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Study of flotation behavior and mechanism of cervantite activation by copper ions

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Abstract: Copper-ion activation plays a highly important role in cervantite (Sb_2O_4) flotation. Without metal-ion activation, cervantite cannot be floated by sodium oleate. In this study, flotation tests were conducted to study the effect of Cu^{2+} on the flotation behaviours of cervantite and quartz (SiO_2) as the main gangue mineral. Metal-ion adsorption capacities, zeta potentials, solution chemistry and X-ray photoelectron spectra were analyzed to study the adsorption behavior and mechanism of copper ions and sodium oleate interaction with the minerals surfaces. The results demonstrate that under weakly acidic conditions, cervantite can be flotated and separated from quartz by the addition of copper ions. The reason is that copper ions can be selectively adsorbed on the cervantite surface under weakly acidic conditions, thereby promoting the adsorption of sodium oleate onto the cervantite surface by chemical adsorption. Conversely, copper ions are weakly adsorbed on quartz surfaces below pH 6.1, and sodium oleate cannot be adsorbed on quartz surfaces by chemical adsorption. The hydroxy copper species are integral to the selective activation of cervantite over quartz.

Keywords: cervantite, flotation, copper ions, activation mechanism

1. Introduction

Antimony is an important strategic metal that is widely used in many industrial fields, such as batteries, metallurgy, fire-retardants, and alloys (Li et al., 2012; Luo et al., 2016; Multani et al., 2016; Takashiri et al., 2016). Antimony is mainly obtained from antimony sulfide minerals, such as stibnite and jamesonite (Gudyanga et al., 1998; Sun et al., 2016). As the balance between the gradual depletion of antimony sulfide resources and the increasing demand for antimony changes, people urgently need to find a way to utilize antimony oxide resources (Wang et al., 2014). However, the recovery of cervantite is currently a problem in the mineral processing industry (Xiao et al., 1987). Antimony oxide is a general name for a group of minerals including: valentinite, senarmontite and cervantite (Gopalakrishnan et al., 1976). The most valuable of them is cervantite, which is the oxidation product of stibnite and often appears in the stibnite oxidation zone (Ashley et al., 2003; Roper et al., 2012). Because of its high density, a gravity-separation method was first used to recover cervantite. Unfortunately, due to its fine particle size and ease of sliming, the recovery of cervantite can only reach approximately 20% using gravity- separation (Guo 1997). Hence flotation would be method better option for cervantite separation. However, due to its strongly hydrophilic nature and similar nature to gangue minerals (Xiao et al., 1987), it is difficult to float cervantite using only anionic collectors without metal ion activation. Metal ions play an important

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role in mineral flotation and can improve the performance of the collector adsorption. Many minerals can achieve satisfactory flotation recoveries after activation by metal ions. Salicylhydroxamic acid can provide a high recovery of cassiterite after activation by lead ions (Feng et al., 2017). Sodium oleate has a poor collecting capacity for unactivated quartz but has a good collecting capacity for quartz activated by calcium and magnesium ions (Ejtemaei et al., 2012; Kou et al., 2016). Aluminium ions or iron ions play a crucial role in the kyanite-oleate flotation system (Jin et al., 2016).

Until now, only a few references have reported the flotation behaviour and mechanism of cervantite activation by metal ions (Guo 1997; Wang et al., 2013). Therefore, the effect of copper ion on the flotation behaviour of cervantite and quartz and the mechanism of this process are explored in this paper. The adsorption of copper ions on mineral surfaces was analysed by atomic adsorption spectrometry, zeta potential measurement and X-ray photoelectron spectroscopy (XPS). The results, which demonstrate efficient recycling of cervantite and other similar minerals by flotation recovery, are significant for guiding further such studies.

2. Material and methods

2.1 Samples and reagents

Bulk samples containing cervantite (Sb_2O_4) and quartz (SiO_2) were obtained from the Xikuangshan mine in China. Handpicked high-grade cervantite and quartz samples were crushed with a hammer, and high-purity cervantite and quartz crystals were manually separated under a microscope. Cervantite and quartz samples were dry-ground in a porcelain ball mill and wet-screened in distilled water to obtain a -0.074 + 0.038 mm sized fraction. The quartz sample was immersed in a 3% w/w hydrochloric acid solution four times to eliminate impurities on the surface. The processed quartz was washed repeatedly with distilled water until the pH of the supernatant reached the natural level. Subsequently, two samples were filtered, vacuum-dried and stored in glass bottles, for use in flotation tests and other measurements. From chemical analysis, the mass fraction of Sb and Si in the cervantite and quartz samples are 71.91% and 46.3%, respectively. By converting these value to Sb_2O_4 and SiO_2 contents, the purity of these were calculated to be 90.8% and 99.3 %, respectively. The XRD patterns of cervantite and quartz are shown in Figs. 1 and 2.

