



Surface modification of ilmenite and its accompanied gangue minerals by thermal pretreatment: Application in flotation process

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Received 9 October 2020; accepted 8 April 2021

Abstract: The effect of conventional thermal pretreatment on the surface properties of ilmenite and its accompanied gangue minerals was investigated using flotation experiments (microflotation and laboratory cell flotation), XRD, XPS and FT-IR analysis and zeta potential and contact angle measurements. After treatment at 600 °C for 25 min as optimal condition, the floatability of ilmenite is improved from 73.5% to 91% at a pH value of 6.3. As demonstrated by XRD and XPS analysis, under this pretreatment condition, the Fe³⁺ content increases by almost 16.5% without any phase decomposition and structural changes in ilmenite. FT-IR analysis and contact angle and zeta potential measurements give evidences that the improvement of ilmenite floatability can be related to the enhancement of collector adsorption and the formation of a more insoluble hydrophobic layer of ferric iron oleate. The ore flotation experiments show that the thermal pretreatment process without making a significant change in TiO₂ content of ilmenite concentrate enhances the TiO₂ recovery from 65.4% to 73.7%.

Key words: ilmenite; thermal pretreatment; flotation; zeta potential; sodium oleate

1 Introduction

By decreasing the ore grades and minerals liberation degree, the common physical separation methods are not efficient enough anymore. For this reason, the froth flotation as an efficient method for beneficiation of fine particle ores has been considered significantly. This method has been used for sulfide minerals easily and successfully for many years. But, in the case of oxide ores, the similar surface properties of minerals make it difficult to achieve a selective flotation [1–3]. However, activation and depressant agents have been commonly used for creating some differences between the surfaces of valuable and gangue minerals but some new methods have been recently applied for changing the surface of minerals and subsequently improving the collector adsorption. In

these methods, the differences between the surface properties of minerals are created by selective removing of some active sites or by converting some surface cations to more active sites for adsorbing the collector [1–10].

Nowadays, ilmenite (FeTiO₃) as one of the most important oxide minerals is used for supplying of titanium dioxide and titanium metal [4]. Ilmenite having some properties such as high density, paramagnetic and conductivity is usually separated from the gangue minerals using gravity separation, high-intensity magnetic separation (HIMS) and electrostatic separation methods. These methods are not able to separate fine ilmenites effectively from the gangue minerals. The froth flotation can be an effective method for beneficiation of these kinds of ilmenites [4–13]. But, in comparison with minerals such as magnetite and rutile, ilmenite has relatively poor floatability [5–7]. For this reason, in recent

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DOI: 10.1016/S1003-6326(21)65697-2

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years, modification of ilmenite surface chemistry and improvement of its flotation behavior have been considered significantly [5–10,14–21]. Fan and ROWSON [6] have used activation by $\text{Pb}(\text{NO}_3)_2$ and the microwave radiation as a pretreatment method to improve the ilmenite floatability. The acid surface dissolution is another pretreatment method which has been applied to improving the ilmenite flotation behavior [9,10,22–24].

In the previous works, the surface oxidation has played a key role in the improvement of ilmenite flotation. The traditional heating is a relatively simple method for oxidizing of minerals which has been received less attention in the previous research works. In addition, in most of these researches, the improvement of ilmenite floatability has been investigated in the presence of iron-free gangue minerals such as quartz and feldspar while the iron-containing silicate minerals such as olivine and pyroxene are dominant gangue minerals accompanying ilmenite [9–10,25–33].

Thus, the aim of this work is the use of thermal pretreatment or oxidation roasting for modifying the surface chemistry of ilmenite and its usual accompanying iron-containing and iron-free gangue minerals. The effect of this pretreatment method on the flotation behavior of ilmenite and different gangue minerals was investigated in micro and cell flotation scales. Also, the minerals surface properties before and after thermal pretreatment were studied in detail using XPS, XRD and FTIR analysis and zeta potential and contact angle measurements.

2 Experimental

2.1 Materials

The samples used in this study were taken from Qara-aghaj titanium deposit located 36 km from Urmia in Azerbaijan province, northwest of

Iran. Based on the mineralogical characterization, this ore deposit contains olivine ($(\text{Mg,Fe})_2\text{SiO}_4$), pyroxene, tremolite ($\text{Ca}_2\text{Mg}_5\text{Si}_8\text{O}_{22}(\text{OH})_2$) and clinocllore ($(\text{Mg,Fe}^{2+})_5\text{Al}(\text{Si}_3\text{Al})\text{O}_{10}(\text{OH})_8$) as the main gangue minerals. Magnetite is the other valuable mineral in this ore [29,30].

The ilmenite ore sample after removing the magnetite by the Eriez low wet intensity magnetic separator was used in the ore flotation experiments. The chemical composition of this feed material is presented in Table 1. Based on the XRD, XRF and microprobe analysis and also the results of heavy liquid separation tests, this ore sample contains almost 20%–25% ilmenite (IL), 45%–50% olivine–pyroxene (Ol–Px), 18%–23% tremolite–clinocllore (Tr–Cch), 8%–13% quartz (Q) and other light minerals [29–31]. The purified samples of ilmenite, Ol–Px, Tr–Cch and quartz were used in micro-flotation experiments to investigate their flotation behavior before and after thermal pretreatment. The first three purified phases were prepared after crushing and grinding of the hand-picked samples taken from the Qara-aghaj area under $150\text{ }\mu\text{m}$ as the ilmenite liberation degree [31]. The quartz sample was purchased from Mijouri Silica Mine, Qazvin province, Iran. The purification of the samples was conducted by sieving and several stages of tabling, low and high intensity magnetic separation methods. The chemical analysis of purified samples determined by XRF is given in Table 1. The TiO_2 content in the ilmenite samples is 46.2% which is relatively low. As determined by microprobe analysis, this can be related to the lower content of TiO_2 (48.02%) in the ilmenite lattice in comparison with theoretical value (56.2%). The lower content of TiO_2 in the ilmenite lattice is due to the replacement of Mg (5.43% MgO), V (1.85% V_2O_3) and Mn (0.30% MnO) in the ilmenite structure [34]. As observed from Table 1, the most important difference between the gangue minerals is their Fe,

Table 1 Chemical compositions of purified and ore samples (wt.%)

Sample	TiO_2	Fe_2O_3	MnO	V_2O_5	P_2O_5	CaO	MgO	SiO_2	Al_2O_3	Na_2O	LOI
Cell flotation feed	11.1	34.9	0.46	0.12	2.9	5.8	15	26.7	2.45	0.25	0.1
Ilmenite	46.2	48.6	1.04	0.29	0.24	0.38	2.53	0.19	0.44	–	0
Olivine–pyroxene (Ol–Px)	0.9	43	0.64	0.015	3.34	5.6	15.8	29.5	1.06	–	0
Tremolite–clinocllore (Tr–Cch)	0.74	17.7	0.17	0.059	0.078	5.9	19.8	43.3	4.8	–	7.1
Quartz	–	0.28	–	–	–	0.35	–	98.1	0.66	–	0.36

LOI–Loss of ignition

Si and Mg contents. The XRD patterns of purified samples [35] and their chemical composition indicate that their purity is almost more than 90%.

Sodium oleate ($C_{18}H_{33}NaO_2$) with a purity of 95% was used as an anionic collector. Sodium silicate (Na_2O_3Si) and lead(II) nitrate ($Pb(NO_3)_2$) were consumed as depressant and activation agents, respectively. The adjustment of pH was carried out using dilute solutions of analytical sulfuric acid and sodium hydroxide. Pine oil was used as a frother in the cell flotation experiments. All the experiments were carried out with distilled water at room temperature.

2.2 Methods

2.2.1 Determination of surface area

The surface area of ilmenite and different gangue mineral samples ground under 15 μm was determined by the BET method using a high-speed gas sorption analyzer (Quantachrome Corporation, NOVA 1000, VERSION 6.10).

2.2.2 Thermal pretreatment

The thermal pretreatment or oxidation roasting was performed in a laboratory muffle furnace at 250, 500, 600, 750 and 950 $^{\circ}C$. Before placing the sample inside the furnace, it was heated to a predetermined temperature. The heating or oxidation roasting was conducted in the ceramic crucible and pan open to air. For microflotation experiments, 30 g of mineral sample was placed in a ceramic crucible and pan, while for carrying out the real ore flotation experiments, 300 g of ore sample was heated in a ceramic pan. At the end of the heating process, the crucible or pan was removed from the furnace, and cooled slowly in air at room temperature.

