Available online at www.sciencedirect.com
ScienceDirect
Trans. Nonferrous Met. Soc. China 32(2022) 3780−3789
Transactions of Nonferrous Metals Society of China
www.tnmsc.cn

Separation and recovery of Ni from copper electrolyte by crystallization of nickel ammonium sulfate double salt

Yi WANG[1,2], Biao LIU[1], Xue-wen WANG[1], Yu-qi MENG[1], Xing-ming WANG[1], Ming-yu WANG[1]

1. School of Metallurgy and Environment, Central South University, Changsha 410083, China;
2. School of Minerals Processing and Bioengineering, Central South University, Changsha 410083, China

Received 24 September 2021; accepted 22 December 2021

Abstract: The separation and recovery of Ni from the copper electrolyte by crystallization of nickel ammonium sulfate double salt were studied. It is found that the solubility of copper sulfate at the same temperature is less than that of nickel sulfate, while the solubility of copper ammonium sulfate is greater than that of nickel ammonium sulfate. So, by adding $(NH_4)_2SO_4$, the Ni can be selectively crystallized from the copper electrolyte. By adding $(NH_4)_2SO_4$ at the molar ratio of $(NH_4)_2SO_4/NiSO_4 \leq 0.8$, and crystallizing at −15 °C for 10 h, the Ni in the copper electrolyte can be crystallized in the form of $Ni(NH_4)_2(SO_4)_2{\cdot}6H_2O$. The qualified product of $NiSO_4{\cdot}6H_2O$ can be obtained by pyrolyzing the crystals, dissolving the pyrolysis product in water, and then concentrating the dissolved solution for crystallization. The method of double salt crystallization is a clean, environmentally-friendly, cost-effective and efficient method for separating and recovering nickel from copper electrolyte.

Key words: copper electrolyte; nickel; crystallization; nickel ammonium sulfate

1 Introduction

Ni is an associated element in copper concentrate. In copper electrolytic refining, Ni enters the electrolyte along with the dissolution of the anode and gradually accumulates in it. When the concentration of Ni in the electrolyte rises above 10 g/L, it begins to have an adverse effect on the current efficiency of copper electrolysis [1]. Separation and recovery of Ni is an important process in copper electrolyte purification [2].

The traditional process of separating and recovering Ni from the copper electrolyte is to first evaporate and crystallize copper sulfate, then conduct electrowinning to remove Cu, As, Sb and Bi in the form of black copper sludge, and further evaporation crystallize or freezing crystallize nickel sulfate [3,4]. The obtained nickel sulfate contains a lot of impurities, such as Cu, Fe, As, Ca, Mg, and Zn [5,6]. Therefore, many methods have been proposed for the refining of the crude nickel sulfate, such as sulfide precipitation [7], gradual oxidation followed by selective hydrolytic precipitation of the impurities [8], solvent extraction [9,10], ion exchange [11], and fluoride salt precipitation [12]. However, the methods described above have the disadvantages of long process route, high production cost, and low metal recovery rate [13].

Recently, it was found that the crystals of copper sulfate or nickel sulfate obtained from copper electrolyte contained the double salt of $Ni(NH_4)_2(SO_4)_2{\cdot}6H_2O$. The $(NH_4)_2SO_4$ is the metabolite of the additive thiourea, and its concentration is ~2.5 g/L in copper electrolyte [14]. This indicates that the nickel in copper electrolyte can be separated and recovered by adding $(NH_4)_2SO_4$. However, due to the lack of basic research and the wrong use of ammonia as the crystallization agent for nickel, the cost of separation

Corresponding author: Biao LIU, Tel: +86-752-5118888, E-mail: 754528868@qq.com
DOI: 10.1016/S1003-6326(22)66057-6

and recovery of nickel has risen sharply, and the method of double salt crystallization has to be abandoned [1]. The motivation of this study is not only to present the method of double salt crystallization is a cost-effective, clean and environmentally-friendly method for separating and recovering Ni from copper electrolyte, but also to let the readers understand the principle of the method.

2 Experimental

2.1 Materials and analysis

To study the separation and recovery of Ni from the copper electrolyte, synthetic and industrial copper electrolytes were used. The composition of the industrial copper electrolytes after evaporating and crystallizing copper sulfate and then removing impurities by self-purification [15] or electro-winning are listed in Table 1. The industrial electrolytes were taken from Guixi Smelter (China). The synthetic copper electrolytes were synthesized with H_2SO_4, $CuSO_4·5H_2O$, $NiSO_4·6H_2O$, $(NH_4)_2SO_4$, and distilled water. All reagents used are in analytical grade.

The compositions of experimental samples were determined by chemical methods and inductively coupled plasma emission spectroscopy (ICP-AES) with a PS−6 PLASMA SPECTROVAC, BAIRD (USA). The ammonia content in the solution is determined by distillation titration [16]. The X-ray diffraction (XRD) patterns were recorded on a Rigaku Miniflex diffractometer with Cu K_α X-ray radiation at 35 kV and 20 mA.

2.2 Experimental procedure

To determine the solubility of $CuSO_4$, $NiSO_4$, $Cu(NH_4)_2(SO_4)_2$ and $Ni(NH_4)_2(SO_4)_2$ in copper electrolyte, the solutions containing $CuSO_4$, $NiSO_4$, $CuSO_4$, and $NiSO_4$ were synthesized by dissolving $CuSO_4·5H_2O$ or/and $NiSO_4·6H_2O$ in different concentrations of H_2SO_4 solutions and adding $(NH_4)_2SO_4$ according to different mole ratios of $(NH_4)_2SO_4/NiSO_4$ or $(NH_4)_2SO_4/CuSO_4$. Solubilities of $CuSO_4·5H_2O$, $NiSO_4·6H_2O$, $Cu(NH_4)_2(SO_4)_2·6H_2O$, and $Ni(NH_4)_2(SO_4)_2·6H_2O$ in copper electrolyte were determined by putting the synthetic solutions in a low-temperature reaction bath at a constant temperature from 40 to −30 °C for 36 h. After filtration, the concentrations of copper, nickel, and ammonia in the solutions were measured.