Sodium oleate of analytical quality was used as the collector in the micro-flotation tests, and $CuCl_2$ of analytical quality was used as an activator. Solutions of HCl and NaOH were used to adjust the pH of the system.

2.2. Flotation tests

Flotation tests for single minerals (2 g) were conducted using a XFG flotation machine with a 40 cm^3 flotation cell. The impeller speed was fixed at 1800 r/min. In each test, desired pH values were obtained by adjustment with 0.01 mol/dm^3 hydrochloric acid and 0.01 mol/dm^3 sodium hydroxide. After adding the desired amount of $CuCl_2$, the suspension was conditioned for 3 min, and afer addition of the desired amount of sodium oleate, the suspension was conditioned for a further 3 min. At this time the pH value was measured. The flotation was sustained for 3 min. The floated and unfloated products were collected, dried, and weighed. The recovery was calculated based on the dry mass of the products obtained. The results presented are the averages of three independent measurements, and their averages were used as the final result.

2.3 Copper-ion adsorption capacity measurements

The copper-ion adsorption capacities of minerals were individually measured, using an atomic adsorption spectrophotometer. Mineral samples (2 g) and 40 cm^3 distilled water were added to a conical flask. After the pH had been adjusted and the required amount of the copper ion had been added (C_0), the pulp was shaken for 30 minutes at a constant temperature (25 ℃). Then, the slurry was centrifuged (20000rpm, 20 min), and the metal ion concentration of the supernatant (C) was detemined using an atomic absorption spectrophotometer. The copper-ion adsorption capacity is represented by the adsorption capacity (AC), where (AC) is defined as (Taseidifar et al., 2017):

$$\mathrm{AC} = \frac{(C_0 - C)}{C_0} \times 100\% \tag{1}$$

where C_0 is the initial concentration of copper ions (mg/dm^3) and C is the measured concentration of metal ions in the supernatant (mg/dm^3).

The results presented are the averages of three independent measurements, and their averages were used as the final result.

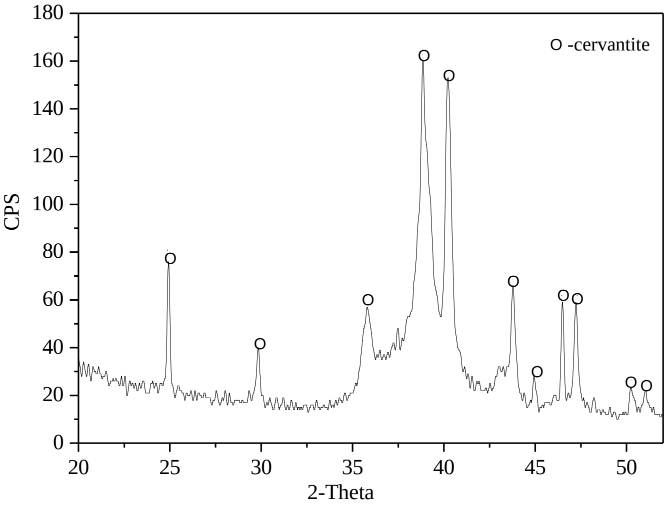

Fig. 1. XRD diffraction pattern of cervantite

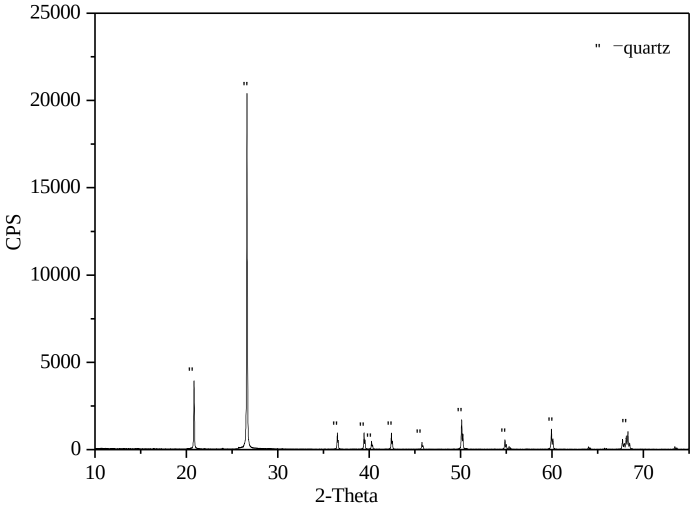

Fig. 2. XRD diffraction pattern of quartz

2.4 Zeta potential measurement

Zeta potentials of minerals were measured using a JS94H zeta potential analyser (Jiang et al., 2012). The mineral samples used for this purpose were ground to a size less than 5 µm with an agate mortar and pestle. The sample size was determined using a Rise-2006 laser particle size analyzer. Mineral samples below 5 µm (20 mg) were added to the 40 cm^3 aqueous solution with or without the desired amounts of reagents, and stirred for 5 min. Then, the pH values were adjusted and measured. The colloidal suspension was transferred to an electrophoresis vessel. The electrodes of the micro electrophoresis meter had been wetted previously to avoid any disturbance due to the presence of air bubbles. Migration of colloidal particles under a potential gradient of 10 V cm^{-1} was observed on a computer screen through a camera and a multimedia system. An average electrophoretic velocity was obtained by the computer, by timing at least 10 particles, first in one direction and then in the opposite direction after reversal of the polarity of the applied electrical field. Values of the zeta potential were calculated using computer software based on the Helmholtz–Smoluchowski equation (Chun et al., 2003). The results presented are the averages of three independent measurements, and their averages were used as the final result.