2.2.3 Microflotation experiments

Microflotation experiments were carried out on purified minerals before and after thermal pretreatment in 300 cm^3 Hallimond tube. In each test, 2 g of samples with size of 45–150 μm was added to the double distilled water and conditioned for 5 min. Then, the collector was added to the suspension and conditioned for 8 min. During the conditioning stage, the pH was adjusted to the required value with an accuracy of ± 0.02 . The prepared pulp was then transferred to the Hallimond tube where the flotation was carried out for 4 min. After the flotation tests, the concentrate and tailing were filtered, dried, and weighed. In the

experiments carried out to investigate the effects of activation and depressant agents, these reagents were added to the solution before the addition of collector, with 2 and 5 min conditioning time, respectively.

2.2.4 Ore flotation experiments

After grinding and desliming, 300 g of ore sample with size of 20–150 μm were subjected to the flotation experiments carried out in 11 Denver cell with a solid percentage of 25–30 wt.%. After mixing the pulp for 5 min, the activator, depressant and collector agents were added and conditioned for 2, 5 and 5 min, respectively. Finally, after adding pine oil (100 g/t) with a conditioning time of 2 min, the froth collection was performed for 4 min, after which the froth phase was brightened. During the experiment, the pH of the pulp was adjusted in a range of 6–6.5 with an accuracy of ± 0.02 . The flotation concentrate and tailing were filtered, dried and weighed, and chemically analyzed for determining the TiO_2 content.

2.2.5 XPS analysis

The XPS analysis was carried out with a Specs EA 10 X-ray photoelectron spectroscope on the ilmenite surface, before and after thermal pretreatment. This analysis was performed using an Al K_{α} X-ray source at 1486.6 eV. The measurements were carried out inside the analysis chamber operating in a high vacuum of about 10^{-7} Pa. Binding energies were calibrated using characteristic carbon (C 1s: 284.7 eV).

2.2.6 FT-IR analysis

The FT-IR analysis was carried out on mineral samples ground under 0.015 mm using NEXU670 FT-IR (Nicolet Corporation, USA) to characterize the nature of the interaction between the collector and the minerals. In each test, the suspension was prepared similar to the microflotation experiments.

2.2.7 Zeta potential measurement

The zeta potential of the mineral samples ground under 15 μm was measured using a Malvern instrument (Nano ZS, ZEN3600, UK). The suspension was prepared by adding 50 mg of pure minerals to 100 mL of distilled, deionized water containing 1×10^{-3} mol/L KCl as a supporting electrolyte. The prepared suspension was conditioned for 15 min during which the suspension pH was measured. The homogenized suspension was injected slowly in a rinsed and cleaned capillary cell by a capacity syringe of 2 mL. The

filled capillary cell was inserted in its own special place and the program was run to measure the zeta potential. The reported results are the average of at least three full repeat experiments. The measurement error was ± 2 mV.

2.2.8 Contact angle measurement

The sessile drop method was used to measure the contact angle of distilled water on a polished section of ilmenite before and after thermal pretreatment. The polished section after cleaning with distilled water in an ultrasonic bath was immersed in a given collector solution for 8 min at a desired pH. For removing the residual collector solutions from the treated surface, the sample was washed with distilled water and then air-dried at ambient temperature. In order to measure the contact angle, a water drop was placed on the sample by a micro syringe and then an image was taken by a camera. The Image J software was used for measuring the contact angle. The reported contact angle is the average of measured contact angles for at least five fresh drops placed at different locations of the sample. Using this measurement procedure, with 95% confidence intervals, the variation in contact angle was found to be within 3° .

3 Results

3.1 Microflotation

3.1.1 Temperature and time of thermal treatment

The flotation recovery of original ilmenite and pretreated ilmenites at different temperatures as a function of pH values is presented in Fig. 1. The maximum flotation recovery of non-treated ilmenite occurring at a pH of 6.3 is almost 73.5%. After thermal treatment up to 600 °C, the flotation recovery of ilmenite is greatly improved across a wide pH range. However, after pretreatment at 600 °C, the maximum increase occurs at pH values between 4.0 and 4.5 but the maximum flotation recovery of pretreated ilmenite (91%) is also achieved at pH 6.3. The improvement in ilmenite floatability in alkaline aqueous solutions is negligible. At temperatures above 600 °C, the ilmenite flotation recovery is not improved significantly. It is even decreased at higher temperatures. Thus, 600 °C at which the maximum improvement in ilmenite flotation recovery occurs is selected as the optimal temperature for the

thermal pretreatment process.

The flotation recovery of pretreated ilmenite at 600 °C as a function of retention time of the thermal treatment process is shown in Fig. 2. In these experiments, the thermal treatment tests were carried out in a ceramic pan. The increase of retention time enhances the ilmenite flotation recovery. The optimal flotation recovery of ilmenite is obtained after thermal pretreatment at 600 °C for 25 min.

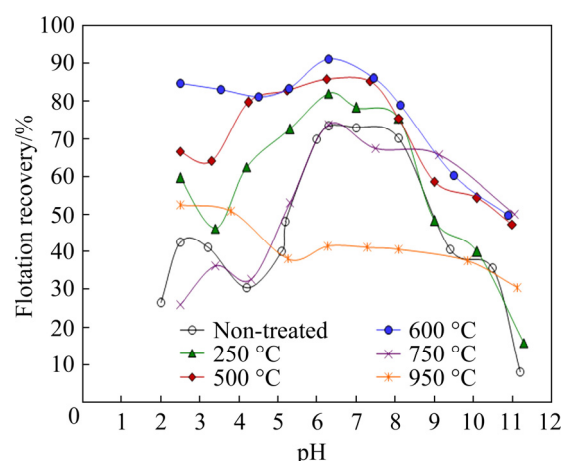


Fig. 1 Flotation recovery of ilmenite and thermally-treated ilmenite at different temperatures as function of pH (Concentration of sodium oleate: 3.65×10^{-4} mol/L)

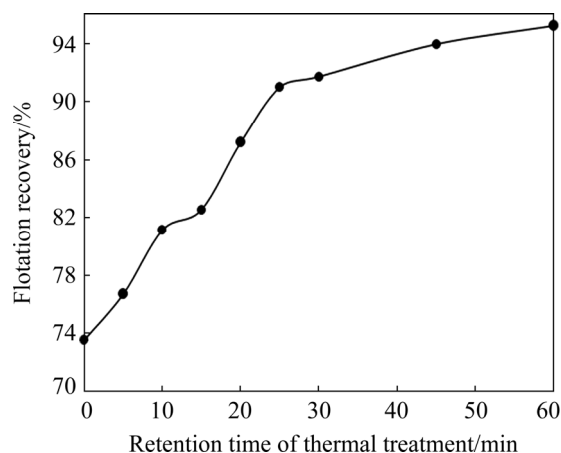


Fig. 2 Flotation recovery of thermally-treated ilmenite at 600 °C as function of retention time of thermal treatment (Concentration of sodium oleate: 3.65×10^{-4} mol/L)

3.1.2 Floatability of gangue minerals

The flotation behavior of Ol-Px and Tr-Cch as the main gangue minerals in the ore sample was also investigated under optimal conditions determined for ilmenite before and after thermal pretreatment. The results are shown in Fig. 3. The gangue minerals are floated in the alkaline solutions

easily. This can be due to presence of Mg or Ca species on the surface of these minerals and consequently their reaction with oleate ions [9]. The Tr-Cch is not floated significantly in the acidic solutions. While the thermal pretreatment increases the flotation recovery of Tr-Cch slightly at pH values less than 7.3, it increases the floatability of Ol-Px in a wide pH range. The maximum flotation recoveries of thermally treated Ol-Px and Tr-Cch are 80% and 58.5%, respectively, which are obtained in a pH range of 8.4–9. At pH 6.3, where ilmenite has the maximum floatability, the thermal pretreatment improves the differences between the flotation recoveries of ilmenite and gangue minerals from 14% to 16% and from 53.4% to 60% for Ol-Px and Tr-Cch, respectively. This shows that the thermal pretreatment can improve the flotation of ilmenite from Tr-Cch more selectively than Ol-Px. Thus, it is necessary to use a suitable depressant agent for Ol-Px.