3 Results and discussion

3.1 Solubility of sulfates of Cu and Ni

After copper electrolyte was evaporated and $CuSO_4·5H_2O$ crystallized, the concentrations of Cu, Ni, and H_2SO_4 in it are 20−30, 25−35, and 350−400 g/L respectively [17]. The recovery of Ni from the crystallization solution is achieved by first electrowinning to remove impurities and then freezing or evaporating to crystallize nickel sulfate. However, the obtained nickel sulfate contains many impurities, such as Cu, Fe, and As [5,6]. The properties of the aqueous solutions of copper sulfate and nickel sulfate are very similar. Therefore, it is necessary to further study the principle of crystallization and separation of Cu and Ni in copper electrolyte.

Figure 1 shows the system of H_2SO_4−H_2O crystallization diagram [18]. The copper electrolyte after $CuSO_4·5H_2O$ crystallization contains 376.5 g/L H_2SO_4 (see Table 1). As can be seen, the crystallized solution freezing point is below −30 °C. This is why freezing crystallization can be used to separate Ni from it. Figure 2 shows the solubility curves of $NiSO_4$ and $CuSO_4$ in different solutions, which were obtained by adding $CuSO_4·5H_2O$ and $NiSO_4·6H_2O$, respectively, in the solutions to supersaturate at 50 °C, and keep for 36 h at different temperatures. Figure 2 shows that the solubility of $NiSO_4$ and $CuSO_4$ decreases with the decrease in temperature and the increase in acidity, and the solubility of $NiSO_4$ is larger than that of

Table 1 Compositions of copper electrolyte after $CuSO_4·5H_2O$ crystallization and then electrowinning or self-purification (g/L)

Copper electrolyte	Cu	Ni	As	Sb	Bi	H_2SO_4	$(NH_4)_2SO_4$
Crystallized solution	11.76	30.15	23.88	2.29	1.51	376.5	5.93
Self-purified solution	11.75	30.14	6.84	0.17	0.09	364.3	5.91
Electrowinning solution	3.71	30.21	7.81	0.28	0.08	391.2	5.98

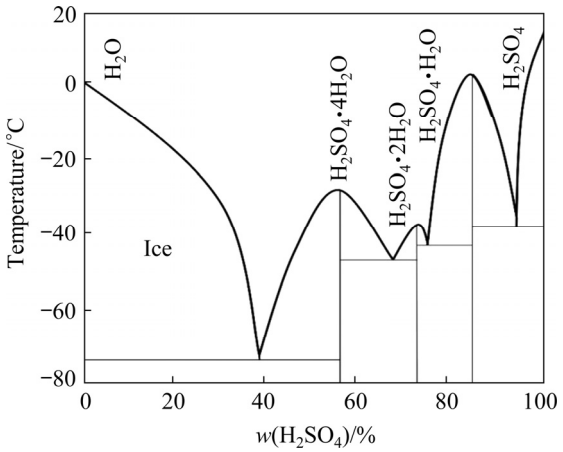

Fig. 1 H_2SO_4−H_2O system crystallization diagram

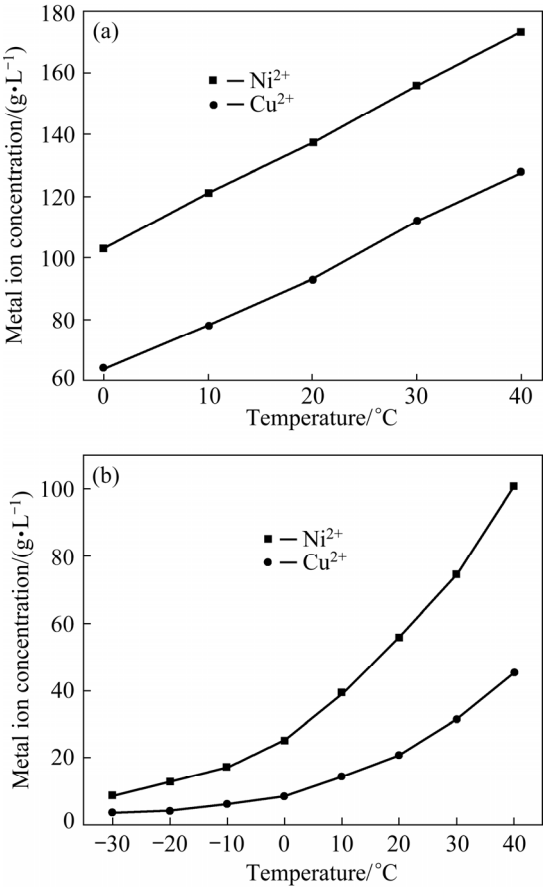

Fig. 2 Solubility of $CuSO_4·5H_2O$ and $NiSO_4·6H_2O$: (a) In water; (b) In 400 g/L H_2SO_4 solution

$CuSO_4$ under the same conditions. Figure 2(b) shows that in 400 g/L H_2SO_4 solution, saturation concentrations of Cu and Ni are 8.34 and 25.01 g/L, respectively, at 0 °C, and then they decrease to 4.15 and 12.47 g/L, respectively, when the temperature drops to −20 °C. This indicates that the crystallized solution listed in Table 1 must undergo electrowinning to remove Cu before freezing crystallization to reduce the content of Cu in nickel sulfate, and the crystallization rate of Ni generally does not exceed 70%. In fact, the crystallization rate of Ni in the electrowinning solution is usually only 55%−65% at −17 °C for 15−16 h, which is the industrial production conditions of nickel sulfate frozen crystallization.

It is well known that the solubility of sulfuric acid double salt of ammonium and copper or nickel is less than that of their sulfate salts. Therefore, using double salt crystallization can improve the crystallization rate of Ni from copper electrolyte. Figure 3 shows solubility curves of $Cu(NH_4)_2(SO_4)_2$ and $Ni(NH_4)_2(SO_4)_2$ in different solutions, which were obtained by adding $Cu(NH_4)_2(SO_4)_2·6H_2O$ and $Ni(NH_4)_2(SO_4)_2·6H_2O$, respectively, in the solutions to supersaturate at 50 °C, and then keeping for 36 h at different temperatures. Figure 3 shows that the solubility of $Cu(NH_4)_2(SO_4)_2$ and $Ni(NH_4)_2(SO_4)_2$ decreases with the decrease in temperature and the increase in acidity, and at the temperature above −25 °C, the solubility of $Cu(NH_4)_2(SO_4)_2$ is greater than that of $Ni(NH_4)_2(SO_4)_2$ under the same

