Shahrood University of Technology
Iranian Society of Mining Engineering (IRSME)
Journal of Mining and Environment (JME)
journal homepage: www.jme.shahroodut.ac.ir
THOMSON REUTERS
Vol. 10, No. 3, 2019, 763-776.
DOI: 10.22044/jme.2019.8257.1700

Studying ilmenite dissolution using mechanical activation method

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Received 3 April 2019; received in revised form 16 May 2019; accepted 24 May 2019

Keywords

Ilmenite

Mechanical Activation

Dissolution

Design of Experiment

Abstract

In this work, the effects of temperature, acid concentration, and mechanical activation on dissolution of ilmenite were studied using the statistical design of experiment technique. Mechanical activation was carried out using a planetary ball mill in dry mode, and the resulting structural changes were characterized by the particle size analysis, specific surface area measurements, and X-ray diffraction method. The results obtained indicated that intensive milling led to a significant decrease in the ilmenite particle size and that after 20 minutes, particles tended to agglomerate. However, after 90 minutes, the BET specific surface area increased to 9.36 m^2/g. In addition to surface changes, mechanical activation led to intense changes and disorders in the crystal structure of ilmenite as amorphization degree increased to 94.30% and the volume weighted crystallite size and lattice strain changed from 346 nm and 0.13% to 14 nm and 1.44%, respectively. The results of the dissolution tests in the form of experimental design indicated that a suitable model could fit the experimental data in 95% confidence level. The coefficient factors for acid concentration, mechanical activation, and temperature were 3.75%, 33.04%, and 9%, respectively. Mechanical activation had the highest effect on titanium extraction in comparison to the other factors involved. Also in addition to its dominant effect on ilmenite dissolution, it also weakened the temperature effect. However, the results of the kinetic tests proved that mechanical activation led to promotion of the temperature effect on increasing the dissolution reaction rate in the initial stages. Finally, a dissolution yield of more than 98% was achieved through 90 minutes of activation at 95° C and 55 wt.% acid concentration.

1. Introduction

Ilmenite mineral ($FeTiO_3$) is one of the most valuable sources of titanium worldwide. As rutile sources are decreasing, currently, ilmenite is the most important resource of titanium extraction and the related compounds [1]. The most important application of ilmenite is in production of titanium dioxide (TiO_2) as a white pigment. The titanium pigment production is carried out through elimination of Fe from the ilmenite structure. Various industrial methods exist for this purpose. Different methods of metallurgical processing of titanium have been reviewed by Zhang *et al*. [2]. Ilmenite dissolution in sulfuric acid has a high applicably for titanium pigment production, and, currently, comprises 40% of titanium pigment production worldwide [3]. Numerous researchers have investigated dissolution of ilmenite by sulfuric acid and its effective parameters. Imahashi and takamatsu [4] have investigated the effects of temperature and sulfuric acid concentration on the ilmenite dissolution. They have concluded that acid concentration has a significant effect on ilmenite dissolution. Han *et al*. [5] have investigated the dissolution rate of ilmenite in sulfuric acid, and the related operational parameters including temperature, acid concentration, particle size, and mixing speed. Their results indicated that temperature, acid concentration, and particle size affected dissolution significantly but the effect of

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mixing speed was not significant. The maximum Ti extraction was obtained at a 14 M acid concentration, and the dissolution rate was characterized by the surface chemical control. Also Jackson and Wadsworth [6] studied the parameters effective on the ilmenite dissolution and concluded that temperature and acid concentration were the effective parameters but the effect of particle size was not significant. Zhang and Nicol [7] studied the kinetics of ilmenite dissolution in sulfuric acid in the presence of a reducing agent, and found that the effects of particle size and acid concentration on the ilmenite dissolution was not significant. However, the effect of temperature was more pronounced for promoting the dissolution rate. Jia *et al*. [8] studied the pressurized dissolution of ilmenite in sulfuric acid. Their results showed that temperature, acid concentration, and Fe^{2+} concentration were effective on the dissolution of iron and titanium from ilmenite. In low acid concentrations (about 20%), iron dissolution is more pronounced than titanium, and by increasing the temperature up to 150° C, the iron dissolution rate increases significantly and the titanium dissolution rate decreases due to the hydrolysis phenomenon.

The sulfate method faces problems due to harsh conditions of titanium dissolution including high sulfuric acid concentration, high temperature, and production of a huge amount of acidic wastes and other related environmental issues. According to the reports, 8 tons of 20 wt.% concentrated acid in each hydrolysis step and vast amounts of low concentration acid in each step of dissolution are produced per ton of titanium pigment. All the produced acids are not reusable in the process [3]. By reusing a low acid concertation in the dissolution step, the mentioned problems have been resolved significantly. Therefore, numerous researchers have investigated promoting the dissolution process and the reactivity of ilmenite in sulfuric acid [1, 3, 9-12]. Mechanical activation is one of the most effective methods involved in the promotion of the ilmenite reactivity. Mechanical activation acts through applying a high mechanical energy by mills including planetary mill. In this process, the resistant structure of the mineral is weakened and the structural changes including decreased particles size, increased specific area, increased structural disorders, decreased crystallite size, increased lattice strain, etc. occur in the sample [13]. As a result of the mentioned changes, reactivity of samples is promoted and application of a low acid concertation for dissolution of samples would be feasible. Welham and Llewellyn [12] investigated the effect of mechanical activation on promoting the dissolution of ilmenite. They concluded that mechanical activation increased active boundaries of crystals, which led to dissolution of ilmenite and a decreased activation energy. Chen *et al*. [9] reported that high energy milling by ball milling led to a complete dissolution of ilmenite from beach sand resource at 100 °C. Hosseini *et al*. [14] studied Ti leaching from an activated ilmenite–Fe mixture by applying mechanical activation and HCl leaching. They reported a maximum recovery of Ti (80%) Ti from activated ilmenite. Other researchers have investigated the effect of mechanical activation on dissolution of ilmenite and the related changes in the kinetics behavior. In summary, mechanical activation had a significant effect on promoting the dissolution rate in every study, which resulted in an improved titanium extraction and decreased activation energy of dissolution [15-23]. Chun Li *et al*. [16] reported that ball milling of Panzhihua ilmenite partially activated ilmenite, and with the mechanically activated ilmenite, leaching conversion at 100 ^{o}C reached 82.1%. They did not report the interaction effects of mechanical activation and leaching temperature. Sasikumar *et al*. [18] studied the dissolution of altered beach sand ilmenite by HCl and H_2SO_4 acid. They concluded that the altered ilmenite showed different physico-chemical characteristics, and it was found to be more resistant to acid leaching in comparison to the less altered ilmenite. They reported that the dissolution of ilmenite increased monotonically with the milling time. They did not mention the main effects of temperature and mechanical activation and their interaction with the leaching process. According to these studies, increased specific surface area, increased structural disorder, decreased crystallite size, and lattice strain in milled samples lead to an increased ilmenite dissolution. However, despite the positive effects of temperature, acid concentration, and mechanical activation on dissolution, there is no study related to evaluating the contribution of these parameters or interaction effects of the mentioned parameters on promoting the dissolution process. Therefore, the goal of the current study was application of the design of experiments technique for investigating effect of temperature, acid concentration, and mechanical activation time on titanium extraction from the ilmenite concentrate. In addition to determining the effect of each parameter, the interaction