2.5 Measurement of adsorbed reagent

Conditioning procedures were similar to that used for micro-flotation tests. Copper chloride and sodium oleate solution (40 cm^3) combined with minerals (2 g) were placed in 100 cm^3 flasks. The pH was adjusted by the addition of HCl and NaOH until the desired pH values had been reached. The pulp was agitated for 30 min at 150 rpm at a constant temperature (25 °C) in an incubator shaker. The solutions were centrifuged at 8000 rpm for 15 min, and the concentration of each component in the supernatant was analyzed. The residual concentrations of reagents were determined by a Total Organic Carbon (TOC) analyzer (TOC-VCPH, Shimadzu, Japan). The experiments were repeated at least three times and the average data were plotted. The amounts of surfactants adsorbed on the mineral (Γ) were calculated from Eq. (2) (Beaussart et al., 2009). The results presented are the averages of three independent measurements, and their averages were used as the final result.

$$\Gamma = \frac{(C_0 - C)V}{m} \tag{2}$$

where C_0 and C are the initial and supernatant concentrations, respectively, V is the solution volume, and m is the mass of the mineral.

2.6 X-ray photoelectron spectroscopy measurements (XPS)

Twenty milligrams of the mineral samples containing particles smaller than 5 µm were added to 40 cm^3 of aqueous solutions with or without the desired amount of reagents, and stirred for 3 min. The pH was adjusted to 6.0 throughout the experiment. After filtration, the sample was washed repeatedly with distilled water whose pH was the same as that required for the tests (6.0). After low-temperature drying, the samples were analyzed by an ESCALAB 250Xi type X-ray photoelectron spectrometer (Omran et al., 2015). Spectra were recorded at the constant pass energy of 20 eV and in intervals of 0.1 eV/step, using an Al Kα X-ray source. Binding energies were referenced to the C 1s value of 284.8 eV.

3. Results and Discussion

3.1 Micro-flotation

The effects of Cu^{2+} on the flotation of cervantite and quartz, using sodium oleate as a collector, are presented in Fig. 3. This shows that flotation separation of cervantite and quartz can be achieved using Cu^{2+} as an activator and sodium oleate as a collector. There is a large difference between the flotation recoveries of cervantite and quartz in the range $5 < pH < 8$, and this difference becomes greatest around pH 6.0. Therefore, a pH value around 6.0 appears suitable to achieve flotation-separation between cervantite and quartz, using Cu^{2+} as an activator and sodium oleate as a collector. According to solution chemical calculations presented in Section 3.5, copper hydroxy complexes are present in the range $2 < pH < 6.1$, whereas the pH range of precipitation of Cu ions as hydroxides is favoured at $pH > 6.1$. This suggests indicating that hydroxy complexes and hydroxide precipitates of Cu ions are important species for activating cervantite.

3.2 Analysis of amount of adsorbed copper ions

The adsorption of copper ions on cervantite and quartz surfaces as a function of pH is shown in Fig.4 . The mechanism of activation of these two mineral surfaces by copper ions can be explained by these adsorption date.

As shown in Fig. 4, with increase of pH, the adsorption of copper ions on the mineral surfaces increases for both minerals and tends to be same under neutral to alkaline conditions. However, the adsorption is greater on the cervantite than on the quartz surface under acidic conditions. Comparing Fig. 4 to Fig. 3, the adsorption of copper ions on cervantite and quartz surfaces is consistent with the activation of the two minerals, indicating that copper ion adsorption plays a crucial role in their flotation behaviours.

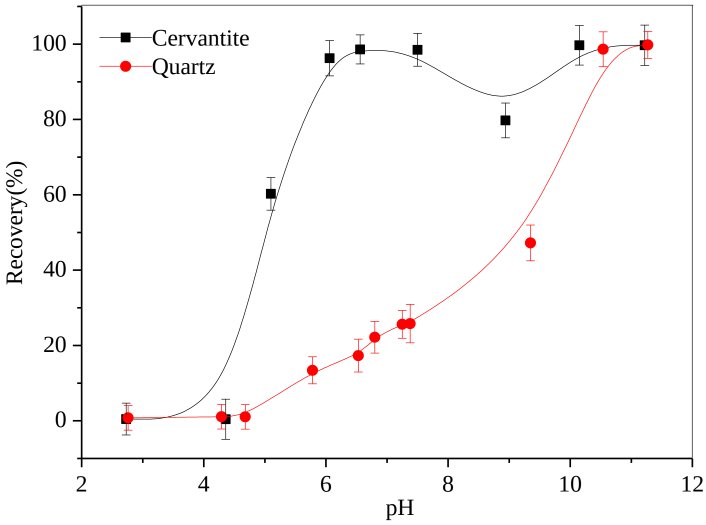

Fig. 3. Effect of pH on mineral recovery using sodium oleate as a collector and Cu^{2+}as an activator (sodium oleate 1.5×10^{-4} M; Cu^{2+} 5×10^{-4} M)

