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Simultaneous extraction of metals from nickel concentrate via NH_4HSO_4 roasting−water leaching process and transformation of mineral phase

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Abstract: Low-temperature NH_4HSO_4 roasting−water leaching process was proposed to extract Ni, Cu and Co from Jinchuan nickel concentrate simultaneously. The effects of some factors on the metal extraction in the process of sulfation roasting and water leaching were systematically investigated. The results showed that 95.7% Ni, 98.9% Cu and 96.8% Co were extracted under optimized roasting and water leaching conditions. The transformation evolution of mineral phases was determined through the means of DTA−TG, XRD, SEM and EDS. The valuable metals were effectively extracted by being transformed to water-soluble metal−ammonium complexes under the sulfation reaction of NH_4HSO_4 and decomposed SO_3 and NH_3. Iron impurities in the leach solution can be removed by elevating leaching temperature to combine iron ions with ammonium ions to form $NH_4[Fe_3(SO_4)_2(OH)_6]$ precipitate. The volatiles collected in the roasting process were determined to be $(NH_4)_2SO_4$ and $(NH_4)_2SO_3$, which can be used as reagents for sulfation roasting.

Key words: nickel concentrate; NH_4HSO_4 roasting; simultaneous extraction; water leaching; mineral phase transformation

1 Introduction

Nickel is an indispensable material for the development of modern aerospace industry, military industry and medical equipment industry. With the rapid development of the non-ferrous metal industry, China has become the world's largest producer and consumer of nickel products [1]. Jinchuan Nickel Mine is the most important copper−nickel sulfide deposit in China and the third largest magmatic polymetallic co-associated deposit in the world [2,3], which can produce 4.25×10^3 t of nickel and 1.13×10^2 t of cobalt every year [4]. In recent years, with the intensified mining of nickel ore, high-grade nickel ore has been exhausted and replaced by low-grade nickel ore with high content of alkaline gangue [5]. Due to the sludging of gangue in the beneficiation process, the produced concentrate has lower nickel grade and higher MgO

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content. When the concentrate is treated by the traditional high-temperature smelting process, the slag with high viscosity is produced in the furnace, resulting in the reduction of metals recovery and nickel matte grade [6]. In addition, in the blowing process of low nickel matte, part of cobalt and nickel is lost due to oxidation into slag. Therefore, it is urgent to elaborate an economical, efficient and clean technology for processing nickel concentrate.

In terms of hydrometallurgy, early pressurized ammonia leaching has been eliminated by industrial production due to high equipment requirements and low extraction of precious metals. HUANG et al [7] developed a high-pressure acid leaching process for low-grade nickel concentrate. The leaching rate of Cu and Ni reached more than 95% and 99%, respectively, when the temperature was 200 °C and the pressure was 1.8 MPa, and only 1% iron entered into the leaching solution. In order to avoid the operation difficulty of high-pressure process, atmospheric acid leaching of concentrated H_2SO_4 or dilute HCl was studied [8−12]. Although the leaching rate of some metals is relatively high in the acid leaching process, the service life of the equipment is shortened due to acid corrosion, and the high Mg content in the concentrate also increases the acid consumption.

Recently, the process of low-temperature roasting followed by leaching has attracted more and more attention due to the improvement of corrosion resistance of materials. Chlorination roasting of the solid chlorinating agents, such as $CaCl_2$ [13], NaCl [14,15], NH_4Cl [16], $AlCl_3$ [17], $FeCl_3·6H_2O$ [18] and $MgCl_2$ [19], has been used to process low-grade nickel sulfide ore. The SO_2 or SO_3 formed by S in the roasting process of sulfide ore concentrates to the chlorination process [20,21]. The resulting soluble salts contain metal chlorides and metal sulfates, so the separation and purification of metals need to be further explored. LI et al [22] conducted sulfated roasting of nickel sulfide concentrate at 650 °C for 2 h, and 90% Ni, 92% Co, 95% Cu and <1% Fe were leached [22]. Compared with the chlorination roasting process, the sulfated product of metal sulfide is only metal sulfate, which is more favorable for the subsequent treatment of leaching solution. However, sulfuric acid roasting seriously corrodes the equipment and the operating environment is poor. The roasting of low-grade nickel sulfide ore with ammonium sulfate was carried out by our research group, but the extraction of valuable metal is slightly low [23,24]. Although adding sodium sulfate can improve the reaction interface and reduce the activation energy of the reaction to increase metal extraction, it also causes some problems of sodium sulfate recovery and recycling [25]. The acidity of ammonium bisulfate is weaker than sulfuric acid, but stronger than ammonium sulfate. Ammonium bisulfate roasting has demonstrated high reaction efficiency and low energy consumption in extracting metals from metal oxide ores. The gas released in the roasting process is easy to recover and recycle. However, it is rare to use the method of ammonium bisulfate roasting to process nickel sulfide ores. The regulation of metal extraction and the transformation mechanism of mineral phase in the roasting process need to be further investigated to provide the basis for the industrial application of the ammonium bisulfate roasting process.

In this work, a process of NH_4HSO_4 roasting−water leaching was proposed to treat Jinchuan nickel concentrate, to simultaneously extract valuable metals. The effect of various factors on the extraction of nickel, iron, copper, cobalt and magnesium in the roasting process was investigated, and suitable process parameters for extracting metals were determined. The effect of temperature, time and liquid-to-solid ratio in the leaching process on metal conversion was optimized to obtain a method to remove iron. XRD, DTA−TG and SEM were used to analyze the composition and morphology of samples to clarify the transformation evolution of metallic minerals.

2 Experimental

2.1 Materials

The raw material used in this work was high-grade nickel concentrate obtained by flotation of low-grade nickel ore from Jinchuan Group, China. After crushing and ball milling, the concentrate powder was dried at 80 °C for the experiments. All chemical reagents used were of analytical grade, and the deionized water was used.

The median diameter and specific surface area of the concentrate powder measured by laser particle size distribution analyzer (BT−2003) and

pore size specific surface area analyzer (SSA−4300) were 22.54 μm and 232.98 m^2/kg, respectively. The chemical composition of the concentrate detected by S8 TIGER II XRF is shown in Table 1. It can be seen that the valuable metals contained in the concentrate are Ni, Cu and Co, and their contents are 9.6%, 6.8% and 0.2%, respectively. The impurity metals are mainly 34.8% Fe and 5.7% MgO.

