



Effect of acidic activators on the flotation of oxidized pyrrhotite

Jie Liu, Er-lei Li*, Kai Jiang, Yan-jun Li, Yue-xin Han

School of Resources and Civil Engineering, Northeastern University, Shenyang 110819, China



ARTICLE INFO

Keywords:

Pyrrhotite
Oxidation
Acidic solution
Activation
Flotation

ABSTRACT

The objectives of the study are to detect the behavior of pyrrhotite oxidation and to determine the effect of acid activators on the flotation of oxidized pyrrhotite. The results showed that the floatability of oxidized pyrrhotite decreased significantly with the increase of oxidation time. The overall recovery dropped to 32.14% when pyrrhotite was oxidized for 30 days. It was proved that the oxidized pyrrhotite can be activated by both oxalic acid and sulfuric acid. The oxalic acid appeared to function better as the activator relative to the sulfuric acid, resulting in a higher recovery efficiency of oxidation pyrrhotite. The Zeta potential of the oxalic-acid-activated pyrrhotite showed a steeper downward trend, compared with that of the sulfuric-acid-activated pyrrhotite. According to observed Fe(2p) and S(2p) spectra, Fe(OH)₃ or FeOOH was produced on the surface of pyrrhotite, forming a hydrophilic film of O-bonded Fe³⁺; hence the floatability of pyrrhotite was decreased. This film could be dissolved in the acid activation and the maximum flotation potential of pyrrhotite was recovered. Moreover, oxalic acid activator would produce a stable complex [Fe(C₂O₄)³⁻ to retrieve the original surface of pyrrhotite, which resulted in better recovery than sulfuric acid.

1. Introduction

The formula of pyrrhotite is Fe_{1-x}S, where x varies from 0 to 0.125. The non-stoichiometric composition of pyrrhotite can also be shown as Fe_{n-1}S_n with n ≥ 8 to give formulae from Fe₇S₈ to Fe₁₁S₁₂. Pyrrhotite has hexagonal, orthorhombic and monoclinic forms (I et al., 2010; Janzen et al., 2000; Thomas et al., 2001; Thomas et al., 2000). Pyrrhotite is found mostly associated with pyrite, chalcopyrite and other sulfide minerals around the world. The pyrrhotite-bearing magnetic iron ores have been found in China (HE et al., 2012). The magnetism of pyrrhotite is similar to magnetite that can easily generates magnetic agglomeration leading to high content of sulfur in the iron concentrate. It is a tough problem to separate pyrrhotite from magnetite. At present, flotation is considered to be the most effective method to remove pyrrhotite from magnetite, but pyrrhotite would be rapidly oxidized when it is exposed to air or water giving unsatisfactory results (Buswell et al., 2002).

Potential factors impacting the oxidation of pyrrhotite have been discussed in many papers, including the crystal structure, oxygen and humidity, ferric iron, pH and temperature (Knipe et al., 1995; Becker et al., 2010; Chiriță et al., 2008). Spectroscopic techniques (XRD, XPS, AES, SEM, etc.) have been used to detect the composition of oxidized pyrrhotite to understand the oxidation mechanism (Belzile et al., 2004). The appearance of Fe(2p), Fe(3p) and S(2p) on XPS spectra corroborates the diffusion of iron through iron (II), iron (III) hydroxyl-oxide or

hydrated iron (III) oxide at the outmost layers and the elemental sulfur along with sulfate (Buckley and Woods, 1985). Intermediates such as thiosulfate and polythionate were also detected (Varnek et al., 2002). The formation of a non-stoichiometric non-equilibrium or metastable layer (NL) resulting from the preferential release of iron over sulfur has been further investigated to understand the oxidation and dissolution behaviour of pyrrhotite (Mikhlin et al., 1998; Mikhlin et al., 2000; Mikhlin, 2000). The formation of hydrated iron (III) and metastable intermediates of sulfate at the surface of pyrrhotite may attribute to the poor floatability because of their natural hydrophilicity.