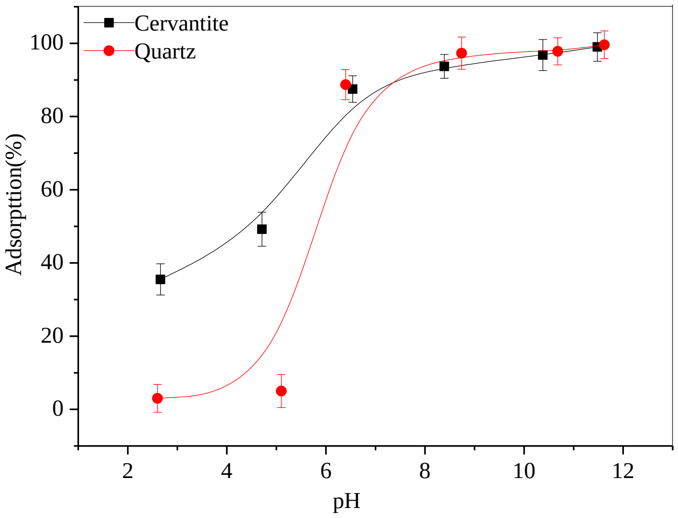

Fig. 4. Effect of pH on the adsorption of Cu^{2+} on mineral surfaces

3.3 Zeta potential analysis

Fig. 5. shows the relationship between the zeta potentials of the two minerals, and the pH before and after treatment by Cu^{2+}. Here, the concentration of copper ions used was 5×10^{-4} M. After addition of copper ions, the zeta potentials of cervantite and quartz were shifted significantly in the positive direction. The PZC values of cervantite and quartz were increased from 2.4 and 2.6 to 4.6 and 3.0, respectively, indicating that positively charged copper ions are adsorbed on both mineral surfaces. Over the entire pH range, the change in zeta potential of cervantite is greater than that of quartz, indicating that copper ions are more strongly adsorbed on the cervantite surface than on the quartz surface. Copper ions do not cause a substantial change in the zeta potential of quartz at low pH, while the zeta potential of cervantite changes by ~20 mV. This may explain why flotation-separation of cervantite from quartz can be achieved using low-pH conditions.

Fig. 6 shows the effect of pH on the zeta potential of minerals before and after treatment with sodium oleate. After treatment with sodium oleate, the zeta potentials of the two minerals with adsorbed copper ions reduced significantly, indicating the adsorption of negatively charged oleate ions on the two copper-ion-activated mineral surfaces. Under acidic conditions, the change of the surface potential of quartz is small, which suggests that the adsorption of sodium oleate on the quartz surface is weak. The surface potential of the cervantite is lower, indicating that the adsorption of sodium oleate on the cervantite surface is relatively strong. When pH > 10, the potential of the two minerals starts increasing, indicating that the adsorption of sodium oleate on two mineral surfaces is relatively weakened. The results are consistent with the results of sodium oleate adsorption capacity analysis on the two mineral surfaces.

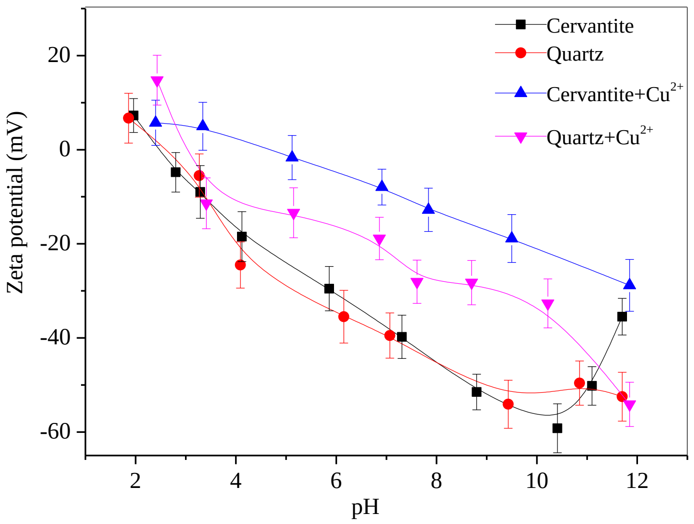

Fig. 5. Effect of pH on zeta potential of minerals before and after treatment with Cu^{2+} (Cu^{2+} 5×10^{-4} M)

