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Effect of chemical composition and crystal chemistry on the zeta potential of ilmenite

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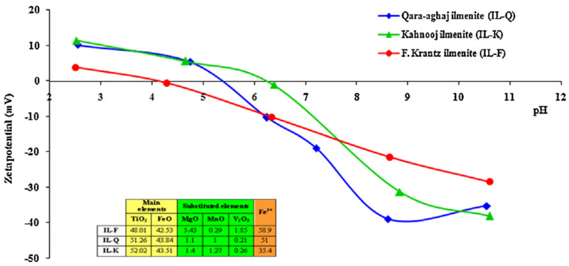
HIGHLIGHTS

- Lattice substitution of Mn, Mg and V influences the zeta potential of ilmenite.
- Hematite exsolutions decrease the isoelectric point of ilmenite by releasing Fe^{3+}.
- Sphene exsolutions containing Ca and Si affect the isoelectric point of ilmenite.
- Chemical composition can be used to predict the IEP of ilmenite.

GRAPHICAL ABSTRACT



	Main elements		Substituted elements			Fe^{3+}
	TiO_2	FeO	MgO	MnO	V_2O_5	
IL-F	48.01	42.53	5.43	0.29	1.85	58.9
IL-Q	51.26	43.84	1.1	1	0.21	51
IL-K	52.02	43.51	1.4	1.27	0.26	35.4

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ABSTRACT

The crystal structure, crystal chemistry and surface properties of three ilmenite samples including IL-F (purchased from the mineral dealership of A. and F. Krantz), IL-Q (Qara-aghaj hard rock deposit, northwest of Iran) and IL-K (placer deposit, south of Iran) were investigated. The microprobe analysis showed that different amounts of Mg, Mn and V have been substituted in the crystal structure of ilmenite. Using SEM, microprobe analysis and X-ray diffraction it was found that there are different amounts of exsolved fine lamellae of hematite inside ilmenite in the studied samples. Some fine lamellae of the sphene mineral were also observed inside the IL-K ilmenite. The isoelectric point (IEP) was determined as 6.25, 5.4 and 4.2 for IL-K, IL-Q and IL-F, respectively. Mn content has a good positive correlation with lattice constants (LC), unit cell volume, crystallinity index and IEP of ilmenite but the increase of Mg and V content in ilmenite was found to decrease them. The crystallinity index of ilmenite was not the major factor for determining IEP. A linear relationship with a correlation coefficient of $r = 0.97$ was found to exist between the measured isoelectric point and Ti content in the ilmenite crystal structure. Fe^{3+} ion sourced from hematite lamellae has a good negative correlation ($r = -0.96$) with the IEP value of ilmenite and it is one of the most important IEP determining ions. Si and Ca content come mainly from sphene exsolutions that tend to increase the IEP value of ilmenite.

1. Introduction

Ilmenite as a titanate of ferrous iron mineral ($Fe^{2+}Ti^{4+}O_3$) is one of the major TiO_2 containing minerals from which titanium dioxide and titanium metal is produced [1]. The conventional methods used in the processing of ilmenite ores are gravity separation, high-intensity magnetic separation (HIMS), Electrostatic separation or a conjunction of them. In some ores, ilmenite is freely disseminated in the gangue, and is not effectively separated from the associated gangue minerals using the mentioned separation methods. Froth flotation as a physico-chemical separation process is an effective tool for separating fine disseminated particles [1–5]. The application of such physico-chemical separation processes (e.g. flotation, flocculation, filtration, etc.) for oxide minerals requires the knowledge of changes in zeta potential with changes in solution conditions [6].

Surface charge plays a significant role in a variety of disciplines, ranging from processing industries to biological functions and life

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sciences. In mineral processing, surface charge often determines the interaction of flotation reagents with minerals and hence selective separation of various minerals for valuable metal extraction. Electrokinetics of colloidal particles is a useful measure of surface charge characteristics. The measurement of electrokinetics, such as electrophoretic mobility or zeta potential, can be considered an in situ technique for determining surface dissolution and adsorption of charged species in a colloidal system [7,8]. The surface charge controls the stability or dispersion of fine particles. Otherwise, electrokinetic properties such as isoelectric point (IEP) and potential determining ions (pdi) of fine particles in aqueous solution play a significant role in understanding the adsorption mechanism of inorganic and organic species at the solid/solution interface [9].

Ilmenite structure is somewhat similar to that of hematite but with some distortion in the oxygen layers. Along the direction of the triad axis, pairs of Ti ions alternate with pairs of Fe^{2+} ions; thus each cation layer is a mixture of Fe^{2+} and Ti^{4+}. The formula of ilmenite may be more fully expressed as (Fe, Mg, Mn) TiO_3 with only a limited amount of Mg and Mn [10]. The elements such as Mn, Mg, and Cr may substitute for Fe or Ti in the original ilmenite lattice, while elements like Al, Si, Th, P, V and Cr are commonly incorporated into the ilmenite grains during chemical weathering. Prolonged exposure to oxidizing and/or acidic environments may also cause changes to the chemistry of ilmenite grains with elements such as Fe and Mn being significantly leached [11].

