Inhibiting effect of citric acid on the floatability of serpentine activated by Cu(II) and Ni(II) ions

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Abstract: The laboratory researches about the inhibiting effect of citric acid on the flotation performance of serpentine activated by Cu^{2+} and Ni^{2+} were carried out through micro flotation tests, zeta potential measurements, collector adsorption capacity measurements and solution chemistry analysis. The flotation results showed that Cu^{2+} and Ni^{2+} could remarkably activate the flotation of serpentine when the pH value was more than 6, however, this activation could be effectively weakened by adding citric acid. Zeta potential measurement and adsorption capacity measurement indicated that the presence of citric acid could prevent the adsorption of Cu^{2+} and Ni^{2+}, and therefore reduce the adsorption amount of potassium butyl xanthate on serpentine surface. Furthermore, solution chemical analysis of the flotation system showed that copper hydroxide $Cu(OH)_{2(s)}$ and the nickel hydroxide $Ni(OH)_{2(s)}$ were the main component in the pH range of 9 to 10, which adsorbed onto serpentine surface and made it activated; while the citric acid could effectively prohibit the formation of these metal hydroxide in slurry so as to inhibit the activation impact.

Keywords: copper ion, nickel ion, serpentine, floatation, activation, inhibiting

1. Introduction

In the flotation of copper and nickel sulfide ore, how to effectively reduce the content of MgO in the flotation concentrates has been the focus in the study of related mineral processing research work (Edwards et al.,1980; Qiao et al.,2005; Malysiak et al.,2004). Serpentine was the main silicate gangue mineral containing MgO in copper and nickel sulfide ore, therefore, inhibition of the serpentine was of great significance for the reduction of MgO content in the copper and nickel flotation concentrates (Zhang and Lei,2013).

In recent years, several research groups in the world had conducted a lot of studies on the reduction of MgO content in Cu-Ni concentrates. Most of them had devoted their efforts to seeking or synthesizing efficient inhibitor of minerals containing magnesium (Zhang and Lei,2013; Zhang et al.,2013; Huang et al.,2014). However, some studies showed that minerals containing magnesium would be mixed into the concentrates due to the activation of metal ions (such as Cu^{2+} and Ni^{2+}) in the copper-nickel sulfide ores flotation process, (Zhang et al.,2012). Lizardite and chlorite could be activated by Cu(II) and Ni(II), and floated with xanthate in the pH range of 9 to 10, in which, copper and nickel hydroxides were the primary stable species to promote xanthate adsorption by adsorbing/precipitating on the mineral surface (Fornasiero and Ralston,2005). FTIR analyses on the adsorption form of xanthate on the surface of chalcopyrite, pentlandite and pyrrhotite (Cao et al., 2014; Zhang et al.,2013) showed that the flotation behaviors of serpentine, chlorite and other gangue minerals containing magnesium were significantly affected by metal ions (such as copper and nickel ions). Undesired activation of these gangue minerals could complicate the regular flotation. Therefore,

the inhibition or elimination of the undesired activation by metal ions was an effective way to inhibit gangue mineral flotation, and guarantee the quality of concentrate. Sun et al. investigated the inhibiting behaviors of several complexing reagents, including oxalic acid, citric acid, EDTA, in the flotation of copper-nickel sulfide ore (Sun et al., 2001), the research results showed that these reagents could remove the Cu and Ni ions adsorbed on the surface of gangue minerals containing magnesium, and reduce adsorption sites of xanthate. Compared with traditional flotation method, the utilization of complexing reagents, especially EDTA, could effectively reduce the content of MgO in Cu-Ni concentrates (Zhang and Liu,2001; Huang et al.,2014). Simultaneously, the above tests results showed that the addition of complexing agents did not affect the flotation behaviors of the target minerals such as pentlandite and chalcopyrite.

The purpose of this work was to investigate the inhibiting effect of citric acid on serpentine activated by Cu^{2+} and Ni^{2+} ions through micro flotation tests, zeta potential measurements and collector adsorption measurements. Then the inhibiting mechanism was further discussed by solution chemistry analysis.