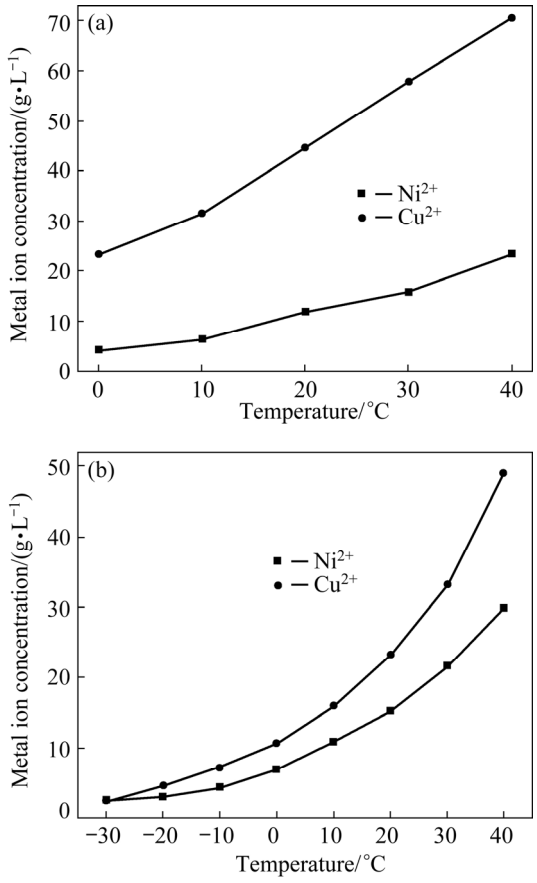

Fig. 3 Solubility of $Cu(NH_4)_2(SO_4)_2·6H_2O$ and $Ni(NH_4)_2(SO_4)_2·6H_2O$: (a) In water; (b) In 400 g/L H_2SO_4 solution

conditions. Figure 3(b) shows that in 400 g/L H_2SO_4 solution, the saturation concentrations of Cu and Ni are 10.71 and 6.99 g/L, respectively, at 0 °C, and then they decrease to 4.15 and 3.09 g/L, respectively, at −20 °C. This indicates that by adding $(NH_4)_2SO_4$ to the electrowinning solution listed in Table 1, and then crystallizing at the temperature above −20 °C, the Ni can be selectively separated and recovered in the form of $Ni(NH_4)_2(SO_4)_2·6H_2O$.

By comparing Figs. 2 and 3, it can be found that after crystallization of copper sulfate from the copper electrolyte, there is no need for electrowinning to remove copper. Directly adding ammonium sulfate can selectively crystallize and separate nickel. This avoids producing harmful substances such as black copper sludges [19].

3.2 Crystallization of Cu and Ni in H_2SO_4 solution containing $(NH_4)_2SO_4$

Figure 4 shows crystallization curves of Cu in different H_2SO_4 solutions, which were obtained by adding $(NH_4)_2SO_4$ into the solutions with 20−40 g/L Cu and different H_2SO_4 concentrations according to $(NH_4)_2SO_4/CuSO_4$ mole ratio of 1:1 and keeping the temperature at −15 °C for different time. As can be seen, the concentration of Cu in the solutions decreases with the increase in the crystallization time, and the crystallization basically reaches the equilibrium after 30 h. The concentration of Cu decreases in the solutions with the increase in acidity under the same conditions.

Figure 5 shows the XRD spectra of Cu crystal products formed in the solutions corresponding to Fig. 4 by keeping the temperature at −15 °C for 36 h. As can be seen, the crystals containing copper sulfate is unstable in the H_2SO_4 solutions. The structure of copper ammonium sulfate is $Cu(NH_4)_2(SO_4)_2·6H_2O$ in water, while in the solution of 200−300 g/L H_2SO_4, it partially becomes $Cu(NH_4)_2(SO_4)_2·2H_2O$, and then it turns into $CuSO_4·2H_2O$ and $CuSO_4·H_2O$ in 400−500 g/L H_2SO_4 solution. It is found by XRD-rietveld analysis that only 40.8 wt.% of the crystals formed in 200 g/L H_2SO_4 solution is $Cu(NH_4)_2(SO_4)_2·6H_2O$, and the rest is $Cu(NH_4)_2(SO_4)_2·2H_2O$. Then, as the

