

Received June 22, 2015; reviewed; accepted November 5, 2015

EFFECT OF pH ON SURFACE CHARACTERISTICS AND FLOTATION OF SULFIDIZED CERUSSITE

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Abstract: The effect of pH on surface characteristic and flotation of sulfidized cerussite was studied by micro-flotation tests, dissolution experiments, scanning electron microscopy (SEM) energy dispersive spectrometer (EDS), and X-ray photoelectron spectroscopy (XPS). The micro-flotation tests demonstrated that higher recovery of cerussite was achieved in acidic solutions than that in alkaline solutions. Despite the addition of high collector concentrations, cerussite flotation did not improved in alkaline solutions. The dissolution performance of sulfide-treated cerussite at different pH values indicated that the lead sulfide layer on the surface of sulfide-treated cerussite could exist in acidic solutions and it was more stable at acidic pH than in alkaline solutions. This finding was proved by the SEM-EDS and XPS analyses.

Keywords: *cerussite, sulfidization, excessive sulfide ions, pH, surface analysis*

Introduction

Lead sulfide ores are gradually becoming depleted. Thus, for future lead demand, oxidized lead minerals have been recognized as an important source of lead metal. The most commonly used commercial process for metal recovery from oxidized ores is sulfidization flotation, since oxidized minerals after sulfide-treatment have characteristics similar to metal sulfide, and thus can be recovered effectively with xanthate-typed collectors (Herrera-Urbina et al., 1998; Fa et al., 2005; Gush, 2005; Kashani and Rashchi, 2008; Lee et al., 2009). However, the sulfidization procedure has been an indispensable challenge for recovery of oxidized minerals by means of sulfidization flotation method. Oxidized lead, zinc and copper minerals are known to undergo more extensive surface hydration compared with sulfide minerals. It results in poor floatability. Thus, sulfidizing agents are frequently added to pulp solutions prior to flotation to enhance the hydrophobicity of the mineral surface (Banza and Gock,

2003; Rashchi et al., 2005; Kuchar et al., 2006). Unfortunately, difficulties in controlling the dosage of sulfidizing agents are a common issue. An excessive amount may cause the depression of oxidized minerals, whereas an insufficient amount results in poor recovery of metal minerals (Fuerstenau et al., 1987; Herrera-Urbina et al., 1999; Irannajad et al., 2009).

In order to overcome drawbacks of the sulfidization flotation method used to recover oxidized minerals, numerous studies have been conducted. Some researchers have been attempting to synthesize a new collector that could selectively float oxidized minerals without requiring any previous sulfidization (Marabini et al., 1989; Cozza et al., 1992; Barbaro et al., 1997; Zhu et al., 2007; Hajati et al., 2010). In addition, some unconventional sulfidization techniques, such as mechanochemical, hydrothermal and roasting sulfidization, have been developed to facilitate the recovery of non-sulfide ores (Wang et al., 2003; Li et al., 2010; Liang et al., 2012; Yuan et al., 2012; Chai et al., 2013; Li et al., 2013). Moreover, Newell et al., (2007) provided a valuable technique for recovery of minerals that were difficult to sulfidize by adding some base-metal ions during the sulfidization process. Furthermore, the control system of sulfide concentration was developed to optimize the accurate addition of sulfidizing agents (Gush, 2005). Although previous techniques can avoid some of the problems caused by conventional sulfidization methods, such methods still appear to be rather restricted to laboratory research and may be unsuitable for industrial application. Therefore, an effective approach for eliminating the effect of excessive sulfide ions on subsequent flotation should be explored.

Sodium sulfide is typically used as a sulfidization agent for metal oxide minerals. However, this agent can be hydrolyzed, and then dissociated in solutions as a function of the solution pH values. The available literature on sulfidization treatment indicates that in acidic solutions ($\text{pH} < 7$) H_2S is the dominant species, whereas the HS^- species are predominant within the pH range from 7 to 13.9, and S^{2-} ions exist in the higher pH range (Sun et al., 2012). Therefore, the distribution of Na_2S in solutions can be adjusted by the solution pH values. Based on this theory, H^+ ions were added into the sulfidized cerussite pulp solutions to cause additional sulfide species to distribute in pulp solutions in the form of H_2S . Besides, gangue minerals, such as quartz, will not be activated in acidic solutions, which will be beneficial for the selective separation of gangue minerals from lead oxide minerals (Ejtemaei et al., 2012).