effects of the parameters involved were also studied.

2. Experimental

2.1. Materials

In this work, the ilmenite concentrate was acquired from the Qara-Aghaj flotation pilot plant. The Qara-Aghaj ore is an *in situ* and rock-type ilmenite deposit, and unlike the placer deposits, it has no alteration so that the electron probe micro-analysis (EPMA) carried out in 67 small points of the ilmenite surface showed that the chemical composition of the existing ilmenite was very close to the ideal ilmenite mineral (TiO_2 = 52.65% and FeO = 47.35%) (Table 1). The chemical composition analysis results are demonstrated in Table 2. These results indicate that high amounts of silicon and magnesium oxides exist in the sample, which are related to gangue minerals of hornblende and olivine type. Table 2 shows that LOI is equal to -3.12. The negative value is due to oxidation of Fe^{2+} ions to Fe^{3+} ions by adsorption of oxygen from the air during the heating step in the analysis. The XRD results (Figure 1) confirmed the presence of ilmenite and magnesium hornblende in the sample.

Table 1. EPMA analysis of small volumes of solid ilmenite in the concentrate.

	MgO	MnO	FeO	V_2O_3	Cr_2O_3	SiO_2	TiO_2	CaO	Al_2O_3	P_2O_5	Total
Average (wt.%)	1.18	1.22	45.04	0.45	0.03	0.20	50.60	0.13	0.26	0.02	98.96
SD*	0.53	0.36	1.09	0.23	0.03	0.30	2.18	0.09	0.32	0.02	1.77

*Standard deviation

Table 2. Chemical composition of the ilmenite concentrate.

Oxide	TiO_2	Fe_2O_3	SiO_2	Al_2O_3	CaO	MgO	MnO	P_2O_5	Cr_2O_3	Na_2O	LOI	Total
(Wt%)	45.50	50.50	3.45	0.35	0.38	2.30	0.88	0.12	0.02	0.2	-3.12	100.58

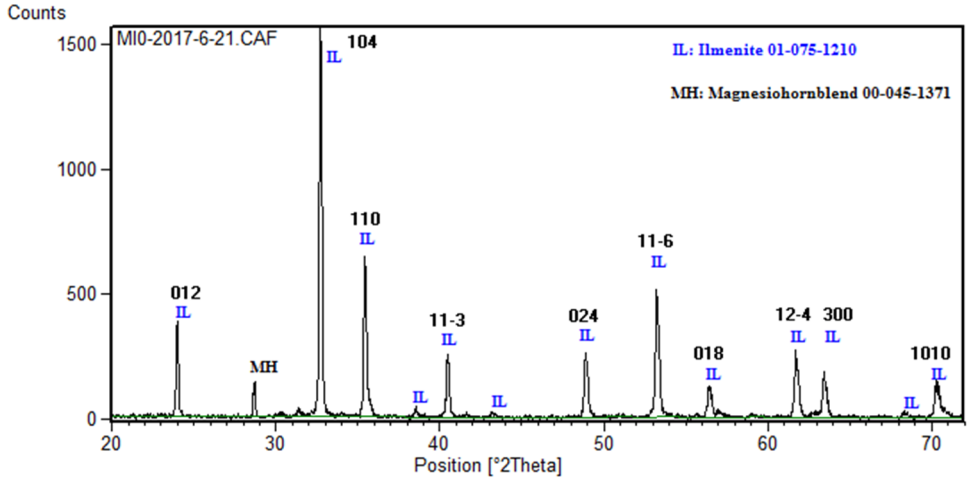

Figure 1. XRD pattern for the Qara-Aghaj ilmenite concentrate sample.

2.2. Characterization

The initial and mechanically activated samples were characterized using XRD, laser particle size analysis, and BET surface area measurements. The XRD patterns were collected by an X-ray powder diffractometer (Bruker Axs D8, Germany) using Cu Kα radiation (λ = 1.5406 Å) at 40 kV and 40 mA. The two theta range of 20–72°, step size of 0.02° and counting time of 3 s were set for all records. The X-ray diffraction patterns were indexed using the JCPDS (Joint Committee on Powder Diffraction Standards) files. The Winfit software [24] was used to line profile analysis of XRD patterns to extract the XRD line parameters. A laser diffraction instrument (Mastersizer 2000, Malvern, UK) was employed for particle size analysis of samples for measurement of granulometric surface area and mean particle size. Belsorp mini II (MicrotracBEL Corp, Japan) was employed for measurement of the specific surface area of the activated and non-activated samples using the BET (Brunauer–Emmett–Teller) method. EPMA analysis of the initial ilmenite concentrate was carried out by an electron probe micro-analyzer (SX100Cameca, France), which determined the chemical composition of small

volumes of mineral grains. Chemical analysis of Ti value in the leach solution was carried out using ultraviolet-visible spectroscopy (SPECORD 200, Germany).

2.3. Design of Experiments

In order to investigate the effects of acid concentration, temperature, and mechanical activation on the ilmenite dissolution process and relative effectiveness of these parameters on titanium extraction, Face-Centered Central Composite Design (FCCD) was used. In this scheme, by considering the upper, lower, and center points, a total of 17 experiments were determined. The levels of factors are depicted in Table 3.

