

## IMPACTS OF SURFACE MODIFICATION ON ISOTHERM AND KINETICS OF COLLECTOR ADSORPTION

Omid Salmani Nuri<sup>1</sup>, Mehdi Irannajd<sup>2\*</sup>, Akbar Mehdilo<sup>3</sup>

<sup>1</sup>PhD Candidate, Department of Mining and Metallurgical Eng., Amirkabir University of Technology, Tehran, Iran, [omidnuri@aut.ac.ir](mailto:omidnuri@aut.ac.ir)

<sup>2</sup>Associate Professor, Department of Mining and Metallurgical Eng., Amirkabir University of Technology, Tehran, Iran, [irannajad@aut.ac.ir](mailto:irannajad@aut.ac.ir)

<sup>3</sup> PhD Candidate, Department of Mining and Metallurgical Eng., Amirkabir University of Technology, Tehran, Iran, [amehdilo@aut.ac.ir](mailto:amehdilo@aut.ac.ir)

**Abstract:** Surface dissolution is one of the surface modification methods which has been used prior to the flotation process to improve minerals flotability. In this study, the effect of surface dissolution has been investigated on isotherm and adsorption kinetics of sodium oleate as a collector on the surface of ilmenite, olivine-pyroxene and quartz. Conditioning time, pH, temperature, activation energy, specific area and contact angle were the parameters which were studied before and after surface dissolution. The results of adsorption isotherms of Langmuir, Freundlich and Temkin, and kinetic models of elovich, lagergerin and pseudo second-order showed that the collector adsorption on the minerals surfaces can be well described by Langmuir isotherm and pseudo second-order kinetic model. The collector adsorption on the minerals surfaces is occurred mainly based on adsorption capacity from solution and single layer. Results indicated that the surface dissolution increases of the collector adsorption on ilmenite surface while decreasing it in gangue minerals. Also, the activation energy of ilmenite is reduced from 57255.4 J/mol to 42437.9 J/mol after surface dissolution which indicates a more favorable collector adsorption on ilmenite. Furthermore, after surface dissolution the activation energies of quartz and olivine-pyroxene are increased from 5746.5 J/mol to 5816.5 J/mol, and from 8326.6 J/mol to 12523.3 J/mol, respectively. Results of contact angle measurements showed that the contact angle of ilmenite is increased and while it is decreased in gangue minerals after surface dissolution. These results were in good agreement with the results of UV-Vis spectroscopy, collector adsorption and ICP analysis.

**Keywords:** Surface dissolution, Adsorption isotherm, Adsorption kinetics, Ilmenite, Sodium oleate.

### INTRODUCTION

Adsorption phenomenon is a vital factor in industrial processes. Mineral flotation, flocculation/coagulation, micellar flooding of oil wells and dewatering are the processes in which performance is controlled by the adsorption of molecules from solution to the solid surfaces. Energetically favorable interactions between mineral and surfactant result in the adsorption phenomenon. The adsorption process can be affected by the characteristics of minerals, ions and solution components of the system. The collector adsorption on the surface of various minerals is an important factor for controlling the flotation selectivity. Surface dissolution, as a surface modification method, has been used to improve the ilmenite flotability. Therefore, the aim of the study is to investigate the effect of surface dissolution on the isotherm and kinetics of collector adsorption, as the essential factors in the flotation output, on the surface of ilmenite, olivine-pyroxene and quartz.

### METHODS

The relatively pure minerals of ilmenite, olivine-pyroxene and quartz were prepared from titanium ore which is located in the northwest of Iran. The  $-150 +45\mu\text{m}$  size fraction was used for the adsorption and flotation experiments. In all experiments, sodium oleate and oxalic acid supplied by Sigma Aldrich were used as the collector and the surface dissolution agent, respectively.

**Surface dissolution** The surface dissolution of the minerals prior to the tests was carried out by mechanical stirring in a 7.5% (w/w) oxalic acid solution for 10 minutes. After filtration of the

---

\* Corresponding author

suspension, solid phase was washed for 5 minutes with double distilled water in a beaker and then dried at 25 °C.

