International Journal of Minerals, Metallurgy and Materials
Volume 24, Number 4, April 2017, Page 377
DOI: 10.1007/s12613-017-1417-2

Extraction of metals from complex sulfide nickel concentrates by low-temperature chlorination roasting and water leaching

Cong Xu, Hong-wei Cheng, Guang-shi Li, Chang-yuan Lu, Xiong-gang Lu, Xing-li Zou, and Qian Xu

State Key Laboratory of Advanced Special Steel & School of Materials Science and Engineering, Shanghai University, Shanghai 200072, China

(Received: 28 June 2016; revised: 18 September 2016; accepted: 22 September 2016)

Abstract: The recovery of valuable metals from complex sulfide concentrates was investigated via chlorination roasting followed by water leaching. A reaction process is proposed on the basis of previous studies and the results of our preliminary experiments. During the process, various process parameters were studied, including the roasting temperature, the addition of NH_4Cl, the roasting time, the leaching time, and the liquid-to-solid ratio. The roasted products and leach residues were characterized by X-ray diffraction and vibrational spectroscopy. Under the optimum condition, 95% of Ni, 98% of Cu, and 88% of Co were recovered. In addition, the removal of iron was studied in the water leaching stage. The results demonstrate that this process provides an effective approach for extracting multiple metals from complex concentrates or ores.

Keywords: extraction; nickel; sulfide; chlorination; ammonium chloride; roasting; leaching

1. Introduction

Nickel is a strategic metal that is widely used in stainless steel, alloys, batteries, and catalysts. The world's available nickel ore deposits mainly consist of sulfide and laterite, and sulfide deposits represent approximately 40wt% of land-based nickel reserves [1]. In China, however, nickel sulfides account for 91wt% of total nickel reserves [2]. With the discrepancy between the growing industrial demand and depleting ore grade, alternative methods applicable to low-grade or complex ores have become an important research topic.

Conventionally, sulfide ores are treated via a flotation-smelting-converting process. However, this technology is limited by concentrate quality and usually results in a low direct yield of metals. Researchers have applied various hydrometallurgical processes to metal recovery from complex sulfide ores, including acid leaching [3–5], heap leaching [6], and pressure oxidation leaching [7]. However, these methods not only require lengthy operations, but also generate substantial concentrations of iron that complicate downstream treatment [8–9].

Concerns have also been raised [10–13] about using roasting pretreatments to overcome the problems of direct leaching. Among the alternative processes, chlorination is an important technique in the recovery of many nonferrous metals from minerals or concentrates [14–16]. Solid chlorinating agents such as NaCl, $CaCl_2$, KCl, and NH_4Cl are extensively used in dry chlorination instead of Cl_2 or HCl because the latter two gases can be a strong corrosion of equipment [17]. In the process involving dry chlorination with raw materials roasted at temperatures above 350°C, nickel, copper, and other valuable metals are selectively converted into soluble dichlorides or sulfates, whereas iron remains predominantly in the form of oxides [18–20].

In China, NH_4Cl is produced mainly as a byproduct of the soda industry and is limited to use in agricultural production. NH_4Cl not only provides a cheaper source of chlorine than KCl, but also reacts with raw materials at a lower temperature than NaCl [21–22]. Roasting with NH_4Cl instead of NaCl has also been studied in oxides as well as sulfides [23–25]. This treatment has generally been conducted at temperatures above 300°C using a large amount of additive (>50wt%) and could achieve high recovery of various

---

Corresponding author: Hong-wei Cheng E-mail: hwcheng@shu.edu.cn

metals. However, the majority of studies have focused on oxide ores, and the roasting mechanism described in literatures is dependent on the thermal decomposition of NH_4Cl to produce HCl as a chlorine source; this procedure is incompatible with the chlorination process that has been reported for sulfides with other chlorinating agents [26–28]. Little attention has been devoted to the reaction process associated with roasting sulfides using NH_4Cl as a chlorinating agent.

In this paper, we investigated the feasibility of chlorination roasting of complex sulfide nickel concentrate with NH_4Cl and the application of the subsequent iron-removing methods through a jarosite process. The role that NH_4Cl plays in the chlorination process was discussed, and its reaction mechanism was elucidated. Furthermore, the effects of roasting temperature, the addition of NH_4Cl, the roasting time, the leaching time, and the liquid-to-solid ratio on the extraction behavior of metals were studied.

2. Experimental

2.1. Materials

The sulfide nickel concentrate sample used in this study was from Jinchuan Co., Ltd. in Gansu Province, China. For this study, the concentrate sample was ground into particles smaller than 75 μm. The chemical composition of the nickel concentrate was measured by inductively coupled plasma optical emission spectrometry (ICP-OES). Table 1 presents the composition of the sulfide nickel concentrate. The X-ray diffraction (XRD) pattern of the concentrate is shown in Fig. 1. The major silicate gangue is lizardite. All chemical reagents used in this study were analytical grade and were purchased from Sinopharm Chemical Reagent Co., Ltd., China. Ammonium chloride was ground into particles passing a 50-mesh screen before use.

Table 1. Chemical composition of the sulfide nickel concentrate wt%

Fe	O	S	Ni	Cu	Co	Si	Mg
34.16	19.75	16.47	9.37	6.63	0.227	5.57	6.88

2.2. Chlorination roasting and water leaching

10 g of concentrate was mixed thoroughly with a certain amount of NH_4Cl, and the mixture was transferred into a 100 mL crucible. The crucible was then placed into a muffle furnace for a certain period of time after the furnace had been preheated to the designated preset temperature. The roasted samples were removed after the furnace cooled to room temperature.

