



Co-extraction of valuable metals and kinetics analysis in chlorination process of low-grade nickel–copper sulfide ore

Wen-ning MU^{1,2,3}, Teng-fei XIAO^{1,2}, Shuang-zhi SHI⁴, Xue-qing XU^{1,2}, Hao CHENG^{1,2}, Yu-chun ZHAI³

1. School of Resources and Materials, Northeastern University at Qinhuangdao, Qinhuangdao 066004, China;

2. School of Materials Science and Engineering, Northeastern University, Shenyang 110819, China;

3. School of Metallurgy, Northeastern University, Shenyang 110819, China;

4. GE-HPEC-NTC Energy Services (Qinhuangdao) Co., Ltd., Qinhuangdao 066000, China

Received 13 April 2021; accepted 26 October 2021

Abstract: To efficiently co-extract Ni and Cu from low-grade nickel–copper sulfide ore, chlorination roasting with NH_4Cl followed by a water leaching process was investigated. The results show that 98.4% Ni and 98.5% Cu can be synchronously extracted when the ore particle size is 75–80 μm , the roasting time is 2 h, the mass ratio of NH_4Cl to ore is 1.6:1 and the roasting temperature is 550 °C. The evolution behavior of various minerals was elucidated using X-ray diffraction (XRD) coupled with scanning electron microscopy (SEM). The kinetics of the chlorination process based on the differential thermal and thermogravimetric analysis (DTA–TG) data was analyzed by Kissinger method and Flynn–Wall–Ozawa (FWO) method. The chlorination process of low-grade nickel–copper sulfide ore mainly contains two stages: the decomposition of NH_4Cl and the chlorination of ore. The maximum apparent activation energies (E_a) at two stages are determined to be 114.8 and 144.6 kJ/mol, respectively. The condensed product of exhaust gas is determined to be ammonium chloride, which can be recycled as the reactant again, making the process economic and clean.

Key words: low-grade nickel–copper sulfide ore; chlorination roasting; synchronous extraction; phase evolution; kinetics

1 Introduction

After years of continuous mining, the high-grade nickel sulfide ore is facing exhaustion and the low-grade nickel–copper sulfide ore will replace it to be the main feedstock in the metallurgical industry [1,2]. In the low-grade sulfide ore, the content of gangue is high, and the mineral phase is complex since the metals coexist in the forms of sulfides, oxides and silicates [3,4]. The traditional pyrometallurgical process is no longer suitable for treating low-grade nickel–copper sulfide ore, due to the changes in the composition, structure and properties of the ore [5,6]. The

difficult separation of gangue in the flotation process, the reduction of the concentrate grade, and the low comprehensive recovery of valuable metals (Ni, Cu, Co, Pt, etc.), coupled with the complicated and lengthy process, have caused a reduction in the overall economic benefit of the enterprise [7,8]. Therefore, the development of the extraction process with low temperature, short process and high metal recovery has become hot research topic.

The mixed acid system with nitric acid as the oxidant and sulfuric acid as the acidolysis agent was used to leach the copper–nickel sulfide lean ore, and 91.5% Ni, 85.0% Cu and 54.6% Co were extracted after 10 days of leaching at room temperature [9]. However, the process has high acid

consumption due to high alkaline gangue content. Some bioleaching methods, such as heap leaching, bottle leaching or column leaching, have been studied for leaching low-grade nickel sulfide ores. The leaching rate of Ni and Co can reach more than 80%, but the leaching rate of copper is relatively low [10–13]. In addition, the biological leaching process is immature and inefficient with a long leaching time.

The medium or low-temperature roasting–leaching technology has highlighted the characteristics of reducing the energy consumption, increasing the yield, and clean production in pyrometallurgy. Currently, our research group has studied the selective extraction of nickel and copper from low-grade nickel sulfide ore by the two-stage roasting method using ammonium sulfate or sulfuric acid as the sulfating reagent, and revealed the behavior and kinetics of metal transformation during the roasting process [14,15]. When sodium sulfate is added to the roasting, the reaction environment can be improved and the activation energy of the sulfation reaction can be reduced [16].

Chlorination roasting has the advantages of low energy consumption, high reactivity and high metal recovery rate when processing various low-grade complex metal ores [17–19]. Solid chlorinating agents are more widely used due to their low cost, low corrosivity and easy availability [20,21]. Compared with CaCl_2 , NaCl , MgCl_2 , KCl and AlCl_3 , NH_4Cl is considered as a promising and eco-friendly chlorination agent for metal sulfides and metal oxides from the viewpoint of chlorination efficiency, no introduction of metal impurities and energy consumption [22,23]. SO_2 or SO_3 produced by S in the sulfide mineral system is beneficial to promoting the chlorination process [24,25]. However, there are few reports on the synchronous extraction of valuable metals by NH_4Cl roasting of low-grade nickel–copper sulfide ore, and the transformation behavior of the minerals and process

kinetics of valuable metals need to be further clarified.

In this study, the NH_4Cl roasting–water leaching process was proposed to synchronously extract Ni and Cu from low-grade nickel–copper sulfide ore. In the chlorination roasting process, the parameters including the roasting temperature, the roasting time, the ore particle size and the mass ratio of NH_4Cl to ore were investigated systematically. The mineral phase evolution in the chlorination process was revealed using X-ray diffraction (XRD). The kinetics of chlorination process was studied by thermogravimetry analysis (DTA–TG) coupled with Kissinger method and Flynn–Wall–Ozawa method.

2 Experimental

2.1 Materials and reagents

The low-grade nickel–copper sulfide ore used in this work was taken from Jinchuan Group Co., Ltd. (JNMC), China. All reagents applied in the experiment were of analytical grade, and the purified water was used.

After crushing and grinding, the ore samples were sieved into five narrow size fractions by vibrating screen: 120–150, 109–120, 96–109, 80–96 and 75–80 μm . The chemical compositions of each size range determined by X-ray fluorescence spectrometer (XRF, S8 TIGER) are given in Table 1.

The results in Table 1 present that the chemical composition of ore powder changes slightly with the different particle sizes. The valuable metals contained in the ore are nickel and copper, the contents of which are around 4.5% and 2.7%, respectively. In addition, the ore also contains iron, sulfur, magnesium, silicon and a small amount of aluminum and calcium as impurities.

The mineralogical data of the ore determined by X-ray diffraction (XRD, Rigaku-Smartlab, Japan

Table 1 Main chemical composition of ore powders in each size range (wt.%)

Particle size/ μm	Ni	Cu	TFe	S	MgO	SiO_2	CaO	Al_2O_3
120–150	4.57	2.68	31.17	20.75	10.69	14.70	1.32	0.87
109–120	4.56	2.67	31.95	20.72	10.57	14.68	1.32	0.97
96–109	4.58	2.66	31.46	20.16	10.80	14.51	1.26	0.92
80–96	4.57	2.72	32.76	22.22	10.42	13.99	1.20	0.89
75–80	4.58	2.65	34.27	23.04	9.63	13.12	1.08	0.86

with Cu K_{α} radiation) are presented in Fig. 1. It can be seen that the mineral phases containing nickel and copper are mainly pentlandite ((Fe,Ni) $_9$ S $_8$) and chalcopyrite (CuFeS $_2$), respectively. Gangue minerals are mainly talc (Mg $_3$ Si $_4$ O $_{10}$ (OH) $_2$) and lizardite (Mg $_3$ Si $_2$ O $_5$ (OH) $_4$), and metallic iron exists in the form of sulfides and oxides. Part of the metallic nickel and copper are distributed in oxides or silicates, which are not seen in the XRD pattern due to the low intensity of diffraction peaks.

