recovery of titanium dioxide increased from about 9.4% to 43.4%. With a further increase in acid concentration, a slight reduction occurred in recovery. With more increase in acid concentration until 6.5 M, the recovery is almost constant. It was therefore clear that the optimum sulfuric acid concentration was 2 M, and that the recovery of titanium dioxide reached its maximum (43.4%) at this concentration.

### 3.4. Effect of liquid to solid ratio

In order to investigate the effect of liquid to solid ratio on the recovery of titanium dioxide, the other parameters were kept constant, and the ratio of liquid to solid was changed. The temperature of 50°C, the sulfuric acid concentration of 2 M (the optimum value obtained in the previous experiments), the particle size of  $106 \mu\text{m}$ , stirring speed of 250 rpm, and two hours of leaching time were determined as constant parameters in this experiment. The results of this series of experiments are presented in Figure 4 (c).

It is well known that higher liquid to solid ratio is associated with decrease in the degree of viscosity of the reacting slurry, which facilitates the transfer of reactants and products during the reaction [31]. According to the results, it can be stated that with increasing the ratio of liquid to solid, the recovery of titanium dioxide increased from five to fifteen depending on the liquid to solid ratio, ranging from 35.8% to 45.7%. Because when the ratio was five, the amount of acid was not enough to dissolve the titanium content. As the liquid to solid ratio increased, the recovery continued to increase. However, this increase was not significant; and while acid consumption increased, recovery increased very marginally (only 1%). Therefore, the optimum ratio of liquid to solid was considered to be 15, and experiments were continued with this liquid to solid ratio.

### 3.5. Effect of temperature

Temperature is usually one of the parameters that influence the chemical dissolution of materials within the experiments. In order to examine the effect of this parameter on the recovery of titanium dioxide, a series of experiments were carried out under conditions of 2 M sulfuric acid concentration, the particle size of  $106 \mu\text{m}$ , liquid to solid ratio of 15, stirring rate of 250 rpm and two hours of reaction time. In these experiments, temperatures of 30, 50, 65, 75, 85 and 100°C were tested. The results obtained are presented in Figure 4 (d).

According to the results, with increasing reaction temperature from 30 to 85°C, the recovery increased from 39.3% to 52.5%. This implies that the effect of temperature on the recovery of titanium dioxide was considerable. By increasing the temperature to 100°C, the recovery was almost constant. This suggests that the optimum reaction temperature was 85°C, and higher temperatures had no significant effect on the recovery of titanium dioxide.

### 3.6. Influence of time

Reaction time is another factor affecting recovery in chemical dissolution; often with an increase in reaction time, the recovery increases. In order to investigate the effect of reaction time on the recovery of titanium dioxide, other parameters were set at their optimal values. Titanium dioxide recovery values were tested and calculated after 10, 20, 30, 60, 90, 120, 240, 360 and 480 minutes. The results of the various time scales are presented in Figure 4 (e).

Figure 4 (e) shows that an increase in reaction time resulted in higher recovery; and after 240 min, about 52.8% of the titanium dioxide was recovered. The same graph also shows that a significant part of the recovery occurred within the first 10 min, as the reaction kinetics was very rapid during this period. The recovery after 10 minutes was 43.58%. After 10 min, the dissolution was progressing at a lower rate, and after 230 min recovery increased from about 10% to 52.8%. Allotting more time, the recovery decreased, and after 480 min, the recovery was approximately 47%. By increasing time (about 8h), the solution began to convert to gel, and the amount of Ti decreased. Therefore, according to the results of various experiments, the optimum reaction time was considered to be 240 min.

