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CARROLLITE LEACHING IN H_2SO_4-NACLO$_3$ MEDIA AT ATMOSPHERIC PRESSURE

A new extraction process suitable for treating refractory $CuCo_2S_4$ under atmospheric pressure acidic leaching conditions was investigated. The effect of variables such as oxidant species, liquid-to-solid ratio, leaching time, oxidizing agent and mineral quality ratio, H_2SO_4 concentration, temperature and sodium chloride concentration on the extraction efficiency of Co, Cu and Fe from $CuCo_2S_4$ were investigated. Under optimal conditions including P_{80}-P_{90} of the sample was d < 0.0074 mm, stirring speed of 400 rpm, leaching time of 8 h with sodium chlorate ($NaClO_3$) and mineral quality ratio of 0.5, 2 mol/L H_2SO_4, liquid-to-solid ratio of 7, leaching temperature of 90°C and 4 mol/L sodium chloride. The leaching efficiency of Co, Cu, and Fe were nearly 97.08%, 100%, and 92.45%, respectively. Furthermore, the contents of cobalt and copper in leaching residue were all less than 0.4 wt.%, which satisfies the requirements of industrial production.

Keywords: $CuCo_2S_4$; atmospheric leaching; H_2SO_4-$NaClO_3$ media

1. Introduction

In recent years, China has become the largest manufacturing center in the world, and a major worldwide foundry of LIB (lithium-ion battery) [1]. The demand for cobalt is predicted to increase steadily due to higher requirements in the manufacturing of electronic devices and new energy materials such as rechargeable batteries, catalysts, and supperalloys. However, cobalt resources are scarce in China and most of them are in lean ore. Almost no native cobalt deposits are relatively rich, and cobalt mainly exists in the form of symbiotic elements in veins and deposits with nickel, copper, iron, and arsenic. Most of the cobalt resources are imported from the Central African Copperbelt, which situated between the Democratic Republic of Congo (DRC) and Zambia and is famous for its abundant cobalt resources. About half of the global production of cobalt originates from this region [2]. These deposits are mainly of sulfide types with carrollite being the major cobalt bearing mineral. The formal oxidation states of the constituent elements in $CuCo_2S_4$, the mineral carrollite, have been controversial for many years, with no clear consensus between $Cu^I Co^{III} Co^{IV} S^{-II}_4$, $Cu^I Co^{III}_2 S^{-II}_3 S^{-I}$, $Cu^{II} Co^{III}_2 S^{-II}_4$ and $Cu^I Co^{III}_2 (S_4)^{-VII}$ [3].

Cobalt in carrollite ore is difficult to extract due to trivalent cobalt and tetravalent cobalt have low solubility. The traditional technology for extracting cobalt from the ore is combined hydro-pyrometallurgical process. Although it is capable of achieving high cobalt recoveries. The significant disadvantages are associated with the pyrometallurgical route to cobalt production: the oxidation of carrollite not only requires high roasting temperatures, which consumes a large amount of energy but also generates a considerable amount of smoke dust, such as sulfur dioxide, which causes environmental pollution [4]. In recent years, with the development of biohydrometallurgy, the technology of cobalt extraction by bacteria has received much attention [5,6]. Biohydrometallurgy can be used to process low-grade copper and cobalt minerals and refractory ores efficiently because of its low investment cost and energy consumption, environmentally eco-friendly process [7-9]. However, it has always been plagued by low recovery of metals and slow dissolution kinetics [10]. Hydrometallurgy is by far the most common way of treating the ore [11-15]. It is typically less energy intensive and more suitable for low grade and complex ore types. Besides, it has small environmental impacts due to lower fuel requirements and lack of SO_2 generation [16-20]. Despite the benefits of hydrometallurgy for the recovery of copper and cobalt from carrollite, hydrometallurgical route showed little commercial success. Because the conventional atmospheric leaching of carrollite ore has poor leaching efficiency and low recovery [21-28].

In this current work, a new extraction process suitable for treating refractory carrollite ore at atmospheric pressure was investigated. The effect of oxidant species, liquid-to-solid ratio,

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leaching time, oxidizing agent and mineral quality ratio, H_2SO_4 concentration, temperature, and sodium chloride concentration on copper, cobalt, and iron extraction were studied. The novelty of this research is based on the high-efficiency leaching of carrollite at atmospheric pressure, provides a powerful theoretical basis and data reference for industrial production.

2. Materials and methods

2.1. Ore samples

The ore used in this study was provided by Guangdong Jiana Energy Technology Co., Ltd. The ore was crushed and sieved to obtain P_{80}-P_{90} of the sample was d < 0.0074 mm. The main chemical composition of the ore is given in Table 1. As shown in this table, the contents of cobalt, copper, and iron are 13.02 wt.%, 9.32 wt.% and 4.96 wt.%, respectively. According to the X-ray diffraction (XRD, D/Max-2550 X-ray diffractometer with Cu Kα radiation from 10° to 80°) pattern of carrollite shown in Fig. 1, the dominant minerals are carrollite, chalcopyrite, and

