



The interaction of cyanide with pyrite, marcasite and pyrrhotite



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ABSTRACT

The adsorption of cyanide ions (CN⁻) on pyrite, marcasite and pyrrhotite surfaces was studied using density functional theory. The depressing effects of CN⁻ on these three minerals were then investigated by flotation tests. The calculated results show that the adsorption energy of CN⁻ on the marcasite surface is the largest, -374.91 kJ/mol; followed by pyrrhotite, -364.34 kJ/mol; and pyrite, -327.94 kJ/mol. These results indicate that the interaction between CN⁻ and marcasite surface is the strongest, then pyrrhotite, followed by pyrite. The depression effect of cyanide on the pyrite, marcasite and pyrrhotite in concentrate with increasing NaCN dosage was analysed by X-ray diffraction (XRD). The results show that the depression effect is in decreasing order of marcasite, pyrrhotite and pyrite, and the greater the cyanide dosage, the stronger depression effect is, which is in good agreement with the calculated results.

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1. Introduction

Cyanide, mainly as sodium cyanide (NaCN) and potassium cyanide (KCN), is an effective depressant of nonferrous metal sulphide minerals during flotation. The hydrolysis products of cyanide are HCN and CN⁻.



$$\frac{[\text{HCN}][\text{OH}^-]}{[\text{CN}^-]} = K_{\text{hydrolysis}} = 2.1 \times 10^{-5} \quad (3)$$

The hydrolysis product – hydrogen cyanide (HCN) is extremely dangerous, so cyanides must always be used in an alkaline medium, because the free alkali in solution will force the hydrolysis reaction (2) to the left.

Cyanide is the most commonly used reagents for increasing the separation efficiency of metal sulphide minerals by flotation. Early on, Sutherland and Wark (Sutherland and Wark, 1955; Wark, 1938) studied the depression of sulphide minerals by cyanide in the presence of several xanthate collectors. Their work illustrates the effectiveness of CN⁻ in mineral separation by flotation, and has been regarded as a standard reference for the industrial application of cyanide in flotation for many years. Since then, expanded studies have been carried out by many researchers (Kostović,

2011; Lu et al., 2002; Rao et al., 2011; Seke and Pistorius, 2006; Teixeira et al., 2013; Yin et al., 2011). For example, Kostović (2011) studied the depressing effect of the cyanide salts (NaCN, K₃[Fe(CN)₆] and K₄[Fe(CN)₆]), as well as ferrous/ferric salts (FeSO₄ and Fe₂(SO₄)₃) on the floatability of pyrite in the presence of xanthates as collector. The results showed that all of tested depressants reduce the collection ability of pyrite with K-butyl xanthate. Different combinations of reagents FeSO₄ and/or Fe₂(SO₄)₃ with NaCN have the greatest depressing effect on the pyrite, while the complex cyanide salts have much less of a depressing effect.

Despite a number of studies on the depression effect of cyanide, the depression mechanism for iron sulphide minerals is not entirely understood. In general, there are two explanations for the depression effect for the cyanide on the flotation of iron sulphide minerals with xanthate as a collector. Some researchers (Elgillani and Fuerstenau, 1968; Wang and Forssberg, 1996) thought that the free cyanide preferentially adsorbs on the iron sulphide mineral surfaces as iron cyanide compounds, hence inhibiting the chemisorption and oxidation of xanthate and thus hampering flotation recovery. Other researchers believed that free cyanide inhibits the electrochemical activities and decreases the mixed potential on the surface of the minerals, preventing the chemisorption and oxidation of xanthate (Wet et al., 1997). The two explanations were analysed further by the thermodynamic calculations and spectrophotometric studies of Guo et al. (2014). However, on the basis of these results, Guo et al. drew the conclusion that the depression effect of free cyanide on iron sulphide minerals may be questionable. According to their analysis, the

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existence of an insoluble iron cyanide surface species remains uncertain, and it is difficult to correlate the spectrophotometric studies to flotation behaviour because much higher cyanide concentrations have to be used in the spectrophotometric studies due to their detection limit.

Common iron sulphides include pyrite (FeS_2), marcasite (FeS_2), and pyrrhotite ($\text{Fe}_x\text{S}_{1-x}$), which often co-exist with other metal sulphides such as copper, lead, and zinc sulphide ores. The depression of iron sulphides is very important for the recovery of other useful metal sulphides. Of all the iron sulphides, the depression of pyrite by free cyanide has been studied the most (Wet et al., 1997; Prestidge et al., 1993). However, there is no such research on the depressing effect of cyanide on marcasite and pyrrhotite. Although pyrite, marcasite, and pyrrhotite consist of iron atoms and sulphur atoms, their crystal structures and properties are very different, which leads to their different flotation behaviour. As a result, it is significant to study the depression effect of cyanide on pyrite, marcasite, and pyrrhotite.

In this paper, the interactions of cyanide ions with the surfaces of pyrite (100), marcasite (010) and pyrrhotite (001) were studied using the DFT method, including adsorption models, adsorption energy, surface charge transfer and density of states (DOS). The flotation separation testing of lead–zinc sulphide minerals was carried out using different dosages of sodium cyanide with the depressing effect of cyanide on pyrite, marcasite, and pyrrhotite. This study provides the theoretical explanations for different interactions between cyanide and pyrite, marcasite, pyrrhotite surfaces.