Table 3. Factors of design of experiments.

Factors	Levels*		
	Lower (-1)	Central (0)	Upper (+1)
Temperature (°C)	80	95	110
Acid concentration (wt.%)	45	55	70
Mechanical activation time (min)	0	45	90

*Number inside the parentheses is the scaled and centered value

2.4. Mechanical activation and microstructure analysis

Mechanical activation of ilmenite by a planetary ball mill (Pulverisette 6, FRITSCH, Germany) was carried out for 20, 45, and 90 min. The mechanical activation was performed using 12 steel balls with a ball diameter of 19 mm, powder weight ratio of 15:1, and a mill rotational speed of 450 rpm. The milling conditions were kept fixed during the milling experiments.

In order to determine the effect of mechanical activation on the ilmenite structure and for measuring the microstructure parameters, the XRD line profile analysis was carried out. The XRD patterns for the initial and activated samples were analysed by the Winfit software and the parameters required for analysing the microstructure such as intensity and width of the peaks were extracted. The relative intensities of peaks were used for calculating the amorphization degree by the following formula, provided by Ohlberg and Strickler [25]:

$$A = 100 - x = 100 - \left(\frac{U_0}{I_0} \times \frac{I_X}{U_X} \times 100\right) \quad (1)$$

In this formula, A is the X-ray amorphization; U_x and U_0 denote the backgrounds of the activated and non-activated samples, while I_x and I_0 refer to the relative integral intensities of diffraction lines of the activated and non-activated samples, respectively. X denotes the degree of crystallinity. The amorphization degree was used as a criterion to consider the disordering of the crystal structure during mechanical activation. Integral breadth of the peaks were used for calculation of the lattice strain and volume weighted crystallite size by the Williamson-hall method using Eq. 2:

$$\beta_{hkl} COS\,\theta_{hkl} = \frac{K\lambda}{D_V} + 4\varepsilon \sin\theta_{hkl} \quad (2)$$

where θ is the Bragg angle of the (h k l) peak, λ is the wavelength of X-rays used, K is a constant (approx. 0.9), and ε is the lattice strain. The intercept and slope of the plot of $\beta_{hkl}\cos\theta_{hkl}$ as a function of $4\varepsilon\sin\theta_{hkl}$ (W-H plot) were used to calculate the domain size and lattice strain, respectively. A detailed explanation of the approach has been given in our previous work [26].

2.5. Dissolution tests

The dissolution tests were carried out in a three-necked balloon flask equipped with a condenser and a thermometer. A hot plate with a magnetic stirrer was used for controlling the temperature. In each test, firstly, 80 mL of a sulfuric acid solution of a given concentration was added to the balloon flask, which was heated up to the desired temperature. Then 4 g of ilmenite powder was added and stirred for 210 min at a constant speed. After filtration, the liquor obtained was analysed by the UV method.

3. Results and discussion

3.1. Effect of mechanical activation on structural changes of ilmenite

The mechanical energy transferred to the samples in high energy mills with a high loading rate initially results in brittle fractures of the particles, and hence, a significant decrease in the particle size. As the milling continues, brittle fracture changes to plastic deformation, and no significant decrease in the particle size is observed [27]. Following the surface energy increase of the

activated samples, welding of the particles leads to agglomeration of small particles, and particle size increases. Figure 2 demonstrates the particle size distribution of the ilmenite concentrate at different time intervals during dry milling. The ilmenite concentrate has a particle size distribution in the range of 10-100 microns. 20 minutes of milling leads to a significant decrease in the concentrate particle size to a range of 0.1-10 microns; however, an extended milling results in a reverse trend due to the agglomeration phenomenon, and causes the particle size to increase. Changes in the particle size results in granulometric, and the BET specific surface area changes. At the beginning of agglomeration, the granulometric surface area decreases. The results obtained are gathered in Figure 3. These results indicate that at the initial stages of milling, namely the initial 20 minutes, BET and granulometric specific surface area are close but by agglomeration and formation of larger particles, the granulometric specific surface area decreases. These changes demonstrate the significant effect of mechanical activation on the structural changes in the concentrate particles, which results in a higher specific surface area for the subsequent processes. After 90 minutes of milling, the BET surface area increases to 9.36 m^2/g.

In addition to the effect of mechanical activation on surface changes of the samples, energy transfer to bulk of particles leads to significant changes in structural order and crystal lattice of the activated samples. A strongly ordered crystal structure leads to a less tendency of the samples to involve in chemical reactions, especially dissolution. Therefore, the disordered structure of the activated samples could be an effective solution to promote reactivity and dissolution of resistant minerals such as ilmenite. Breaking of bonds in crystal lattice of minerals leads to a lower required activation energy and an increased dissolution rate [13]. Therefore, structural changes of ilmenite during high energy milling were determined by XRD analysis. The results of amorphization degree and decrease in relative XRD peak intensities are depicted in Table 4 and Figure 4. These results indicate that peak intensities are decreased significantly, and therefore, an amorphous structure should be formed. In the initial 20 minutes of milling, the amorphization degree is 66.41%, and in 90 minutes, it reaches 94.30%. By applying a high mechanical energy to the crystal lattice, the scattering domains are affected and shrunk. In addition, continuous loading in high energy mills leads to an increase in the strains applied on the lattice, which eventually leads to plastic deformations and a lattice strain [27].

The crystallite size and lattice strain were calculated using the Williamson-Hall method. The Williamson-Hall plots for the activated and non-activated ilmenite samples are depicted in Figure 5. The crystallite size and lattice strain inside the ilmenite lattice were calculated using plots of Figure 5, and the variations are shown in Figure 6. Accordingly, the crystallite size is decreased significantly from 346 nm at the initial state to 14.5 nm after 90 minutes of mechanical activation. Also the lattice strain increased from 0.13% to 1.44%. Altogether, significant changes in peak intensities, amorphous structure, lattice strain, and crystal size remarks the effectiveness of mechanical activation in creating structural disorders in the ilmenite particles.