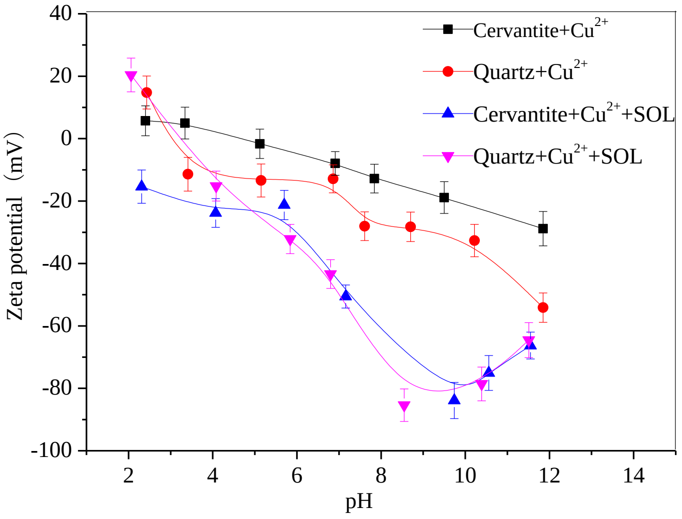

Fig. 6. Effect of pH on zeta potential of minerals before and after treatment with sodium oleate (Cu^{2+} 5×10^{-4} M, sodium oleate 1.5×10^{-4}M)

Fig. 7 shows the effect of pH on the zeta potential differences of the minerals before and after treatment with sodium oleate. The concentration of sodium oleate was 1.5×10^{-4} M, and the concentration of copper ions was 5×10^{-4} M. The two curves are effectively parallel for pH > 6 but differ significantly at pH <6. The figure suggests the difference in behavior between the two minerals occurs for pH < 6 and is greatest at around pH 4. There is slight change in the zeta potential variation of quartz with pH to ~4. On the other hand, the zeta potential of cervantite becomes small as the pH decreases below 6, indicating oleate ions are more strongly adsorbed on the cervantite surface than on the quartz. This is consistent with the different flotation behaviors of the two minerals at pH < 6.

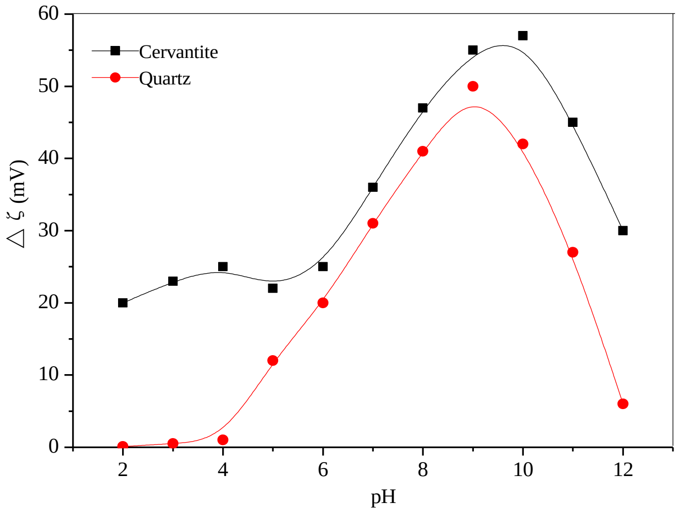

Fig. 7. Effect of pH on zeta potential difference of minerals before and after treatment with sodium oleate

3.4 Sodium oleate adsorption capacity analysis

Fig. 8 shows the relationship between pH and the adsorption capacity of sodium oleate on cervantite with or without Cu^{2+}. Without copper ions, the cervantite surface has a lower adsorption capacity for sodium oleate. As the pH is increased, the adsorption capacity of sodium oleate on cervantite also increases gradually, and reaches a maximum at pH 9.5. As the pH is increased further, the concentration of hydroxyl ions increases in the pulp and the adsorption capacity of sodium oleate decreases. This may be caused by competitive adsorption of hydroxyl ions and oleate ions. Upon addition of copper ions, the adsorption capacity of sodium oleate increases significantly, compared to the capacity without copper ions. This change is even more obvious at low pH, indicating that copper ions play an important role in increasing the adsorption capacity of sodium oleate on the cervantite surface at pH < 6.