2.   Materials and methods

2.1. Materials

Serpentine sample was obtained from Shandong Linqu deposits in China. The hand-picked high-grade serpentine sample was first crushed with a hammer, then ground in a porcelain mill with agate balls, and finally screened by stainless steel screens. The 45~74μm size fractions were used for pure mineral flotation tests and collector adsorption capacity measurements. A portion of the sample was further ground to -2μm for X-ray diffraction (XRD) and chemical analysis. The XRD pattern was shown in Figure.1, indicating that serpentine sample was of a high purity without observable existences of other minerals. As presented in Table 1, the chemical analysis results showed that this sample contained a bit of Fe and Ca elements as impurities, and the content of serpentine reached 97%.

Table 1. Chemical compositions of serpentine sample (%)

MgO	SiO₂	Al₂O₃	CaO	TFe	LOSS
40.75	42.21	0.77	0.13	1.86	12.79
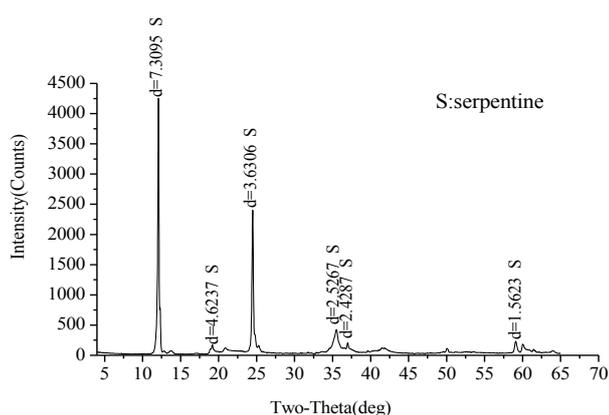
Fig. 1. XRD spectrum of serpentine sample

Industrial pure potassium butyl xanthate was obtained from dressing plant and used as serpentine's collector. Copper and nickel sulfates were used as the ions source. Citric acid was utilized to reduce or eliminate the effect of metal ions. Chemical pure sulfuric acid and sodium hydroxide were diluted to 0.1mol/L and 0.01mol/L and used to adjust the pulp pH value. The water used in this

study was distilled water, with resistivity as $16.13 \times 10^6 \, \Omega \cdot cm$（298.15K. Reagents used for the tests: citric acid, copper sulfate pentahydrate and nickel sulfate hexahydrate were all analytically pure. The frother was chemically pure methyl isoamyl alcohol (MIBC).

2.2. Methods

2.2.1. Micro flotation tests

The micro flotation tests were performed by using XFG-type laboratory flotation machine (Figure. 2) with 40 cm³ micro-flotation cell (GAO, YUESHENG et al.,2016; GAO, ZHIYONG et al.,2016). The slurry was prepared by dispersing 2 g of serpentine sample (45~74µm) in 40 cm³ of distilled water, and agitated for 120 s. Then, the target pH value was adjusted by 0.1 mol/L H_2SO_4 and 0.01 mol/L NaOH solutions before adding flotation reagents. For each reagent, the stirring time was 180 s, and the flotation time was set as 300 s. All flotation tests were carried out at room temperature around 298.15 K. The concentrates and tailings were filtered, dried, and weighed to calculate the flotation recovery of serpentine under various flotation conditions.

Fig. 2. XFG flotation machine for micro flotation tests

2.2.2. Zeta potential measurements

The zeta potentials of the sample were measured by using Brookhaven Zeta plus zeta meter (USA). The sample was further ground to -2 µm in the agate mortar. 0.05 g sample was placed in a beaker, and stirred for 900 s with 50 cm³ distilled water and reagents. Then, a series of pH values were regulated, and zeta potentials of sample were measured. The average of four independent measurements was adopted to ensure the reasonability and credibility of tests.

2.2.3. Measurement of Collector adsorption Capacity

In each test, 0.1 g of sample and a certain amount of distilled water and potassium butyl xanthate solution were placed into a beaker. After the slurry pH value was adjusted to 9.5, the solution was stirred for 1800 s to ensure adsorption equilibrium. Then the supernatant liquid was sufficiently centrifuged separation from solution, and the concentration of residual collector was measured by UV3000PC ultraviolet spectrophotometer. The collector adsorption capacity on the surface of minerals could be calculated through formula 1:

$$\Gamma = \frac{(C_0 - C) \times V}{m} \tag{1}$$

Γ is the collector adsorption capacity on the surface of minerals (mol/g), C_0 is the initial concentration of collector in slurry (mol/L), C is the residual concentration of collector in slurry (mol/L), V is slurry volume (L), m is the quality of sample (g).