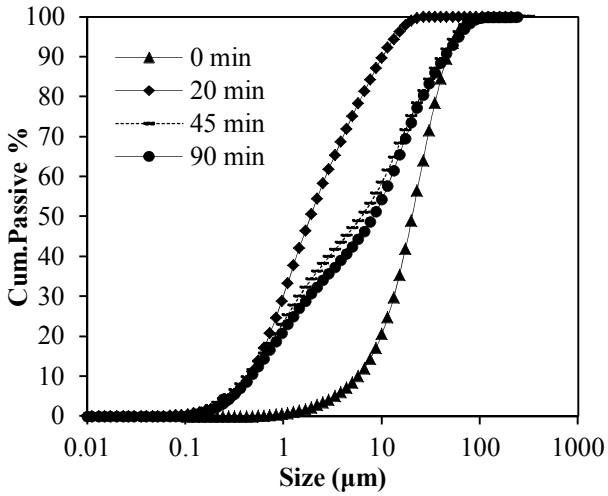

Figure 2. Changes in particle size distribution due to mechanical activation with different durations.

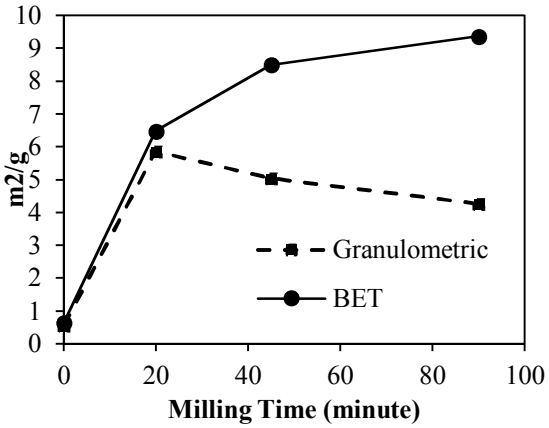

Figure 3. Changes in granulometric and BET specific surface area due to mechanical activation.

Table 4. Data of the amorphization degree calculations.

Time (min)	Average Intensity (cps)	Relative Intensity (%)	Background (cps)	X (%)	A=100-X (%)
0	357.5	100	8	100	0.00
20	150.1	41.98	10	33.58	66.41
45	82	22.93	14	13.10	86.89
90	33.1	9.26	13	5.69	94.30

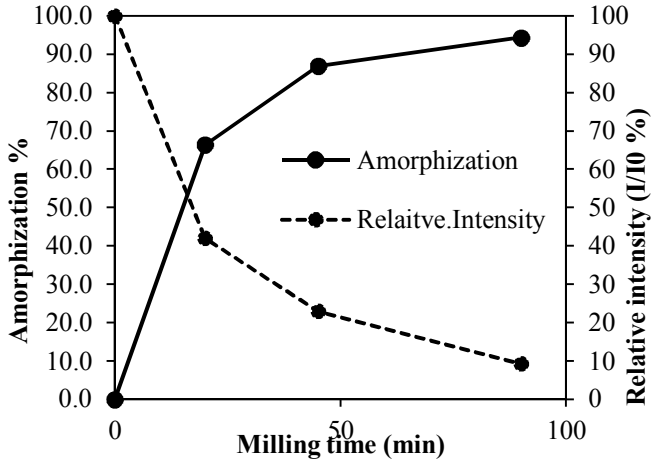

Figure 4. Increase in amorphization degree and relative decrease of ilmenite XRD pattern peak intensities with mechanical activation.

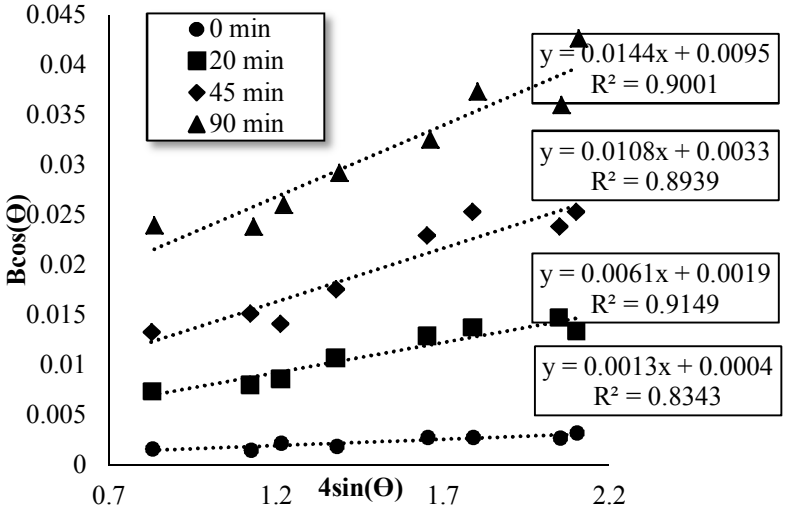

Figure 5. Williamson–Hall plots for the activated and non-activated ilmenite samples milled for different times.

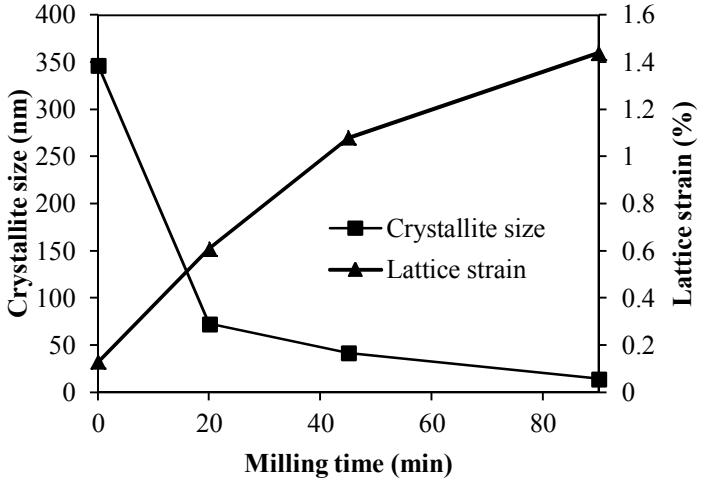

Figure 6. Crystal lattice strain increase and ilmenite crystal size decrease as functions of mechanical activation duration.

3.2. Dissolution tests

Once the experiments were performed according to the CCFD statistical design, the liquor samples obtained were analyzed, and the results obtained were summarized in Table 4. In Table 5, it can be seen that Ti extraction varies from 8.19% to 98.83% depending on the treatment conditions. It is clear that mechanical activation improved the Ti yield more significantly compared with the non-activated ilmenite.

