Korean J. Chem. Eng., 39(3), 706-716 (2022)
DOI: 10.1007/s11814-021-0919-9

pISSN: 0256-1115
eISSN: 1975-7220

Separation of Cu, Co, Ni and Mn from acid leaching solution of ocean cobalt-rich crust using precipitation with Na_2S and solvent extraction with N235

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(*Received 10 April 2021 • Revised 6 July 2021 • Accepted 8 August 2021*)

Abstract−In order to effectively separate and recover copper, cobalt, nickel and manganese from the leaching solution of ocean cobalt-rich crusts, a process of selective precipitation and extraction using precipitation with Na_2S solution and solvent extraction with N235 extractant, was proposed. The optimum separation and recovery process conditions were determined through single factor condition experiments. The results show the precipitation efficiency of copper can reach 99.87%, while the precipitation efficiency of cobalt and nickel was 1.23% and 1.08%, respectively, at the initial pH of 0.60. Similarly, under the condition of initial pH of 4.00, 99.18% cobalt and 98.31% nickel were precipitated and only 0.89% manganese was co-precipitated. The mixed cobalt-nickel precipitation was completely dissolved with HCl solution, then N235 extractant was used to extract cobalt from solution. The extraction efficiency of cobalt can exceed 99% though three stages countercurrent extraction under optimal extraction conditions (chloride ion concentration of 9 mol/L, the N235 concentration of 30% (v/v), the phase ratio (O/A) of 2, and at 298.15 K for 8 min). In addition, thermodynamic calculations showed that the extraction of cobalt from acid leaching solution of ocean cobalt-rich crust with N235 as the extractant was an exothermic reaction.

Keywords: Acid Leaching Solution of Cobalt-rich Crust, Separation, Precipitation, Extraction, Copper, Cobalt, Nickel and Manganese

INTRODUCTION

Oceanic cobalt-rich crusts as an important submarine solid mineral have attracted much attention due to high economic potential of various metals [1], a series of investigations and studies have been carried out since the 1970s [2-5]. Cobalt-rich crusts generate growing economic interest owing to potential of metal production, including manganese, cobalt, nickel, copper and rare earth elements (REE) [6,7]. In particular, the grade of cobalt is 2.5 times that of terrestrial mines [8]. Global estimated reserve of deep sea crust minerals is about 500 billion tons of which Indian Ocean reserves account for about 150 billion tons [9]. Therefore, with the depletion of terrestrial mineral resources, the development and utilization of marine cobalt-rich crust resources have become an important trend [10-12]. Cobalt-rich crusts mainly contain Mn and Fe elements [13,14], and because cobalt-rich crusts are formed in the deep-sea within the oxygen-rich bottom zone (ORZ) [15], Mn and Fe primarily occur in their oxidized forms as Mn-or Fe-oxyhydroxides and produce secondary colloids[16], and valuable metals such as Cu, Co and Ni are present in iron-manganese hydrate oxide in the form of isomorphism [17]. Therefore, the key to extracting valuable metals (Mn, Co, Ni, Cu) from cobalt-rich crusts is to destroy the original crystal lattice of iron-manganese oxide minerals via pyrometallurgy or hydrometallurgy [18]. Such as, Zhang et al. [10] and G. Senanayake [18] reviewed previous studies on reductive leaching of manganese nodules by various organic and inorganic reagents including phenols, SO_2, Na_2SO_3, H_2O_2, CH_3OH, FeS_2, coal, sucrose, glucose, lignite, pyrrhotite and sawdust (cellulose) in the media of solutions of H_2SO_4. At present, most research has focused on the reduction roasting of ocean cobalt-rich crusts, while ignoring the separation of copper, cobalt, nickel and manganese in the leachate. Due to the increasing demand for valuable metals, the separation of copper, cobalt, nickel and manganese in the leachate of ocean cobalt-rich crusts has attracted wide attention.

A large number of researchers have explored various methods to remove or separate copper from the solution, including electrolysis [19], precipitation [20-22], ion-exchange [23], adsorption [24], membrane filtration [25] and titanium oxidation (TiO_2) photocatalysis [26]. Among these, chemical precipitation is widely used due to low cost, simple process, etc. [22]. For example, Sezin et al. [27] investigated and showed pH is an important factor in sulfide precipitation, and when Na_2S is added in acidic pH range, Cu is totally precipitated and eliminated. Mamta et al.'s [28] research has shown that copper removal from wastewater sparged with biogenic $H_2S(g)$ varied depending on the ratio of metal to sulfide; maximum removal efficiency of copper was 100%, and as the amount of copper in solution exceeds the amount of sulfide in solution, the percentage removal of copper decreases.

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However, the separation of cobalt from nickel is still challenging due to the similar aqueous chemical behavior [29]. Various techniques have been reported to separate cobalt from nickel and other impurities (iron, aluminum, and magnesium), such as ion exchange resins [30,31], selective oxidative precipitation [32], electrolysis [33] and solvent extraction [34-36]. Among these, ion exchange resins lack selectivity for cobalt and are more suitable for nickel extraction [29], while solvent extraction is an efficient way to separate cobalt from nickel compared with precipitation and ion exchange [37]. The common extractant in Co/Ni separation is PC88A (also known as EHEHPA, P507 and Ionquest 801) [37]. The previous research reports that Co was successfully separated from sulfate solutions using the 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester (PC88A) [38-40]. However, it is not suitable to separate cobalt and nickel with PC88A extractant in solutions with high concentration of manganese ions, due to the extraction order of these metals has been established as Mn>Cu>Co>Ni when the loading of the metal in the organic phase is low, and on high loading the extraction order is Cu>Mn>Co>Ni [38]. Three thiophosphinic extractants, Cyanex 272, Cyanex 301and Cyanex 302, can efficiently separate Co and Ni from high Ni/Co ratio systems due to its excellent Co selectivity [41-45]. Nevertheless, the saturated extraction capacity of Cyanex solvents is much lower than that of PC88A, which heavily discounts the extraction and separation efficiency [46]. Besides, Cyanex solvents are usually most expensive despite the fact that these extractants have demonstrated good potential for recovery of Co and Ni and for their separation from aqueous solutions [45,47,48]. According to the above literature, a large number of studies have confirmed that solvent extraction can separate cobalt and nickel in the solution, but most of studies are to separate cobalt and nickel from solutions with relatively simple impurity components. However, the leaching solution of ocean cobalt-rich crusts has high impurity content and complex composition, and it is difficult to obtain high-purity cobalt and nickel products even with solvent extraction methods. Previous studies have shown that in chloride solution, amine extractant such as N235 can completely separate cobalt and nickel due to the different characteristics of cobalt and nickel [49]. But, at present, there are few studies on the separation of cobalt and nickel using amine extractants from the leaching solution of ocean cobalt-rich crusts.

To effectively separate and recover the copper, cobalt, nickel and manganese in the leaching solution of ocean cobalt-rich crusts, the precipitation-solvent extraction process has been studied. In this study, the process conditions for removing iron in the leaching solution by adjusting the pH value were explored and the effects of main process parameters on separation copper by precipitation using the Na_2S solution were investigated. Furthermore, the feasibility of co-precipitation (Na_2S)-dissolution (HCl)-solvent extraction (N235) to efficiently separate cobalt and nickel has been confirmed and the main parameters of this process were determined; the thermodynamic behavior of the extraction process of cobalt in the extraction system of N235 was also investigated. Efficient separation and recovery of copper, cobalt, nickel and manganese from the leachate of oceanic cobalt-rich crusts has been realized.

