

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/341139592>

Recovery of valuable metals from copper slag

Article in *Mining Metallurgy & Exploration* · May 2020

DOI: 10.1007/s42461-020-00224-7

CITATIONS

14

READS

195

5 authors, including:



Changda Zhang

Central South University

11 PUBLICATIONS 66 CITATIONS

[SEE PROFILE](#)



Huaguang Wang

Michigan Technological University

11 PUBLICATIONS 182 CITATIONS

[SEE PROFILE](#)



Mingyu Wang

Central South University

105 PUBLICATIONS 1,922 CITATIONS

[SEE PROFILE](#)



Xuewen Wang

Shih Hsin University

68 PUBLICATIONS 2,949 CITATIONS

[SEE PROFILE](#)

Some of the authors of this publication are also working on these related projects:



Ceramic fabricating [View project](#)



Luminescent materials [View project](#)



Recovery of valuable metals from copper slag

Changda Zhang¹ · Bin Hu¹ · Huaguang Wang² · Mingyu Wang¹ · Xuewen Wang¹

Received: 15 February 2020 / Accepted: 17 April 2020 / Published online: 4 May 2020
© Society for Mining, Metallurgy & Exploration Inc. 2020

Abstract

The copper smelting process produces plenty of copper slag every year, which is a hazardous solid waste, but a secondary resource. In the present study, the extraction of copper, nickel, and cobalt from copper slag was investigated through the process of sulfation roasting–water leaching and the process of sulfation roasting–sulfate decomposition roasting–water leaching respectively. Compared with the process of sulfation roasting–water leaching, the process of sulfation roasting–sulfate decomposition roasting–water leaching is a better choice, which could not only get almost the same leaching of copper, nickel, and cobalt as the former process, but has a lower leaching of iron and aluminum. For the process of sulfation roasting–sulfate decomposition roasting–water leaching, the leaching of Cu, Ni, and Co reached up to 74.2%, 71.1%, and 69.6% respectively, under the optimal conditions including sulfation roasted with 80 wt% sulfuric acid addition at 200 °C for 60 min and sulfate decomposition roasted at 650 °C for 60 min, followed by water leached at 90 °C for 30 min with a liquid–solid ratio of 2 ml/g. The leaching of Fe and Al was only 4.9% and 17.6%.

Keywords Copper slag · Sulfation roasting · Sulfate decomposition roasting · Water leaching

1 Introduction

Copper is the third most extensively used metal after iron and aluminum, with 80% of it coming from the pyrometallurgical process [1]. After pyrometallurgical smelting, plenty of copper slag is produced. In China alone, the annual production of copper slag is more than 10 million tons. In general, copper slag has a low content of copper, nickel, and cobalt and a high content of iron and silicon, and fayalite is the main crystalline phase. Nickel and cobalt are mainly distributed in fayalite phase in the form of ferrite and silicate [2]. From the viewpoint of environmental protection, copper slag is classified as a hazardous solid waste. However, it also contains a large amount of valuable metals such as nickel and cobalt as well as iron, with huge potential economic benefits. Hence, it is also an important secondary resource.

A wide variety of processes for the recovery of valuable metals from copper slag have been proposed, which can be summed up in three types: pyrometallurgical, hydrometallurgical, and pyro-hydrometallurgical processes. The typical pyrometallurgical techniques are used to treat copper with processes involving calcining or smelting reduction followed by wet magnetic separation, which can recover metals such as Fe, Cu, and Co from copper slag in the form of iron-rich alloy [3, 4]. However, using these techniques to treat copper slag, fayalite cannot obtain a high conversion rate. The addition of CaO in the process of reduction smelting is beneficial to the decomposition of fayalite [5]; furthermore, the recovery of metals can be significantly improved by adding a certain amount of sodium salt [6]. However, whether using smelting reduction or direct reduction, the reaction temperature for all of them is more than 1200 °C. In contrast, the hydrometallurgical process has lower energy consumption; and environment-friendly advantages, such as atmospheric direct leaching processes using several acids, bases, and salts with or without an oxidizing agent addition have been tested for extracting valuable metals from copper slag [7–10]. However, the metals extraction of these processes is not high enough as well as providing poor selectivity. High-pressure oxidative acid leaching [11, 12] can not only achieve a higher leaching rate, but also requires significantly less sulfuric acid

✉ Mingyu Wang
wmydxx@163.com

¹ School of Metallurgy and Environment, Central South University, Changsha 410083, China

² Department of Materials Science and Engineering, Michigan Technological University, Houghton, MI 49931, USA

due to the released iron which is re-precipitated as hematite and then leads to acid regeneration. However, it is hard to achieve a high metal leaching rate from water-quenched copper slag by using this technology [13]. To overcome the problems of pyrometallurgical and hydrometallurgical processes, pyro-hydrometallurgical processes have been proposed, which mainly include the process of chlorination roasting–water leaching and the process of sulfation roasting–water leaching. Chlorination roasting using Cl_2 , HCl , NaCl or other chloride salts as chlorinating agents followed by water leaching can obtain high leaching of valuable metals from copper slag [14, 15]; however, the roasting waste gas contains Cl_2 and HCl , which severely impact the environment. Compared with chlorination roasting, the process of sulfation roasting using pyrite, sulfur, sulfuric acid, or other sulfates as vulcanizing agents followed by water leaching also can achieve high leaching of valuable metals [16–18], and the roasting waste gas is easily treated; however, the leaching of iron is very high, which is not conducive to the separation and extraction of valuable metals such as copper and nickel from the leaching solution.

The content of nickel, cobalt, and copper in copper slag are relatively low, so it's hard to make any process that is extracting just them economically valuable. However, copper slag also contains a lot of iron, so an ideal way of copper slag utilization should be first selective leaching of nickel, cobalt, and copper, and destabilizing fayalite structure at the same time; then, the iron is enriched and extracted from the leach residue by a simple mineral separation method. Following this idea, in this study, the extraction of copper, nickel, and cobalt from copper slag was investigated through two methods. One is the process of sulfation roasting–water leaching and the other is sulfation roasting–sulfate decomposition roasting–water leaching. The motivation of this study is to develop an efficient leaching method with high leaching of Ni and Co as well as Cu, and low leaching of iron and aluminum.

2 Experimental process

2.1 Materials and analysis

The copper slag used in this study was obtained from China Minmetals Corporation. The copper slag was first crushed and ground into –200 mesh powder before the experiment. XRF-1800 X-ray Fluorescence spectrometry (XRF) (Shimadzu,

Japan) was used for chemical analysis of the sample, and the result is shown in Table 1. In copper slag, the copper mainly exists in the form of Cu_2S , while cobalt and nickel mainly exist in the form of CoO and NiO respectively [19]. All the reagents used in roasting, leaching, and chemical analysis were of analytical grade.