Table 5. Results of the experiments.

Exp. Name	Acid conc. (wt.%)	Activation time (min)	T (°C)	Ti extraction (%)
N1	-1	-1	-1	8.19
N2	+1	-1	-1	15.95
N3	-1	+1	-1	80.26
N4	+1	+1	-1	98.61
N5	-1	-1	+1	44.42
N6	+1	-1	+1	46.47
N7	-1	+1	+1	98.83
N8	+1	+1	+1	93.79
N9	-1	0	0	84.03
N10	+1	0	0	98.48
N11	0	-1	0	24.87
N12	0	+1	0	98.79
N13	0	0	-1	85.72
N14	0	0	+1	95.24
N15	0	0	0	80.9
N16	0	0	0	83.88
N17	0	0	0	85.74

3.2.1. Statistical analysis and modeling

For an accurate analysis of the results and interpreting relations between factors and response, existence of out of range data is investigated. Therefore, the Deleted Studentized Residual analysis was carried out (Figure 7). The results obtained indicate that none of the data obtained is out of range. Therefore, modeling for the obtained data is reasonable. By accurate modeling, a correct understanding of the main effects and mutual effects of parameters is achievable. The established model (Eq. 3) is able to predict the response with a probability of 95% for specified values of factors. The fitting between the observed values and the predicted values for titanium extraction has a high correlation factor ($R^2 = 0.98.32$) (Figure 8).

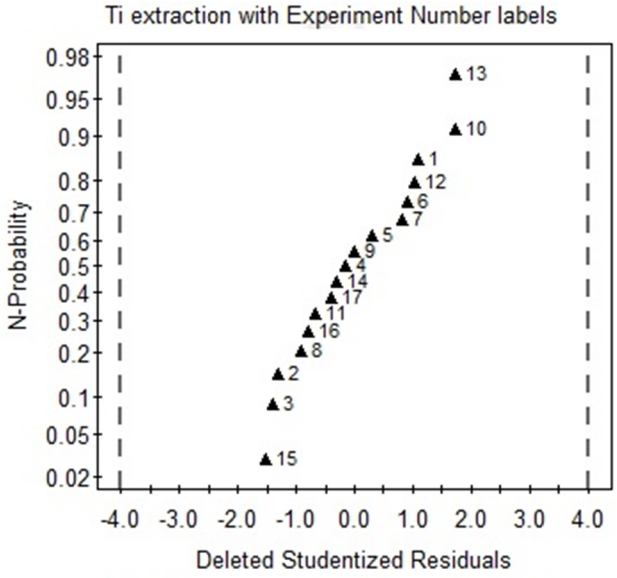

Figure 7. Deleted studentized residual analysis.

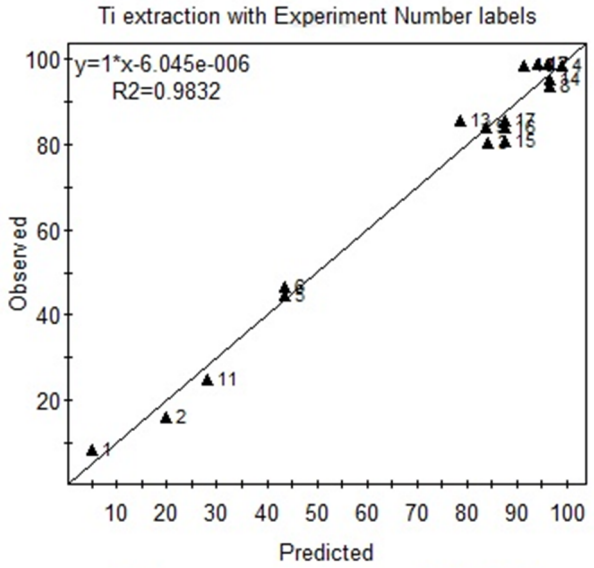

Figure 8. Correlation of observed and predicted values by the proposed model for titanium extraction.

The final model for titanium extraction based on the scaled and centered values is in the form of Eq. 3, where *ETi* is the percent of titanium extraction, X_1 is the acid concentration, X_2 is the duration of mechanical activation, and X_3 is the dissolution temperature.

$$ETi = 3.75x_1 + 33.045x_2 + 9x_3 - 26.7x_2^2 - 3.64x_1x_3 - 6.63x_2x_3 + 87.71 \quad (3)$$

In order to evaluate the model accuracy, four criteria, namely reproducibility, model validity, R^2 value, and productivity (Q^2) of the proposed model are investigated. An accurate model possesses a Q^2 value higher than 0.5, a confidence level more than 0.25, and a reproducibility more than 0.5. If the R^2 value for the model is close to 1, the model will possess a high accuracy but this criterion alone is not sufficient for commenting on the model accuracy. Also the difference between the R^2 and Q^2 values must not be more than 0.3 [28]. Figure 9 represents a summary of model fitting for the current model. The values obtained for R^2, Q^2, model validity, and reproducibility are 0.98, 0.94, 0.55, and 0.99, respectively. These values confirm the accuracy of the proposed model for evaluating the ilmenite dissolution data from temperature, mechanical activation time, and acid concentration as the factors involved. This plot indicates that within the determined ranges for the factors, the effects of main factors and interactions of factors on titanium extraction from ilmenite can be investigated.

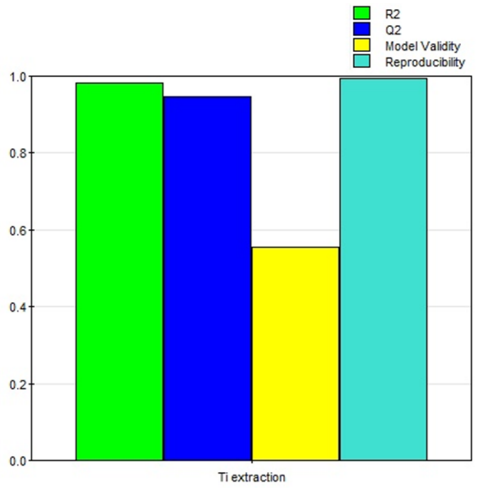

Figure 9. Summary of model fit.

