



## Efficient separation of copper and nickel from ammonium chloride solutions through the antagonistic effect of TRPO on Acorga M5640



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### ABSTRACT

In this study, copper and nickel in ammoniacal/ammonium chloride solutions were separated by using an extractant mixture of Acorga M5640 and trialkylphosphine oxide (TRPO). The effects of contact time, Acorga M5640 concentration, modifier concentration, total ammonia concentration, and phase ratio on the extraction and separation of both metals were determined. The addition of TRPO into Acorga M5640 organic phase exerted antagonistic effects on copper and nickel extractions. The antagonistic effect of the extractant mixture was significantly stronger on the extraction of nickel than on that of copper. More than 99.96% of copper and less than 6.6% of nickel were extracted using a mixture of 10 vol.% Acorga M5640 and 2 vol.% TRPO in kerosene from an ammoniacal solution initially containing 3.0 g/L each of copper and nickel under optimal extraction conditions. The separation factor of copper over nickel reached 35,250.

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### 1. Introduction

The associated metals copper and nickel in oxidized ores, ocean manganese nodules, or other secondary materials are normally leached using ammoniacal solutions as their ammine complexes (Liu et al. 2014; Mishra et al. 2011; Silva et al. 2005). Solvent extraction is a state-of-the-art process for the recovery and separation of copper and nickel from metal-rich ammoniacal medium; this technique offers several advantages, including flexible operations, capacity to handle a wide range of feed concentrations, controllable selectivity, and low energy consumption (Hu et al. 2013a). In general, commercially available extractants for the separation of copper and nickel from ammoniacal solutions can be subdivided into two main categories: hydroxyoximes and  $\beta$ -diketones. Hydroxyoximes include LIX84 (Parija and Sarma 2000), LIX84I (Sengupta et al. 2007), LIX 973N (Alguacil 1999), LIX64N (Pandey et al. 1989), and Acorga M5640 (hereafter abbreviated as M5640) (Sridhar et al. 2010).  $\beta$ -diketones include LIX54 (Gameiro et al. 2008), DK-16 (Rao and Sahoo 1993), MX 80A (Mickler and Uhlemann 1992), and other sterically hindered derivatives (Wang et al. 2015). Ketoximes and aldioximes are suitable extractants for copper separation because of their high affinity for copper in ammoniacal solutions. However, these extractants are often limited by the poor

selectivity of copper over nickel in ammoniacal media. Parija and Sarma (2000) studied the extraction of copper and nickel from ammoniacal-sulfate leach liquors using LIX84 as an extractant; the two metals were quantitatively coextracted into the organic phase. Sridhar et al. (2010) used M5640 to quantitatively extract copper and nickel from an aqueous solution containing 3 g/L each of copper and nickel and 60 g/L ammonium carbonate by using an appropriate concentration of the extractant. Alguacil and Cobo (1998) extracted nickel from ammoniacal/ammonium carbonate solutions using M5640 in Iberfluid and found that nickel almost completely transferred into the organic phase containing 2.5 vol.% M5640. These studies indicate that hydroxyoximes exhibit weaker selectivity of copper over nickel in ammoniacal solutions. The procedure of coextraction and subsequent selective stripping under different acidity conditions was established as a feasible route for the separation and recovery of copper and nickel (Parija and Sarma 2000; Sridhar et al. 2009). However, this technique is limited by the fact that high nickel concentrations in the organic phase decrease copper load capacity and increase the number of extraction and stripping stages (Hu et al. 2013b). Considerable efforts have been exerted to develop other appropriate alternative methods for the recovery and separation of copper and nickel from ammoniacal solutions. A recently developed strategy (Hu et al. 2013b) for the selective recovery of copper and nickel was based on the synergistic effect of different extractants. Hu et al. (2013b) found that adding Aliquat 336 into LIX84I can evidently enhance the separation efficiency of Cu(II) and Ni(II) through the antagonistic effect of Aliquat 336 on LIX84I. Thus, this new method may be used for the separation of copper and nickel in ammoniacal solutions.

