Depression of pyrite in alkaline medium and its subsequent activation by copper

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ABSTRACT

The adsorption of hydroxyl and calcium hydroxyl ions (OH⁻ and CaOH⁺) on pyrite (100) surfaces was studied using first-principles calculations to investigate the depression of pyrite by NaOH and CaO. The calculation results showed that the adsorption of CaOH⁺ on pyrite surfaces was stronger than the adsorption of OH⁻. The surface Fe atoms were the active sites for the two adsorbates, which is not conducive to the interaction of xanthate with the pyrite surface. In addition, partial surface S atoms were covered by Ca in CaOH⁺, which would not be favourable for the copper activation of pyrite. The OH⁻ obtained electrons from the surface, whereas CaOH⁺ lost electrons to the surface. The loss of electrons resulted in the accumulation of electrons on the surface, which hindered the oxidation of pyrite and the formation of dixanthogen. Flotation tests showed that the Cu activation of pyrite after depression by CaO was more difficult than after depression by NaOH. This result was consistent with the calculated result that partial surface S sites, which were the active sites of Cu adsorption, were covered by Ca; this coverage resulted in the Cu activation becoming difficult.

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1. Introduction

Pyrite is one of the most common sulphide minerals encountered in nature. Pyrite often exists in sulphide mining and coal mines, where it is usually undesired and is often removed by the flotation method. The flotation behaviour of pyrite is greatly influenced by the pH of the pulp. Sodium hydroxide (NaOH) and lime (CaO) are the most common pH modifiers for pulp and are also effective depressants of pyrite. The depressing effects of NaOH and CaO on pyrite are different, and CaO is more effective. It is shown that pyrite would be effectively depressed at lower pH levels regulated by CaO.

Suggested reasons for NaOH depressing pyrite include the hydrophilic compounds of iron hydroxyl forming on the pyrite surface hindering the adsorption of xanthate anion. Another view suggests that OH⁻ could exchange with xanthate anion, which then desorbs from the pyrite surface. Wang and Forssberg (1996) have shown that OH⁻ would first chemically adsorb on the pyrite surface:

$$FeS_2 + OH^- \rightarrow FeS_2 - OH_{ads} + e \qquad (1)$$

The main components after the dissolution of lime (CaO) in water are calcium ion (Ca²⁺) and hydroxyl ion (OH⁻). At a pH below 12.5, calcium hydroxyl ion (CaOH⁺) is the main component in lime solution. Chen et al. (2011) have shown that when CaO was used to adjust the pH of pulp, the zeta potential of pyrite was more posi-

tive than when NaOH was used; furthermore, at a pH range of 9–12, the zeta potential of pyrite in CaO solution increased as the pH value was increased. This result suggests that the interaction of CaOH⁺ with the pyrite surface is stronger than the interaction of OH⁻ with the pyrite surface at high pH levels.

Different views exist with respect to the roles of calcium on the depression of pyrite. The adsorption of calcium on surface has been suggested to inhibit the oxidation of pyrite and thus reduce the formation of dixanthogen on the surface. Szargan et al. (1992) have suggested that the adsorption sites of dixanthogen on a pyrite surface were reduced due to the adsorption of calcium, which resulted in the depression of pyrite. Based on evidence gathered using the X-ray photoelectron spectroscopy (XPS) method, Hu et al. (2000) have suggested that the surface CaSO₄ species on pyrite accounted for the depression of pyrite by CaO.

In this paper, using first-principles calculations, the adsorption of hydroxyl and calcium hydroxyl ions (OH⁻ and CaOH⁺), respectively, on a pyrite (100) surface were used to investigate the depression of pyrite by NaOH and CaO. The copper (Cu) activation of pyrite depressed by NaOH and CaO was predicted based on the calculation results. Flotation tests were performed, and the prediction was confirmed.