Table 1 Chemical composition of nickel concentrates (wt.%)

S	TFe	Ni	Cu	Co
27.9	34.8	9.6	6.8	0.2
MgO	SiO_2	Al_2O_3	CaO	Others
5.7	7.3	0.5	0.6	6.6

The mineral phase composition of the concentrate was determined by Rigaku-Smart lab XRD, and the results in Fig. 1 show that the main minerals contained in the concentrate are $CuFeS_2$, $(Ni,Fe)_9S_8$, FeS_2 and $Mg_3Si_4O_{10}(OH)_2$.

The morphology of the concentrate powder was analyzed by ZEISS-Sigma scanning electron microscope (SEM). Figures 2(a) and (b) present that the ground concentrate powders are of irregular shapes and different sizes. The particles exhibit two

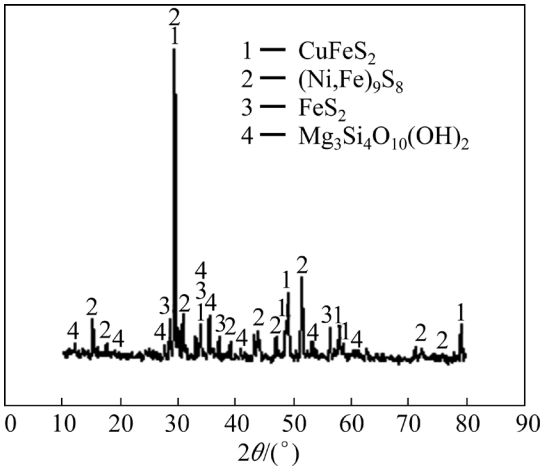

Fig. 1 XRD pattern of nickel concentrate

morphologies: loose layered structure and smooth surface. The smooth structure at Spot 1 is enriched with sulfur, iron and copper as chalcopyrite, as seen in Fig. 2(c). While the layered structure at Spot 2 contains high content of magnesium, oxygen and silicon forming gangue according to EDS analysis in Fig. 2(d).

2.2 Experimental procedure

A scale of 10 g of dry concentrate powder was weighed and evenly mixed with NH_4HSO_4 according to a certain mass ratio. Then, the mixture

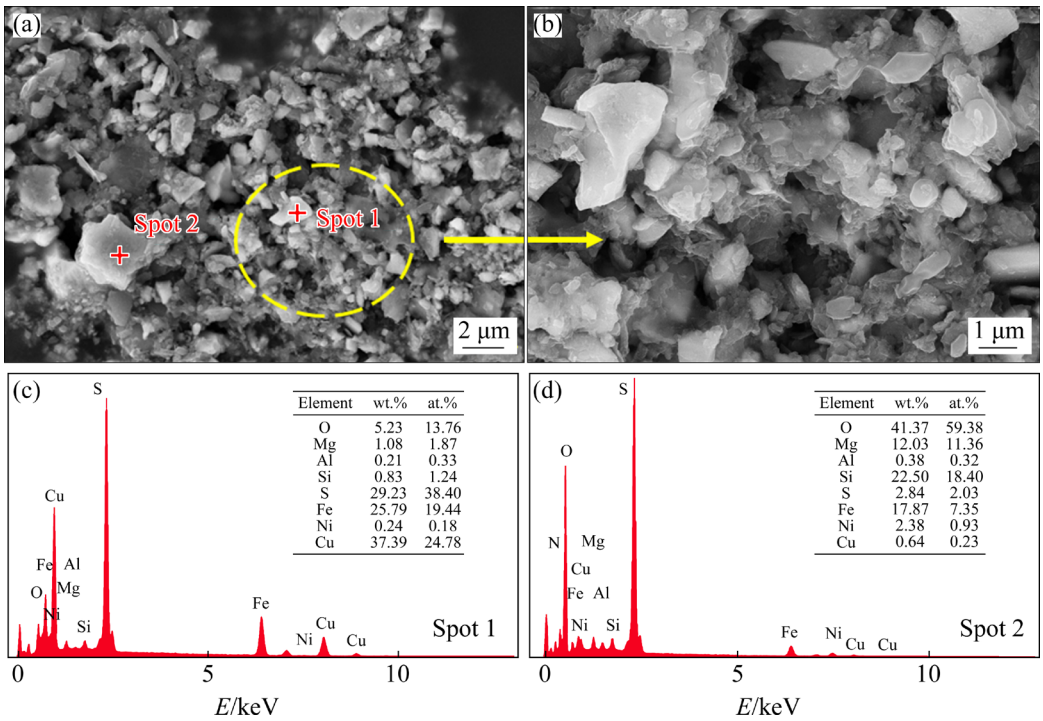

Fig. 2 SEM images (a, b) and EDS analyses (c, d) of concentrate powder

was placed in a ceramic crucible and roasted in a closed tube furnace with an exhaust gas absorber. The heating rate of the furnace was controlled at 10 °C/min. When the preset temperature was reached, the sample was held at this temperature for a period of time. After that, the heating was stopped, and when the furnace temperature dropped to 80 °C, the roasted clinker was leached and washed with water to collect the leach solution. The concentration of Ni, Cu, Co, Fe and Mg in the leach solution was measured by atomic absorption method, and the extraction of metal was calculated according to Eq. (1).

$$x_i = \frac{\rho_i V_i}{10 w_i} \times 100\% \quad (1)$$

where x_i is the extraction of metal (%), ρ_i is the concentration of a metal ion in the leach solution (g/L), V_i is the volume of leach solution (L), and w_i is the mass fraction of metal in the concentrate (%).

When the optimal conditions of the roasting process were investigated, the leaching conditions were fixed as follows: liquid-to-solid ratio (mL/g) of 6:1, leaching temperature of 80 °C, stirring speed of 450 r/min, and leaching time of 60 min. When the leaching experiment was carried out, the raw material used was 10 g of clinker obtained under the optimized roasting conditions. The entire process flow is shown in Fig. 3.

