



Full Length Article

Activation mechanism of ammonium ions on sulfidation of malachite (–201) surface by DFT study



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ABSTRACT

The activation mechanism of ammonium ions on the sulfidation of malachite (–201) was determined by density functional theory (DFT) calculations. Results of DFT calculations indicated that interlayer sulfidation occurs during the sulfidation process of malachite (–201). The absorption of both the ammonium ion and sulfide ion on the malachite (–201) surface is stronger than that of sulfur ion. After sulfidation was activated with ammonium ion, the Cu 3d orbital peak is closer to the Fermi level and characterized by a stronger peak value. Therefore, the addition of ammonium ions activated the sulfidation of malachite (–201), thereby improving the flotation performance.

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1. Introduction

Copper oxide ore is an important part of copper resources [1]. Malachite is a typical representative of copper oxide ores [2]. Malachite is a carbonate mineral containing copper, belonging to monoclinic system [3]. Its crystal form is needle-like and columnar. Its aggregate shows massive, hull-like, nodular and its structure has fiber radial and concentric layer. Malachite is arguably the best know Cu secondary mineral typically formed in the oxidation zone of copper deposits as weathering product of copper sulphides, always symbiosis with other copper-containing minerals, such as azurite, chalcocite, cuprite and other natural copper ore.

Sulfidation xanthate flotation is the most widely used method for dealing with copper oxide ore [4–7]. The sulfidation process converts the oxide mineral surface using Na₂S, whereas the adsorption of S^{2–} ions on the oxide mineral surfaces generates a metal sulfide film in favor of oxide mineral flotation [8,9]. However, in the sulfidation process of copper oxide ore, there are some problems, such as a large amount of sulfidizing agent consumption and low sulfidation efficiency, which puts forward new challenges for the sulfidation xanthate flotation of copper oxide ore.

Minerals fracture along the surface with the weakest bonding force in a crystal structure through mechanical breaking. Smooth surface fracturing along a certain crystalline direction is called dissociation surface, and irregular and rugged mineral surface fracturing not along a certain crystalline direction is called fracture surface [10]. In practice, the structure of a mineral is composed of many crystals. The fracture surface of a mineral is always complex. The unsaturated degree of chemical bonds from a fracture is different because of various fracture positions. These unsaturated bonds remarkably affect the polarity and native floatability of mineral surfaces. The dissociation surface of minerals has been extensively investigated [11]. However, the dissociation surface of malachite has been rarely examined. Lebernegg et al. [12], selected the surface of malachite (201) to conduct related studies through quantum chemical calculation and demonstrated that a common edge is used with two small surfaces of malachite (201) approximate to CuO₄ to form a Cu₄O₆ dipolymer with a double bridge and create a (201) parallel surface with carbonate rocks at an angle of 2.37 Å. This formation is the dissociate surface of a malachite crystal with a complete structure. In addition to the (201) surface, a (010) surface is an equivalent dissociation surface, that is, orthogonal to surfaces and parallel to chains [12–14]. However, the dissociation of this surface involves the destruction of dipolymers and carbonate rocks and requires a considerable amount of energy [12]. Com-

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Table 1
Crystal lattice parameters of malachite under different exchange correlation functions.

Exchange- Correlation Functional	Calculated value				Experimental value	
	Lattice parameter/Å		Axis angle/°		Lattice parameter/Å	Axis angle/°
GGA-PBE	a	21.892	α	90	a = 9.502	$\alpha = 90$
	b	12.083	β	150.71		
	c	8.586	γ	90		
GGA-PW91	a	10.096	α	90	b = 11.974	$\beta = 98.75$
	b	12.023	β	103.39		
	c	3.334	γ	90		
GGA-SOL	a	14.332	α	90	c = 3.240	$\gamma = 90$
	b	11.886	β	133.963		
	c	5.693	γ	90		

pared with the (201) surface, the (010) surface is more difficult to dissociate.

In this study, based on the electronic geometry and surface atomic properties of malachite crystal, the research results of structural analysis were applied to the flotation research field. The sulfidation mechanism of malachite and the activation mechanism of NH_4^+ on sulfidation of malachite were studied by DFT calculations.