The content of copper, nickel, cobalt, iron, aluminum, and magnesium in copper slag and leach residue was determined using a PS-6 Inductively Coupled Plasma (ICP) spectroscopy (BAIRD, USA). The X-ray diffraction (XRD) patterns of the solid material were recorded by a Rigaku D/MAX 2200 Diffractometer (Rigaku, Japan) with $\text{Cu-K}\alpha$ radiation at 35 kV and 20 mA using a scan speed 8°min^{-1} in 2θ ranges from 10° to 80° . The thermal analysis curves were obtained on a STD Q600 TG-DSC thermal analyzer (TA Instruments, USA) in the temperature range 20–1000 °C at a heating rate of 10 °C/min under nitrogen gas atmosphere, and the amount of the sample was 30.00 ± 0.20 mg.

2.2 Experimental procedures

2.2.1 Sulfation roasting–water leaching

Prior to the sulfation roasting process, 50 g ground copper slag powder was placed in a porcelain crucible, and then uniformly mixed with the desired 98% sulfuric acid. And then the mixture was heated in a muffle furnace at a predetermined temperature. After sulfation roasting, the roasted product was leached with tap water at 90 °C for 30 min with a liquid–solid ratio of 2 ml/g. Subsequently, the leaching solution and residue were separated by vacuum filtration, and the leaching residue was successively washed with 50 ml water and then dried, weighed, and analyzed for the content of copper, nickel, cobalt, iron, aluminum, and magnesium. The leaching of valuable metal was calculated by mass balance from the analysis of the copper slag and the leach residue.

2.2.2 Sulfation roasting–sulfate decomposition roasting–water leaching

In the process of sulfation roasting–sulfate decomposition roasting, the first stage roasting process is the same as the sulfation roasting process. In the second-stage roasting process, a certain amount of sulfation roasted mixture was prepared according to the optimum conditions of the first stage roasting experiment. And then, 50 g sulfation roasted mixture was also heated in a muffle furnace at a predetermined temperature. After the second-stage roasting, the leaching solution and residue were separated by vacuum filtration and the leach residue was successively washed with 50 ml water. Finally, the washed leach residues were dried, weighed, and analyzed for the content of copper, nickel, cobalt, iron, aluminum, and magnesium.

Table 1 XRF elemental analysis of the copper slag (mass fraction, %)

O	Ca	Mg	Al	Si	Fe	Co	Ni	Cu	S
34.47	2.35	3.53	3.90	18.50	36.98	0.16	0.53	0.26	1.14

3 Results and discussion

3.1 Sulfation roasting–water leaching

3.1.1 Effect of H_2SO_4 addition

To determine the consumption of H_2SO_4 in the sulfation roasting process, a predetermined weight of 98% H_2SO_4 was mixed with the raw copper slag and then roasted at 200 °C for 1 h. The H_2SO_4 addition varied in a range of 30–80 wt% (mass ratio of 98% H_2SO_4 to raw copper slag). The subsequent water leaching was carried out at 90 °C for 30 min with a liquid/solid ratio of 2 ml/g. The leaching of metals versus sulfuric acid addition is shown in Fig. 1.

As can be seen from Fig. 1, the leaching of Ni, Co, Fe, and Mg have similar trends, all of which increased gradually with addition of H_2SO_4 from 30 wt% to 75 wt%. Further additions of H_2SO_4 resulted in an insignificant increase in the leaching of Co, but the leaching of Ni, Fe, and Mg continued to increase. The leaching of Al increased from 15.3% to 34.5% as the H_2SO_4 addition increased from 30 to 60 wt%. A further increase of H_2SO_4 addition can result in a rapid increase in the leaching of Al. Compared with Ni, Co, Fe, Mg and Al, the leaching of Cu was much lower than when the addition of H_2SO_4 was less than 70 wt%. However, once the addition of H_2SO_4 was over 70 wt%, the leaching of copper increased sharply. By measuring the pH of the leaching solution, it was found that the pH value of the leaching solution was about 4 when the sulfuric acid addition was below 70 wt%. However, once the addition of sulfuric acid exceeded 70 wt%, the pH value of the leaching solution dropped to about 2, which might explain the sudden change in Cu

leaching. Additionally, it was found in the experimental process that once the addition of sulfuric acid was more than 80 wt%, liquid sulfuric acid would appear in the mixture, that is to say, 80 wt% sulfuric acid addition was the largest amount. Copper is one of the valuable metals in copper slag. To achieve a high copper leaching rate, the addition of sulfuric acid must exceed 70 wt%. Given these considerations, 80 wt% H_2SO_4 addition was chosen as the optimized amount in the later experiments.

3.1.2 Effect of roasting temperature

The effect of roasting temperature on the leaching of metals was studied at a roasting time of 1 h and the addition of H_2SO_4 was 80 wt%. The roasting temperature varied in a range of 160–320 °C. The leaching condition was constant and the results are shown in Fig. 2.

It can be seen from Fig. 2 that the effect of roasting temperature on the leaching of Ni was insignificant. The leaching of Mg, Co, Fe, and Al all tended to decrease with the increase of roasting temperature, but the effect of roasting temperature on the leaching of Fe and Al is much greater. On the contrary, with the increase of roasting temperature from 160 to 200 °C, the leaching of Cu increased from 43.9 to 69.6%; with further increase in temperature, the leaching of Cu did not change significantly. Since the vapor pressure of H_2SO_4 at over 200 °C is high, the possibility of a reaction with H_2SO_4 (g) is also high. On the other hand, the possibility of the formation of water during the reactions with liquid or gaseous H_2SO_4 is considerable. Water formation will decrease the H_2SO_4 concentration, and so the vapor pressure of H_2SO_4 at lower H_2SO_4 concentrations will be lower at the same temperatures,

