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Effect of solution potential on selective separation of metals from acid wastewater by controlling potential

ABSTRACT

In view of the difficulties in separating similar metals from acidic wastewater, a new process is proposed to selectively separate metals by controlling potential. In this study, the effects of solution potential on precipitation ratio and separation efficiency were investigated. The potential was controlled by adding sodium sulfide or xanthate and was monitored by an MT320-SpH instrument with a Pt electrode and a calomel electrode. E-pH diagrams of Me-S-H$_2$O system were plotted through thermodynamic calculations. The results revealed that with the drop of solution potential, the metal precipitation ratios increased. Cu^{2+}, Co^{2+}, and Zn^{2+} can be selectively separated and completely precipitated under controlling potential at 330 mV, 125 mV and 30 mV, respectively. Mn^{2+} could be recovered by carbonate precipitation from the residual solution after Zn removal. The precipitation ratios of Cu^{2+}, Co^{2+}, Zn^{2+}, and Mn^{2+} were as high as 99%.

1. Introduction

Co is widely used in hard alloys, heat-resistant alloys and pigments due to its excellent physical and chemical properties. In recent years, the unprecedented boom in the Li-ion battery industry has increased the demand for Co dramatically [1,2], owing to its application as cathode material. A by-product in Co extraction processes is a solution containing Cu^{2+}, Co^{2+}, Zn^{2+}, and Mn^{2+}, obtained by stripping the loaded organic P204(di-2-ethylhexylphosphinate) with HCl—named P204 stripping solution. Typically, P204 stripping solution is categorized as a kind of acidic wastewater because of its low pH. In addition, it also is a polymetallic solution. Many methods have been developed to treat P204 stripping solution; however, currently, none of them are ideally suited for the effective disposal of this solution.

In the most common process, P204 stripping solution is neutralized before storage [3]. However, the stockpiling of this precipitates not only occupies land but also leads to potential environment threat and the major loss of valuable metals. Consequently, neutralization should be replaced by an appropriate treatment approach that is more environmentally friendly and allows recycling. Common treatments such as displacement [4], solvent extraction [5,6], ion exchange [7], and adsorption [8–10] can be used to remove heavy metals from P204 stripping solution [11]. Nonetheless, most of these treatment methods have some disadvantages, for example, separating metals with low-efficiency results in an inferior beneficiation of valuable precipitates.

With the advantages of fast reaction rates, a high precipitation ratio, and excellent thickening and dewatering characteristics, sulfide precipitation has been widely used in treating wastewater [12,13]. However, the dosage of sulfide is difficult to control and the obtained precipitates are mixtures of multiple metal sulfides [13]. Moreover, excess metal ions and excess sulfides in solution have side-effects to treatment process [14]. All these disadvantages make it difficult to recover valuable metals in subsequent steps. Veeken et al. [15] selectively separated Zn^{2+} from solution by utilizing a combination of a sulfide ion-

selective electrode and a pH electrode meter as the monitors to control the molar ratio of Zn^{2+} and S^{2-}. They reported that when Zn^{2+}/S^{2-} molar ratio reached a certain value, Zn could be selectively removed to less then 0.03 mg/L.

Each metal ions has its own electrode potential in aqueous solution. Therefore, it is possible to selectively separate different metals in the leaching and precipitating process by taking advantages of this character. Liu et al. [16] proposed a technology to selectively separate valuable metals from cobalt white alloy under controlling potential. Cobalt white alloy was leached by sulfate solution with catalytic HF and, subsequently, H$_2$O$_2$ was added as an oxidant to control solution potential, resulting in Co and Fe being selectively leached while Cu remained in residue. Yang et al. [17] selectively leached Cu smelting dust in sulfate solution under controlling potential by adding H$_2$O$_2$. After leaching, Cu^{2+} was selectively precipitated under controlling potential by adding Na$_2$S.