The chelating extractant M5640 is a salicylaldoxime derivative commercially used to extract copper in both acidic and alkaline media; this

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extractant is superior to other copper extractants because it has higher selectivity toward copper than iron and readily allows stripping (Deep et al., 2010). The active substance of M5640 is 2-hydroxy-5-nonylbenzaldehyde oxime. The extraction abilities of hydroxyoximes can be modified by adding compounds that can form hydrogen bonds with these extractants (Kyuchoukov et al. 1998). M5640 is already modified by a fatty ester (2,4,4-trimethyl-1,3-pentanediol diisobutyrate) and facilitates stripping; however, it still shows poor selectivity of copper over nickel. Neutral organophosphorus compounds containing P = O groups (electron donors) are powerful extractants because of their excellent coordination ability, high chemical stability, and low toxicity. M5640 can associate with organophosphorus derivatives by hydrogen bonding between —OH and P = O groups when two extractants are present in the organic phase. This observation indicates that a phosphorus-based extractant can modify the reactivity of the strong chelating extractant M5640 and thus improve the separation of copper and nickel in ammoniacal solutions. In the present work, a mixture of M5640 and trialkylphosphine oxide (TRPO) was employed for the selective extraction of copper over nickel from ammoniacal/ammonium chloride solutions. To the best of our knowledge, this study is the first to use an approach based on the synergistic effect of M5640 and TRPO to separate copper and nickel in ammoniacal solutions.

## 2. Experimental

### 2.1. Chemicals

The extractant M5640 was received from Cognis Co., Ltd. TRPO (a mixture of C<sub>6</sub> and C<sub>8</sub> trialkylphosphine oxide with 93% purity and average molecular weight of 348) and tri-*n*-butylphosphate (TBP, A.R.) were obtained from Shanghai Laiyashi Chemical Co., Ltd. The organic phase was prepared by dissolving 10 vol.% M5640 and 2 vol.% TRPO in kerosene.

An ammoniacal solution containing copper and nickel was prepared by dissolving copper chloride and nickel chloride in ammoniacal/ammonium chloride solutions. The concentration of both Cu(II) and Ni(II) in the solution was maintained at 3.0 g/L. Extraction experiments were performed in aqueous solutions with a total ammonia concentration of 4.0 mol/L (containing 3.0 mol/L ammonia and 1.0 mol/L ammonium chloride,  $[\text{NH}_3]_{\text{total}} = [\text{NH}_3] + [\text{NH}_4^+]$ ). All other chemicals used in this work were of A.R. grade.

### 2.2. Extraction procedure

In the extraction experiments, 10.0 mL of the organic phase was equilibrated with 10.0 mL of the aqueous phase in a 60 mL separating funnel by shaking at  $25 \pm 1$  °C on an automatic shaker with a shaking speed of 150 rpm and reciprocating amplitude of 20 mm for 3 min. After contact, the mixture was centrifuged for clear phase separation. The equilibrium pH of the aqueous phase ( $\text{pH}_{\text{equ}}$ ) was measured using a Mettler FE20 pH meter. The concentrations of copper and nickel in raffinate were determined through atomic absorption spectrometry (Hitachi Z2000 spectrophotometer). The concentrations of copper and nickel in the loaded organic phase were calculated using a mass balance. The distribution coefficient (*D*) was calculated by taking the ratios of the equilibrium concentration of the metal in the organic and aqueous phases. From the *D* values, the extraction percentage was obtained by using  $\% E = D \times 100 / [D + (V_{\text{aq}}/V_{\text{org}})]$  where  $V_{\text{aq}}$  and  $V_{\text{org}}$  are the volume of aqueous and organic phases, respectively. The copper-to-nickel separation factor ( $\beta_{\text{Cu/Ni}}$ ) was calculated from the *D* ratio of copper to nickel ( $\beta_{\text{Cu/Ni}} = D_{\text{Cu}}/D_{\text{Ni}}$ ).