2. Methods

2.1. Computational details

All the calculations were performed using CASTEP, GGA-PW91 (Perdew et al., 1992) based on density functional theory. Only va-

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lence electrons were considered explicitly through the use of ultrasoft pseudopotentials (Vanderbilt, 1990). Based on the test results, a plane wave cut-off energy of 270 eV was used for all calculations. The surfaces were obtained from the relaxed bulk structure. Adsorption studies were performed using surface supercells that corresponded to (2×2) surface unit cells, and a Monkhorst–Pack (Monkhorst and Pack, 1976; Pack and Monkhorst, 1977) k-point sampling density of $2 \times 2 \times 1$ was used for all adsorption calculations. In addition, a vacuum thickness of 15 Å was placed between the slabs. The slab thickness was tested to determine the slab size that produced a convergence of the surface energy to within 0.005 J/m^2, and a slab size with 15 atomic layers was determined (see Fig. 1). Geometric constraints were placed on the bottom nine atomic layers of slab. Before adsorption, the hydroxyl and calcium hydroxyl molecules (OH$^-$ and CaOH$^+$) were placed inside a $15 \times 15 \times 15$ Å cubic cell for the optimisation calculation, and the gamma point was used. The convergence tolerances for the geometry optimisation calculations were set to a maximum displacement of 0.002 Å, a maximum force of 0.08 eV Å^{-1}, a maximum energy change of 2.0×10^{-5} eV atom^{-1} and a maximum stress of 0.1 GP; the SCF convergence tolerance was set to 2.0×10^{-6} eV atom^{-1}. In addition, the spin polarisation was used for all calculations.

The adsorption energy of each adsorbate (OH$^-$ or CaOH$^+$) on a pyrite surface was calculated as

$$E_{ads} = E_{adsorbate/slab} - (E_{adsorbate} + E_{slab}), \quad (2)$$

where E_{ads} is the adsorption energy, $E_{adsorbate}$ is the energy of the OH$^-$ or CaOH$^+$ calculated in a cubic cell, E_{slab} is the energy of the FeS$_2$ slab and $E_{adsorbate/slab}$ is the energy of the OH$^-$-adsorbed or CaOH$^+$-adsorbed FeS$_2$ slab. A more negative value of E_{ads} indicated

Fig. 1. Slab model of (2×2) pyrite $(1\,0\,0)$ surface with 15 atomic layers and vacuum thickness of 15 Å. The atoms on the same level occupy one layer.

stronger adsorption of molecule on surface. The slab model of a (2×2) pyrite $(1\,0\,0)$ surface with 15 atomic layers and a vacuum thickness of 15 Å is shown in Fig. 1. Each Fe atom is coordinated to five S atoms, and each S atom is coordinated to two Fe atoms and one S atom, thereby retaining a perfect S$_2^{2-}$ dimer on the pyrite $(1\,0\,0)$ surface.

2.2. Flotation

Samples of pyrite were obtained from the Dachang Tongkeng Mine in Nandan, China. High-purity samples were hand-picked from the mine, and a chemical analysis revealed that the pyrite content was 95.7%. The samples were dry-ground in a porcelain ball mill and dry-screened to obtain $-0.09 + 0.06$ mm particles.

In each test, 2.0 g of the material was added to a XFGC-80 single-trough floatation cell. Prior to the test, the sample was cleaned with supersonic waves. The reagents were added in the following order: (a) NaOH with 3 min of conditioning; (b) 1×10^{-4} mol/L CuSO$_4$ with 5 min of conditioning; and (c) 5×10^{-5} mol/L xanthate with 5 min of conditioning. The flotation time was set to 3 min in all of the single-mineral experiments.