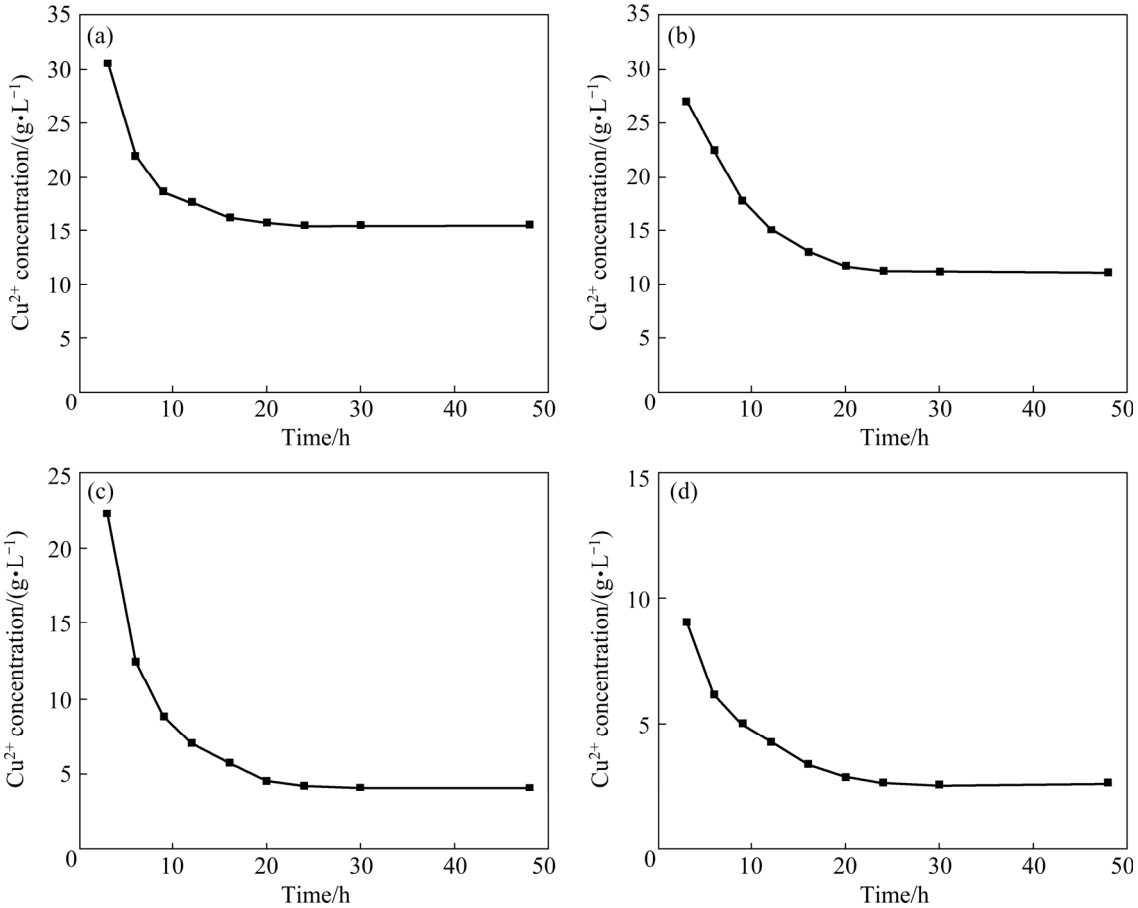

Fig. 4 Crystallization curves of Cu in different concentrations of H_2SO_4 solutions at −15 °C: (a) 200 g/L; (b) 300 g/L; (c) 400 g/L; (d) 500 g/L

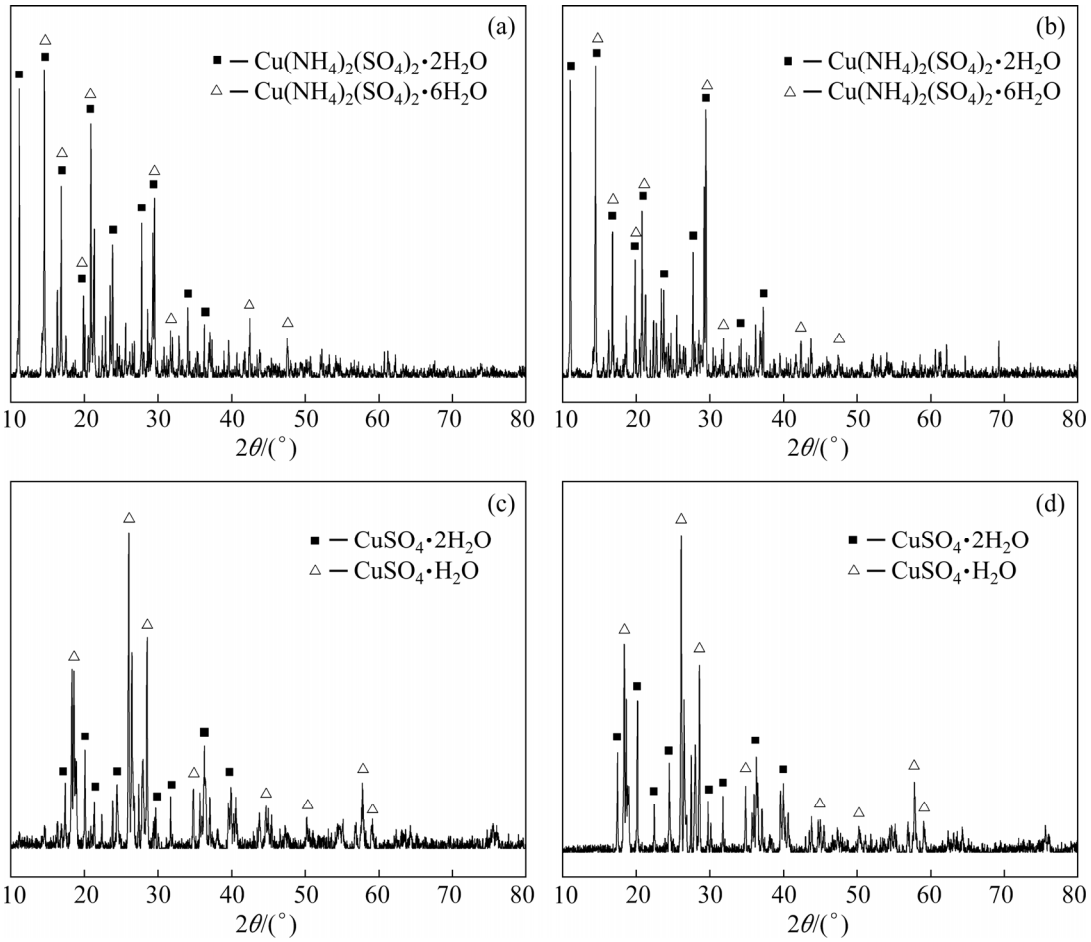

Fig. 5 XRD spectra of Cu crystal products formed in different concentrations of H_2SO_4 solutions by keeping at −15 °C for 36 h: (a) 200 g/L; (b) 300 g/L; (c) 400 g/L; (d) 500 g/L

concentration of H_2SO_4 increases to 300 g/L, the content of $Cu(NH_4)_2(SO_4)_2·6H_2O$ decreases to 32.8 wt.%. When the concentration of H_2SO_4 increases to 400 g/L, the phases of $Cu(NH_4)_2(SO_4)_2·6H_2O$ and $Cu(NH_4)_2(SO_4)_2·2H_2O$ in the crystals disappear, replaced by $CuSO_4·2H_2O$ and $CuSO_4·H_2O$. The contents of $CuSO_4·2H_2O$ and $CuSO_4·H_2O$ in the crystals formed in 400 g/L H_2SO_4 solution are 30.7 and 69.3 wt.%, respectively. The content of $CuSO_4·2H_2O$ in the crystals formed in 500 g/L H_2SO_4 solution is only 19.9 wt.%. This is because H_2SO_4 has dehydration properties, and the higher the concentration is, the stronger the dehydration properties are.

Figure 6 shows crystallization curves of Ni in different concentrations of H_2SO_4 solutions, which were obtained by adding $(NH_4)_2SO_4$ into the solutions with 20−40 g/L Ni and different H_2SO_4 concentrations according to $(NH_4)_2SO_4/NiSO_4$ mole ratio of 1:1 and keeping the temperature at −15 °C for different time. As seen, the concentration of Ni decreases rapidly with keeping time from 3 to about 10 h, and then it decreases slowly till 48 h. The concentration of Ni decreases in the solutions with the increase in acidity under the same conditions. This can explain why during copper sulfate crystallization, the loss of Ni in the form of nickel ammonium sulfate increases with the increase in the density of the copper electrolyte evaporation endpoint and when the evaporation endpoint density is controlled at 1.38−1.40 g/mL, the crystallized copper sulfate contains almost no Ni [14]. From Fig. 6(c), it can be found that by adding $(NH_4)_2SO_4$ into the electrowinning solution and freezing at −15 °C for 10 h, the crystallization rate of Ni can reach >80%. This shows that the method of double salt crystallization can not only significantly increase the crystallization rate of Ni, but also greatly shorten the crystallization time compared with nickel sulfate crystallization.