In this study, micro-flotation tests, dissolution experiments, SEM-EDS and XPS studies of sulfide-treated cerussite were carried out to investigate the effect of pH on surface characteristics and flotation of sulfidized cerussite.

Experimental

Materials and reagents

Samples of cerussite from the Lanping lead-zinc mine in the Yunnan province of China were obtained after the manual removal of gangue minerals. The X-ray

fluorescence (XRF) and X-ray diffraction (XRD) analyses of materials are demonstrated in Table 1 and Fig.1a, respectively. It shows that cerussite contains 76.70% Pb, 4.48% C and 18.30% O with only PbCO_3 crystals. The pure cerussite sample was manually ground in an agate mortar and then sieved to produce a size range from -74 to $+45$ μm cerussite for micro-flotation tests, and a fraction with particle size less than 20 μm for dissolution experiments.

All reagents, except sodium amyl xanthate, and solvents used in the experiments were of analytical grade. The pH was adjusted by the addition of HNO_3 or NaOH (Tianjin HengXing Chemical Reagent Co., Ltd., Tianjin, China). $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ (Sinopharm Chemical Reagent Co., Ltd., Beijing, China) was added as a sulfidizing agent. The commercial-grade sodium amyl xanthate (Yunnan Tiefeng High Tech Mining Chemicals Co., Ltd., Kunming, China) was used as a collector, and its purity was about 88%. Pure deionized water with a resistivity of 18 $\text{M}\Omega$ produced by a Milli Q50 system (Billerica, MA, USA) was used throughout the experimental work.

Preparation of sulfide-treated cerussite

Sulfide-treated cerussite was prepared as follows: firstly, natural pure cerussite samples were charged into 0.05 mol/dm^3 $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ aqueous solution used as a sulfidization agent at the natural pH of the sulfide solution. The slurry was then conditioned for 30 min using a magnetic stirrer for agitation at 650 rpm. Subsequently, the slurry was filtered using a filter paper with pore size of 1 μm , and then rinsed with pure deionized water several times to eliminate superficial ions until the pH of the filtrate was identical to that of pure deionized water. At the end of experiments, the solid was dried under an argon-saturated atmosphere at room temperature and stored for subsequent experiments. The XRF analysis results and XRD pattern of sulfide-treated cerussite are shown in Table 1 and Fig. 1b, respectively.

Table 1. XRF analysis results of cerussite samples: (a) original, and (b) sulfide-treated

Sample	Component Content, wt%				
	Pb	C	O	S	Si
a	76.70	4.48	18.30	0.14	0.38
b	78.12	3.81	15.74	1.92	0.41

The XRF and XRD analyses demonstrate that the content of S in the treated sample reached up to 1.92%. Besides PbCO_3 crystals, PbS crystals were also detected and the diffraction peaks of PbS were well in accordance with the values of the JCPDS card (No. 77-0244). In addition, the C and O contents of sulfide-treated cerussite decreased compared with that of original cerussite samples, which further revealed that lead sulfide layers formed on the cerussite surface.