3. Results and discussion

3.1. Adsorption of OH$^-$ and CaOH$^+$ on the pyrite surface

The adsorption sites of hydroxyl and calcium hydroxyl molecules (OH$^-$ and CaOH$^+$) were tested to determine the stable adsorption configuration of the molecules on pyrite surfaces. Fig. 2 shows the possible adsorption sites of OH$^-$ and CaOH$^+$ on pyrite surfaces, and the values shown in the figure indicate the atomic distance in angstroms. The calculation results shown in Table 1 suggest that the adsorption energy of a hydroxyl O atom on the surface Fe site (-264.99 kJ mol^{-1}) was far less than that on a surface S site (-163.65 kJ mol^{-1}), which indicates that the surface Fe atom was the active site for OH$^-$ adsorption. The adsorption energy of CaOH$^+$ on Hollow 1 (the configuration shown in Fig. 2c) was -191.60 kJ mol^{-1}, which was higher than that on Hollow 2 (configuration shown in Fig. 2d, with an O atom adsorbed on a surface Fe atom and a Ca adsorbed on surface S atoms) at -276.62 kJ mol^{-1}. This result suggests that the latter site (Hollow 2) would be the stable configuration for CaOH$^+$ adsorption on the pyrite surface. Based on the calculated adsorption energies, the depression of pyrite by lime (CaO) was expected to be stronger than the depression by sodium hydroxide (NaOH). In addition, we have found that the adsorption energy of H$_2$O molecule on pyrite surface was only -63.68 kJ/mol. This suggested that although water molecule may have influence on the pyrite surface properties, the strong chemical adsorption of OH$^-$ and CaOH$^+$ still plays a dominant role on the pyrite surface.

The Fe–O atomic distance on the OH$^-$ adsorption surface (1.843 Å) was shorter than that on the CaOH$^+$ adsorption surface (2.092 Å). In addition, the Mulliken population of the Fe–O bond shown in Table 2 suggests that the population of Fe–O bond on the OH$^-$ adsorption surface (0.42) was greater than that on the CaOH$^+$ adsorption surface (0.25). Furthermore, the electron density map shown in Fig. 3 indicates that the Fe–O interaction on the OH$^-$ adsorption surface was apparently more covalent (i.e., exhibited greater electron density in the interatomic region) than that on the CaOH$^+$ adsorption surface. However, a comparison of the adsorption energies of OH$^-$ and CaOH$^+$ on the pyrite surface indicated that the adsorption of CaOH$^+$ was stronger than that of OH$^-$. This result suggested that the presence of Ca would greatly enhance the adsorption of CaOH$^+$ on the pyrite surface, although the adsorption of the –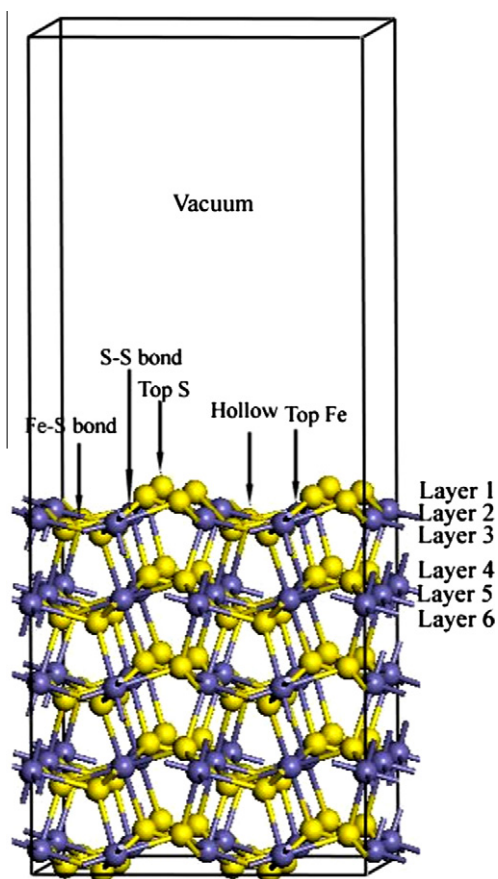OH group in CaOH$^+$ was weaker than the