Figure 7 shows the XRD spectra of Ni crystal products formed in the solutions corresponding to

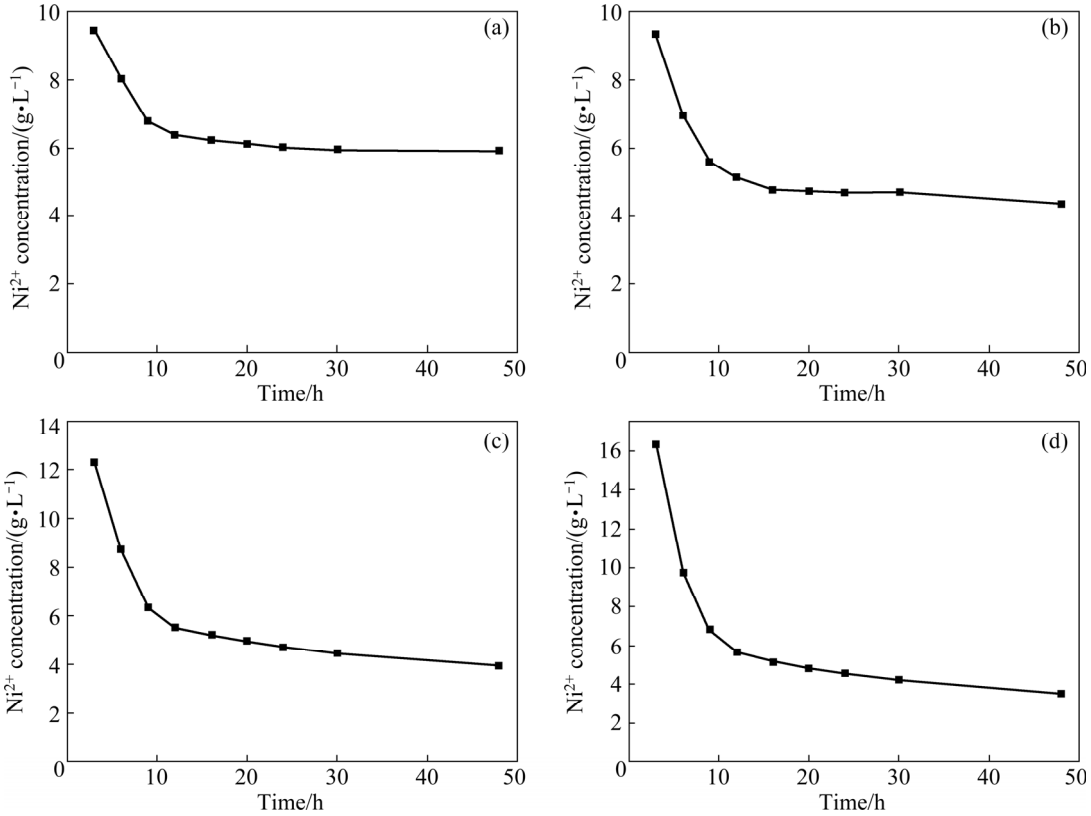

Fig. 6 Crystallization curves of Ni in different concentrations of H_2SO_4 solutions at −15 °C: (a) 200 g/L; (b) 300 g/L; (c) 400 g/L; (d) 500 g/L

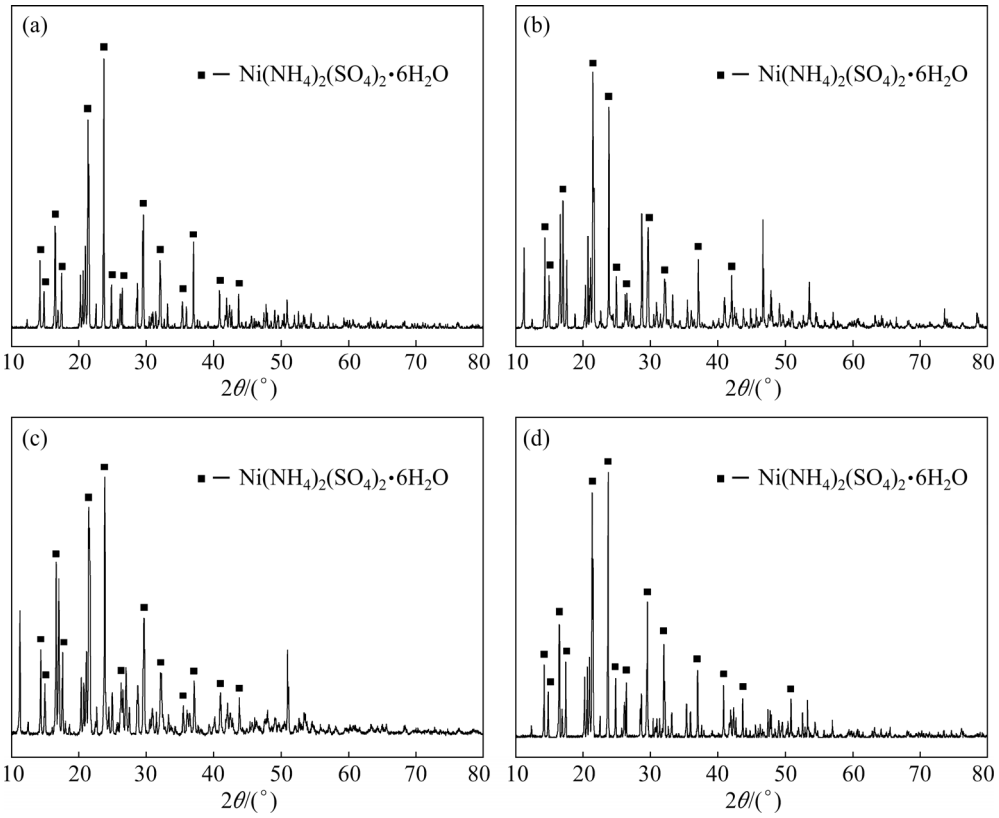

Fig. 7 XRD spectra of Ni crystal products formed in different concentrations of H_2SO_4 solutions by keeping at −15 °C for 36 h: (a) 200 g/L; (b) 300 g/L; (c) 400 g/L; (d) 500 g/L