The morphology and surface composition of the ore analyzed by scanning electron microscopy (SEM, ZEISS-Sigma, Germany) are shown in Figs. 2(a–c). It can be seen from Fig. 2(a) that the

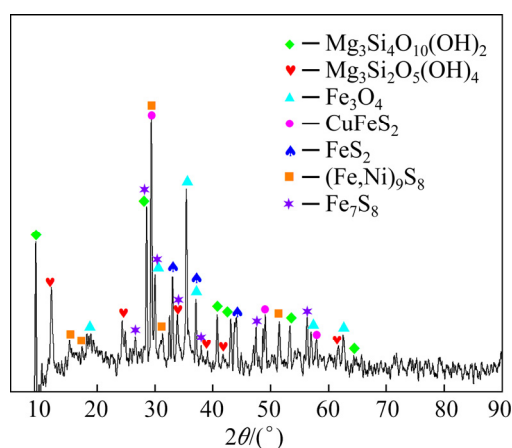


Fig. 1 XRD pattern of low-grade nickel–copper sulfide ore

particles have irregular shape, with loose layered structure and the concave surface. Moreover, some small particles adhere to the surface of the large particles. The EDS energy spectrum analysis of Fig. 2(b) shows that the elements contained at Spot 1 are mainly O, Si, Mg, Fe, Ni, Cu, and S. The EDS surface scan of Fig. 2(c) determines that the distribution of O is mainly coincident with that of Si and Mg, and Particle A is enriched with O, Si, and Mg as a gangue structure. The distributions of Ni, Cu, S and Fe overlap to form metal sulfides, while part of Fe overlaps with O to form Fe $_3$ O $_4$.

2.2 Roasting and leaching experiments

The thoroughly dried 20 g ore powder with a certain particle size was mixed evenly with NH $_4$ Cl according to the required mass ratio. Then, the mixture was placed in a closed furnace connected with an exhaust gas absorption device and atmosphere control device, and roasted at the preset temperature (300–650 °C) for a period of time. Various factors such as roasting temperature, roasting time, NH $_4$ Cl dosage and particle size of ore powder were changed to investigate their effects on the chlorination of ore. The atmosphere in the furnace was controlled as a mixed gas composed of 20% oxygen and 80% nitrogen with a flow rate of 20 mL/min. When the roasting process was over, the sample was taken out after being cooled to room

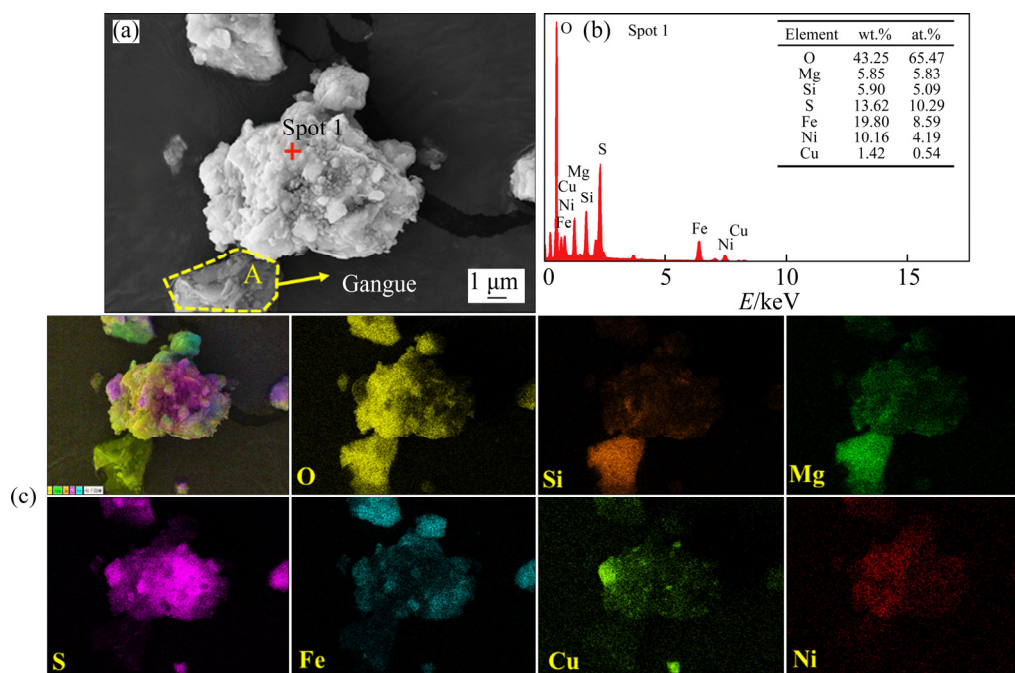


Fig. 2 SEM image (a), EDS analysis results of Spot 1 (b) and elemental distributions (c) of low-grade nickel–copper sulfide ore

temperature in the furnace and leached with hot water to transfer metal salts into the solution. The leaching conditions were as follows: temperature 80 °C, time 1 h, stirring speed 350 r/min and liquid-to-solid ratio 6:1. When the water leaching process was finished, the mixture was separated by vacuum filtration to collect the leaching solution and residue.

2.3 Assessment indexes

The extraction of Ni, Cu Fe and Mg calculated according to Eq.(1) was used to evaluate the chlorination process under different experimental conditions:

$$\alpha_m = \frac{C_m V}{20W_m} \times 100\% \quad (1)$$

where α_m (%) is the extraction of metal ($m = \text{Ni, Cu, Fe or Mg}$), C_m (g/L) is the concentration of a metal ion in the leaching solution, V (L) is the volume of leaching solution, and W_m (%) is the mass fraction of metal in the ore. The concentration of metal ions was tested by an atomic absorption spectrophotometer (AA-6800F/G, Shimadzu, Japan).

2.4 TG-DTA experiment

The differential thermal and thermogravimetric analysis (DTA-TG, Diamond 6300, USA) was used to investigate the chlorination roasting kinetics of low-grade nickel-copper sulfide ore. The homogeneous mixture of the ore and NH_4Cl was placed in the analysis instrument in a corundum crucible and heated from room temperature to 800 °C in a stable mixed gas atmosphere (20% O_2 + 80% N_2) at a flow rate of 20 mL/min. The mass ratio of NH_4Cl to the ore was selected to be 1.6:1 and experiments were conducted at different heating rates of 5, 10, 15 and 20 °C/min, respectively.

3 Results and discussion

3.1 Effect of roasting temperature and phase evolution

The roasting temperature is an important parameter that affects the chlorination of the ore. The curves of metal extractions are shown in Fig. 3 in the temperature range of 300–650 °C. It can be seen from Fig. 3 that the extraction of Ni, Cu, and

Fe increases first and then decreases with the increase of temperature. The extractions of Cu and Ni show similar increasing trends, and reach the maximum values of 95.3% and 97.5% at 550 °C, respectively. The increase of temperature is beneficial to the decomposition of NH_4Cl to produce hydrogen chloride. However, when the temperature is higher than 550 °C, as a result of NH_4Cl gasification (boiling point is about 520 °C), the production of hydrogen chloride is inhibited, and the extraction of Cu and Ni decreases with the increase of temperature.

