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Thermodynamics and density functional theory study of potassium dichromate interaction with galena

Jian-Hua Chen[1,2], *Xian-Hao Long*[1], *Li-Hong Lan*[3], *and Qian He*[2]

1) College of Chemistry and Chemical Engineering, Guangxi University, Nanning 530004, China
2) College of Resources and Metallurgy, Guangxi University, Nanning 530004, China
3) Key Laboratory of Chemical and Biological Transformation Process of Guangxi Higher Education Institutes, School of Chemistry and Chemical Engineering, Guangxi University for Nationalities, Nanning 530006, China

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Abstract: The adsorption heat and reaction rate constant of potassium dichromate on the surface of galena were studied. The results indicate that potassium dichromate tends to adsorption on the galena surface. The reaction order is only 0.08385, suggesting that the concentration of potassium dichromate has little influence on its adsorption on the galena surface. In addition, the simulation of CrO_4^{2-} adsorption on the PbS (100) surface in the absence and presence of O_2 was carried out by density functional theory (DFT). The calculated results show that CrO_4^{2-} species adsorb energetically at the Pb–S bond site, and the presence of O_2 can enhance this adsorption.

Keywords: flotation; potassium dichromate; galena; adsorption; thermodynamics; density functional theory

1. Introduction

Ever since the use of sodium dichromate in flotation was deemed as a depressant for lead minerals in 1921 [1], the interactions of chromates or dichromates with complex sulfide minerals containing galena have been highly studied [2–6]. It is generally accepted that the depressing mechanism of galena in the presence of a dichromate is based on two aspects [7–8]. First, the formation of lead chromate with high hydrophobicity on the surface is favored when oxidized galena is treated with a dichromate, which depresses galena. Furthermore, a xanthate can be desorbed from the galena surface in the presence of potassium dichromate. Although studies on adsorption and depression of a dichromate on the galena surface have been reported, the micro-mechanism of dichromate adsorption on galena is not yet fully understood.

It has been found that the pulp must be stirred for an extended period to oxidize galena surfaces when a dichromate is used as a depressant in flotation [9]. This suggests that the oxidation of galena surfaces by oxygen molecules plays a very important role in galena depression. However, the detail of dichromate–galena surface interactions is rare in the literature. In particular, the effect of oxygen molecules has been neglected in the investigations of interaction between galena surfaces and dichromates.

Microcalorimetry with high sensitivity and accuracy is an important and effective method for the analysis of thermodynamics and dynamics. It provides useful and reliable information about the thermodynamics and kinetics of reaction processes [10–11]. In addition, computational methods, such as the density functional theory (DFT), are effective tools for the acquisition of microscopic details about configuration and electronic structure during reagent adsorption on mineral surfaces [12–16].

In this study, the kinetics and thermochemistry of CrO_4^{2-} adsorption on the galena surface were measured with microcalorimetry. At the same time, the simulation and modeling of CrO_4^{2-} adsorption on the (100) surface of PbS in the absence and presence of O_2 were performed by DFT. The combined results from computational simulation and thermodynamic analysis gave an insight into the properties and interactions between the galena surfaces and dichromates, the mechanism of reagent adsorption, and the subse-

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Corresponding author: Li-Hong Lan E-mail: lanlihong2004@163.com

quent flotation behavior of galena.

2. Experimental

2.1. Pure mineral flotation

A pure galena sample was obtained from Dachang Mine in Guangxi Province, China. The hand-picked sample had a purity of 95.1%. The sample, defined as clean galena, was cleaned with a supersonic apparatus for 8 min before flotation experiments. Another sample, defined as oxidized galena, was baked in an oven for 20 min at 60°C. Mineral particles with the sizes of −148 μm were selected for flotation experiments and sealed in glass bottles.

Flotation experiments on the pure mineral were carried out in a suspended style flotator with a capacity of 40 mL. In each experiment, 4.0 g of the sample was used. During flotation, the reagents were added in order. The depressant, potassium dichromate, was first added followed by a 5×10^{-5} mol/L butyl-xanthate while agitating for 3 min. The total flotation time was at least 5 min. In addition, $CuSO_4$ was used to activate galena, and the activating time was 2 min.