Fig. 1 Effect of H_2SO_4 addition on metals leaching

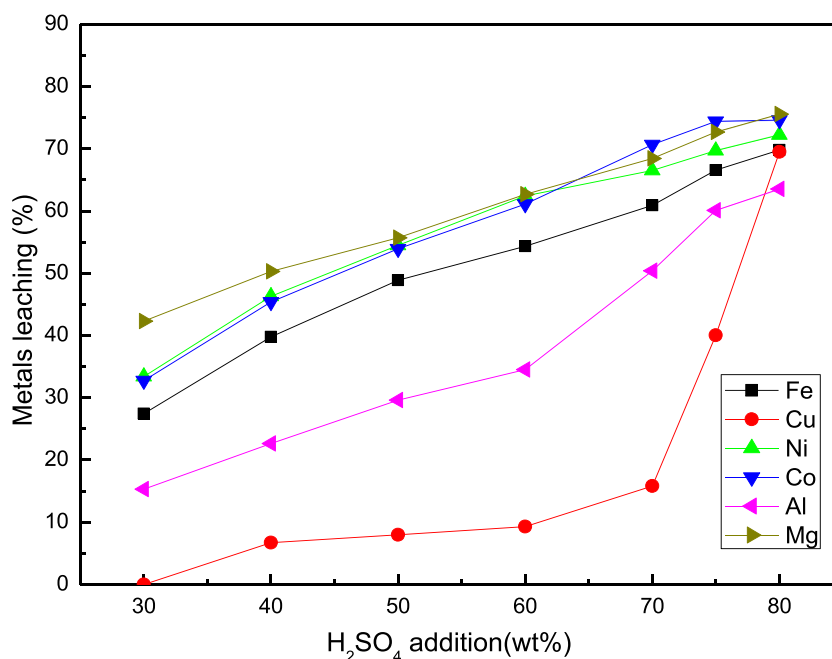
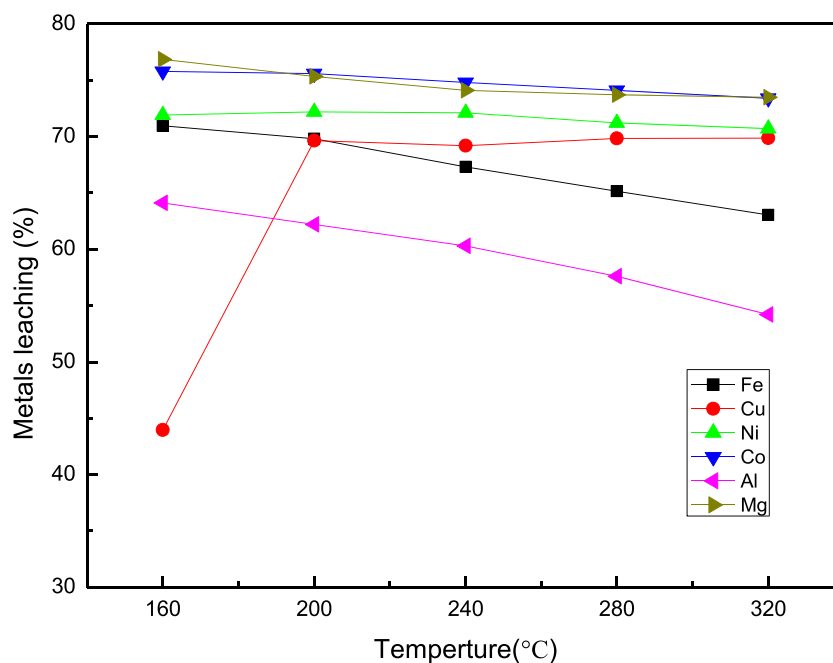


Fig. 2 Effect of roasting temperature on the leaching of metals



and thus, the reaction seems to be more likely to reach equilibrium at around 200 °C [20]; so 200 °C is chosen as the optimal roasting temperature.

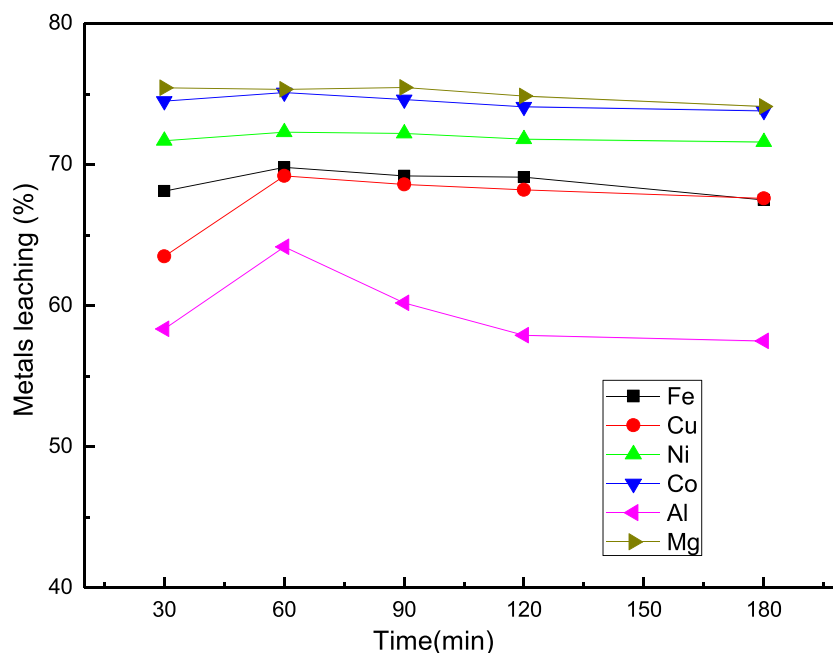
3.1.3 Effect of roasting time

To examine the influence of roasting time on the leaching of metals, the roasting time was varied from 30 to 180 min at 200 °C with 80 wt% H₂SO₄ addition. The results shown in Fig. 3 indicated that the effect of roasting time on the leaching of Mg, Co and Ni was relatively insignificant. But for Fe, Cu,

and Al, the leaching of them all increased gradually, with the roasting time increased from 30 min to 60 min, and then approximately reached the optimal condition. A further increase of time did not significantly affect the leaching of Fe and Cu. However, when the roasting time exceeded 60 min, the leaching of Al decreased rapidly. Therefore, a roasting time of 60 min was chosen as the most suitable roasting time.

According to the above condition experiments, the most suitable conditions in sulfation roasting process were: raw copper slag roasted with 80 wt% H₂SO₄ addition at 200 °C for 60 min. Under the most suitable roasting conditions

Fig. 3 Effect of roasting time on the leaching of metals



followed by water leached at 90 °C for 30 min with a liquid/solid ratio of 2 ml/g, the leaching of Fe, Cu, Ni, Co, Mg, and Al was 69.8%, 69.4%, 72.2%, 75.1%, 75.4%, and 63.3% respectively (average of the three results).

3.2 Sulfation roasting–sulfate decomposition roasting–water leaching

The process of sulfation roasting–water leaching can effectively extract nickel, cobalt, and copper, but the leaching of Fe, Al, and Mg was also very high, especially iron. These impurities were not conducive to the subsequent separation and extraction of nickel, cobalt, and copper from the leaching solution. Therefore, the process of sulfating roasting–sulfate decomposition roasting was proposed.

Figure 4 is the ΔG^0 -T relation diagram of sulfate decomposition [21]. It can be seen from Fig. 4 that the stability of FeSO_4 , CuSO_4 , NiSO_4 , CoSO_4 , MgSO_4 , $\text{Al}_2(\text{SO}_4)_3$, and CaSO_4 all decreased as the temperature increased. At the same temperature, the arrangement of decomposition of metal sulfate is determined by $\text{Fe} > \text{Al} > \text{Cu} > \text{Ni} > \text{Co} > \text{Mg} > \text{Ca}$, that is to say, the sulfates of Fe and Al can be decomposed to oxides easily at around 700 °C, but the sulfates of Cu, Ni, and Co are thermodynamically relatively stable, which makes it possible for selective leaching of Cu, Ni, and Co through sulfate decomposition roasting followed by water leaching. Although calcium sulfate has thermodynamic stability, the solubility of calcium sulfate in aqueous solution is small. Magnesium sulfate also has thermodynamic stability, so the separation of Mg and Ni, Co as well as Cu cannot be achieved by the method of sulfate decomposition roasting, and can only be separated during the extraction of Ni, Co, and Cu from the subsequent leach solution. Since the sulfation roasting process

has been studied in detail above, this section mainly studies the sulfate decomposition roasting process. The effects of the several parameters that included roasting mode, roasting temperature, and roasting time, as well as the water leaching process, were investigated.

