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Removal of Cu from the nickel electrolysis anolyte using amorphous MnS

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ABSTRACT

In this research, amorphous MnS was used to remove Cu from the nickel electrolysis anolyte. Through condition experiments, the effects of amorphous MnS dosage, reaction temperature, pH value and reaction time on copper removal were investigated. The experimental results showed that amorphous MnS had high reaction activity, and 99.2% of Cu in the nickel electrolyte was removed in 30 min. Under the optimal operating conditions, 1.6–1.8 times the theoretical amount of amorphous MnS, mean particle size 1.6 μm, reaction temperatures 60–80 °C, pH values 3.5–4.5 and retention time of more than 45 min, the concentration of Cu was reduced to less than 3 mg/L in the nickel electrolysis anolyte and Cu/Ni mass ratio in the Cu removal precipitates exceeded 15. The nickel electrolyte after Cu removal directly met the production requirement of qualified electrodeposited nickel and the precipitate was eligible for Cu matte smelting. The enlarged scale experiment confirmed that amorphous MnS can be used as a high-efficiency reagent to remove copper from the nickel electrolysis anolyte in large-scale industrial production.

1. Introduction

At present, during electrolytic nickel refining process, the purification of impurities, such as iron and cobalt, has been well controlled at home and abroad, but the removal of Cu is still a challenging and intriguing task. As Cu and Ni have similar chemical properties, the effective separation of Cu and Ni has been a long-term problem, which plagued the domestic and international metallurgical industry (Chen et al., 2013). According to the national standard of China (GB/T 6516-1997 Ni9996), the Cu content should be less than 0.01% (Huang et al., 1990). Many methods have been put forward to remove Cu from the Ni electrolysis anolyte (Zhao et al., 2009). Such as Ni powder or Ni powder plus sulfur powder (Li and Thomas, 2004), electro-deposition method (Kudelski et al., 1999; Read et al., 2004), and ion exchange processes (Ting-Chia et al., 1988). However, these treatments cannot satisfy the requirement in industry due to their low efficiency and high cost.

Sulfide precipitation has some obvious advantages for metal removal, including the lower solubility of metal sulfide precipitates, potential for selective metal removal, fast reaction rates, better settling properties and potential for re-use of sulfide precipitates by smelting (Yeligar et al., 1981). Sulfide precipitation can be effected using either solid (FeS, CaS), aqueous (Na_2S, NaHS, NH_4S) or gaseous sulfide sources (H_2S). One process that has been discovered to be effective in the removal of Cu is insoluble sulfide treatment (Allen et al., 1994; Bazza et al., 1987). The attractiveness of Cu removal using metal sulfide results from the extremely low solubility of CuS, which leads to a desired ion exchange reaction motive power. Also the use of insoluble metal sulfide overcomes some of the obstacles associated with using Na_2S (D. Bhattacharyya et al., 1979), since it can be overfed without major odor problems, due to the slight solubility of metal sulfide and minimal formation of H_2S (Lazaridis et al., 2004). Based on this, Cu removal reagents containing insoluble S, such as active Ni sulfide, active sulfur powder and Ni thiosulfate (Lewis and Van-Hille, 2006) were investigated by many researchers. These reagents indeed can efficiently remove Cu from Ni electrolysis anolyte. But the preparation process for these Cu removal reagents is very complex. In addition, their active ingredients easily lose its reaction activity over time, which would reduce greatly the effectiveness of Cu removal. For example, when the active Ni sulfide was exposed to the air, it would be ultimately oxidized to Ni(OH)S and lost its activity easily in 6 h (Wang et al., 1993), which would reduce the Cu removal effectiveness dramatically. In the case of nickel sulfide concentrate which had been used as the Cu removal reagent in Jinchuan Group Ltd. of China for a long time, because the reaction activity of these Cu removal reagents was low, substantial excess of Ni sulfide concentrate must be added. As a result, a great amount of Cu removal precipitates is produced. Therefore, the Ni content of precipitates can be very high, as a fact the mass ratio of Ni/Cu is only 2.

Therefore, to find an efficient and chemically stable Cu removal reagent, simple preparation of which is necessary. Meanwhile, to aim

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for higher mass ratio of Cu/Ni, the new Cu removal reagent should have better selectivity for Cu^{2+} and Ni^{2+}. Furthermore, if the new reagent introduces new impurity, the element needs to be easily removed before electrolytic refining process.

Compared to the above Cu removal reagent, amorphous MnS may be an ideal option. The precipitation and separation of metal sulfides are based on different sulfide solubilities of metals at a certain pH and temperature. The thermodynamic equilibria involved in the sulfide precipitation can be expressed as:

$$H_2S(g) = 2H^+ + S^{2-}, \qquad Kp = \frac{[H^+]^2[S^{2-}]}{P_{H_2S}} \tag{1}$$

$$Me^{n+} + S^{2-} = MeSn/2, \qquad K = \frac{1}{[Me^{n+}][S^{2-}]^{\frac{n}{2}}} = \frac{1}{Ks} \tag{2}$$

where Ks is the solubility product of the metal sulfide. These relationships can be written in the form:

$$pH = -\frac{n}{2}(\log Kp - \log P_{H_2S} + \log[S^{2-}] \tag{3}$$

$$\log[Me^{n+}] = \log Ks - \frac{n}{2}\log[S^{2-}]. \tag{4}$$

For a given P_{H_2S}, each can be plotted on a sulfide solubility diagram as shown in Fig. 1. It can been seen that the line of Mn^{2+} is far to the right side of the diagram, indicating that manganese sulfide is more soluble than Cu and Ni sulfides. This offers a theoretical basis for the separation of Cu^{2+} and Ni^{2+}.