2.2.4. Solution chemistry analysis

To understand the inhibition mechanism of citric acid, the main species in solution and on minerals surface were identified through solution chemistry analysis. Based on the necessary data of various reactions acquired from IUPAC SC-database, the distribution relationships among different species were calculated. The calculation software was SCDbase Species.exe and Microsoft Excel, and the drawing software was Origin Pro8.0. Then the logC-pH graphs of Cu(II)-H$_2$O system, Ni(II)-H$_2$O system, Cu(II) -citric acid system and Ni(II)-citric acid system were drawn.

3. Results and discussion

3.1. Micro-flotation of serpentine

The micro-flotation tests were conducted to reveal flotation behaviours of serpentine in the presence and absence of Cu^{2+} or Ni^{2+}, and to evaluate the inhibition effect of citric acid on flotation. In these tests, the concentrations of potassium butyl xanthate, copper sulfate pentahydrate and nickel sulfate hexahydrate were 1×10^{-4} mol/L, 5×10^{-4} mol/L and 5×10^{-4} mol/L, respectively. Citric acid was added as complexing reagent at concentration of 2×10^{-4} mol/L, 4×10^{-4} mol/L and 6×10^{-4} mol/L.

As shown in Figure.3, the natural floatability of serpentine was poor, and the highest recovery was under 10% at the whole pH range. Under the activation of Cu^{2+} or Ni^{2+}, the highest recovery of serpentine reached about 60% or 45% in the pH range of 8.5 to 9.5, and the adsorption of Cu^{2+} on serpentine surface was more efficient than that of Ni^{2+}. In addition, the existence of Cu^{2+} or Ni^{2+} had little influence on serpentine flotation in the pH<6 range, and the recovery rate of serpentine remained low. The reasonable explanation was that the main ion species (free state) of Cu^{2+} or Ni^{2+} couldn't adsorb on the surface of serpentine at acidic pH values, therefore, no enough adsorption sites available for the adsorption of potassium butyl xanthate.
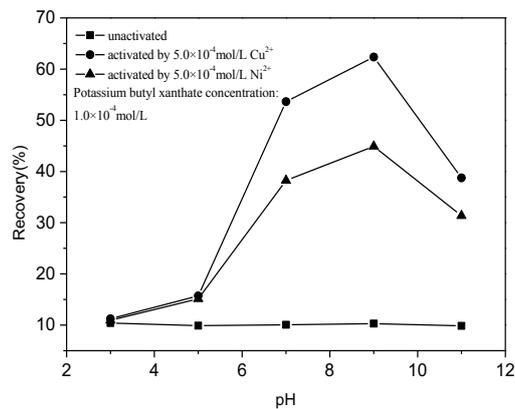
Fig. 3. Flotation recovery of serpentine as a function of pH
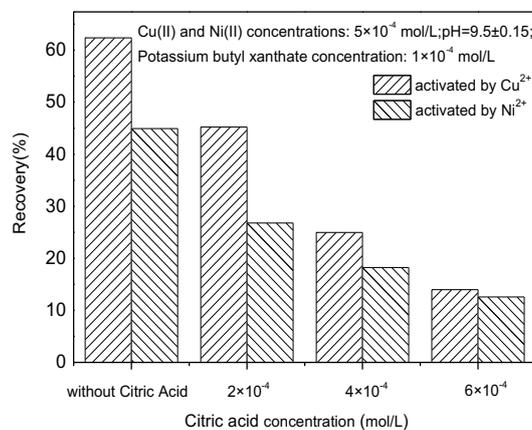
Fig. 4. Effect of adding Citric Acid on the flotation of serpentine activated by Cu^{2+}, Ni^{2+}

It could be seen from Figure. 4 that after adding citric acid, the flotation recovery of serpentine decreased rapidly, though it was activated by Cu^{2+}or Ni^{2+}. The flotation recovery almost declined to the non-activated level when citric acid concentration was 6×10^{-4} mol/L, it showed that the citric acid could effectively inhibit the serpentine which activated by copper ions and nickel ions. The mechanism may be that citric acid could effectively stabilize the Cu^{2+}or Ni^{2+} in the solution to avoid the generation of $Cu(OH)_{2(s)}$ or $Ni(OH)_{2(s)}$, therefore, to prevent the activation of Cu^{2+} or Ni^{2+} on serpentine.