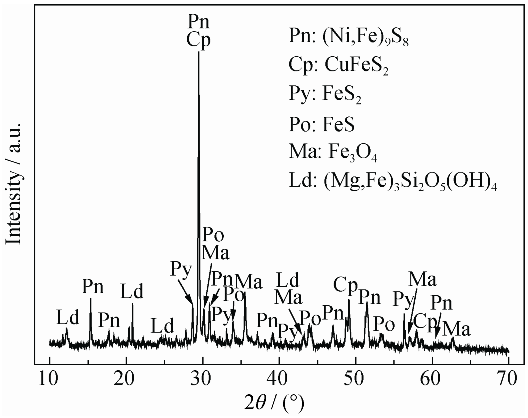


Fig. 1. XRD pattern of the sulfide concentrate.

The roasted residues were then leached with deionized water at 90°C with a liquid-to-solid ratio of 5:1 mL/g for 120 min to extract valuable metals. The leaching solution was then filtered and transferred to a 1000 mL volumetric flask. Fig. 2 shows the flowsheet for the experimental procedure. And in order to precipitate ferric ions even better, in the iron-removal process, the residues were pre-oxidated with a certain amount of H_2O_2, and then the pH values of solutions were adjusted by $NH_3 \cdot H_2O$ by adding slowly to maintain the appropriate pH values as shown in Fig. 2. The extractions of Ni, Cu, Fe, and Co (η) were calculated according to the following equation:

$$\eta = \frac{CV}{1000 m\omega} \times 100\% \tag{1}$$

where C is the content of metals from the leach liquor, mg/L; V is the volume of leach liquor, L; m is the mass of sulfide concentrate used in the experiments, g; and ω is the content of metals in the raw ore. Parallel experiments were conducted twice, and the average extractions were obtained to ensure the reproducibility of the results.

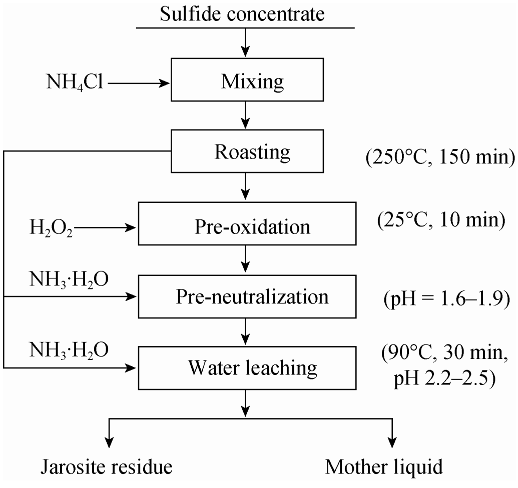


Fig. 2. Flowsheet for the chlorination-leaching process.

2.3. Analytical methods

The contents of nickel, copper, and cobalt in the leach liquor were determined by ICP-OES (Perkin-Elmer 7300DV), and the amount of iron was analyzed by chemical titration. The solution before iron removal was obtained by acid-washing the calcine with 40 mL of 5wt% HCl solution. The ammonium, chloride, and sulfate ion contents were determined by the formaldehyde method, the Mohr method, and the gravimetric method, respectively. The pH values of the leach liquor were measured using a pH meter (pH, Shanghai INESA, PHS-3C). The phases of sulfide concentrate, roasted products, and leach residues were characterized by XRD (Rigaku, 18KW D/MAX2500V+/PC, Cu K_α radiation, 40 kV/40 mA). The infrared spectra of the leach residues were collected by Fourier transform infrared (FTIR) spectroscopy (Nicolet Avatar370) in the wavenumber range from 400 to 4000 cm^{-1} using the KBr pellet technique. Laser Raman scattering spectra of calcines and leach residues were recorded at room temperature in the wavenumber range from 100 to 1600 cm^{-1} using a Renishaw Invia confocal micro-Raman system; the 633 nm line was used as the excitation source.

3. Results and discussion

3.1 Chlorination roasting

3.1.1. Phase changes during chlorination roasting

To investigate the reaction process of chlorination roasting, a series of roasting experiments were conducted at various temperatures from 200 to 325°C at intervals of 25°C. The roasted products were sealed in an N_2 atmosphere. XRD analyses were carried out as soon as possible because of the hygroscopic nature of the reaction products. As shown in Table 2, the size of the arrows indicated the relative content of different phases. The presence of NH_4FeCl_3 is indicated in the sample roasted at 200°C, in addition to unreacted pentlandite, chalcopyrite, pyrite, and magnetite. Compared with the phases of unreacted pentlandite and chalcopyrite at 200°C, the formation of Fe_2O_3 indicates that the oxidation of iron sulfides may occur readily or preferentially in the presence of NH_4Cl. The main reactions related to iron sulfides are assumed to be as follows:

$$4FeS + 3O_2 \rightarrow 2Fe_2O_3 + 2S_2 \tag{2}$$

$$2FeS + 2Cl_2 \rightarrow 2FeCl_2 + S_2 \tag{3}$$

$$FeCl_2 + NH_4Cl \rightarrow NH_4FeCl_3 \tag{4}$$

In the XRD pattern of the sample roasted at 225°C, the peaks associated with pentlandite and chalcopyrite started to decrease in intensity, and NH_4NiCl_3, $(NH_4)_2CuCl_4$ and $(NH_4)_2Ni_2(SO_4)_3$ were detected in the roasted products. Of course, significant unreacted metal sulfides were also detected in the roasted products. Pentlandite, chalcopyrite, and pyrite had disappeared completely by 250°C. In addition, double salts with different molar ratios were abundant; these salts included chloride salts such as $(NH_4)_2FeCl_5$ and sulfate salts such as $(NH_4)_3Fe(SO_4)_3$, $NH_4Fe(SO_4)_2$, and $(NH_4)_2Fe(SO_4)_2$. The main reactions about iron at this temperature could be assumed to be as follows:

