

A Sustainable and Selective Roasting and Water-Leaching Process to Simultaneously Extract Valuable Metals from Low-Grade Ni-Cu Matte

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Due to stringent environmental requirements and the complex occurrence of valuable metals, traditional pyrometallurgical methods are unsuitable for treating low-grade nickel-copper matte. A clean and sustainable two-stage sulfating roasting and water-leaching process was used to simultaneously extract valuable metals from low-grade nickel-copper matte. Ammonium and sodium sulfate were used as sulfating agents. The first roasting temperature, mass ratio of ammonium sulfate to matte, roasting time, dosage of sodium sulfate, second roasting temperature and leaching temperature were studied. Under optimal conditions, 98.89% of Ni, 97.48% of Cu and 95.82% of Co, but only 1.34% of Fe, were extracted. X-ray diffraction (XRD) and scanning electron microscopy (SEM) were used to reveal the sulfating mechanism during the roasting process.

INTRODUCTION

Low-grade Ni-Cu matte, which is processed using the flash smelting method, is an intermediate in the conversion of concentrate into high-grade Ni-Cu matte.

Traditionally, pyrometallurgical methods involve placing low-grade Ni-Cu matte into a converter to blow it into high-grade Ni-Cu matte. The Jinchuan group then uses a floatation-magnetic method to separate Ni and Cu.¹ However, because valuable metals occur in multiple states in concentrate, the smelting low-grade Ni-Cu matte contains a quantified amount of Fe. In the subsequent conversion process, more than 70% of Co and a portion of Ni and Cu are lost. Furthermore, the blowing conversion method yields environmentally hazardous gases (SO₂ or SO₃), which are typically converted into sulfuric acid. However, Jinchuan is located in the western Gobi Desert of China, and due to high transportation costs, there is a significant overstock of sulfuric acid.

Hydrometallurgical methods are adopted to treat low-grade Ni-Cu matte; these methods have the advantages of low temperature, environmental friendliness and economical equipment investment. These methods include oxidative ammonia/ammonium sulfate leaching, acid-oxygen pressure leaching, atmospheric acid-oxygen leaching, FeCl₃-HCl leaching, Cu(II)-Cl-HCl-Cl₂ system leaching and CuCl₂-NaCl-HCl system leaching.²⁻⁸ However, the above-mentioned methods have a moderate recovery of valuable metals and limited selectivity for precious metals compared with their selectivity for Fe. In some methods, like FeCl₃-HCl and Cu(II)-Cl-HCl-Cl₂, the existence of Cl⁻ is harmful for electrolytic deposition.

In this work, a two-stage ammonium sulfating roasting and water-leaching process was used to convert metals into their respective water-soluble metal sulfates in a controllable manner, and the sulfating roasting mechanism was revealed.

EXPERIMENTAL

Materials

Low-grade Ni-Cu matte was obtained from a flash smelter in Jinchuan, China. Figure 1 shows the x-ray diffraction (XRD) patterns and a micrograph of low-grade Ni-Cu matte (for EDS scanning mapping images of matte, see supplementary Fig. S1; for SEM images of crushed matte, see supplementary Fig. S2). The low-grade Ni-Cu matte primarily consisted of magnetite (Fe_3O_4), pentlandite ($\text{Fe}_{4.005}\text{Ni}_{4.995}\text{S}_8$), iron nickel alloy (FeNi_3) and bornite (Cu_5FeS_4). Table I shows the chemical composition by using the XRF method and each phase's content by using the Highscore Plus 3.0 Rietveld method in matte.

Methods

The low-grade Ni-Cu matte was first crushed in a jaw crusher, pulverized in a planetary ball mill and sifted into different particle sizes. Then, the sifted powder was mixed. Na_2SO_4 (CAS#: 7757-82-6, AR), $(\text{NH}_4)_2\text{SO}_4$ (CAS#: 7783-20-2, AR), dimethylglyoxime (CAS#: 95-45-4, AR), BCO (CAS#: 370-81-0, AR) and other common reagents were purchased from Kermel, China.

This article describes a sulfating roasting water-leaching process. Before the roasting test, the matte sample was crushed, ground and screened into

fractions with a predetermined particle size. Then, the fraction was mixed with ammonium sulfate in a particular mass ratio, pelletized with a diameter range of 5–10 mm and dried at 80°C for 24 h. The pellets were transferred to a corundum crucible, which was roasted in a vertical furnace with an intelligent temperature control instrument (maximum, 1200°C). The leaching process was executed in a water bath with an intelligent temperature control instrument and magnetic stirring equipment.