3.2. Zeta potential measurements

In the absence and presence of Cu^{2+}/Ni^{2+} or citric acid, the zeta potentials of serpentine as a function of pH were measured, and the results were shown in Figure.5 and 6. Figure.5 and 6 described the changes of the zeta potential as the result of the activation of the mineral surface. When there were no copper or nickel ions added in the solution, the zeta potential of serpentine decreased with the increase of pH value in distilled water. The point of zero charge (PZC) of serpentine was about 9.5, which was consistent with the result of other researchers (Yoon et al., 1979; Cao et al., 2014). The surface charge of serpentine was positive at pH range of 3 to 9.5. Meanwhile, significant changes of zeta potential were observed in the presence of activator ions (Cu^{2+}or Ni^{2+}) and complexant (citric acid).

Zeta potentials of serpentine shifted towards positive values in the presence of Cu^{2+} or Ni^{2+}. When pH < 6, the zeta potential of serpentine increased slightly, combined with the results of micro-flotation in Figure 3, it indicated that the adsorption of copper or nickel ions on the serpentine surface was low. When the pH > 6, zeta potential of serpentine made a positive shift, which suggested that copper ions, nickel ions and/or their hydrolysate adsorbed on the mineral surface. Furthermore, and the zeta potential of the serpentine surface increased, it indicated that the adsorbed Cu^{2+}or Ni^{2+}may lie closer to the outer stern planes of the electrical double layer of the serpentine. With the addition of citric acid, zeta potential of serpentine shifted back to negative values, but which still remained between the zeta potential of pure serpentine and that of serpentine activated by metal ions. This phenomenon implied that the complexation reaction between citric acid and Cu^{2+} or Ni^{2+} could effectively eliminate the influence of serpentine zeta potential caused by Cu^{2+} and Ni^{2+}, then thus serpentine was suppressed.

Meanwhile, the Figure. 3 and results of zeta potential measurements showed that Cu^{2+} had a better activation effect on the xanthate flotation of serpentine than Ni^{2+}, it may be related to the higher affinity of xanthate for copper than for nickel, and nickel sulphide was more soluble than copper sulphide (Fornasiero and Ralston,2005). As shown in Figure. 5 and 6, the interaction of critic acid with Ni^{2+} was stronger than with Cu^{2+} , confirmed by the zeta potential changes before and after the interaction of critic acid and cationic ions. It was consistent with that the complexing ability of citric acid to nickel was stronger than to copper.

3.3. Adsorption capacity measurement

In order to study the influence of Cu^{2+}, Ni^{2+} and citric acid on the adsorption capacity of potassium butyl xanthate on serpentine surface, the adsorption capacity of potassium butyl xanthate on serpentine surface were measured under three conditions （the pH value was 9.5±0.15）: (1) serpentine + potassium butyl xanthate; (2) serpentine + Cu^{2+} (or Ni^{2+}) + potassium butyl xanthate; (3) serpentine + Cu^{2+} (or Ni^{2+}) + citric acid + potassium butyl xanthate. Each agent was added in sequence and stirred for 180 s separately. The results were depicted in Figure 7 and Figure 8.