In order to improve the recovery of pyrrhotite, an effective activator is urgently needed, such as Cu²⁺, Pb²⁺, HS⁻, S²⁻, etc. (Allison and O'Connor, 2011; Newell et al., 2006; Bradshaw et al., 2006; Lee et al., 2009). Copper sulfate together with sulfuric acid has been applied widely in China to obtain acidic solution. In the lately reported studies (Buswell and Nicol, 2002; Bunkholt and Kleiv, 2015) Fe²⁺ is exchanged by Cu²⁺ on the surface of pyrrhotite, which helps improve the pyrrhotite flotation.

It has long been researched on oxidation of pyrrhotite and activation by copper, while most studies focus on the short-term oxidation in the air or in aqueous solution. The research on mechanisms with the increase of oxidation time upon environment is very limited at this stage. Therefore, this paper focuses on the surface property of pyrrhotite with extended oxidation time and its activation behaviour by acids. XPS and Zeta potential measurements will be applied to

* Corresponding author.

E-mail address: lel1261644587@163.com (E.-l. Li).

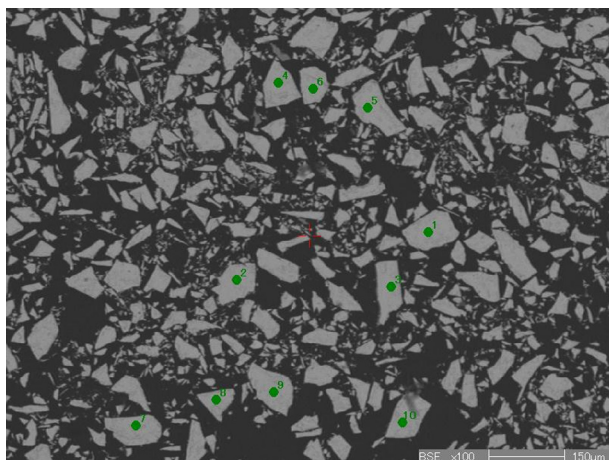


Fig. 1. Detection electron probe of pyrrhotite.

investigate the surface composition and flotation behaviour of oxidation pyrrhotite.

2. Experimental

2.1. Minerals

The pyrrhotite sample provided by the North Mining Corporation in Henan Province was used in the experiments. After crushing, sorting, grinding by a ceramic ball mill and dry screening, pure pyrrhotite mineral sample with a size distribution between 0.038 mm and 0.074 mm was prepared for the test. The mineral was stored in a wild-mouth bottle filled with nitrogen gas. Vaseline was smeared uniformly on the bottleneck to seal the bottle to avoid oxidation.

The results of Electron Probe Microanalysis of pyrrhotite are shown in Fig. 1 and Table 1. Table 1 indicates the contents of Fe and S are 60.25 wt% and 37.85 wt% respectively. The mole percentages of Fe and S are 47.63% and 52.37%, respectively. As a results, the pyrrhotite formula is calculated as Fe₁₀S₁₁. In addition, the contents of Cu, Zn and As are 0.025 wt%, 0.018 wt% and 0.06 wt%, respectively.

2.2. Oxidation treatment

2.0 g pyrrhotite sample was placed in a 50 mL beaker. 1 mL ethanol was then added and the beaker was gently shaken by hand to ensure uniform distribution of the sample in the beaker. After being dried quickly in the ventilation hood, samples were then exposed to air with relative humidity 60% at 293 K. Samples were checked daily to observe the oxidation process.

2.3. Flotation tests

In the experiments, the collector of sodium butyl xanthate and the frother of 2# oil with industry grade were used. For all other reagents, the chemical pure standard were adopted. Water used in all the tests refers to distilled water. Solutions of hydrochloric acid of 0.10 mol/L and sodium hydroxide of 0.10 mol/L were applied to adjust pH.

