



Full Length Article

Combined DFT and XPS investigation of enhanced adsorption of sulfide species onto cerussite by surface modification with chloride



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ABSTRACT

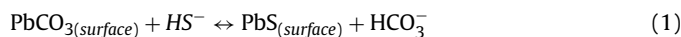
This study systematically investigates the enhanced adsorption of sulfide species onto cerussite by surface modification with chloride through density functional theory calculations and X-ray photoelectron spectroscopy (XPS) measurements. Calculation results demonstrate obvious differences in the surface structures and electronic properties of cerussite after HS⁻ adsorption in the absence and presence of chloride species. Surface modification with chloride promotes the stable adsorption of HS⁻ onto the cerussite surface, and the hybridization of Pb 6p orbital at the surface layer and S 3p orbital from HS⁻ is enhanced. Moreover, the reactivity of cerussite surfaces is enhanced by the occurrence of new DOS peaks of Pb 6p and S 3p near the Fermi level and by the transfer of additional electrons between the bonding atoms in the presence of chloride. Meanwhile, Mulliken population and XPS analysis results indicate that a slight oxidation is involved in the interaction between sulfide species and cerussite surfaces because of the presence of disulfide and polysulfide in the sulfidization products. In addition, a higher proportion of disulfide and polysulfide relative to the overall S is exhibited in the presence of chloride, facilitating the sulfidization flotation of cerussite.

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1. Introduction

Lead oxide minerals are a potential lead resource that can fill the gap caused by the gradual reduction of lead sulfide minerals [1–3]. Among multitudinous beneficiation methods, surface sulfidization flotation is the most promising to concentrate lead oxide minerals in consideration of technical and economic factors [4–6]. The surface hydration and solubility of lead sulfide minerals are particularly weaker than those of lead oxide minerals. As such, the sulfidizing agent sodium sulfide (Na₂S) is usually added into pulp suspensions containing lead oxide minerals to generate lead sulfide species on their surfaces [7–10]. Hydrolysis easily occurs in Na₂S solutions, and the dissociated product varies as a function of solution pH. For instance, H₂S is the dominating S species at pH lower than 7.0, HS⁻ is predominant within the pH range of 7.0–13.9, and S²⁻ is the primary S species at pH higher than 13.9 [11–13]. The optimum flotation recovery of cerussite occurs at mild alkaline pH [8,10,13]. Thus, HS⁻ is a substantial reactant with cerussite sur-

faces. The sulfidization reaction occurring at the cerussite surface can be depicted as follows:



Despite many experimental studies on surface sulfidization flotation, this process remains to have limitations, such as unsatisfactory sulfidization efficiency, inferior sulfidization products, massive consumption of sulfidizing agents and collectors, as well as inadequate flotation recovery of lead. To address these issues, chloride ions were introduced into the pulp solution to modify the surface composition and property of cerussite, which is the most representative lead oxide mineral [10,14,15]. The positive contribution of chloride ions to the sulfidization flotation of cerussite was confirmed through surface analysis, liquid detection and solution chemistry calculation. In addition, the flotation recovery was increased by 10%–16% after cerussite was pretreated with chloride ions before addition of Na₂S [10,14]. Such an improvement was attributed to the increase in the number of active sites and enhancement in the activity of active sites on cerussite surfaces as determined by dissolution experiments, zeta potential measurements, X-ray photoelectron spectroscopy (XPS), and density functional theory (DFT) calculations [15]. These experimental

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results provide a macroscopic foundation for the positive effect of chloride ions on the sulfidization of cerussite.

Recently, computational chemistry has developed into an important research field that complements and consummates experimental studies. It focuses on the atomic arrangement, adsorption, and interaction between flotation reagents and mineral surface. Wen et al. [16] found through DFT calculations that the surface relaxation and reconstruction occurring on the natural chalcopyrite (001) surface could significantly affect its flotation performance. Chen et al. [17] studied the interactions among pyrite, galena surfaces, and xanthate species with and without oxygen by using first-principles calculations and indicated that dixanthogen could be generated on the pyrite (100) surface but not on the galena (100) surface. Sarvaramini et al. [18] simulated the adsorption of collectors on the activated sphalerite surface through DFT. Long et al. [19,20] conducted a DFT study on the attachment of collectors to sphalerite (110) and galena (100) surfaces in the presence of H₂O. The adsorption of flotation reagents on quartz and kaolinite surfaces was also simulated based on DFT [21–23]. Recently, a DFT simulation of the adsorption of hydrogen sulfide ions onto the cerussite (110) surface has been reported, and the sulfidization mechanism has been elucidated at the atomic level [24]. These studies played a significant role in the computational chemistry applied to the flotation field for demonstrating the interaction mechanism of flotation reagents with the mineral surface.

In the present work, we systematically investigated the effect of chloride on the adsorption of sulfide species onto the cerussite surface by using DFT and XPS. DFT calculations were performed to explore the adsorption configuration, electronic structures, and charge transfer of interactions between HS⁻ and cerussite (110) surface in the presence of chloride. Meanwhile, XPS measurements were conducted to provide insights into the chemical states of S in sulfide-treated cerussite samples in the presence of chloride. This study provides a comprehensive understanding of the enhanced sulfidization of cerussite induced by chloride species.