3.2.2. Main effects and interaction of factors

The main effects of factors on the ilmenite dissolution is obtained from the model coefficient plot. This plot provides coefficients of factors for the obtained model. Therefore, it is possible to determine the relative effects of factors on the response. Figure 10 presents the model coefficients for titanium extraction. Accordingly, model coefficients for acid concentration, mechanical activation time, and temperature are 3.75%, 33.04%, and 9%, respectively. Therefore, the mechanical activation duration is the most effective factor. On the next level, temperature and then acid concentration have the highest effectiveness. Studies in the literature have remarked the important role of temperature on reactivity and dissolution of ilmenite, and their results indicate that titanium extraction increases as the temperature increases [5-7, 15, 18-20]. The results of the current work indicate that mechanical activation could have a more significant effect on promoting dissolution and reactivity of ilmenite in comparison to temperature. The reason is related to the interface where the reaction occurs. Increasing the temperature leads to more collisions between the reactant materials with an energy greater than the activation energy, and therefore, the reaction rate increases. However, for samples with a rigid crystal structure wherein each atom is constrained with strong bonds on each side, more energy is required for separating one atom from the surface and possibly participating in the reaction. Reaction of materials requiring breakage of bonds or formation of new bonds is usually slow [29]. Mechanical activation, and subsequently, specific surface area increase, lattice order reduction increases in defects, and finally, increase in free energy of materials leads to decreased activation energy and increased possibility of reaction between reactants. Due to increased free energy and weakened bonds in surface activated materials, collisions with lower energy could lead to reaction, and therefore, the possibility of reaction occurrence in lower temperatures will increase. Therefore, the temperature effect will decrease. The results obtained from the current study point out to the mentioned phenomenon as it is obvious that the mechanical activation time is more effective on titanium extraction from ilmenite in comparison to temperature and acid concentration.

Plots of mutual interactions of mechanical activation time and acid concentration with temperature are shown in Figures 11 and 12. The results of the current work suggest that the mechanical activation possesses the highest effectivity in dissolution of ilmenite in comparison to the other factors involved. Moreover, the mechanical activation affects the temperature dependency of ilmenite dissolution. As mentioned earlier, mechanical activation reduces the temperature effect. According to Figure 11 for non-activated ilmenite, temperature has its highest effect on dissolution, achieving up to 30% titanium extraction improvement but as mechanical activation time increases, this effect reduces and the two curves slowly approach each other.

Acid concentration acts similar to temperature in increasing the reactivity. As the acid concentration increases, concentration of the dissolution agent (H^+) and its effective collisions with ilmenite surface increase. Therefore, dissolution rate and reactivity increase. As the temperature increases, this effect reduces, and high or low acid concentration results in similar titanium extraction values.

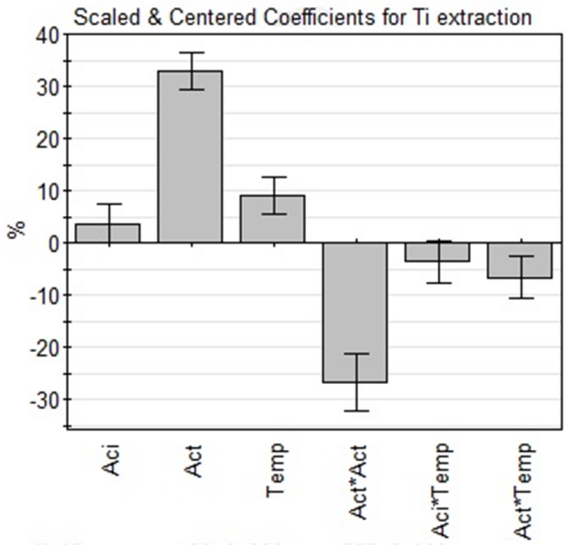

Figure 10. Plot of model coefficients for titanium extraction.

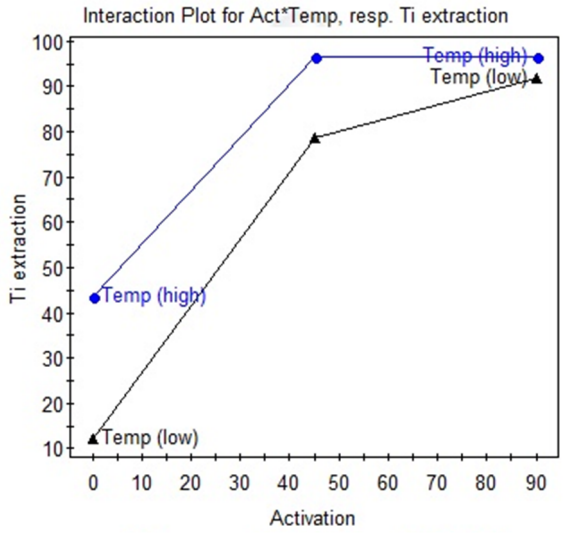

Figure 11. Plot of mutual interactions of temperature (high = 110 °C and low = 80 °C) and mechanical activation time.

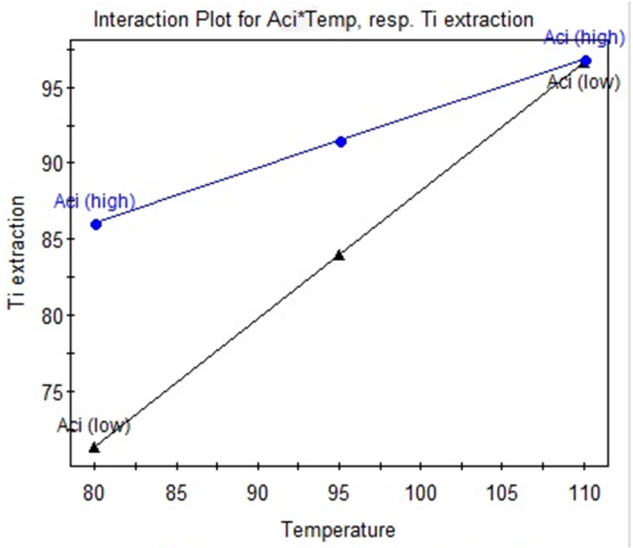

Figure 12. Plot of mutual interactions of acid concentration (high = 45 wt.% and low = 70 wt.%) and temperature.