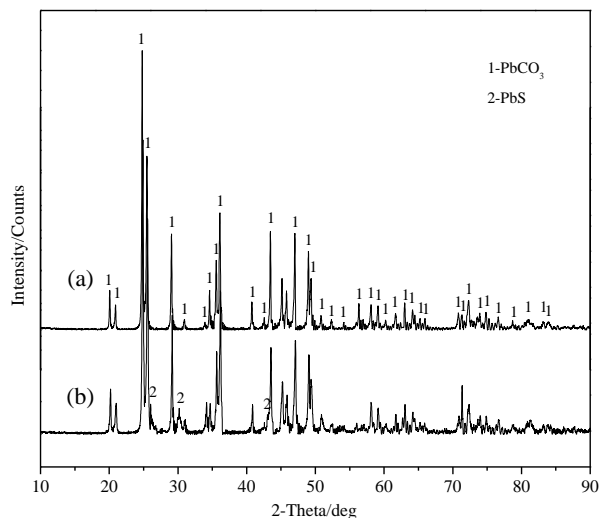


Fig. 1. XRD pattern of cerussite samples: (a) original, and (b) sulfide-treated

Micro-flotation experiments

Micro-flotation experiments were conducted in a mechanical agitation flotation machine with a micro-flotation cell of 40 cm³. The conditioning period was conducted outside the micro-flotation cell. The mineral suspension was prepared by adding 2.0 g of minerals to 40 cm³ of $5 \cdot 10^{-3}$ mol/dm³ Na₂S·9H₂O aqueous solutions conditioned for 15 min. After sulfidization, the solution was conditioned with either HNO₃ or NaOH solution until a desired pH value was reached, and the slurry was conditioned for 15 min at 650 rpm. The pulp was then transferred to the micro-flotation cell and conditioned with collector for 3 min. The flotation time was 3 min. After the flotation tests, the concentrate and tailings were filtered and dried before being weighed. The flotation recovery was calculated based on solid weight distributions between these two products. Micro-flotation tests were conducted in duplicate and the maximum standard error in the flotation recovery results was $\pm 2.5\%$.

Dissolution experiments

Dissolution experiments were performed after dispersing 2.0 g of sulfide-treated cerussite samples into 38 cm³ of aqueous solution with fixed pH ranging from 2.0 to 12.0 (± 0.1 pH units) determined by a radiometer pH-stat (PHM 290). The suspensions were magnetically stirred at 650 rpm. The dissolution experiments were conducted for 1 h, when an equilibrium state was considered to be achieved.

Upon completion of each dissolution experiment, a centrifuge was used for solid-liquid separation. The liquid obtained from separation was stored in closed vials and analyzed for the total concentrations of S by means of inductively coupled plasma-atomic emission spectrometry (ICP-AES) (ICPS-1000II, Shimadzu, Japan). The solid

was collected and rinsed with pure deionized water, dried in argon-saturated atmosphere at room temperature, and then stored in closed plastic bags for surface analysis. The maximum standard deviation for measurement was within $\pm 2\%$.

SEM-EDS analysis

The morphology of sulfide-treated cerussite conditioned under different conditions was analyzed using a scanning electron microscope (XL30ESEM-TM, Philips, Holland), which was performed using a high resolution electron microscope. The elemental chemical compositions of samples were determined by an energy dispersive spectrometer (Genesis 2000, EDAX, USA).

XPS analysis

Sulfide-treated cerussite conditioned under different conditions was analyzed using PHI5000 Versa Probe II (PHI5000, ULVAC-PHI, Japan) equipped with a monochromatic Al K_{α} X-ray source. The analyzed sample was first subjected to a survey scan to identify chemical components, followed by high-resolution scans on a certain element. Carbon is ubiquitous and is present on all surfaces for XPS analysis, so all spectra were calibrated using the carbon 1s (C1s) spectral peak at 284.8 eV. The obtained spectra were analyzed by peak fitting and separation and the relative contents of different compositions were determined after removal of the proportion from the contamination by means of the MultiPak Spectrum software.

Results and discussion

Micro-flotation tests

The distribution of Na_2S in solutions as a function of pH values will be proposed because HS^- ions are the dominant species existed in the pulp solutions when $7.0 < \text{pH} < 13.9$, whereas H_2S and S^{2-} become the dominant species in the Na_2S solutions when $\text{pH} < 7.0$ and $\text{pH} > 13.9$, respectively. In order to determine the distribution of S species in the pulp solutions after cerussite was conditioned with $5 \times 10^{-3} \text{ mol/dm}^3$ $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ aqueous solutions, the solution pH and residual concentrations of S in pulp solutions were measured. The changes of pH and residual concentrations of S in pulp solutions as a function of sulfidization time are demonstrated in Table 2. As shown in the data from Table 2, the pH in pulp solutions was decreasing from 11.76 to 11.31 within 15 min as the sulfidization reaction proceeded. The residual concentrations of S in pulp solutions exhibited the similar trend to the changes of pulp solution pH, i.e., the residual concentrations of S in the pulp solutions was decreasing from 178.7 mg/dm^3 to 63.4 mg/dm^3 when cerussite was sulfidized for 15 min. As sulfidization time further extended, the pH and residual S concentrations in the pulp solutions remained nearly unchanged. When the pulp pH and residual S concentration were about 11.3 and 60 mg/dm^3 , respectively. It indicated that there was a lot of S

retained in the sulfidized cerussite pulp solutions and they existed in the form of HS^- ions with a small amount of S^{2-} ions which were negatively charged.