MATERIALS AND METHODS

1 Reagents and Solutions

$Na_2S{\cdot}9H_2O$ (Sodium sulfide nonahydrate) were kindly supplied by Shanghai Macklin Biochemical Co., LTD, N235 (trioctyl tertiary amine) and TBP (tributyl phosphate) were kindly supplied by Zhengmao Industries Inc. Organic solutions were prepared by dissolving N235 in the diluent kerosene provided by Shanghai Science and Technology Co., LTD. All inorganic chemicals used were analytical grade and without any purification treatment.

The acid leaching solutions used throughout the study were obtained from the oceanic cobalt-rich crusts after reduction roasting (mass ratio of oceanic cobalt-rich crusts and sawdust was 5) at 723.15 K and sulfuric acid leaching at 298.15 K. The results showed that under the condition of a liquid-to-solid ratio of 10, leaching with 0.5 mol/L H_2SO_4 at room temperature for 50 min, the leaching efficiencies of copper, cobalt, nickel and manganese were 98.14%, 98.47%, 98.79% and 99.32%, respectively. The concentration of metals in the leaching solution was analyzed with inductively coupled plasma optical emission spectroscopy (ICP-OES, iCAP Duo6300, Thermo Scientific, UK) and results obtained are shown in Table 1.

2. Procedure Experiments

The pH value of the solution during the whole experiment was modified by adding either 1 mol/L H_2SO_4 or 200 g/L NaOH. The precipitant is a sodium sulfide solution with a mass fraction of 20%. Precipitation experiments were carried out in conical flasks (250 ml) by magnetic stirring (with a stirring speed of 500 r/min) at 298.15 K for 10 min. The mixed cobalt-nickel precipitation is dissolved with hydrochloric acid. At 289.15 K, the solvent extraction experiments were performed by mechanical shaking (oscillation frequency of 300 r/min) in 150 ml conical flasks, the extraction time for all extraction experiments is 8 min. After phase disengagement, the organic and aqueous phases were separated by using separating funnels. With pure water as stripping agent for cobalt, at 298.15 K, stripping experiments were carried out by mechanical shaking (oscillation frequency of 300 r/min) in 150 ml conical flasks, and then left standing for 15 min to separate the phases using a separatory funnel. During the entire extraction experiment, the concentration of Co and Ni in the aqueous phase was analyzed by spectrophotometry while other metals were analyzed by ICP-OES, and the metal concentration in the organic phase was calculated according to the principle of conservation of mass, and the distribution ratio (D) was calculated according to the concentration of Co and Ni in the organic phase and aqueous phase. The calculation equations are shown as follows:

Table 1. Chemical components of leaching solution

Element	Mn	Fe	Cu	Co	Ni	Mg	Al	Na	Si
Content (g/L)	27.881	21.483	0.080	0.942	0.631	0.950	0.362	1.394	0.010

$$E=\frac{C_M-C_A}{C_F}\times 100\% \tag{1}$$

$$C_O=\frac{(C_M-C_A)V_F}{V_O} \tag{2}$$

$$D=\frac{C_O}{C_A} \tag{3}$$

where, E is the extraction ratio (%) of metal, C_M represents the concentration (g/L) of each metal ion in the acid leaching solution, C_A is the concentration (g/L) of each metal ion in the raffinate, C_O represents the concentration (g/L) of metal ion in loaded organic phase, V_O and V_F are, respectively, the volume of organic phase and aqueous phase, and D is the distribution ratio (%) of metal.

RESULTS AND DISCUSSION

1. Removal of Iron Impurity

The 50 mL of the actual acid leaching solution was added to a 150 mL beaker, and 200 g/L NaOH was used to adjust the pH (1.5-5.0) of the solution to carry out the iron precipitation experiments. The solutions with different pH values were heated in a water bath for 30 minutes, cooled, filtered, and the filtrate was analyzed for ion concentration. The experimental results are shown in Fig. 1.

It can be seen from Fig. 1 that the removal efficiency of iron was very high at higher pH values, and the precipitation efficiency of iron increased from nil (pH 1.5) to 99.98% (pH 5.0). Although the co-precipitation of other metal ions was observed during the precipitation of iron in the higher pH range, the co-precipitation of metals such as cobalt, nickel, and manganese in the acid leaching solution was not observed when the pH value was less than 4. The total aluminum was precipitated as $Al(OH)_3$ and it was increased from nil (at pH 1.5) to 82.12% (at pH 5.0). The co-precipitation of Co, Ni and Mn can be clearly observed when the pH value exceeded 4.0. For example, at pH values of 4.2, 4.3, 4.4 and 5.0, the precipitation of cobalt (as $Co(OH)_2$) was of 0.10%, 0.16%, 0.36% and 1.42%, the precipitation of nickel (as $Ni(OH)_2$) was of 0.09%, 0.17%, 0.32% and 1.28%, and the precipitation of manganese (as $Mn(OH)_2$) was of 1.03%, 3.87%, 5.12% and 10.98%. Copper ions would not be precipitated when the pH value was less than 3.5, but co-precipitation occurred when the pH value exceeded 3.5. For example, at pH values of 4.0, 4.2, 4.3 and 4.4, the precipitation of copper (as $Cu(OH)_2$) was of 1.26%, 5.62%, 9.45% and 13.87%. The amount of copper precipitation was significantly increased with the increasing pH above 4.4. In the entire pH range of the experiment, the co-precipitation of magnesium was very small; even at pH 5.0, the co-precipitation of magnesium metal was only 0.87%. From this study, the co-precipitation of these metals follows the order as Al>Cu>Mn>Co>Ni>Mg. Therefore, it was ascertained that the iron precipitation as $Fe(OH)_3$ was highly selective and almost quantitative at pH 4.0, which condition can selectively remove iron from the acid leaching solution of oceanic cobalt-rich crust.

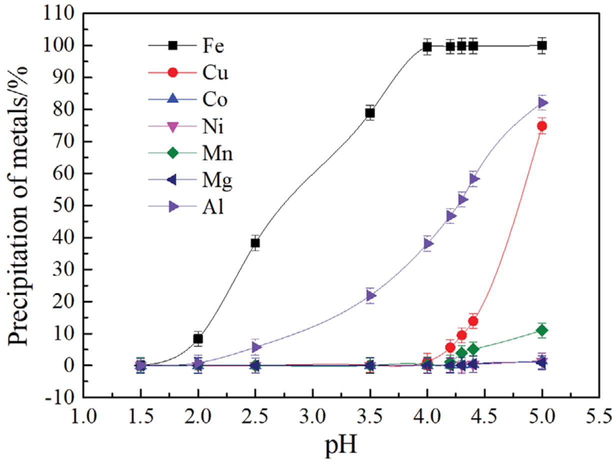

Fig. 1. Precipitation of iron at different pH.

Based on the above research, the pH value of the solution was adjusted to 4.0 with 200 g/L NaOH, and the iron removal experiments were carried out at room temperature for 30 min. The concentration of metals in the filtrate after precipitation of iron was analyzed with inductively coupled plasma optical emission spectroscopy (ICP-OES, iCAP Duo6300, Thermo Scientific, UK) and results obtained are shown in Table 2.