2. Calculation method and simulation

CASTEP module in Materials Studio (MS) is used to simulate calculations [15]. In the calculation, the exchange correlation function uses the PW91 gradient correction function under GGA to provide description and an ultrasoft pseudo potential of PW base cluster to describe the interaction between an ion core and a valence electron [16–20]. The following valence electrons are considered to calculate the pseudo potential of each atom: Cu– $3d^{10} 4s^1$, C– $2s^2 2p^2$, O– $2s^2 2p^4$, S– $3s^2 3p^4$, N– $2s^2 2p^3$, and H– $1s^1$. The cut-off energy is appropriately set at 351 eV. The total system energy and charge density are subjected to integral calculation in Brillouin area by using the Monkhorst–Pack scheme. The selected k grid point is $2 \times 2 \times 6$ in size to ensure the convergence of system energy and configuration on the level of a quasi complete surface wave base. In self-consistent field operation, Pulay density mixture method is used. Its convergence accuracy is set at 2.0×10^{-5} eV atom⁻¹. BFGS algorithm is utilized to optimize the model structure. The convergence criteria for the interaction force between atoms, the internal stress of the crystal, and the maximum atomic displacement are set at 0.005 eV nm⁻¹, 0.1 GPa, and 0.002 Å, respectively.

The sulfidation mechanism of malachite is investigated mainly to analyze sulfide adsorption configuration and S^{2-} adsorption energy on the surface of malachite or among the layers. The activated sulfidation mechanism of malachite is also explored to examine the adsorption effects of S^{2-} and NH_4^+ on the surface of malachite. As calculation and construction models, CASTEP module is used to construct the structures of S^{2-} and NH_4^+ , and BFGS optimization algorithm is applied to optimize these structures. The optimized particles are placed on the surface of the optimized malachite to simulate and calculate its interaction process. It is regarded as the convergence after the system energy reaches equilibrium in the self-consistent process. The adsorption energy (ΔE_{ads}) of an atom adsorbed on the surface of malachite is calculated as follows:

$$\Delta E_{ads} = E_{malachite+\chi} - E_{malachite} - E_{\chi} \quad (1)$$

where $E_{malachite}$ and $E_{malachite+\chi}$ respectively refer to the total energy of a cell model on the surface of malachite (–201) before and after the corresponding particles are adsorbed; E_{χ} refers to the energy of each particle; and ΔE_{ads} refers to the adsorption energy of each particle after it is adsorbed on the surface of malachite. A negative ΔE_{ads} indicates that the reaction can be performed

spontaneously. A more negative ΔE_{ads} shows that stronger adsorption more likely occurs. Density functional simulation is conducted in a vacuum. Thus, adsorption energy is calculated differently because calculation systems vary [21]. However, these systems provide a qualitative basis but do not represent the actual energy. The charge of adsorbents or adsorbates can affect the absorption energy obtained by the DFT calculation. The DFT calculation on charged systems presents a few limitations. The current research aimed to obtain change trend of interaction energy and charge transfer mechanism between malachite surface and sulfur ion or ammonium ion. The results can be used to explain experimental phenomena and provide useful information.

3. Results and discussion

3.1. Surface geometry structure of malachite

Calculation was performed on malachite crystals by use of three different gradient-corrected functionals under the generalized gradient approximation (GGA). The best calculation method could be obtained through comparison with the experimental values. The comparison results are shown in Table 1.

The calculation results show that using GGA-PW91 is appropriate for the obtained lattice constants of malachite unit cell are comparatively close to the experimental values. Hence, the GGA-PW91 was used in the subsequent study.

The calculated surface energy of the malachite crystal (–201) surface is relatively small. Therefore, this surface is a dominant dissociation surface and mainly selected as the object of this study. To examine the structure and properties of malachite surface atoms, we optimize the structure of the malachite surface. A malachite crystal cell model is initially optimized and the (–201) surface with three atomic layers is cut on the basis of the optimized cell. The vacuum layer with a thickness of 20 Å is constructed on the z axis (Fig. 1). Fig. 1(a) and (b) respectively illustrate the side view and the top view of malachite (–201) surface.

As shown in Fig. 1, two Cu of malachite (–201) surface and other atoms constitute two kinds of approximate tetrahedral and hexahedral structures; four Cu atoms, two carbonate rocks, and one hydroxyl form a large polyhedron. After the structure is optimized, the surface atoms exhibit evident displacement called relaxation phenomenon if the force and energy among atoms reach convergence balance. This phenomenon is mainly reflected in the changes in bond angle and bond length.

Table 2 shows the geometric parameters of the surface atoms of the malachite (–201) surface before and after optimization. Furthermore, Table 2 reveals that the bond angles of $\text{Cu}_1\text{—O—Cu}_2$ and $\text{O}_{[\text{CO}_3]}\text{—Cu—O}_{[\text{OH}]}$ changed. The bond angles $\hat{\alpha}_1$ and $\hat{\alpha}_2$ in approximate tetrahedral composed of Cu1 and Cu2 atoms change. In particular, for the bond angle of $\text{Cu}_1\text{—O—Cu}_2$, $\hat{\alpha}_1$ and $\hat{\alpha}_3$ increase whereas $\hat{\alpha}_2$ decreases; for the bond angle of $\text{O}_{[\text{CO}_3]}\text{—Cu—O}_{[\text{OH}]}$, $\hat{\alpha}_1$

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