$$6FeCl_2 + 3O_2 \rightarrow 2FeCl_3 + 2Fe_2O_3 + 3Cl_2\uparrow \tag{5}$$

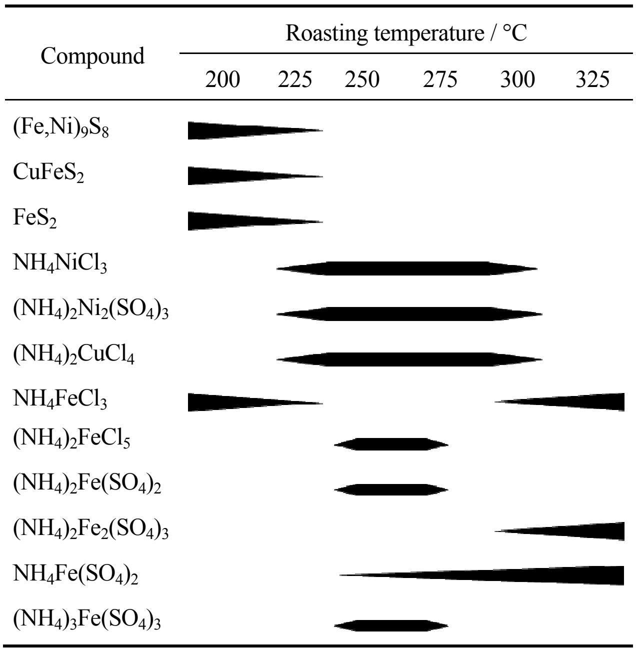
$$FeCl_3 + 2NH_4Cl \rightarrow (NH_4)_2FeCl_5 \tag{6}$$

$$Fe_2O_3 + 6(NH_4)_2SO_4 \rightarrow 2(NH_4)_3Fe(SO_4)_3 + 6NH_3\uparrow + 3H_2O \tag{7}$$

$$Fe_2O_3 + 4(NH_4)_3Fe(SO_4)_3 \rightarrow 6NH_4Fe(SO_4)_2 + 6NH_3\uparrow + 3H_2O \tag{8}$$

At a roasting temperature of 325°C, these double salts started to decompose into simple chlorides and sulfates such as $NiCl_2$, $CuCl$, $CuCl_2$, $Fe_2(SO_4)_3$, $NiSO_4$, which were not listed here but reflected in the XRD result.

Table 2. Compounds identified by XRD after roasting at different temperatures



Compound	Roasting temperature / °C					
	200	225	250	275	300	325
$(Fe,Ni)_9S_8$	▬	▬				
$CuFeS_2$	▬	▬				
FeS_2	▬	▬				
NH_4NiCl_3		▬	▬	▬	▬	
$(NH_4)_2Ni_2(SO_4)_3$		▬	▬	▬	▬	
$(NH_4)_2CuCl_4$		▬	▬	▬	▬	
NH_4FeCl_3	▬	▬			▬	▬
$(NH_4)_2FeCl_5$			▬	▬		
$(NH_4)_2Fe(SO_4)_2$			▬	▬		
$(NH_4)_2Fe_2(SO_4)_3$					▬	▬
$NH_4Fe(SO_4)_2$			▬	▬	▬	▬
$(NH_4)_3Fe(SO_4)_3$			▬	▬		

The reaction mechanism during the roasting process is presented in Fig. 3. It involves the following steps. (1) Iron sulfide formation is catalyzed by HCl and O_2, and binary metal sulfides are thermally decomposed into simple sulfides and elemental sulfur. (2) Sulfur is oxidized into SO_3 or SO_2, and the produced SO_2 can be further oxidized into SO_3 via catalysis with Fe_2O_3 [29]. SO_3 or SO_2 then reacts with NH_4Cl to produce Cl_2 in the presence of oxygen, and metal sulfides are chlorinated by Cl_2. (3) Iron oxides or metal chlorides undergo combination reactions with ammonium salts.

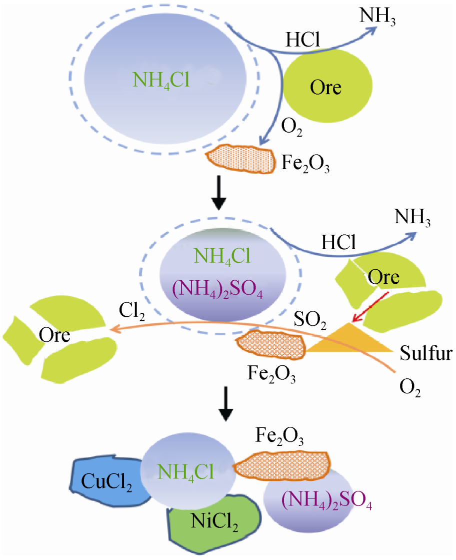


Fig. 3. Reaction mechanism of sulfide concentrate with NH_4Cl.

The *in situ* chlorination mechanism has been widely confirmed in previous studies involving other chlorinating agents [18,28], and the chlorination of sulfides is more thermodynamically favorable than the chlorination of oxides [22]. This scenario can be also compared with the chlorination of oxides by NH_4Cl at temperatures above 300°C [30], where the chlorination of sulfides was demonstrated to occur at lower temperatures than the chlorination of oxides. Possible chemical reactions during the roasting process are as follows:

$$4NH_4Cl + O_2 + 2SO_3 \rightarrow 2(NH_4)_2SO_4 + 2Cl_2\uparrow \quad (9)$$

$$(Ni,Fe)_9S_8 + 22NH_4Cl + 16.5O_2 \rightarrow 4NH_4NiCl_3 + 5FeCl_2 + 8(NH_4)_2SO_4 + 2NH_3\uparrow + H_2O \quad (10)$$

$$CuFeS_2 + 6NH_4Cl + 4O_2 \rightarrow (NH_4)_2CuCl_4 + FeCl_2 + 2(NH_4)_2SO_4 \quad (11)$$

The oxidation process primarily facilitates the conversion of iron sulfides into hematite or magnetite. The sulfation of these iron oxides can then be achieved through reaction with $(NH_4)_2SO_4$ generated from the chlorine-forming reaction in Eq. (9) [31]. In the presence of O_2, Cl_2, HCl, NH_3, SO_2, and SO_3, competing reactions exist between chlorination and sulfation of different metal sulfides or oxides [32]. On the basis of the thermodynamics of some reactions shown in Fig. 4, the sulfation sequence for various metal oxides is Fe, Co, Ni, Cu; in addition, iron chlorides are not stable in the range of experimental reaction temperatures. Thus, iron oxides are first generated and readily converted into double sulfates ($(NH_4)_xMe_y(SO_4)_z$, Me = Fe, Ni). By contrast, the behavior of copper runs counter to that of iron, which is almost in the form of double chlorides. And notably, compared with Table 2, the formation of double chlorides contributes to the stability of iron chlorides in the roasting process.