2. Separation Copper by Precipitation Using the Na_2S Solution

It can be seen from Fig. 1 that copper can also be precipitated from the acid leaching solution by adjusting the pH. However, the precipitation efficiency of copper was increased from nil (at pH 1.5) to 74.86% (at pH 5.0), co-precipitation of other metal ions (such as Al, Mn, Co and Ni) was obviously observed during precipitation of Cu at higher pH range. Therefore, the selective precipitation of copper from the acid leaching solution by adjusting pH is not feasible. It has been documented that metal ions in a solution can combine with S^{2-} (Eq. (6)) and HS^- (Eq. (7)) to form insoluble metal sulfides (MS) precipitate, thereby separating the heavy metals from the solution [50]. Different metal ions have different solubility product of metal sulfides (*K*sp), and the smaller the solubility product, the easier it is to form a precipitate.

Therefore, the ionic product constants of metal sulfides provide a theoretical basis for the selective precipitation of ions.

$$H_2S \rightleftharpoons HS^- + H^+ \quad K_{p1}=\frac{[HS^-][H^+]}{H_2S} \quad pK_1=6.99 \tag{4}$$

$$HS \rightleftharpoons S^{2-} + H^+ \quad K_{p2}=\frac{[S^{2-}][H^+]}{HS^-} \quad pK_2=17.4 \tag{5}$$

$$M^{2+}+S^{2-} \rightleftharpoons MS(S) \tag{6}$$

$$M^{2+}+HS^{2-} \rightleftharpoons MS(S)+H^+ \tag{7}$$

Table 2. Chemical components of the filtrate after precipitation of iron

Element	Mn	Fe	Cu	Co	Ni	Mg	Al	Si
Content (g/L)	27.823	0.006	0.079	0.939	0.630	0.950	0.223	0.01

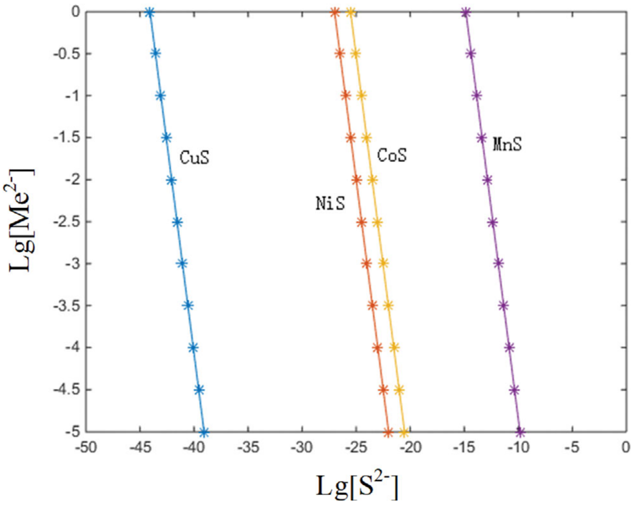

Fig. 2. The relationship between the S^{2-} concentration and the concentration of several metal ions.

Cu, Co, Ni and Mn are the main valuable metals in the acid leaching solution. The separation of copper using Na_2S solution is based on the difference in the solubility of these metal sulfides in water. When Na_2S solution is added to the acid leaching solution, the concentration of S^{2-} in the solution continues to increase, so that the residual concentration of the target metal is continuously reduced. The relationship between the S^{2-} concentration and the concentration of several metal ions at 18 °C is shown in Fig. 2.

It can be seen from Fig. 2 that the order of the sulfide solubility products of copper, cobalt, nickel and manganese was MnS>CoS>NiS>CuS, so, the first precipitation produced by adding appropriate Na_2S solution to the acid leaching solution was CuS, achieving its separation with other metal ions.

The main factors affecting the sulfide precipitation copper are the initial pH of the precipitation and the amount of sulfide added. Under the conditions of stirring speed of 500 r/min and precipitation for 10 min at 298.15 K, in order to study the effect of the initial precipitation pH and the amount of Na_2S on the precipitation efficiency of copper, experiments of precipitating copper were carried out at different initial pH values and different Na_2S dosage. The experimental results are shown in Fig. 3.

It can be seen from Fig. 3(a) that the Cu was precipitated as CuS and it was increased from 76.12% (the dosage of Na_2S was 1.0 times the theoretical dosage) to 88.49% (the dosage of Na_2S was 1.3 times the theoretical dosage) at initial pH of 0.45. Although no co-precipitation of Mn was observed during precipitation of Cu at higher Na_2S dosage, co-precipitation of Co and Ni was observed. It can be clearly seen from the figure that when the Na_2S dosage was greater than 1.2 times the theoretical dosage, the precipitation efficiency of Cu increased slowly, but the co-precipitation efficiency of Co and Ni increased rapidly. For example, when the Na_2S dosage was 1.1,1.2 and 1.3 times the theoretical dosage, the precipitation efficiency of Cu was of 84.42%, 87.08% and 88.49%. Therefore, at the initial pH of 0.45, the precipitation efficiency of Cu was not high, and precipitation and separation of Cu was not feasible. As can be seen from Fig. 3(b), at initial pH of 0.60, the

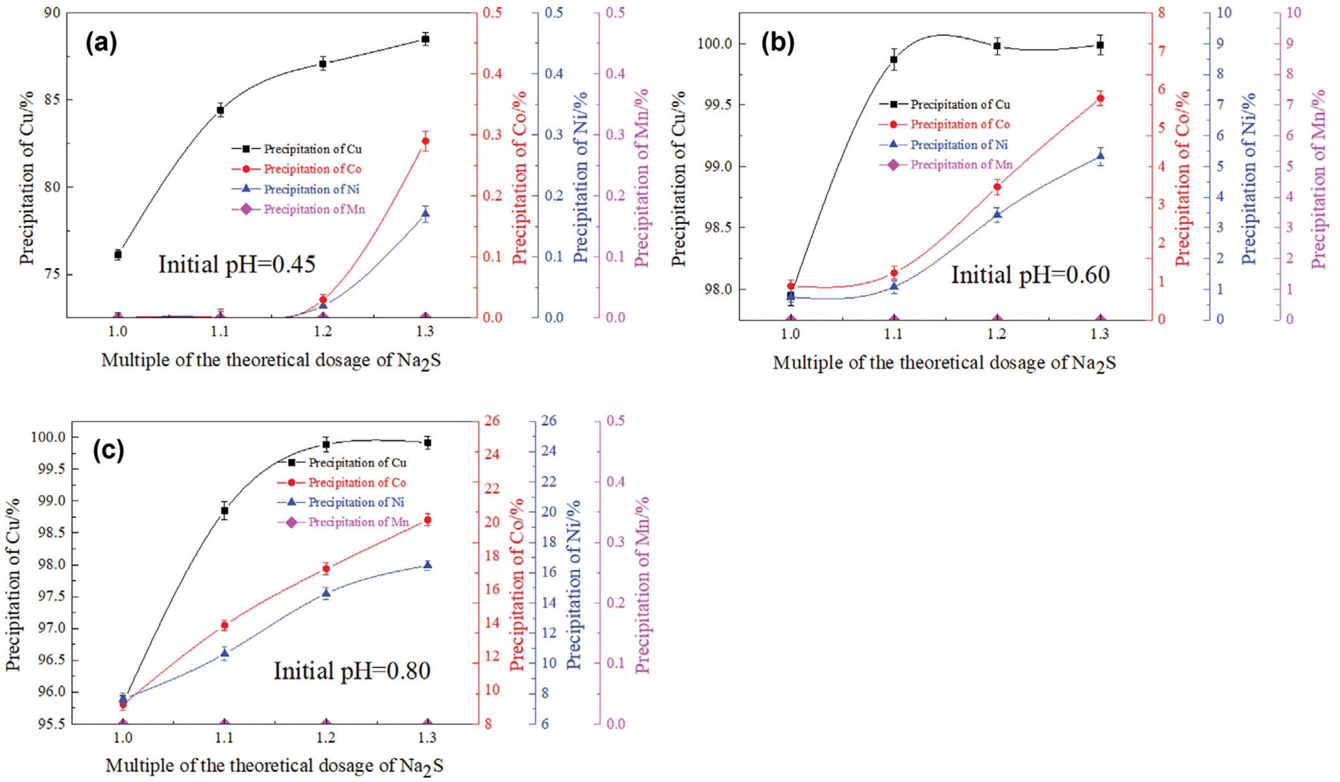

Fig. 3. The effect of sodium sulfide dosage on precipitation efficiency of copper at different pH. (a) Initial pH=0.45, (b) Initial pH=0.60, (c) Initial pH=0.80.