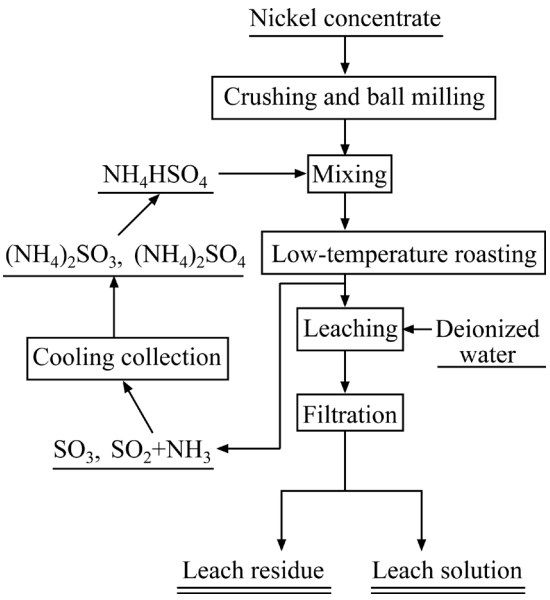

Fig. 3 Flow chart of roasting−water leaching process of concentrate

3 Results and discussion

3.1 Roasting process

3.1.1 Roasting mechanism

NH_4HSO_4 is decomposed in the heating process according to the following reaction equations, and the products produced such as $(NH_4)_2S_2O_7$, SO_2 and SO_3 can be used as acidifiers [26].

$$2NH_4HSO_4=(NH_4)_2S_2O_7+H_2O(g) \quad (2)$$

$$3(NH_4)_2S_2O_7=6SO_2(g)+2N_2(g)+2NH_3(g)+9H_2O(g) \quad (3)$$

$$NH_4HSO_4=NH_3(g)+SO_3(g)+H_2O(g) \quad (4)$$

The DTA−TG curves of the mixture of NH_4HSO_4 and concentrate (at a mass ratio of 8:1) between room temperature and 800 °C were measured by a differential thermogravimetric analyzer (Diamond 6300, USA), and the results are shown in Fig. 4(a). It can be seen that there are four endothermic peaks (141, 430, 488 and 672 °C) and one exothermic peak (305 °C) on the DTA curve, corresponding to the mass changes at four stages on the TG curve. The endothermic peak at 141 °C can be attributed to the decomposition of NH_4HSO_4,

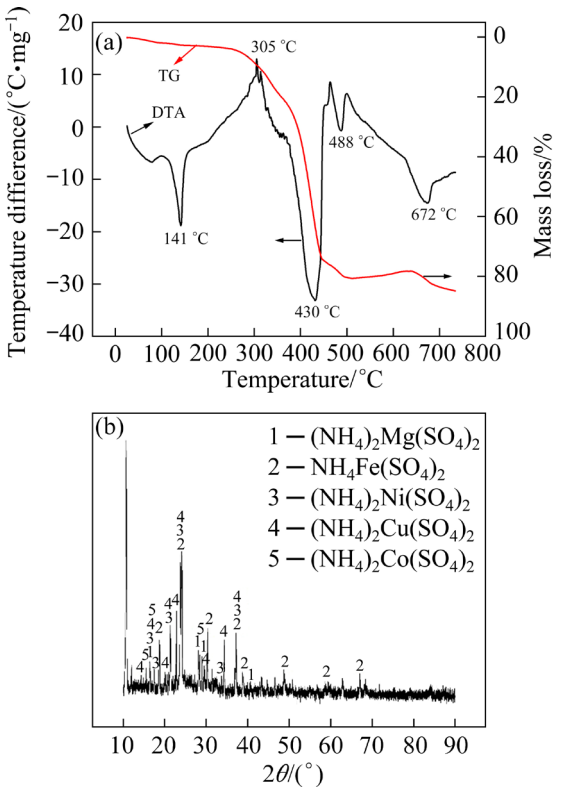

Fig. 4 DTA−TG analysis results of mixture of concentrate and NH_4HSO_4 (a), and XRD pattern of roasted clinker (b)

with a mass loss of approximately 6.6%. The exothermic peak at 305 °C is caused by the oxidation of metal sulfides. The endothermic peak at 430 °C corresponds to the sulfation reaction of metal-bearing minerals. These two reactions result in a mass loss of approximately 66.67%. The endothermic peak at 488 °C is generated by the decomposition of some metal−ammonium complexes and ferric sulfates, with a mass loss of approximately 8.6%. The endothermic peak at 672 °C is caused by the decomposition of $CuSO_4$, causing a mass loss of 8.6 %.

The XRD pattern of the clinker obtained at 400 °C in Fig. 4(b) shows that the main phases in the clinker are $NH_4Fe(SO_4)_2$, $(NH_4)_2Cu(SO_4)_2$, $(NH_4)_2Ni(SO_4)_2$, $(NH_4)_2Co(SO_4)_2$, and $(NH_4)_2Mg(SO_4)_2$. Compared with the XRD pattern in Fig. 1, the diffraction peaks of $CuFeS_2$, $(Ni, Fe)_9S_8$, FeS_2 and $Mg_3Si_4O_{10}(OH)_2$ disappear, indicating that they have been transformed into metal−ammonium complexes. The chemical reaction equations can be expressed as Eqs. (5)−(9).

$$4CuFeS_2+16NH_4HSO_4+13O_2=4(NH_4)_2Cu(SO_4)_2+4NH_4Fe(SO_4)_2+4NH_3+8SO_2+10H_2O \quad (5)$$

$$FeS_2+3NH_4HSO_4+2O_2=NH_4Fe(SO_4)_2+2NH_3+3SO_2+2H_2O \quad (6)$$

$$2(Ni,Fe)_9S_8+149NH_4HSO_4=18NH_4Fe(SO_4)_2+18(NH_4)_2Ni(SO_4)_2+95NH_3+93SO_2+122H_2O \quad (7)$$

$$Mg_3Si_4O_{10}(OH)_2+6NH_4HSO_4=3(NH_4)_2Mg(SO_4)_2+4SiO_2+4H_2O \quad (8)$$

$$2NH_4Fe(SO_4)_2=Fe_2(SO_4)_3+2NH_3+SO_3+H_2O \quad (9)$$

The SEM images of the clinker in Fig. 5 show that the concentrate particles are completely disintegrated after roasting, resulting in irregular shapes and different sizes of the clinker. Many flaky particles and whiskers gather together separately. The EDS analysis in Fig. 5(c) shows that the flaky particles located at Spot 3 contain high content of nitrogen, oxygen and sulfur, forming metal−ammonium complexes. The EDS analysis in Fig. 5(d) shows that the whiskers located at Spot 4 contain high content of sulfur, iron and oxygen, forming iron-bearing sulfates. The transformation evolution of nickel concentrate in the roasting process using NH_4HSO_4 is shown in Fig. 6. The main product at a roasting temperature below 400 °C is metal−ammonium complex. When the temperature is higher than 400 °C, some metal−ammonium complexes are transformed into metal sulfates [27]. As the temperature increases from 400 to 488 °C, ammonium ferric sulfate is