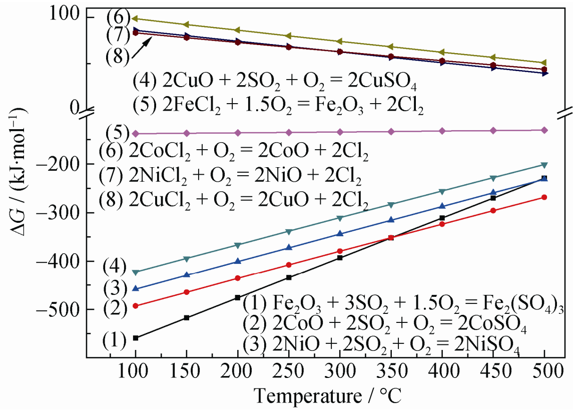


Fig. 4. Relationship between ΔG and T for some relevant reactions.

3.1.2. Effect of roasting temperature

A series of chlorination roasting experiments were carried out between 200 and 325°C with the addition of NH_4Cl and with the reaction time kept constant. The extraction of metals was determined by the methods described in section 2.2. The effect of roasting temperature on the extraction of metals is shown in Fig. 5. A significant improvement was observed in the extraction of nickel, copper, iron, and cobalt as the temperature was increased to 250°C; thereafter, however, the extraction of nickel, copper, and cobalt decreased slightly. This decrease is attributed to the dramatic decomposition of ammonium chloride at high temperatures, which results in a smaller portion available to react with sulfides at

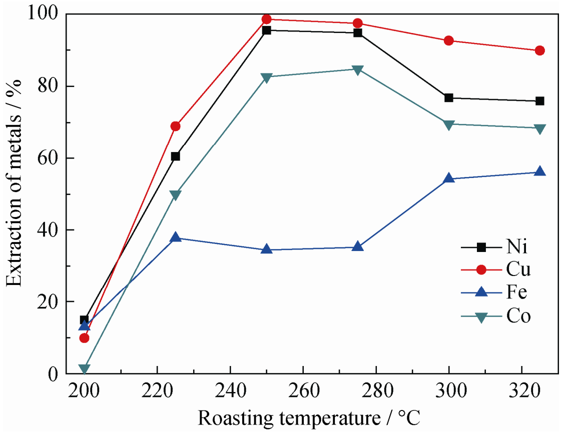


Fig. 5. Effect of roasting temperature on the extraction of metals (90°C, 100 mL water for 60 min).

temperatures above 300°C. In the leach residues, iron is present as ammoniojarosite. Furthermore, as the roasting temperature increases, ammonium chloride decomposes quickly; this decomposition leads to a decrease in the ammonium content during leaching. As a result, at temperatures above 300°C, iron extraction increases remarkably. Obviously, roasting at approximately 250°C resulted in a good leaching performance.

3.1.3. Effect of NH_4Cl addition

The influence of NH_4Cl addition on the extraction of metals is presented in Fig. 6. The results show that increasing the amount of ammonium chloride up to 100wt% promotes the extraction of metals, and then the extractions of metals decrease slowly when the amount of ammonium chloride added is increased further. These results stem from excess NH_4Cl particles restraining the diffusion of O_2 because of the sintering of reaction products. The extraction of iron increases with the amount of NH_4Cl added from 20wt% to 50wt% and thereafter remains constant until the amount of NH_4Cl added reaches 100wt%. The extractions of Ni, Cu, and Co decrease as the amount of NH_4Cl added exceeds 100wt%, and the extraction of iron increases slightly. This behavior is attributed to the decrease of the concentration of SO_4^{2-} in the leaching solution. The extractions of Ni, Cu, and Co were sufficient with the excess addition of NH_4Cl; thus, the amount of NH_4Cl added was fixed at 80wt% in the subsequent experiments.

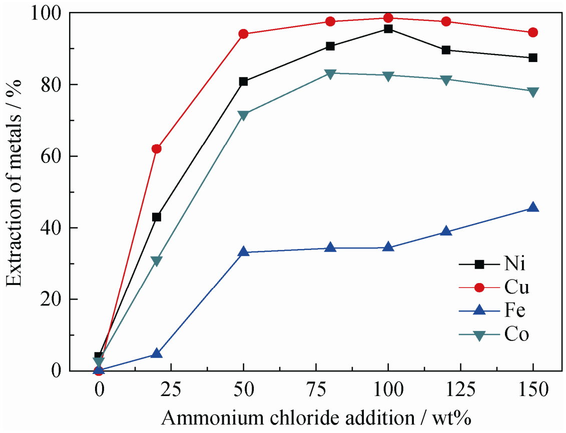


Fig. 6. Effect of NH_4Cl addition on the extraction of metals (90°C, 100 mL water for 60 min).

3.1.4. Effect of roasting time

The effect of roasting time on the extraction of valuable metals is shown in Fig. 7. The extraction of metals increases sharply as the roasting time increases to 60 min; further increases in roasting time beyond 60 min lead to increases in extractions of no more than 20%. When the roasting time is extended from 60 min to 180 min, the extraction results remain constant. However, the extraction of iron decreases when the roasting time is increased from 60 min to 300 min. The decrease in iron recovery to the leach liquor after 60 min may be caused by the formation of Fe_2O_3 or $NH_4Fe(SO_4)_2$, which is poorly soluble [8]. Hence, a roasting time of 150 min is sufficient to extract more than 88% Co, 94% Ni, and 98% Cu.