2.2. Microcalorimetry examination

The heat generated by the adsorption process characterizes the intensity of adsorption between the reagent and mineral [17]. Hence, the adsorption heat of galena was measured using an RD496-III type microcalorimeter (Southwest Institute of Electronic Engineering, China), an automatic instrument controlled by computer, as shown in Fig. 1(a). Fig. 1(b) shows the cuvette and sleeve employed in the adsorption reaction setup.

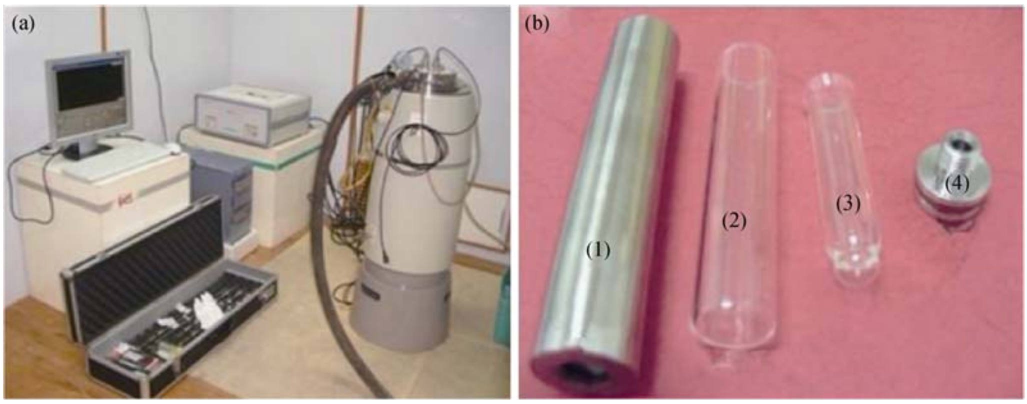

Fig. 1. Microcalorimetry experimental equipment: (a) microcalorimetry device; (b) (1) stainless steel casing, (2) large sample cell, (3) small sample cell, (4) stainless steel cover.

The first step in the microcalorimetry experiment was the preparation of samples. The studied galena samples were natural minerals with a purity of 95.1%. A 1.0 g sample and 20 mL distilled water were put in a 50 mL conical flask. The mixture was vibrated by ultrasonic wave for 5 min and then allowed to rest. The mixture components separated into two layers. After removing the clear liquid layer, 20 mL distilled water was added to produce the mineral samples.

In the second step, the heat of adsorption was measured. Distilled water (1 mL) and the mineral sample (1 mL) were shaken and injected into small (3 mL) and large (6 mL) sample cells using an injector. The small sample cell was then put into the large sample cell, and both were put in a 15 mL stainless steel sleeve. The sealed sleeve was placed into the microcalorimetry device. The temperature of the calorimetric experiment was kept constant at 298.15 K. The reaction parameters were set, and when the baseline was stable, the small sample cell was pierced, allowing distilled water to flow into the large sample cell. As a result, the distilled water was mixed with the mineral sample in the large cell. The thermal effect was then recorded automatically by computer.

2.3. Computational and modeling methods

Calculations were performed using the Castep module (Cambridge Serial Total Energy Package) based on the first principle pseudopotential method [18–23]. The DFT calculations employed the plane wave (PW) basis sets and the ultrasoft pseudopotentials [24]. The exchange correlation functional used was the Perdew–Wang generalized gradient approximation (GGA) [25]. A kinetic energy cutoff of 280 eV for the PW basis was used throughout. The Brillouin zone was sampled with Monkhorst and Pack special k-points of a $2 \times 2 \times 1$ grid for all structure calculations, which demonstrated that the cutoff energy and the k-points meshes were sufficient for the system [26–27]. The convergence tolerances for geometry optimization calculations were set to the maximum displacement of 0.02 nm, the maximum force of 0.5 eV/nm, the maximum energy change of 2.0×10^{-5} eV/atom, the maximum stress of 0.1 GPa, and the self-consistent field (SCF) convergence tolerance of 2.0×10^{-6} eV/atom. The valence electron configurations considered in the study were Pb $5d^{10}6s^{2}6p^{2}$, S $3s^{2}3p^{4}$, Cr $3s^{2}3p^{6}3d^{5}4s^{1}$, and O $2s^{2}2p^{4}$. Before adsorption, O_2 and CrO_4^{2-} were placed inside a 1.5 nm × 1.5 nm × 1.5 nm cubic cell for optimization calculation with a vacuum thickness of 1 nm between the surfaces slabs. Fig. 2 shows the computational models of galena surfaces and the unit cells of CrO_4^{2-} and O_2. The molecules were constructed in the simulation program, and all structures were optimized before analysis.

