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# Investigation on the promoted flotation behavior of pentlandite by ammoniacal copper(II) solution

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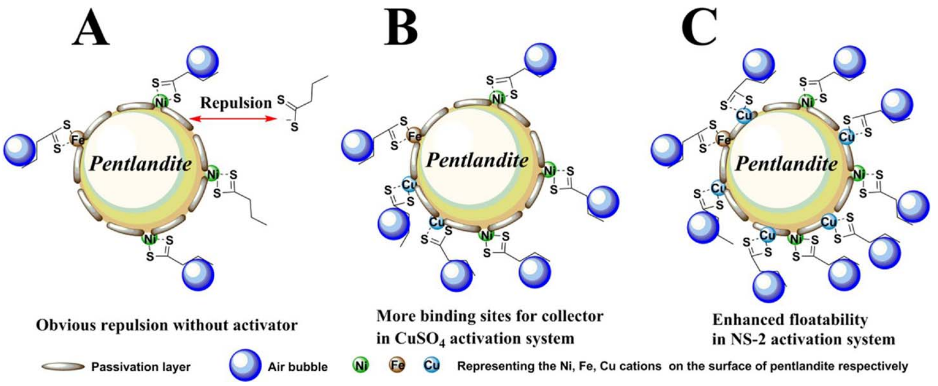
## GRAPHICAL ABSTRACT

Model for the physicochemical processes occurred on the pentlandite surfaces without an activator (A), in $CuSO_4$ activation system (B) and in NS–2 activation system (C).



## ARTICLE INFO

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## ABSTRACT

In this paper, we studied the improved flotation behavior of pentlandite by ammoniacal copper(II) solution. The microflotation tests showed that ammoniacal copper(II) solution exhibited better activation effect for the flotation of pentlandite in alkaline pulping (pH 8–11) than $CuSO_4$. Ultraviolet–visible spectroscopy analysis further comfirmed that ammoniacal copper(II) complexes were the dominant species in ammoniacal copper(II) solution, which was responsible for the superior activation effect. Systematic electrochemical studies including cyclic voltammetry (CV) measurements, polarization curves (Tafel plots) and electrochemical impedance spectroscopy (EIS) demonstrated that the electrochemical processes were improved and the hydrophilic hydroxide layers were converted to hydrophobic species on the surfaces of pentlandite in ammoniacal copper(II) solution.

## 1. Introduction

In mineral froth flotation processes, flotation reagents are crucial for increasing the hydrophobicity of the valuable minerals and therefore achieving an efficient flotation separation [1]. Among various types of flotation reagents, copper sulphate is a versatile activator as it promotes the interaction of collector molecules with mineral surfaces [2]. Addition of copper sulphate has been used as a universal, effective and inexpensive method for the activation of common sulfide minerals such as sphalerite (ZnS) [3], marmatite ($Zn_xFe_{1-x}S$) [4], pyrite ($FeS_2$) [5],

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pyroxene ((Mg, Fe, Ca) $Si_2O_6$) [6] and pentlandite ($(Fe, Ni)_9S_8$) [7]. The activation effect of Cu(II) comes mainly from the stoichiometric replacement, the noticeable monolayer coverage and the immunization of $O_2$ [8].

In most cases, the flotation of the sulfide minerals occurs in alkaline pulping. In such condition, however, the predominant species of copper is insoluble $Cu(OH)_2$ [9], which leads to the deactivation of Cu(II) and the undesired negative impact on the flotation of valuable minerals. To solve this issue, the synergism of $Cu^{2+}$ with additional amine compounds was proved to be effective. For instance, Tong and co–workers reported that ammoniacal copper(II) solution effectively activated the flotation of high–iron marmatite particles in alkaline flotation system, performing much better than copper sulfate [10]. As another example, an operating plant used ammonia as a pH regulator in the treatment of a copper/zinc ore, which demonstrated the utilization value of ammoniacal Cu(II) species in processing sulfide ores [11]. Similarly, some concentrators in China employed ammonium sulfate, ammonium hydrocarbonate and ammonium chloride instead of lime to process iron sulfides. These ammonium salts could improve the floatability of pyrite in the absence of copper sulfate [12].

In our previous work on the processing of copper–nickel sulfide ore, we found that NS–2 solution (a mixed solution of copper sulphate and ammonium sulfate) could also replace copper sulphate and exhibit a superior activation effect for the flotation of pentlandite. To the best of our knowledge, there is little report on the application of such an activator in the flotation of pentlandite in alkaline condition, and there is no reported research work on the systematic electrochemical investigation of the interaction of mineral surfaces with ammoniacal copper(II) complexes. Herein, we compare the activation effects of copper sulphate and the NS–2 solution in the flotation of pentlandite in alkaline condition, and studies the electrochemical processes of corresponding activation modes to obtain a better understanding of the improved flotation behavior of pentlandite by ammoniacal copper(II) solution in alkaline pulping.