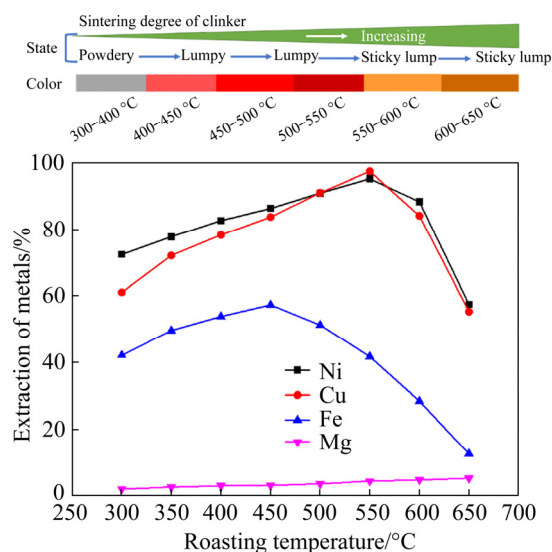


Fig. 3 Effect of roasting temperature on extraction of metals (roasting time 2 h, mass ratio of NH_4Cl to ore 2:1, and ore particle size 75–80 μm), state and color of roasted clinkers at different roasting temperatures

While the extraction of Fe reaches its maximum at 450 °C, and then decreases with the increase of the temperature. In addition to the reasons stated above, it is also attributed to the formation of water-insoluble ferric oxide through the decomposition of ferric sulfate and the oxidation of ferric chloride. The dissolved iron will increase the cost of subsequent iron removal. To decrease the extraction of iron, the clinker can be roasted for the second time (400–550 °C) under oxidizing conditions to convert iron into iron oxide to achieve pre-separation [25]. The Mg extraction is less affected by the roasting temperature, and it increases slightly with the increase of the temperature. The state and color of roasted clinkers at the different roasting temperatures shown in Fig. 3 present that the sintering degree and hardness of clinker increase with the increase of roasting

temperature, and the color of clinker also changes, from grey (300–400 °C) to dark red (500–550 °C) and then to yellowish brown (600–650 °C). By considering the separation of the clinker and the crucible, the roasting temperature of 550 °C is more appropriate.

The XRD patterns of roasted clinker and leaching residue at different roasting temperatures are shown in Figs. 4(a,b), and their phase compositions are labeled in Fig. 4(c). The following conclusions can be obtained by analyzing Fig. 4:

(1) In the temperature range of 350–520 °C, NH_4Cl is partially decomposed, and NH_3 , HCl and NH_4Cl coexist in the roasting system.

(2) The undecomposed NH_4Cl can directly react with the iron to form $(\text{NH}_4)_3\text{FeCl}_5$ and NH_4FeCl_3 (350–450 °C), and then they decompose to FeCl_2 (450–550 °C). The iron can also react with HCl to generate FeCl_2 , which can be further oxidized to Fe_2O_3 (450–650 °C).

(3) Nickel and copper can react with the

undecomposed NH_4Cl to form $(\text{NH}_4)_6\text{NiCl}_2$ and NH_4CuCl_3 (450–550 °C), respectively, and then they decompose into CuCl_2 and NiCl_2 (550–650 °C). The copper and nickel can also react with HCl to produce CuCl_2 and NiCl_2 , respectively.

(4) The obvious diffraction peaks of $\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$ and $\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$ in the clinker and residue (350–550 °C) indicate that they are difficult to react with NH_4Cl or HCl , so the extraction of magnesium is low, which is consistent with our previous work [3]. However, the disappearance of diffraction peaks of $\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$ at 650 °C is caused by its thermal decomposition.

In general, the NH_4Cl roasting of the ore is a complex process, including the decomposition of NH_4Cl , the reaction of metal sulfide with HCl , the reaction of metal sulfide with NH_4Cl , the decomposition of intermediate product chlorinated metal–ammonium complexes, and the oxidation of ferrous chloride. In addition, metal sulfides can also

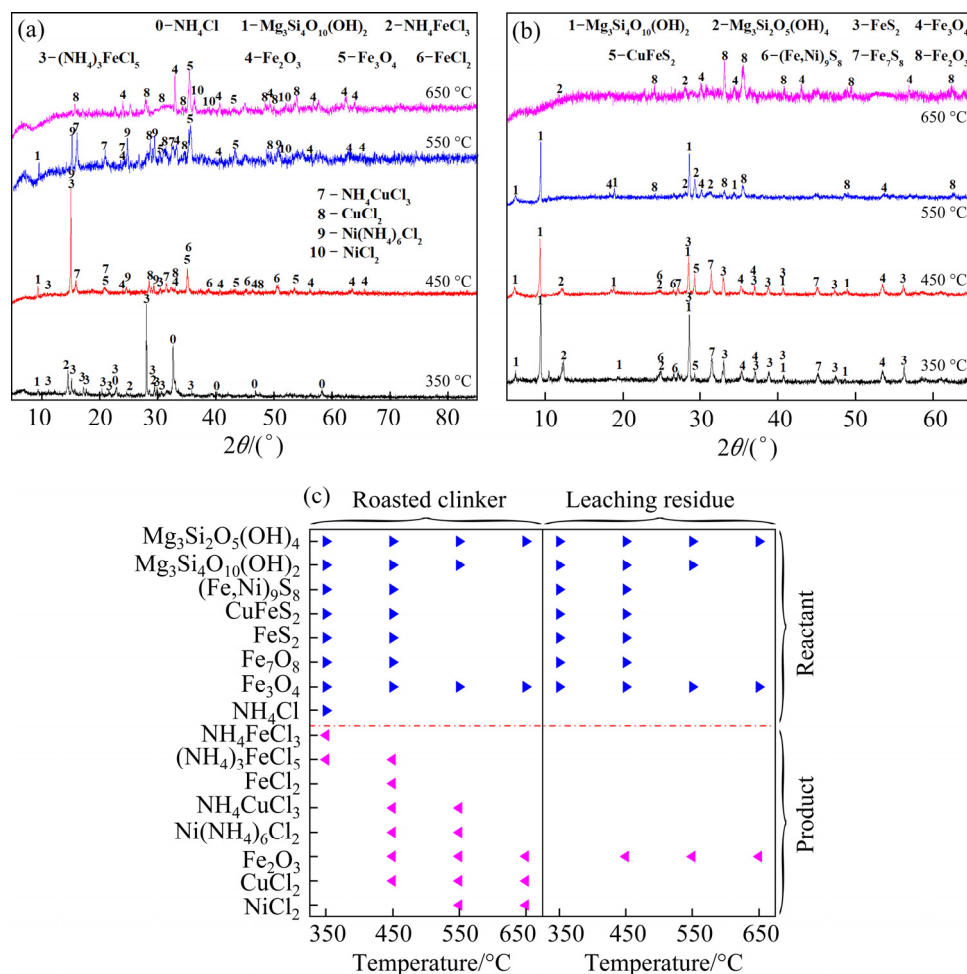


Fig. 4 XRD patterns of roasted clinkers (a) and leaching residues (b) at different roasting temperatures, and phase composition of roasted clinker and leaching residue (c)

be oxidized by oxygen in the furnace atmosphere to form metal oxides. These metal oxides can be directly or indirectly converted into metal chlorides by reacting with HCl or NH_4Cl , or directly oxidized to produce metal sulfates. The evolution of valuable metals is consistent with the literature [23], but the final products in this study are mainly controlled as soluble metal chlorides. Schematic representation of the chlorination roasting–water leaching process is shown in Fig. 5.

3.2 Effect of roasting time

The effect of roasting time on the metal extractions was investigated ranging from 1 to 3 h. The results in Fig. 6(a) show that the extraction of Ni and Cu increases rapidly as the roasting time

increases from 1 to 2 h, and reaches the maximum value of 95.3% and 97.5%, respectively, with 2 h roasting process. After that, when the roasting time continues to prolong, the extraction of Ni and Cu improves slowly, which indicates that they are almost completely reacted. The extraction of Fe gradually decreases with the increase of roasting time, because the roasting temperature is higher than the boiling point of ferric chloride ($315\text{ }^\circ\text{C}$), causing it to overflow in a gaseous state, and the longer the roasting time is, the more the ferric chloride is oxidized to ferric oxide. The extraction of Mg is less than 4.5% and there is no obvious change with the increase of roasting time, indicating that the talc and serpentine are difficult to be chlorinated.