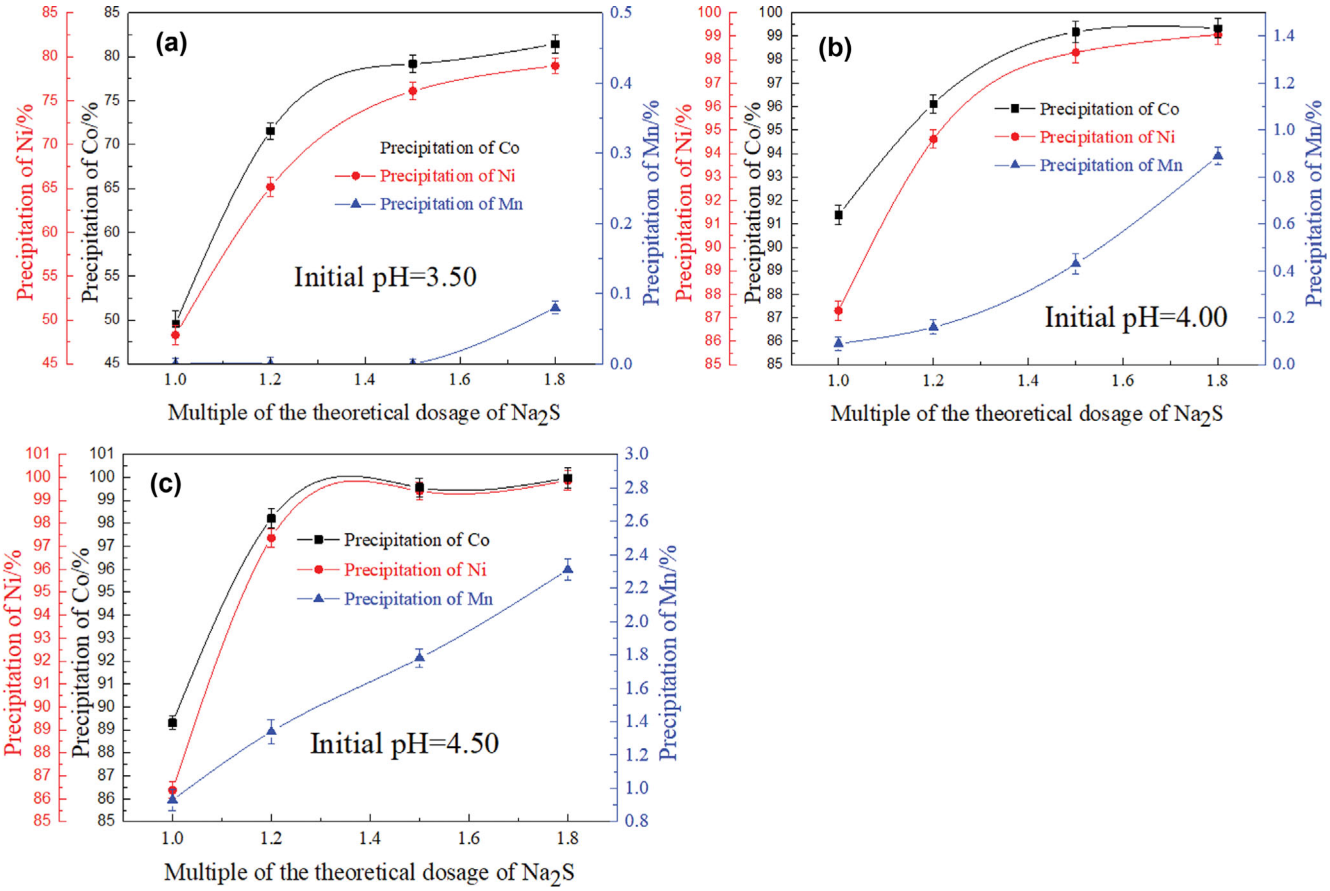

Fig. 4. The effect of sodium sulfide dosage on precipitation efficiency of cobalt and nickel under different pH. (a) Initial pH=3.50, (b) Initial pH=4.00, (c) Initial pH=4.50.

precipitation efficiency of Cu was ideal and it increased from 97.95% (the dosage of Na_2S was 1.0 times the theoretical dosage) to 99.99% (the dosage of Na_2S was 1.3 times the theoretical dosage). Even if the Na_2S dosage was 1.3 times the theoretical dosage, the co-precipitation of Mn was still not observed. When the Na_2S dosage was 1.1 times the theoretical dosage, the precipitation efficiency of copper had reached the best. After that, further increasing the dosage of Na_2S, the precipitation efficiency of Cu remained basically unchanged. However, the precipitation efficiency of Co and Ni continued to increase, which was undesirable. It can be seen from Fig. 3(c), at initial pH of 0.80, the precipitation efficiency of Cu was also very good. However, even if the Na_2S dosage was 1.0 times the theoretical dosage, the co-precipitation efficiencies of Co and Ni were very high at 9.16% and 7.65%, respectively. At this pH, although Mn not was co-precipitated, the co-precipitation efficiency of Co and Ni was clearly observed, which was not suitable as the initial pH for separating Cu from acid leaching solution.

Based on the above experimental results analysis, the separation of Cu from the solution after iron precipitation was carried out under optimal extraction conditions. The filtrate after precipitation of Cu containing 27.823 g/L Mn, 0.006 g/L Fe, 0.928 g/L Co, 0.624 g/L Ni, 0.950 g/L Mg and 0.223 g/L Al was taken to use for separate Co, Ni and Mn study.

3. Co-precipitation of Cobalt and Nickel Using the Na_2S Solution

The obtained filtrate from the previous precipitation of copper experiment as the feed solution of the co-precipitation of cobalt and nickel experiments were carried out at different pH and different Na_2S. The effect of precipitation initial pH and the Na_2S dosage was investigated under the conditions of a stirring speed of 500 r/min and precipitation for 10 min at 298.15 K, and the experimental results are shown in Fig. 4.