As seen from Figure 7 and Figure 8, the potassium butyl xanthate adsorption on the surface of pure serpentine was very low in distilled water. When Cu^{2+} and Ni^{2+} existed in solution, the adsorption capacity of potassium butyl xanthate on serpentine surface increased greatly, this indicated that collector absorbed on the surface of serpentine minerals was based on the adsorption of copper and nickel ions (or their hydrolysates). However, citric acid could effectively reduce the adsorption capacity of potassium butyl xanthate on serpentine surface that had been activated by metal ions. The adsorption capacity was still higher than pure serpentine surface, suggesting that citric acid could not completely eliminate the existences of copper and nickel ions on serpentine.
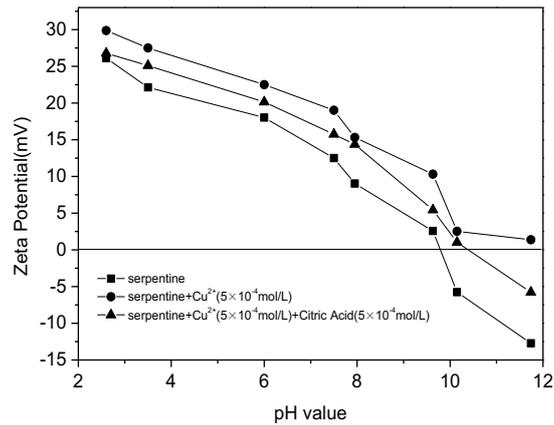
Fig. 5. Effect of citric acid on the zeta potential of serpentine activated by Cu^{2+} as a function of pH
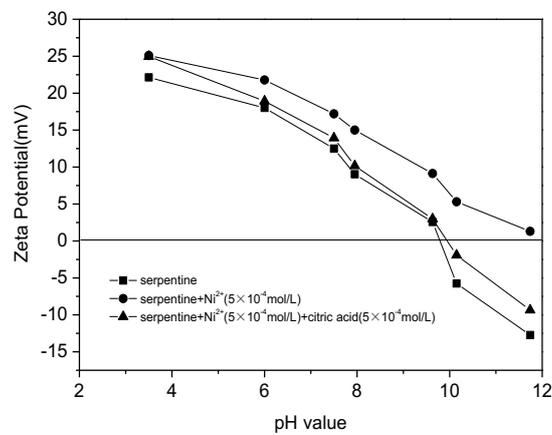
Fig. 6. Effect of citric acid on the zeta potential of serpentine activated by Ni^{2+} as a function of pH
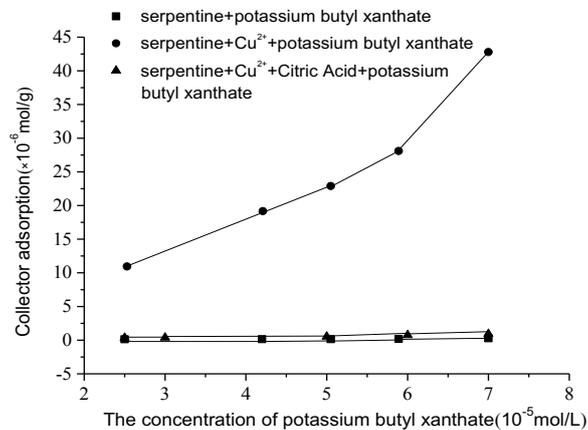
Fig. 7. The influence of Cu^{2+} and citric acid on collector adsorption capacity on the serpentine surface

3.4. Solution chemistry analysis

According to the hydrolysis reactions of copper and nickel ions and their equilibrium constants, the main hydrolysis species in solution were determined.

With the concentration of Cu^{2+} in solution of $1×10^{-4}$ mol/L, the distribution of the hydrolysis components of Cu^{2+} was drawn and the results were shown in Figure 9. When the concentrations of citric acid ion (Cit^{2-}) and Cu^{2+} were $1×10^{-2}$ mol/L and $1×10^{-4}$ mol/L respectively, the LgC-pH graph of Cu^{2+}-citric acid system was drawn and the results were shown in Figure 10.

As seen from Figure 9, in acidic pH range, copper ions were the main species in solution, which couldn't activate the flotation of serpentine. Copper hydroxide $Cu(OH)_{2(s)}$ was the primary component in cupric solution at pH＞6.34, which could cover up serpentine surface, react with xanthate, and thus activating the flotation of serpentine. This was consistent with the results of serpentine flotation tests, of which the recovery rate of serpentine started to increase greatly when pH>6, and the zeta potential on serpentine surface moved to positive direction when pH>6. Therefore, it could be speculated that the activation of Cu^{2+} on serpentine mainly depended on the amount of copper hydroxide $Cu(OH)_{2(s)}$.