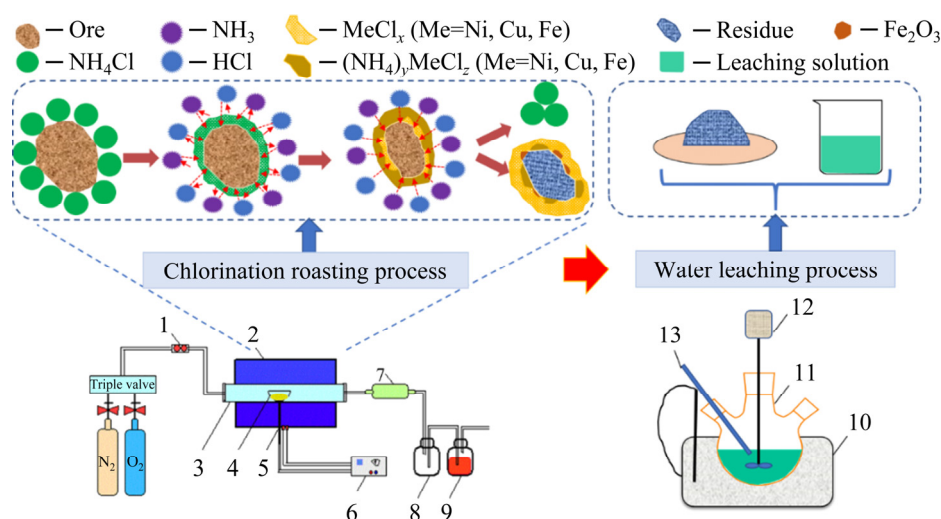


Fig. 5 Diagram of experimental device and schematic representation of chlorination roasting–water leaching process: 1–Flow meter; 2–Tube furnace; 3–Quartz tube; 4–Ceramic crucible; 5–Thermocouple; 6–Temperature control instrument; 7–Condensing apparatus; 8–Safety bottle; 9–Offgas absorption bottle; 10–Water bath; 11–Flask; 12–Mechanical agitation; 13–Thermometer

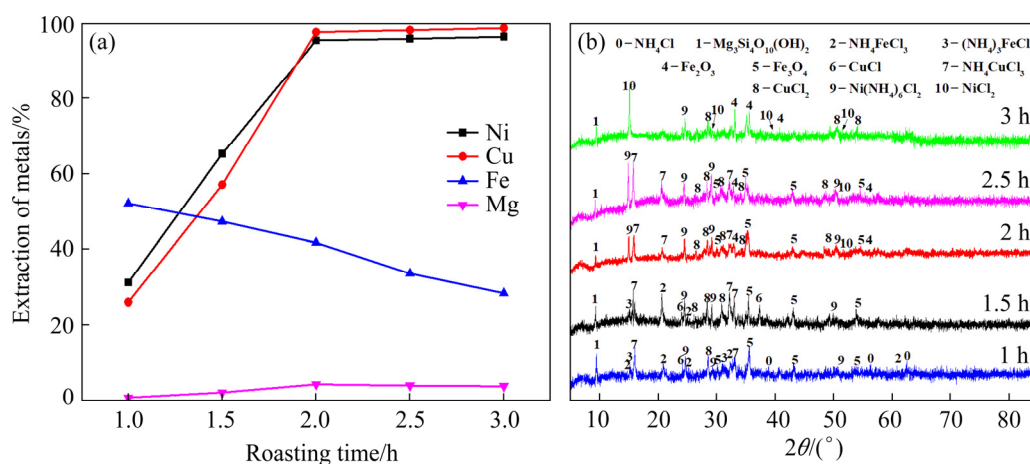


Fig. 6 Effect of roasting time on extraction of metals (roasting temperature $550\text{ }^\circ\text{C}$, mass ratio of NH_4Cl to ore 2:1, and ore particle size $75\text{--}80\text{ }\mu\text{m}$) (a) and XRD patterns of roasted clinkers with different roasting time (b)

According to the XRD patterns of the clinkers at different roasting time in Fig. 6(b), with the increase of roasting time, the diffraction peaks of chlorinated metal–ammonium complexes, metal chlorides and ferric oxides appear in the clinker in sequence. After 1 h roasting, Ni-bearing and Fe-bearing minerals are transformed into the corresponding chlorinated metal–ammonium complexes, and the copper in chalcopyrite is transformed into NH_4CuCl_3 , CuCl and CuCl_2 . As the roasting time is increased to 1.5 h, the diffraction peaks of NH_4Cl disappear due to its complete decomposition. When the roasting time is 2 h, the diffraction peaks of $(\text{NH}_4)_3\text{FeCl}_5$ and NH_4FeCl_3 are replaced by the diffraction peaks of ferric oxide, indicating that they have been decomposed and then oxidized to ferric oxide. Also, the diffraction peaks of CuCl disappear because it is converted to CuCl_2 . When the roasting time is increased to 3 h, the diffraction peaks of $(\text{NH}_4)_6\text{NiCl}_2$ and NH_4CuCl_3 disappear, as they are converted into NiCl_2 and CuCl_2 through decomposition, respectively. The diffraction peaks of Fe_3O_4 also disappear due to being oxidized to ferric oxide.

Figures 7(a–c) show the SEM images of the roasted clinkers obtained at the different roasting time. A lot of undecomposed and unreacted NH_4Cl

adheres to the surface of the clinker in 1 h roasting process, and the decomposition of NH_4Cl results in a loose and porous surface structure. When the roasting time is increased to 2 h, large pits and pore structures appear on the surface of the clinker, and many small particles are bonded together, which is caused by the generation of a large number of chlorinated metal–ammonium complexes. As for 3 h roasting, the chlorinated metal–ammonium complexes are completely decomposed into metal chlorides, and the clinker presents many fine and loose powders, and an octahedral block structure. The block structure is determined to be Fe_2O_3 crystals based on the molar ratio of Fe to O analyzed by EDS, as seen in Fig. 7(d).

These results show that when the roasting time is longer than 2 h, only the phase transaction occurs, but the extractions of Ni and Cu are not significantly improved. Therefore, the roasting time is selected as 2 h in subsequent experiments.

3.3 Effect of mass ratio of NH_4Cl to ore

The dosage of NH_4Cl is an important factor that affects the economics and cleanliness of the process. The influence of the mass ratio of NH_4Cl to ore on the metal extraction is shown in Fig. 8(a). When the mass ratio of NH_4Cl to ore is less than 1:1, the extractions of Cu and Ni are both lower