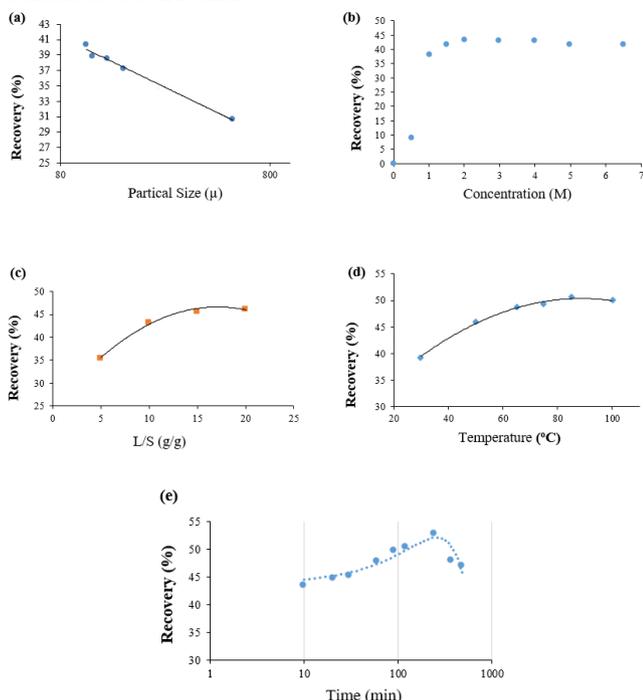


Figure 4. The effect of various parameters on the recovery of titanium dioxide, particle size (a), sulfuric acid concentration (b), liquid to solid ratio (c), temperature (d), time (e)

## 4. Reaction models

Two major processes in series, i.e., 1) The extraction of solute molecules from the solid surface, and 2) The diffusion of mentioned molecules into the bulk liquid phase can define the dissolution of solid particles in liquids [32]. Based on the conditions of the experiments, the dissolution rate can be under control of one of these two steps [33-35]. The most critical non-catalytic fluid-solid reactions models are the shrinking core, shrinking particle, homogeneous, and finally the grain

models [36]. The shrinking core model has been widely used to model the leaching systems [37]. There are some steps in shrinking core model: 1) diffusion through the liquid film, 2) diffusion through the ash/product layer and 3) the chemical reaction at the surface of the solid particles [38].

The leaching of the roasted slag in the presence of sulfuric acid occurs based on Equations 8 and 9.

With a spherical geometry of particles and the surface chemical reaction as the slowest step, the following shrinking core model (Equation 10) can be used to define the dissolution kinetics [38].

$$kt = 1 - (1 - x)^{\frac{1}{3}} \quad (10)$$

Likewise, when the ash layer diffusion is the controlling step factor, the shrinking core model can be used in the form of Equation 11 [38].

$$kt = 1 - \frac{2}{3}x - (1 - x)^{\frac{2}{3}} \quad (11)$$

When both parameters of chemical reaction and diffusion control the process, some various models are suggested to define the reactions [39, 40].

In the systems with a high amount of sulfuric acid, the silicates will be dissolved to form silicic acid in the form of gel or condensate product and will attach to the surface of un-reacted particles. As a result, the leaching process will be controlled by the ash or product layer diffusion [15,46]. Thus, it is critical to recognize the rate-controlling step.

In order to recognize the kinetic mechanism of the dissolution of roasted slag, the reactions were modeled at various temperatures and plotted versus time. Table 3 shows the several kinetic models, in which "X" defines the fraction reacted, "K" denotes the kinetic constant, and "t" represents the time.

Table 3. Several kinetic models

| Eq. no. | Model   | Mechanism  | References |
|---------|---|--|------------|
| 12      | $kt = 1 - (1 - x)^{\frac{2}{3}}$  | Mixed control model by shrinking core model (diffusion control; chemical reaction control) | [41]       |
| 13      | $kt = (1 - (1 - x)^{\frac{1}{3}})^2$                                      | Diffusion through product layer  | [42]       |
| 14      | $kt = -\ln(1 - x)$  | Mixed control model (surface reaction control; and diffusion through sulfur layer)         | [43]       |
| 15      | $kt = 1 - \frac{2}{3}x - (1 - x)^{\frac{1}{3}}$                           | Diffusion through a porous product layer by shrinking core model                           | [44]       |
| 16      | $kt = \frac{1}{3} \ln(1 - x) + \left[ (1 - x)^{-\frac{1}{3}} - 1 \right]$ | Interfacial transfer and diffusion across the product layer                                | [20]       |
| 17      | $kt = 1 - 3(1 - x)^{\frac{2}{3}} + 2(1 - x)$                              | Diffusion of hydrogen ions through a product layer by shrinking core model                 | [45]       |
| 18      | $kt = \ln \frac{1}{1 - x} - \beta x$                                      | Diffusion through product layer  | [46]       |