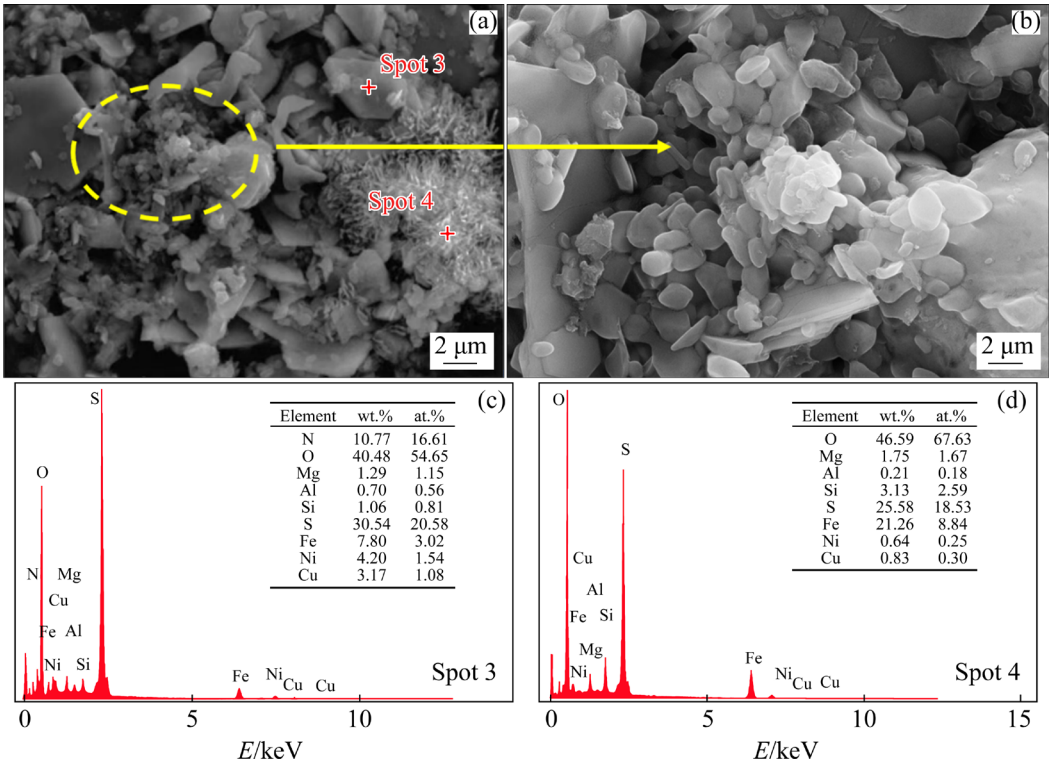

Fig. 5 SEM images (a, b) and EDS analyses (c, d) of clinker

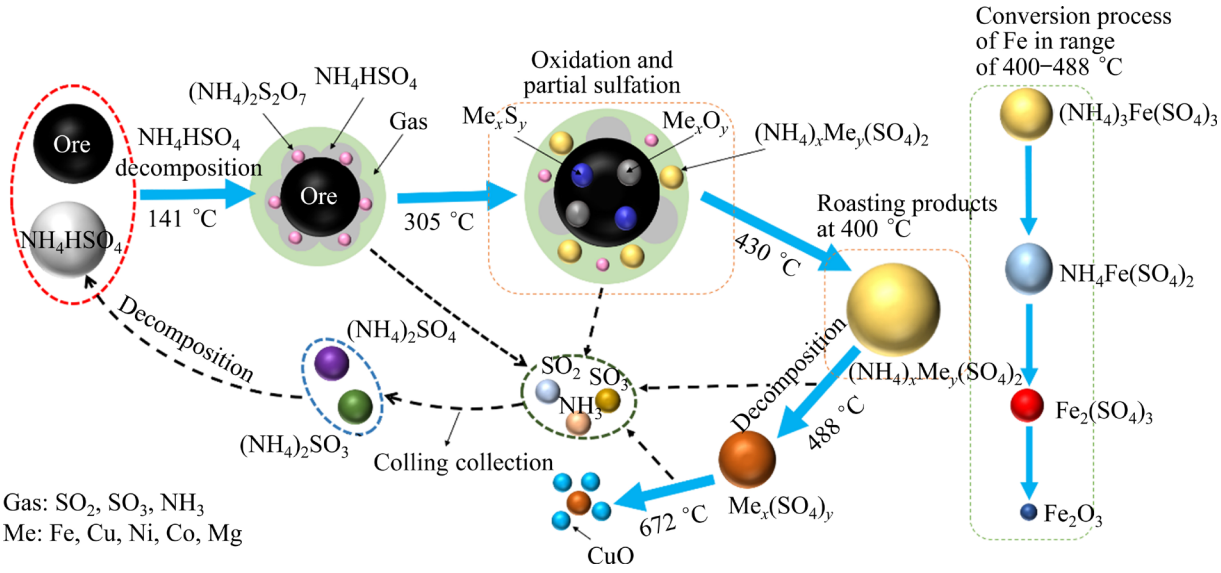

Fig. 6 Phase transformation of nickel concentrates in NH_4HSO_4 roasting process

firstly decomposed into ferric sulfate and finally transformed into insoluble ferric oxide. When the temperature is higher than 650 °C, copper sulfate can be decomposed into copper oxide [28,29].

3.1.2 Effect of concentrate particle size

The concentrate powder was sieved into six particle size fractions by electric vibrating screen as: 120−150, 109−120, 96−109, 80−96, 75−80 and <75 μm. The effect of particle size on the extraction of metal was investigated under the following conditions: NH_4HSO_4-to-concentrate mass ratio (N/C) 8:1, roasting time 180 min, and roasting temperature 400 °C. The results are shown in Fig. 7.

From Fig. 7(a), it can be seen that the concentrate particle size has a great effect on the extraction of Ni and Co, but little effect on the extraction of Cu, Fe and Mg. As the particle size decreases from 120−150 to 80−96 μm, the extraction of Ni, Co and Cu increases from 86%, 83.5% and 97% to 95.6%, 96.2% and 98.9%, respectively. When the particle size is smaller than 80−96 μm, the extraction of Cu decreases slightly, while the extraction of other metals remains constant. The specific surface area and reactivity of particles can be improved by reducing the particle size of concentrate. This not only strengthens the diffusion process of the sulfation reagent but also increases the reaction interface area, thereby improving the extraction of the metal. The Ni, Co and Cu in the concentrate with a particle size of