## 3. Results and discussion

### 3.1. Effect of contact time

The effect of different contact time (0.5 min to 10 min) on the extraction of copper and nickel from the ammoniacal solutions containing

3.0 g/L each of copper and nickel were studied using 10 vol.% M5640 or 10 vol.% M5640 + 2 vol.% TRPO. Copper equilibrium was reached more rapidly than nickel equilibrium (Fig. 1), indicating the faster extraction kinetics of copper than nickel (Sridhar et al. 2010). The maximum and constant extraction of copper was reached after approximately 3 min, and more than 99.96% of copper transferred into the organic phase in both systems. Meanwhile, the extraction percentage of nickel markedly increased with prolonged contact time. In specific, the nickel extraction percentages reached 82.4% and 31.8% after 10 min of contact with M5640 and M5640 + TRPO, respectively. Therefore, prolonging the contact time is unfavorable to the separation of copper and nickel. Thus, an extraction contact time of 3 min was used in subsequent experiments. Comparison of the two extraction systems revealed that the addition of TRPO did not deteriorate the extraction ability of M5640 toward copper but significantly enhanced the separation efficiency. The copper-to-nickel separation factor ( $\beta_{\text{Cu/Ni}}$ ) reached 35,250, and <6.6% of nickel was coextracted when 2 vol.% TRPO was added into 10 vol.% M5640 organic phase after 3 min of mixing.

### 3.2. Effect of M5640 concentration

The effect of M5640 concentration varying from 0 to 20 vol.% in the organic phase on the extraction and separation of copper and nickel was investigated from the ammoniacal solutions containing 3.0 g/L each of copper and nickel. The concentration of TRPO was fixed at 2 vol.% in the organic phase. As shown in Fig. 2, the copper extraction percentage enhanced significantly from 2.3% to 99.96% as the M5640 concentration increased from 0 to 10 vol.% in the organic phase, while that of nickel increased slightly, with extraction efficiencies remaining below 6.6%. It is noticeable that the copper extraction percent kept stable at about 100% with further increasing of the M5640 concentration from 10 vol.% to 20 vol.%, whereas the nickel extraction percentage enhanced sharply and reached 61.7%. A maximum separation factor of 35,250 at M5640 concentration of 10 vol.% was achieved. The coextraction of nickel increased obviously when the M5640 concentration exceeded 10 vol.%, which is unfavorable for the separation of copper and nickel. Therefore, optimal M5640 concentration of 10 vol.% corresponds to best separated effect for this system.

### 3.3. Effect of modifier concentration

The effects of different concentrations (0 to 10 vol.%) of modifiers in 10 vol.% M5640 diluted in kerosene on the extraction and separation of copper and nickel were studied. Fig. 3 shows that the phosphorus-based modifiers exerted an antagonistic effect on M5640 for both copper and nickel extraction. However, the modifiers exhibited a stronger effect on the extraction of nickel than on that of copper. The difference of antagonistic effect strength on nickel and copper allowed the efficient separation of copper and nickel in ammoniacal solutions. As the modifier concentration was increased from 0 to 10 vol.%, the percentage extraction of nickel sharply decreased from 51.0% to 5.3% for TBP and 2.0% for TRPO, whereas that of copper slightly decreased from 99.99% to 99.3% for TBP and 93.7% for TRPO. These results suggest that the antagonistic effect of TRPO was stronger than that of TBP, which is consistent with the basicity order of the Lewis bases. Compared with TBP, TRPO has a higher tendency to interact with M5640 through hydrogen bonding, which could explain the stronger antagonistic effect of TRPO than TBP on M5640. Fig. 3 also shows the copper-to-nickel separation factor as a function of the modifier content in the organic phase. The separation factor between copper and nickel in the M5640 + TRPO extraction system sharply increased from 4812 to 35,250 as the TRPO concentration increased from 0 to 2 vol.% and then decreased when the concentration was further increased. A similar trend was also observed in the M5640 + TBP system. Hence, 2 vol.% TRPO was used as the modifier in the subsequent experiments in consideration of the copper extraction efficiency and the separation factor between copper and nickel.

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