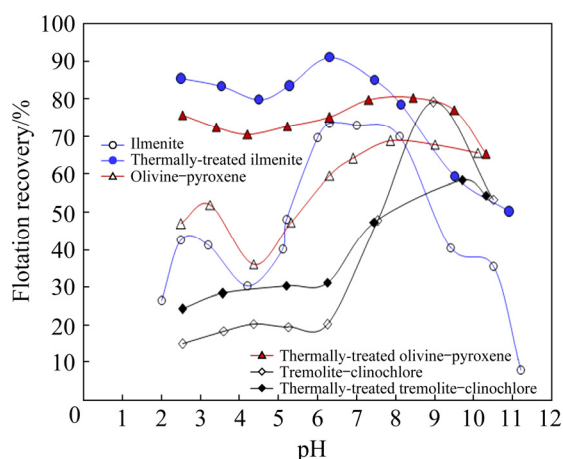


Fig. 3 Effect of thermal treatment on flotation recovery of ilmenite and gangue minerals (Sodium oleate: 3.65×10^{-4} mol/L, retention time of thermal treatment: 25 min, and temperature of thermal treatment: 600 °C)

3.1.3 Flotation reagents

The effect of sodium oleate dosage on the flotation recovery of non-treated ilmenite and thermally treated ilmenite at different temperatures at a constant pH of 6.3 is illustrated in Fig. 4. Before thermal pretreatment, the maximum flotation recovery of ilmenite is almost 73.5% which is achieved at 3.65×10^{-4} mol/L of sodium oleate. After pretreatment at temperatures of 500 and 600 °C, using only 1.83×10^{-4} mol/L of sodium oleate, the floatability of ilmenite reaches 83.3% and 85%, respectively. This shows that the thermal

pretreatment process decreases the consumption rate of the collector. However, after thermal pretreatment at 600 °C, the maximal and optimal flotation recovery of ilmenite also occurs in the presence of 3.65×10^{-4} mol/L sodium oleate.

The effect of $\text{Pb}(\text{NO}_3)_2$ as an activation agent on the flotation of ilmenite and thermally pretreated ilmenite and gangue minerals is presented in Fig. 5. Before thermal pretreatment, the maximum flotation recovery of ilmenite achieving in the presence of 4.2×10^{-5} mol/L $\text{Pb}(\text{NO}_3)_2$ is about 87%, while it increases to 93.5% for thermally pretreated ilmenite by consuming 2.1×10^{-5} mol/L $\text{Pb}(\text{NO}_3)_2$ only. Using this dosage of activator, differences between the flotation recovery of ilmenite and gangue minerals are 16.7% and 59% for Ol-Px and Tr-Cch, respectively. Thus, the highest difference

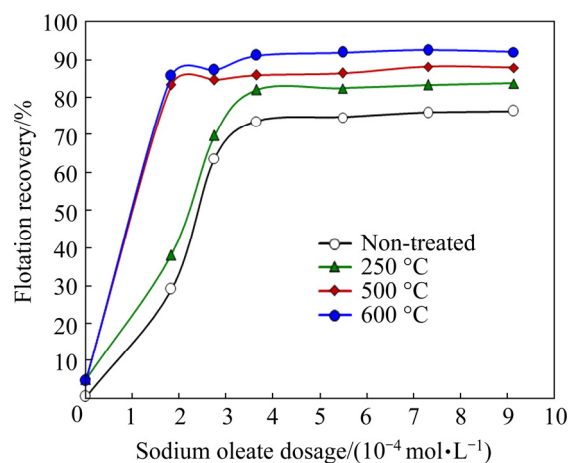


Fig. 4 Flotation recovery of ilmenite and thermally-treated ilmenite at different temperatures as function of sodium oleate concentration (pH 6.3)

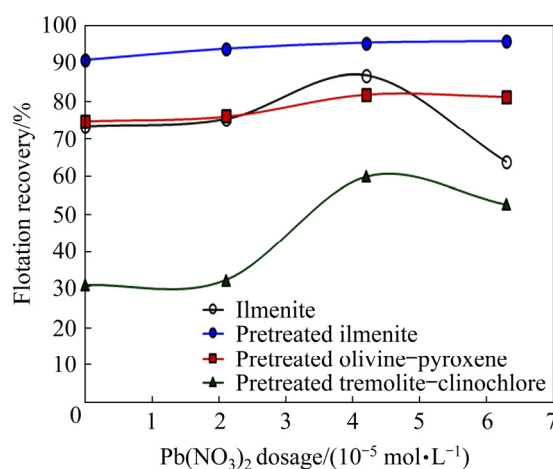


Fig. 5 Flotation recovery of ilmenite, olivine-pyroxene and tremolite-clinocllore as function of activator dosage before and after thermal pretreatment (Sodium oleate: 3.65×10^{-4} mol/L, and pH 6.3)

between the flotation recoveries of ilmenite and gangue minerals is achieved when the activation agent is used after thermal pretreatment process.

After investigation, various depressants including sodium hexa metaphosphate (SHM), quebracho and acidified sodium silicate (SS) with sulfuric acid (SA) at ratios of 1:1 and 1:2, and the acidified sodium silicate (SS) with sulfuric acid (SA) at ratios of 1:2, were selected as depressant agents for gangue minerals [35]. Figure 6 shows the effect of depressant dosage on the flotation recovery of ilmenite, Ol-Px and Tr-Cch before and after thermal pretreatment.

Using the acidified sodium silicate, Ol-Px is depressed more than ilmenite. The maximum differences between the flotation recoveries of ilmenite and Ol-Px before and after thermal pretreatment occurring at 400 and 600 g/t acidified sodium silicate are 38.4% and 25.7%, respectively. The highest differences between flotation recovery

of ilmenite and Tr-Cch occurring in the absence of depressant are 53.4% and 59.7% for non-treated and thermally treated states, respectively. This shows that without any depressant agent, the thermal pretreatment improves the separation of ilmenite from tremolite and clinocllore gangues through the froth flotation. As displayed in Fig. 6, after thermal pretreatment, the optimal amount of depressant is 200 g/t which results in the decrease of flotation recovery of ilmenite, Ol-Px and Tr-Cch from 91% to 63%, from 75% to 39.6% and from 31.2% to 15.1%, respectively. After thermal pretreatment, the depressant agent does not increase the differences between the flotation recovery of ilmenite and gangue minerals but it inhibits the further reduction of ilmenite floatability. Another point which should be noted is that the thermal pretreatment method decreases the consumption rate of depressant agent.

3.2 Ore flotation

Firstly, in order to investigate the effect of various gangue minerals on the separation of ilmenite by the froth flotation technique, the flotation experiments were carried out on the mixed samples. In these experiments, the pure ilmenite (20 wt.%) was mixed with each of the gangue minerals (80 wt.%). The results of these flotation experiments carried out on a synthetic ore sample before and after thermal pretreatment are given in Table 3. The separation efficiency (SE) and Gaudin's selectivity index (SI) were calculated using metallurgical parameters including TiO_2 grade and recovery. When the flotation feed is a mixture of ilmenite and quartz, the ilmenite concentrate has higher TiO_2 grade and recovery than those gained from other mixtures. The separation efficiency and

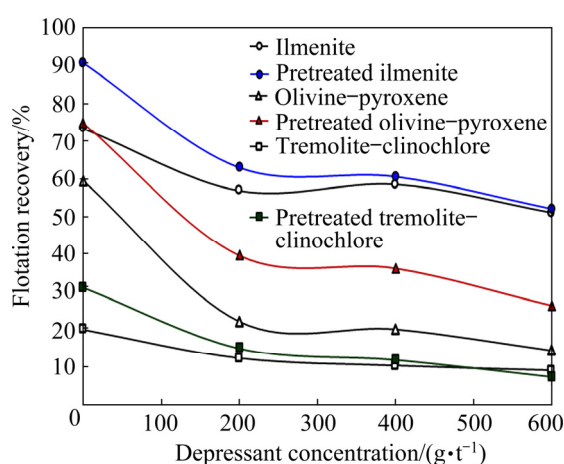


Fig. 6 Flotation recovery of ilmenite and gangue minerals as function of depressant concentration (SS:SA=1:2) before and after thermal pretreatment (Sodium oleate: 3.65×10^{-4} mol/L, and pH 6.3)