## 2. Materials and methods

### 2.1. Materials

Pure pentlandite samples used for microflotation tests and as the electrode materials were obtained from Jinchuan, Gansu Province, China. The mineral purity was confirmed by chemical analysis and X–ray powder diffraction (XRD) as described in our previous work [13,14]. The pentlandite samples used as the electrode materials were ground in an agate ball mill and the pentlandite samples for microflotation tests were crushed to the average particle size of below 75 μm. Copper sulfate hydrate ($CuSO_4 \cdot 5H_2O$), ammonium sulfate ($(NH_4)_2SO_4$) were used to prepare the activator solution, and hydrochloric acid (HCl), sulfuric acid ($H_2SO_4$), sodium hydroxide (NaOH) and ammonium hydroxide ($NH_3 \cdot H_2O$) were used to adjust the pH of solutions. All reagents described above were of analytic grade (obtained from Tianjin Guangfu Technoligy Development Co., Ltd., China). For other flotation reagents, Sodium Butyl Xanthate (NaBX) was used as the collector and Methyl Isobutyl Carbinol (MIBC) acted as the frother. $KNO_3$ solution ($10^{-3}$ M) used in the experiments was prepared using deionized water.

### 2.2. Preparation of NS–2 solution and pure $Cu(NH_3)_4SO_4$ solid

The NS–2 solution was prepared by dissolving $CuSO_4 \cdot 5H_2O$ and $(NH_4)_2SO_4$ successively in water with a molar ratio of 1:2, the required pH was achieved by the addition of $NH_3 \cdot H_2O$ (4 mol/L). The pure $Cu(NH_3)_4SO_4$ solid was prepared according to the method described [15]. The $CuSO_4$ solutions of different pH values were prepared by using $CuSO_4 \cdot 5H_2O$, NaOH solution (4 mol/L) and $H_2SO_4$ solution (4 mol/L).

### 2.3. Methods

#### 2.3.1. Ultraviolet–visible spectroscopy analysis

Ultraviolet–visible spectroscopies of the samples were recorded on a UV2800 spectrometer (China) according to the test method described [16].

#### 2.3.2. Microflotation tests

Mineral flotation tests were carried out in an inflatable hanging slot flotation machine ($XFGC_{II}$), and the impeller rotation speed was set at 2000 r/min. The pentlandite suspension was prepared by adding 2.0 g of pentlandite to 50 mL of $KNO_3$ solutions ($10^{-3}$ M) of different pH values. The conditioning time was allotted as follows: 2 min for the activators (NS–2 or $CuSO_4$), 2 min for the collector (NaBX) and 2 min for the frother (MIBC). Then flotation was performed for a total of 4 min. After flotation, the floated and unfloated particles were filtered and dried for calculating the flotation recovery by weight.

#### 2.3.3. Electrochemical measurements

All of the electrochemical experiments in this study were performed on a CHI660E electrochemical workstation (CH Instruments Ins). A typical three–electrode system (a saturated Ag/AgCl electrode as the reference electrode, a platinum wire as the auxiliary electrode, and a pentlandite–graphite paste electrode as the working electrode) was used for the measurments. High purity nitrogen gas was bubbled into the solution prior to each measurement. Unless otherwise stated, all potentials reported here were referred to the saturated Ag/AgCl which could be corrected for the standard hydrogen electrode (SHE) according to the equation: E (SHE) = E (Ag/AgCl) + 0.197 V (in KCl saturated solution).

To prepare the working electrodes, pentlandite samples were fully ground (with particle diameter less than 10 μm), and then washed with anhydrous ethanol in an ultrasonic oscillator and dried at 45 °C in a vacuum oven. The pentlandite–graphite paste electrode was constructed by the method described [17]: (1) 400 mg of a fresh pentlandite sample was mixed with 100 mg of graphite; (2) 50 mg of a copolymer binder (nafion, w/w 0.5% in anhydrous ethanol) was added dropwise into the mixture, and then the resulting paste was thoroughly mixed; (3) The resulting product was transferred into a cylinder, after a piece of copper wire (with a diameter of 0.5 mm) was plugged into the bottom of the cylinder, the electrode surface was pressed tightly. The area of this prepared pentlandite–graphite paste electrode was 0.67 $cm^2$.

## 3. Results and discussion

### 3.1. Ultraviolet–visible spectroscopy analysis of the species distribution of NS–2 solution

Fig. 1 indicated the species distribution of NS–2 in an alkaline environment. As showed in Fig. 1(a), for NS–2 solutions at pH 8, 9 and 10, there were two sharp peaks emerging at approximately 290 nm and 600 nm, respectively, which were the distinguishing characteristics of $Cu(NH_3)_4{}^{2+}$ complexes (comparing with the green line of the pure $Cu(NH_3)_4SO_4$ solution at pH 8). However, for NS–2 solution at pH 11, the absorption peaks shifted to 310 nm and 636 nm, respectively, which indicated the formation of $Cu(NH_3)_5{}^{2+}$ (due to the coordination of $Cu(NH_3)_4{}^{2+}$ with $NH_3$) [18]. On the other hand, no characteristic peaks could be observed for $CuSO_4$ and $(NH_4)_2SO_4$ solution at 290 nm and 600 nm at pH 8 (Fig. 1(b)), which further verified the formation of ammoniacal copper(II) complexes in the NS–2 solution in an alkaline environment. The results of ultraviolet–visible spectroscopy provided the evidence that the activation ability of NS–2 for pentlandite was probably attributed to ammoniacal copper(II) complexes rather than $CuSO_4$.