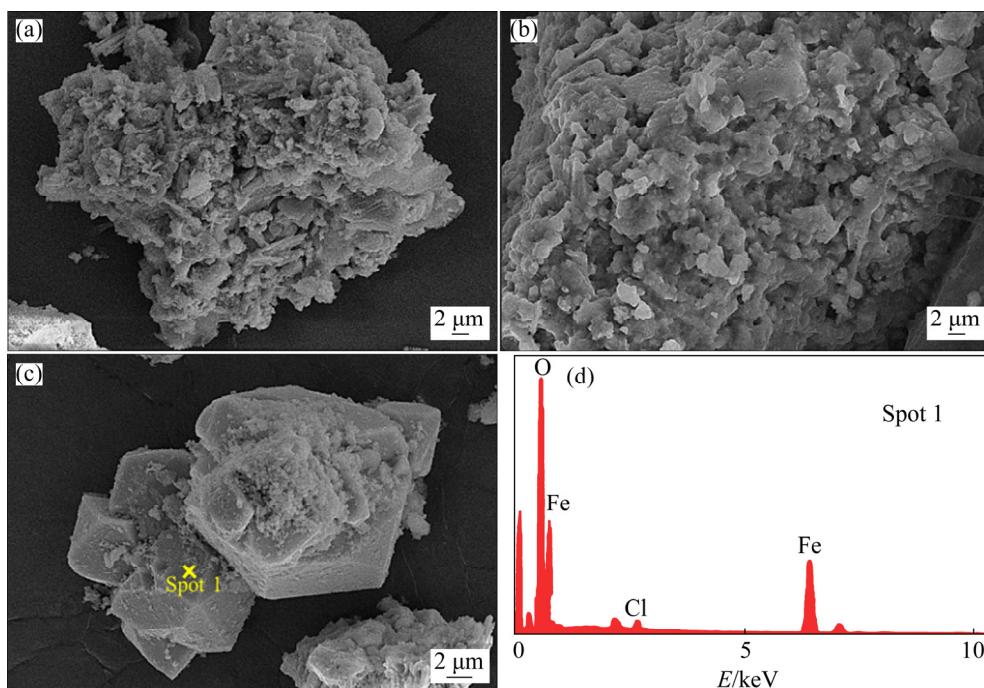


Fig. 7 SEM images of clinkers obtained at roasting time of 1 h (a), 2 h (b) and 3 h (c), and EDS analysis results of Spot 1 (d)

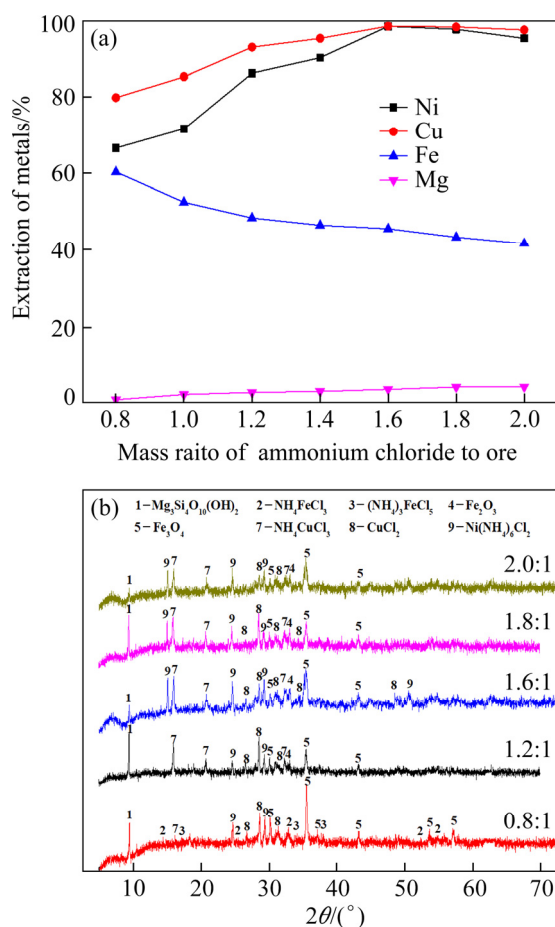


Fig. 8 Effect of mass ratio of NH₄Cl to ore on extraction of metals (roasting temperature 550 °C, roasting time 2 h, and ore particle size 75–80 μm) (a) and XRD patterns of roasted clinkers at different mass ratios of NH₄Cl to ore (b)

than 80% as a result of the insufficient dosage of NH₄Cl. Noticeably, the extraction of Cu is higher than that of Ni, while the extraction of Fe is higher than that with other mass ratios. These indicate that Cu and Fe are chlorinated preferentially than Ni. The XRD in Fig. 8(b) shows that when the mass ratio of NH₄Cl to ore is 0.8:1, the product is mainly chlorinated metal–ammonium complexes containing Fe and Cu, which further proves that Fe and Cu are easier to be chlorinated than Ni. This is because nickel mainly exists in (Ni,Fe)₉S₈ with a relatively stable structure. Then, with the increase in the dosage of NH₄Cl, the extractions of Ni and Cu gradually increase, while the extraction of Fe decreases significantly, and the extraction of Mg remains low (<5%). When the mass ratio of NH₄Cl to ore is 1.6:1, the extractions of Ni and Cu reach the maximum, 98.4% and 98.5%, respectively, and then slightly decrease with the increase of NH₄Cl

dosage, which is caused by a large amount of HCl hindering the generation of stronger chlorination agent (Cl₂). The decrease of Fe extraction is due to the volatilization and oxidation of the product ferric chloride at 550 °C. When the mass ratio of NH₄Cl to ore reaches 1.6:1 or above, the diffraction peaks of phase in the clinker have no obvious change (in Fig. 8(b)), indicating that the dosage of NH₄Cl is sufficient for the chlorination of the ore. In order to prevent the waste of chlorinating agent and ensure the economic efficiency of the process, the mass ratio of NH₄Cl to ore is selected as 1.6:1.

3.4 Effect of ore particle size

The effect of ore particle size on the metal extraction is carried out in five different sieving scale ranges. Figure 9 shows that the effect of ore particle size on the extraction of metals is relatively small compared with other factors. As the particle size becomes finer, the extractions of Ni and Cu gradually increase, while the extractions of Fe and Mg only increase a little. When the sieving scale is 75–80 μm, the extractions of Ni and Cu reach the maximum of 98.4% and 98.5%, respectively, while the extraction of Fe is 45.6%, and the extraction of Mg is less than 4%. The particle size of the ore determines the contact area of the reactants. The finer the particle size is, the larger the contact area between the ore and chlorinating agents is, and the greater the probability of reaction between them is. However, with the decrease of particle size, the gap between the ore powders becomes smaller, which hinders the flow of gas and is not conducive to the contact between the reaction interface and the gas.

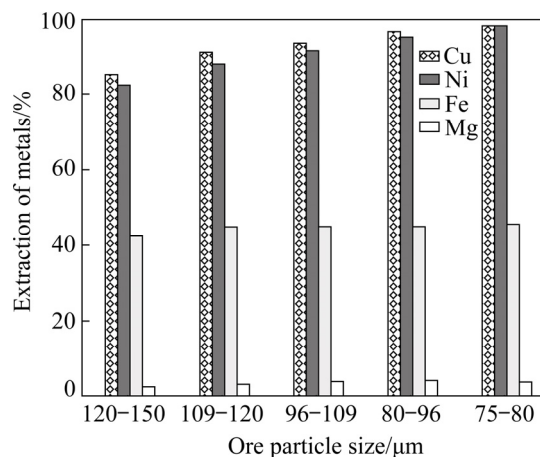


Fig. 9 Effect of ore particle size on extraction of metals (roasting temperature 550 °C, roasting time 2 h, and mass ratio of NH₄Cl to ore 1.6:1)

Therefore, the particle size of the ore is not as fine as possible. Based on these experiments, 75–80 μm is determined as the appropriate experimental condition.

3.5 Analysis of condensate

SEM and XRD are used to analyze the microscopic morphology and phase of the condensate of the exhaust gas, and the results are shown in Fig. 10. In Fig. 10(a), the condensate particles are irregular spheres stuck together with a smooth surface. Figure 10(b) shows that the diffraction peaks of the condensate match very well with the standard diffraction peak of NH_4Cl (JCPDS No. 73-0365), indicating that condensate is NH_4Cl which can be recycled as the chlorinating agent.