Table 2. Changes of pH and residual concentrations of S in pulp solution as a function of sulfidization time

Time, min	Pulp solution pH	Residual concentrations of S in pulp solutions, mg/dm^3
0	11.76	178.7
1	11.65	136.5
3	11.55	111.4
5	11.48	94.7
7	11.41	81.6
10	11.34	66.8
15	11.31	63.4
20	11.30	62.7
25	11.30	61.4
30	11.29	60.2

The results for sulfide-treated cerussite conditioned at different pH values using sodium amyl xanthate as the collector are shown in Fig. 2. According to Fig. 2, with increasing pH values in the pulp solutions, the recovery of cerussite decreased within the pH range from 4 to 12. The recovery of cerussite decreased from approximately 90 to 60% at $5 \cdot 10^{-4}$ mol/dm^3 sodium amyl xanthate concentration. The poor recovery of cerussite at pH 12 demonstrated that excessive sulfide ions in the sulfidized cerussite pulp solutions adversely affected cerussite flotation because such ions in the pulp solutions not only inhibited the interaction between xanthate ions and the mineral surface but also excluded the adsorbed xanthate ions on the surface of sulfidized cerussite. It corresponded well with the initial research results presented elsewhere (Fuerstenau et al., 1987; Herrera-Urbina et al., 1998; Herrera-Urbina et al., 1999; Feng et al., 2015). In addition, the flotation results of sulfide-treated cerussite at pH 4 also indicated that mineral floatability was improved after elimination of excessive sulfide ions in the sulfidized cerussite pulp solutions. The irregular result of cerussite flotation at pH 2 may be attributed to the decomposition of the majority of sodium amyl xanthate in the pulp solutions (Sirkeci, 2000; Bulut and Atak, 2002; Kantar, 2002). In order to avoid the influence of low concentration of collector at pH 2 caused by decomposition, the concentration of $5 \cdot 10^{-3}$ mol/dm^3 sodium amyl xanthate was introduced to float the mineral samples (Fig. 2).

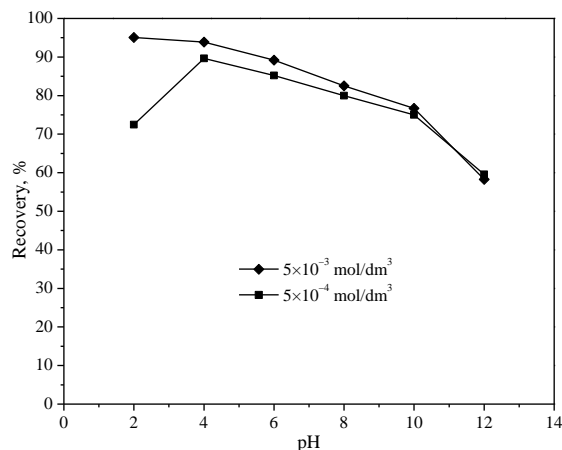


Fig. 2. Flotation recovery of cerussite as a function of pH values in the presence of different concentrations of sodium amyl xanthate