The metal extraction results also indicate a common sequence of recovery rates under certain conditions: Cu > Ni > Co > Fe. This order is the reverse of that related to the oxygen affinity of various nonferrous metals. Furthermore, Fe also exhibits a stronger affinity for chlorine than Co, Ni, and Cu, consistent with the roasted products obtained at roasting temperatures ranging from 200 to 250°C. The difference in roasting behaviors among these four metals may be due to the different oxidation rates of the corresponding metal sulfides and to the differences in chemical stability of the corresponding metal chlorides.

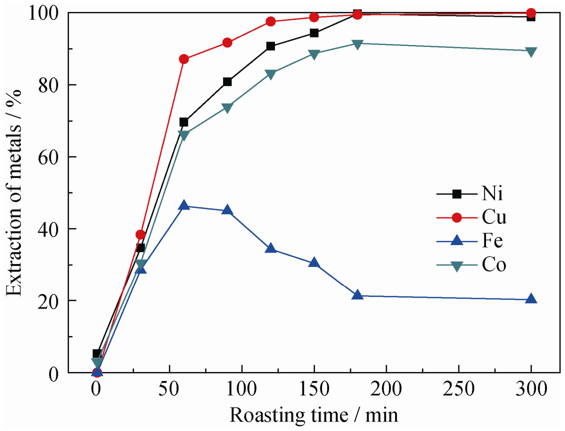


Fig. 7. Effect of roasting time on the extraction of metals (90°C, 100 mL water for 60 min).

3.2. Water leaching

After chlorination roasting under the optimum conditions (roasting temperature of 250°C; 80wt% NH_4Cl addition; roasting time of 150 min), the calcines were subjected to leaching by water. As evident in Fig. 7, the extraction of iron does not exceed 50% over various roasting time periods. Results reported in literatures [32–33] indicate that the control of iron plays a critical role in the hydrometallurgical processes of non-ferrous metals and that high leaching temperatures contribute greatly to the formation of ammoniojarosite. Here we expect iron to be removed completely as a precipitate during the hot-water leaching stage. As a result of its successful implementation in the zinc metallurgy industry [34], the jarosite process was introduced to lower the concentration of iron in the leach liquor while fixing the leaching temperature at 90°C.

3.2.1. Effect of leaching time

Fig. 8 shows the effect of leaching time on the leaching behavior of metals. The FTIR spectra of residues leached for different periods of time are given in Fig. 9. The leaching time is observed to strongly affect the extraction of iron. As the leaching time increases from 10 to 120 min, the dissolution of iron decreases by approximately 17%. Not surprisingly, the extractions of nickel, copper, and cobalt remain almost constant as the leaching time is extended. In addition, Fig. 9 shows that the crystallization of ammoniojarosite is not accomplished when calcine is leached for only 10 min. Clearly, leaching for 30 min is necessary to precipitate ammoniojarosite effectively.

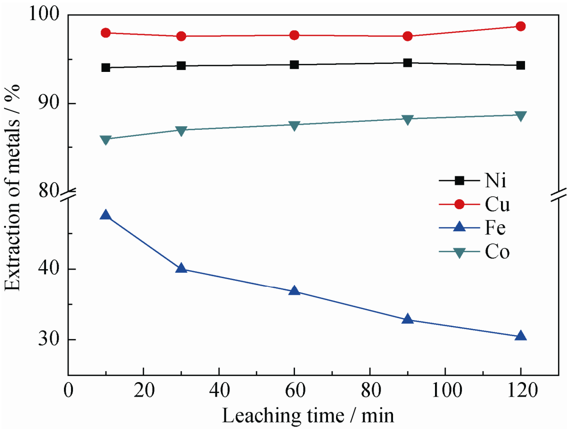


Fig. 8. Effect of leaching time on the extraction of metals (90°C, 100 mL water).

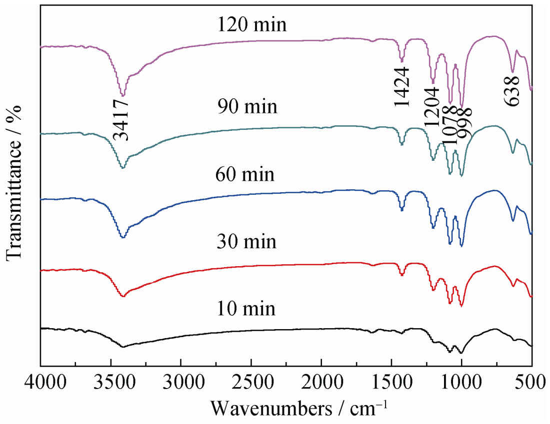


Fig. 9. FTIR spectra of residues leached for different periods of time (90°C, 100 mL water).

3.2.2. Effect of liquid to solid ratio

Fig. 10 shows the effect of the liquid-to-solid ratio on the extraction of metals. These results suggest that the extractions of nickel, copper, and cobalt are weakly dependent on the liquid-to-solid ratio in the range from 1 to 5 mL/g. However, the extraction of iron changes drastically as a result of a decrease in the initial ferric ion concentration when too much water is added. However, excessive water in the leaching process can lower the concentration of metal ions in the solution, which adversely affects the subsequent separation and purification. Therefore, a liquid-to-solid ratio of 2 mL/g is appropriate in the leaching stage to extract 95% of Ni, 98% of Cu, 30% of Fe, and 88% of Co.