### 4.1. Kinetics analysis and modeling

After the conduct of experiments which evaluated various parameters affecting the recovery of titanium dioxide, the leaching tests were performed at temperatures of 50, 65, and 85°C in order to study the prepared sample dissolution kinetics in sulfuric acid. About 80% of the prepared sample was in size range of +90 to -106 μm. Since the recovery of titanium dioxide is about 50% after 120 min, and with increasing time up to 240 min, the recovery increases only for 2%, leaching tests were carried out at the period of 120 min. A series of experiments was carried out under conditions of 2 M sulfuric acid concentration, solid to liquid ratio of 1/15, and stirring rate of 250 rpm. Some experiments were randomly chosen to be repeated (the data were not shown); it was found that the results were nearly close to each other and the error values were insignificant. Figure 5 shows the effect of temperature on the leaching process.

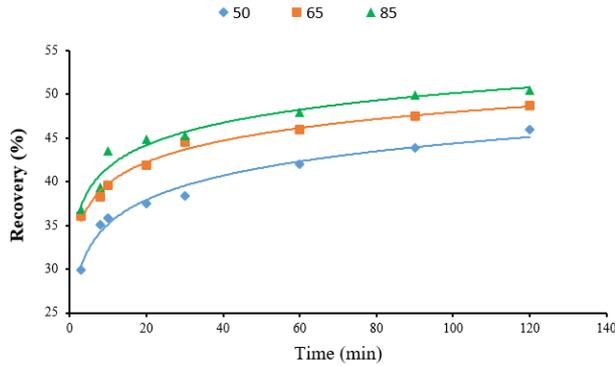


Figure 5. The Effect of temperature: (50 °C (◆), 65 °C (■), 85 °C (▲)) on the dissolution rate of 90-106 μm size

Linear regression, using the given equations in Table 3, was performed for all of the experimental data. The results show that Equation (7) can convert the empirical hyperbolic data to a linear trendline. The reaction rate constant ( $k$  ( $\text{min}^{-1}$ )) is intercepted, and the retardation coefficient ( $\beta$ ) is the slope [46].

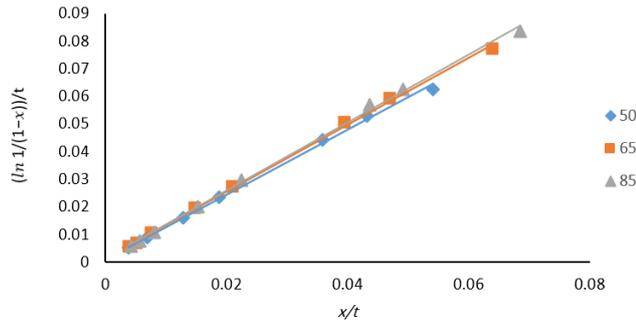


Figure 6. The plot of  $(\ln 1/(1-x))/t$  vs.  $x/t$  versus temperature for the recovery of  $\text{TiO}_2$

The Arrhenius equation shows the relationship between reaction temperature and  $k_r$  (Equation 19) [47].

$$k = A \exp\left(\frac{-E_a}{RT}\right) \rightarrow \ln k = \ln A - \frac{E_a}{RT} \quad (19)$$

The Arrhenius plot is presented in Figure 7. The values of the reaction rate, the correlation coefficient, and the retardation coefficient under different temperature are shown in Table 4. The correlation coefficient ( $R^2$ ) of the straight line in Figure 6 proves that the model is suitable [40-42]. The activation energy of the reaction is calculated from the slope of the line. This value which is 5.85 kJ/mol, confirms that the dissolution rate was controlled by diffusion. It was reported that the activation energy of the reaction controlled by diffusion was smaller than 40.0 kJ/mol [48, 49].

Table 4. The value of  $k$ ,  $\beta$  and  $R^2$  under different conditions

| Temperature °C | $k$    | $\beta$ | $R^2$  |
|----------------|--------|---------|--------|
| 50             | 0.0010 | 1.1779  | 0.9984 |
| 65             | 0.0013 | 1.2088  | 0.9989 |
| 85             | 0.0014 | 1.2309  | 0.9983 |

According to SEM image and WDX analyses, the effects of diffusion were observed on the particles, which included the dissolution of titanium compounds. The ash layer was formed on the surface of some particles. This layer is generally consisted of Ca, Si, and Fe. The formation of this layer on the surface of the particles shows that the leaching rate was controlled by diffusion.