3.2.1 Effect of roasting mode

The process of sulfation roasting–sulfate decomposition roasting can be carried out in two ways; one is continuous heating roasting and the other is intermittent heating roasting. Continuous heating roasting refers to when sulfation roasting is completed and then continues to increase the temperature for the sulfate decomposition roasting. Intermittent heating roasting refers to when after sulfation roasting is completed, then the roasted materials are taken out of the muffle furnace and ground fine, and then put back into the muffle furnace to finish the second-stage of roasting. Figure 5 is the comparison of the leaching of Ni, Co, and Cu under the different roasting modes.

As can be seen in Fig. 5, among three roasting modes, the process of intermittent heating roasting had the highest leaching of nickel, cobalt, and copper. In particular, the increases in nickel and cobalt leaching are more pronounced. Therefore, the mode of intermittent heating roasting was chosen as the optimal heating method.

3.2.2 Effect of sulfate decomposition roasting temperature

The effect of sulfate decomposition roasting temperature on the leaching of metals was studied over a temperature range from 500 to 700 °C at a roasting time of 1 h. The subsequent water leaching was carried out at 90 °C for 30 min with a

Fig. 4 ΔG^0 -T relation diagram of sulfate decomposition. 1. $1/4\text{O}_2 + \text{FeSO}_4 = 1/2\text{Fe}_2\text{O}_3 + \text{SO}_3$; 2. $1/3\text{Al}_2(\text{SO}_4)_3 = 1/3\text{Al}_2\text{O}_3 + \text{SO}_3$; 3. $1/3\text{Fe}_2(\text{SO}_4)_3 = 1/3\text{Fe}_2\text{O}_3 + \text{SO}_3$; 4. $\text{CuSO}_4 = \text{CuO} + \text{SO}_3$; 5. $\text{NiSO}_4 = \text{NiO} + \text{SO}_3$; 6. $\text{CoSO}_4 = \text{CoO} + \text{SO}_3$; 7. $\text{MgSO}_4 = \text{MgO} + \text{SO}_3$; 8. $\text{CaSO}_4 = \text{CaO} + \text{SO}_3$

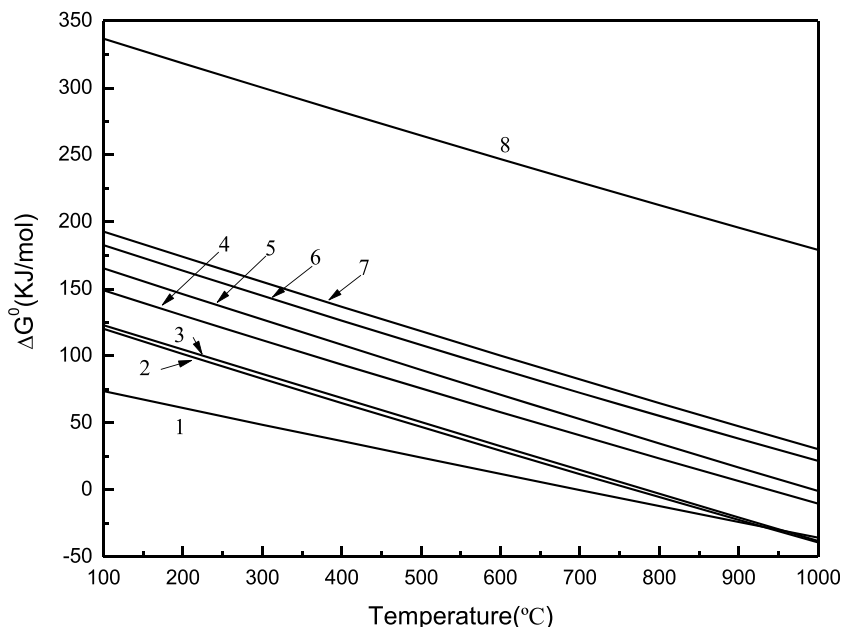
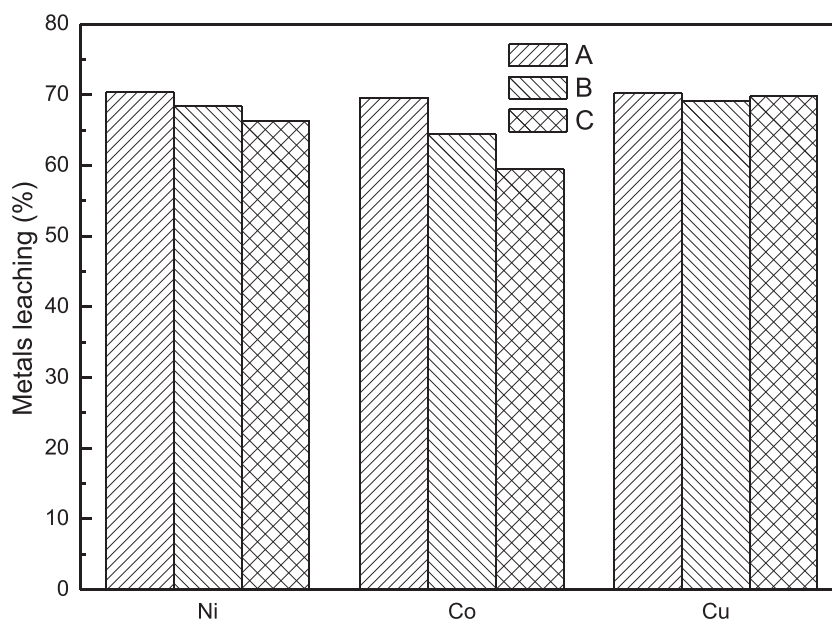


Fig. 5 Effect of roasting mode on the leaching of metals. A. Intermittent heating roasting (200 °C roasting for 1 h, crushed, 650 °C roasting for 1 h, water leaching). B. Continuous heating roasting (200 °C roasting for 1 h, 650 °C roasting for 1 h, crushed, water leaching). C. Direct sulfation roasting (650 °C roasting for 1 h without first-stage roasting, crushed, water leaching)



liquid/solid ratio of 2 ml/g. The leaching rate of metals versus sulfate decomposition roasting temperature is shown in Fig. 6.