Table 3 Results of flotation separation of ilmenite from different gangue minerals before and after thermal pretreatment (Sodium oleate: 1000 g/t, and pH 6.3)

Process	Feed	Yield/%			TiO_2		SE/%	SI
		C	T	F	Grade/%	Recovery/%		
Before thermal pretreatment	IL+Q	32.3	67.7	100	27.1	85.3	69.0	5.47
	IL+Tr-Cch	35.8	64.2	100	21.3	71.0	50.6	3.3
	IL+Ol-Px	43.8	56.2	100	16.6	66.9	36.1	2.45
After thermal pretreatment (25 min at 600 °C)	IL+Q	33.6	66.4	100	28	92.0	75.6	7.66
	IL+Tr-Cch	38.9	61.1	100	22.3	80.3	59.81	4.0
	IL+Ol-Px	49.6	50.4	100	15.6	70.6	34.72	2.1

C-Concentrate; T-Tailing; F-Feed

selectivity index, and also the TiO_2 grade and recovery of ilmenite concentrate decrease by the increase of iron content in the gangue minerals. After thermal pretreatment, the TiO_2 grade and recovery in the ilmenite flotation concentrate is improved in the cases of IL+Q and IL+Tr–Cch, while they decrease slightly in the case of IL+OI–Px. As shown in Table 3, the separation efficiency and selectivity index also have the same trend.

The influence of thermal pretreatment on the flotation of ilmenite from ore sample was also investigated. The ore sample composed mainly of ilmenite, olivine, pyroxene, tremolite and clinocllore minerals (with chemical composition presented in Table 1) was used in the ore flotation experiments before and after thermal pretreatment at a pH value of 6.3. This feed was prepared by removing the magnetite from the Qara-aghaj ore sample by the magnetic separation method. Table 4 presents the flotation results obtained under optimal conditions for the ore sample before and after thermal pretreatment. The results show that the recovery of TiO_2 in the flotation concentrates improves from 65.4% to 73.7%, while the TiO_2 content is relatively constant.

3.3 Phase analysis

Figure 7 presents the XRD patterns of ilmenite and thermally pretreated ilmenite at different temperatures. After heating up to 600 °C, significant changes do not occur in the ilmenite structure. Decomposition of ilmenite to the hematite and rutile starts at the temperatures immediately above 600 °C. By increasing the temperature, ilmenite is oxidized to $\text{Fe}_2\text{O}_3\text{--}2\text{TiO}_2$ as an intermediate phase [36] which gradually is

converted to hematite and rutile. When the temperature reaches 750 °C, ilmenite is completely decomposed into the hematite and rutile phases. Further increase in the temperature (950 °C) results in the formation of pseudobrookite (Fe_2TiO_5) by recombination of hematite and rutile.

3.4 XPS analysis

The XPS spectra of $\text{Fe } 2p_{3/2}$ and $\text{Fe } 2p_{1/2}$ for original ilmenite and thermally pretreated ilmenite are illustrated in Fig. 8. Table 5 and Fig. 8 show the binding energies for Fe^{2+} and Fe^{3+} and their relative contents on the surface of ilmenite before and after thermal pretreatment. In the case of original ilmenite, the binding energies for $\text{Fe}^{2+} 2p_{3/2}$, $\text{Fe}^{3+} 2p_{3/2}$, $\text{Fe}^{2+} 2p_{1/2}$ and $\text{Fe}^{3+} 2p_{1/2}$ are 711.09, 714.39, 723.60 and 726.67 eV, respectively, which are shifted to 710.27, 712.48, 723.55 and 725.97 eV after thermal treatment at 600 °C. Moreover, the results indicate that the relative contents of total Fe^{2+} ($\text{Fe}^{2+} 2p_{3/2} + \text{Fe}^{2+} 2p_{1/2}$) and Fe^{3+} ($\text{Fe}^{3+} 2p_{3/2} + \text{Fe}^{3+} 2p_{1/2}$) on the surface of non-treated ilmenite are 51.7% and 48.3%, respectively. The content of Fe^{3+} on the surface of ilmenite is somewhat higher than that in usual state, which can be due to the dissemination of hematite exsolution lamellae in ilmenite [34]. After pretreatment at 600 °C, the total content of Fe^{3+} ($\text{Fe}^{3+} 2p_{3/2} + \text{Fe}^{3+} 2p_{1/2}$) on the surface of ilmenite reaches 64.6%. The increase of Fe^{3+} content through thermal pretreatment is in good agreement with the improvement of ilmenite floatability.

3.5 FT-IR analysis

Figure 9 shows the FT-IR spectra of non-treated and thermally treated ilmenite and gangue minerals conditioned with sodium oleate at a pH

Table 4 Results of ore flotation experiments before and after thermal pretreatment (1000 g/t sodium oleate, 1000 g/t acidified sodium silicate as depressant, 100 g/t $\text{Pb}(\text{NO}_3)_2$ as activator, 100 g/t pine oil as frother, and pH 6.3)

Process	Product	Proportion/%	TiO_2 content/wt. %	Recovery/%	SE/%
Before thermal pretreatment	Concentrate	34.4	21.1	65.4	
	Tailing	65.6	5.85	34.6	39.8
	Feed	100	11.1	100	
After thermal pretreatment (25 min at 600 °C)	Concentrate	39.3	20.8	73.7	
	Tailing	60.7	4.81	26.3	44.2
	Feed	100	11.1	100	

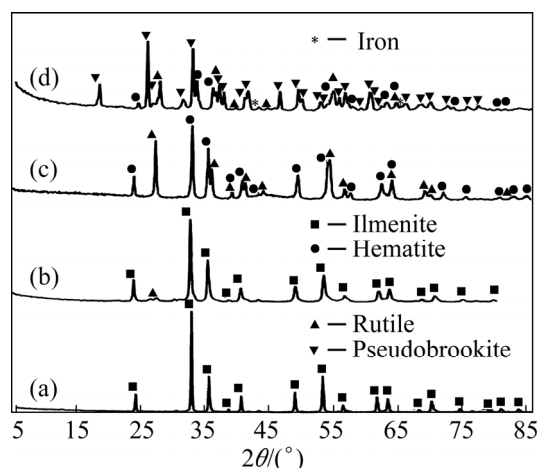


Fig. 7 XRD patterns of ilmenite and thermally-treated ilmenite at different temperatures: (a) Ilmenite; (b) Pretreated ilmenite at 600 °C; (c) Pretreated ilmenite at 750 °C; (d) Pretreated ilmenite at 950 °C

value of 6.3. The FT-IR spectra of ilmenite and gangue minerals show absorption around $1620\text{--}1635\text{ cm}^{-1}$ attributed to the bending mode of adsorbed water [37]. The bands around 2923 and 2852 cm^{-1} for different minerals are attributed to —CH_2 stretching of acyclic compounds [9,36–38].

The new bands around $1710\text{--}1750$ and $1500\text{--}1550\text{ cm}^{-1}$ are also related to the carboxyl (C=O) and carboxylate group of sodium oleate, respectively [37]. The formation of these bands indicates that sodium oleate is adsorbed on the surface of ilmenite and gangue minerals before and after pretreatment. The much weaker intensities of the bands for quartz in comparison with other minerals can be due to the less adsorption of oleate ions on the surface of quartz. In the case of ilmenite and iron containing gangue minerals, the new bands appearing at around 1580 and 1467 cm^{-1} are attributed to iron oleate [9,38–40]. This component showing the chemisorption of sodium oleate on the surface of ilmenite and iron containing gangue minerals is responsible for flotation of these minerals. The above new bands are not observed in the case of quartz mineral. Thus, the lack of quartz flotation can be due to the lack of oleate chemisorption on its surfaces. After thermal pretreatment, the new band appearing at $1570\text{--}1580\text{ cm}^{-1}$ for ilmenite and iron containing gangue minerals can be attributed to the formation of ferric iron oleate [16].