It can be seen from Fig. 4 that the precipitation efficiencies of cobalt and nickel remained consistent, because the solubility products of cobalt sulfide and nickel sulfide were very close. But by adjusting the initial pH of precipitation and the Na_2S dosage can made cobalt and nickel precipitate (as CoS and NiS) while manganese remained in the solution. When the initial pH of the precipitation was 3.50 (Fig. 4(a)), even if the Na_2S dosage was increased to 1.8 times the theoretical dosage, the precipitation efficiencies of cobalt and nickel only were 81.64% and 78.96%, respectively; at this time, the precipitation efficiency of manganese was clearly observed. When the initial pH of precipitation was 4.00 (Fig. 4(b)), the precipitation efficiency of cobalt and nickel under the same Na_2S dosage was significantly higher than the initial pH of precipitation of 3.50. When the Na_2S dosage was 1.5 times the theoretical dosage, the precipitation efficiency of cobalt and nickel reached the maximum, respectively, 99.18% and 98.31%. At this time, the

Table 3. Chemical components of the filtrate after precipitation of cobalt and nickel

Element	Mn	Fe	Co	Ni	Mg	Al
Content (g/L)	27.692	0.003	0.005	0.008	0.948	0.211

precipitation efficiency of manganese was only 0.43%, which was acceptable to us. But continuing to increase the Na_2S dosage, the precipitation efficiency of cobalt and nickel was not increased, and the precipitation efficiency of manganese could reach 0.89%, so when the initial pH of the precipitation was 4.00 and the Na_2S dosage 1.5 times the theoretical dosage could effectively separate cobalt and nickel. When the initial pH was increased to 4.50 (Fig. 4(c)), it can be seen from the figure that the separation effect was very poor. When the Na_2S dosage was 1.0 times the theoretical dosage, there was a large amount of manganese co-precipitation, continuing to increase the Na_2S dosage, the precipitation efficiency of manganese would increase rapidly, so, it was not suitable to precipitate cobalt and nickel from solution.

According to the above experimental results, the precipitation of cobalt and nickel with Na_2S solution from solution was carried out under optimal extraction conditions. The concentrations of metals in the filtrate after precipitation of cobalt and nickel were analyzed with inductively coupled plasma optical emission spectroscopy and the results are shown in Table 3. This filtrate is used as the raw material for manganese recovery.

4. Separation of Co and Ni by Extraction Using N235 Extractant

4-1. Influence of Chloride Ion Concentration

The separation of cobalt and nickel with N235 extractant needs to be carried out in a high concentration of chloride solution. At high concentrations of chloride ion solution, cobalt can form tetrahedral $CoCl_4^{2-}$ ions, which readily dissolve in protonated amines [49]. In contrast, nickel was forming neutral $NiCl_2$ complexes which was difficult to extract by amines. The mixed cobalt-nickel precipitation was completely dissolved with hydrochloric acid. To investigate the influence of concentration chloride ions on the extraction of cobalt, extraction experiments were conducted in the initial chloride ion concentration of 6-11 mol/L adjusted with concentrated hydrochloric acid solution. The N235 concentration was 30% (v/v), the phase ratio (O/A) was 2, and the extraction experiments of cobalt ions under different concentrations of chloride ions were carried out at 298.15 K for 8 min; the results are shown in Fig. 5.

It can be seen from Fig. 5 that with the increase of initial chloride ions concentration from 6 to 11 mol/L, the extraction efficiency of cobalt increased from 78.32% to 98.12%, and the extraction efficiency of nickel can reach 0.16% at initial chloride ion concentration of 11 mol/L. It can be clearly seen from figure that when the chloride ion concentration reached 9 mol/L, the extraction efficiency of cobalt reached the best at 97.89%, and then keeping increasing the chloride ion concentration had very little contribution to improving the extraction efficiency of cobalt. However, when the chloride ion concentration exceeded 9 mol/L, co-extraction of nickel was observed, resulting in poor separation of cobalt and nickel. Therefore, the optimal the initial chloride ion concentration was chosen to be 9 mol/L in the subsequent studies.

4-2. Influence of the Concentration of N235 (v/v)

When the initial concentration of chloride ion was 9 mol/L, the phase ratio (O/A) was 2, and the extraction was performed at 298.15 K for 8 minutes, the effect of different N235 concentrations (v/v) on the extraction efficiency of cobalt was studied. The relationship between the extraction efficiency of cobalt and the concentration of N235 (v/v) is shown in Fig. 6.

It can be observed from the Fig. 6 that as the concentration of N235 increased from 15% to 30% (v/v), the extraction efficiency of cobalt was also increasing, from 75.29% to 97.95%. When the N235 concentration was 30% (v/v), the extraction efficiency of cobalt was 97.95%. After that, increasing the N235 concentration had no obvious effect on the improvement of the extraction efficiency of cobalt. However, the N235 concentration increased from 15% to 40% (v/v), and the extraction efficiency of nickel continued to increase. The extraction efficiency of nickel was 0.13% at a

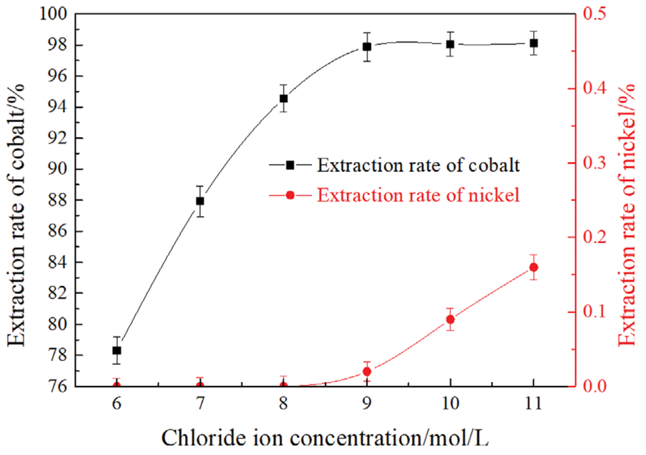

Fig. 5. The extraction efficiency of cobalt at varying concentration chloride ions.

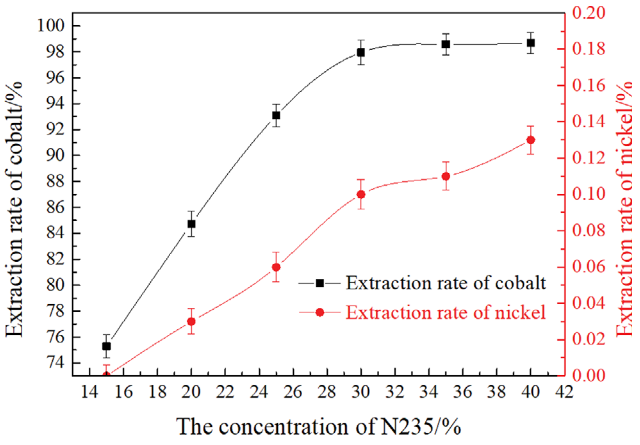

Fig. 6. The extraction efficiency of cobalt versus the concentration of N235 (v/v).

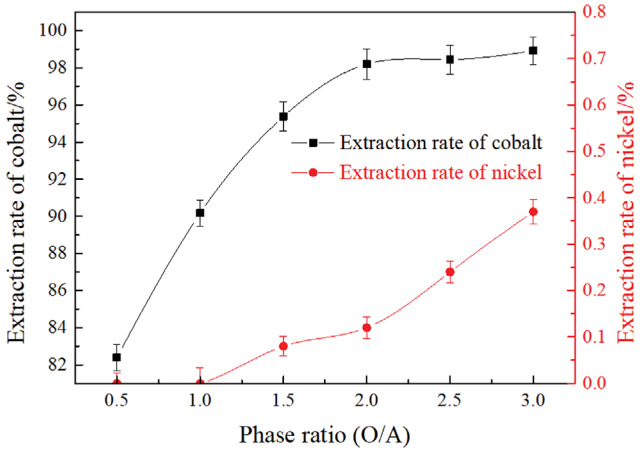

Fig. 7. Effect of phase ratio (O/A) on extraction of cobalt.