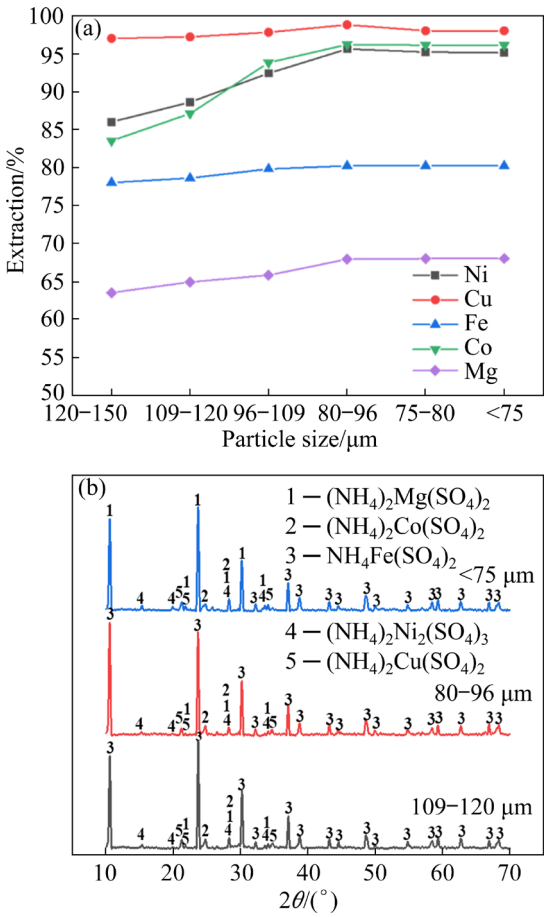

Fig. 7 Effect of concentrate particle size on extraction of metal (a), and XRD pattern of clinker with different particle sizes (b)

80−96 μm can be fully reacted, and the extraction of Fe and Mg can reach 80.2% and 67.9%, respectively. Therefore, 80−96 μm is selected as the

suitable condition for subsequent experiments. From Fig. 7(b), it can be seen that the metal-bearing minerals in the concentrate with different particle sizes after sulfation roasting are transformed into metal−ammonium complexes.

3.1.3 Effect of N/C ratio

When the concentrate particle size was 80−96 μm, the roasting time was 180 min, and the roasting temperature was 400 °C, the effect of N/C on the extraction of metal was investigated. The results in Fig. 8(a) show that N/C has a significant effect on the extraction of metal. The extraction of Co increases continuously with the increase of N/C, reaching 96.2% at the N/C of 8:1, then remains constant with the further increase of N/C. The extraction of Cu increases rapidly from 61% (N/C 2:1) to 95% (N/C 3:1), and then there is no significant change with the further increase of N/C. The extraction of Fe and Mg increases slowly with the increase of N/C. The extraction of Ni increases first and then tends to be stable with the increase of N/C, reaching the maximum value of 95.6% when N/C is 8:1. As NH_4HSO_4 dosage increases, the reaction interface between the concentrate particles and NH_4HSO_4 increases, thereby improving the sulfation rate of metal. From the XRD pattern of Fig. 8(b), it can be seen that with the increase of N/C from 3:1 to 9:1, the diffraction peak intensity of $(NH_4)_2Cu(SO_4)_2$, $(NH_4)_2Fe(SO_4)_2$, and $(NH_4)_2Ni(SO_4)_2$ gradually increases. Considering the high extraction of valuable metals, the optimal N/C ratio is chosen to be 8:1.

3.1.4 Effect of roasting time

The effect of roasting time on the extraction of metal was investigated when the concentrate particle size was 80−96 μm, the N/C was 8:1, and the roasting temperature was 400 °C, and the results are shown in Fig. 9(a). It can be seen that the extraction of Ni and Mg increases by 11.5% and 12% to reach 95.6% and 67.9%, respectively, with the increase of roasting time from 60 to 180 min. However, when the roasting time is further

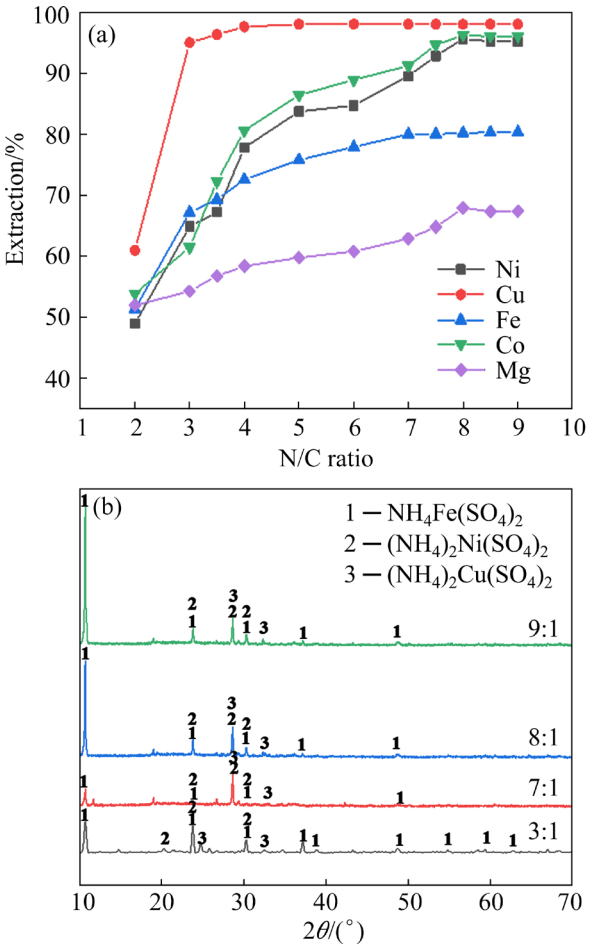

Fig. 8 Effect of N/C ratio on extraction of metal (a), and XRD pattern of clinker at different N/C ratios (b)

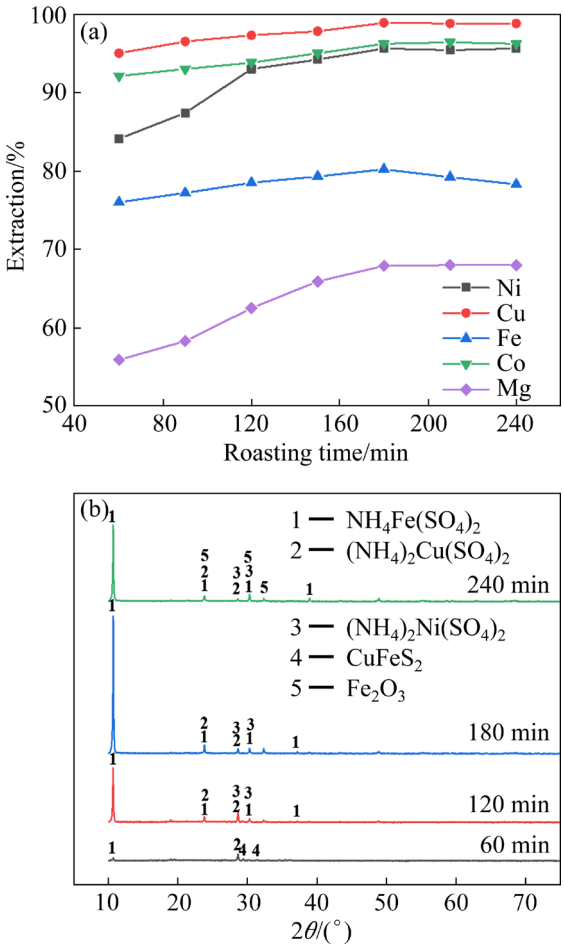

Fig. 9 Effects of roasting time on extraction of metal (a), and XRD pattern of clinker at different roasting time (b)