The concentrations of Ni and Cu were analyzed by spectrophotometry using an ultraviolet spectrophotometer (PUXI, Beijing); Co was analyzed using atomic absorption spectrometry (Shimadzu-AA6680, Japan), and Fe was analyzed using chemical titration of the filtrate. The initial and post-roasting phase compositions of the samples were determined using XRD (Rigaku-SmartLab, Cu/K α , Japan). Microtopographies of the sample were determined using scanning electron microscopy (SEM) (Zeiss-Sigma 300, German).

RESULTS AND DISCUSSION

First Roasting Process

In the first roasting process, the leaching conditions were fixed with a leaching temperature of 80°C , leaching time of 90 min, liquid–solid ratio of 6:1 and stirring speed of 600 r/min.

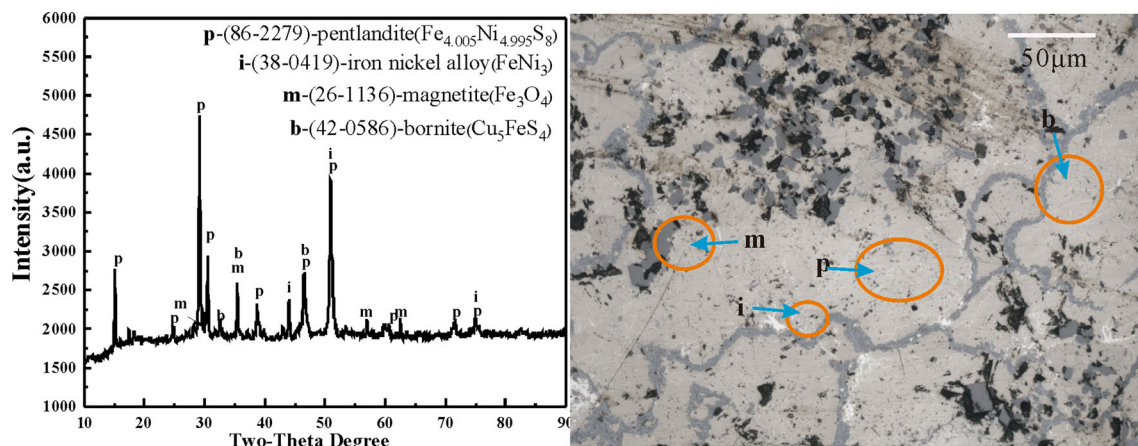


Fig. 1. XRD patterns and an optical micrograph of low-grade Ni-Cu matte. (a) XRD patterns. (b) Optical micrograph image.

Table I. Chemical composition and quantitative content of phases in low-grade nickel-copper matte

Element	S	Fe	Ni	Cu	Co	Si	Mg
(wt.%)	23.91	20.29	14.28	9.70	0.31	0.09	0.04
Phase	Pentlandite	Bornite	Magnetite	Iron nickel alloy			
(wt.%)	56	19	18	7			

Effect of the Roasting Temperature

Figure 2a illustrates the effect of roasting temperature on the metal extraction under the following conditions: an $(\text{NH}_4)_2\text{SO}_4$ to matte mass ratio of 5:1, Na_2SO_4 dosage of 60% (relative to the weight of the matte), roasting time of 4 h and matte particle size of 80–75 μm .

As shown in Fig. 2a, the extraction of Ni, Cu, Co and Fe first increases over the roasting temperature range of 350–500°C, reaching their highest values of 92.09%, 93.87% and 89.18% at 500°C and 57.42% at 450°C, respectively, but then they decrease as the

roasting temperature increases. The decomposition of $(\text{NH}_4)_2\text{SO}_4$ can be divided into two stages,⁹ as shown in Eqs. 1 and 2 [DTA-TG curves of $(\text{NH}_4)_2\text{SO}_4$, see supplementary Fig. S3]. The sulfating activation becomes violent as the roasting temperature increases, accompanied by the decomposition of $(\text{NH}_4)_2\text{SO}_4$. However, when the roasting temperature exceeds 550°C, the decomposition rate of $(\text{NH}_4)_2\text{SO}_4$ is too rapid, which leaves insufficient time for the reactions between NH_4HSO_4 or SO_3 with the mineral phases in the matte to occur. Therefore, the extraction of Ni, Cu and Co decreases when the roasting temperature exceeds 550°C. The