N235 concentration of 40% (v/v). From Fig. 6, a rule can be found that when the N235 concentration increased from 30% to 40%, the extraction efficiency of cobalt remained unchanged, but the extraction efficiency of nickel continued to increase. To obtain a better separation effect, the optimal extraction concentration of N235 was determined to be 30% (v/v).

4-3. Influence of Phase Ratio (O/A)

The effect of the phase ratio (O/A) on extraction of cobalt was studied in the range of 0.5-3 at an initial chloride ion concentration of 9 mol/L, N235 concentration of 30% (v/v), at 298.15 K for 8 min. The extraction efficiencies of cobalt and nickel under different phase ratio (O/A) are shown in Fig. 7.

As can be seen from Fig. 7 that when the phase ratio (O/A) increased from 0.5 to 2.0, the extraction efficiency of cobalt continued to increase from 82.39% to 98.20%. Although the extraction efficiency of nickel was not observed when the phase ratio (O/A) was 0.5 to 1.0, but as the phase ratio (O/A) increased from 1.0 to 2.0 the extraction efficiency of nickel increased from nil to 0.12%. After that, continuing to increase the phase ratio (O/A), the extraction efficiency of cobalt was no longer clearly improved, but the extraction efficiency of nickel continued to increase. Based on the above experimental results, the phase ratio (O/A) of 2.0 was determined as the best value.

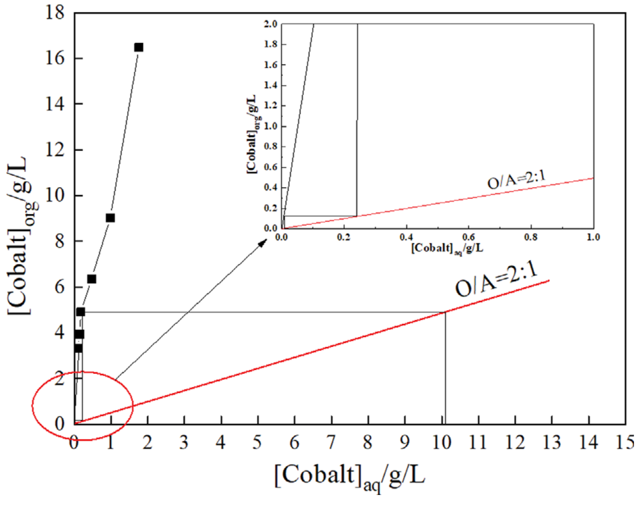

Fig. 8. The McCabe-Thiele diagrams of extraction cobalt.

Table 4. Three-stage countercurrent extraction experiment results

Items	Co	Ni
C_o ($g \cdot L^{-1}$)	10.0820	6.5950
C_{aq} ($g \cdot L^{-1}$)	0.0003	6.5772
C_{org} ($g \cdot L^{-1}$)	5.0409	0.0089
E (%)	99.997	0.270
D	50,409.2	0.0014

4-4. McCabe-Thiele Diagrams

To determine the count of series demanded for countercurrent extraction at a certain phase ratio, which aim to achieve the complete separation of cobalt and nickel, a simulated countercurrent extraction was carried out to determine the number of stages required for extraction of cobalt with N235. The McCabe-Thiele equilibrium isotherm was established by changing the phase ratio (O/A) at an initial chloride ions concentration of 9 mol/L, N235 concentration of 30% (v/v) and a temperature of 298.15 K extract for 8 min (shown in Fig. 8).

It can be seen from Fig. 8 that, at the phase ratio (O/A) of 2, with two theoretical extraction series, a few cobalt ions (<0.01 g/L) remained in the raffinate. However, to ensure the extraction efficiency of cobalt, the extraction stage usually needs one more stage than the theoretical stage in the actual operation process. Furthermore, a three-stage countercurrent extraction simulation study was carried out at O/A ratio of 2 : 1 to confirm the prediction. The results of the three-stage countercurrent extraction experiment are shown in Table 4.

The experimental results show that the content of cobalt and nickel in the organic phase after three-stage countercurrent extraction was 5.0409 g/L and 0.0089 g/L, respectively. Simultaneously, the extraction efficiency of cobalt was 99.997%, and the distribution ratio was as high as 50409.5. The extraction efficiency of nickel was only 0.270%, indicating that nickel was difficult to extract by N235 under the optimal conditions determined above. To sum up, three-stage countercurrent extraction can achieve a perfect separation of cobalt and nickel in the hydrochloric acid solution. More than 99% of the cobalt was extracted into the loaded organic phase, while less than 1% of the nickel was extracted into the loaded organic phase. The experimental results were highly consistent with the predicted results of the McCabe-Thiele diagrams of extraction cobalt.

5. Stripping Cobalt from the Loaded Organic Phase

Stripping of cobalt and recycling of the organic phase are very important for continuous extraction systems. When N235 is used to extract and separate cobalt and nickel, the stripping agent is usually pure water. Therefore, in subsequent stripping experiments, pure water was used as a stripping agent for stripping cobalt from the loaded organic phase.

5-1. Influence of Phase Ratio (O/A)

The influence of the phase ratio (O/A) on stripping of cobalt was studied in the range of 3-0.5 at temperature of 298.15 K stripping for 5 min. The stripping efficiency of cobalt under different

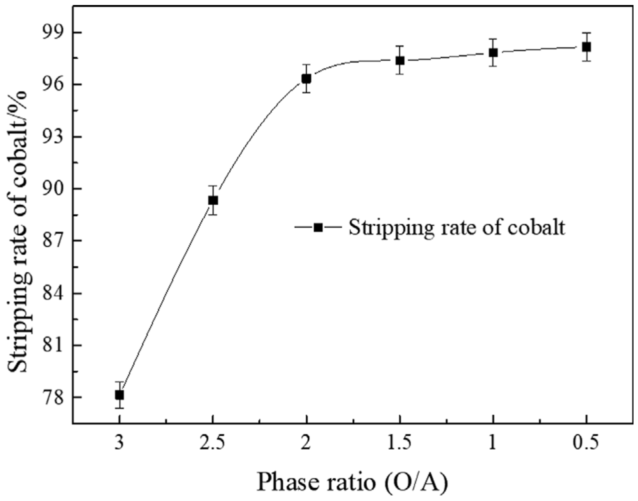

Fig. 9. The stripping efficiency of cobalt under different phase ratio (O/A).

phase ratio (O/A) is shown in Fig. 9.

It can be seen from the results of the stripping experiments that when the phase ratio (O/A) decreased from 3.0 to 0.5, the single-stage cobalt stripping efficiency increased from 78.16% to 98.16% (shown in Fig. 9), and as the phase ratio (O/A) was reduced from 3.0 to 1.5, the stripping efficiency of cobalt increased from 78.16% to 97.38%, but as the phase ratio (O/A) was reduced from 1.5 to 0.5, the stripping efficiency of cobalt remained basically unchanged. Therefore, when pure water was used as a stripping agent for stripping cobalt from the loaded organic phase, the best phase ratio (O/A) was determined to be 1.5.

5-2. McCabe-Thiele Diagrams

To determine the number of stripping stages, the experiment of stripping cobalt from the organic phase containing 5.0409 g/L cobalt was performed with pure water under different the phase ratio (O/A) conditions; after phase separation, the cobalt ion concentration of the two phases was analyzed. The McCabe-Thiele diagram is illustrated in Fig. 10.