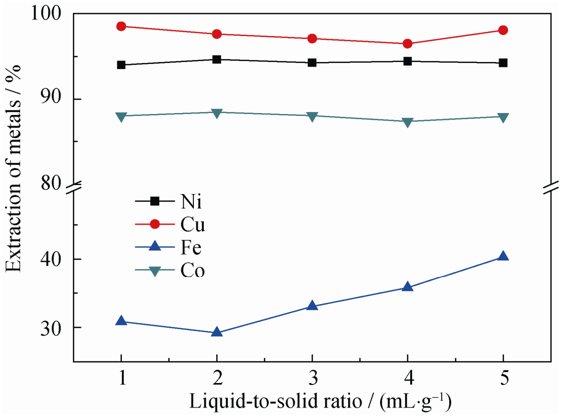


Fig. 10. Effect of the liquid-to-solid ratio on the extraction of metals (90°C for 60 min).

3.2.3. Iron removal process

As presented in Fig.10, under the optimum condition, about 30% of Fe were transferred into the leach liquor. And so, an iron-removal step is adopted to separate iron from the solution to the fullest. The iron-removal process includes two steps: chemical reaction and crystallization [35]. The reaction can be written as

$$3Fe^{3+} + NH_4^{+} + 2SO_4^{2-} + 6H_2O \rightarrow NH_4Fe_3(OH)_6(SO_4)_2 + 6H^{+} \qquad (12)$$

On the basis of this reaction, sufficient monovalent cation and sulfate ion are necessary to precipitate ferric ions. Roasted products can provide sufficient sulfate ions, and the majority of ammonium in the additive is fixed in the form of double salts. Therefore, a supply of extra sulfate salts is not needed to maintain the precipitation reaction. Notably, ferrous compounds were identified in the roasted products (Table 2). Thus, moderate amounts of oxidizing agent are required to maximize the precipitation of iron. Meanwhile, the precipitation reaction will generate acid, which decreases the removal rate of iron. Thus, a neutralizing agent is used to adjust the initial acidity and pH value of the solution during the reaction process. In these experiments, the roasted samples were dissolved in water and per-oxidized with 0.4 mL of 20wt% H_2O_2 for 10 min at room temperature. Then, 5wt% $NH_3 \cdot H_2O$ was slowly injected to maintain the initial pH value at 1.6–1.9 and the final pH value at 2.2–2.5 at the leaching temperature of 90°C for 30 min. The insoluble gangue minerals and minor unreacted sulfides may serve as nucleation seeds to accelerate the kinetics of crystallization. Agitation can also improve the dispersion of nucleation seeds [36].

The results of iron precipitation are presented in Fig. 11. Based on the the mass balance of elements with Table 1, the calculation from these results indicates that 84.68% of iron was removed in the form of ammoniojarosite. The remaining 11.88% of iron was in the leach residue in the form of hematite and minor unreacted iron sulfides. More importantly, approximately 92% of chloride ion from NH_4Cl, 36% of ammonium, and 99% of sulfur were fixed in the calcine. This result indicates that the emission of SO_2 is negligible and the released ammonia gas can be absorbed by water.

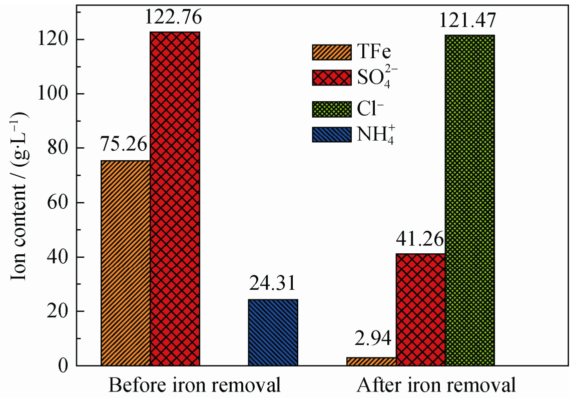


Fig. 11. Ion content of the leach liquor before and after iron removal.

3.2.4. Characteristics of the leach residue

The XRD pattern of the residue after the iron-removal process is given in Fig. 12. The main phases are ammoniojarosite and lizardite. Lizardite is the main gangue in the flotation concentrate. In addition, the FTIR and Raman spectra of the residue are shown in Fig. 13. Three bands are observed in the region from 1000 to 1200 cm^{-1} in both spectra. The two peaks at 1082 and 1196 cm^{-1} in the FTIR spectrum and the two bands at 1095 and 1163 cm^{-1} in the Raman spectrum are the vibrational modes of $\nu_3(SO_4^{2-})$, and the strong peak at 1001 cm^{-1} in the FTIR spectrum and at 1005 cm^{-1} in the Raman spectrum are assigned to the symmetric stretching mode of SO_4^{2-} [37]. The splitting of the $\nu_3(SO_4^{2-})$ mode is consistent with the C_{2v} point symmetry of SO_4^{2-} ions in jarosite-group compounds [38]. In the FTIR spectrum of the leach residue, the sharp peaks at 3414 and 1425 cm^{-1} are due to the stretching modes of N–H bonding. The peak at 1629 cm^{-1} is the bending stretching of H_2O. The bending stretching modes of SO_4^{2-} are observed at 451 and 624 cm^{-1} in the Raman spectrum [39]. Other bands in the Raman spectrum are related to the external modes of Fe–O bonding; the appearance of these bands indicates that some iron oxides remained in the leach residue, although they were not detected in the XRD pattern.

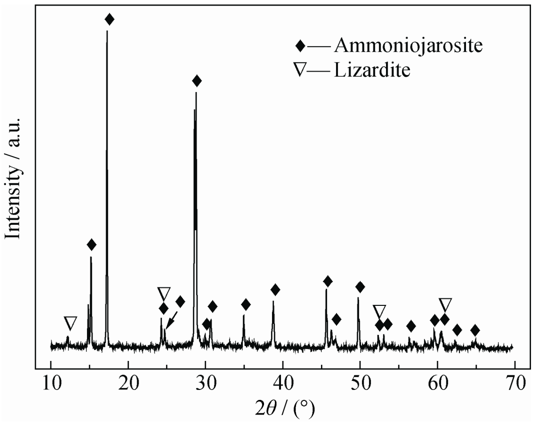


Fig. 12. XRD pattern of the residue after the iron removal process.

