Technical note

Decoppering capability of nickel thiocarbonate in nickel electrolyte

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ABSTRACT

This technical note reports the decoppering capability of a synthesized nickel thiocarbonate ($NiCS_3$), which is a highly efficient reagent for removing copper from nickel electrolyte. It is observed that the decoppering capability of nickel thiocarbonate decreases with increasing standing time (t_s, the time when nickel thiocarbonate is kept at room temperature) and aging time (t_a, the time when nickel thiocarbonate is kept at 60 °C). Nickel thiocarbonate retains an effective decoppering capability in the standing time of at least 62 days, which completely satisfies the demand of industrial production. It is also found that nickel thiocarbonate keeps a good decoppering capability when $t_a < 34$ min, essentially due to the stable amorphous structure of nickel thiocarbonate within the time period. When the aging time is prolonged to 900 min, nickel thiocarbonate tends to decompose and/or oxidize with the formation of S, Ni_3S_2, NiS_2 and Ni_3S_4, which matches well with the decrease in intensity of C = S bands and C–S bands in the FTIR spectra of nickel thiocarbonate after long aging ($t_a = 4680$ min). These results clearly demonstrate that to maintain high decoppering capability it is necessary to prevent decomposition and oxidization of nickel thiocarbonate.

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1. Introduction

Nickel electrolyte, also called nickel electrolysis anode solution, is produced from nickel sulfide anode plate during the process of electro-winning. Some impurities, such as copper and iron, will concentrate in the nickel electrolyte, which is harmful to the nickel product. Because even a small amount of other heavy metals can significantly affect nickel application, the contents of heavy metals with electric potential lower than nickel (e.g., Cu) in the nickel electrolyte have to be strictly controlled (Pickles, 2004). Generally, the residual copper concentration of nickel electrolyte should not exceed 3 mg/L after copper removal (Chen et al., 2013).

Much work has focused on developing reagents to remove copper from nickel electrolyte. For example, nickel powder is used for copper removal by the displacement reaction. To meet the production require-ment, the particle size of nickel powder should be very fine, leading to a high cost (Chen et al., 2013). Among available reagents for copper removal, sulfur bearing reagents are able to separate copper from nickel solution because of the stronger affinity of sulfur with copper than with nickel (Gu et al., 1996; Lazaridis et al., 2004; Li and Thomas, 2004; Wu et al., 1995). Several decoppering sulfide reagents, such as hydrogen sulfide (H_2S), sodium sulfide (Na_2S), active sulfur powder (S) and active nickel sulfide (NiS), have been used for removing copper. These

reagents are effective for decoppering; however, they have obvious disadvantages. For instance, the additions of H_2S and Na_2S cause air pollution (Al-Tarazi et al., 2004). Active sulfur powder and active nickel sulfide are difficult to prepare and their decoppering capability usually lasts within several hours (Zhang et al., 1998; Zhao et al., 2009, 2010). The application of active nickel sulfide for copper removal in industrial production showed that the sulfide would lose decoppering capability in the standing time (t_s, the time when the decoppering reagent is kept at room temperature) of 6 h, which is too short to meet the demand of industrial production ($t_s \geq 24$ h) (Zhao et al., 2009).

Recently, nickel thiocarbonate ($NiCS_3$) has been proposed as a promising decoppering reagent for nickel electrolyte (Chen et al., 2013; Zhao et al., 2009). It offers many advantages over other reagents, such as low cost and high reactivity. Laboratory-scale experiments dem-onstrated that 98.8% of copper could be removed in 15 min and the removal process was affected by the reagent dosage, pH value, reaction temperature and time (Chen et al., 2013). To make it further satisfy the requirement of industrial applications, a clear understanding of the decoppering capability of nickel thiocarbonate is essential. This can be achieved by studying the effect of the standing time on the decoppering capability of nickel thiocarbonate, which has not yet been reported.