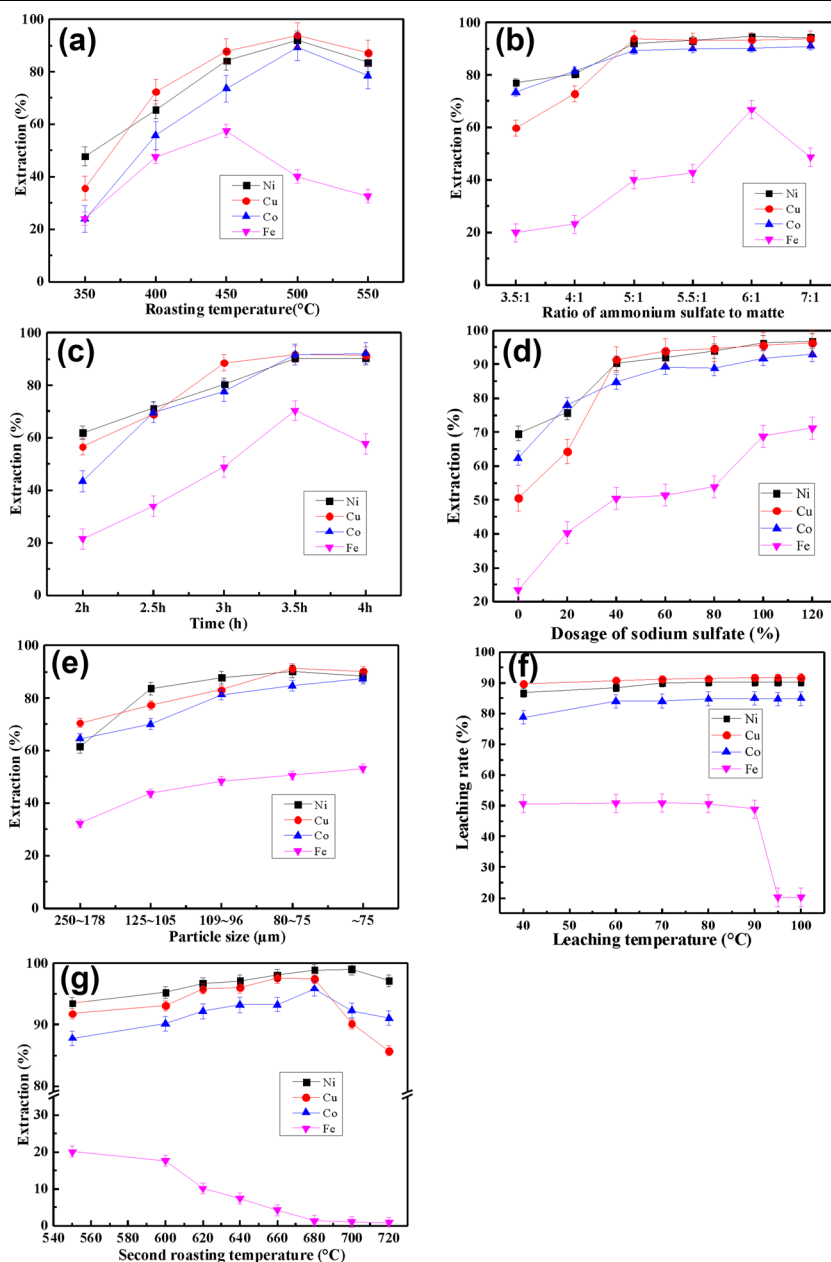
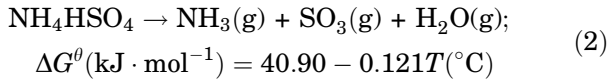
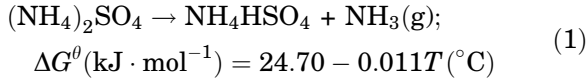


Fig. 2. Effect of the following parameters on the metal extractions: (a) effect of roasting temperature; (b) effect of ratio of ammonium sulfate on matte; (c) effect of time; (d) effect of dosage of sodium sulfate; (e) effect of particle size; (f) effect of leaching temperature; and (g) effect of second roasting temperature.

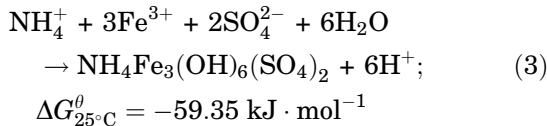
significant decrease in Fe from 450°C to 500°C can be attributed to the decomposition of iron sulfates.^{10,11} Hence, the roasting temperature of 500°C was recommended for the following experiments. (For the collected volatiles, see supplementary Fig. S4.)



Effect of the Mass Ratio of Ammonium Sulfate to Matte

Figure 2b shows the effect of the mass ratio of ammonium sulfate to matte under the following conditions: a roasting temperature of 500°C, Na₂SO₄ dosage of 60%, roasting time of 4 h and matte particle size of 80–75 μm.