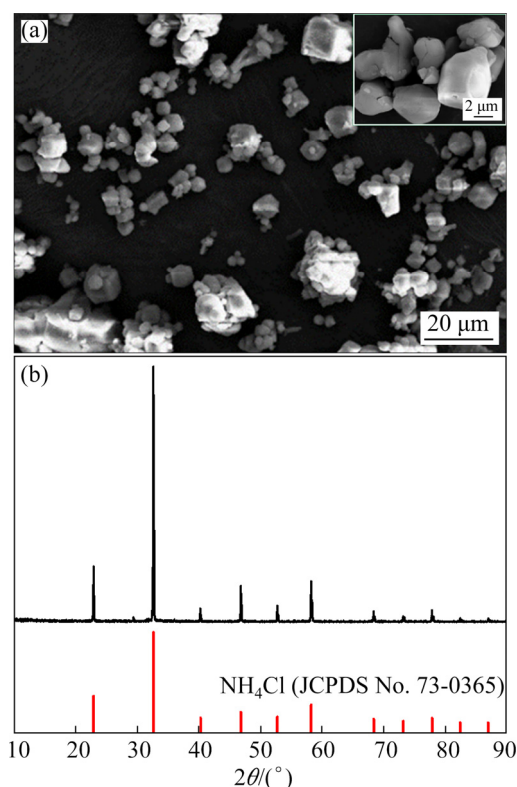


Fig. 10 SEM image (a) and XRD pattern (b) of condensate collected on cooling

3.6 Analysis of chlorination kinetics

The non-isothermal DTA, TG and DTG curves of the mixture of NH_4Cl and the ore at different heating rates are shown in Fig. 11. From the TG and DTG curves of Figs. 11(a, b), it can be determined that there are two mass loss stages in the chlorination roasting process of the ore. Combined with the analysis of the DTA curve in Fig. 11(c), it

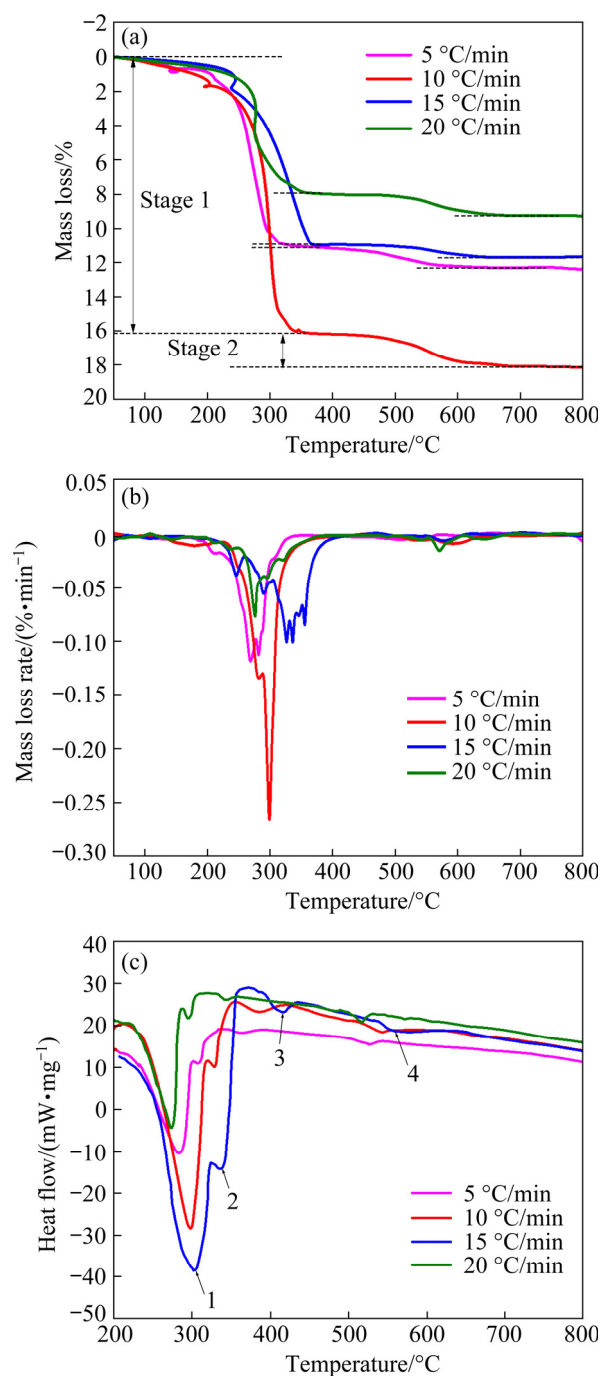


Fig. 11 TG (a), DTG (b) and DTA (c) curves at different heating rates for mixture of NH_4Cl and ore

can be seen that the mass reduction of Stage 1 is mainly caused by the decomposition of NH_4Cl , which corresponds to the endothermic Peaks 1 and 2 on the DTA curve; the mass reduction of Stage 2 is mainly attributed to the chlorination reaction of the ore, which corresponds to the endothermic Peaks 3 and 4 on the DTA curve. The peak temperature of each endothermic peak is given in Table 2.

Table 2 Peak temperature at different heating rates (K)

Heating rate/(K·min ⁻¹)	Peak 1	Peak 2	Peak 3	Peak 4
5	549.6	569.2	616.4	783.0
10	562.5	584.3	641.0	801.0
15	573.7	604.1	663.6	817.2
20	577.8	614.1	681.6	831.5

The two methods of Flynn–Wall–Ozawa (FWO) [26] and Kissinger [27] are used to calculate apparent activation energies (E_a) and apparent pre-exponential factor (A). The kinetic equations based on the experimental data of Fig. 11(c) are obtained at a variable heating rate.

The kinetic analysis of solid–solid reactions is generally performed based on the following Arrhenius equation [28]:

$$\frac{d\alpha}{dt} = A \exp\left(-\frac{E_a}{RT}\right) (1-\alpha)^n \quad (2)$$

where α is the conversion of reaction, t is the time, T is the thermodynamic temperature, R is the molar gas constant and n is reaction order.

The expression of Kissinger method modified by STARINK [29] and FWO method can be expressed as Eqs. (3) and (4), respectively:

$$\ln \frac{\beta}{T_m^{1.8}} = -\frac{E_a}{RT_m} + \ln \frac{AR}{E_a} \quad (3)$$

$$\lg \beta = \lg \frac{AE_a}{Rg(\alpha)} - 2.315 - 0.4567 \frac{E_a}{RT_m} \quad (4)$$

where T_m is the peak temperature on the DTA curves, β is the heating rate, and $g(\alpha) = \int_0^\alpha \frac{d\alpha}{(1-\alpha)^n}$.

At different heating rates β , the value of α at the peak temperature on the DTA curve is approximately equal, so $g(\alpha)$ can be regarded as a constant.

The plots of $\ln(\beta/T_m^{1.8})$ versus $1/T_m$ and $\ln \beta$ versus $1/T_m$ are shown in Figs. 12(a, b), respectively. It can be seen that at each endothermic peak on the DTA curve, there is a good linear relationship between $\ln(\beta/T_m^{1.8})$ and $1/T_m$, and between $\ln \beta$ and $1/T_m$. According to the slope and intercept of the straight line, E_a and A are calculated by the modified Kissinger method and FWO method, respectively, and the results are listed in Table 3. The data in Table 3 show that the reaction activation energies of the two methods are in agreement. In the decomposition process of NH_4Cl , the average value of reaction activation energy at Peak 1 is 116.8 kJ/mol, which is higher than the value of