It can be seen from Fig. 6 that the leaching of Fe decreased sharply from 53.5% to 4.7% as the temperature increased from 500 to 650 °C; with further increase in temperature, the decrease of Fe did not change significantly. For aluminum, the leaching rate decreased continuously with the increase in the roasting temperature. The leaching of Co decreased slightly with the increase of roasting temperature. In the range of 500 to 650 °C, the leaching of Ni did not change much, but it would decrease significantly when the temperature exceeded 650 °C. For copper, the leaching increased with an increase in temperature from 500 to 600 °C, and then it decreased when

the temperature was over 600 °C. In particular, the leaching of Cu decreased significantly after the temperature exceeded 650 °C. For magnesium, the leaching increased slowly with the increase of roasting temperature. Given these considerations, 650 °C was chosen as the optimal roasting temperature.

Figure 7 displays the TG-DSC curves of the sulfation roasted mixture. It can be seen from the DSC curve that there were three endothermic peaks at about 280 °C, 636 °C, and 800 °C; correspondingly, the TG curve also showed that there are three considerable weight losses in the range of 200 to 300 °C, 550 to 650 °C, and 750 to 850 °C respectively. The first endothermic peak at 280 °C was thought to be caused by

Fig. 6 Effect of sulfate decomposition roasting temperature on the leaching of metals

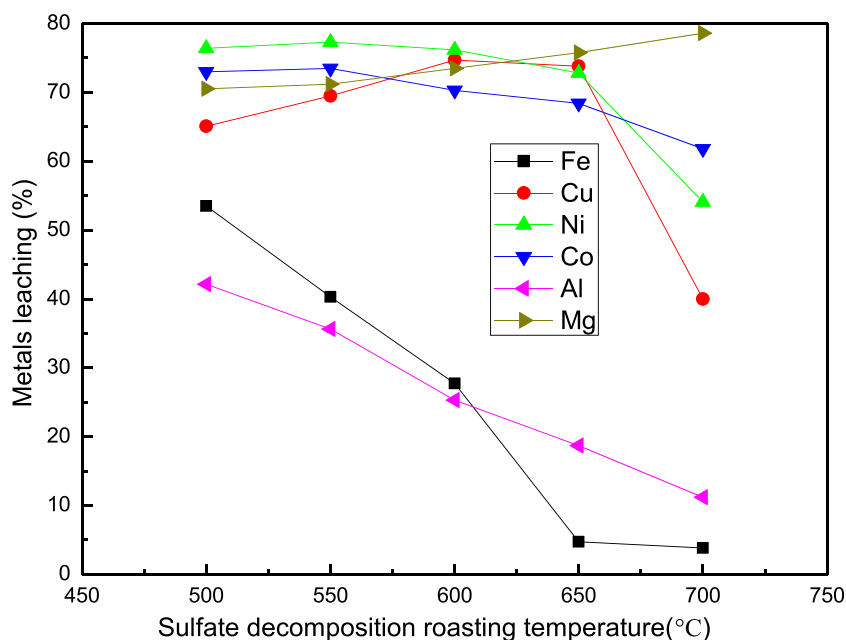
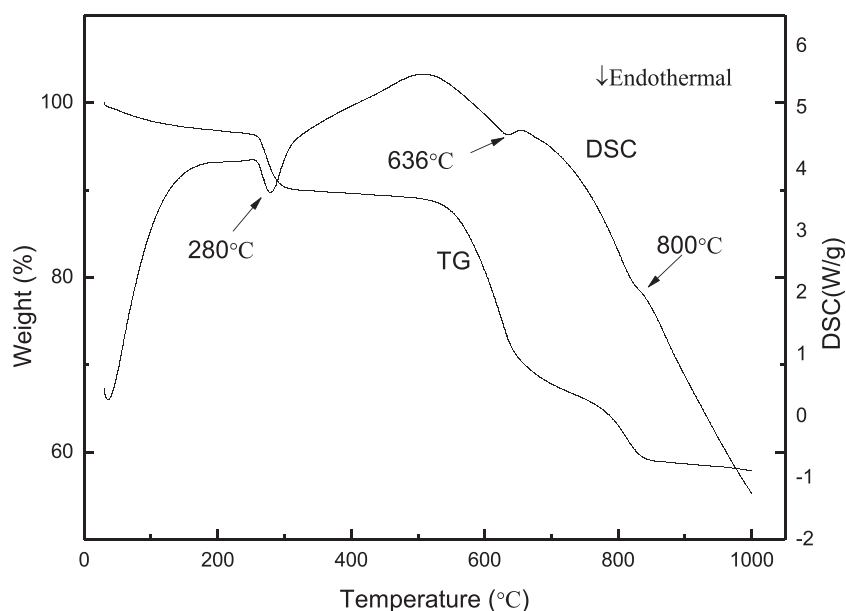


Fig. 7 TG-DSC curves of the sulfation-roasted mixture



the dehydration of the sulfation roasted mixture. The second endothermic peak at 636 °C was caused by the decomposition reaction of ferrous sulfate and aluminum sulfate, which is consistent with the experiment result. When the temperature reached the critical value of the decomposition temperature of ferrous sulfate and aluminum sulfate, the reaction continued to generate SO_3 , resulting in a rapid weight loss process. The third endothermic peak at 800 °C may be caused by the decomposition of other sulfates such as Ni, Co, and Cu.

3.2.3 Effect of roasting time

To examine the effect of sulfate decomposition roasting time on the leaching of metals, the roasting time was varied from 30 to 180 min at 650 °C. The results shown in Fig. 8 indicated that the leaching of Fe can be reduced from 8.7% to 4.9% with the roasting time increased from 30 min to 180 min. The leaching of aluminum decreased slowly with the increase of roasting time. The effect of sulfate decomposition roasting time on the leaching of magnesium was insignificant. But it is also noted that when the roasting time exceeded 60 min, the leaching of nickel, cobalt, and copper also decreased. To enable a higher leaching of valuable metals of Ni, Cu and Co, a roasting time of 60 min was chosen as the most suitable roasting time.

3.2.4 Effect of leaching time

Figure 9 is the experimental results obtained by adding 80 wt% H_2SO_4 into copper slag followed by sulfation roasting (200 °C for 60 min) and sulfate decomposition roasting (650 °C for 60 min), and leaching the roasted materials in

water with a liquid–solid ratio of 2 ml/g at 90 °C for different times.