Figure 2b shows that the extractions of Ni, Cu and Co increase with the enhanced mass ratio of (NH₄)₂SO₄ to matte. However, a mass ratio of (NH₄)₂SO₄ to matte exceeding 5:1 has little effect on the extractions of Ni, Cu and Co. The extraction of Fe first increases with the higher mass ratio of (NH₄)₂SO₄ to matte and then decreases when the mass ratio exceeds 6:1, which can be attributed to the formation of NH₄Fe₃(OH)₆(SO₄)₂, as shown in Eq. 3. Therefore, the mass ratio of 5:1 was used in the following experiments.



Effect of Roasting Time

The roasting temperature was maintained at 500°C, the dosage of Na₂SO₄ at 60%, the roasting time at 4 h and the matte particle size at 80–75 μm. The results are presented in Fig. 2c.

Figure 2c shows that as the roasting time increased to 2–3.5 h, the extraction of Ni, Cu, Co and Fe increased, reaching values of 90.18%, 91.78%, 91.65% and 70.32%, respectively. Then, the extraction of Ni, Cu and Co remained almost constant after 3.5 h; the decreased extraction of Fe could be attributed to the decomposition of iron sulfates.

As shown in Fig. 3, the diffraction peaks of (NH₄)₂Fe₂(SO₄)₃ appear in sample 1, indicating that Fe is initially converted into ammonium ferric sulfate. With a prolonged roasting time, the diffraction peaks of the phases in sample 1 disappear, while the diffraction peaks of Fe₂(SO₄)₃, Na₃Fe(SO₄)₃ and Na₂Cu(SO₄)₂ appear in sample 2,

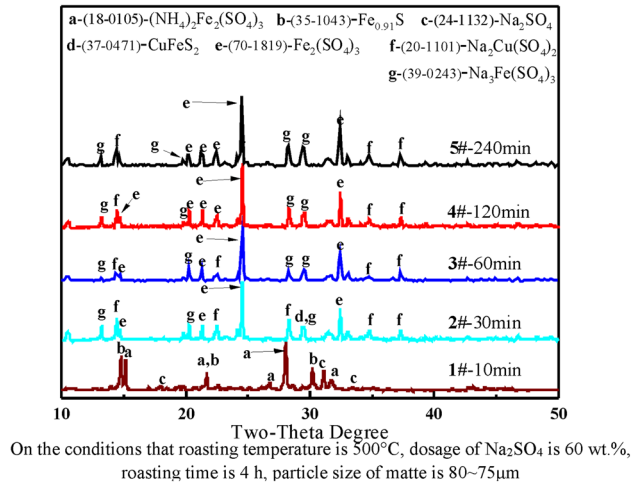


Fig. 3. XRD patterns of the samples for different roasting times.