2.4. Calculation of adsorption energy

The adsorption energy of CrO_4^{2-} on galena surface was calculated as

$$E_{ads} = E_{CrO_4^{2-}/surface} - E_{CrO_4^{2-}} - E_{surface} \quad (1)$$

where E_{ads} is the adsorption energy, $E_{CrO_4^{2-}}$ the energy of CrO_4^{2-} calculated in a cubic cell, $E_{surface}$ the energy of a galena slab, and $E_{CrO_4^{2-}/surface}$ is the energy of a galena slab with adsorbed CrO_4^{2-}.

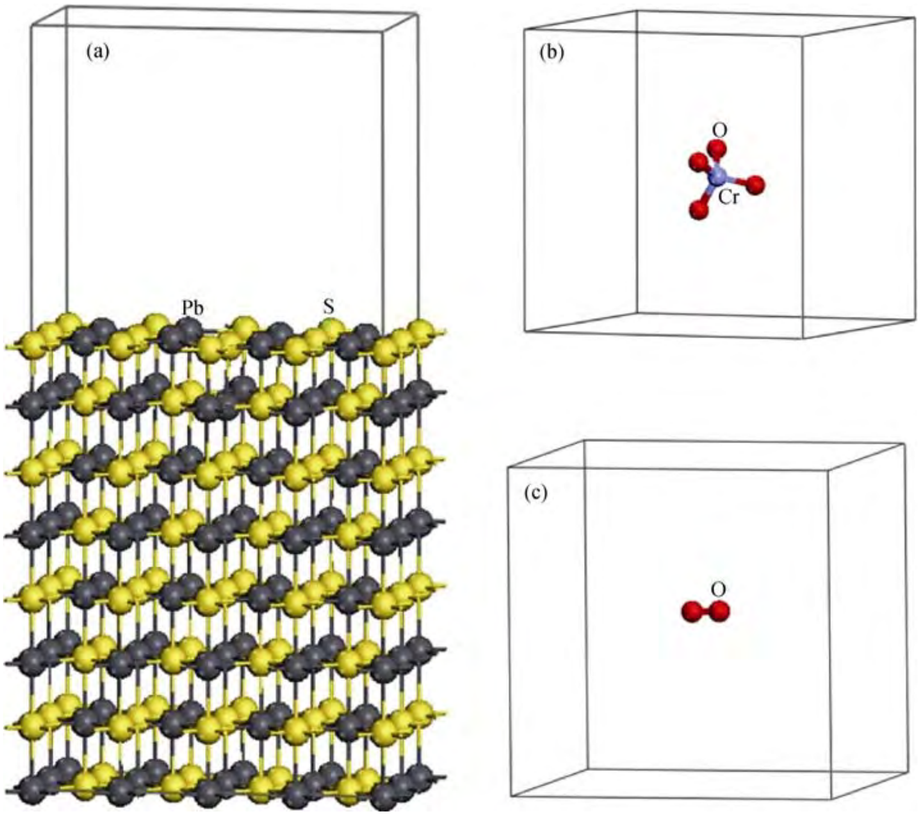

Fig. 2. Computational model of galena surfaces (a), unit cell of CrO_4 (b), and unit cell of O_2 (c).

3. Results and discussion

3.1. Separation of copper-lead concentrates in the presence of potassium dichromate

Potassium dichromate, one of the most effective depressants for galena, plays a very important role in the flotation process. In this research, the depressing behavior of potassium dichromate was investigated during the separation of copper-lead concentrates. Fig. 3 shows the recovery of galena along with the grade of galena and chalcopyrite as a function of stirring time in copper-lead concentrates in the presence of potassium dichromate.

As shown in Fig. 3(a), the recovery of galena in copper-lead concentrates changes significantly with increasing stirring time. A longer stirring time results in a less recovery of galena from copper-lead concentrates, suggesting that galena is strongly depressed by a long period of agitation in the presence of potassium dichromate. The addition of potassium dichromate reduces the grade of galena in copper-lead concentrates, whereas the grade of chalcopyrite is increased after adding potassium dichromate, as shown in Fig. 3(b). These observations reveal that the stirring time is very important for the depression of galena in the presence of potassium dichromate.