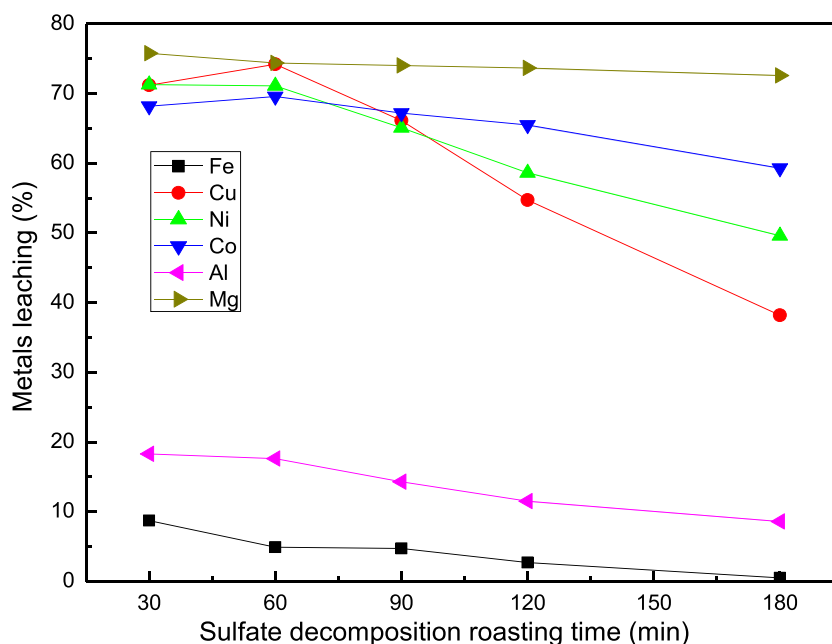
It can be seen from Fig. 9 that the leaching of Al and Fe was less influenced by the increase in leaching time, and their maximum leaching percentages are about 17% and 5% respectively. On the other hand, the leaching of Ni, Cu, Co, and Mg all first increased with the increase of leaching time, and reached their maximum amounts at 30 min. After that, the leaching of Ni, Co, and Mg decreased slightly, whereas Cu decreased significantly up to 180 min. The result of measuring the pH changes of the leaching solution indicated that the pH increased slowly from 1.6 to 2.7 as the leaching time increased from 10 min to 180 min, which may be caused by the H^+ consumption during the leaching of silicates. As can be seen from the concentration of silicon in the leaching solution, the changing trend of silicon leaching is consistent with that of pH, which indicates that the longer the leaching time, the more the leaching of silicate. Not surprisingly, the concentration of Ca was almost dependent on the pH of leaching solution. Higher pH is not helpful for the dissolution of calcium sulfate. Given these considerations, for subsequent experiments the leaching time was kept to 30 min.

3.2.5 Effect of leaching temperature

The effect of temperature on the leaching of metals was studied at a fixed leaching time of 30 min with a liquid–solid ratio of 2 ml/g; the results are shown in Fig. 10.

As can be seen in Fig. 10, there is a slow increase in the leaching of Cu, Co, and Ni for leaching temperature from 30 °C to 50 °C; above that, as the leaching temperature increases, the leaching of Cu, Co, and Ni has no obvious change. The effect of temperature on the leaching of Al and

Fig. 8 Effect of sulfate decomposition roasting time on the leaching of metals



Fe was insignificant. The leaching of Mg and the concentration of Ca and Si all increased with the increase of leaching temperature. However, the experimental process showed that with an increase in leaching temperature, the filterability of the mixture consisting of leach solution and leach residue significantly enhanced. Therefore, a leaching temperature of 90 °C was chosen for subsequent temperature.

3.2.6 Effect of liquid–solid ratio

The effect of liquid–solid ratio on the leaching of metals was investigated by changing the liquid–solid ratio from 2 ml/g to

5 ml/g at 90 °C for 30 min of leaching. The results obtained are illustrated in Fig. 11.

It can be seen from Fig. 11 that the effect of the liquid–solid ratio on the leaching of Mg, Ni, Cu, Co, Fe, and Al was insignificant for all of them, and that the liquid–solid ratio was not a main factor for the leaching of Mg, Ni, Cu, Co, Fe, and Al. In the liquid–solid ratio range of 2 to 4 ml/g, the concentration of Ca in leach solution did not change much, but it decreased significantly when the liquid–solid ratio exceeded 4 ml/g. For Si, the concentration decreased slowly with the increase in liquid–solid ratio. In general, the higher content of Cu, Ni, and Co in leaching solution corresponds to more favorable conditions for the subsequent separation and

Fig. 9 Effect of leaching time on the leaching of metals

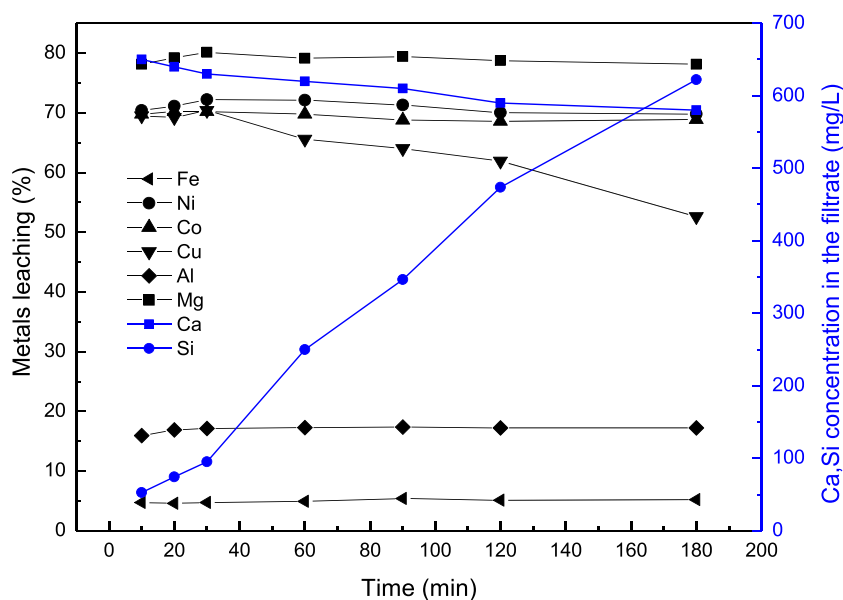
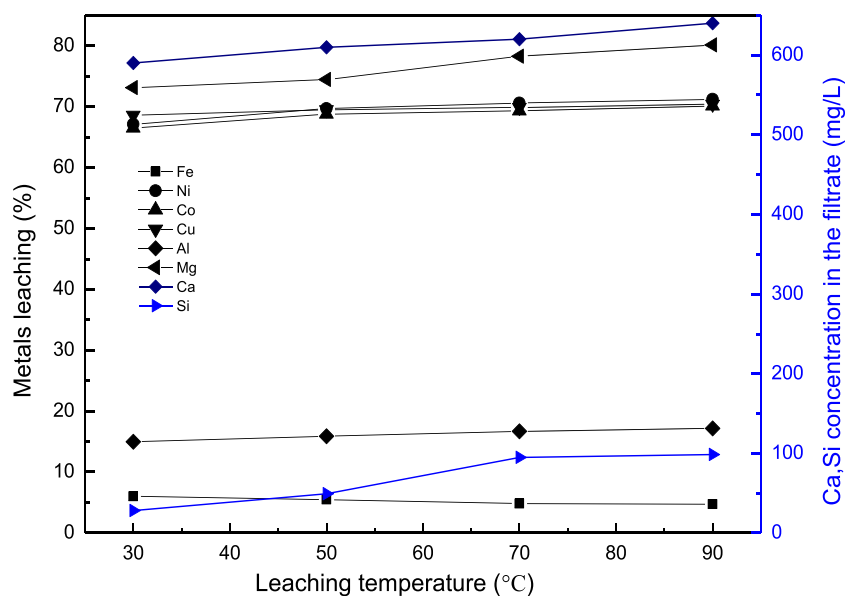


Fig. 10 Effect of leaching temperature on the leaching of metals



extraction of them. Therefore, the liquid/solid ratio of 2 ml/g was chosen as the optimized amount.