However, the effect of mechanical activation on temperature is controversial at 210 minutes of dissolution. It is expected that not only mechanical activation does not reduce the temperature effect but also promotes it. This is because as the reactivity of reactant particles increases, small changes in temperature lead to increases in collisions with sufficient energy, and therefore, possibility of reaction increases. In order to investigate this possibility, kinetic tests for initial sample and activated sample were carried out at lower and upper levels of mechanical activation and temperature and at the middle level of acid concentration. The results obtained are shown in Figures 13 and 14. Comparing the kinetic plots of titanium extraction from non-activated and activated ilmenite samples at different temperatures indicate that the effects of temperature for the two samples are different. As it was expected, for the activated sample, due to the increased free energy of particles, activation energy of dissolution reaction is decreased so temperature increases the reaction rate significantly. These changes are more pronounced at the initial stages in comparison to late dissolution times. As activated particles promptly react at the initial stages, percentage of activated particles decreases over time and effect of temperature decreases during dissolution process so the two curves approach each other. Contrary to the activated sample, two kinetic curves separate slowly for the non-activated sample, and temperature effect becomes more significant in the late times. Table 6 presents the kinetic coefficients for activated and non-activated samples at different temperatures for times of 200 and 35 minutes. Ratio of kinetic coefficients indicate that at 200 minutes, this ratio is higher for the non-activated sample in comparison to the activated one but at 35 minutes, the ratio is higher for the activated sample.

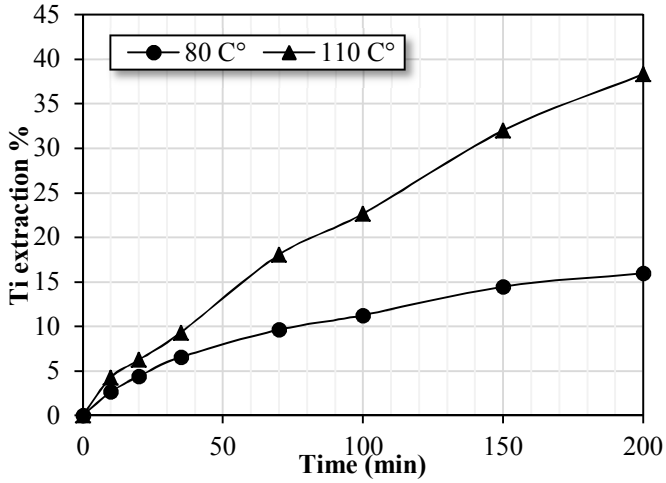

Figure 13. Effect of temperature on titanium extraction from non-activated ilmenite (acid = 55 wt.%).

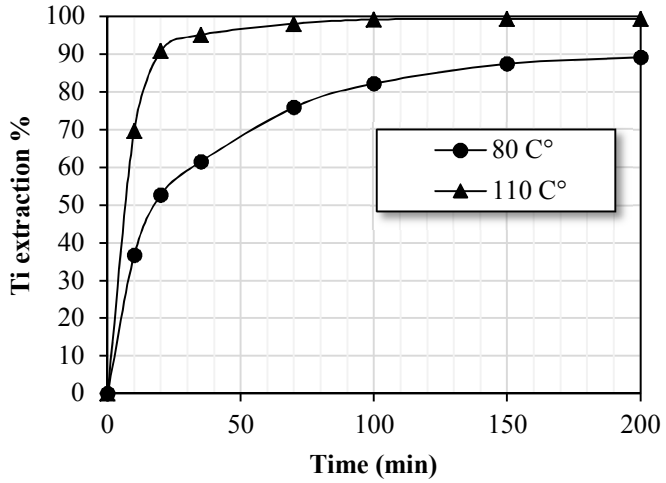

Figure 14. Effect of temperature on titanium extraction from activated ilmenite (acid = 55 wt.%).

Table 6. Kinetics coefficients for activated and non-activated samples.

Time (min)	Leaching kinetic coefficients of activated ilmenite (k (1/min))			Leaching kinetic coefficients of non-activated ilmenite(k (1/min))		
	80 C°	110° C	Ratio	80° C	110° C	Ratio
200	0.165	0.419	2.53	0.003	0.0096	3.2
35	0.158	0.505	3.2	0.0047	0.0067	1.42

3.2.3. Contour plot

The contour plot for titanium extraction versus temperature and mechanical activation time is plotted in Figure 15. Accordingly, the lowest titanium extraction is obtained at low temperatures and mechanical activation time. As activation time and temperature increase, titanium extraction increases. Contour plot indicates that maxima are obtained at elevated temperatures; however, the contour lines are extended towards longer times of mechanical activation. Therefore, as the mechanical activation time increases, maxima migrate towards lower temperatures. This is due to the higher reactivity of activated ilmenite, which results in a higher reactivity and an increased possibility of reaction at lower temperatures. The results obtained indicate that by 90 minutes of mechanical activation, at a temperature of 95 °C and with a 55 wt.% acid concentration, a dissolution yield more than 98% is achieved. Interestingly, in order to achieve a similar ilmenite dissolution yield in industrial processing, an acid concentration more than 80 wt.% and a temperature more than 150 °C are required. Despite the high efficiency of mechanical activation in improving the ilmenite dissolution recovery, there is no industrial scale mechanical activation pre-treatment of ilmenite in pigment production plants because of high energy consumption of the mechanical activation process. Some mills such as attrition mill, vibratory mill, and IsaMill were developed to industrialize the ultrafine grinding in minerals processing, and they had a high potential to become applicable in the industry [30]. 'Xstrata Technology' introduced the world's largest ultrafine grinding mill-2.6 MW M10000 IsaMill (10000 L volume) that can treat 50 tons of material per hour [31]. The Activox process is an alternative method to process the sulfide mineral concentrates. This process, which uses ultrafine grinding by IsaMill, is practical and cost effective [32].

In this research work, a maximum recovery of 98% was achieved, which was the highest when compared with the other researches, the results of which had reported maximum recoveries below 80% [3, 12, 17, 18].