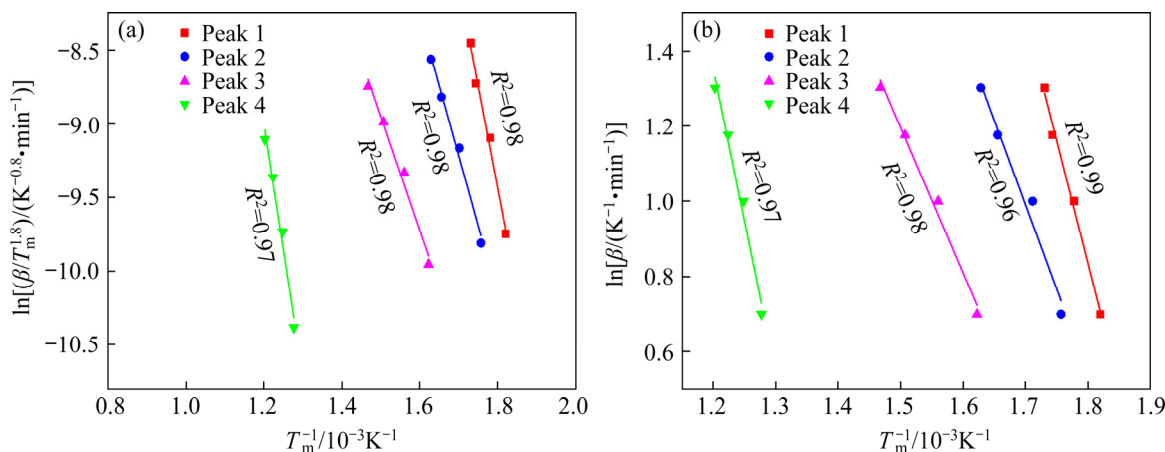


Fig. 12 Relationship between $\ln(\beta/T_m^{1.8})$ and $1/T_m$ of Kissinger method (a) and relationship between $\ln \beta$ and $1/T_m$ of FWO method (b)

Table 3 Apparent activation energies (E_a) and frequency factor (A) of different peaks by different methods

Method	$E_a/(\text{kJ} \cdot \text{mol}^{-1})$				$\ln(A/\text{min})$			
	Peak 1	Peak 2	Peak 3	Peak 4	Peak 1	Peak 2	Peak 3	Peak 4
Modified Kissinger	115.1	79.0	64.2	142.3	25.02	16.1	11.6	21.3
FWO	118.5	81.7	70.3	146.8				
Average	116.8	80.3	67.3	144.6				

80.3 kJ/mol at Peak 2. In the chlorination process of ore, the average value of reaction activation energy at Peak 3 is calculated to be 67.3 kJ/mol, which is lower than the value of 144.6 kJ/mol at Peak 4.

The reaction order (n) of each endothermic peak at different heating rates can be calculated according to the relationship of $I=0.63n^2$ [30], where I is the peak shape index. In an infinitely small interval, a non-isothermal process can be considered as an isothermal process [31], so the reaction rate equations of Peaks 1, 2, 3 and 4 are expressed as follows:

$$\frac{d\alpha}{dt} = \begin{cases} 7.3 \times 10^{10} \exp\left(-\frac{116800}{RT}\right) (1-\alpha)^{0.7} & \text{(for Peak 1)} \\ 9.7 \times 10^6 \exp\left(-\frac{80300}{RT}\right) (1-\alpha)^{0.4} & \text{(for Peak 2)} \\ 10.7 \times 10^4 \exp\left(-\frac{67300}{RT}\right) (1-\alpha)^{1.5} & \text{(for Peak 3)} \\ 17.7 \times 10^8 \exp\left(-\frac{144600}{RT}\right) (1-\alpha)^{2.4} & \text{(for Peak 4)} \end{cases} \quad (5)$$

4 Conclusions

(1) The optimum chlorination conditions demonstrated by the roasting experiments are the ore particle size 75–80 μm , the roasting time 2 h, the mass ratio of NH_4Cl to ore 1.6:1 and the roasting temperature 550 $^\circ\text{C}$. After conducting water leaching of the clinker, 98.4% Ni and 98.5% Cu can be co-extracted, the extraction of Fe is 45.6%, while the extraction of Mg is less than 4%.

(2) In the chlorination process, nickel, iron, and copper can be converted into metal chlorides. Iron chloride can be further oxidized to iron oxide and release Cl_2 or HCl to promote the chlorination reaction. Gangue is difficult to react under low-temperature chlorination conditions. The exhaust gas can be condensed into ammonium chloride for recycling.

(3) The kinetics results of the chlorination process show that both the decomposition of NH_4Cl and the chlorination of minerals include two-step reactions: the decomposition of NH_4Cl and the chlorination of ore.

Acknowledgments

The authors thank the National Natural

Science Foundation of China (No. 52074069), the Natural Science Foundation of Hebei Province (No. E2020501022), the National Basic Research Program of China (No. 2014CB643405) and the Fundamental Research Funds for the Central Universities, China (No. N2223027) for the financially supported of this research.

References

- [1] ZHEN Shi-jie, QIN Wen-qing, YAN Zhong-qiang, ZHANG Yan-sheng, WANG Jun, REN Liu-yi. Bioleaching of low grade nickel sulfide mineral in column reactor [J]. Transactions of Nonferrous Metals Society of China, 2008, 18: 1480–1484.
- [2] YUAN Shuai, ZHOU Wen-tao, LI Yan-jun, HAN Yue-xin. Efficient enrichment of nickel and iron in laterite nickel ore by deep reduction and magnetic separation [J]. Transactions of Nonferrous Metals Society of China, 2020, 30: 812–822.
- [3] MU Wen-ning, CUI Fu-hui, XIN Hai-xia, ZHAI Yu-chun, XU Qian. A novel process for simultaneously extracting Ni and Cu from mixed oxide–sulfide copper–nickel ore with highly alkaline gangue via $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ chlorination and water leaching [J]. Hydrometallurgy, 2020, 191: 105187.
- [4] CUI Fu-hui, MU Wen-ning, ZHAI Yu-chun, GUO Xue-yi. The selective chlorination of nickel and copper from low-grade nickel–copper sulfide–oxide ore: Mechanism and kinetics [J]. Separation Purification Technology, 2020, 239: 116577.
- [5] MAREE W, KLOPPERS L, HANGONE G, OYEKOLA O. The effects of mixtures of potassium amyl xanthate (PAX) and isopropyl ethyl thionocarbamate (IPETC) collectors on grade and recovery in the froth flotation of a nickel sulfide ore [J]. South African Journal of Chemical Engineering, 2017, 24: 116–121.
- [6] CUI Fu-hui, MU Wen-ning, WANG Shuai, XIN Hai-xia, XU Qian, ZHAI Yu-chun, LUO Shao-hua. Sodium sulfate activation mechanism on co-sulfating roasting to nickel–copper sulfide concentrate in metal extractions, microtopography and kinetics [J]. Minerals Engineering, 2018, 128: 104–116.
- [7] GERICKE M, GOVENDER Y. Bioleaching strategies for the treatment of nickel–copper sulphide concentrates [J]. Minerals Engineering, 2011, 24: 1106–1112.
- [8] ZHAO Kai-le, GU Guo-hua, WANG Chang-liang, RAO Xi-ying, WANG Xiao-hui, XIONG Xia-xu. The effect of a new polysaccharide on the depression of talc and the flotation of a nickel–copper sulfide ore [J]. Minerals Engineering, 2015, 77: 99–106.
- [9] XIE Yan-ting, XU Yan-bin, YAN Lan, YANG Ru-dong. Recovery of nickel, copper and cobalt from low-grade Ni–Cu sulfide tailings [J]. Hydrometallurgy, 2005, 80: 54–58.
- [10] QIN Wen-qing, ZHEN Shi-jie, YAN Zhong-qiang, CAMPBELL M, WANG Jun. Heap bioleaching of a low-grade nickel-bearing sulfide ore containing high levels of