The main aim of this study is to determine the capability of nickel thiocarbonate for decoppering nickel electrolyte at different t_s, indicated by the residual copper concentration of the electrolyte (C_{Cu}) and/or the mass ratio of copper to nickel in the residue ($R_{Cu/Ni}$). It demonstrates that the standing time of nickel thiocarbonate with an effective decoppering capability is at least 62 days, which fully satisfies the technical requirement of nickel production from the electrolyte. To obtain the upper limit of the decoppering capability, nickel

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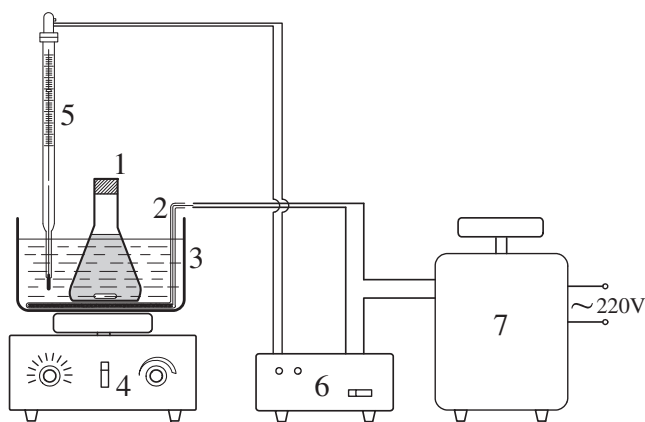*E-mail address:* zhaozw@csu.edu.cn (Z. Zhao).

Fig. 1. Experimental apparatus for copper removal. 1—tapered reactor, 2—glass tube heating device, 3—water bath pot, 4—magnetic blender, 5—temperature controller, 6—power relay, 7—transformer.

thiocarbonate was aged at 60 °C for different time periods (t_a). The variation of the decoppering capability of aged nickel thiocarbonate with t_a up to 4680 min was also investigated.

2. Experimental

2.1. Materials

The materials used in this study include nickel electrolyte and several analytical grade reagents for synthesizing nickel thiocarbonate. Nickel electrolyte was provided by the Jinchuan Group Co. Ltd., China. The electrolyte contains 75 g/L Ni^{2+}, 0.53 g/L Cu^{2+}, 74.0 g/L Cl^-, 100 g/L SO_4^{2-}, and 25.0 g/L Na^+ ions at pH 4.50. To prepare nickel thiocarbonate with high decoppering capability, three analytical grade chemical reagents including nickel sulfate ($NiSO_4$), sodium sulfide (Na_2S), and carbon disulfide (CS_2) were used.

2.2. Experimental procedure and analysis

Aqueous sodium sulfide and carbon disulfide were mixed for 8 h at room temperature using a magnetic stirrer. The mixture obtained was separated into an organic layer and an inorganic layer to which nickel sulfate was added with the formation of a slurry. The slurry was then filtered and the solid obtained was nickel thiocarbonate.

The nickel electrolyte was decoppered by the synthesized nickel thiocarbonate after different standing times (t_s) or aging times (t_a) in a 500 mL flask (heated by a water bath, Fig. 1) at 60 °C for 1 h with a stirring rate of 250 r/min. After cooling to room temperature, the decoppered electrolyte was filtered. The residual copper concentration (C_{Cu}) of the filtered solution was measured using an atomic absorption spectrophotometer (3510 model, China) while the mass ratio of copper to nickel in the residue ($R_{Cu/Ni}$) was determined by chemical titration. The phase compositions of the decoppering reagent after different aging times were identified by X-ray diffraction (XRD) using a D8 ADVANCE diffractometer with Cu Kα X-ray radiation at 35 kV and 20 mA. The functional group structures of the decoppering reagent aged for different time periods were determined by Fourier transform infrared spectroscopy (FTIR) using the KBr disk method

with a VERTEX70 (Japan) spectrophotometer operating in the wavenumber range 4000–400 cm^{-1}.