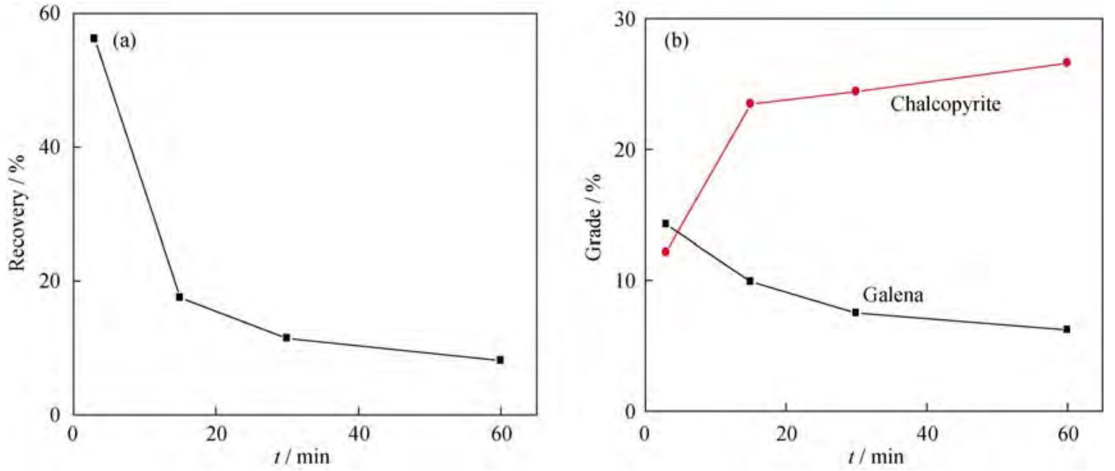

Fig. 3. Effects of stirring time on the recovery of galena (a) in copper-lead concentrate and the grade of galena and chalcopyrite (b) in copper-lead concentrate.

It is generally believed that galena is depressed when it is oxidized, meaning that the oxidation of galena may influence the flotation behavior in the presence of potassium dichromate. To gain a complete understanding of this issue, the flotation of pure galena was examined in the presence of potassium dichromate as a depressant.

3.2. Depression behaviors of galena in the presence of potassium dichromate

Fig. 4 shows the recovery of clean galena and oxidized galena as a function of potassium dichromate dosage. The depressant dosage strongly influences the recovery of both galena samples. The recovery of galena decreases with increasing potassium dichromate dosage, indicating that galena is depressed in the presence of potassium dichromate, either of clean galena or oxidized galena. A higher content of potassium dichromate leads to a better depression. Additionally, the synergistic effect of oxidation and potassium dichromate in galena depression was investigated. Zhang [28] proposed the synergistic effect equation in the combined use of flotation reagents as the following equation:

$$E_{sv} = E_z - E_s \tag{2}$$

where E_{sv} is the synergy efficiency value, E_z the depression efficiency for the combined use of depressant reagents, and E_s the weighted average for the depression efficiency of the individual reagent. Here, the oxidation effect can be taken as one kind of depressant, and the synergy efficiency of oxidation and potassium dichromate can be calculated by Eq. (2). The calculation results are listed in Table 1.

Results in Table 1 show that the synergy efficiency values (E_{sv}) are all positive, indicating that an obvious synergistic effect between oxidation and potassium dichromate exists. In addition, the value of E_{sv} increases with increasing potassium dichromate content, suggesting that the oxidation of galena surfaces can enhance the depression effect of potassium dichromate.

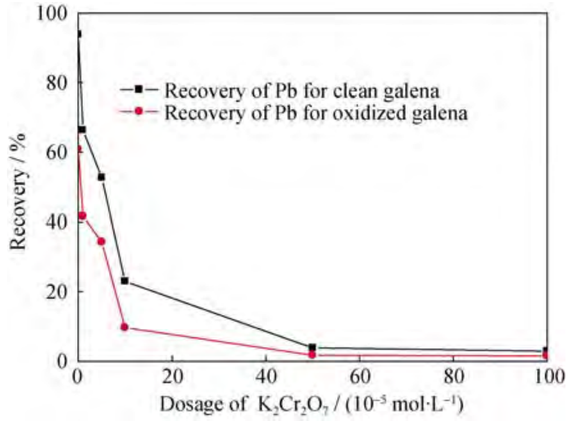

Fig. 4. Effect of depressant dosage on the recovery of clean and oxidized galena.