- magnesium as olivine, chlorite and antigorite [J]. Hydrometallurgy, 2009, 98: 58–65.
- [11] YANG Cong-ren, QIN Wen-qing, LAI Shao-shi, WANG Jun, ZHANG Yan-sheng, JIAO Fen, REN Lu-yi, ZHUANG Tian, CHANG Zi-yong. Bioleaching of a low grade nickel–copper–cobalt sulfide ore [J]. Hydrometallurgy, 2011, 106: 32–37.
- [12] NORRIS P R. Selection of thermophiles for base metal sulfide concentrate leaching. Part II: Nickel–copper and nickel concentrates [J]. Minerals Engineering, 2017, 106: 13–17.
- [13] CUI Fu-hui, MU Wen-ning, WANG Shuai, XU Qian, ZHAI Yu-chun, LUO Shao-hua. Controllable phase transformation in extracting valuable metals from Chinese low-grade nickel sulphide ore [J]. JOM, 2017, 69: 1–7.
- [14] MU Wen-ning, CUI Fu-hui, HUANG Zhi-peng, ZHAI Yu-chun, XU Qian, LUO Shao-hua. Synchronous extraction of nickel and copper from a mixed oxide–sulfide nickel ore in a low-temperature roasting system [J]. Journal of Cleaner Production, 2018, 177: 371–377.
- [15] ZHENG Shi-li, Li Ping, Tian Lei, CAO Zhan-min, ZHANG Ting-an, CHEN Yong-an, ZHANG Yi. A chlorination roasting process to extract rubidium from distinctive kaolin ore with alternative chlorinating reagent [J]. International Journal of Mineral Processing, 2016, 157: 21–27.
- [16] LIU Jian, WEN Shu-ming, CHEN Yu, LIU Dan, BAI Shao-jun, WU Dan-dan. Process optimization and reaction mechanism of removing copper from an Fe-rich pyrite cinder using chlorination roasting [J]. Journal of Iron Steel Research International, 2013, 20: 20–26.
- [17] ALEKSANDROV P V, MEDVEDEV A S, MILOVANOV M F, IMIDEEV V A, KOTOVA S A, MOSKOVSKIKH D O. Molybdenum recovery from molybdenite concentrates by low-temperature roasting with sodium chloride [J]. International Journal of Mineral Processing, 2017, 161: 13–20.
- [18] ALEKSANDROV P V, MEDVEDEV A S, IMIDEEV V A, MOSKOVSKIKH D O. Nickel sulphide concentrate processing via low-temperature calcination with sodium chloride. Part 1—Identification of interaction products [J]. Minerals Engineering, 2019, 134: 37–53.
- [19] BAI Shao-jun, BI Yun-xiao, DING Zhan, LI Chun-long, YU pan, WEN Shu-ming. Innovative methodology for the utilization of low-grade pyrite cinder containing heavy metals via hydrothermal alkali melting followed by chlorination roasting [J]. Journal of Alloys and Compounds, 2020, 840: 155722.
- [20] NADIROV R K, SYZDYKOVA L I, ZHUSSUPOVA A K, USSERBAEV M T. Recovery of value metals from copper smelter slag by ammonium chloride treatment [J]. International Journal of Mineral Processing, 2013, 124: 145–149.
- [21] PANDA R, JADHAO P R, PANTA K K, NAIK S N, BHASKAR T. Eco-friendly recovery of metals from waste mobile printed circuit boards using low temperature roasting [J]. Journal of Hazardous Materials, 2020, 395: 122642.
- [22] XU Cong, CHENG Hong-wei, LI Guang-shi, LU Chang-yuan, LU Xiong-gang, ZOU Xing-li, XU Qian. Extraction of metals from complex sulfide nickel concentrates by low-temperature chlorination roasting and water leaching [J]. International Journal of Minerals, Metallurgy and Materials, 2017, 24(4): 377–385.
- [23] LI Guang-shi, ZOU Xing-li, CHENG Hong-wei, GENG Shu-hua, XIONG Xiao-lu, XU Qian, ZHOU Zhong-fu, LU Xiong-gang. A novel ammonium chloride roasting approach for the high-efficiency co-sulfation of nickel, cobalt, and copper in polymetallic sulfide minerals [J]. Metallurgical and Minerals Transactions B, 2020, 51: 2769–2784.
- [24] ZHANG Guo-quan, LUO Dong-mei, DENG Chen-hui, LV Li, LIANG Bin, LI Chun. Simultaneous extraction of vanadium and titanium from vanadium slag using ammonium sulfate roasting–leaching process [J]. Journal of Alloys Compounds, 2018, 742: 504–511.
- [25] CUI Fu-hui, MU Wen-ning, WANG Shuai, XIN Hai-xia, SHEN Hong-tao, XU Qian, ZHAI Yu-chun, LUO Shao-hua. Synchronous extractions of nickel, copper, and cobalt by selective chlorinating roasting and water leaching to low-grade nickel–copper matte [J]. Separation and Purification Technology, 2018, 195: 149–162.
- [26] OZAWA T. A new method of analyzing thermogravimetric data [J]. Bulletin of the Chemical Society of Japan, 1965, 38(11): 1881–1886.
- [27] KISSINGER H E. Reaction kinetics in differential thermal analysis [J]. Analytical Chemistry, 1957, 29(11): 1702–1706.
- [28] CAI Jun-meng, XU Di, DONG Zhu-jun, YU Xi, YANG Yang, BANKS S W, BRIDGWATER A V. Processing thermogravimetric analysis data for isoconversional kinetic analysis of lignocellulosic biomass pyrolysis: Case study of corn stalk [J]. Renewable and Sustainable Energy Reviews, 2018, 82: 2705–2715.
- [29] STARINK M J. A new method for the derivation of activation energies from experiments performed at constant heating rate [J]. Thermochimica Acta, 1996, 288: 97–104.
- [30] GAO Chuan-hui, LI Xian-guo, FENG Li-juan, XIANG Zhan-chang, ZHANG Da-hai. Preparation and thermal decomposition of $5\text{Mg}(\text{OH})_2 \cdot \text{MgSO}_4 \cdot 2\text{H}_2\text{O}$ nanowhiskers [J]. Chemical Engineering Journal, 2009, 150: 551–554.
- [31] VYAZOVKIN S, WIGHT C A. Isothermal and non-isothermal kinetics of thermally stimulated reactions of solids [J]. International Reviews in Physical Chemistry, 2010, 17: 407–433.

低品位镍铜硫化矿氯化焙烧同步提取 有价金属及过程的动力学

牟文宁^{1,2,3}, 肖腾飞^{1,2}, 石双志⁴, 徐雪晴^{1,2}, 程皓^{1,2}, 翟玉春³

1. 东北大学秦皇岛分校 资源与材料学院, 秦皇岛 066004;

2. 东北大学 材料科学与工程学院, 沈阳 110819;

3. 东北大学 冶金学院, 沈阳 110819;

4. 通用电气-哈动力-南汽轮能源服务(秦皇岛)有限公司, 秦皇岛 066000

摘 要: 研究低品位镍铜硫化矿氯化铵氯化焙烧-水浸工艺高效同步提取镍和铜。结果表明, 当矿粉粒度为 75~80 μm , 焙烧时间为 2 h, 氯化铵与矿的质量比为 1.6:1, 焙烧温度为 550 $^{\circ}\text{C}$ 时, 可同步提取 98.4% 的镍和 98.5% 的铜。采用 X 射线衍射(XRD)结合扫描电子显微镜(SEM)分析各种矿物的演化行为。通过 Kissinger 法和 Flynn-Wall-Ozawa(FWO)法处理差热-热重分析(DTA-TG)数据, 研究氯化过程动力学。结果表明, 低品位镍铜硫化矿的氯化过程主要包括 NH_4Cl 的分解和矿物的氯化两个阶段, 最大的表观活化能(E_a)分别为 114.8 kJ/mol 和 144.6 kJ/mol。废气经冷凝回收确定为氯化铵, 可作为反应物再次利用, 实现工艺的经济性和清洁性。

关键词: 低品位镍铜硫化矿; 氯化焙烧; 同步提取; 物相演变; 动力学

(Edited by Bing YANG)