As shown in Fig. 2, the recovery of cerussite at pH 2 reached approximately 95% in the presence of high concentrations of sodium amyl xanthate, which confirmed the speculation that the decomposition of the majority of sodium amyl xanthate in pulp solutions at pH 2 resulted in a sharp decline in cerussite recovery with low collector concentrations. Meanwhile, the recovery of cerussite consistently decreased within the entire pH range with increasing pH values in pulp solutions when the concentration of sodium amyl xanthate was $5 \cdot 10^{-3} \text{ mol/dm}^3$. The high recovery of sulfidized cerussite at acidic pH was similar to the result achieved for galena (Ralston, 1994). Compared with the flotation results with $5 \cdot 10^{-4} \text{ mol/dm}^3$ of sodium amyl xanthate, the increase in the collector concentration improved the cerussite recovery in the acidic pulp solutions, particularly at pH 2, whereas negligible change occurred for the cerussite recovery at alkaline pH. This phenomenon further revealed that excessive sulfide ions in pulp solutions would affect floatability of minerals regardless of collector concentrations because in the acidic solutions, excessive sulfide ions existed in the form of H_2S , whereas HS^- species or S^{2-} ions were the dominant species at alkaline pH (Gush, 2005; Sun et al., 2012). Thus, for elimination of excessive sulfide ions in the sulfidized cerussite pulp solutions, the addition of H^+ ions was effectively proven.

Dissolution performance of sulfide-treated cerussite at different pH

The dissolution experiments were conducted to investigate the effect of pH values on the cerussite surface after treatment with sulfidizing agents. Figure 3 shows the S concentration in filtrates and S contents in solids are determined as a function of pH values after the dissolution experiments.

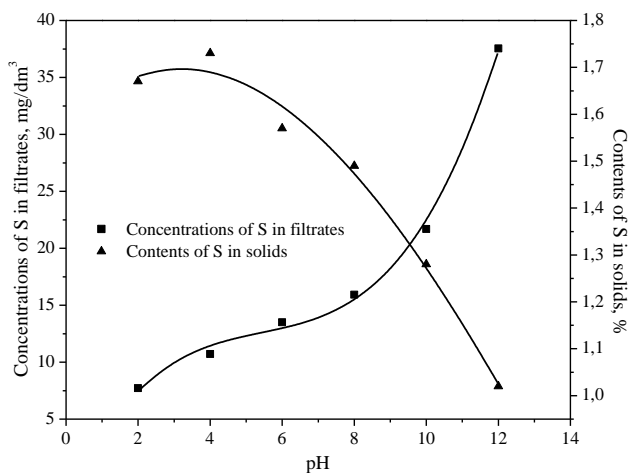
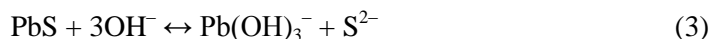
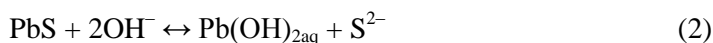
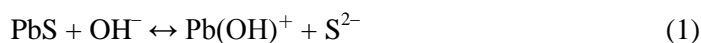


Fig. 3. Concentrations of S in filtrates and contents of S in solids as a function of pH values

It can be seen from Fig. 3 that the S concentration in filtrates increased, whereas the S content in solids decreased with increasing pH values in the pulp solution. The foregoing analysis result showed that the lead sulfide layer formed on the cerussite surface after treatment with $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$. Thus, it was considered that the lead sulfide layer on the surface of sulfide-treated cerussite was more stable at acidic pH than that in alkaline solutions. This mechanism can be discussed through the reaction between the lead sulfide layer on the mineral surface and H^+ or OH^- in the pulp solution.

In a $\text{PbCO}_3\text{-PbS-H}^+$ solution system, H^+ in solution could easily react with CO_3^{2-} in PbCO_3 crystals according to the conditions of chemical reaction. Thus, H^+ in the acidic solutions would be prior to react with cerussite by internal diffusion through superficial lead sulfide layers. Another possibility was for inhomogeneous lead sulfide layers on the surface of cerussite. In this way, H^+ would continue to combine with PbCO_3 after it damaged the weaker lead sulfide layer. Both kinds of interaction between H^+ and minerals would protect the lead sulfide layers on the mineral surface from damage. Thus, the concentration of S in filtrates was lower, whereas, the content of S in the solids kept higher in the acidic solutions.