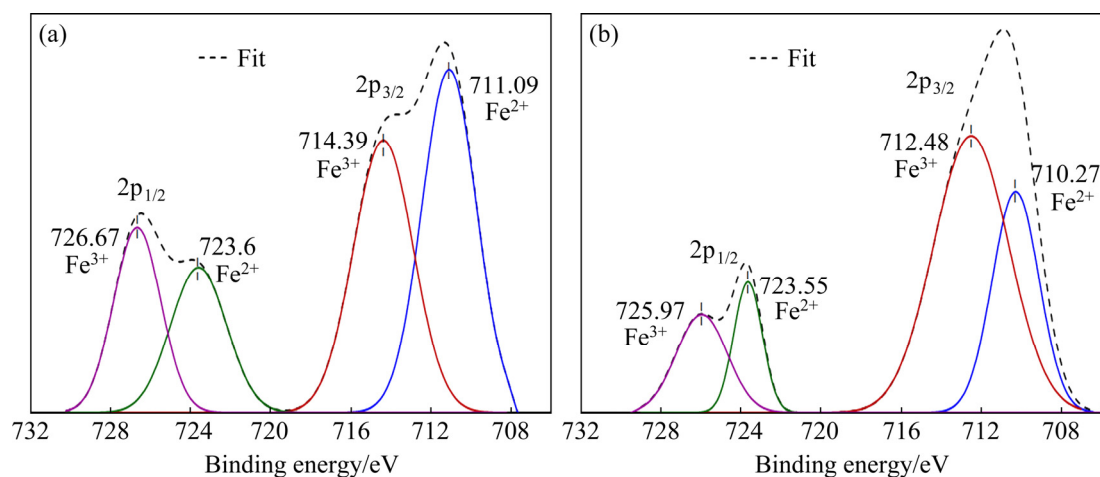


Fig. 8 XPS spectra of Fe $2p_{3/2}$ and Fe $2p_{1/2}$ for non-treated (a) and thermally-treated (b) ilmenite

Table 5 Binding energies and relative contents of Fe^{2+} and Fe^{3+} based on XPS analysis of ilmenite before and after pretreatment

Sample	Binding energy/eV				Fe content/%			
	$2p_{3/2}$		$2p_{1/2}$		$2p_{3/2}$		$2p_{1/2}$	
	Fe^{2+}	Fe^{3+}	Fe^{2+}	Fe^{3+}	Fe^{2+}	Fe^{3+}	Fe^{2+}	Fe^{3+}
Original ilmenite	711.09	714.39	723.6	726.67	36.1	31.5	15.6	16.8
Pretreated ilmenite	710.27	712.48	723.55	725.97	26	52.2	9.4	12.4

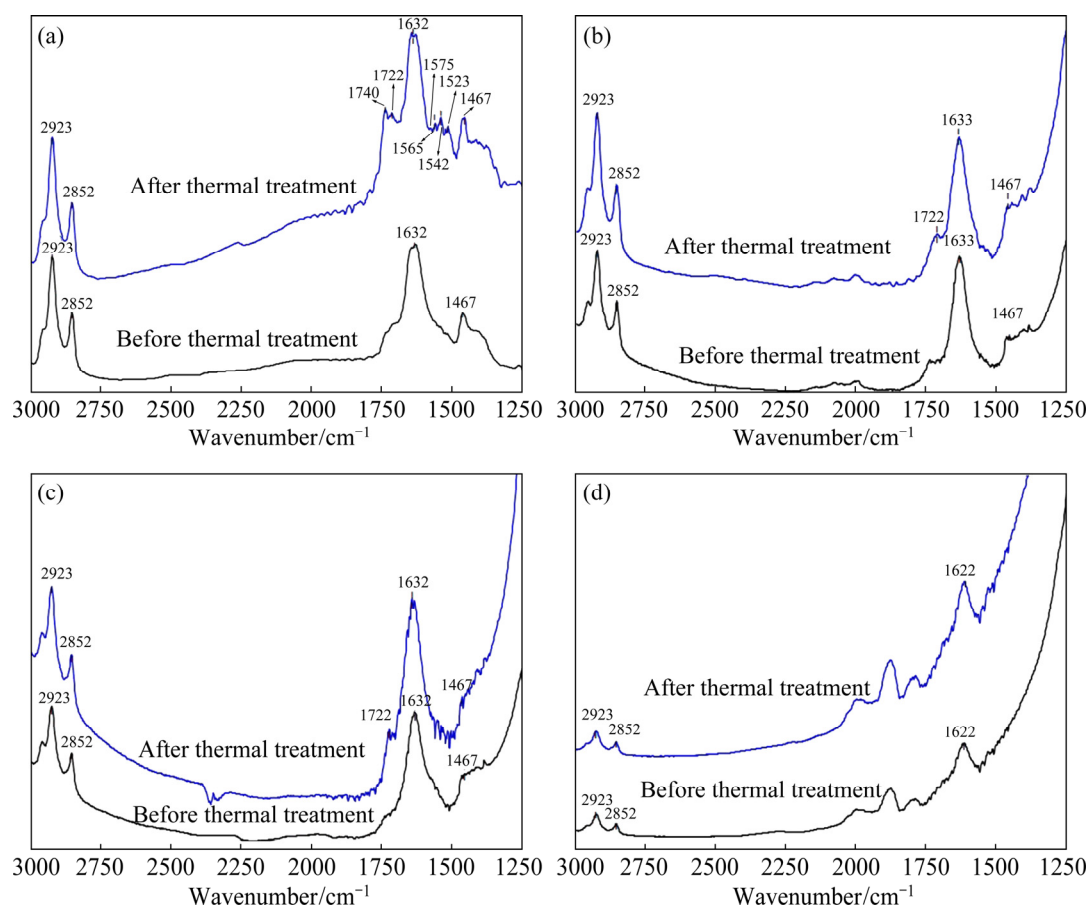


Fig. 9 FT-IR spectra of ilmenite and gangue minerals conditioned with sodium oleate before and after thermal pretreatment: (a) Ilmenite; (b) Olivine–pyroxene; (c) Tremolite–clinocllore; (d) Quartz (3.65×10^{-4} mol/L sodium oleate, pH 6.3, thermal pretreatment time: 25 min, and temperature of thermal pretreatment: 600 °C)

3.6 Zeta potential

The zeta potentials of ilmenite and thermally-treated ilmenite at various temperatures measured as a function of pH using 2×10^{-3} mol/L KCl solution as an electrolyte, are shown in Fig. 10. The IEP (iso-electric point) of ilmenite is located at a pH value of 5.4. After thermal pretreatment process, the zeta potential of ilmenite decreases over a pH range from 2.5 to 7.5. The IEP of ilmenite occurs at pH values of 4.6, 3.9, 2.9 and 3 for treated ilmenite at temperatures of 500, 600, 750 and 950 °C, respectively.

As shown in Fig. 11(a), using 3.65×10^{-4} mol/L sodium oleate, the zeta potential of different ilmenites displays a negative value over a wide pH range from 3 to 11. The IEP of ilmenite is shifted to a pH between 2.6 and 3.2. At a pH of 6.3, the zeta potential is -66.3 , -73.1 and -55.9 mV for raw ilmenite, thermal treated ilmenite at 600 °C and thermal treated ilmenite at 950 °C, respectively. Figures 11(b–d) present the zeta potential–pH

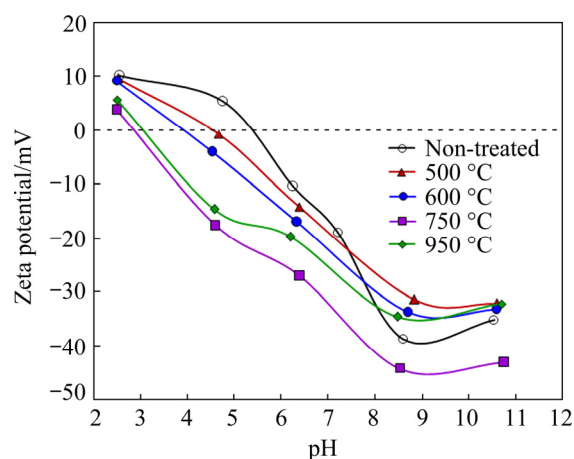


Fig. 10 Zeta potential of non-treated and thermally-treated ilmenite as function of pH

profiles of non-treated ilmenite and pretreated ilmenites at 600 and 950 °C in the presence and absence of sodium oleate. The collector adsorption changes the zeta potential significantly. At pH values between 3 and 11, in the presence of oleate