Furthermore, Wu and Yang (1976) noted that exchange reaction rates of metal sulfide correspond to the value of solubility products only for fresh, amorphous metal sulfides. Therefore, a newly synthesized metal sulfide having a higher solubility than the sulfide of copper may be an ideal Cu removal reagent. Considering the relatively high solubility product of MnS $10^{-10.5}$, (the solubility product of common insoluble metal sulfide is presented in Table 1) which is greater than that of NiS by eight orders of magnitude and that of CuS by 25.6 orders of magnitude. The reaction rate of Cu removal would be much higher than active NiS.

Another advantage of using MnS in Cu removal is the easy disposal of Mn^{2+} after the ion exchange reaction of MnS and Cu^{2+}. In the subsequent process of nickel electrolysis anolyte purification, removal of Co with Cl_2 is the last process. Since the oxidation reduction potential of Mn^{2+} is 600 mV vs. SCE, which is much less than that of Co^{2+} with 1000–1200 mV vs. SCE, the Mn^{2+} would precipitate as MnO_2 before Co^{2+}. We have carried out experiments based on the analysis and confirmed the feasibility of this method.

Table 1
Metal sulfide and its solubility product constants.

Metal sulfide	pKsp	Metal sulfide	pKsp
MnS	10.5	NiS(β)	24.9
FeS	18.1	CoS(β)	25.6
NiS(α)	18.5	NiS(γ)	26.6
CoS(α)	21.3	PbS	27.5
ZnS(α)	24.7	CuS	35.2

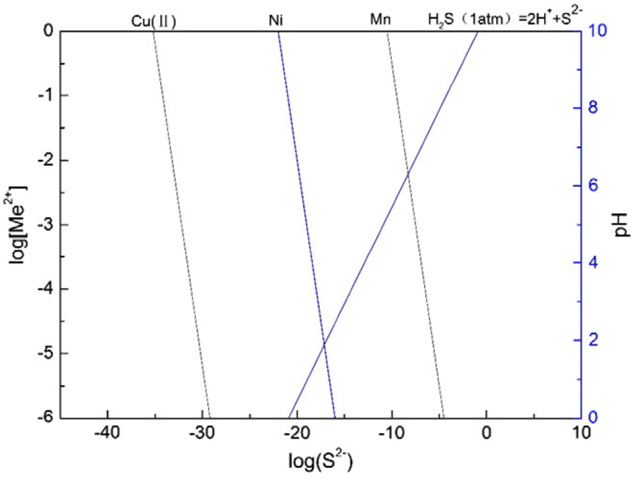

Fig. 1. Sulfide solubility diagram at 25 °C.

Based on the above analysis, amorphous MnS was prepared to remove Cu from the nickel electrolysis anolyte in this paper. Several operating parameters like MnS dosage, reaction temperature, retention time and pH value were examined.

2. Experimental method

2.1. Preparation of amorphous MnS

In each experiment, amorphous MnS was synthesized by adding quantitative 0.1 mol/L Na_2S to 0.1 mol/L $MnSO_4$ solution in a conical flask. The solution was agitated vigorously with a magnetic stirrer for 15 min at room temperature. The reaction of Na_2S with $MnSO_4$ was as follows:

$$Na_2S + MnSO_4 \rightarrow MnS\downarrow + Na_2SO_4. \tag{5}$$

During the reaction, the solution turned pink immediately and became brown with vigorous stirring after a few minutes. Then the brown amorphous MnS can be obtained by using vacuum filter. However the nascent amorphous MnS contained a great amount of water, which couldn't be easily measured in small scale, the slurry was used together without filtration to remove Cu in the experiments. As a consequence, Cu concentration of the nickel anolyte after Cu removal was calculated from the results of diluted solution.

2.2. Removing Cu with amorphous MnS

Cu removal experiments were conducted in a 250 mL pyrex reaction flask. The flask, equipped with an agitator, was heated using a thermostatically controlled water bath. In each experiment, 100 mL nickel electrolysis anolyte (from the Jinchuan Group Ltd. of China, the composition was listed in Table 2) was first added into the flask and was heated to the required temperature (±0.5 °C). Then the nickel electrolysis anolyte was poured into the prepared amorphous MnS, accompanied with vigorous stirring. In order to investigate the effects of operation parameters on Cu removal, amorphous MnS addition amount, reaction temperature, reaction time, and pH value of solution would be changed in each experiment. After reaction, the reaction solution was filtered and the precipitate was obtained. The Cu and Mn concentrations in the solution were analyzed by Inductively Coupled Plasma (ICP, Thermo Electron, IRIS Intrepid II XSP). Additionally the Cu removal precipitates were dissolved with 30 wt.% HCl and 20 wt.% H_2O_2 and the Cu/Ni contents were also analyzed by ICP. By calculation, the mass ratio of Cu/Ni in the Cu removal precipitates was obtained.

Table 2
Composition of nickel electrolysis anolyte.

Element	Ni	Pb	Zn	Cu	Cl^-	Na^+	SO_4^{2-}	pH
Concentration/g/l	75.5	0.15	0.008	0.5	74.9	25	99.84	4.5