3.2.7 Phase changes during sulfation roasting–sulfate decomposition roasting–water leaching process

Based on the preceding experimental results, in the process of sulfation roasting, the optimum conditions would be: raw copper slag roasted with 80 wt% H_2SO_4 addition at 200 °C for 60 min. In the process of sulfate decomposition roasting, the most suitable conditions were: roasting at 650 °C for 60 min, then followed by water leached at 90 °C for 30 min with a liquid–solid ratio of 2 ml/g. The leaching of Cu, Ni, and Co reached 74.2%, 71.1%, and 69.6% respectively, and the

leaching of Fe and Al was only 4.9% and 17.6% (average of the three results).

To further understand the reaction mechanism during the sulfation roasting–sulfate decomposition roasting–water leaching process, XRD analysis was conducted and the results are shown in Fig. 12.

It can be seen from Fig. 12a that the main crystalline phase in raw copper slag was fayalite. The diffraction line of sulfides and oxides including Cu, Ni, and Co was not detected, which means that all metals exist in amorphous phases in the copper slag or that they are too low in quantity for XRD. Compared with Fig. 12a, new characteristic reflections of $Fe(SO_4)(H_2O)$ appeared in Fig. 12b due to sulfation roasting, which means that the fayalite phase has been converted into the $Fe(SO_4)(H_2O)$ phase after sulfation roasting. The main

Fig. 11 Effect of liquid–solid ratio on the leaching of metals

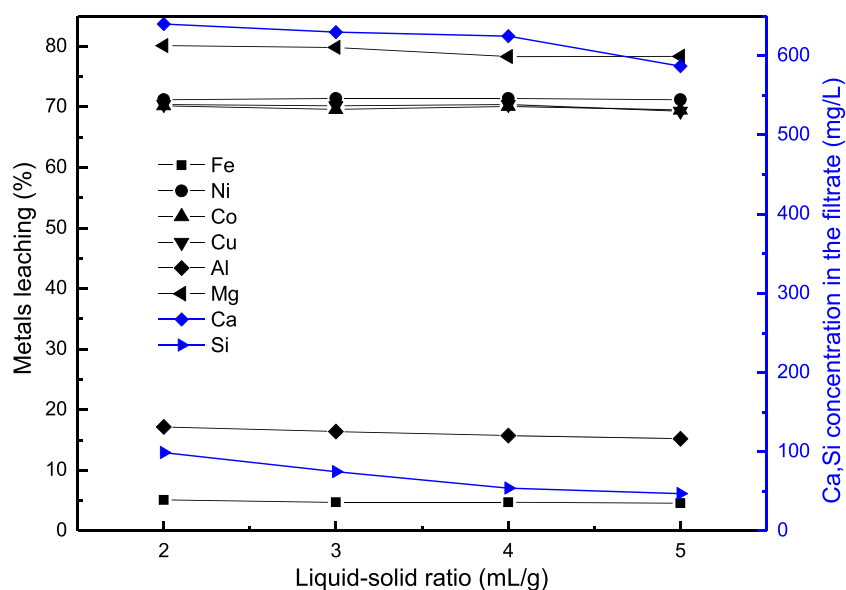
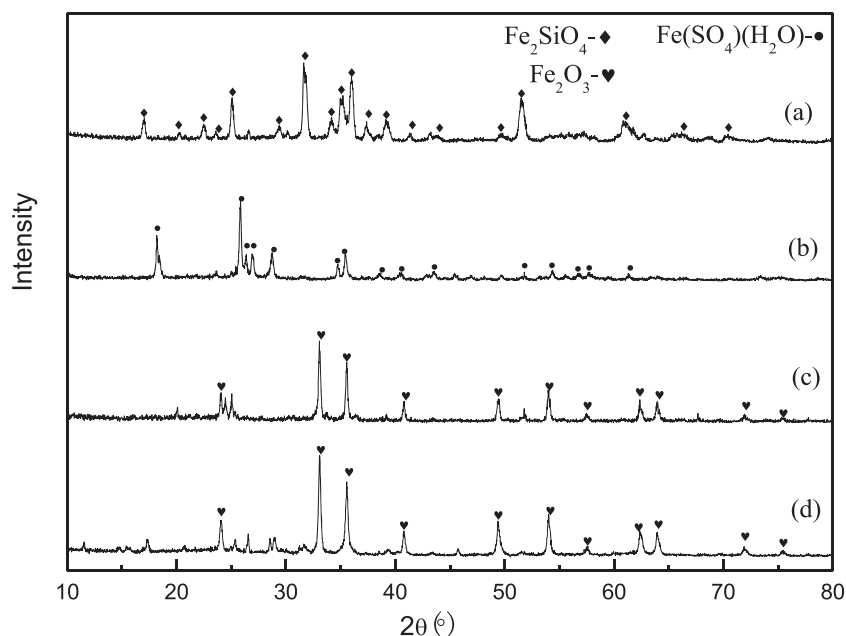
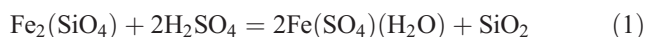


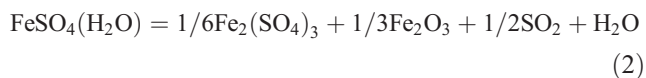
Fig. 12 XRD patterns of **a** Raw copper slag, **b** sulfation roasted mixture, **c** sulfate decomposition roasted mixture, **d** leach residue



reaction in the process of sulfation roasting can be expressed by the following equation:



In Fig. 12c, new characteristic reflections of Fe_2O_3 appeared due to sulfate decomposition roasting, which cannot be leached by water. The main reaction in this process can be expressed by the following equation:



As can be seen from Fig. 12d, the crystalline phase in the water leaching residue was Fe_2O_3 , which was the same as that in the sulfate decomposition roasted mixture.

4 Conclusions

The present work focused on the extraction of valuable metal nickel, cobalt, and copper from the copper slag. Two methods were adopted to perform the leaching procedure. For the process of sulfation roasting–water leaching, the leaching of nickel, cobalt, and copper is relatively high, but about 70% of iron and 63% of aluminum are also leached, which can result in the further separation becoming more difficult. Compared with the process of sulfation roasting–water leaching, the process of sulfation roasting–sulfate decomposition roasting–water leaching appears to be a good option, since it was characterized by high extraction of nickel, cobalt, and copper as well as

low extraction of iron and aluminum. For the process of sulfation roasting–sulfate decomposition roasting–water leaching, the leaching of Cu, Ni, and Co reached up to 74.2%, 71.1%, and 69.6% respectively, under the optimal conditions including sulfation roasted with 80 wt% sulfuric acid addition at 200 °C for 60 min and sulfate decomposition roasted at 650 °C for 60 min, followed by water leached at 90 °C for 30 min with a liquid–solid ratio of 2 ml/g. The leaching of Fe and Al was only 4.9% and 17.6%.