2. Computational methods and models

2.1. Computational method

Density functional theory (DFT) calculations were carried out using the CASTEP program module developed by Payne et al. (1992). The generalised gradient approximation (GGA) developed by Perdew and Wang (PW91) (Perdew and Wang, 1992) was used to describe the exchange correlation effects. A Monkhorst–Pack k-point sampling density of $2 \times 2 \times 1$ was used for all adsorption calculations (Monkhorst and Pack, 1976). In all calculations, a plane wave cutoff energy of 270 eV was used based on the test results. The convergence tolerances for geometry optimization calculations are shown in Table 1.

2.2. Computational model

The crystal structures and models of pyrite, marcasite and pyrrhotite have been described in detail elsewhere (Zhao et al., 2015a, 2015b). Different crystal faces of pyrite, marcasite and pyrrhotite were studied to obtain the most stable faces, including (100), (001), (010), (101), (110), (011) and (111). The most stable faces of pyrite, marcasite and pyrrhotite through optimization test of various faces are (100), (101), and (001), respectively.

All surfaces were obtained from the optimum unit cell volume of the bulk sulphides. The pyrite (100), marcasite (101), and pyrrhotite (001) surfaces were modelled using $(2 \times 2 \times 1)$, $(2 \times 2 \times 1)$, and $(1 \times 2 \times 1)$ supercell geometries, respectively,

Table 1
The convergence tolerances for geometry optimization calculations.

Convergence tolerance parameters	Tolerances
Maximum displacement	0.002 Å
Maximum force	0.08 eV Å ⁻¹
Maximum energy change	2.0×10^{-5} eV atom ⁻¹
Maximum stress	0.1 Gpa
Self-consistent field (SCF)	2.0×10^{-6} eV atom ⁻¹

where the central cell contains a slab with two surfaces and a 15 Å vacuum gap above and below the surfaces separating adjacent mirror images of the slab. The surface energies of a range of surfaces with varying slab thicknesses were calculated to determine the slab size. The most stable surface models resulting from the DFT calculations are shown in Fig. 1(a)–(c). The bottom several atomic layers of the slab were kept fixed during all geometry optimization calculations. The surface atomic layers were relaxed. According to these three models (Fig. 1), the adsorption energies of CN^- on the pyrite, marcasite and pyrrhotite surfaces, Mulliken populations and DOS of the interaction between CN^- and the pyrite, marcasite and pyrrhotite surfaces were calculated using the first principles density functional calculation package CASTEP.

2.3. Calculation of adsorption energy

The adsorption energies of cyanide ions on sulphide surfaces were calculated as:

$$E_{\text{ads}} = E_{\text{CN}^-/\text{surface}} - E_{\text{CN}^-} - E_{\text{surface}} \quad (4)$$

where E_{ads} is the adsorption energy; $E_{\text{CN}^-/\text{surface}}$ is the energy of the pyrite, marcasite, or pyrrhotite slab with the adsorbed CN^- ; E_{CN^-} is the energy of the CN^- calculated in a cubic cell; and E_{surface} is the energy of the pyrite, marcasite, or pyrrhotite slab.

2.4. Flotation experiment

Ore samples were obtained from Dachang of Guangxi, China. The assays of the ore for multiple elements are shown in Table 2.

The main minerals in the ore are cassiterite, jamesonite, galena, pyrite, marmatite, pyrrhotite, and marcasite. The Pb and Sn exist mainly in the form of jamesonite with very little galena. The Zn and Sn exist in the form of marmatite and cassiterite, respectively. The gangue minerals include mainly quartz, mica, feldspar and carbonates. The proportion of the minerals in the feed is shown in Table 3.

The test ore is ground to 55% passing -0.074 mm. To this ore, 400 g/t butyl xanthate and 400 g/t copper sulphate were added. From this concentrate cassiterite was separated by gravity concentration. After the cassiterite removal, the bulk concentrate was ground to 85% passing -0.074 mm, this material was used as the feed for separating the lead minerals and marmatite. In the bulk concentrate, the assays of iron, lead, antimony, zinc and sulphur were 23.4%, 0.81%, 0.72%, 5.2%, and 30.1%, respectively. Hence a large amount of iron sulphides (pyrite, marmatite, and pyrrhotite) need to be depressed in the separation of lead–zinc minerals. It should be noted that the flotation behaviour of jamesonite is different with galena. Jamesonite is sensitive to the pulp pH, especially when using lime (Zhao et al., 2015a, 2015b). The pulp pH of flotation for jamesonite is lower than 9.5; however, iron sulphides could not have been depressed under such a low-alkaline condition. As a result, a certain amount of sodium cyanide was added in the flotation operation. A flowsheet for the flotation of the ore feed is shown in Fig. 2.

To understand the effect of the NaCN dosage on pyrite, marcasite, and pyrrhotite, the recovery of iron, zinc and lead in the concentrate were chemically analysed. The low content of iron means a strong depressing effect of sodium cyanide on the iron sulphide minerals. In addition, the effect of NaCN on the pyrite, marcasite and pyrrhotite in the concentrate with increasing NaCN dosage was analysed by X-ray diffraction (XRD) (Cu $K\alpha$ radiation) using a Rigaku D/MAX-2500 V diffractometer.

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