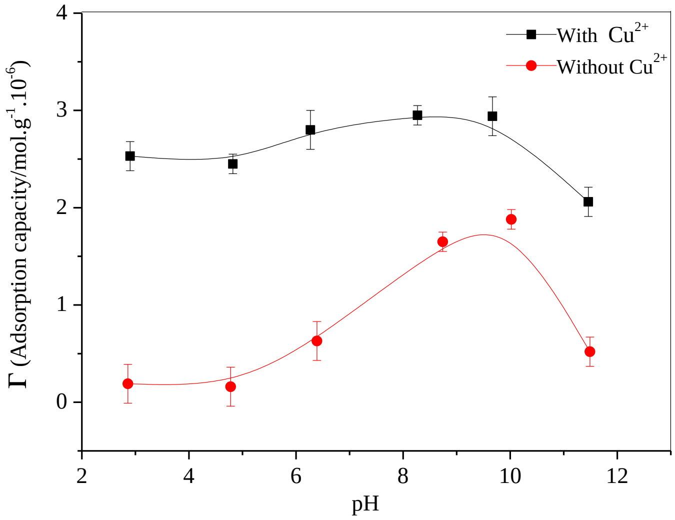

Fig. 8 Relationship between pH and adsorption capacity of sodium oleate on cervantite, with or without Cu^{2+}

Fig. 9 shows the relationship between pH and the adsorption capacity of sodium oleate on the two mineral surfaces. The adsorption capacity of sodium oleate on the cervantite surface is higher than on the quartz surface at low pH, which is consistent with zeta potential changes of the two minerals by sodium oleate (Fig.7). This suggests the stronger adsorption of copper ion on the cervantite surface than on the quartz surface at low pH. The adsorption capacity of sodium oleate on the two mineral surfaces increases gradually with the increase of pH, and reaches a maximum at pH 9.5. As the pH is increased further, the adsorption capacity of sodium oleate on the two mineral surfaces gradually decreases. This is because the concentration of hydroxyl ions increases as the pH is increased, resulting in competitive adsorption with sodium oleate at the mineral surfaces.

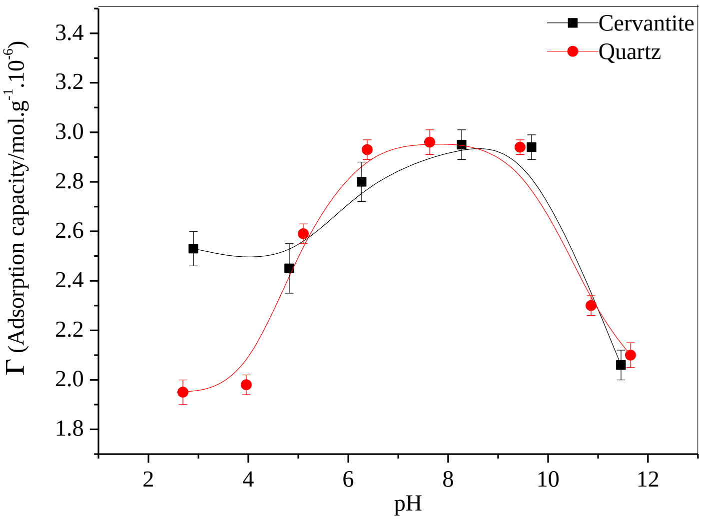

Fig. 9. Effect of pH on the adsorption capacity of sodium oleate on minerals in the presence of Cu^{2+}

3.5 Solution chemistry analysis

According to the theory of flotation solution chemistry (Albrecht et al., 2016), the logC-pH diagram for the hydrolysis species of copper ions (5×10^{-4}M) is shown in Fig. 10. A comparison between Fig. 10 and Fig. 3 shows that flotation recovery of cervantite corresponds to the concentration of hydroxy copper and copper hydroxide precipitate. The positively charged Cu^{2+} species dominates at pH < 3, and the recovery of cervantite approximates to zero, indicating that copper ions do not activate cervantite. When pH > 3, the concentration of hydroxy copper species increases, and corresponding recovery of cervantite increases. When pH > 6.1, copper hydroxide precipitate becomes predominant. Hydroxy complexes or hydroxide precipitates of copper ions can be adsorbed on the surfaces of the two minerals. However, copper hydroxy complexes are more readily adsorbed on the cervantite surface than on the quartz surface. This appears to be the fundamental reason for the flotation-separation of cervantite from quartz. In comparison hydroxide precipitates of copper ions show similar adsorption behaviors on the two mineral surfaces. Therefore, it is difficult to achieve flotation-separation of these two minerals under conditions that are in the range of neutral to highly alkaline.

