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Comparison of microwave irradiation and oxidation roasting as pretreatment methods for modification of ilmenite physicochemical properties

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ABSTRACT

The effect of microwave irradiation and oxidation roasting (as a conventional heating method) on ilmenite surface properties and its flotation behavior were compared. This comparison was performed by carrying out micro and laboratory scales flotation tests, XPS, XRD, FTIR, SEM and microprobe analyses, zeta potential and contact angle measurements. The micro scale flotation experiments indicated that the ilmenite flotation recovery improves from 73.5% to almost 94% and 91% after pretreatment by microwave irradiation and oxidation roasting, respectively. This is in good concordance with the results of XPS analysis showing the increase of Fe^{3+} content from 48.5% to 66% after pretreatment by microwave irradiation and 64.8% after oxidation roasting. As evidenced by FTIR analysis, zeta potential and contact angle measurements, the improvement in ilmenite floatability and hydrophobicity after pretreatment is due to the entrance of more oleate ions into the Helmholtz layer and the increase of the formation of ferric iron oleate which is more insoluble than the ferrous one. The surface properties and floatability of quartz does not change significantly after pretreatment by both methods.

In ore flotation experiments, when the grinded ore was pretreated by microwave irradiation and oxidation roasting, without significant changes in the TiO_2 grade of flotation concentrate, the recovery of TiO_2 improves from 65.4 to 76.2% and 73.7%, respectively. In the case of non-grinded ore, the recovery of TiO_2 increases up to 79.8% and 70.2% after microwave irradiation and oxidation roasting, respectively. The decrease of iron content in the gangue minerals increases the improvement of TiO_2 grade and recovery after pretreatment by both methods. Using microwave irradiation as a pretreatment process, the improvement in the recovery of TiO_2 and separation efficiency is more than those of oxidation roasting. In addition, microwave irradiation reduces the consumption of activation and depressant agents.

Introduction

Ilmenite is the most important titanium mineral, which is used to produce titanium dioxide and titanium metal [1]. Due to the various properties of ilmenite including high density, paramagnetic property and electrical conductivity, the gravity separation, high-intensity magnetic separation (HIMS), electrostatic separation and/or a combination of them are commonly used for its processing [2–6]. Nowadays, by decreasing the high-grade titanium deposits and also the ilmenite liberation degree, the low grade ores in which ilmenite is freely disseminated in the gangue minerals, have been considered significantly [3–6]. For these ores in which the conventional methods do not have good efficiency, the froth flotation is an effective method for ilmenite beneficiation [1,3–7]. In the anionic flotation, in comparison with magnetite and rutile, ilmenite has poor floatability. This can be due to the interaction of just half of the ilmenite metallic ions (Ti^{4+} and Fe^{2+}) with the collector anions at different pH ranges [3–5]. Various studies have been conducted for improving the ilmenite flotation recovery [3–13]. Hot flotation [8], agglomeration flotation [9], Aeration into the pulp [10], reverse flotation [11], activation with $Pb(NO_3)_2$ [4], surface dissolution [6] and microwave irradiation [3–5,12,13] are pretreatment methods which have been used to improve ilmenite floatability. Microwave irradiation, as a rapid

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heating technique, has recently been used in some processes such as comminution, magnetic separation, flotation, extractive metallurgy and etc. The literature review indicates that the microwave irradiation can increase mineral liberation, comminution efficiency, magnetic susceptibility, minerals floatability and leachability and also it can decrease the energy consumption of some processes [3,5,12–34]. In some previous works, the efficiency of microwave irradiation in the improvement of some minerals properties has been compared with the traditional thermal treatment method [14–17,20,21].

In this research, the efficiencies of microwave irradiation and oxidation roasting (as a conventional heating method) for improving ilmenite floatability and also its flotation behavior in the presence of different gangue minerals are investigated and compared with each other.