In the $\text{PbCO}_3\text{-PbS-OH}^-$ solution system, OH^- was attracted to Pb^{2+} , and no noticeable difference existed when OH^- combined with Pb^{2+} in PbS and PbCO_3 crystals. Thus OH^- in solutions would be prior to react with superficial lead sulfide layers. Therefore, OH^- ions would first react with PbS as follows:





Based on reactions (1) to (3), soluble lead hydroxyl complexes would form in alkaline solutions, and these lead hydroxyl species were hydrophilic. If solid lead hydroxide particles were formed (reaction (4)), they would greatly affect the flotation of minerals because the hydrophobicity of lead hydroxide was worse than that of lead sulfide (Ralston, 1994). Formation of hydrophilic products at the PbS-H₂O interface would inhibit the interaction between the xanthate ions and mineral surface. This finding provided a further evidence of the low recovery of cerussite at alkaline pH, which corresponded well with the results of micro-flotation tests.

SEM-EDS analysis

The dissolution performance of sulfide-treated cerussite at different pH values indicated that the lead sulfide layer on the surface of sulfide-treated cerussite can exist in the acidic solution. To help in further interpreting the mechanism that made the lead sulfide layer on the surface of sulfide-treated cerussite more stable at acidic pH than in alkaline solutions, SEM-EDS was conducted. The results are presented in Fig. 4.

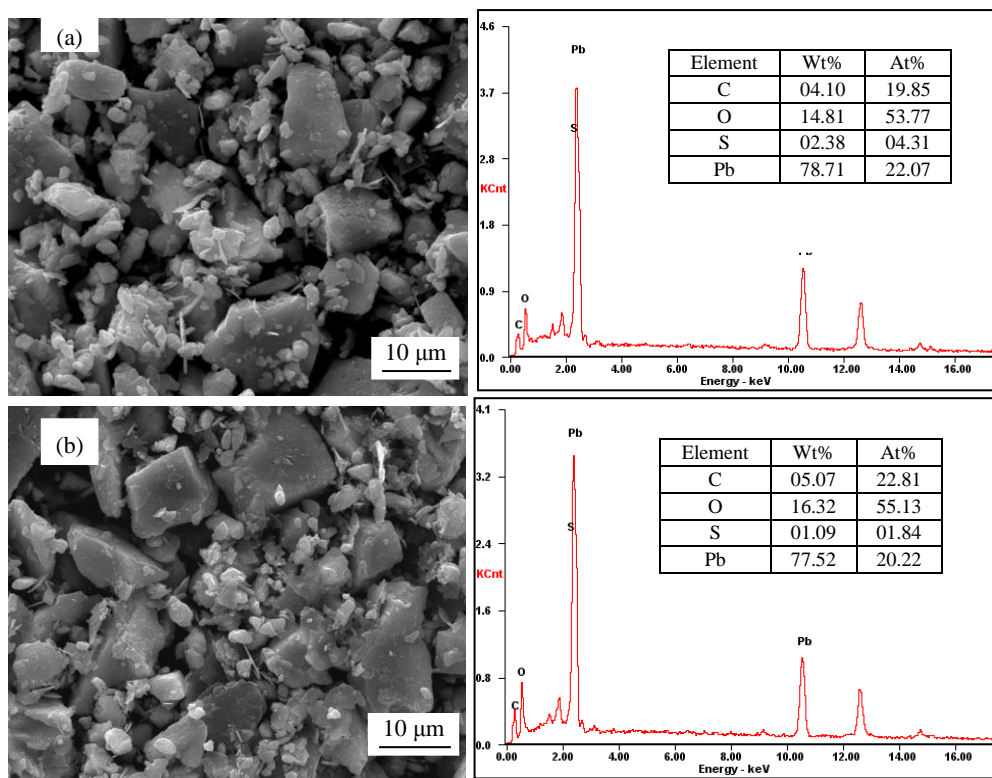


Fig. 4. SEM-EDS for sulfide-treated cerussite samples dissolved in aqueous solutions with different pH values: (a) 4.5, and (b) 9.5