increased from 180 to 240 min, the extraction of Ni and Mg remains constant. The extraction of Cu, Co and Fe increases slightly with the increase of roasting time, reaching 98.9%, 96.2% and 80.2% at 180 min. While the extraction of Fe decreases at a roasting time longer than 180 min due to the decomposition of ferric sulfate into insoluble iron oxide. From XRD pattern of Fig. 9(b), it can be clearly seen that, the metal-bearing minerals disappear after roasting for 120 min due to being transformed into metal−ammonium complexes. When the roasting time reaches 240 min, the peak intensity of $NH_4Fe(SO_4)_2$ decreases significantly, indicating that a part of $NH_4Fe(SO_4)_2$ has been decomposed, thus reducing the extraction of Fe. Considering the effect of the increase of roasting time on the production efficiency, a suitable roasting time is selected as 180 min.

3.1.5 Effect of roasting temperature

The effect of temperature on the extraction of metal was investigated when the concentrate with the particle size of 80−96 μm was mixed with NH_4HSO_4 at N/C of 8:1 and roasted for 180 min. Figure 10(a) shows that roasting temperature has a significant effect on the extraction of Ni, Cu and Co. When the temperature is raised from 250 to 400 °C, the extraction of Ni, Cu and Co increases by 51.2%, 59.9% and 44.3% to reach the maximum of 95.6%, 98.8% and 96.2%, respectively. Afterwards, the extraction of Ni, Cu and Co decreases with the further increase of the temperature. The extraction of Fe and Mg also reaches the maximum of 80.2% and 67.9% at 400 °C, and then decreases slightly with the increase of the temperature. This is mainly attributed to the insufficient sulfation reagents caused by the rapid decomposition of NH_4HSO_4 at temperatures above 400 °C [26]. From Fig. 10(b), it can be seen that the metal-bearing minerals have been transformed into metal−ammonium complexes at 350 °C, while iron mainly exists in the form of $(NH_4)_3Fe(SO_4)_3$ and Fe_2O_3. At 400 °C, the diffraction peaks of $NH_4Fe(SO_4)_2$ are very obvious, which is generated by the decomposition of $(NH_4)_3Fe(SO_4)_3$. The diffraction peak of $(NH_4)_2S_2O_7$ is produced by the decomposition of NH_4HSO_4 and disappears at 450 °C due to its full decomposition. The diffraction peaks of the metal−ammonium complexes are also greatly reduced at 450 °C, indicating that the sulfation reaction of metal-bearing minerals was not complete. The result is consistent with the reduction of metal extractions in Fig. 10(a). In summary, the most suitable roasting temperature is chosen to be 400 °C.

3.1.6 Comparison with $(NH_4)_2SO_4$ roasting process

Compared with the $(NH_4)_2SO_4$ roasting process [24,26], NH_4HSO_4 roasting process in this study has the following improvements: (1) The roasting temperature is lower, and the products are mainly metal−ammonium complexes; (2) High metal extractions can be obtained without adding sodium sulfate; (3) There is no problem of sodium sulfate recovery in the subsequent solution, which simplifies the process. The specific comparisons are given in Table 2.

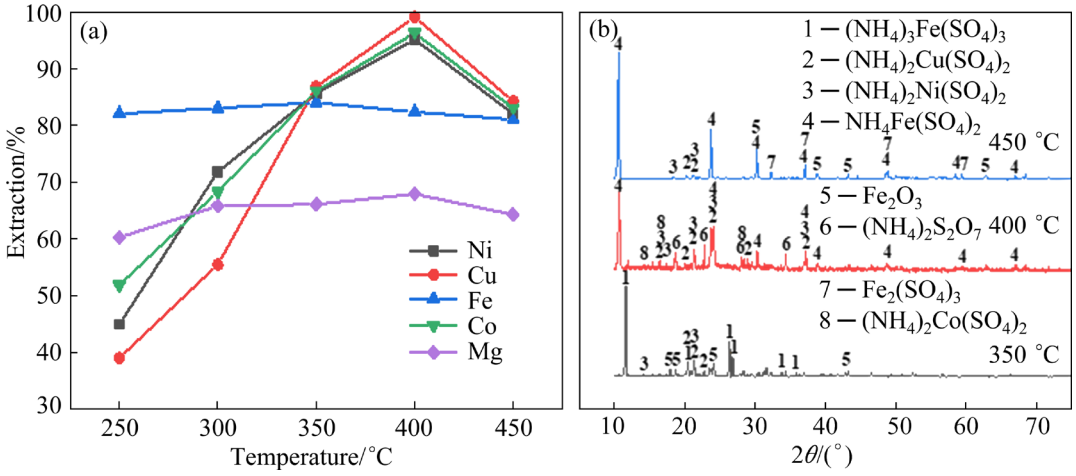

Fig. 10 Effect of roasting temperature on extraction of metal (a), and XRD pattern of clinker at different temperatures (b)

3.2 Water-leaching process

3.2.1 Effect of leaching temperature

Under the following conditions: leaching time 60 min, liquid-to-solid ratio 6:1, and stirring speed 450 r/min, the effect of leaching temperature on metal extractions was investigated. The results given in Fig. 11(a) show that the extraction of Ni, Cu, Co and Mg increases with the increase of leaching temperature and finally remains constant at the temperature above 80 °C. The leaching process of roasted clinker is the process of dissolving soluble metal−ammonium complexes in water. The increase of temperature can significantly increase the dissolution rate of the substance. However, the extraction of Fe decreases with the increase of temperature, because a large number of iron ions combine with NH_4^+ ions to form jarosite $NH_4[Fe_3(SO_4)_2(OH)_6]$ precipitation according to the step of Eq. (10). The increase of leaching temperature can accelerate the formation of jarosite to decrease iron concentration in the solution. Comprehensive consideration, the appropriate leaching temperature is chosen to be 80 °C.

$$NH_4Fe(SO_4)_2 \rightarrow Fe_2(SO_4)_3 \rightarrow FeOHSO_4 \rightarrow Fe_2(OH)_4SO_4 \rightarrow NH_4[Fe_3(SO_4)_2(OH)(OH)_6] \quad (10)$$

Table 2 Comparison between $(NH_4)_2SO_4$ roasting and NH_4HSO_4 roasting processes