Table 1. Synergistic effect of oxidation and potassium dichromate in the process of galena depression

Addition of potassium dichromate / (10^{-5} mol·L^{-1})	E_z / %	E_s / %	E_{sv} / %
1	58.21	36.4	21.81
5	65.63	43.39	22.24
10	90.31	58.10	32.21
50	98.32	50.06	48.26

The effect of stirring time on the recovery of clean galena was investigated, and the results are shown in Fig. 5. It is clearly observed that the recovery of clean galena is reduced with increasing stirring time in the presence of potassium dichromate, which is in accordance with industrial production. To further study the reaction between galena and potassium dichromate in the flotation process, and to understand why such a long pulp stirring time is need, the heat of adsorption and kinetic parameters of potassium dichromate were examined on the galena surface.

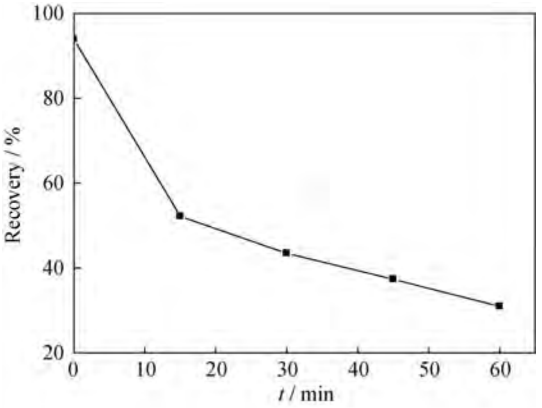

Fig. 5. Effect of stirring time on the recovery of clean galena.

3.3. Heat of adsorption and kinetic parameters of potassium dichromate on galena

To understand the process of potassium dichromate adsorption on the surface of galena, the heat of adsorption was measured at 298.15 K; the measured adsorption heat is –4.45 J/m^2 (as shown in Table 2), suggesting that the adsorption of potassium dichromate on the surface of galena was chemical in nature and occurred exothermically. In addition, the adsorption heat of the xanthate (–2.976 J/m^2) [11] was more positive than that of potassium dichromate, indicating that potassium dichromate adsorbed stronger than the xanthate on the surface of galena. Therefore, the xanthate adsorbed on the galena surface was easy desorbed by potassium dichromate during flotation.

Table 2. Thermodynamic and kinetic parameters of potassium dichromate adsorption on the galena surface at 298.15 K

Adsorption heat, ΔH / (J·m^{-2})	Rate constant, k / (10^3 s^{-1})	Reaction order, n
−4.45	3.19	0.08385

The adsorption of potassium dichromate on the surface of galena depends on not only thermodynamic parameters but also kinetic parameters. Thermodynamic parameters only show the trend of reaction, while kinetic parameters determine the rate of adsorption reaction.

The reaction rate of potassium dichromate adsorption is shown in Eq. (3).

$$v = kC^{n}_{\mathrm{K_2Cr_2O_7}} \tag{3}$$

where v is the rate of reaction, k the rate constant, $C_{\mathrm{K_2Cr_2O_7}}$ the concentration of potassium dichromate in the solution, and n the reaction order.

The reaction rate constant (k) and the reaction order (n) of the adsorption reaction can be obtained by

$$\ln\left(\frac{1}{H_0}\cdot\frac{\mathrm{d}H_i}{\mathrm{d}t}\right) = \ln k + n\ln\left(1-\frac{H_i}{H_0}\right) \tag{4}$$

where H_0 is the total enthalpy of the system. The rate constant (k) is calculated from ln$k$, which is determined as the intercept of the plot of $\ln\left(\frac{1}{H_0}\cdot\frac{\mathrm{d}H_i}{\mathrm{d}t}\right)$ against $\ln\left(1-\frac{H_i}{H_0}\right)$. The slope of the line (n) represents the reaction order. The calculation results are presented in Table 2.

The reaction rate constant and order can elucidate the relationship between the concentrations of species and the reaction rate. As shown in Table 2, the rate constant for potassium dichromate on the surface of galena is 3.19, indicating the depression of galena in the presence of potassium dichromate. In addition, the reaction order for potassium dichromate adsorption on galena is calculated as 0.08385, close to a zero-level reaction, suggesting that the concentration of potassium dichromate has little influence on its adsorption. At a given concentration, the rate of potassium dichromate adsorption on galena is very slow due to small value of n. Thus, a long stir time is necessary in industrial practice to complete the reaction between potassium dichromate and galena.