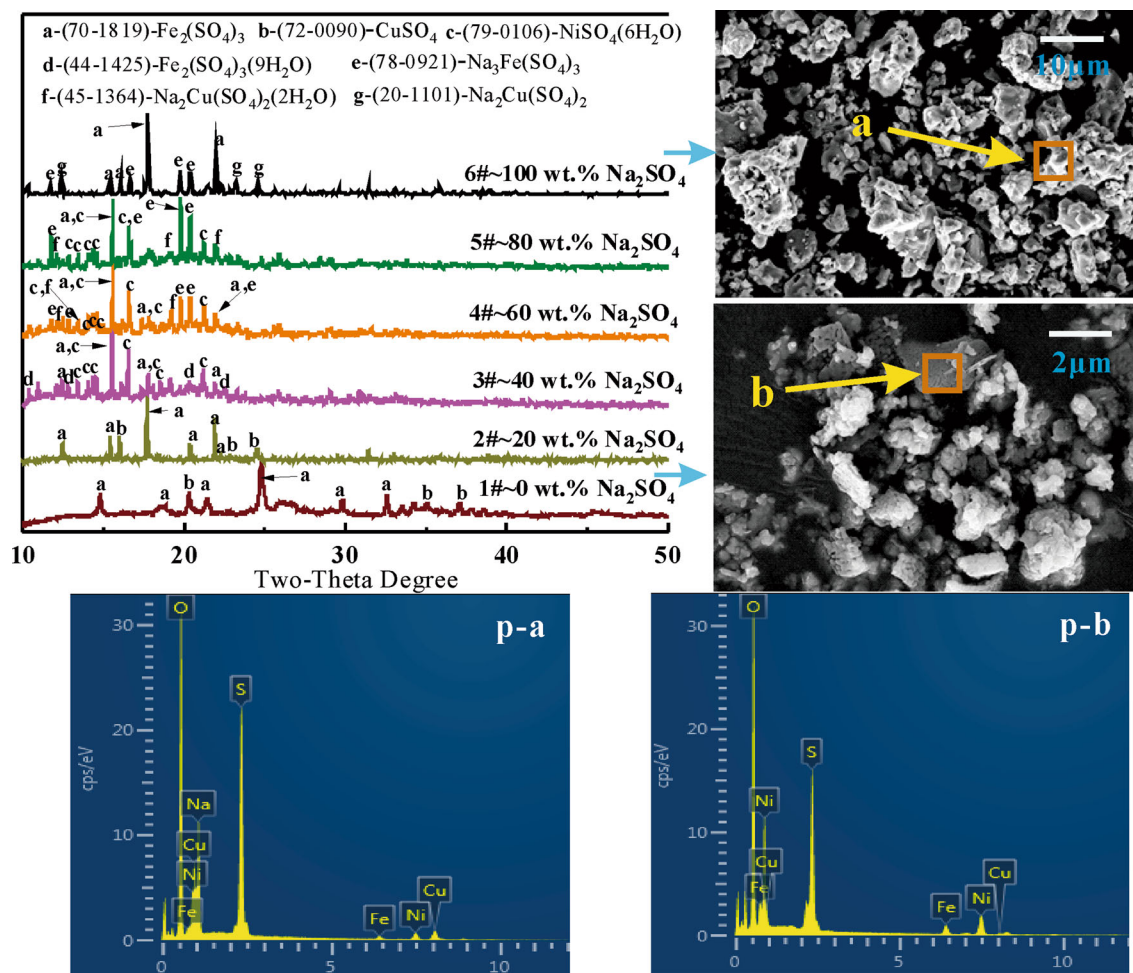
indicating that (NH₄)₂Fe₂(SO₄)₃ was completely decomposed and that sodium-metal (Cu, Fe) sulfate was formed. As the roasting time increases, the diffraction peaks of metal sulfides disappear, while the diffraction peaks of Fe₂(SO₄)₃, Na₃Fe(SO₄)₃ and Na₂Cu(SO₄)₂ intensify. Therefore, initially, the metal sulfides are converted to ammonium-metal sulfates. Then, the ammonium-metal sulfates decompose and are converted to metal sulfates or sodium-metal sulfates. Hence, a roasting time of 3.5 h was recommended in the subsequent experiments.

Effect of the Sodium Sulfate Dosage

Sodium sulfate is a common active agent in the sulfating roasting process, as it can promote the sulfation of metals, especially Ni, Cu and Co.^{12–15} Hence, Na₂SO₄ was added to activate the sulfating process to metal sulfides. The roasting temperature was maintained at 500°C, the mass ratio of (NH₄)₂SO₄ to matte was 5:1, the roasting time was 3.5 h, and the particle size of the matte was 80–75 μm. The results are shown in Fig. 2d.

As shown in Fig. 2d, the extractions of Ni, Cu and Co increase as the Na₂SO₄ dosage increases. Specifically, the extractions of Ni, Cu and Co initially increase rapidly by 20.75% (from 69.53% at 0% to 90.28% at 40%), 40.85% (from 50.53% at 0% to 91.38% at 40%) and 22.40% (from 62.38% at 0% to 84.78% at 40%), respectively, and then they increase slowly with the continued increase in dosage of Na₂SO₄; moreover, the extraction of Fe increases by 47.75% (from 23.48% at 0% to 71.23% at 120%).

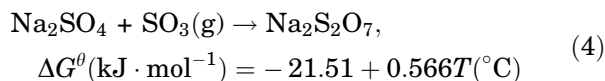
As shown in Fig. 4, the main phases in sample 1 are Fe₂(SO₄)₃ and CuSO₄. After adding 20% of Na₂SO₄, the intensities of the diffraction peaks of CuSO₄ in sample 2 become stronger than those in 1, which corresponds with the increase of the Cu extraction. When 20% of Na₂SO₄ is continuously



On the conditions that the roasting temperature is 500°C, mass ratio of (NH₄)₂SO₄ to matte is 5:1, roasting time of 4 h, particle size of matte of 80~75µm

Fig. 4. XRD patterns and SEM images of the samples with the addition of different amounts of sodium sulfate: p-a, EDS of point a; p-b, EDS of point b.