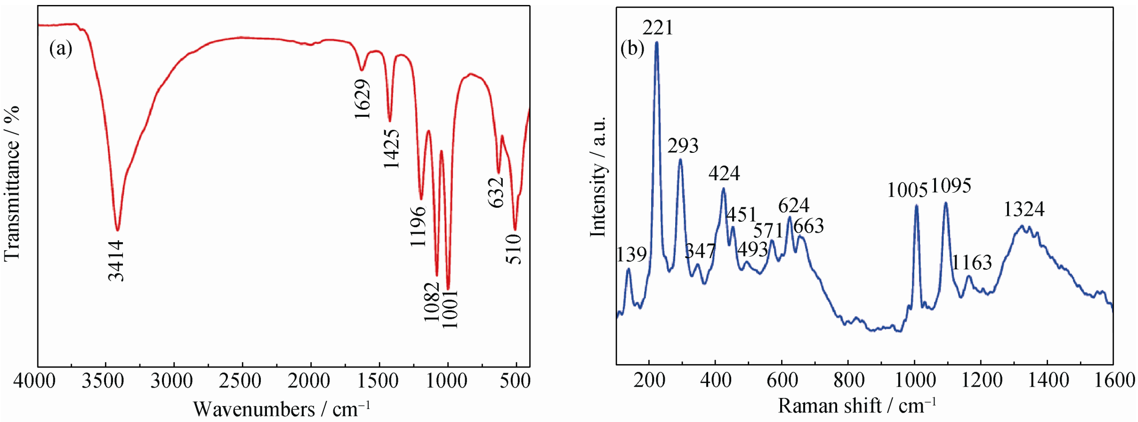


Fig. 13. FTIR (a) and Raman spectra (b) of the residue after the iron removal process.

4. Conclusions

(1) A low-temperature chlorination-water leaching process with NH_4Cl as a chlorinating agent was investigated for the extraction of valuable metals from complex sulfide concentrates via chlorination roasting at 250°C.

(2) Iron was precipitated effectively in the form of ammoniojarosite using a jarosite process with pre-oxidation and pH control.

(3) The whole roasting process included the breakdown of binary metal sulfides, the formation of chlorine and iron oxides, the chlorination of metal sulfides, and the sulfation of metal oxides. The generation of double chlorides promoted the stability of iron chlorides in the roasting process.

(4) The roasting process resulted in the emission of almost no SO_2, and NH_3 was used as $NH_3·H_2O$ to adjust the solution pH value in the subsequent water-leaching step.

Acknowledgements

This work was financially supported by the National Key Basic Research Program of China (No. 2014CB643403) and the National Science Fund for Distinguished Young Scholars (No. 51225401).

References

[1] G.M. Mudd, Nickel sulfide versus laterite: the hard sustainability challenge remains, [in] *The 48th Annual Conference of Metallurgists*, Sudbury, 2009, p. 214.

[2] H.R. Watling, The bioleaching of nickel–copper sulfides, *Hydrometallurgy*, 91(2008), No. 1-4, p. 70.

[3] O.G. Olvera, M. Rebolledo, and E. Asselin, Atmospheric ferric sulfate leaching of chalcopyrite: Thermodynamics, kinetics and electrochemistry, *Hydrometallurgy*, 165(2016), p. 148.

[4] P.A. Olubami, J.O. Borode, and S. Ndlovu, Sulphuric acid leaching of zinc and copper from Nigerian complex sulphide ore in the presence of hydrogen peroxide, *J. S. Afr. Inst. Min. Metall.*, 106(2006), No. 11, p. 765.

[5] T.C. Veloso, J.J.M. Peixoto, M.S. Pereira, and V.A. Leao, Kinetics of chalcopyrite leaching in either ferric sulphate or cupric sulphate media in the presence of NaCl, *Int. J. Miner. Process.*, 148(2016), p. 147.

[6] J. Petersen, Heap leaching as a key technology for recovery of values from low-grade ores: a brief overview, *Hydrometallurgy*, 165(2016), p. 206.

[7] D.J. Lane, N.J. Cook, S.R. Grano, and K. Ehrig, Selective leaching of penalty elements from copper concentrates: a review, *Miner. Eng.*, 98(2016), p. 110.

[8] Y.L. Zhang, X.J. Yu, and X.B. Li, Zinc recovery from franklinite by sulphation roasting, *Hydrometallurgy*, 109(2011), No. 3-4, p. 211.

[9] X.Y. Guo, D. Li, K.H. Park, Q.H. Tian, and Z. Wu, Leaching behavior of metals from a limonitic nickel laterite using a sulfation-roasting-leaching process, *Hydrometallurgy*, 99(2009), No. 3-4, p. 144.

[10] X.W. Liu, Y.L. Feng, H.R. Li, Z.C. Yang, and Z.L. Cai, Recovery of valuable metals from a low-grade nickel ore using an ammonium sulfate roasting-leaching process, *Int. J. Miner. Metall. Mater.*, 19(2012), No. 5, p. 377.

[11] N. Kanari, I. Gaballah, E. Allain, and N. Menad, Chlorination of chalcopyrite concentrates, *Metall. Mater. Trans. B*, 30(1999), No. 4, p. 567.

[12] X.Y. Guo, D. Li, Z. Wu, and Q.H. Tian, Application of response surface methodology in optimizing the sulfation-roasting-leaching process of nickel laterite, *Int. J. Miner. Metall. Mater.*, 19(2012), No. 3, p. 199.

[13] Y.L. Liao, J. Zhou, F.R. Huang, and Y.Y. Wang, Leaching kinetics of calcification roasting calcinate from multimetallic sulfide copper concentrate containing high content of lead and iron, *Sep. Purif. Technol.*, 149(2015), p. 190.

[14] Z.K. Chen, The research progress and prospect of chlorination method used to realizing separation and enrichment in metallurgical industry, *Hunan Nonferrous Met.*, 30(2014), No. 6, p. 29.