It may be expected that the zeta potential of ilmenite will be affected by the chemical composition. Due to the variations in the composition, the parameters measured at the ilmenite–water interface could be expected to vary according to the degree of ionic substitution in a particular ilmenite. That is, the electrochemical properties of ilmenites from different sources may not be essentially the same, and therefore, the electrochemical properties determined for a particular ilmenite mineral should be considered as pertaining only to that mineral. Thus if the electrochemical properties of the ore constituents are known, it is possible to define pH ranges in which specific minerals are made to selectively interact with such collectors and therefore result in selectivity of floatation. It is therefore of vital importance to understand the effect of bulk chemical composition on the electrokinetics of a solid.

The zeta potential of ilmenite came from Panzhihua has been determined about 5.6 by Song et al. and Choi [1,12]. Fan et al. have also determined the zeta potential in the range of 5.4–5.7 for ilmenite of Norway [2–4]. The electrokinetic properties of some other minerals like kaolinite [13–15], sepiolite [16], perlite [17,18], TiO_2 [19,20], diaspore [7,15], chromite [6], hematite [21], magnetite [22], dolomite [9], Scheelite [23], cassiterite [24] and phyllosilicate minerals [25] have been investigated. In most of these researches, surface properties of minerals and some effective parameters on surface charge and zeta potential such as pH, electrolyte type and concentration, solid content, solution ion strength and charged chemical species in solution have been studied. The effect of mineral chemical composition on surface zeta potential was studied only in the cases of chromite, diaspore and kaolinite [6,7,13].

The aim of the present work is to study the chemistry and electrokinetic properties of ilmenite mineral. The mineralogical features, chemical composition and the most important impurities in the ilmenite crystal lattice were identified and their effects on zeta potential have been evaluated.

2. Materials and methods

2.1. Materials

Three kinds of ilmenite samples from different localities were used in this study. IL-K and IL-Q ilmenite samples were taken from Kahnooj mine as a placer deposit (south of Iran) and Qaraaghaj hard rock deposit (northwest of Iran), respectively. The IL-F sample was received from a laboratory of mineralogy as a hand sample which had been purchased from the mineral dealership of August and Friedrich Krantz. These samples were crushed and ground under 150 μm. The purification procedure of samples was performed using steps of sieving and several stages of tabling, low intensity magnetic separation and high intensity magnetic separation methods. The pure concentrates were washed several times with distilled water and dried at room temperature. Examination under binocular microscope showed ilmenite grains with clean surface, and free from gangue minerals.

Analytical grade H_2SO_4 and NaOH were used for pH adjustment and doubly distilled water was used throughout this study.

2.2. Methods

2.2.1. Materials characterization

The chemical composition of the samples was determined using X-ray fluorescence (XRF, Philips X Unique2). The phase composition was analyzed with XPERT MPD diffractometer employing Cu Ka radiation. Microscopic studies for evaluation of textural and structural features were performed using Philips XL30 model scanning electron microscopy (SEM). The electron microprobe (EMP) analysis of the samples was carried out using Cameca SX 100 equipped with five wavelength dispersive (WD) spectrometers. In order to prepare the samples for SEM and EMP analysis, the grains of ilmenite were set into a mold (typically 30 mm diameter) with epoxy resin to form a hardened block. The block was then ground down to expose a representative cross section of particles which was subsequently polished and then coated with carbon before being presented to the SEM and EMP. Accelerating voltage of 15 kV and 100 s counting time were used to perform analysis in 25 μm^2 areas.

2.2.2. Zeta potential measurement

The zeta potential of mineral suspension was measured using a Malvern instrument (UK). The samples were ground under 15 μm. The suspension was prepared by adding 50 mg of mineral samples to 100 ml of distilled, deionized water containing 1 mM KCl as a supporting electrolyte. The resultant suspension was conditioned for 15 min during which suspension pH was measured. The pH was adjusted using either NaOH or H_2SO_4 over the pH range of 2–11. Zeta potential was measured following the procedures described in the instrument manual. The reported results are the average of at least three full repeat experiments. The repeated tests showed a measurement error of ±2 mV.

2.2.3. XPS analysis

XPS spectra were measured with Specs EA 10 X-ray photoelectron spectroscope to study the distribution density and binding energy of the elements on the mineral surface.

3. Results

3.1. Chemical composition

The chemical analysis of the various mineral samples is shown in Table 1. It is evident that ilmenite samples exhibit some variation in chemical compositions. The presence of some impurities such as Mg, Mn, Si and Ca decreases the Ti content of the samples. The X-ray diffraction method was used to identify various phases in the samples. The XRD patterns of the samples shown in Fig. 1 suggest that all the samples examined were essentially composed of ilmenite. Another mineral which is observed at a minor amount in the IL-F sample is hematite while its content in the other samples is low to be detected by the X-ray diffraction method. The higher