Flotation tests for pure pyrrhotite mineral were conducted in a micro-flotation cell with 25 mL effective volumes. 2.0 g sample through a 5-min ultrasonic cleaning was used in each experiment. The flotation

Table 1
Analysis results of electron probe of pyrrhotite (mass fraction, %).

Detection element	Fe	S	As	Cu	Zn
Average	61.819	38.648	0.06	0.025	0.018

time was proceeded for about 3 min under the following condition: stirring speed at 1800 r/min, activator and collector with a concentration of 10⁻⁴ mol/L and frother concentration of 13 mg/L. Activation tests were conducted for the samples which have been oxidized for 30 days. Recovery (R) is calculated by the Eq. (1).

$$R = \frac{m_1}{m_1 + m_2} \quad (1)$$

where *m*₁ is the mass of floated fractions and *m*₂ is the non-floated fractions.

2.4. XPS measurements

The XPS was conducted by Surface Analysis System (ESCALAB250, supplied by Thermo VG of America) with AlKα (1486.6 eV) as the photon source at 50.0 eV electron analysis pass energies. Binding Energy (B.E.) was measured using C 1s peak (284.6 eV) as a reference. Gaussian-Lorentzian bands were fitted and the peak in Fe (2p) and S (2p) were investigated to analyse the compositions on the pyrrhotite surface. To prepare the samples for XPS, the pyrrhotite was exposed to air for 30 days with 60% relative humidity at 293 K, leached and then dried. The leaching was carried out at 293 K for 1 h in oxalic acid and sulfuric acid with concentrations of 4 × 10⁻³ mol/L, respectively.

2.5. Zeta potential measurements

Zeta apparatus (Nano-ZS90, Made in England) was used to measure the zeta potential of pyrrhotite samples by the measurements of electrophoresis. In each test, 30 mg of mineral was ground to less than 2 μm in the agate mortar, and mixed with 50 mL distilled water in a 100 mL beaker. The collector and activators were added to the pulp, and then stirred for 5 min with a magnetic stirring apparatus. The pH of the suspension was regulated to prepare for the Zeta potential measurement and each sample was measured three times to calculate the average value.

3. Results and discussion

3.1. Effect of oxidation time on recovery of pyrrhotite

The recovery of pyrrhotite as the function of oxidation time was presented in Fig. 2. At the beginning, pyrrhotite had good natural floatability with recovery of 95.56%. After oxidation for 15 days, its recovery reduced sharply by almost 30 percentage. When oxidation time was extended to 30 days, the recovery of pyrrhotite was reduced

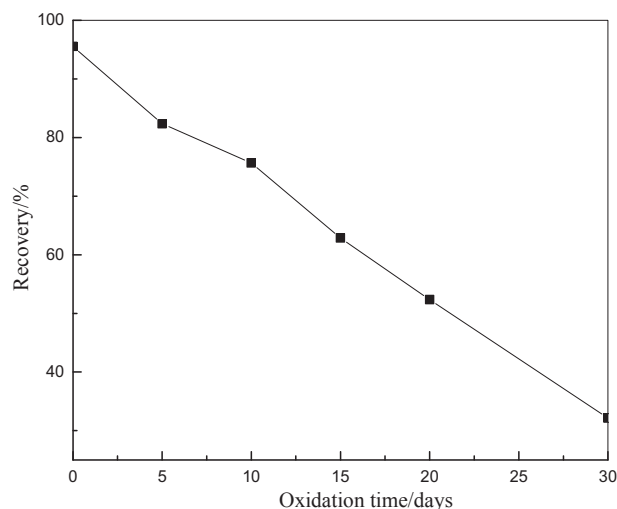


Fig. 2. Relationship of recovery of pyrrhotite with oxidation time.

Download English Version:

<https://daneshyari.com/en/article/6672425>

Download Persian Version:

<https://daneshyari.com/article/6672425>

[Daneshyari.com](https://daneshyari.com)