**Adsorption test** Langmuir, Freundlich and Temkin models are the most common isotherm models which are used for investigating the adsorption isotherms. Kinetic study of the adsorption process is a vital factor which is governed by the rate of adsorbed oleate ion on the surface of minerals. Elovich, Pseudo first and second order models are the most common kinetic models which are used for modeling the kinetic rates. In each test, 1 g of purified mineral samples in a size range of +45 -150 micron was added to the 50 ml of double deionized water. These experiments were carried out under different experimental conditions including reagent dosages, temperatures, times, and pH values. Thus, the adsorption density of collector on the mineral surfaces ( $q_t$ ) at  $\lambda = 192$  nm [6] is calculated by equation (1):

$$q_t = \frac{(C_0 - C_t) \times V}{M \times A} \quad (1)$$

Where,  $C_0$  and  $C_t$  present the initial and final concentrations of sodium oleate in solution (mol/L), respectively.  $V$  is the volume of solution (L),  $M$  is the mass of mineral sample (g),  $A$  is the specific surface area of mineral sample ( $m^2/g$ ) and  $q_t$  is the adsorption density ( $mol/m^2$ ).

**BET Analysis** The NOVA-1000 instrument manufactured by Quantachrome with nitrogen gas as the absorbent was applied to measure the surface area of the minerals. In each test, a 0.5 g of purified minerals with a size of -150  $\mu m$  was used.

**ICP-Mass** In each test, 10 g of purified samples was placed into a beaker which contains the acid solution. After agitating with a mechanical stirrer for 15 minutes, the suspension was filtered, and the remaining liquid phase was analyzed by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) to determine the concentration of elements which were transferred from surface to solution after surface dissolution.

**Contact angle** Sessile drop method was used for measuring the contact angle of the minerals before and after surface dissolution. Cleaned samples were immersed in a given collector solution of 120 mL for 15 min with the desired pH value. A water drop was created on the sample using a micro syringe. After the drop was in contact with the sample, an image was captured using a camera. The contact angle was measured using Image J software.

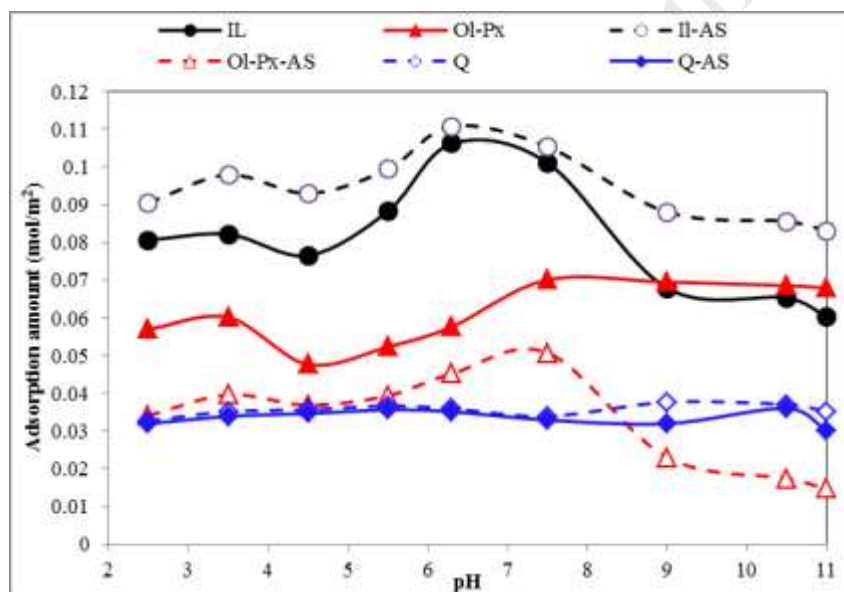
## FINDINGS AND ARGUMENT

**Surface area (BET analysis)** The surface area is a necessary factor for determining the adsorption densities of collector on the surface of minerals. The surface areas of ilmenite and two gangue phases were measured by BET method before and after surface dissolution. The results showed that the surface areas of all minerals are increased after pretreatment. After surface dissolution of all three minerals, the liquid phases were analyzed separately by the ICP-Mass method. Results showed that  $Fe^{2+}$ ,  $Mg^{2+}$ ,  $Ca^{2+}$  and  $Al^{3+}$  ions are dissolved through pretreatment and this affects the surface properties of the minerals (Table 1).

**Table 1.** Ions dissolved from ilmenite and two gangue minerals after surface dissolution by ICP-Mass analysis

Sample	Content of dissolved element (ppm)				
	Ca	Fe	Mg	Si	Ti
Ilmenite	-	129.5	45.2	-	0.31
Olivine-Pyroxene	628.15	1254.8	551.7	259.4	-
Quartz	-	89.5	34.5	421.6	-

**Effect of pH** Fig. 1 shows the adsorption densities of oleate ions on the surface of original and treated minerals as a function of pH. Results showed that the maximum values of collector adsorption densities of non-treated and treated ilmenite occur at a pH of 6-6.5. It can be due to the presence of Fe ions on ilmenite surface [5]. Also, the adsorption density of collector on original olivine-pyroxene is reached to the maximum value at a pH of 9. It can be due to presence of surface-active ions such as  $\text{Fe}^{2+}$ ,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  on their surfaces. After surface dissolution, the collector adsorptions on the surface of olivine-pyroxene are decreased in whole pH range, especially in alkali pH values. This can be related to the removal of surface-active ions from their surfaces [6-8].