3. Results and discussion

As mentioned before, the decoppering capability of nickel thiocarbonate can be indicated by the effect of standing time on the residual copper concentration in the nickel electrolyte and on the mass ratio of copper to nickel in the residue. Table 1 shows the variation of C_{Cu} with standing time up to 92 days. It is seen that the residual copper concentration decreases with increasing standing time. This is because copper ions in the nickel electrolyte react with nickel thiocarbonate, generating the precipitation of $CuCS_3$ with dissolution of nickel. The reaction between nickel thiocarbonate and copper can be given as

$$NiCS_3 + Cu^{2+} \rightarrow Ni^{2+} + CuCS_3 \downarrow \tag{1}$$

Table 1 also shows that the variation of $R_{Cu/Ni}$ with standing time exhibits an opposite changing tendency to that of C_{Cu}. For example, C_{Cu} increases from 0.78 to 2.41 mg/L when t_s is extended from 0 days to 62 days. On the contrary, $R_{Cu/Ni}$ is decreased from 25.33 to 16.77. When $t_s = 92$ d, C_{Cu} continues to increase to 3.75 mg/L, which exceeds the required residual copper concentration (≤ 3 mg/L Cu). This means that nickel thiocarbonate loses its "effective" decoppering capability when $t_s = 92$ days. The standing time of nickel thiocarbonate with an effective decoppering capability is thus at least 62 days, which completely meets the technical requirement of industrial production. On the other hand, it is also noted that $R_{Cu/Ni}$ will satisfy the demand of copper removal ($R_{Cu/Ni} \geq 15$) when C_{Cu} is lower than 3 mg/L (Chen et al., 2013); hereafter, our discussion will focus on the variation in C_{Cu} during the decoppering process.

To obtain the upper limit of the decoppering capability, nickel thiocarbonate was aged at 60 °C for different time periods (t_a). Table 2 shows the effect of aging time on the residual copper concentration of the electrolyte. C_{Cu} is found to be 1.72 mg/L for nickel thiocarbonate without aging ($t_a = 0$ min). As the aging time increases from 16 to 1800 min (30 h), C_{Cu} increases from 2.69 to 342 mg/L. The value even goes up to 634 mg/L when $t_a = 4680$ min (78 h), which is very close to the initial copper concentration of the electrolyte (635 mg/L). The increase in C_{Cu} suggests the decreased capability of nickel thiocarbonate with copper, essentially caused by the phase changes during the aging of the decoppering reagent, as revealed by the XRD results in Fig. 2.

Fig. 2 shows that there are obvious phase transformations during the aging process. The newly synthesized nickel thiocarbonate is amorphous and its structure remains stable within the aging time of 34 min. When t_a is prolonged to 900 min, several new phases including S, Ni_3S_2, NiS_2 and Ni_3S_4 are observed. This phenomenon can be attributed to the decomposition and oxidization of nickel thiocarbonate, as indicated by the following reactions (Speight, 2005):

$$NiCS_3 \rightarrow NiS + CS_2 \tag{2}$$

$$NiCS_3 + O_2 \rightarrow NiS_2 + S + CO_2 \tag{3}$$
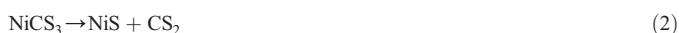
The reaction products, NiS_2 and NiS, may undergo further decompositions to S, Ni_3S_4 and Ni_3S_2 (Peng, 2005):

$$3NiS_2 \rightarrow 2S + Ni_3S_4 \tag{4}$$

Table 1
Effect of standing time (t_s) on C_{Cu} and $R_{Cu/Ni}$.

t_s (d)	0	1	2	6	18	27	62	92
C_{Cu} (mg/L)	0.78	0.77	0.79	1.09	1.57	2.19	2.41	3.75
$R_{Cu/Ni}$	25.33	25.17	24.96	23.09	20.91	19.62	16.77	14.55