3.4. DFT simulation

To obtain the adsorption configuration of potassium dichromate on the surface of galena, DFT was used to simulate the potassium dichromate adsorption on the surface of PbS. Potassium dichromate exists in the solution as $\mathrm{CrO_4^{2-}}$ ($\mathrm{Cr_2O_7^{2-} + H_2O = 2\,CrO_4^{2-} + 2\,H^+}$); therefore, the model of $\mathrm{CrO_4^{2-}}$ was used in the simulations.

The most stable adsorption configuration was obtained after geometry optimization. Fig. 6 shows the stable adsorption configuration of $\mathrm{CrO_4^{2-}}$ on the surface of galena. Spheres represent the adsorbed atoms, while the atoms of the galena surface are shown in stick format. The stick between Pb and S atoms is the Pb− S bond. In this configuration, two single-bonded oxygen atoms of $\mathrm{CrO_4^{2-}}$ are arranged, facing Pb and S atoms of the bond site on the galena surface.

The oxidation of the galena surface is necessary for galena depression by potassium dichromate. To explore the role of oxygen in this process, the adsorption of $\mathrm{CrO_4^{2-}}$ on the galena surface in the presence of oxygen was simulated. The adsorption model is shown in Fig. 7.

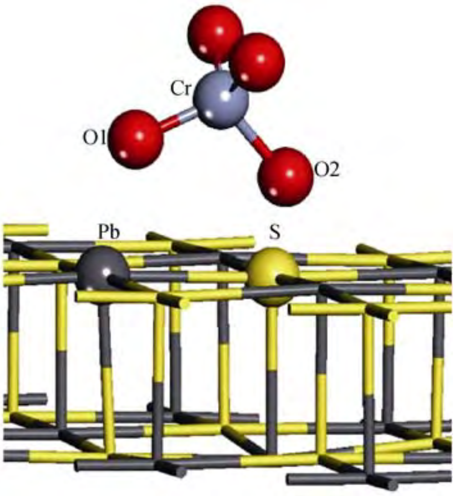

Fig. 6. Model of CrO_4^{2-} adsorption on the galena surface.

The adsorption configuration of the galena surface is obviously distorted in the presence of oxygen. The oxygen molecule on the galena surface is forced into the surface layers in the presence of CrO_4^{2-}. It is found that the adsorption energy of CrO_4^{2-} in the presence of O_2 (–520.18 kJ/mol) is more negative than that in the absence of O_2 (–418.94 kJ/mol), indicating that the adsorption of CrO_4^{2-} on the surface of galena is energetically enhanced in the presence of O_2.

Density of states (DOS), especially partial density of states (PDOS), gives the qualitative information on the nature of electron hybridization in the adsorption system. Hence, the PDOS of atoms for CrO_4^{2-} adsorption on galena was calculated in the absence and presence of O_2. The results are shown in Fig. 8, and the zero of energy is set at the Fermi level (E_F). The Pb 6s, O1 2s, and O2 2s states contribute little to DOS, which are not shown in the figure.

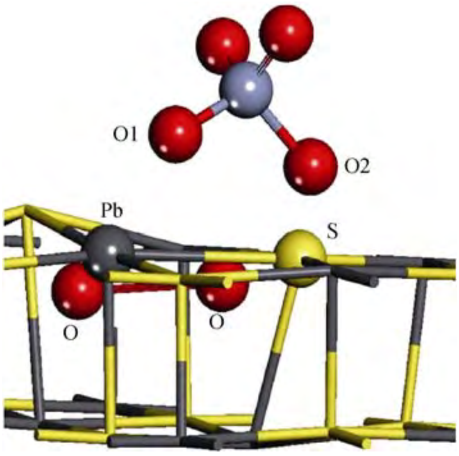

Fig. 7. Model of CrO_4^{2-} adsorption on the galena surface in the presence of O_2.