Figure 10 showed that citric acid could effectively stabilize the Cu^{2+} in solution and make the critical pH value of $Cu(OH)_{2(s)}$ increase from 6.34 to 9.03. The addition of citric acid expanded the stable regions of Cu^{2+} and then inhibited the activation of Cu^{2+} on serpentine, and that was consistent with the results of pure minerals flotation test, Zeta potential measurement and adsorption capacity measurement of collector.

In case of nickel ions, the analysis results were similar to those of copper ions.

The LgC-pH graphs of Ni^{2+}-H_2O system and Ni^{2+}-Citric Acid system were drawn and depicted in Figure 11 and Figure 12, respectively. As shown in Figure 11 the critical pH in this system was 8.67, which indicated that $Ni(OH)_{2(s)}$ was the dominant component in flotation (optimal pH=9). While in the presence of citric acid, the critical pH increased to 10.91, which was more than normal flotation pH, so that the activation of nickel ions was also weakened.

However, impeccable explanation of metal ions activation and Citric Acid inhibition mechanism on the serpentine required further detailed studies.
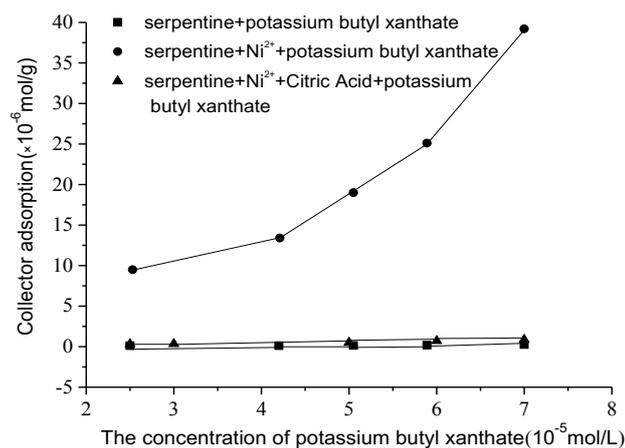
Fig. 8. The influence of Ni^{2+} and citric acid on collector adsorption capacity on the serpentine surface
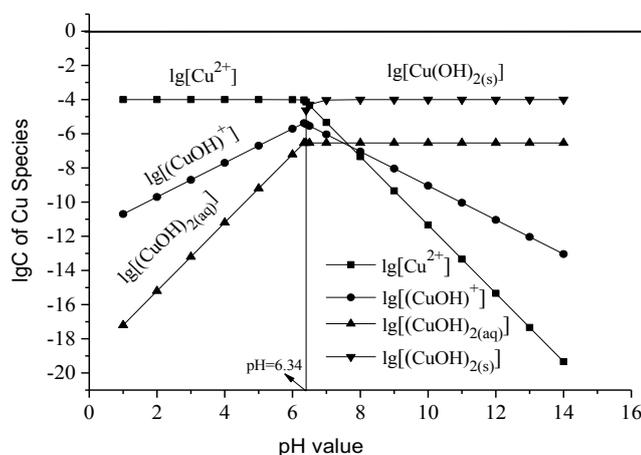
Fig. 9. The LgC-pH graph of the Cu^{2+}-H_2O system
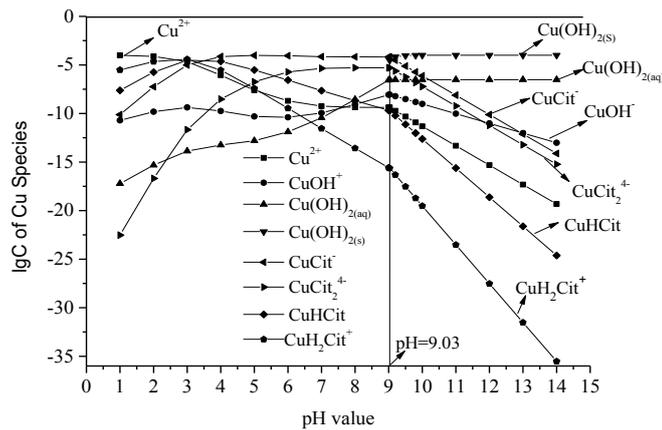
Fig. 10. The LgC-pH graph of the Cu^{2+}-citric acid system
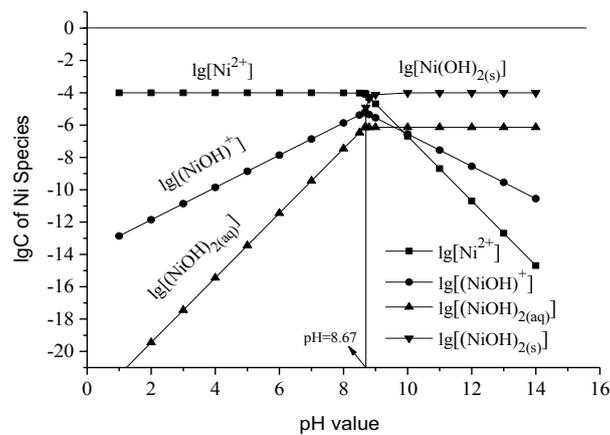
Fig. 11. The LgC-pH graph of the Ni^{2+}-H_2O system
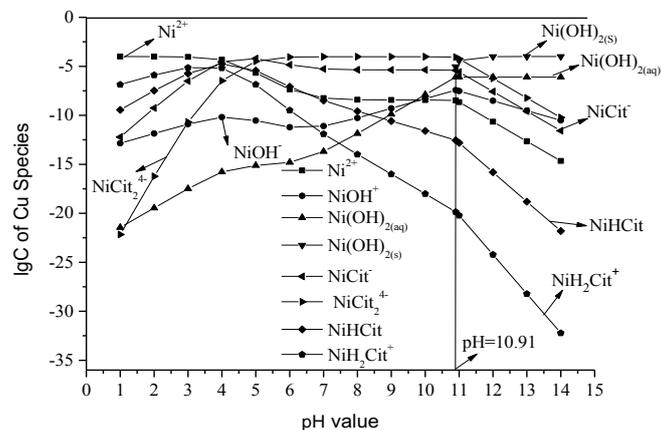
Fig. 12. The LgC-pH graph of the Ni^{2+}-citric acid system