Above all these discussion, a new method is proposed to selectively separate and recover Cu, Co, and Zn from acid wastewater by controlling solution potential in this paper. The effect of potential on both precipitation ratio and separation efficiency were investigated and the optimal precipitation potentials were obtained finally. Thus, this study provides a reference for selective separation of valuable metals from acidic wastewater.

2. Experimental

2.1. Materials

The raw material used is P204 stripping solution supplied by a cobalt extraction company of China. The main chemical composition of P204 stripping solution is listed in Table 1.

Sodium sulfide nonahydrate (Na$_2$S·9H$_2$O, ≥98 wt%), sodium hydroxide (NaOH, ≥96 wt%), sodium carbonate (Na$_2$CO$_3$, ≥99.8 wt%), and hydrochloride acid (HCl, ≥36.5 wt%) were of analytical grade. Sodium ethyl xanthate (C$_3$H$_5$OS$_2$Na, ≥90.0 wt%) was of industrial grade.

Table 1
Main composition of P204 stripping solution.

Components	Cu	Co	Zn	Mn	Cl
Concentration/(g/L)	32.50	2.50	10.20	110.10	181.30

2.2. Experimental setup and procedure

Selective separation experiments were performed in a 250-mL flask. A known volume of the solution (150 mL) was added into the flask and was heated to 50 °C in a constant-temperature water bath equipped with a magnetic agitator. Stirring speed was kept constant during experiments. NaOH or HCl and precipitant were added into solution to adjust pH value and potential, respectively. In order to control pH value and potential accurately, NaOH, HCl and precipitant were added gradually in several times. Potential and pH value were monitored by MT320-SpH instrument and pH meter, respectively. After the reaction, the slurry was vacuum filtered, and the filtrate was collected after measuring the volume. The precipitates were washed with water at 90 °C , dried at 110 °C, and weighted.

The precipitation ratio, representing the proportion of the precipitated quantity to the total quantity in solution, was calculated as shown in Eq. (1):

$$P_{Me} = \left[1 - \frac{V_{removal} \times C_{removal}}{V_{material} \times C_{material}} \right] \times 100\% \tag{1}$$

where P_{Me} is the precipitation ratio (%); $V_{material}$ and $V_{removal}$ are the volumes of the original solution (L) and the Me-removed solution (L), respectively; and $C_{material}$ and $C_{removal}$ represent the metal concentrations of the original solution (g/L) and the Me-removed solution (g/L), respectively.

2.3. Analysis and characterization

The metals contents of precipitates and solutions were determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES, IRIS Intrepid III XRS, USA). Precipitates were dissolved in a combination of nitric acid and sulfuric acid and diluted to 100 mL with 2.0 mol/L nitric acid. Solutions were diluted to 100 mL with 2.0 mol/L nitric acid before analyzing. The phases of precipitates were determined by a Jeol TTRAX-3 X-ray diffractometer, operating at 40 kV, 250 mA, and with a scan rate of 10°/min. The surface morphologies of precipitates were imaged by scanning electron microscopy (Jeol JSM-6360LV instrument), operating at 20 kV.