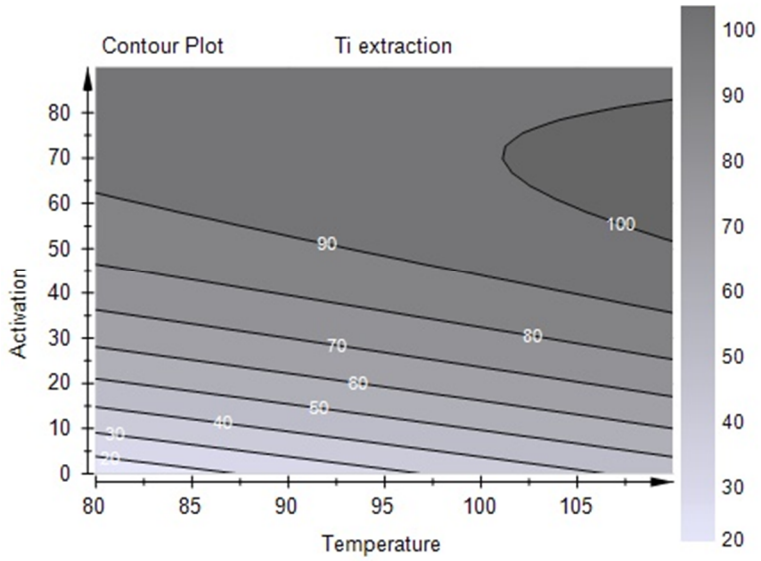

Figure 15. Contour plot for titanium extraction versus temperature and mechanical activation time at a mild acid concentration.

4. Conclusions

Mechanical activation and dissolution of ilmenite were studied by investigating temperature, acid concentration, and mechanical activation time through the design of experiment technique. The results obtained are summarized below:

1. Mechanical activation with dry planetary ball mill leads to decreased particle size, particle agglomeration, and increasing of BET specific surface up to 9.36 m^2/g
2. Mechanical activation leads to significant structural changes in the ilmenite structure as amorphization degree increases to 94.30% and also volume weighted crystallite size and lattice strain changes from 346 nm and 0.13% to 14 nm and 1.44%, respectively.
3. Modeling by experiment design technique provides an accurate model for data fitting with values of R^2, Q^2, model validity, and reproducibility as 0.98, 0.94, 0.55, and 0.99, respectively.
4. Model coefficients for factors, namely acid concentration, mechanical activation time, and temperature were obtained as 3.75%, 33.04%, and 9%, respectively. These values point out to their promoting effect on the dissolution process, and the mechanical activation has the most important effect in comparison to other factors.
5. In addition to the dominant effect of increasing ilmenite dissolution due to formation of defects and breakage of bonds inside the solid structure, mechanical activation leads to an increased reaction rate in lower temperatures and reduced effect of temperature factor. However, the kinetic tests revealed that mechanical activation also led to a promoted effect of temperature at the initial stages of dissolution process.
6. The results of dissolution tests revealed that mechanical activation and implementing structural defects was a powerful method for promoting the ilmenite reactivity, and therefore, by 90 minutes of mechanical activation at 95 °C and 55% acid concentration, a dissolution yield more than 98% was achievable.

Acknowledgments

The support from the Mineral Processing Research Center of the Sahand University of Technology is gratefully acknowledged. The authors also acknowledge the Iranian Mines & Mining Industries Development & Renovation, IMIDRO, for financial supporting of this research (No. 6210, Cod. 622).

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مطالعه انحلال ایلمنیت با استفاده از روش فعال‌سازی مکانیکی

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ارسال ۲۰۱۹/۴/۳، پذیرش ۲۰۱۹/۵/۲۴

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چکیده:

در این پژوهش، تأثیر دما، غلظت اسید و فعال‌سازی مکانیکی بر انحلال ایلمنیت با استفاده از تکنیک آماری طراحی آزمایش مطالعه شده است. فعال‌سازی مکانیکی با استفاده از یک آسیای سیاره‌ای در مد خشک انجام شد و تغییرات ساختاری ایجاد شده با روش‌های آنالیز اندازه ذرات، اندازه‌گیری سطح مخصوص و پراش پرتو ایکس مورد شناسایی قرار گرفت. نتایج حاصل نشان داد که آسیا کاری شدت بالا منجر به کاهش شدید در اندازه ذرات می‌شود و بعد از مدت زمان ۲۰ دقیقه ذرات اگلومره می‌شوند. با این وجود بعد از زمان ۹۰ دقیقه سطح مخصوص BET به میزان $9.36\ m^2/g$ افزایش یافت. علاوه بر تغییرات سطحی، فعال‌سازی مکانیکی منجر به تغییرات شدید و بی‌نظمی در ساختار کریستال ایلمنیت می‌شود به طوری که درجه بی‌شکل شدگی به ٪۹۴/۳۰ افزایش و اندازه کریستالیت و کرنش شبکه به ترتیب از مقدار ۳۴۶ نانومتر و ٪۰/۱۳ به ۱۴ نانومتر و ٪۱/۴۴ تغیر یافت. نتایج آزمایش‌های انحلال در قالب طرح آزمایشی نشان داد که یک مدل مناسب در سطح اعتماد مهندسی ۹۵ درصد قادر به برازش داده‌های تجربی می‌باشد. فاکتور ضرایب مدل برای غلظت اسید، زمان فعال‌سازی مکانیکی و دما به ترتیب برابر با ٪۳/۷۵، ٪۳۳/۰۴ و ٪۹ می‌باشد. در مقایسه با دیگر متغیرها فعال‌سازی مکانیکی دارای بیشترین تأثیر در استخراج تیتانیوم می‌باشد. علاوه بر تأثیر عمده بر انحلال ایلمنیت، فعال‌سازی مکانیکی منجر به تضعیف اثر دما می‌شود. با این وجود نتایج آزمایش‌های سینتیکی ثابت کرد که فعال‌سازی مکانیکی منجر به بهبود اثر دما در افزایش میزان نرخ واکنش انحلال در زمان‌های ابتدایی می‌گردد. در نهایت راندمان انحلال بیش از ٪۹۸ با فعال‌سازی مکانیکی ۹۰ دقیقه در دمای ۹۵ درجه سانتی‌گراد و غلظت اسید ۵۵ درصد وزنی به دست آمد.

کلمات کلیدی: ایلمنیت، فعال‌سازی مکانیکی، انحلال، طراحی آزمایش.