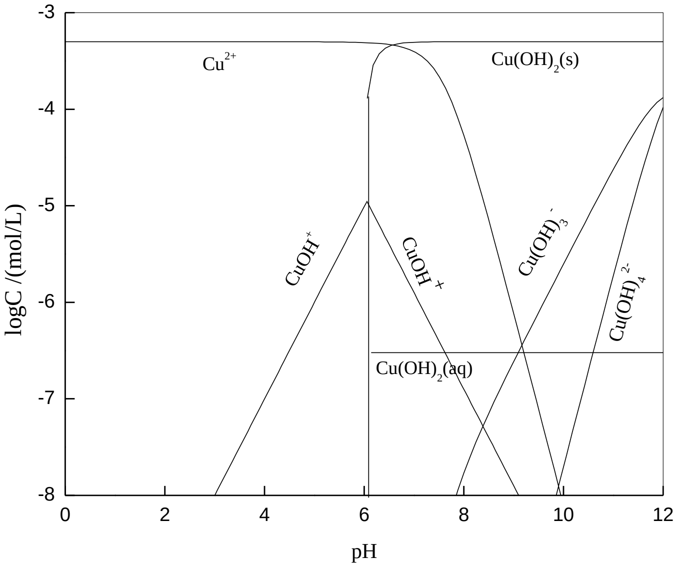

Fig. 10. The logC-pH diagram for hydrolysis species of Cu ions

3.6 XPS analysis

For further analysis of the mechanism of flotation-separation of cervantite and quartz at pH 6.0, this section describes the differences in the photoelectron spectra of the two minerals before and after treatment with copper ions and sodium oleate. The XPS spectra of cervantite before and after treatment with copper ions and sodium oleate are shown in Fig. 11, and the surface element binding energies and relative contents are shown Table 1.

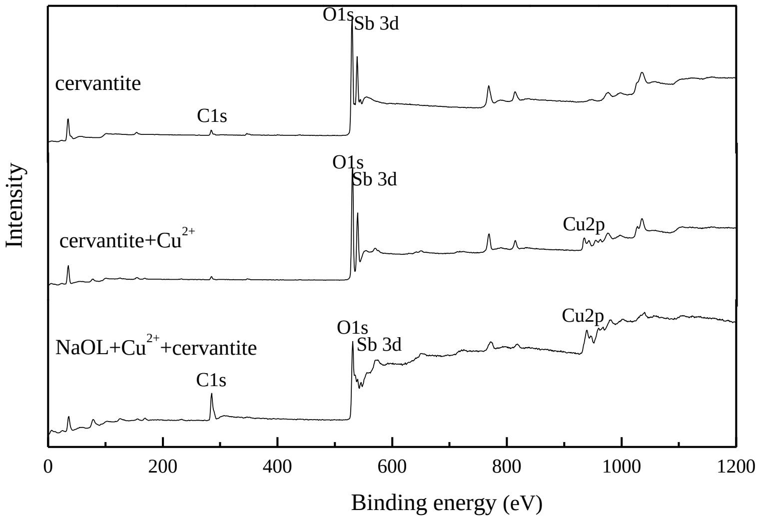

Fig. 11. XPS spectrograms of cervantite before and after treatment with copper ions and sodium oleate at pH 6.0

Table 1. Surface elements, measured by XPS, of cervantite before and after treatment with copper ions and sodium oleate at pH 6.0

Surface	Surface element	Binding energy (eV)	Relative content
Cervantite surface	Sb3d	530.17	20.05
	C1s	284.79	21.72
	O1s	530.79	58.23
Cervantite surface treated with copper ions	Sb3d	530.12	15.69
	C1s	284.81	26.05
	O1s	531.62	46.51
	Cu2p	935	11.75
Cervantite surface treated with copper ions and sodium oleate	Sb3d	530.67	6.66
	C1s	284.8	54.36
	O1s	532.23	31.35
	Cu2p	938.91	7.63

As shown in Fig. 11 and Table 1, the copper content of the cervantite surface was 11.75 % after the addition of copper ions, indicating that copper ions are adsorbed on the cervantite surface. The binding energy of oxygen on the cervantite surface increases from 530.79eV to 531.62eV, showing a difference of 0.83eV. The displacement value is greater than the instrumental error of 0.4eV, indicating chemical adsorption of species onto the surface oxygen of cervantite. The most likely of these are the hydrolysis species generated by the added copper ions.

Upon activation by copper ions and adsorption of sodium oleate, the surface carbon content of cervantite increases substantially (from 21.72 % to 54.36 %). The surface antimony content decreases significantly (from 20.05 % to 6.66 %). The surface oxygen content decreases (from 58.23 % to 31.35 %). The surface copper content decreases (from 11.75 % to 7.63 %) as a result of oleate adsorption. While decreases in the surface Sb and O contents are expected, the carbon content increases due to the adsorption of sodium oleate. The O1s binding energies on the cervantite surface before and after oleate adsorption are 531.62 eV and 532.23 eV, respectively, with a difference of 0.61 eV. The Cu 2p binding energies before and after the reaction are 935 eV and 938.91 eV, respectively, with a difference of 3.91 eV, excluding the uncertainty of measurements. This indicates that chemical reaction occurs between sodium oleate and Cu ions adsorbed on the cervantite surface, and the precipitation of copper oleate enables the flotation of cervantite.