4.   Conclusions

The micro flotation tests showed that the natural flotation of serpentine was poor using potassium butyl xanthate as collector. While Cu^{2+} and Ni^{2+} could remarkably activate the flotation when pH>6, and Cu^{2+} displayed a better performance than Ni^{2+}. Citric acid could effectively inhibit the activation of Cu^{2+} and Ni^{2+} on serpentine.

Adsorption of nickel or copper ions on the serpentine surfaces changed the values of zeta potential and isoelectric point. However, citric acid could reduce the variation, and maintain zeta potentials between those of the pure and the activated.

The results of collector adsorption capacity measurements showed that potassium butyl xanthate could hardly adsorb on pure serpentine surface. While in the existence of Cu^{2+} and Ni^{2+}, adsorption capacity was increased by more than a hundred times. Citric acid could depress the adsorption capacity back to the previous level, but couldn't eliminate the effect of metal ions completely.

The solution chemical calculation analysis showed that: in pH range of 8.5-9.5 (flotation pH value of copper-nickel sulfide ores), Cu^{2+} and Ni^{2+} mainly existed in the form of $Cu(OH)_{2(s)}$ and $Ni(OH)_{2(s)}$. Based on the results of flotation test and several analyses, activation mechanism was attributed to precipitation and coverage of $Cu(OH)_{2(s)}$ and $Ni(OH)_{2(s)}$. Citric acid could effectively complex the Cu^{2+} and Ni^{2+} in solution, and make the pH value of sediment (critical pH) increase from 6.34 and 8.67 to 9.03 and 10.81, respectively. These variations resulted in much less $Cu(OH)_{2(s)}$ and $Ni(OH)_{2(s)}$ forming on serpentine surface, and the flotation was depressed. The calculation results of solution chemistry were consistent with the results of pure minerals flotation test and adsorption capacity measurement of collector.

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