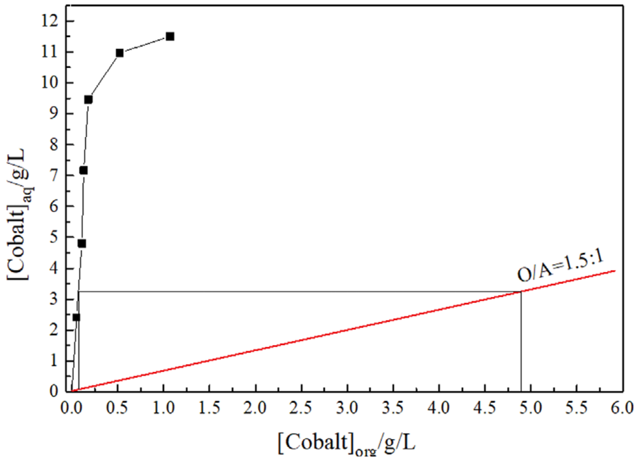

Fig. 10. McCabe-Thiele equilibrium isotherm for Co stripping.

Experimental results illustrated that the single-stage stripping extraction of cobalt can be exceed 99% at an O/A ratio of 1.5 : 1 and contact time of 8 min, and the residual cobalt concentration was lower than 0.1 g/L. The stripping stage usually needs one more stage than the theoretical stage in the actual operation process. Furthermore, a two-stage countercurrent stripping simulation study was carried out at the phase ratio (O/A) of 1.5; experimental results showed that the stripping efficiency of cobalt can reach 99.964%. The concentration of cobalt in the organic phase had dropped from 5.0409 g/L to 0.0018 g/L, indicating that the use of pure water as a stripping agent can basically achieve complete cobalt removal from the organic phase.

6. Thermodynamic Analysis

In the high concentration chloride ion solution, the reason why the amine extractant N235 can extract and separate cobalt and nickel is because N235 has a good extraction effect on the tetrahedral $CoCl_4^{2-}$ ions formed by cobalt ions. The reaction formula of the extraction process is as follows:

$$Co^{2+}+6Cl^{-}+2H^{+}+2R_3N_{(org)}=(R_3NH)_2CoCl_4 \tag{8}$$

$$K_{ex}=\frac{[(R_3NH)_2CoCl_4]}{[Co^{2+}]\times[Cl^{-}]^6\times[H^{+}]^2\times[R_2N]^3} \tag{9}$$

$$D=\frac{[(R_3NH)_2CoCl_4]}{[Co^{2+}]} \tag{10}$$

where, K_{ex} is the extraction equilibrium constant at a certain temperature, D is the metal distribution efficiency.

After modification of Eq. (10), Eq. (11) can be obtained, and after taking differentiation T of the Eq. (9), the Eq. (12) can be obtained.

$$lgD=lgK_{ex}+lg[Co^{2+}]+6lg[Cl^{-}]+2pH+2lg[R_3N] \tag{11}$$

$$\frac{dlgD}{dT}=\frac{dlgK_{ex}}{dT} \tag{12}$$

The Eq. (13) and Eq. (14) can be obtained from the van't Hoff equation.

$$\frac{dlgK}{dT}=\frac{\Delta H}{2.303RT^2} \tag{13}$$

$$lgD=-\frac{\Delta H}{2.303RT}+C \tag{14}$$

where, R is the gas constant (8.314 kJ·mol^{-1}), T is the absolute temperature, and C is the integral constant.

Based on the analysis of the above extraction theory, the initial chloride ion concentration was 9 mol/L, the O/A ratio was 2, and the N235 concentration was 30% (v/v); the extraction was performed at different temperatures for 8 minutes (298.15-338.15 K), and the extraction efficiencies and distribution efficiencies of cobalt

Table 5. Extraction efficiency (E) and distribution efficiency (D) of cobalt at different temperatures

T (K)	298.15	308.15	318.15	328.15	338.15
E (%)	97.73	96.62	95.26	94.05	92.08
D	21.526	14.293	10.049	7.903	5.813

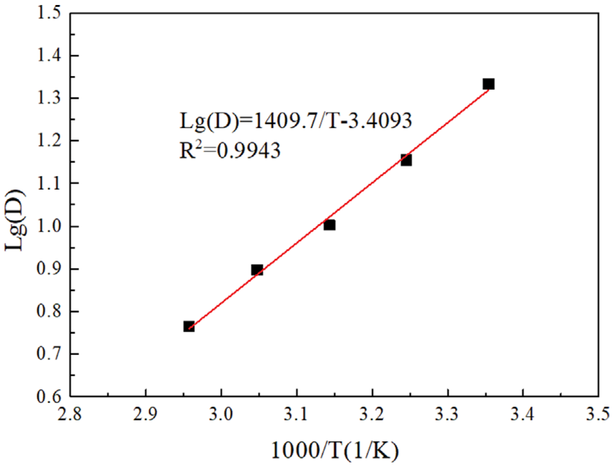

Fig. 11. Linear fitting result of log D versus 1000/T for cobalt separation using N235 as extractant.

were analyzed. The results are shown in Table 5.

According to the experimental results in Table 5, the linear regression equation (lgD-1000/T) was obtained, and the results are shown in Fig. 11. It can be clearly seen from the figure that the linear correlation coefficient was 0.9943, indicating that the fitting degree of the equation was very high. The enthalpy change of cobalt extraction at a certain temperature can be calculated as follows:

$$\Delta H = -2.303 R \times k = -2.303 \times 8.314 \times 1.4097 = -26.993\ \mathrm{kJ \cdot mol^{-1}}$$

where K is is the slope of the fitting equation.

The results show that the enthalpy change of the cobalt extraction process with N235 was $-26.993\ \mathrm{kJ \cdot mol^{-1}}$ ($\Delta H<0$), indicating that the extraction process of cobalt was an exothermic reaction, so low temperature is more conducive to the extraction of cobalt by N235.

