

## Floatability and oxidation of pyrite with different spatial symmetry



Yongjun Xian<sup>a,b</sup>, Yijie Wang<sup>a,b</sup>, Shuming Wen<sup>a,b,\*</sup>, Qi Nie<sup>c,\*</sup>, Jiushuai Deng<sup>a,b</sup>

<sup>a</sup>State Key Laboratory of Complex Nonferrous Metal Resources Clean Utilization, Kunming University of Science and Technology, Kunming 650093, China

<sup>b</sup>Faculty of Land Resource Engineering, Kunming University of Science and Technology, Yunnan, Kunming 650093, China

<sup>c</sup>Faculty of Mining Engineering, Kunming Metallurgy College, Yunnan, Kunming 650033, China

### ARTICLE INFO

#### Article history:

Received 26 September 2014

Accepted 10 December 2014

Available online 9 January 2015

#### Keywords:

Pyrite  
Spatial symmetry  
Space group  
Flotation  
Oxidation

### ABSTRACT

The spatial symmetry of mineral crystals has a strong potential for the unintentional floatability variation of minerals. In this study, the flotation and oxidation behaviors of two pyrites with the same FeS<sub>2</sub> stoichiometry but with different spatial symmetry were evaluated. The results show that an increase of pH and aerating time significantly increases the depression of pyrite with space group Pa3 during flotation, whereas pyrite with space group Pca21 is more difficult to depress compared to Pa3 pyrite with increasing pH. The aerating time inappreciably increases the depression of Pca21 pyrite. XPS analyses of the surface species of both pyrite samples with the same oxidation treatment confirm that more hydrophilic species (e.g., ion oxy-hydroxy species and sulfate) are present on Pa3 pyrite than Pca21. This result indicates that Pa3 pyrite is more easily oxidized than Pca21 pyrite. DFT was introduced to study the crystal structures and electronic structure of the two pyrites at the atomic scale. The cell models show that Pa3 pyrite has a central symmetry structure, whereas Pca21 pyrite forms with a non-centrosymmetry structure. The calculated values of the band gap of Pa3 and Pca21 pyrites suggests that the two pyrites have similar features of semiconduction. The DOS comparison implies that there are less Fe 3d orbit on the Pca21 pyrite surface crossing the Fermi level and suggests that the stability and oxidizability of Pca21 pyrite surface would be greater than Pa3. The stability and oxidizability of pyrite surfaces are most likely responsible for the difference of flotation and oxidation behaviors of the two pyrites.

© 2014 Elsevier Ltd. All rights reserved.

## 1. Introduction

Pyrite (FeS<sub>2</sub>) is the most common and widely distributed sulfide mineral in the Earth's crust and is usually associated with other sulfide minerals. It is generally considered to be a worthless mineral (i.e., gangue type) and is ideally removed during the processing of complex ores. The conventional practice of sulfide flotation takes advantage of the depression of pyrite in alkaline solutions. In practice, however, this technique is unsatisfactory for the removal of pyrite in many cases. One of the key factors is that the metal ions, such as Cu and Pb, that commonly exist in the flotation pulp result in the unintentional activation of pyrite, even in alkaline solutions (Finkelstein, 1999; He et al., 2005, 2006; Pecina et al., 2006; Prestidge et al., 1997; Skinner et al., 1996; Voigt et al., 1994; von Oertzen et al., 2005, 2007; Weisener and Gerson, 2000; Xian et al., 2013a,b).

Recently, some researchers proposed that the presence of lattice defects is another key factor affecting the flotation of pyrite. For instance, pyrite may float in the presence of copper and gold impurities in the crystal structure even in strong alkaline pulp (Chanturiya et al., 2000). During ore-forming, lattice defects of pyrite always result from the loss of its anions or cations, causing a vacancy defect. In addition, extraneous ions, such as Pb, Cu, Se, Zn, Au, and Ag ions, substitute for lattice sites or occupy the interstitial void of sulfide crystals causing impurity defects. The lattice defects in the pyrite crystal change the electrochemical properties and affect the electrochemical processes of pyrite, which is responsible for the varying pyrite oxidation and flotation (Abraitis et al., 2004). In a series of experiments, it was demonstrated that the presence of Co, As, and Ni in pyrites results in the semiconductor type conversion of pyrites and influences the oxidation of the pyrite surface under moist-air conditions (Lehner et al., 2006, 2007; Savage et al., 2008). In recent years, first principle calculations were increasingly introduced to assist the understanding of flotation mechanisms due to their ability to provide direct observations of atomic-scale phenomena in complete isolation. In a study using density functional theory (DFT), Li et al. (2010) found that vacancy defects significantly influence the covalence and electrochemical