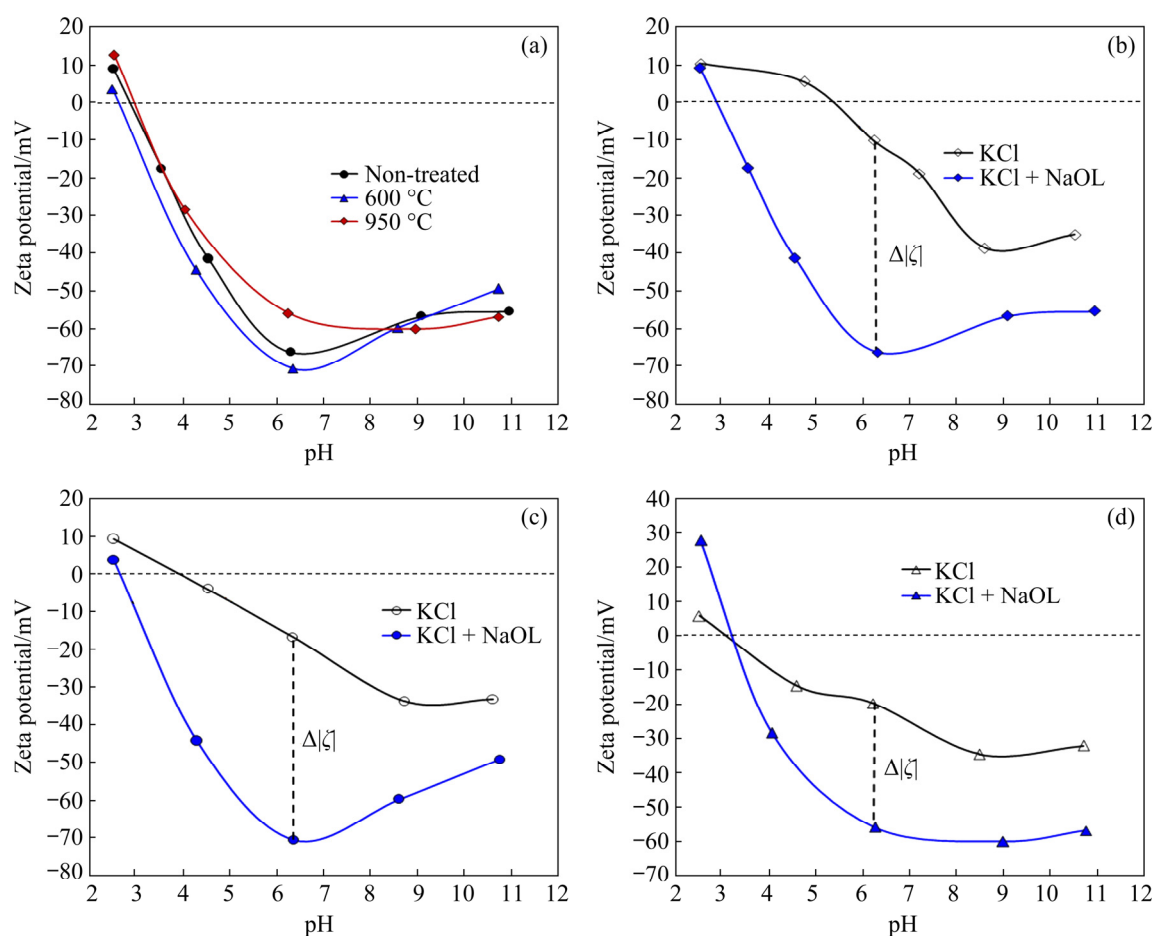


Fig. 11 Zeta potential of ilmenite and thermally-treated ilmenite as function of pH in presence of KCl (2×10^{-3} mol/L) and KCl + NaOL (3.65×10^{-4} mol/L sodium oleate and 2×10^{-3} mol/L KCl): (a) Different ilmenite in presence of KCl + NaOL; (b) Non-treated ilmenite; (c) Pretreated ilmenite at 600 °C; (d) Pretreated ilmenite at 950 °C

ions, the zeta potential of non-treated ilmenite and thermally treated ilmenite at 600 °C is considerably more negative than when only KCl is present. The more negative zeta potential is due to the strong adsorption of oleate ions.

Figure 12 displays the zeta potential–pH profiles of the non-treated and thermally-treated ilmenite and different gangue minerals in the absence and presence of sodium oleate. The IEP values of non-treated ilmenite, Ol–Px and Tr–Cch are located at pH values of 5.4, 3.8 and 4.4, respectively, while after thermal pretreatment these values are shifted to pH values between 2.5 and 3, respectively. This is due to the decrease of zeta potential by converting Fe^{2+} to Fe^{3+} ions on the surface of minerals. This relationship between Fe^{3+} content and IEP or zeta potential is in good agreement with the previous work [34].

In the presence of sodium oleate, the zeta

potential of ilmenite, Ol–Px and Tr–Cch display a negative value over a wide pH range from 3 to 11. The IEP values of all three phases are shifted to a pH between 2.5 and 3. As seen from Fig. 12, by using sodium oleate, the zeta potential of ilmenite at a pH of 6.3 before and after thermal treatment is more negative than that of other minerals. From this viewpoint, Ol–Px, Tr–Cch and quartz are ranked in the next places. This shows that at a pH value of 6.3, the negativity of zeta potential is proportional with the flotation recovery of these minerals (Fig. 3 and Table 3).

After thermal pretreatment, the decrease in the zeta potential of ilmenite, Ol–Px and Tr–Cch is due to the conversion of Fe^{2+} to Fe^{3+} on the surface of minerals, which results in the more attraction of negatively charged ions or polar groups entering the Helmholtz layer. This increases the floatability of all three phases and hence makes it difficult to