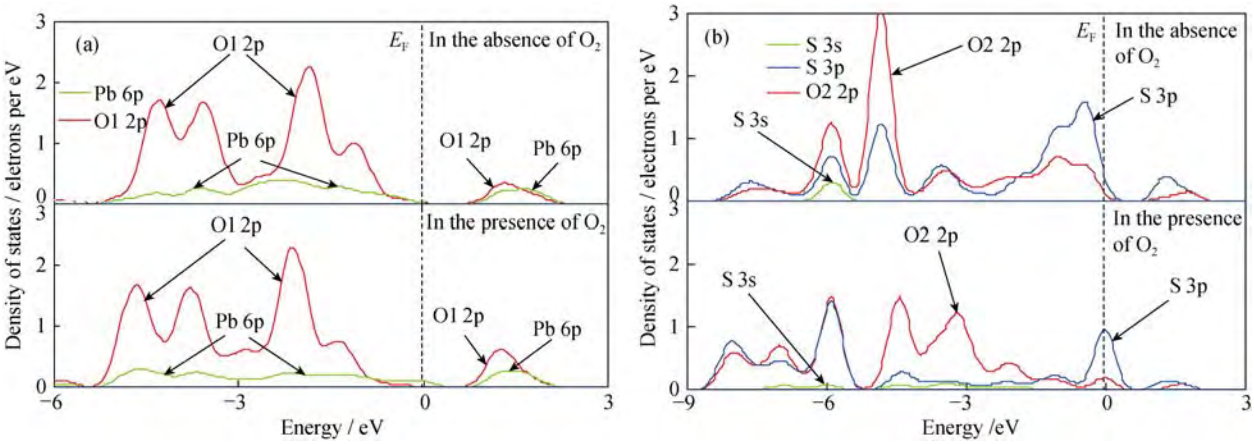

Fig. 8. PDOS of Pb and O1 atoms (a) and S and O2 atoms (b) for CrO_4^{2-} adsorption on the galena surface in the absence and presence of O_2.

As revealed in Fig. 8(a), the PDOS of Pb and O1 atoms are divided into two regions: the O1 2p and Pb 6p bonding states between –5.5 and 0.35 eV, and the corresponding anti-bonding states are located from 0.68 to 2.4 eV. It is worth noting that the PDOS of Pb and O1 atoms shift slightly towards the lower energy side, indicating that the bonding between Pb and O1 atoms becomes more stable in the presence of O_2.

Fig. 8(b) clearly shows that the PDOS of S and O2 atoms are different before and after oxidation. In the absence of O_2, the bonding state between S 3p and O2 2p changes from –6.7 to –4 eV, resulting in two sharp hybridized peaks located at –5.9 and –4.8 eV, respectively. The corresponding anti-bonding states are located near the Fermi level. In the presence of O_2, the PDOS of S and O2 atoms move towards the lower energy side. It is worth noting that the bonding of S 3p and O2 2p states is split into two parts. Particularly, the overlap between S 3p and O2 2p states is nearly perfect from −8.7 to −5.3 eV. There are three obvious hybridized peaks located at −8, −7, and −5.9 eV, indicating that the bonding interaction between S and O2 atoms becomes stronger in the presence of O_2. In addition, the overlap of anti-bonding at the Fermi level becomes smaller in the presence of O_2, indicating that the anti-bonding interaction between S and O2 atoms is weakened by O_2. These results of PDOS analyses show that the adsorption of CrO_4^{2-} on the surface of galena is effectively enhanced in the presence of O_2.

4. Conclusions

(1) The heat of adsorption of potassium dichromate (–4.45 J/m^2) is more negative than that of the xanthate (–2.976 J/m^2), indicating the potassium dichromate is more strongly adsorbed on the surface of galena than the xanthate. Therefore, the xanthate adsorbed on galena easily is desorbed by potassium dichromate during flotation.

(2) The rate constant for potassium dichromate adsorption on the galena surface is 3.19, which indicates that the depression of galena in the presence of potassium dichromate is favorable. Additionally, the reaction order is calculated as 0.08385, suggesting that the concentration of potassium dichromate has little influence on its adsorption on galena. The reaction rate of potassium dichromate adsorption on galena is slow at a given concentration. Thus, it is necessary to stir for a long period of time in industrial practice to complete the reaction between potassium dichromate and galena.

(3) The adsorption energy of CrO_4^{2-} adsorbed on PbS is the lowest at the Pb− S bond site (–418.94 kJ/mol), suggesting that this site is the most favorable for adsorption. The influence of O_2 on the interaction of CrO_4^{2-} with the galena surface is also investigated. The results indicate that the adsorption of CrO_4^{2-} on PbS is energetically enhanced in the presence of O_2.

Acknowledgements

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