\* Corresponding authors at: State Key Laboratory of Complex Nonferrous Metal Resources Clean Utilization, Kunming University of Science and Technology, Kunming 650093, China (S. Wen), Faculty of Mining Engineering, Kunming Metallurgy College, Yunnan, Kunming 650033, China (Q. Nie).

E-mail addresses: [shmw@126.com](mailto:shmw@126.com) (S. Wen), [158961326@qq.com](mailto:158961326@qq.com) (Q. Nie).

properties of pyrite and adversely affect pyrite flotation. They also studied the influences of As, Co and Ni impurities on pyrite (100) surface oxidation by O<sub>2</sub> molecules and reported that the pyrite surface bearing As impurities would lose the greatest quantity of electrons and suffer a higher level of oxidation than Co- or Ni-bearing pyrite surfaces (Li et al., 2011b). Through DFT and experimental investigations, Xian et al. (2012) demonstrated that the stability of pyrites increases in the following order: As-substituted < perfect < Co-substituted < intercrystalline Au. As-substituted pyrite is more easily depressed than perfect pyrite, whereas Co-substituted and intercrystalline Au pyrites are more difficult to depress than perfect pyrite. Li et al. studied the effect of various impurities on the electronic properties and reactivity of pyrite and reported that the presence of As, Co and Ni can enhance the oxidation of pyrite, whereas Se and Te do not affect the oxidation of pyrite. Co and Ni can significantly enhance the interaction of pyrite with butyl-dixanthogen, whereas As, Se and Te have little effect on the interaction of pyrite with butyl-dixanthogen (Li et al., 2011a).

These investigations provide novel research methods and valuable information for understanding the effect of factors on the flotation behavior of pyrite. However, some important science issues remain unresolved. Much of our geochemistry and crystal chemistry knowledge represents the fact that in addition to the above-mentioned lattice defects, the external mineralogical conditions, including temperature, pressure and volume, also result in structure variation of FeS<sub>2</sub> crystals, which change the chemical properties of the FeS<sub>2</sub> crystals, such as pyrite and marcasite (Bachhuber et al., 2014; Garcia et al., 2007; Huang and Rowson, 2001). By XRD analysis, we found two pyrites from two deposits belonging to the cubic system and have the same stoichiometry of FeS<sub>2</sub> but with different spatial symmetry (space groups). The different spatial symmetry has a strong influence on the unintentional floatability variation of pyrite. Unfortunately, so far, there has been little discussion on the correlation between spatial symmetry and the oxidation on the flotation of pyrite. By combining the computational and experimental methods (von Oertzen et al., 2005, 2007), the present investigation aims to understand the difference of the floatability and oxidation behaviors of two FeS<sub>2</sub> pyrites with different spatial symmetries and to elucidate the crystal and electronic structure of the pyrites to determine the reason responsible for the difference of floatability and oxidation. The present study provides a new perspective about a key factor, i.e., spatial symmetry, affecting the oxidation and flotation behavior of pyrite and aids in the further development of new methods for the treatment of hard-handle sulfide ores containing pyrite.