Figure 4a shows that the sulfide-treated cerussite sample immersed in the aqueous solutions with pH 4.5 presented a relatively rough surface with numerous fine granular solid particles, which were considered to be PbS crystals or mainly made up of PbS crystals. Such a surface was favorable for subsequent collector adsorption. Combined with the EDS elemental analysis result, this sample contained 4.10% C, 14.81% O, 2.38% S, and 78.71% Pb. After the sample was contacted with pH 9.5 aqueous solutions, a flat and smooth surface emerged, as shown in Fig. 4b. Agglomeration between fine and bulk particles weakened in SEM images. Formation of the bare surface was attributed to the reaction between OH^- ions in solutions and superficial lead sulfide layers. In this case, the thickness of lead sulfide layers would decrease, thus reducing adsorption of collectors and resulting in a substantial decrease in the hydrophobicity of cerussite. Figure 4b shows that the composition of sample was 5.07% C, 16.32% O, 1.09% S, and 77.52% Pb. Comparing Fig. 4b with Fig. 4a, the content of S on the mineral surface after treatment with acidic pH was more than twice than that treated with alkaline solutions. Meanwhile, the content of C and O in Fig. 4a is lower than those in Fig. 4b, and the content of Pb in Fig. 4a is higher than that in Fig. 4b. These results indicated that more lead sulfide existed on the mineral surface. Lead sulfide layers on the surface of sulfide-treated cerussite were considered to be more stable at acidic pH than that in alkaline solutions. Therefore, we can reasonably assume that alkaline solutions would be unsuitable for the existence of lead sulfide layers on the cerussite surface, as confirmed by micro-flotation tests and the dissolution experiments of sulfide-treated cerussite.

XPS studies

XPS is a surface analysis technique that provides information on the qualitative and quantitative composition of a superficial layer from a few tens of Å thick. It can identify both of the chemical composition and chemical state of the element in the measured samples based on the chemical shift of the photoelectron peaks. Thus, the XPS analysis was employed to show the difference of sulfide-treated cerussite samples conditioned under different conditions. For this study, the Pb4f spectra were used to represent the change of the surface for sulfide-treated cerussite treated in aqueous solutions with different pH values, and the results are given in Fig. 5, Table 3 and Table 4.

Table 3. Atomic concentration of sulfide-treated cerussite samples dissolved in aqueous solutions with different pH values: (a) 2.0, (b) 4.5, (c) 9.5, and (d) 12.0

Sample	Atomic concentration, %			
	C1s	O1s	S2p	Pb4f
a	12.35	39.24	17.85	30.56
b	13.98	42.73	14.91	28.38
c	16.67	50.25	9.82	23.26
d	17.85	55.69	6.36	20.10

Table 4. Binding energy and relative contents of Pb4f_{7/2} in different compositions determined by peak fitting and separation in XPS analysis of sulfide-treated cerussite samples dissolved in aqueous solutions with different pH values: (a) 2.0, (b) 4.5, (c) 9.5, and (d) 12.0

Sample	Binding energy, eV		Percentage in total Pb, %	
	Pb in PbCO ₃	Pb in PbS	Pb in PbCO ₃	Pb in PbS
a	138.79	137.39	74.62	25.38
b	138.78	137.37	77.11	22.89
c	138.79	137.36	82.92	17.08
d	138.78	137.35	85.55	14.45