**Fig 1.** Adsorption density of collector on ilmenite and gangue minerals before and after surface dissolution as a function of pH (collector concentration=  $3.65 \times 10^{-4}$  mol/L,  $T = 25^\circ\text{C}$ )

**Adsorption Isotherm** Table 2 showed that the Langmuir isotherm model with the highest  $R^2$  value is the best describing model for the adsorption process before and after surface dissolution. This model postulates that the adsorption of collector molecules on the mineral surface, with all adsorption sites, is a monolayer adsorption while they are all energetically equivalent [9]. The  $q_m$  value of the Langmuir isotherm model for the treated ilmenite and quartz increased 17.3 % and 4.72%, respectively, while it decreased 34.1 % for the treated olivine-pyroxene.

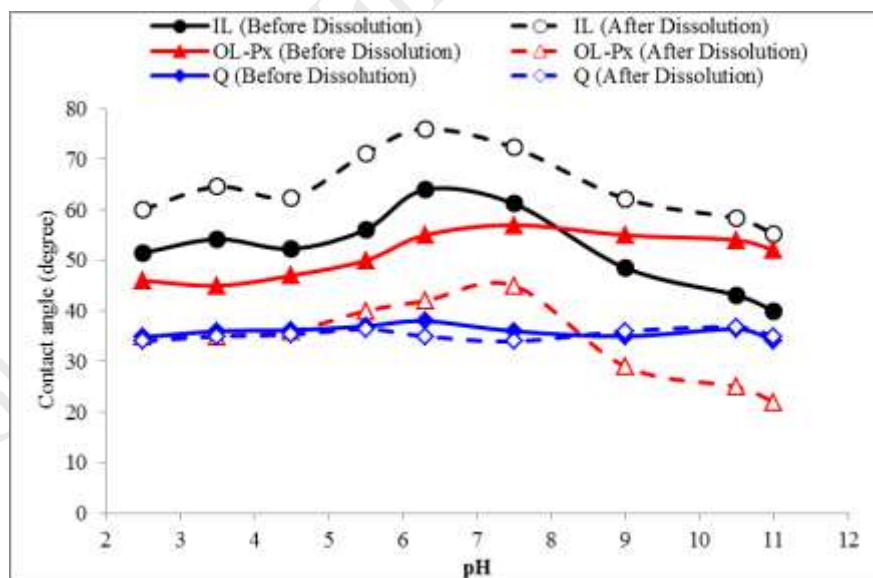
**Adsorption Kinetics** The results of adsorption kinetics showed that the pseudo second order model can well describe the adsorption kinetics of oleate ions on the surface of minerals among the three kinetic models (Table 3). This shows that the adsorption phenomenon is based on the adsorption capacity of the mineral [10-11].

**Activation energy** The positive values of  $E_a$  for all minerals showed that the adsorption of oleate on the surface of the minerals is an endothermic reaction. Results showed that activation energy of ilmenite decreases from 57.255 kJ/mol to 42.437 kJ/mol, indicating the easily adsorption of oleate ions on the surface of treated ilmenite after surface dissolution. This is due to the conversion of  $Fe^{2+}$  ions to  $Fe^{3+}$  ones on the surface of ilmenite. Increasing the  $E_a$  for Ol-Px and Q minerals from 8.326 kJ/mol and 5.746 kJ/mol to 12.523 kJ/mol and 5.816 kJ/mol, respectively, indicate less adsorption of oleate ions on the surface of these gangue minerals. This is due to the removal of Fe, Ca, and Mg ions from the surface of those minerals.