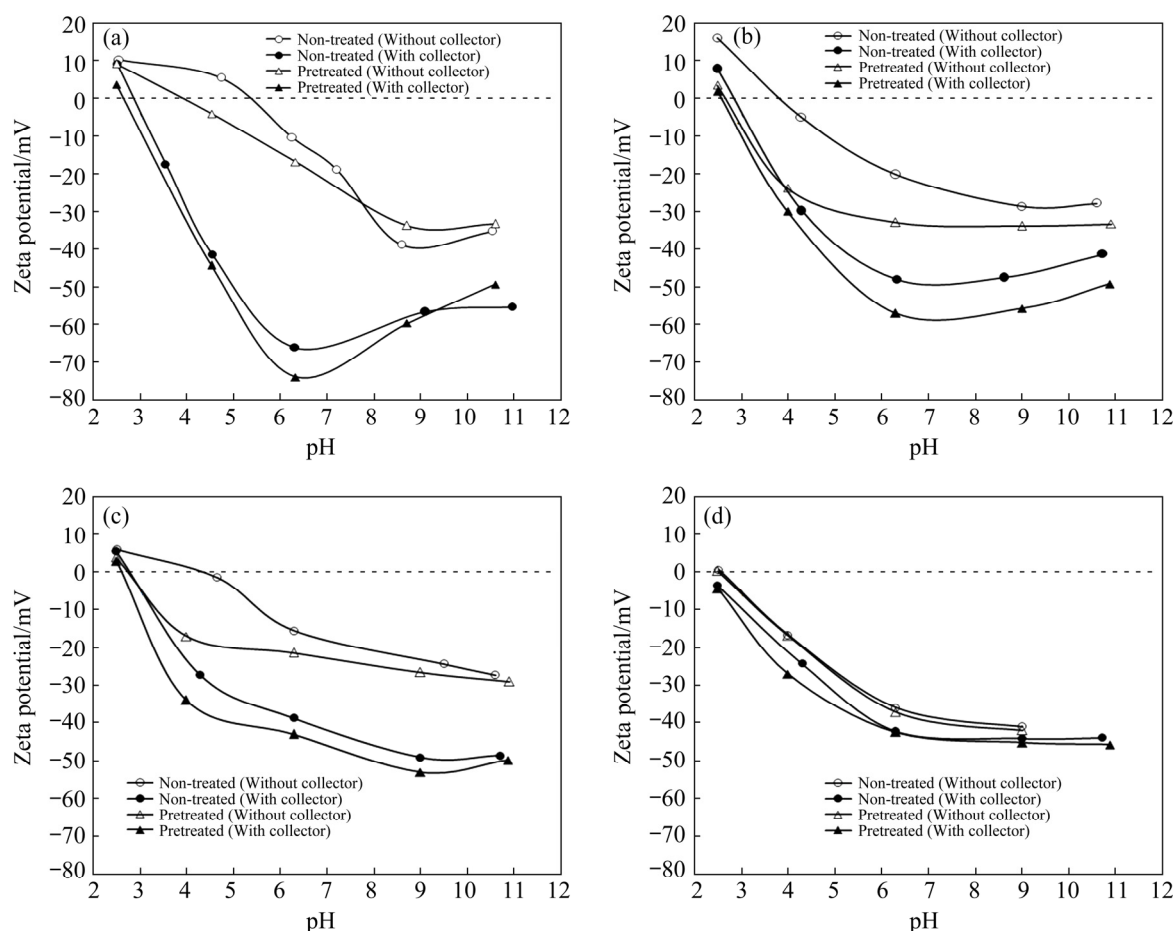


Fig. 12 Zeta potential of non-treated and thermally-treated ilmenite and gangue minerals as function of pH in presence of KCl (2×10^{-3} mol/L) and KCl + NaOL (3.65×10^{-4} mol/L sodium oleate and 2×10^{-3} mol/L KCl) (Thermal pretreatment time: 25 min, temperature of thermal pretreatment: 600°C): (a) Ilmenite; (b) Olivine-pyroxene; (c) Tremolite-clinocllore; (d) Quartz

achieve a selective flotation of ilmenite from iron containing gangue minerals.

3.7 Hydrophobicity

The hydrophobicity of ilmenite and thermally pretreated ilmenite conditioned with sodium oleate was determined by measuring the contact angle as a function of pH (Fig. 13). These results are in good consistent with the flotation results presented in Fig. 3. By increasing the pH value, the contact angle on the surface of both states of ilmenite is increased. The measured contact angle for thermally treated ilmenite is always more than that of non-treated ilmenite in whole pH range. The maximum contact angles occurring at a pH of 6.3 are achieved at 74.7° and 80.3° for original ilmenite and thermally pretreated ilmenite, respectively. The decrease of oleate ions adsorption on the surface of

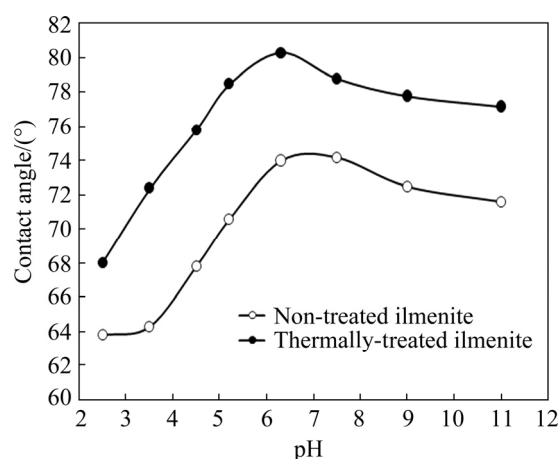


Fig. 13 Contact angle as function of pH for ilmenite and thermally-treated ilmenite at 600°C (Sodium oleate solution: 3.65×10^{-4} mol/L)

both states of ilmenite results in the decrease of contact angle in alkaline solutions. The contact

angle was also measured as a function of time for ilmenite and thermally treated ilmenite conditioned with sodium oleate (Fig. 14). As seen from Fig. 14, the decrease of contact angle for thermal treated ilmenite occurs slower than that of non-treated ilmenite. After 10 min, the contact angle is almost 38.7° and 67.8° for non-treated and thermal treated ilmenite, respectively.

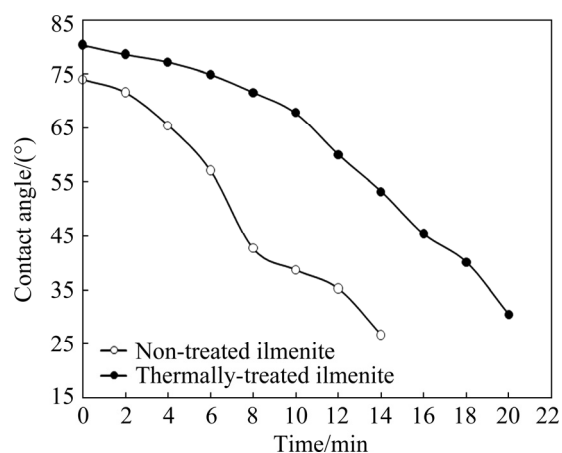


Fig. 14 Contact angle as function of time for ilmenite and thermally-treated ilmenite at 600 °C (Sodium oleate solution: 3.65×10^{-4} mol/L)

4 Discussion

4.1 Ilmenite flotation

Based on the distribution diagram of surface species on ilmenite [7,41,42], Ti and Fe species are responsible for the recovery peaks in the acidic and intermediate pH ranges, respectively. In the strong acidic pH values, titanium ions appearing as $\text{Ti}(\text{OH})^{3+}$ and $\text{Ti}(\text{OH})^{2+}$ species react with the oleate ions. In this pH range, the adsorption of collector can also take place through the colloidal precipitation of oleate molecules [40,42]. In the intermediate pH values, ferrous ions existing in the forms of Fe^{2+} and FeOH^+ are active sites for adsorption of oleate species including oleate ion (RCOO^-), oleate dimer ($(\text{RCOO})_2^{2-}$) and acid-soap ($(\text{RCOO})_2\text{H}^-$). The ion molecular species ($(\text{RCOO})_2\text{H}^-$) play an important role in the high flotation recovery of ilmenite in weakly acidic or weakly alkaline solutions [41–47].

The increase of pretreatment temperature enhances the conversion of Fe^{2+} into Fe^{3+} ions on the surface of ilmenite. The highest amount of conversion without any significant phase decomposition in the crystal structure occurs when

ilmenite is thermally treated at 600 °C. The increase of Fe^{3+} ions improves the ilmenite floatability in a wide pH range. As schematically shown in Fig. 15, the chemisorption of oleate ions on the surface of ilmenite causes the increase of ferric iron oleate ($K_{\text{sp}}=10^{-29.7}$ [48]) which is more insoluble than ferrous iron oleate ($K_{\text{sp}}=10^{-15.5}$ [48]). The greater insolubility of ferric iron oleate improves the hydrophobicity of the ilmenite surface, enhancing the bubble–particle attachment time and flotation recovery (Figs. 15(c, d)).

4.2 Collector adsorption density

The adsorption density of collector ions in the stern plane is given by the Stern–Grahame equation [49]:

$$\Gamma_s = (\text{const} \tan t) C \exp\left(-\frac{\Delta G_{\text{ads}}^0}{RT}\right) \quad (1)$$

where C is the collector bulk concentration, R is the gas constant, T is the absolute temperature, and ΔG_{ads}^0 is the standard free energy of adsorption. For indifferent electrolytes, ΔG_{ads}^0 is approximated as $\Delta G_{\text{ads}}^0 = zF\zeta$ where the zeta potential (ζ) approximates the stern layer potential, z is the valence of the adsorbing ion ($z=1$ for oleate ions), and F is the Faraday constant (96485 C/mol).

FUERSTENAU and SHIBATA [49] showed that if the collector concentration is constant and the pH is variable, the relative adsorption density of collector in the stern plane can be proportional to $\exp(\Delta|\zeta|)$. So, Eq. (1) can be rewritten as follows:

$$\Gamma_s = (\text{const} \tan t) C \exp(\Delta|\zeta|) = K \exp(\Delta|\zeta|) \quad (2)$$

where K is constant; $\Delta|\zeta| = \zeta_2 - \zeta_1$; ζ_1 and ζ_2 are the measured zeta potentials before (in the presence of KCl) and after anionic collector adsorption, respectively. The difference between the two values of the zeta potential can be due to the strong adsorption of the collector in the stern plane, which is a necessary condition for good flotation. This difference can also be taken as a measure of the free energy of adsorption in the stern plane.