The XPS spectra of quartz before and after treatment with copper ions and sodium oleate are shown in Fig. 12, and the surface element binding energies and relative concentrations are shown in Table 2. After adding copper ions, the copper content of the quartz surface increases to 7.83 %, indicating that adsorption of copper ions occurs on the quartz surface. However, changes in the binding energies of the quartz-surface elements are small and within the uncertainty of measurements. This indicates that copper ions are physically adsorbed on the quartz surface. There is an increase in the surface carbon content of quartz activated by copper ions with sodium oleate (from 6.27 % to 37.38 %). The surface silicon content decreases (from 31.56 % to 16.62 %). The surface oxygen content decreases (from 62.17 % to 40.32 %). The surface copper content decreases (from 7.83 % to 5.68 %) after sodium oleate addition. There is a decrease in the relative contents of Si and O on the quartz surface while the content of C increases, indicating that sodium oleate is adsorbed on the quartz surface.

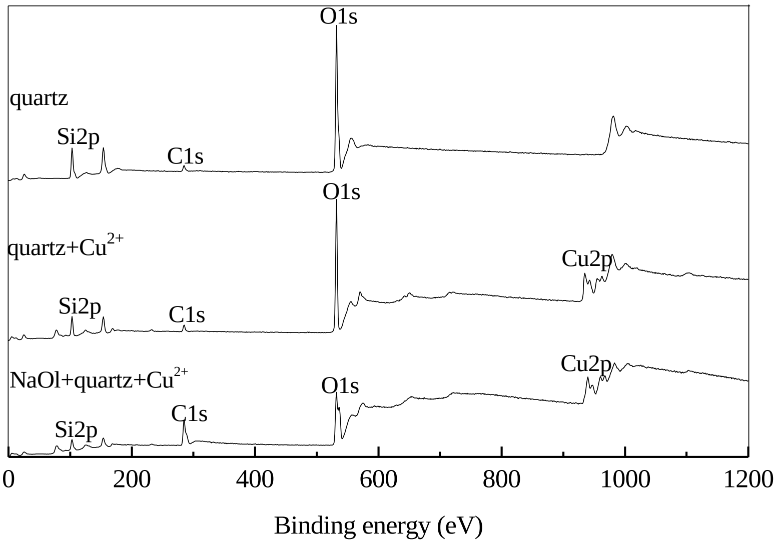

Fig. 12. XPS spectrogram of quartz before and after treatment with copper ions and sodium oleate at pH 6.0

A comparison of Table 1 and Table 2 shows that the copper content is higher on the cervantite surface than on the quartz surface, indicating that copper ions are more readily absorbed on the cervantite surface at pH 6.0. This indicates that the cervantite surface has more active sites than the quartz surface for the adsorption of sodium oleate. After adsorption of sodium oleate, there are slight changes in the binding energies of the surface-elements of quartz. These changes are within the uncertainty of measurements, indicating that no chemical adsorption of sodium oleate and copper ion occurs on the quartz surface at pH 6.0.

3.7 Summary

With copper ions as activator, flotation separation of cervantite and quartz can be realized at pH 6.0 using sodium oleate as collector. The adsorption capacity of copper ions on the cervantite surface is greater than on the quartz surface under weak acid conditions, which results in zeta potential differences between the two minerals, and the greater adsorption capacity of sodium oleate on the cervantite surface than on the quartz surface. Hence flotation separation of cervantite from quartz can be realized at pH 6.0. According to the solution chemical analysis, both hydroxyl complexes and hydroxide precipitates of copper ions can activate the cervantite, while hydroxide precipitates of copper ions can also activate quartz. This results in the inability to separate the two minerals under alkaline conditions. Hydroxy copper complexes are the crucial component to achieve selective activation of cervantite from quartz. XPS analysis results suggest that copper and oleate ions are chemically adsorbed on the cervantite surface at pH 6.0, whereas copper and oleate ions are physically adsorbed on the quartz surface at this pH. These differences enable the separation of the two minerals.

Table 2. Surface elements measured by XPS of quartz before and after treatment with copper ions and sodium oleate at pH 6.0

Surface	Surface element	Binding energy (eV)	Relative concentration
Quartz surface	Si2p	103.14	31.56
	C1s	284.42	6.27
	O1s	532.51	62.17
Quartz surface treated by copper ions	Si2p	103.48	24.04
	C1s	284.84	8.72
	O1s	532.54	59.4
	Cu2p	935.08	7.83
Quartz surface treated by copper ions and sodium oleate	Si2p	103.17	16.62
	C1s	284.78	37.38
	O1s	532.26	40.32
	Cu2p	935.24	5.68

4. Conclusions

1) Using sodium oleate as a collector, flotation-separation of cervantite from quartz can be accomplished by the addition of copper ions under weakly acidic conditions.
2) Copper ions are chemically adsorbed on the cervantite surface under weakly acidic conditions. Therefore, the adsorption capacity of sodium oleate on the cervantite surface is greater than on the quartz surface. Hydroxy copper complex ions are critical to the selective activation of the cervantite
3) Chemical reaction occurs between sodium oleate and the Cu ions adsorbed on the cervantite surface at pH 6.0. On the other hand, no chemical reaction between sodium oleate and copper ions occurs on the quartz surface at pH 6.0.

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