Acknowledgements This study was financially supported by the National Natural Science Foundation of China (51974369) and the Natural Science Foundation of Hunan Province (2016JJ2142).

Compliance with ethical standards

Conflict of Interest On behalf of all authors, the corresponding author states that there is no conflict of interest.

References

- Potysz A, van Hullebusch ED, Kierczak J, Grybos M, Lens PNL, Guibaud G (2015) Copper metallurgical slags—current knowledge and fate: a review. *Crit Rev Environ Sci Technol* 45(22):2424–2488. <https://doi.org/10.1080/10643389.2015.1046769>
- Hu JH, Wang H, Zhao LM, Li L, Liu HL (2011) Characterization of copper slag from impoverishment. *J Saf Environ* 11(2):90–93. <https://doi.org/10.3969/j.issn.1009-6094.2011.02.022>
- Sarfo P, Das A, Wyss G, Young C (2017) Recovery of metal values from copper slag and reuse of residual secondary slag. *Waste Manag* 70:272–281. <https://doi.org/10.1016/j.wasman.2017.09.024>
- Guo ZQ, Zhu DQ, Pan J, Zhang F (2018) Innovative methodology for comprehensive and harmless utilization of waste copper slag via

- selective reduction-magnetic separation process. *J Clean Prod* 187: 910–922. <https://doi.org/10.1016/j.jclepro.2018.03.264>
5. Yang HF, Jing LL, Dang CG (2011) Iron recovery from copper-slag with lignite-based direct reduction followed by magnetic separation. *Chin Nonferrous Met* 21(5):1165–1170. <https://doi.org/10.1016/B978-0-444-53599-3.10005-8>
 6. Li SW, Pan J, Zhu DQ, Guo ZQ, Xu JW, Chou JL (2019) A novel process to upgrade the copper slag by direct reduction-magnetic separation with the addition of Na_2CO_3 and CaO. *Powder Technol* 347:159–169. <https://doi.org/10.1016/j.powtec.2019.02.046>
 7. Herreros O, Quiroz R, Manzano E, Bou C, Vinals J (1998) Copper extraction from reverberatory and flash furnace slags by chlorine leaching. *Hydrometallurgy* 49(1):87–101. [https://doi.org/10.1016/S0304-386X\(98\)00010-3](https://doi.org/10.1016/S0304-386X(98)00010-3)
 8. Zang Y, Man RL, Ni WD, Wang H (2010) Selective leaching of base metals from copper smelter slag. *Hydrometallurgy* 103(1):25–29. <https://doi.org/10.1016/j.hydromet.2010.02.009>
 9. Altundogan HS, Boyrazli M, Tumen F (2004) A study on the sulphuric acid leaching of copper converter slag in the presence of dichromate. *Miner Eng* 17(3):465–467. <https://doi.org/10.1016/j.mineng.2003.11.002>
 10. Banza AN, Gock E, Kongolo K (2002) Base metals recovery from copper smelter slag by oxidising leaching and solvent extraction. *Hydrometallurgy* 67(1):63–69. [https://doi.org/10.1016/S0304-386X\(02\)00138-X](https://doi.org/10.1016/S0304-386X(02)00138-X)
 11. Huang FR, Liao YL, Zhou J, Wang YY, Li H (2015) Selective recovery of valuable metals from nickel converter slag at elevated temperature with sulfuric acid solution. *Sep Purif Technol* 156:572–581. <https://doi.org/10.1016/j.seppur.2015.10.051>
 12. Khalid MK, Hamuyuni J, Agarwal V, Agarwal V, Pihlasalo J, Haapalainen M, Lundströmlm M (2019) Sulfuric acid leaching for capturing value from copper rich converter slag. *J Clean Prod* 215:1005–1013. <https://doi.org/10.1016/j.jclepro.2019.01.083>
 13. Perederiy I, Papangelakis VG (2017) Why amorphous FeO-SiO_2 slags do not acid-leach at high temperatures. *J Hazard Mater* 321: 737–744. <https://doi.org/10.1016/j.jhazmat.2016.09.055>
 14. Aleksandrov PV, Medvedev AS, Imideev VA, Moskovskikh DO (2019) Nickel sulphide concentrate processing via low-temperature calcination with sodium chloride. Part 1-identification of interaction products. *Miner Eng* 134:37–53. <https://doi.org/10.1016/j.mineng.2019.01.001>
 15. Cui FH, Mu WN, Wang S, Xin HX, Shen HT, Xu Q, Zhai YC, Luo SH (2018) Synchronous extractions of nickel, copper, and cobalt by selective chlorinating roasting and water leaching to low-grade nickel–copper matte. *Sep Purif Technol* 195:149–162. <https://doi.org/10.1016/j.seppur.2017.11.071>
 16. Sukla LB, Panda SC, Jena PK (1986) Recovery of cobalt, nickel and copper from converter slag through roasting with ammonium sulphate and sulphuric acid. *Hydrometallurgy* 16(2):153–165. [https://doi.org/10.1016/0304-386X\(86\)90040-X](https://doi.org/10.1016/0304-386X(86)90040-X)
 17. Tümen F, Bailey NT (1990) Recovery of metal values from copper smelter slags by roasting with pyrite. *Hydrometallurgy* 25(3):317–328. [https://doi.org/10.1016/0304-386X\(90\)90047-6](https://doi.org/10.1016/0304-386X(90)90047-6)
 18. Guo XY, Li D, Park K-H, Tian QH, Wu Z (2009) Leaching behavior of metals from a limonitic nickel laterite using a sulfation–roasting–leaching process. *Hydrometallurgy* 99(3):144–150. <https://doi.org/10.1016/j.hydromet.2009.07.012>
 19. Zhang LN, Zhang L, Wang MY, Sui ZT (2005) Treatment and resourceful disposal of copper slag. *Multipurpose Util Miner Resour* 5:22–26. <https://doi.org/10.3969/j.issn.1000-6532.2005.05.006>
 20. Arslan C, Arslan F (2002) Recovery of copper, cobalt, and zinc from copper smelter and converter slags. *Hydrometallurgy* 67(1): 1–7. [https://doi.org/10.1016/S0304-386X\(02\)00139-1](https://doi.org/10.1016/S0304-386X(02)00139-1)
 21. Tagawa H (1984) Thermal decomposition temperatures of metal sulfates. *Thermochim Acta* 80(1):23–33. [https://doi.org/10.1016/0040-6031\(84\)87181-6](https://doi.org/10.1016/0040-6031(84)87181-6)

Publisher's Note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.