Process	Roasting temperature/°C	Sulfating reagent	Roasting product	Treatment of leaching solution
$(NH_4)_2SO_4$ roasting	450−500	$(NH_4)_2SO_4$, NH_4HSO_4, mixed gas of NH_3, SO_2 and SO_3, Na_2SO_4	Metal sulfates	Considering recovery of sodium sulfate
NH_4HSO_4 roasting	400	NH_4HSO_4, mixed gas of NH_3, SO_2 and SO_3	Metal−ammonium complexes	–

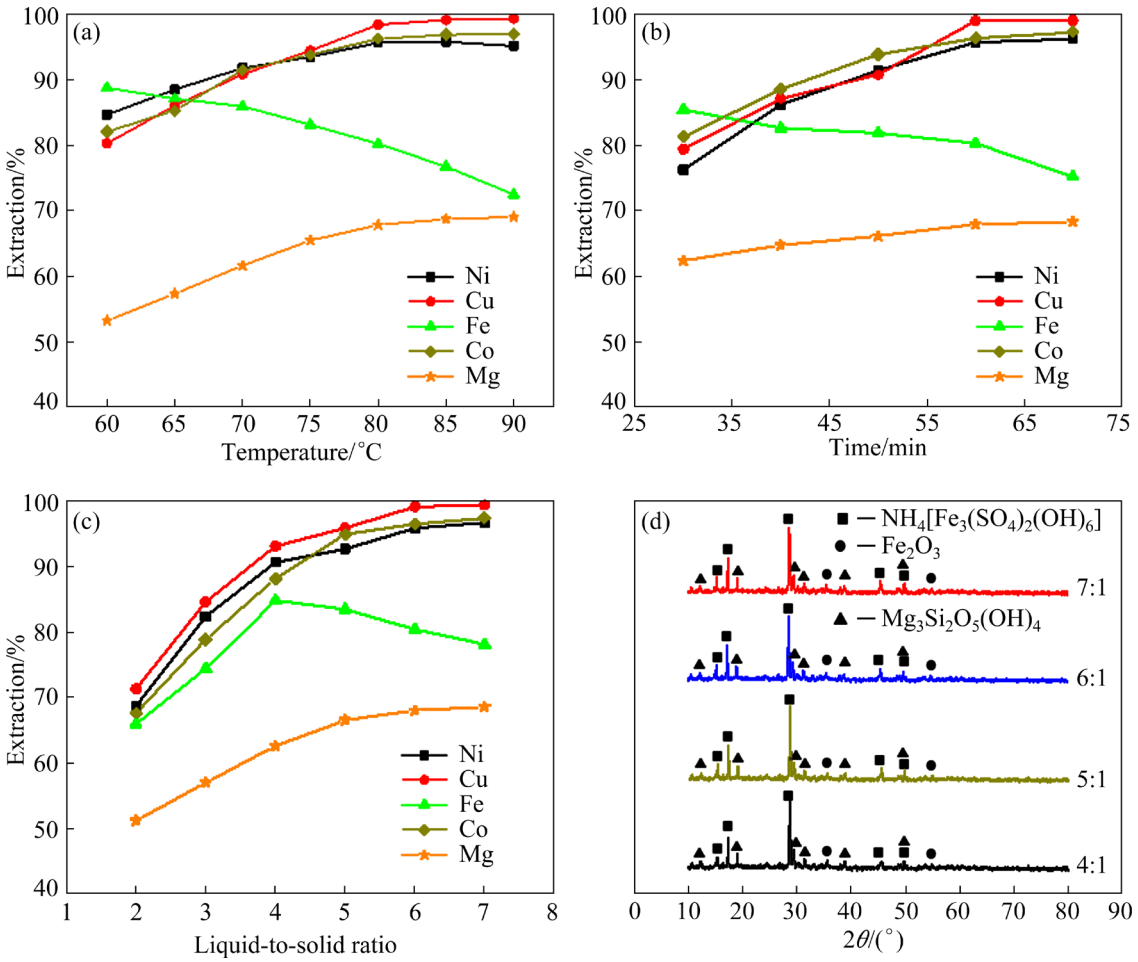

Fig. 11 Effect of various factors on extraction of metal: (a) Leaching temperature; (b) Leaching time; (c) Liquid-to-solid ratio; (d) XRD pattern of leach residue at different liquid-to-solid ratios

3.2.2 Effect of leaching time

The effect of leaching time on the extraction of metal was investigated when the leaching temperature is 80 °C, the liquid-to-solid ratio is 6:1, and the stirring speed is 450 r/min. The results in Fig. 11(b) shows that the extractions of Ni, Cu and Co all increase with the increase of leaching time, and then tend to be constant when the leaching time is greater than 60 min. While the extraction of Fe decreases with the increase of leaching time due to the increase of jarosite yield at 80 °C. The extraction of Mg is less affected by leaching time. Thus, the leaching time of 60 min is used for subsequent experiments.

3.2.3 Effect of liquid-to-solid ratio

The effect of liquid-to-solid ratio on the extraction of metal was carried out under the following conditions: leaching temperature 80 °C, leaching time 60 min, and stirring speed 450 r/min. From Fig. 11(c), it can be seen that the extraction of Ni, Cu and Co increases significantly with the increase of liquid-to-solid ratio from 2:1 to 6:1, and remains constant in the liquid-to-solid ratio range of 6:1 to 7:1. When the liquid-to-solid ratio is low, the metal−ammonium complexes produced in the roasting process cannot be fully dissolved, resulting in low metal extractions. With the increase of liquid-to-solid ratio, the viscosity of the leach solution decreases, which is conductive to the dissolution and diffusion of metal−ammonium complexes, thus improving the extraction of metal. The extraction of Fe decreases when the liquid-to-solid ratio exceeds 4:1 due to the increase of iron ion precipitation rate. The XRD pattern in Fig. 11(d) shows that when the liquid-to-solid ratio is greater than 4:1, the diffraction peak intensity of jarosite in the residue slightly increases, indicating that the amount of iron precipitation is slightly increased. In summary, 6:1 is selected as the suitable liquid-to-solid ratio.