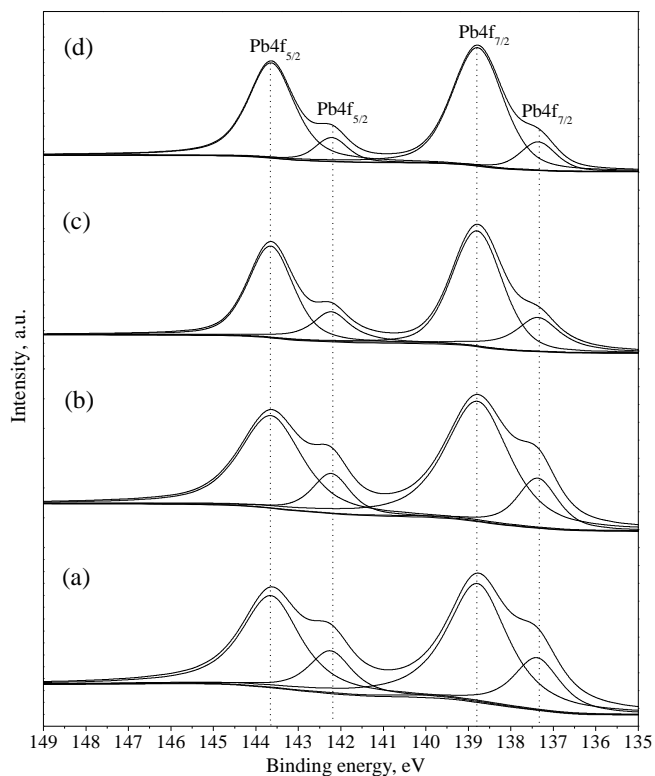


Fig. 5. Pb4f spectra for sulfide-treated cerussite samples dissolved in aqueous solutions with different pH: (a) 2.0, (b) 4.5, (c) 9.5, and (d) 12.0

As shown in Table 3, the atomic concentrations of S and Pb greatly decreased, while the atomic concentrations of C and O gradually increased with the increasing pH value. After the sample was contacted with pH 4.5 aqueous solutions, the atomic concentrations of C, O, S and Pb were 13.98, 42.73, 14.91 and 28.38%, respectively. When the sulfide-treated cerussite sample was treated with pH 9.5 aqueous solutions,

the atomic concentrations of C and O increased to 16.67 and 50.25%, and the atomic concentrations of S and Pb decreased to 9.82 and 23.26%, respectively, indicating that alkaline solutions would be unsuitable for the existence of lead sulfide layers on the cerussite surface.

As shown in Fig. 5, the area under the peaks represents the relative Pb4f contents in different compositions of various sulfide-treated cerussite samples, whereas the position of the peaks indicates the binding energy. It can be seen from Fig. 5a, the Pb4f spectrum appeared two pairs of Pb4f_{7/2} and Pb4f_{5/2} doublet for the sulfide-treated cerussite sample immersed in aqueous solutions with pH 2. The Pb4f_{7/2} at binding energy of 138.79 eV was assigned to Pb in PbCO₃ (Cozza et al., 1992; Grano et al., 1997), and the Pb4f_{7/2} at 137.39 eV was attributed to Pb in PbS (Grano et al., 1997). Combined with the data in Table 4, the percentage of Pb in the form of PbCO₃ and PbS was 74.62% and 25.38%, respectively. As the pH value increased, the proportion of lead sulfide dramatically decreased. After the sample was contacted with pH 4.5 aqueous solutions as shown in Fig. 5b and Table 4, the percentage of Pb in the form of PbS in the total Pb decreased to 22.89%. When the sample was contacted with pH 9.5 aqueous solutions, the percentage of Pb in the form of PbS in the total Pb was 17.08%, and it decreased to only 14.45% when pH increased to 12.0. The main reason for the decrease in the proportion of lead sulfide in the alkaline solution was due to the reaction between OH⁻ ions in solutions and superficial lead sulfide layers besides the detachment of weak-linked surface layer of lead sulfide during the stirring process. These results further indicated that lead sulfide layers on the surface of sulfide-treated cerussite were more stable at the acidic pH than that in the alkaline solutions based on the qualitative and quantitative analysis.

Conclusions

The recovery of cerussite consistently decreased with increasing pH values in the pulp solutions with sufficient collector concentrations. The existence of some H⁺ ions was favorable for cerussite flotation after sulfidization treatment because of the conversion of excessive sulfide ions in the pulp solutions into H₂S. The poor cerussite recovery was achieved because HS⁻ species or S²⁻ ions were dominant species at alkaline pH. Despite the addition of high collector concentrations, cerussite floatability will not be improved in the alkaline solutions.

Lead sulfide layers on the surface of sulfide-treated cerussite were considered to be more stable at acidic pH than that in the alkaline solutions. The mechanism was attributed to the interaction between the lead sulfide layer on the mineral surface and H⁺ or OH⁻ in pulp solutions. This finding was successively proven by the dissolution performance, SEM-EDS analysis and XPS studies of sulfide-treated cerussite at different pH values.

Acknowledgements

The authors would like to acknowledge the financial support provided by the Analysis and Testing Foundation of Kunming University of Science and Technology (No. 20130534 & 20140876), and Academic New Artist Award for Doctoral Post Graduate in Yunnan Province (2014).

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