Fig. 6 by keeping the temperature at −15 °C for 36 h. Figure 7 shows that the crystals formed by $NiSO_4$ and $(NH_4)_2SO_4$ in 200−500 g/L H_2SO_4 solutions are pure matters of $Ni(NH_4)_2(SO_4)_2{\cdot}6H_2O$. This indicates that the structure of $Ni(NH_4)_2(SO_4)_2{\cdot}6H_2O$ is stable in H_2SO_4 solutions. Based on the difference in solubility of Cu and Ni in the H_2SO_4 solution containing $(NH_4)_2SO_4$ in Figs. 4 and 6, by comparing Figs. 5 and 7, it can be found that by adding $(NH_4)_2SO_4$ into the electrowinning solution listed in Table 1 and freezing at −15 °C, the $Ni(NH_4)_2(SO_4)_2{\cdot}6H_2O$ crystals without Cu can be obtained. Moreover, by freezing the self-purified solution listed in Table 1 at −10 °C to further remove Cu, and then adding $(NH_4)_2SO_4$ to crystallize Ni at −15 °C, the crystals of $Ni(NH_4)_2(SO_4)_2{\cdot}6H_2O$ without Cu can be obtained as well. That is to say, to obtain copper-free nickel ammonium sulfate crystals from copper electrolyte using the method of double salt crystallization, the concentrations of H_2SO_4 and Cu should be maintained at ≥400 and ≤6 g/L, respectively. In this way, the production of black copper sludge can be avoided, and the method of double salt crystallization become a clean, environmentally-friendly, cost-effective and efficient method for separating and recovering Ni from copper electrolyte.

3.3 Separation of Ni from copper electrolyte

Table 2 gives the experimental results of double salt crystallization to separate Ni from the self-purified solution listed in Table 1, which were obtained by adding $(NH_4)_2SO_4$ into it according to different $(NH_4)_2SO_4/NiSO_4$ mole ratios and keeping the temperature at −20 °C for 16 h. As can be seen, the Cu and Ni contents remaining in the solution both decrease with the increase in $(NH_4)_2SO_4/NiSO_4$ mole ratio, and the decreasing rate of Ni is faster than that of Cu. This indicates that $NiSO_4$ in the copper electrolyte is easier to combine with $(NH_4)_2SO_4$ to form a double salt than $CuSO_4$. Figure 8 shows the XRD spectra of the crystals obtained by adding $(NH_4)_2SO_4$ according to $(NH_4)_2SO_4/NiSO_4$ mole ratio of 1:1 into the solution and keeping at −20 °C for 16 h. As seen, the obtained crystals are mixtures of $Cu(NH_4)_2(SO_4)_2{\cdot}6H_2O$ and $Ni(NH_4)_2(SO_4)_2{\cdot}6H_2O$. The contents of $Cu(NH_4)_2(SO_4)_2{\cdot}6H_2O$ and $Ni(NH_4)_2(SO_4)_2{\cdot}6H_2O$ in the crystals obtained by XRD-rietveld analysis are 12.1 and 87.9 wt.%, respectively, which is consistent with the results calculated from Tables 1 and 2. This shows that as long as $Ni(NH_4)_2(SO_4)_2{\cdot}6H_2O$ exists, $Cu(NH_4)_2(SO_4)_2{\cdot}6H_2O$ can also be formed even in the solution containing 300−400 g/L H_2SO_4. This is due to the similar structure of $Ni(NH_4)_2(SO_4)_2{\cdot}6H_2O$ and $Cu(NH_4)_2(SO_4)_2{\cdot}6H_2O$. Cu^{2+} ions can exist in the form of isomorphism in the crystals.

Table 2 shows that the utilization rate of $(NH_4)_2SO_4$ becomes higher and higher with the decrease in $(NH_4)_2SO_4/NiSO_4$ mole ratio, and its utilization rate is close to 100% when the molar ratio is ≤0.8. This indicates that as long as the $(NH_4)_2SO_4/NiSO_4$ mole ratio is ≤0.8, $(NH_4)_2SO_4$ will not accumulate in the solution, and if the solution contains Cu ≤8.5 g/L, by controlling $(NH_4)_2SO_4/NiSO_4$ mole ratio ≤0.8, the $(NH_4)_2SO_4$ can be quantitatively combined with Ni to form the crystals of $Ni(NH_4)_2(SO_4)_2{\cdot}6H_2O$ without Cu. Therefore, to recover Ni from the copper electrolyte by double salt crystallization, the mole ratio of $(NH_4)_2SO_4/NiSO_4$ should be maintained at ≤0.8.

Table 3 gives the experimental results obtained by freezing the electrowinning solution listed in

Table 2 Experimental results of double salt crystallization to separate Ni from self-purified solution

$(NH_4)_2SO_4/NiSO_4$ mole ratio	Concentration of residual Ni/ ($g{\cdot}L^{-1}$)	Concentration of residual Cu/ ($g{\cdot}L^{-1}$)	Concentration of residual $(NH_4)_2SO_4$/ ($g{\cdot}L^{-1}$)	Ni crystallization rate/%	$(NH_4)_2SO_4$ utilization rate/%
0.7	11	10.7	5.59	64.98	100.52
0.8	9.2	10.02	6.4	70.71	99.31
0.9	7.08	8.97	7.42	77.46	97.8
1	5.31	8.44	8.17	83.09	96.69
1.1	4.22	7.8	9.79	86.56	94.3
1.2	2.54	6.7	11.29	91.91	92.11

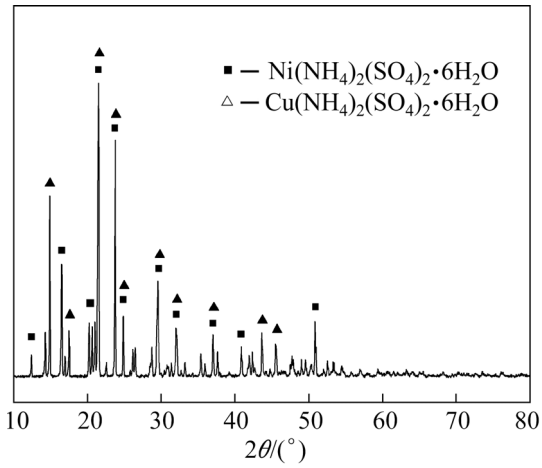

Fig. 8 XRD spectra of crystals formed in copper electrolyte listed in Table 1 by adding $(NH_4)_2SO_4$ according to $(NH_4)_2SO_4/NiSO_4$ mole ratio of 1:1 and then keeping at −20 °C for 16 h