The relative adsorption densities of oleate (Γ_s) and the standard free energy of adsorption (ΔG_{ads}^0) were calculated for ilmenite and thermally treated ilmenites with Eq. (2). The results are presented in Table 5. These results show that the relative adsorption densities of oleate in a wide pH range for ilmenite and thermally-treated ilmenites are in

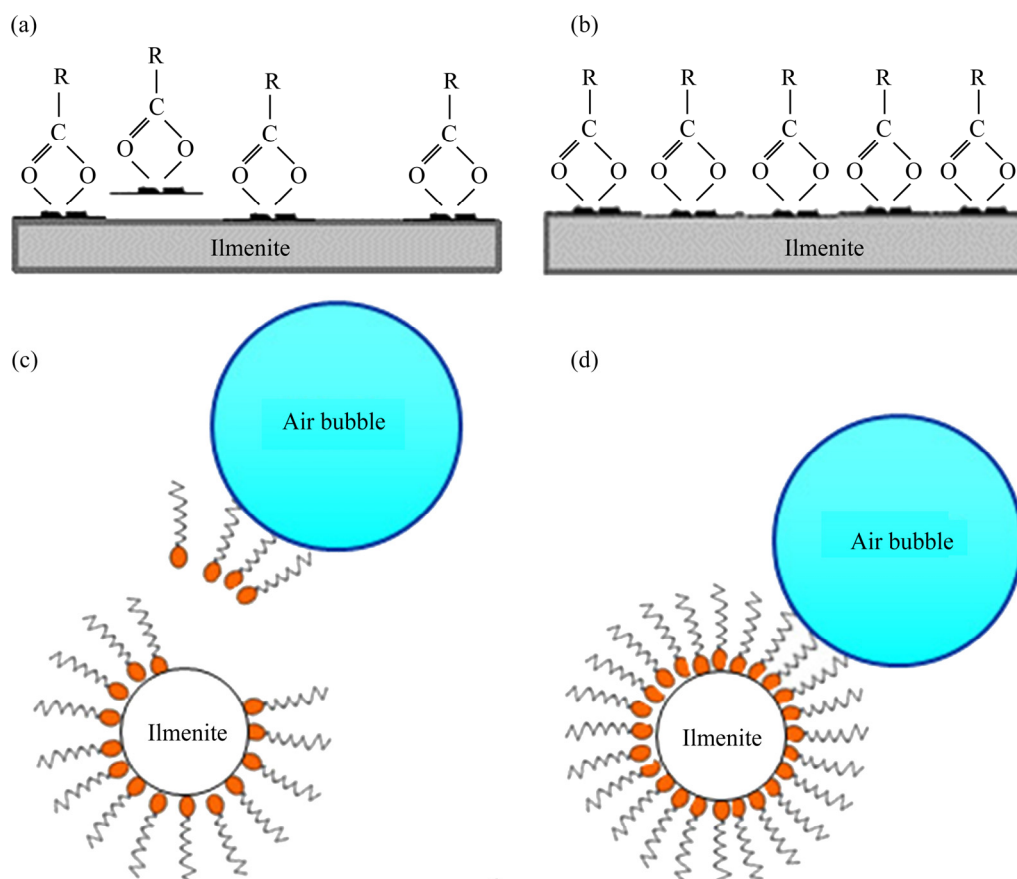


Fig. 15 Schematic model of oleate adsorption and formation of iron oleate layer on surface of ilmenite and its attachment to air bubble before and after thermal treatment: (a) Formation of iron oleate before thermal treatment; (b) Formation of iron oleate after thermal pretreatment; (c) Dissolution of ferrous iron oleate and detachment of ilmenite from air bubble before thermal treatment; (d) Stability of ferric iron oleate and enhancing of bubble–ilmenite attachment time after thermal treatment

Table 5 Zeta potential, oleate adsorption densities and the standard free energy of adsorption at pH of 6.3 for original ilmenite and pretreated ilmenite samples

Sample	pH at IEP	pH at IEP after collector adsorption	ζ_1/mV	ζ_2/mV	$\Delta \zeta /\text{mV}$	Γ_s	$\Delta G_{\text{ads}}^0/\text{kJ}$
Ilmenite	5.4	2.8	−10.3	−66.3	56	$K_{\text{exp}}(0.056)$	$-66.3zF=-6.4$
Pretreated ilmenite at 600 °C	3.85	2.6	−16.9	−73.1	57.2	$K_{\text{exp}}(0.0572)$	$-73.1zF=-7.1$
Pretreated ilmenite at 950 °C	3.05	3.2	−19.7	−55.9	36.2	$K_{\text{exp}}(0.0362)$	$-55.9zF=-5.4$

good accordance with the flotation recoveries (shown in Fig. 2). The average value of ΔG_{ads}^0 for all three ilmenite samples is negative, which proves that the adsorption of oleate on the surface of ilmenite takes place through the chemisorptions mechanism. The more negative value of ΔG_{ads}^0 for ilmenite treated at 600 °C indicates that the thermal pretreatment under this condition facilitates the reaction of oleate ions with Fe species on the surface of ilmenite.

With the surface area under the quantitative analysis of FT-IR spectra at 2923 cm^{-1} and the specific surface area of minerals (determined by BET method), the relative adsorption density of sodium oleate on the surface of ilmenite and different gangue minerals was determined, as given in Table 6. The results show that the adsorption density of oleate for pretreated ilmenite and iron containing gangue minerals is more than that of non-treated ones. This can be attributed to the

Table 6 Surface area under spectra at 2923 cm⁻¹ and relative adsorption density of sodium oleate on surface of ilmenite and different gangue minerals

Sample	Surface area/ (m ² ·g ⁻¹)	Before thermal treatment		After thermal treatment	
		Surface area under spectra at 2923 cm ⁻¹	Adsorption density	Surface area under spectra at 2923 cm ⁻¹	Adsorption density
Ilmenite	5.038	0.3283	0.0652	0.3788	0.0752
Olivine–pyroxene	7.53	0.2686	0.0357	0.3805	0.0505
Tremolite–clinochlore	12.87	0.1948	0.0151	0.2448	0.0190
Quartz	9.56	0.1657	0.0173	0.1687	0.0176

conversion of Fe²⁺ to Fe³⁺ ions and hence more adsorption of oleate ions on the surface of pretreated minerals in comparison with raw mineral samples. The adsorption density of oleate for treated and non-treated ilmenite is more than that of gangue minerals, and this is in good agreement with the flotation results obtained before and after thermal pretreatment. In addition to the low adsorption of the collector, there is no significant difference between the adsorption density of oleate on the surface of non-treated quartz and thermally-treated one.

5 Conclusions

(1) The thermal pretreatment method converting Fe²⁺ ions to Fe³⁺ ones modifies the ilmenite surface chemistry and hence improves its floatability in a wide range of pH.

(2) The maximum amount of improvement occurs after thermal pretreatment at 600 °C, a temperature at which the phase decomposition of ilmenite starts immediately.

(3) The improvement of gangue minerals floatability is directly related to their iron content. Thus, in the flotation of ilmenite, the improvement of separation efficiency, selectivity index and recovery of TiO₂ have negative correlation with the iron content of the gangue minerals.

(4) After thermal pretreatment at 600 °C, the maximum improvement of separation efficiency, selectivity index and recovery of TiO₂ in the ilmenite flotation concentrate are achieved when the gangue minerals are free from iron.

(5) When ilmenite is accompanied by iron-free gangue minerals such as quartz, plagioclase, etc, the thermal pretreatment process can be used as an effective method for improving the flotation separation of ilmenite.

Acknowledgments

The authors would like to thank Amirkabir University of Technology for the financial support of this research.

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加热预处理对钛铁矿及其伴生脉石矿物的表面改性： 在浮选过程中的应用

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摘 要：通过浮选实验(微量浮选和实验室浮选槽)、XRD、XPS 和 FT-IR 分析以及 Zeta 电位和接触角测量，研究常规加热预处理对钛铁矿及其伴生脉石矿物表面性质的影响。在 600 °C、25 min 的最佳条件下进行预处理，pH 为 6.3 时钛铁矿的可浮性由 73.5% 提高到 91%。XRD 和 XPS 分析表明，在此预处理条件下，钛铁矿的 Fe^{3+} 含量提高约 16.5%，而没有出现任何相分解和结构变化。FT-IR 分析以及接触角和 Zeta 电位测量结果证明，钛铁矿可浮性的提高是由于捕收剂吸附作用的增强和较难溶的油酸铁疏水层的形成。矿石浮选实验表明，加热预处理使 TiO_2 回收率由 65.4% 提高到 73.7%，而钛铁矿精矿的 TiO_2 含量没有明显变化。

关键词：钛铁矿；加热预处理；浮选；Zeta 电位；油酸钠

(Edited by Bing YANG)