[15] T.K. Mukherjee and C.K. Gupta, Base metal resource processing by chlorination, *Miner. Process. Extr. Metall. Rev.*, 1(1983), No. 1-2, p. 111.

[16] P.K. Jena and E.A. Brocchi, Metal extraction through chlorine metallurgy, *Miner. Process. Extr. Metall. Rev.*, 16(2008), No. 4, p. 211.

[17] O. Terakado, T. Saeki, R. Irizato, and M. Hirasawa, Pyrometallurgical recovery of indium from dental metal recycling sludge by chlorination treatment with ammonium chloride, *Mater. Trans.*, 51(2010), No. 6, p. 1136.

[18] T.K. Mukherjee, P.R. Menon, P.P. Shukla, and C.K. Gupta, Chloridizing roasting process for a complex sulfide concentrate, *JOM*, 37(1985), No. 6, p. 29.

[19] V.A. Imideev, P.V. Aleksandrov, A.S. Medvedev, O.V. Bazhenova, and A.R. Khanapieva, Nickel sulfide concentrate processing using low-temperature roasting with sodium chloride, *Metallurgist*, 58(2014), No. 5-6, p. 353.

[20] I. Iwasaki, Non-sulfuric acid generation type copper smelting by chlorination roasting, *Resour. Process.*, 44(1997), No. 3, p. 159.

[21] M. Chakravortty and S. Srikanth, Kinetics of salt roasting of chalcopyrite using KCl, *Thermochim. Acta*, 362(2000), No. 1-2, p. 25.

[22] N.V. Ngoc, M. Shamsuddin, and P.M. Prasad, Salt roasting of an off-grade copper concentrate, *Hydrometallurgy*, 21(1989), No. 3, p. 359.

[23] A.A. Andreev, A.N. D'yachenko, and R.I. Kraidenko, Processing of oxidized nickel ores with ammonium chloride, *Theor. Found. Chem. Eng.*, 45(2011), No. 4, p. 521.

[24] M.Z. Zhang, G.C. Zhu, Y.N. Zhao, and X.J. Feng, A study of recovery of copper and cobalt from copper–cobalt oxide ores

by ammonium salt roasting, *Hydrometallurgy*, 129-130(2012), p. 140.

[25] R.K. Nadirov, L.I. Syzdykova, A.K. Zhussupova, and M.T. Usserbaev, Recovery of value metals from copper smelter slag by ammonium chloride treatment, *Int. J. Miner. Process.*, 124(2013), p. 145.

[26] R.Ž. Vračar and K.P. Cerović, The study of chlorination kinetics of copper(I) sulfide by calcium chloride in the presence of oxygen, *Metall. Mater. Trans. B*, 31(2000), No. 4, p. 723.

[27] R.F. Pilgrim and T.R. Ingraham, Thermodynamics of the chlorination of iron, cobalt, nickel and copper sulphides, *Can. Metall. Q.*, 6(1967), No. 1, p. 39.

[28] A. Dahlstedt, S. Seetharaman, and K.T. Jacob, Thermodynamics of salt roasting of sulphide ores, *Scand. J. Metall.*, 21(1992), No. 6, p. 242.

[29] M. Aneesuddin, P.N. Char, M.R. Hussain, and E.R. Saxena, Studies on thermal oxidation of chalcopyrite from Chitradurga, Karnataka State, India, *J. Therm. Anal.*, 26(1983), No. 2, p. 205.

[30] V.A. Borisov, A.N. D'yachenko, and R.I. Kraidenko, Reaction of ammonium chloride with the copper(II) sulfide and oxide, and identification of the reaction products, *Russ. J. Gen. Chem.*, 81(2011), No. 7, p. 1430.

[31] T. Nagaishi, S. Ishiyama, M. Matsumoto, and S. Yoshinaga, Reactions between ammonium sulphate and metal oxides (metal=Cr, Mn and Fe) and thermal decomposition of the products, *J. Therm. Anal.*, 29(1984), No. 1, p. 121.

[32] G. Bayer and H.G. Wiedemann, Thermal analysis of chalcopyrite roasting reactions, *Thermochim. Acta*, 198(1992), No. 2, p. 303.

[33] J.Y. Chen, S.Q. Yu, and Z.C. Wu, *The Separation and Utilization of Iron in Hydrometallurgy*, Metallurgical Industry Press, Beijing, 1991, p. 173.

[34] J.E. Dutrizac, Comparative rates of precipitation of ammonium jarosite and sodium jarosite in ferric sulphate-sulphuric acid media, *Can. Metall. Q.*, 49(2013), No. 2, p. 121.

[35] Q.K. Wang, Y.J. Ma, and J.C. Tan, The studies and applications of iron precipitations as alkali jarosites, *Min. Metall. Eng.*, 6(1986), No. 1, p. 30.

[36] J.E. Dutrizac, The effect of seeding on the rate of precipitation of ammonium jarosite and sodium jarosite, *Hydrometallurgy*, 42(1996), No. 3, p. 293.

[37] P.J. Murphy, A.M.L. Smith, K.A. Hudson-Edwards, W.E. Dubbin, and K. Wright, Raman and IR spectroscopic studies of alunite-supergroup compounds containing Al^{3+}, Cr^{3+}, Fe^{3+} and V^{3+} at the *B* site, *Can. Mineral.*, 47(2009), No. 3, p. 663.

[38] K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*: *Part B*. *Applications in Coordination*, *Organometallic*, *and Bioinorganic Chemistry*, 5th Ed., John Wiley & Sons, Inc., New York, 1997, p. 184.

[39] A. Adamou, G. Manos, N. Messios, L. Georgiou, C. Xydas, and C. Varotsis, Probing the whole ore chalcopyrite-bacteria interactions and jarosite biosynthesis by Raman and FTIR microspectroscopies, *Bioresour. Technol.*, 214(2016), p. 852.