Table 1 by adding or without adding $(NH_4)_2SO_4$ to crystallize nickel at −15 °C for 16 h. The addition of $(NH_4)_2SO_4$ in the solution is according to $(NH_4)_2SO_4/NiSO_4$ mole ratio of 0.8. It can be seen from Table 3 that after adding $(NH_4)_2SO_4$ with an $(NH_4)_2SO_4/NiSO_4$ mole ratio of 0.8, the recovery of Ni is 80.02%, and the concentration of $(NH_4)_2SO_4$ in the solution hardly changes before and after crystallization. However, without the addition of $(NH_4)_2SO_4$, the crystallization rate of Ni is only ~60%, and copper must be removed by electrowinning before Ni crystallization. Therefore, the double salt crystallization not only effectively improves the crystallization efficiency of Ni in the copper electrolyte, but also greatly reduces the cost of Ni separation and recovery.

Table 4 gives the compositions of the crystals obtained from the solutions listed in Table 3. It can be seen from Table 4 that the purity of nickel sulfate obtained by freezing crystallization without adding $(NH_4)_2SO_4$ is only 86.94 wt.%, while the purity of nickel ammonium sulfate obtained by adding $(NH_4)_2SO_4$ to freeze crystallization is 99.39 wt.%. This fully shows the purification advantage of double salt crystallization in separating nickel from the copper electrolyte.

3.4 Production of nickel sulfate

The decomposition temperature of $NiSO_4$ is above 840 °C, while that of $(NH_4)_2SO_4$, $CuSO_4$, and $FeSO_4$, etc is below 700 °C [20]. The $Ni(NH_4)_2(SO_4)_2·6H_2O$ listed in Table 4 was recrystallized and pyrolyzed at 760 °C for 3 h. Recrystallization can deeply separate the impurities, such as Ca, Na and As. Then, the pyrolysis product was added into boiling water under stirring to dissolve. During the dissolution, some $Ni(OH)_2$ was added to maintain the pH to 6.5−6.7. After filtration, the main components of the solution are listed in Table 5. As can be seen, the purity of $NiSO_4$ solution obtained by $Ni(NH_4)_2(SO_4)_2·6H_2O$ recrystallization, pyrolysis, dissolution and filtration has met the needs of nickel sulfate crystallization. The product of nickel sulfate with a purity of 99.9 wt.% was obtained by concentrating

Table 3 Compositions of electrowinning solution after freezing crystallization nickel sulfate or nickel ammonium sulfate (g/L)

Copper electrolyte	Cu	Ni	As	Sb	Bi	H_2SO_4	$(NH_4)_2SO_4$
Without adding $(NH_4)_2SO_4$	3.83	12.14	14.20	0.29	0.08	400.6	2.53
Adding $(NH_4)_2SO_4$	3.83	6.01	14.21	0.29	0.08	401.4	5.91

Table 4 Compositions of crystals obtained from solutions listed in Table 3 (wt.%)

Copper electrolyte	Ni	Cu	As	Sb	Bi	Fe	Zn	Ca	Pb
Without adding $(NH_4)_2SO_4$	19.57	0.61	0.18	0.02	0.01	0.21	0.24	0.12	0.02
Adding $(NH_4)_2SO_4$	14.78	0.14	0.03	0.01	0.01	0.03	0.05	0.01	0.01

Table 5 Composition of dissolved solution of $Ni(NH_4)_2(SO_4)_2·6H_2O$ pyrolysis product (mg/L)

Ni	Na	Cu	As	Sb	Bi	Fe	Zn	Ca	Mg
56.89*	19	3	<1	<1	<1	2	35	15	11

*—g/L

crystallization. The flue gas produced in the pyrolysis is absorbed by water to recover $(NH_4)_2SO_4$. The dissolved residue obtained by filtration is used for comprehensive recovery. The production mechanism of nickel sulfate by $Ni(NH_4)_2(SO_4)_2·6H_2O$ pyrolysis and dissolution can be expressed by the following reactions:

$$3Ni(NH_4)_2(SO_4)_2·6H_2O \triangleq 3NiSO_4+4NH_3\uparrow+3SO_2\uparrow+9H_2O\uparrow+N_2\uparrow \quad (1)$$

$$2FeSO_4 \triangleq 2FeO+O_2\uparrow+2SO_2\uparrow \quad (2)$$

$$2CuSO_4·5H_2O \triangleq 2CuO+O_2\uparrow+2SO_2\uparrow+10H_2O\uparrow \quad (3)$$

$$4ZnSO_4·7H_2O \triangleq 2ZnO·ZnSO_4+O_2\uparrow+2SO_2\uparrow+28H_2O\uparrow \quad (4)$$

$$ZnSO_4+Ni(OH)_2=NiSO_4+Zn(OH)_2\downarrow \quad (5)$$

$$2NH_3+SO_2+H_2O_2=(NH_4)_2SO_4 \quad (6)$$

4 Conclusions

(1) Both $NiSO_4$ and $CuSO_4$ can combine with $(NH_4)_2SO_4$ to form the double salts containing ammonium. The double salts are $Ni(NH_4)_2(SO_4)_2·6H_2O$ and $Cu(NH_4)_2(SO_4)_2·6H_2O$, respectively. At the same temperature, the solubility of $CuSO_4$ is less than that of $NiSO_4$, while the solubility of $Ni(NH_4)_2(SO_4)_2·6H_2O$ is less than that of $Cu(NH_4)_2(SO_4)_2·6H_2O$.

(2) In copper electrolyte, $(NH_4)_2SO_4$ is preferentially combined with $NiSO_4$ to form a double salt. As long as the amount of $(NH_4)_2SO_4$ added is well controlled, selective crystallization of $Ni(NH_4)_2(SO_4)_2·6H_2O$ can be achieved in the purification of copper electrolyte.