Materials and methods

Materials

Samples

The purified samples of ilmenite, olivine–pyroxene (Ol–Px), tremolite–clinochlore (Tr–Cch) and quartz were used in this study. The first three samples were prepared from the hand-picked samples taken from the Qara-aghaj deposit; a hard rock titanium deposit located 36 km from Urmia in Azerbaijan province northwest of Iran which contains olivine, pyroxene, tremolite and clinochlore as the main gangue minerals and ilmenite and magnetite as valuable minerals [35,36]. The hand-picked samples were crushed and ground under 150 μm as the ilmenite liberation degree [35]. Then, the sieving and several stages of tabling, low and high intensity magnetic separation methods were applied for achieving the purified samples. Olivine and pyroxene minerals containing Fe, Si and Mg as the main component have similar chemical and physical properties, and their separation from each other is almost impossible. This situation also exists between the tremolite and clinochlore minerals. Therefore, the main gangue minerals of the Qara-aghaj deposit having differences between their densities were separated by the shaking table into two mineral phases including olivine–pyroxene (Ol–Px) and tremolite–clinochlore (Tr–Cch). The quartz sample was taken from a silica mine in Qazvin province, Iran. The chemical composition of the purified samples determined by XRF is presented in Table 1. As seen from Table 1, there are significant differences between Fe, Si and Mg contents of the gangue minerals. Fig. 1 shows the XRD patterns of ilmenite, olivine–pyroxene (Ol–Px) and tremolite–clinochlore (Tr–Cch). Fig. 1a–c suggests that the purified samples including ilmenite, olivine–pyroxene and, tremolite–clinochlore are essentially composed of their minerals.

The ore samples including representative ore sample, low grade ore sample and high grade ore sample were used in the ore flotation experiments after removing the magnetite and titanomagnetite minerals by the low wet intensity magnetic separator. Table 2 shows the chemical composition of the ore samples. The low grade ore sample containing lower amounts of olivine and pyroxene was taken from block H of eleven blocks in Qara-aghaj area while the high grade ore sample with higher content of olivine and pyroxene was taken from block G.

Reagents

In this study, sodium oleate ($C_{18}H_{33}O_2Na$) with a purity of 95% was used as a collector. Sodium silicate (Na_2SiO_3) and lead nitrate ($Pb(NO_3)_2$) with 99% purities were consumed as depressant and activator agents, respectively. The pH adjustment was carried out using the analytical grade H_2SO_4 (97%) and NaOH (98%). In the ore flotation experiments, pine oil was used as a frother. Distilled water was used in both micro and ore flotation experiments throughout this study.

Methods

Materials characterization

The XPERT MPD diffractometer equipped with Cu *K*a radiation was used to determine the phase composition of the samples. The chemical analysis of the samples was conducted using X-ray fluorescence (XRF, Philips X Unique II). The textural and morphological characteristics of the samples were investigated by Philips XL30 model scanning electron microscopy (SEM). The electron microprobe (EMP) analysis of the samples was performed using a Cameca SX 100 instrument equipped with five wavelength dispersive (WD) spectrometers.

BET analysis

The BET analysis method with a high speed gas sorption analyzer (Quantachrome Corporation, NOVA 1000, VERSION 6.10) was used to determine the surface area of ilmenite and different gangue minerals. This analysis was carried out on the mineral samples with a size of −15 μm.

Microwave irradiation pretreatment

Microwave pre-treatment was conducted in a 2.45 GHz microwave oven (Black & Dicker model MG34EP-B1, rated power1000 W, and cavity dimension 333 × 356 × 210 mm). The prepared samples in defined size ranges were placed in the oven in a microwave transparent Pyrex glass vessel. In order to minimize the effect of the field pattern variation in the oven, the vessel was located in the center of the cavity. After irradiation for a desired exposure time, the samples were removed from the oven and were prepared for flotation experiments.

Oxidation roasting

The oxidation roasting pretreatment was conducted in a laboratory muffle furnace. When the furnace heated up to a predetermined temperature the sample placed in a ceramic pan was put into the furnace and roasted open to air. For carrying out the microflotation experiments, 30 g of the mineral sample was placed in a small ceramic pan while in the ore flotation experiments, 300 g of the ore sample was spread in a ceramic pan. When the sample roasted at adjusted temperature for a desired retention time, the pan was removed from the furnace, and cooled slowly in air at room temperature.

Microflotation experiments

A 300 cm^3 Hallimond tube was used for carrying out the microflotation experiments. In each test, before and after pretreatment, 2 g of purified minerals with a size of −150 + 45 μm were used. The suspension of the sample and the

Table 1
Chemical composition (wt%) of purified samples.

Composition	TiO_2	Fe_2O_3	MnO	V_2O_5	P_2O_5	CaO	MgO	SiO_2	Al_2O_3	L.O.I
Ilmenite	46.2	48.6	1.04	0.29	0.24	0.38	2.53	0.19	0.44	0.0
Olivine–pyroxene (Ol–Px)	0.9	43.0	0.64	0.015	3.34	5.6	15.8	29.5	1.06	0.0
Tremolite–clinochlore (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