Solution potentials were monitored by an MT320-SpH analyzer (Mettle Toledo Inc.). Pt and calomel electrodes were used as the working and reference electrodes, respectively. The solution potential was determined using Eq. (2).
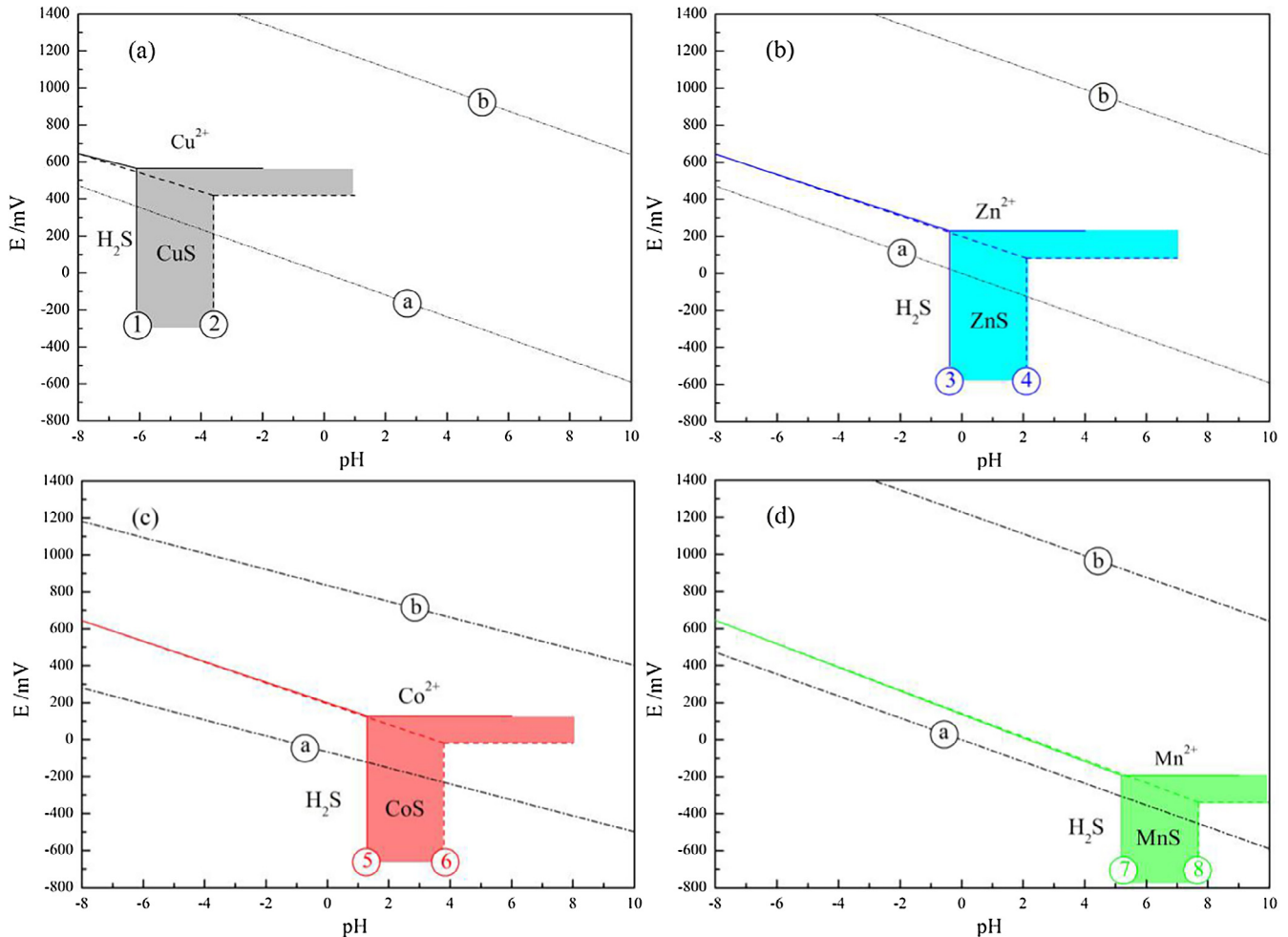
$$E_T = E_A + E_R \tag{2}$$

Fig. 1. E-pH diagrams of Me-S-H$_2$O system. (a) Cu-S-H$_2$O; (b) Zn-S-H$_2$O; (c) Co-S-H$_2$O; (d) Mn-S-H$_2$O. (Line a $-O_2$ Line; Line b $-H_2$ Line. ① [Cu^{2+}] = 1.0 mol/L, ② [Cu^{2+}] = 10^{-5} mol/L, ③ [Zn^{2+}] = 1.0 mol/L, ④ [Zn^{2+}] = 10^{-5} mol/L, ⑤ [Co^{2+}] = 1.0 mol/L, ⑥ [Co^{2+}] = 10^{-5}mol/L, ⑦ [Mn^{2+}] = 1.0 mol/L, ⑧ [Mn^{2+}] = 10^{-5}mol/L).