added, the diffraction peaks of NiSO₄(6H₂O) appear in sample 3, indicating that the extent to which Ni is sulfated depends on the amount of Na₂SO₄. The diffraction peaks of Na₃Fe(SO₄)₃ and Na₂Cu(SO₄)₂(2H₂O) appear in sample 4, and after adding 100% of Na₂SO₄, the main phases in sample 6 are Fe₂(SO₄)₃, Na₃Fe(SO₄)₃ and Na₂Cu(SO₄)₂. The SEM images of 1 and 6 show that after adding Na₂SO₄, the polyporous particles transform into adhesive particles. The accepted activation mechanism of Na₂SO₄ in the sulfating roasting process is the formation of Na₂S₂O₇, as shown in Eq. 4, with the extensive erosion effect and the cycle phase transformation of the liquid phase to the solid phase.^{12,16,17} This mechanism explains the increase in the metal extraction with the enhanced dosage of Na₂SO₄. Therefore, a Na₂SO₄ dosage of 40% was used in the subsequent experiment.



Effect of Particle Size

Figure 2e shows the effect of particle size on the extraction of Ni, Cu, Co and Fe by keeping the roasting temperature at 500°C, the mass ratio of (NH₄)₂SO₄ to matte at 5:1, the dosage of sodium sulfate at 40% and the roasting time at 3.5 h.

As shown in Fig. 2e, the extractions of Ni, Cu, Co and Fe increase as the matte particle size decreases from 250–178 µm to 80–75 µm, although the extractions of Cu and Ni show a small decrease with particle sizes less than 75 µm. For solid–solid–gas reactions, smaller particles induce more contiguous opportunities for each of the reactants. However, a

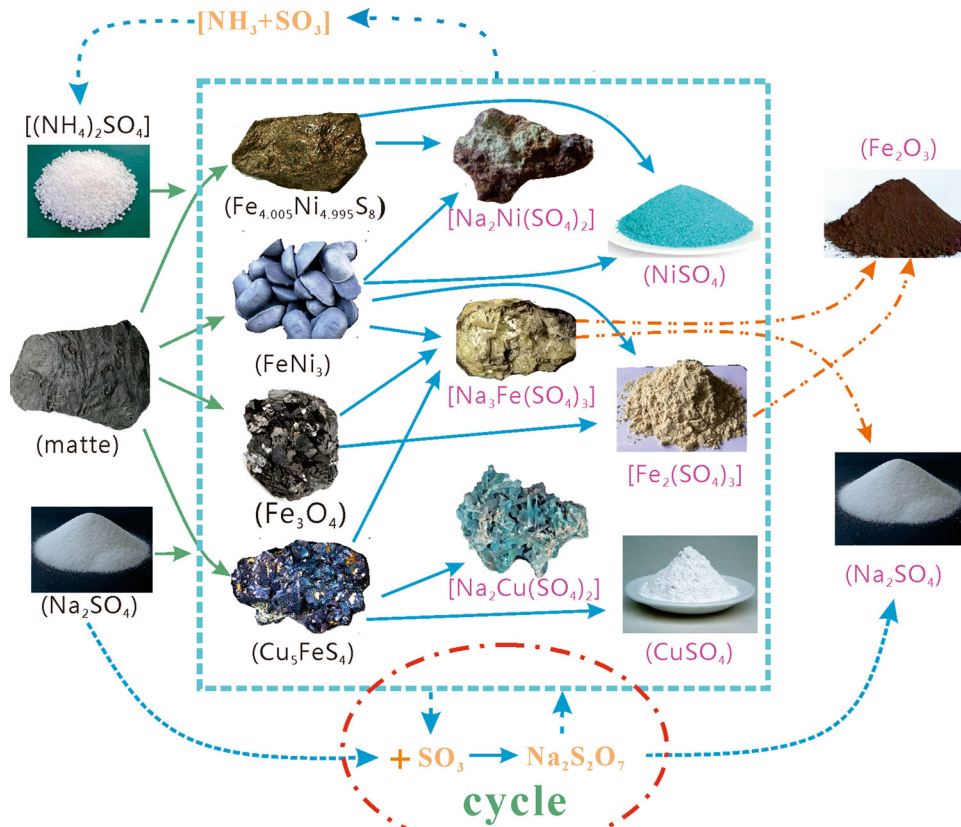


Fig. 5. The mechanism of the two-stage selective sulfating roasting process.

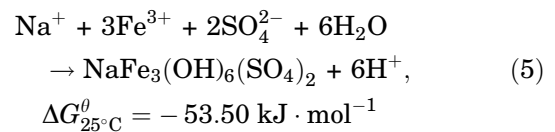
too small particle size narrows the gap and gets a tight contact between particles; this leaves insufficient space to exchange gases, which explains why the extractions of Cu and Ni slightly decrease when the particle size is smaller than $75\ \mu\text{m}$. Hence, the particle size of $80\text{--}75\ \mu\text{m}$ was adopted in the later experiments.