(3) If Cu concentration is ≤6 g/L in the copper electrolyte containing 380−400 g/L H_2SO_4, by adding $(NH_4)_2SO_4$ according to $(NH_4)_2SO_4/NiSO_4$ mole ratio ≤0.8, not only the crystal of $Ni(NH_4)_2(SO_4)_2·6H_2O$ without Cu can be obtained, but also the accumulation of $(NH_4)_2SO_4$ can be avoided after freezing crystallization at −15 °C for 8−10 h. The obtained $Ni(NH_4)_2(SO_4)_2·6H_2O$ can be used to produce qualified nickel sulfate products.

Acknowledgments

The authors are grateful for the financial supports from the National Natural Science Foundation of China (No. 50274075).

References

[1] NYIRENDA R L, PHIRI W S. The removal of nickel from copper electrorefining bleed-off electrolyte [J]. Minerals Engineering, 1998, 11: 23−37.

[2] ZHAO Tian-cong. Metallurgy of heavy metals [M]. Beijing: Metallurgical Industry Press, 1981. (in Chinese)

[3] AGRAWAL A, BAGCHI D, KUMARI S, KUMARI S, KUMAR V, PANDEY B. Recovery of nickel powder from copper bleed electrolyte of an Indian copper smelter by electrolysis [J]. Powder Technology, 2007, 177: 133−139.

[4] WANG Xue-wen, CHEN Qi-yuan, YIN Zhou-lan, WANG Ming-yu, XIAO Bing-rui, ZHANG Fan. Homogeneous precipitation of As, Sb and Bi impurities in copper electrolyte during electrorefining [J]. Hydrometallurgy, 2011, 105: 355−358.

[5] JI Li-lei. The preparation of superfine nickel oxide from crude nickel sulfate [D]. Zhenjiang: Jiangsu University of science and Technology, 2018. (in Chinese)

[6] HAVLÍK T, ŠROBIAN M, KAMMEL R, KURILLA J, CMOREJOVÁ D. Refining of crude nickel sulphate obtained from copper electrolyte [J]. Hydrometallurgy, 1996, 41: 79−88.

[7] ALISON L, ROB H. An exploration into the sulphide precipitation method and its effect on metal sulphide removal [J]. Hydrometallurgy, 2006, 81: 197−204.

[8] HAVLÍK T, ŠKROBIAN M, KAMMEL R, CURILLA J, CMOREJOVÁ, D. Refining of crude nickel sulphate obtained from copper electrolyte [J]. Hydrometallurgy, 1996, 41: 79−88.

[9] GUPTA B, DEEP A, SINGH V, TANDON S. Recovery of cobalt, nickel, and copper from sea nodules by their extraction with alkylphosphines [J]. Hydrometallurgy, 2003, 70: 121−129.

[10] SILVA J, PAIVA A, SOARES D, LABRINCHA A, CASTRO F. Solvent extraction applied to the recovery of heavy metals from galvanic sludge [J]. Journal of Hazardous Materials, 2005, 120: 113−118.

[11] ZBIGNIEW H. Purification of nickel sulfate using chelating ion exchangers and weak-base anion exchangers [J]. Hydrometallurgy, 1986, 16: 361−375.

[12] ZENG Gui-sheng, LING Bo, LI Zhong-jun, LOU Sheng-lian, SUI Xin-zhen, GUAN Qian. Fluorine removal and calcium fluoride recovery from rare-earth smelting wastewater using fluidized bed crystallization process [J]. Journal of Hazardous Materials, 2019, 373: 313−320.

[13] WU Xiao-li. Study on purification of crude nickel sulfate [J]. Copper Engineering, 2018(5): 52−56. (in Chinese)

[14] LIU Biao. A new technology of copper electrolyte purification [D]. Changsha: Central South University, 2018. (in Chinese)

[15] WANG Xing-ming, WANG Xue-wen, LIU Biao, WANG Ming-yu, WANG Hua-guang, LIU Xue-hui, ZHOU Sheng-fan. Promotion of copper electrolyte self-purification with antimonic oxides [J]. Hydrometallurgy, 2018, 175: 28−34.

[16] ILEANA Z G, FERNANDO E C T, URIEL H H B,

VICTOR A R, JUAN P R P. Mobile digital colorimetry for the determination of ammonia in aquaculture applications [J]. Computers and Electronics in Agriculture, 2021, 181: 105960.

[17] WANG Xue-wen. Study on the mechanism of the formation and action of arsenato antimonic acid in copper electrorefining [D]. Changsha: Central South University, 2003. (in Chinese)

[18] CHEN Si-wei, DING Yi, YANG Chun-rong. Chromium salt production process [M]. Beijing: Chemical Industry Press, 1988. (in Chinese)

[19] PAZ D C, PÉREZ S M, RUIZ O I, RÍOS G, BOLÍVAR J P. Copper recovery from sludges generated in the electrolyte treatment plant of a pyrometallurgical complex [J]. Hydrometallurgy, 2021, 206: 105769.

[20] LIANG Yin-jiao, CHE Yin-chang, LIU Xiao-xia, LI Nai-jun. Handbook of inorganic thermodynamic data [M]. Shenyang: Northeastern University Press, 1993. (in Chinese)

硫酸镍铵复盐结晶法分离回收铜电解液中的镍

王 懿[1,2]，刘 彪[1]，王学文[1]，孟钰麒[1]，王兴明[1]，王明玉[1]

1. 中南大学 冶金与环境学院，长沙 410083；
2. 中南大学 资源加工与生物工程学院，长沙 410083

摘 要：研究采用硫酸镍铵复盐结晶从铜电解液中分离回收镍的方法。研究发现，在相同温度的溶液中，硫酸铜的溶解度小于硫酸镍的溶解度，而硫酸铜铵的溶解度大于硫酸镍铵的溶解度。因此，加入$(NH_4)_2SO_4$可使铜电解液中的镍选择性结晶析出。按$(NH_4)_2SO_4/NiSO_4$摩尔比≤0.8加入$(NH_4)_2SO_4$，在−15 ℃冷冻结晶10 h，可使其中的镍以$Ni(NH_4)_2(SO_4)_2·6H_2O$的形式结晶析出。将所得结晶物热解，再将热解产物加水溶解，最后将溶解液浓缩结晶得到合格的$NiSO_4·6H_2O$产品。复盐结晶法是一种清洁环保、经济高效的从铜电解液中分离回收镍的方法。

关键词：铜电解液；镍；结晶；硫酸镍铵

(Edited by Bing YANG)