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Effect of crystal chemistry and surface properties on ilmenite flotation behavior

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ABSTRACT

The crystal chemistry, surface properties and flotation behavior of three ilmenite samples: IL-F (purchased from the mineral dealership of A. and F. Krantz), IL-Q (Qara-aghaj deposit, Iran) and IL-K (Kahnuj deposit, Iran) were investigated. The substitution of different amounts of Mg, Mn and V in the crystal structure of ilmenite was identified by microprobe analysis. Different amounts of hemoilmenite exsolution were observed inside all three ilmenite samples using SEM, electron microprobe and X-ray diffraction analyses. Using these analytical techniques, the titanite phase was found inside the IL-K ilmenite. The XPS analysis indicated that the contents of Fe^{3+} are 5.66, 5.33 and 3.72% for IL-F, IL-Q and IL-K, respectively which are in good agreement with the amounts of hemoilmenite exsolution.

The IEP was determined to be 4.2, 5.4 and 6.3 for IL-F, IL-Q and IL-K, respectively. Using sodium oleate as a collector, the maximum flotation recovery was obtained at 78.4, 73.5 and 51.5% for IL-F, IL-Q and IL-K samples, respectively, at a pH range of 5 to 7 where iron cations are active ions. The IEP has a negative correlation with Fe^{3+} ions, collector adsorption density and ilmenite floatability. Mg and V have negative correlation with ilmenite flotation recovery. Si and Ca sourced mainly from the titanite phase affect the flotation recovery of ilmenite negatively.

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 are produced (Song and Tsai, 1989). The ilmenite structure is 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 (Deer et al., 1991; Didenko and Efremov, 2004). 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 (Pownceby et al., 2008).

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 gangues, and is not effectively separated from the accompanying gangue minerals using these separation methods. Froth flotation as a physico-chemical separation process is an effective tool for separating fine disseminated particles (Song and Tsai, 1989; Fan and Rowson, 2000a,b; Fan et al., 2009; Zhu et al., 2011). However, ilmenite displays poor floatability under conventional flotation conditions in comparison with other oxide minerals, such as magnetite and rutile. Even a large dosage of collectors gave a froth flotation recovery of less than 80% (Fan and Rowson, 2000a,b; Fan et al., 2009). A series of studies have been carried out to improve ilmenite recovery, including surface modification of ilmenite (Fan et al., 2009; Zhu et al., 2011; Bulatovic and Wyslouzil, 1999), reverse flotation (Behera and Mohanty, 1986), hot flotation (Liimatainen and Techn, 1977) and agglomeration flotation (Runolinna and Rinne, 1960). Liimatainen and Techn studied the flotation of ilmenite at various pulp temperatures (Liimatainen and Techn, 1977). Agglomeration flotation of ilmenite was studied by Runolinna and Rinne (1960). Gutierrez suggested aeration into ilmenite pulp as an effective method to improve ilmenite flotation recovery (Gutierrez, 1976). Reverse flotation methods were applied for upgrading of massive ilmenite ore by Behera and Mohanty (1986). Fan and Rowson used the pre-treatment by microwave radiation to modify ilmenite surface properties prior to flotation and to improve ilmenite recovery (Fan and Rowson, 2000a; Fan et al., 2009; Fan and Rowson, 2002; Fan et al., 2000). The modification of ilmenite surface properties and improvement of its floatability using lead ions (lead nitrate) were also investigated by Fan and Rowson (2000b). The other method used for improvement of ilmenite flotation behavior is the acid surface dissolution (Zhu et al., 2011; Bulatovic and Wyslouzil, 1999). After the treatment using microwave radiation and surface dissolution the Fe^{2+} ions on ilmenite surfaces are converted into Fe^{3+} ions and the zeta potential of ilmenite is decreased; and the capability to chemically bind with oleate ions (in the presence of sodium oleate

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as collector) is significantly increased (Fan and Rowson, 2000a,b; Fan et al., 2009; Zhu et al., 2011).

The previous works have mainly focused on the improvement of ilmenite floatability using flotation reagents and some surface modification methods. In these works the effect of ilmenite chemistry on its flotation behavior has not been evaluated. So, the aim of this work is to study the influence of ilmenite mineralogical features, chemical composition and crystal chemistry on its surface properties and floatability. By knowing these factors, a suitable flotation process can be considered for effective separation of ilmenite from accompanying gangue minerals.