7. Recovery Process of Copper, Cobalt, Nickel and Manganese from the Acid Leaching Solution of Ocean Cobalt-rich Crust

According to the research in chapter 3.1-3.6, the process of sep-

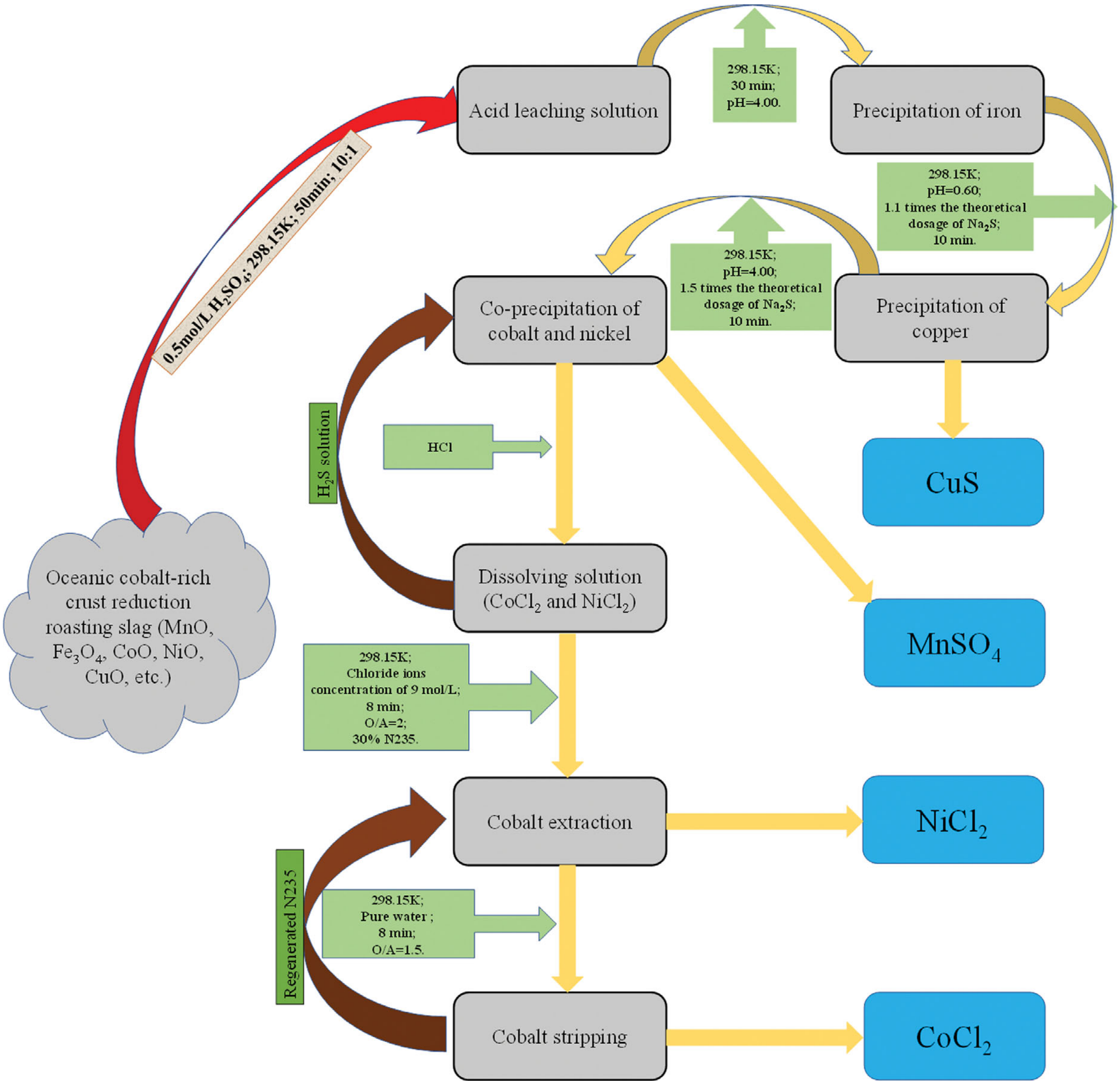

Fig. 12. Process flow of separation and recovery of copper, cobalt, nickel and manganese from the acid leaching solution of ocean cobalt-rich crust.

aration recovery of copper, cobalt, nickel and manganese from the acid leaching solution of ocean cobalt-rich crust was proposed (in Fig. 12).

First, the acid leaching solution of ocean cobalt-rich crust was pretreated, which the iron was removed as $Fe(OH)_3$ precipitation from the acid leaching solution by adjusting the pH value. Under the condition of the initial acid leaching solution pH value of 4.00 and precipitation at a temperature of 298.15 K for 30 minutes, 99.58% iron was precipitated, while valuable metals such as copper, cobalt, nickel and manganese in the acid leaching solution were hardly producing corresponding precipitation.

Then, based on the difference in sulfide solubility products of copper, cobalt, nickel and manganese, the experiments of precipitation of copper and co-precipitation of cobalt and nickel were carried out. The precipitation efficiency of copper can reach 99.87% under the condition of the initial pH of 0.60, Na_2S dosage 1.1 times the theoretical dosage, stirring speed of 500 r/min, precipitation 10 min at 298.15 K, while the precipitation efficiencies of cobalt and nickel were 1.23% and 1.08%, respectively, and the precipitation of manganese was not observed, which basically realized the complete precipitation (as CuS) of copper. Similarly, under the condition of the initial pH of 4.00, the Na_2S dosage was 1.5 times the theoretical dosage, a stirring speed of 500 r/min, precipitation 10 min at 298.15 K, 99.18% cobalt and 98.31% nickel were co-precipitated; a 70.082 g/L $MnSO_4$ solution was obtained.

Finally, the mixed cobalt-nickel precipitation was completely dissolved with hydrochloric acid. When the initial chloride ion concentration was 9 mol/L, the N235 concentration was 30% (v/v), the phase ratio (O/A) was 2, and the extraction temperature was 298.15 K for 8 min, the extraction efficiency of cobalt could reach 99.997%; through three-stage countercurrent extraction, complete extraction of cobalt was achieved, and a 14.522 g/L $NiCl_2$ solution was obtained. And, by using pure water as stripping agent, two-stage countercurrent stripping was carried out under the condition that the phase ratio (O/A) was 1.5; the results showed that the extraction efficiency of cobalt could could reach 99.964%, and the concentration of cobalt in the loaded organic phase was reduced to 0.0018 g/L. A 16.653 g/L $CoCl_2$ solution was obtained.

CONCLUSIONS

Separation of Cu, Co, Ni and Mn from the acid leaching solution of ocean cobalt-rich crust using precipitation (using Na_2S solution) and solvent extraction (using N235 extractant) was presented in this paper. The primary conclusions are summarized as follows:

(1) The actual ocean cobalt-rich crust acid leaching solution bearing 27.881 g/L Mn, 21.483 g/L Fe, 0.080 g/L Cu, 0.942 g/L Co and 0.631 g/L Ni was used to remove iron by precipitation method. When the pH of the solution was adjusted to 4.0 using NaOH solution at room temperature for 30 min, the iron removal efficiency reached 99.58%, and the filtrate after iron precipitation mainly contained 27.823 g/L Mn, 0.006 g/L Fe, 0.079 g/L Cu, 0.939 g/L Co and 0.630 g/L Ni.

(2) The precipitation efficiency of copper can reach 99.87% under the condition of the initial pH was 0.60, Na_2S dosage was 1.1 times the theoretical dosage, a stirring speed of 500 r/min, precipitation 10 min at 298.15 K, while, the precipitation efficiencies of cobalt and nickel were 1.23% and 1.08%, respectively, and the precipitation of manganese was not observed. Similarly, under initial pH of 4.00, the Na_2S dosage was 1.5 times the theoretical dosage, a stirring speed of 500 r/min, precipitation 10 min at 298.15 K, 99.18% cobalt and 98.31% nickel were precipitated, obtaining a 76.082 g/L $MnSO_4$ solution.

(3) When the initial chloride ion concentration was 9 mol/L, the N235 concentration was 30% (v/v), the phase ratio (O/A) was 2, and the extraction temperature was 298.15 K for 8 min, the extraction efficiency of cobalt can reach 99.997% through three-stage countercurrent extraction, and a 14.522 g/L $NiCl_2$ solution was obtained. When the phase ratio was 1.5, using pure water as a stripping agent, more than 99% of the cobalt in the loaded organic phase can be extracted after two-stage countercurrent stripping, and a 16.653 g/L $CoCl_2$ solution can be obtained. In addition, the thermodynamic analysis results of the extraction process showed that the extraction process of cobalt was an exothermic reaction; low temperature was more conducive to the extraction of cobalt by N235.

ACKNOWLEDGEMENTS

We are deeply grateful to COMRA for providing samples of this study. We gratefully acknowledge the financial support from long-term special project for National (Project No. JS-KTHT-2019-01) and the key Laboratory of Biochemical Engineering, Institute of Process Engineering, Chinese Academy of Sciences, Beijing 100190, China. Help from the Analytical & Testing Center of University of Science and Technology Beijing is also greatly appreciated.

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