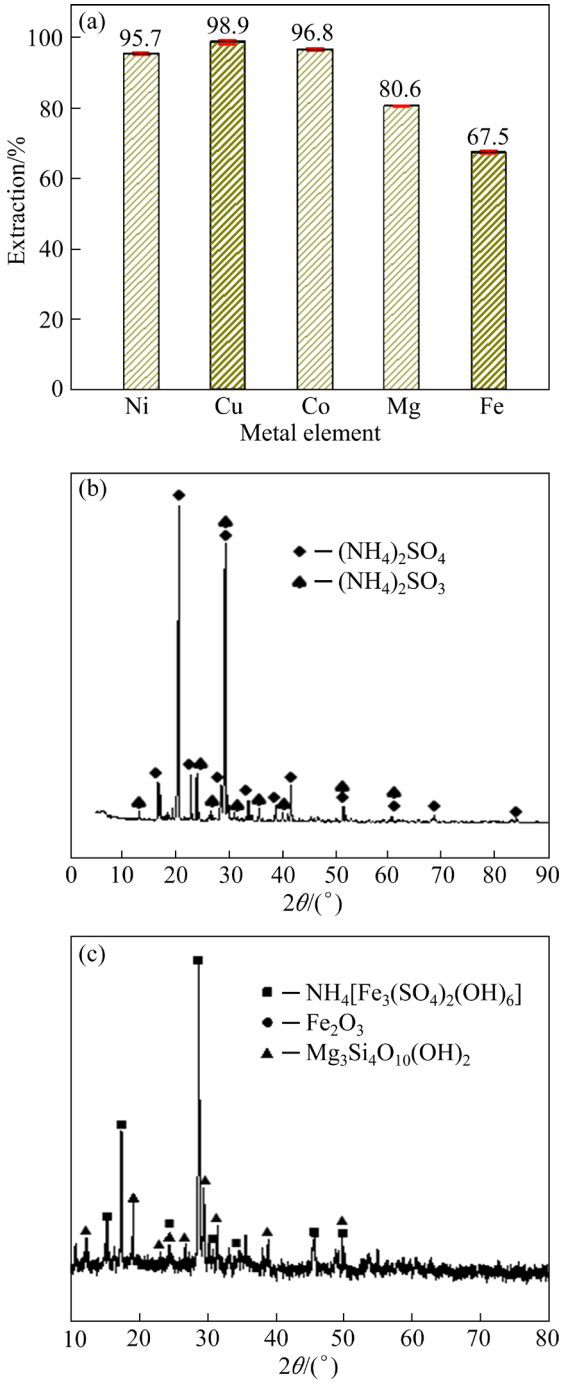

Fig. 12 Error bar of repeated experiments conducted under optimized roasting and leaching conditions (a), XRD pattern of collected volatiles (b), and XRD pattern of leach residue (c)

3.3 Analysis of volatiles and leach residue

Three repeated experiments were carried out under the above optimized roasting and leaching conditions, and the average extractions of Ni, Cu, Co, Mg and Fe was 95.7%, 98.9%, 96.8%, 80.6% and 67.5%, respectively, as shown in Fig. 12(a). The error bars in the figure show that there are small errors in the extraction of each metal, which indicates that the experiments of extracting metals are repeatable and the data are accurate and reliable. After the volatiles produced in the roasting process were recovered, their phase compositions were analyzed by XRD, and the results are shown in Fig. 12(b). It can be determined that the volatiles

mainly consist of $(NH_4)_2SO_4$ and $(NH_4)_2SO_3$, which can be used as reagents for sulfation roasting to achieve recycling. The XRD pattern of the leach residue obtained under optimized roasting and water leaching conditions in Fig. 12(c) shows that the main phases contained in the residue are the residual $Mg_3Si_4O_{10}(OH)_2$, Fe_2O_3 and $NH_4[Fe_3(SO_4)_2(OH)_6]$. According to the previous research results of our group, the iron in the leach solution can be removed by two-stage selective roasting to transform it into insoluble Fe_2O_3 or increasing the leaching temperature to transform it into jarosite [25], so the iron removal process will not be discussed in this paper.

4 Conclusions

(1) A process of NH_4HSO_4 roasting−water leaching was proposed to treat nickel concentrate. The metal-bearing minerals were mainly transformed into metal−ammonium complexes under the sulfation of NH_4HSO_4 and its decomposed SO_3 and NH_3. The transformation evolution of iron-bearing phases with the increase of temperature was as: $(NH_4)_3Fe(SO_4)_3 \rightarrow NH_4Fe(SO_4)_2 \rightarrow Fe_2(SO_4)_3 \rightarrow Fe_2O_3$.

(2) The optimal conditions of roasting nickel concentrate were obtained as follows: concentrate particle size 80−96 μm, N/C 8:1, roasting time 180 min, roasting temperature 400 °C, and 95.7% Ni, 98.9% Cu and 96.8% Co were extracted. The volatiles collected in the roasting process were determined to be $(NH_4)_2SO_4$ and $(NH_4)_2SO_3$, which can be used as reagents for sulfation roasting to achieve recycling.

(3) By exploring the effect of main factors on the metal extraction in the leaching process, suitable leaching conditions were determined as: temperature 80 °C, time 60 min, and liquid- to-solid ratio 6:1. The iron ions in the leach solution can be transformed into $NH_4[Fe_3(SO_4)_2(OH)_6]$ precipitation by increasing the leaching temperature, which provides an effective way for removing iron from the solution.

CRediT authorship contribution statement

Shou-ming DU: Investigation, Writing − Original Draft; **Wen-ning MU:** Conceptualization, Methodology, Writing − Reviewing and Editing; **Li-ying LI:** Investigation, Methodology, Software; **Shu-zheng SHI:** Formal analysis, Data curation; **Huan-huan CHEN:** Data curation, Validation; **Xue-fei LEI:** Project administration, Validation; **Rui GUO:** Project administration, Resources; **Shao-hua LUO:** Project administration, Resources; **Le WANG:** Supervision, Resources.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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硫酸化焙烧—水浸法从镍精矿中同步提取金属及矿相转化

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摘 要：提出低温 NH_4HSO_4 焙烧—水浸工艺从金川镍精矿中同步提取 Ni、Cu 和 Co，并系统研究硫酸化焙烧和水浸出过程中一些因素对金属提取的影响。结果表明，在优化的焙烧和水浸条件下，95.7% Ni、98.9% Cu 和 96.8% Co 被提取。利用 TG−DTA、XRD、SEM 和 EDS 等手段分析矿相的转化机理，在 NH_4HSO_4 及其分解的 SO_3 和 NH_3 的硫酸化反应下，有价金属被转化为水溶性金属—铵配合物从而得到有效的提取。通过提高浸出温度使铁离子与铵离子结合形成 $NH_4[Fe_3(SO_4)_2(OH)_6]$沉淀可除去浸出液中的杂质铁。在焙烧过程中收集的挥发物为 $(NH_4)_2SO_4$ 和$(NH_4)_2SO_3$，可用作硫酸化焙烧的试剂。

关键词：镍精矿；NH_4HSO_4 焙烧；同步提取；水浸出；矿相转化

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