Effect of Leaching Temperature

Figure 2f shows the effect of leaching temperature when the roasting temperature is 500°C , the mass ratio of $(\text{NH}_4)_2\text{SO}_4$ to matte is 5:1, the dosage of sodium sulfate is 40%, the roasting time is 3.5 h and the particle size is $80\text{--}75\ \mu\text{m}$.

Figure 2f also shows that the leaching rates of Ni, Cu and Co slightly increase with the enhanced leaching temperature. However, the leaching rate of Fe significantly decreases when the leaching temperature is higher than 90°C because of the rapid formation of $\text{NaFe}_3(\text{SO}_4)_2(\text{OH})_6$, as shown in Eq. 5. The solution temperature plays a key role in the formation of $\text{NaFe}_3(\text{SO}_4)_2(\text{OH})_6$; when the temperature is below than 85°C , the reaction rate of Eq. 5 is slow, resulting in a lower generation amount of $\text{NaFe}_3(\text{SO}_4)_2(\text{OH})_6$ at a fixed leaching amount of 90 min. However, when the solution temperature is higher than 90°C , the reaction rate of Eq. 5

accelerates several times more than at lower temperature, while when the solution temperature is higher than 95°C , it has less effect on the reaction.^{18,19} Therefore, a leaching temperature of 95°C is suggested for the following experiments.



Effect of the Second Roasting Process

During the following separation of metal ions, there is a significant cost for removing iron. Due to the different thermodynamic stabilities of metal sulfates,^{10,11} a second roasting process was used to achieve an initial separation of the metals. The second roasting process is based on the products after the first roasting process (the conditions are the same as those used in the first roasting process, with a leaching temperature of 95°C), and the roasting time is 2 h. The results are shown in Fig. 2g.

Figure 2g shows the extractions of Ni, Cu and Co increase with an enhanced roasting temperature ranging from 540°C to 680°C . The extractions

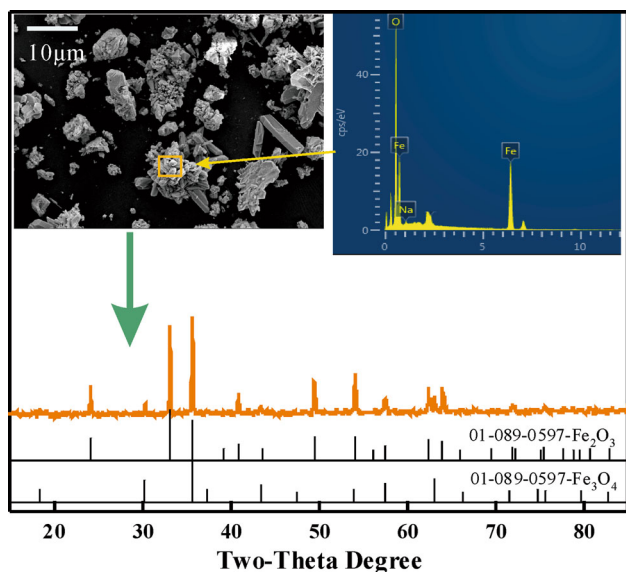


Fig. 6. XRD patterns and SEM images of the leaching residue.

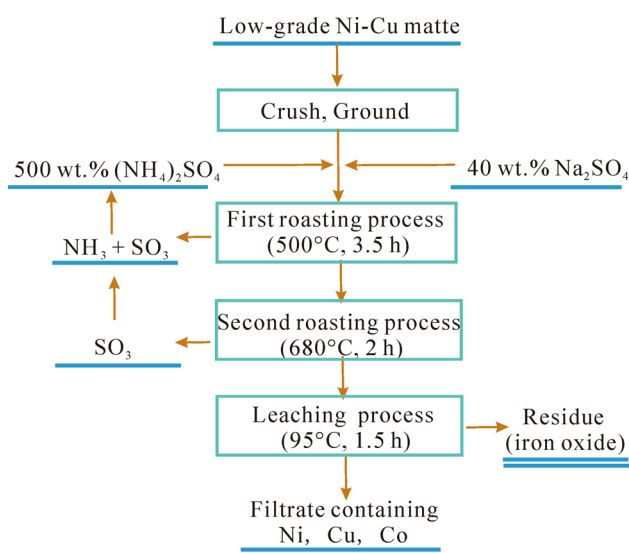
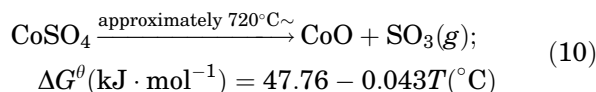
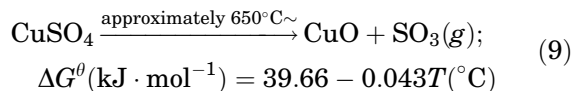
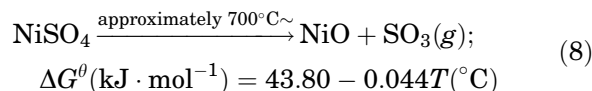
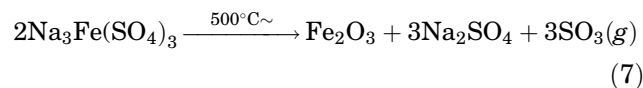
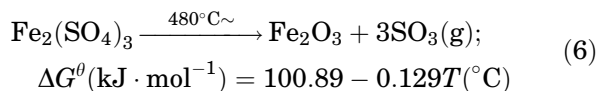