2. Materials and methods

2.1. Materials

Three ilmenite samples from different localities were used in this study. The IL-K and IL-Q ilmenite samples were taken from the Kahnuj deposit (south of Iran) and Qara-aghaj hard rock deposit (northwest of Iran), respectively. The IL-F sample was received from a laboratory of mineralogy as a hand sample (purchased from the mineral dealership of Friedrich Krantz). The samples were crushed and ground to a size of 150 μm; and were then purified using steps of sieving, several stages of tabling, and low and high intensity magnetic separation methods. The pure ilmenite samples were washed several times with distilled water and dried at room temperature. Examination under a binocular microscope showed ilmenite grains with a clean surface, and almost free from gangue minerals.

Sodium oleate (with 95% purity) was used as a collector in flotation experiments and FTIR analysis. Analytical grade H_2SO_4 and NaOH were used for pH adjustment and double 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. The microscopic studies for evaluation of textural and structural features were performed using Philips XL 30 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 in 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 EMP analysis. The SEM images were taken under accelerating voltage of 25 kV.

2.2.2. Flotation experiments

The flotation experiments were carried out in a 300 cm^3 Hallimond tube. In each test, 2 g of material was used with a size of 45–150 μm. The sample was added to the double distilled water and conditioned for 5 min. After this period, the collector was added to the suspension, the pH was adjusted to the required value, and a second conditioning stage of 8 min was given to the suspension. The prepared pulp was then transferred to the Hallimond tube where flotation was carried out for 4 min. After the flotation tests, the concentrate and tailing were filtered, dried, and weighed.

2.2.3. XPS analysis

XPS spectra were measured with a Specs EA10 X-ray photoelectron spectroscope to study the distribution density and binding energy of the elements on the mineral surface. The XPS analysis was carried out with an Al K_α X-ray source at 1486.6 eV and the peaks deconvoluted using SDP software (version 4.1) with 80% Gaussian–20% Lorentzian peak fitting. The XPS measurements were performed inside the analysis chamber operating in a high vacuum of about 10^{-7} Pa. Binding energies were calibrated using characteristic C1s carbon peak (C1s = 284.7 eV).

The ilmenite samples with a size of 45–150 μm which were used in the flotation tests were applied in XPS analysis experiments.

2.2.4. FT-IR spectroscopy

The FT-IR spectra were obtained with NEXU670 FT-IR (Nicolet Corporation, USA) to characterize the nature of the interaction between the collector and the minerals. The mineral sample was ground to smaller than 0.015 mm before contacting the collector. In each test, the conditioning of suspension was performed similar to the flotation experiments. In the quantitative analysis the ratio of KBr to sample was 300:1, wt/wt.

2.2.5. 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 2×10^{-4}, 2×10^{-3} and 2×10^{-2} M KCl as a supporting electrolyte. For determination of zeta potential after collector interaction, 3.65×10^{-4} M sodium oleate was used in the presence of 2×10^{-3} M KCl as an indifferent 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 repeating tests showed a measurement error of ± 2 mV.

3. Results and discussion

3.1. Chemical composition

The chemical analysis of the various mineral samples is shown in Table 1. It is evident that the ilmenite samples exhibit some variation in chemical composition. The presence of some impurities such as Mg, Mn, Si and Ca decreases the Ti content of the samples. The XRD patterns of the samples shown in Fig. 1 suggest that all three samples are 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 content of iron in the IL-F sample is related to the amount of hematite. The higher content of CaO and SiO_2 in the IL-K sample is due to the presence of minor titanite ($CaTiSiO_5$) or sphene phase which was detected by X-ray diffraction. The other important impurities in these samples are MgO and MnO which are probably sourced from the geikielite ($MgTiO_3$)– pyrophanite ($MnTiO_3$) solid solution series in ilmenite. The IL-F sample has higher content of MgO (4.11%) while the MnO content (0.26%) is at the least level.

3.2. SEM microanalysis

The microstructure of the samples was studied by SEM and the various observed phases were analyzed using the electron microprobe analyzer. The results are given in Fig. 2 and Table 2. Ilmenite analysis showed that the TiO_2 content of the IL-F sample varies from 47.64 to 48.71% (average 48.01%) which is lower than the theoretical value (52.6%). The average content of FeO with 42.53% (varying from 41.9 to 42.98%) is about 5% lower than the theoretical content in the ilmenite structure. The most important impurity in the ilmenite structure is Mg