**Table 2.** Comparison of different parameters for various isotherm models at  $T=25^\circ C$ .

Isotherms		Langmuir			Freundlich			Temkin		
Parameters		$R^2$	$q_m$	$K_L$	$R^2$	N	$K_f$	$R^2$	$K_T$	B
IL	Before	0.99	1.068 E-05	10732.3	0.94	2.06	0.00046	0.96	90069.2	2.5 E-06
	After	0.99	1.214 E-05	31175.5	0.95	2.70	0.00026	0.94	324760	2.6 E-06
Ol-PX	Before	0.99	1.642 E-05	9522.21	0.92	1.75	0.00085	0.96	83563.5	2.2 E-06
	After	0.99	1.082 E-05	4879.28	0.94	1.44	0.00197	0.95	52519	2.1 E-06
Quartz	Before	0.99	0.74	4195.1	0.92	1.47	0.00011	0.96	43458.6	1.6 E-06
	After	0.99	0.775	3699.6	0.93	1.42	0.00013	0.95	40656.8	1.6 E-06

**Contact angle** The results of contact angle (Fig. 2) showed that the surface dissolution increases the hydrophobicity of ilmenite in whole pH range which can be caused by the presence of  $Fe^{2+}$  and  $Fe^{3+}$  ions on ilmenite surface interacting with oleate ions. Also, the hydrophobicity of olivine-pyroxen decreased after surface dissolution which is described by the removal of Ca and Mg ions from that surface [12-13].



**Fig 2.** The results of contact angle for the minerals before and after surface dissolution

**Table. 3** Adsorption kinetic parameters of oleate ions on IL, Ol-Px and Q surfaces before (BS) and after (AS) surface dissolution (collector concentration=  $3.65 \times 10^{-4}$  mol/L, T= 25 °C).

Kinetic models		Pseudo second order		
Minerals		R <sup>2</sup>	S <sub>2</sub> ( $\times 10^{-4}$ mol/m <sup>2</sup> )	K <sub>2</sub>
Ilmenite (IL)	BS	0.998	0.097	3.8593
	AS	0.999	0.105	8.4408
Olivine-Pyroxene (Ol-Px)	BS	0.996	0.0706	6.3320
	AS	0.999	0.0603	5.0341
Quartz (Q)	BS	0.997	0.0536	7.774
	AS	0.996	0.0514	7.371

## CONCLUSIONS

In this study, the effect of surface dissolution on the behavior of collector adsorption on ilmenite, olivine-pyroxene, and quartz was studied. The surface dissolution changes the surface properties of the minerals such as position and distribution of surface ions, surface area, hydrophobicity, and also kinetics and isotherm behaviors of collector adsorption on the mineral surfaces. Results showed that the collector adsorption on treated ilmenite increased, while it decreased in gangue minerals. It should be noted that the surface dissolution can be used as the method of surface modification for minerals with similar ions on their surfaces.

## REFERENCES

- Fuerstenau, M. C; Rice, D. A., Somasundaran, P; and Fuerstenau, D. W; 1965, "Metal ion hydrolysis and surface charge in beryl flotation", Inst. Min. Metall. Trans, 74, 381.
- Freundlich, H; 1906, "Over the adsorption in solution", J. Phys. Chem, 57, 1100-1107.
- Haghseresht, F; and G. Q. Lu; 1998, "Adsorption characteristics of phenolic compounds onto coal-reject-derived adsorbents", Energy & Fuels, 12(6), 1100-1107.
- Ho, Yuh-Shan; 2006, "Review of second-order models for adsorption systems", Journal of hazardous materials, 136(3), 681-689.
- Jie, Zhang; Wang Weiqing; Liu Jing; Huang Yang; Feng Qiming; and Zhao Hong; 2014, "Fe (III) as an activator for the flotation of spodumene, albite, and quartz minerals", Minerals Engineering, 61, 16-22.
- Kundu, Sanghamitra; and Gupta, A. K.; 2006, "Arsenic adsorption onto iron oxide-coated cement (IOCC): regression analysis of equilibrium data with several isotherm models and their optimization", Chemical Engineering Journal, 122(1), 93-106.
- Wick, Roger; Peter Walde; and Pier Luigi Luisi; 1995, "Light microscopic investigations of the autocatalytic self-reproduction of giant vesicles", Journal of the American Chemical Society, 117(4) 1435-1436.
- Wills, Barry A; and James Finch; 2015, "mineral processing technology: an introduction to the practical aspects of ore treatment and mineral recovery", Butterworth-Heinemann,.
- Zhong, Kangnien; and Lin Cui; 1987, "Influence of Fe 2+ ions of ilmenite on its flotability", International Journal of Mineral Processing, 20(3), 253-265.
- Zhu, Yang-ge; Guo-fan Zhang; Qi-ming Feng; Dai-cui Yan; and Wei-qing Wang; 2011, "Effect of surface dissolution on flotation separation of fine ilmenite from titanite", Transactions of Nonferrous Metals Society of China, 21(5), 1149-1154.