2. Computational and experimental methods

2.1. Computational details

The calculations in this work were performed using DFT on the basis of the generalized gradient approximation with the Perdew–Burke–Ernzerhof for solids (GGA–PBESOL) functional implemented in the CASTEP 8.0 program [25]. A norm-conserving pseudo potential was employed to describe electron–ion interactions with a kinetic energy cutoff of 340 eV [26]. In energy calculations, the K-point grid was set to 4 × 3 × 1. With respect to self-consistent electronic minimization, the Pulay density mixing method was adopted with an energy tolerance of 1.0 × 10⁻⁵ eV/atom, a force tolerance of 3.0 × 10⁻² eV/Å, and a displacement tolerance of 1.0 × 10⁻³ Å. The configuration of valence electrons in this work involved C 2s²2p², O 2s²2p⁴, Pb 5d¹⁰6s²6p², H 1s¹, and S 3s²3p⁴ states.

The cerussite crystal with cell parameters of $a = 5.1807 \text{ \AA}$, $b = 8.5698 \text{ \AA}$, $c = 6.1067 \text{ \AA}$, and $\alpha = \beta = \gamma = 90^\circ$ was utilized to model the primitive unit cell in this work [27]. The adsorption surface was acquired through a cleavage along the (110) plane of an optimized bulk cerussite structure [15,24]. The slab model of the cerussite (110) surface with 20 Å atomic layers was used to simulate the adsorption of flotation reagents on the mineral surface in the absence and presence of chloride. An optimized vacuum space of 20 Å along the z-axis perpendicular to the surface was determined to avoid the spurious interaction between nearby slabs.

Adsorption energy is an indicator in estimating the adsorption stability of sulfide species on the cerussite surface. A negative

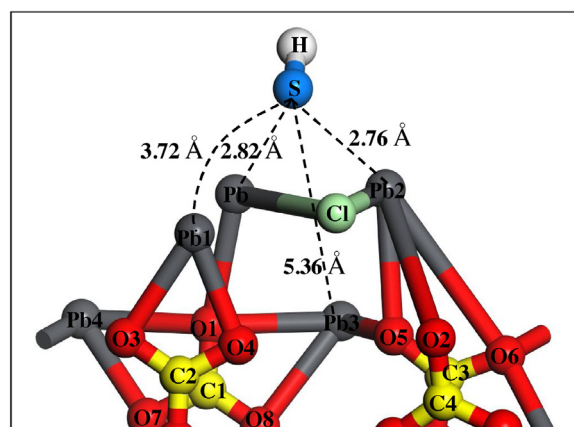


Fig. 1. Adsorption configurations of HS⁻ on the cerussite (110) surface in the presence of chloride.

value of calculated adsorption energy signifies the occurrence of adsorption, and a more negative value implies easier and stronger adsorption of sulfide species on the cerussite surface. HS⁻ was taken as the dominating sulfide species, and PbCl⁺ was calculated as the primary lead chloride complex in the cerussite sulfidization flotation enhanced by chloride ions [10,14,15]. Thus, the adsorption energies of sulfide species on the mineral surface in the absence and presence of chloride were calculated as follows:

$$\Delta E_{ads-1} = E_{\text{surface}+\text{HS}^-} - E_{\text{surface}} - E_{\text{HS}^-} \quad (2)$$

$$\Delta E_{ads-2} = E_{\text{surface}+\text{PbCl}^++\text{HS}^-} - E_{\text{surface}} - E_{\text{PbCl}^+} - E_{\text{HS}^-} \quad (3)$$

where ΔE_{ads-1} and ΔE_{ads-2} denote the adsorption energy in the absence and presence of PbCl⁺, respectively; $E_{\text{surface}+\text{HS}^-}$ and $E_{\text{surface}+\text{PbCl}^++\text{HS}^-}$ denote the energy of the cerussite (110) surface with HS⁻ adsorbed in the absence and presence of PbCl⁺, respectively; E_{surface} denotes the energy of the cerussite (110) surface without HS⁻ adsorbed; and E_{PbCl^+} and E_{HS^-} denote the energy of PbCl⁺ and HS⁻ before interaction with the mineral surface.

2.2. Experimental details

Natural cerussite samples were purchased from Yunnan Province, China, and all reagents employed in the present work were of analytical grade and used as received. The samples used in the XPS measurement were obtained by dispersing 5 g of pure cerussite particles with sizes ranging from -74 μm to +45 μm into 500 mL of aqueous solution. First, a desired concentration of NaCl stock solution was added into the mineral suspension and then stirred for 10 min as necessary. Then, a fresh Na₂S·9H₂O stock solution was poured and stirred for 30 min. Subsequently, the mixture was filtered, and the produced solid particle was collected, dried, and stored to assure the following XPS measurements.

The interaction product was examined using PHI5000 Versa Probe II (PHI5000, ULVAC-PHI, Japan) with an Al K_α X-ray source. A survey scan of the analyzed sample was first conducted to detect elemental compositions, and then a precise scan was performed to obtain the XPS spectrum of a specific element. Subsequently, the MultiPak Spectrum software was used to calculate and analyze each spectrum and the atomic proportions of the measured samples. The C1s spectrum at 284.8 eV was obtained and used as an internal standard to calibrate the measured spectra for charge compensation.

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