Fig. 7. Flow sheet of the selective roasting and water-leaching process.

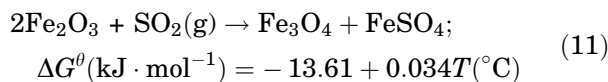
of Cu and Co reach their peaks of 97.48% and 95.82%, respectively, and the extraction of Ni reaches its maximum of 99.01% at 700°C; all of the extractions decrease as the roasting temperature continues to increase because of the decomposition of their corresponding metal sulfates, as show in Eqs. 6–10.¹⁰ The extraction of Fe significantly decreases with the increased roasting temperature; the quick decrease in 600–620°C is attributed to the fast decomposition rate of $\text{Fe}_2(\text{SO}_4)_3$ and $\text{Na}_3\text{Fe}(\text{SO}_4)_3$ at higher temperature.^{20,21} Compared with the first roasting process, the extractions of Ni, Cu and Co increase by 8.61%, 6.1% and 11.04% at the second roasting

temperature of 680°C, respectively. At a higher roasting temperature, Na_2SO_4 effectively promotes the sulfating process of the metals because of the generated strong sulfation ability intermediate of $\text{Na}_2\text{S}_2\text{O}_7$, as shown in Eq. 5, and its cycle phase transforms from solid to liquid.^{12,16,22,23} Overall, the second roasting temperature of 680°C was adopted as the optimal condition. The mechanism diagram of the two-stage selective sulfating roasting process is shown in Fig. 5. [For possible reactions in the two-stage roasting process, see supplementary Eqs. 1–23.]



Leaching Residue

Figure 6 shows the leaching residue of the two-stage roasting product. The main phases in the leaching residue contain Fe_2O_3 and Fe_3O_4 . In the first stage of the roasting process, metal-bearing phases in matte were converted to corresponding metal sulfates and sodium metal sulfates, while some of $\text{Fe}_2(\text{SO}_4)_3$ was decomposed into insoluble Fe_2O_3 at the first roasting temperature of 500°C, as shown in Eq. 3. In the ensuing second roasting process, $\text{Na}_3\text{Fe}(\text{SO}_4)_3$ and $\text{Fe}_2(\text{SO}_4)_3$ were decomposed rapidly at 680°C. However, when the partial pressure of O_2 is lower than a certain value, Fe_2O_3 will react with SO_2 to generate Fe_3O_4 and FeSO_4 as in Eq. 11,²⁴ so the leaching residue contains a small amount of Fe_3O_4 . Figure 7 shows the flow sheet of the selective roasting and water-leaching process.



CONCLUSION

In this work, a two-stage roasting and water-leaching process was used to simultaneously extract valuable metals from low-grade nickel-

copper matte. Ammonium sulfate and sodium sulfate were used as the sulfating agents. During both the first and second roasting processes, sodium sulfate significantly improved the extractions of Ni, Cu and Co. After adding sodium sulfate, metal sulfides were converted to sodium-metal sulfates, not metal sulfates, by using a single sulfating agent, ammonium sulfate. Under optimal conditions (a first roasting temperature of 500°C, mass ratio of $(\text{NH}_4)_2\text{SO}_4$ to matte of 5:1, sodium sulfate dosage of 40%, roasting time of 3.5 h, particle size of 80–75 μm , second roasting temperature of 680°C and leaching temperature of 95°C), the extractions of Ni, Cu and Co reached 98.89%, 97.48% and 95.82%, respectively. However, the extraction of Fe was only 1.34%. This process was clean and sustainable for treating low-grade nickel matte.

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ELECTRONIC SUPPLEMENTARY MATERIAL

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