## 2. Method

### 2.1. Experimental method

#### 2.1.1. Material

The pyrite (FeS<sub>2</sub>) mineral samples used in this study were acquired from Weixian Mine (Pa3) and Lijiang Mine (Pca21) of Yunnan province, China, respectively. The ore was crushed into +0.5–1 mm particles, and impure minerals liberated from the pyrite were hand-removed under a microscope to obtain pure pyrite crystals. The elemental compositions of these samples were determined by Inductively Coupled Plasma Mass Spectroscopy (ICP-MS,

**Table 1**  
Chemical composition of the samples.

Sample no.	Elements (wt%)					
	Fe	S	SiO <sub>2</sub>	Cu	Ca	Mg
1#	44.84	53.31	0.21	<50 (ppm)	0.12	<0.01
2#	43.78	52.77	<0.05	0.034	0.31	<0.01

EIAN-DRCCII, PE, USA), and the results are shown in Table 1. An X-ray diffraction (D/Max 2200, Rigaku, Japan) analysis showed that pyrite was the only phase present, with no apparent impurities in both samples.

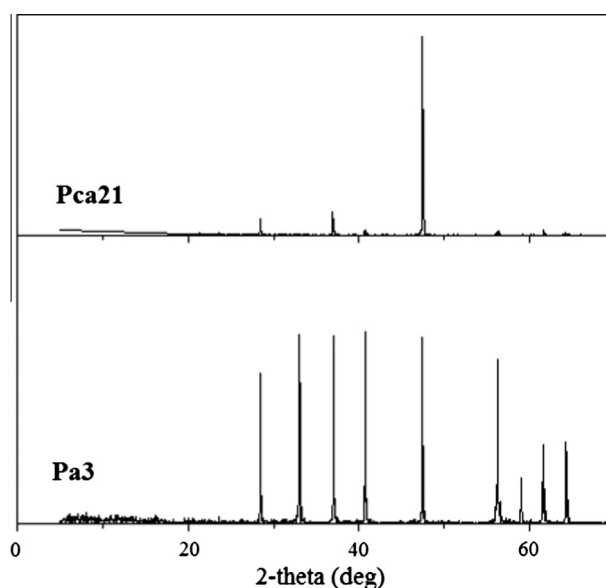
The X-ray diffractograms of the untreated pyrites and the corresponding lattice parameters from the Jade PDF database are presented in Fig. 1 and Table 2, respectively. The results showed that both pyrites belong to the cubic system and have the same stoichiometry but different space groups, i.e. pyrite with space group of Pa3 and pyrite with space group of Pca21 and which are responsible for the difference of the X-ray diffraction on the crystal structure.

#### 2.1.2. Flotation process

Pure deionized water with a resistivity of <18.0 mS/m produced from a Mill-Q50 (USA) was used throughout the flotation tests. The pyrite samples were washed with a deoxygenated 0.1 M H<sub>2</sub>SO<sub>4</sub> solution, rinsed 30 times with deoxygenated deionized water, and air-dried in an Ar environment. The purified pyrite (100 g) was dry-ground in an agate cup mill (MM400, Retsch, Germany) for 4.5 min at a frequency of 15/s, and the particle size of the final sample was  $d_{85} = 74 \mu\text{m}$ . After grinding, the pyrite was combined with 400 g of water and transferred into a 0.5 L XJC laboratory single-trough flotation cell, which has a bottom driven agitator and an aeration device. Before aerating, agitator was turn on at a revolving speed of 1200 r/min. The pH value of the flotation pulp was adjusted by NaOH and HCl (analytical reagent) solutions with a series of concentrations. The collector (Ethyl xanthogenate, 100 g/t) and frother (pine oil, 40 g/t) were added and conditioned for 2 and 1 min, respectively. The frother and collector used in this study were technically pure. Then, the flotation pulp was aerated for a predetermined time at flow rate of 3 L/min air. After aerating, the concentrate was collected for 5 min by a manual froth scraper device and was recovered on a filter. Each test was repeated three times, and the average value was obtained.

#### 2.1.3. XPS analysis

XPS measurements were performed with a Perkin Elmer Physical Electronics Division (PHI, 5100) spectrometer using an Mg Ka irradiation X-ray source operated at 300 W. A pass energy of 17.9 eV was used for all elemental spectral regions. The pressure in the analyzer chamber was 10<sup>-7</sup> Pa. Before the XPS analysis, both pyrite samples were oxidation treated with the same flotation



**Fig. 1.** X-ray diffractograms of untreated pyrites.

Download English Version:

<https://daneshyari.com/en/article/233116>

Download Persian Version:

<https://daneshyari.com/article/233116>

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