## 5. Conclusion

This research was conducted on a blast furnace slag sample acquired

from Esfahan Steel Company, located in Esfahan province, Iran. The aim was to investigate the recovery of titanium dioxide by roasting and leaching through sulfuric acid. Several experiments were carried out to determine the optimal values of the influencing parameters on the process. The following conclusions were made following the results of this study. Titanium dioxide recovery increased from 31% to 39%, when the sample and sodium carbonate were combined in a ratio of 4 to 1 and heated at a temperature of 500°C in a muffle furnace for two hours. Water solubility (55°C, 30 min, solid to liquid ratio of 10/1) eliminated water soluble impurities and extra alkali from the roasted sample. The optimum conditions were obtained by leaching at the temperature of 85°C, the sulfuric acid concentration of 2 M, the solid/liquid ratio of 1/15, the particle size of 106 μm, and a reaction time of 240 min. Under such conditions, the recovery of titanium dioxide was 52.8%.

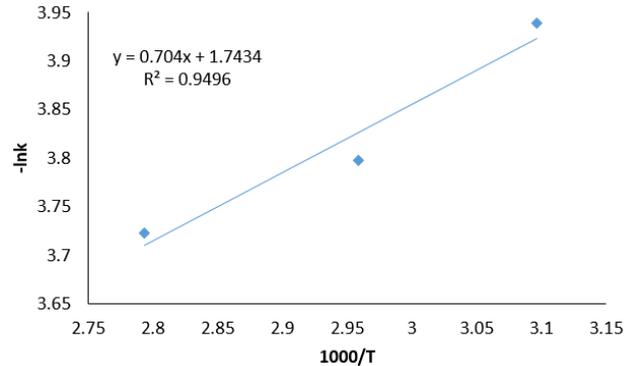


Figure 7. The Arrhenius plot

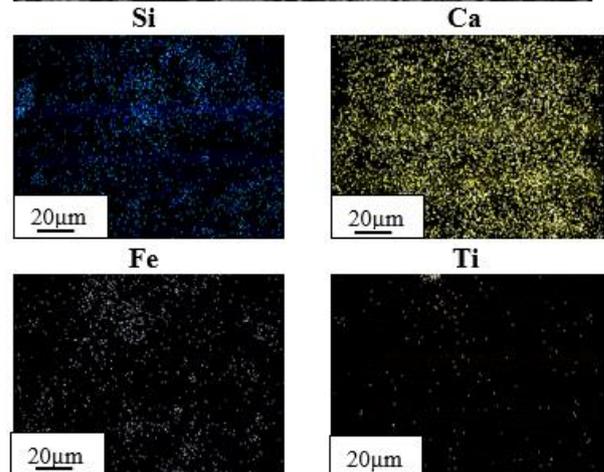
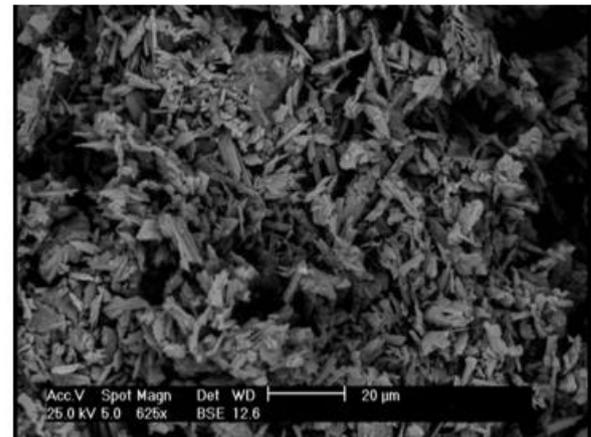


Figure 8. The SEM image and the WDX analysis of the sample surface after leaching

Kinetic studies showed that the leaching process was controlled by diffusion. The calculated activation energy of the reaction was equal to 5.85 kJ/mol.

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