TABLE 1

The main chemical analysis of carrollite ore

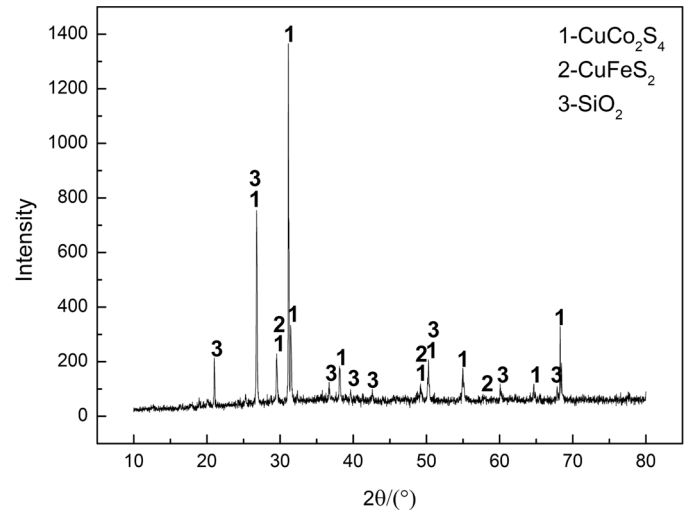| Element	Co	Cu	Fe	S	Si	O	Mn	Mg	Al	Ca
wt.%	13.02	9.32	4.96	11.76	24.33	21.63	0.69	5.70	5.49	2.91

Fig. 1. The X-ray diffraction pattern of carrollite ore
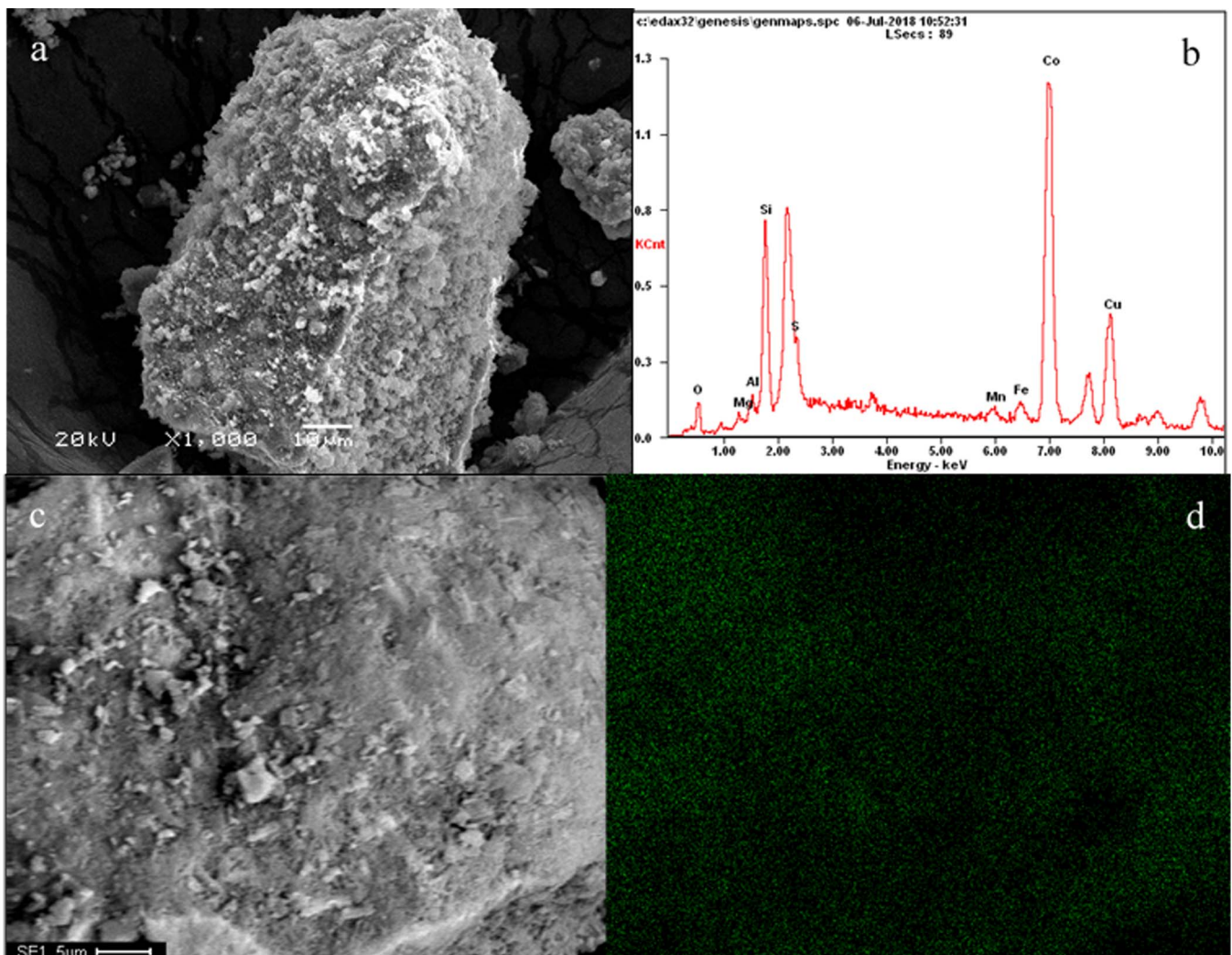

Fig. 2. (a, c) the scanning electron microscopy image of carrollite ore (b) EDX patterns (d) EDX elemental mapping of Co

silica. The surface morphology analyses were obtained in Fig. 2 by using a JSM-6360LV spectrometer coupled with energy-dispersive X-ray spectroscopy (EDX-GENESIS60S).

2.2. Methods and conditions

The leaching experiments were conducted in a 500 mL three-neck round bottom flask fitted with an overhead mechanical stirrer. For each leaching experiment, according to the predetermined liquid-solid ratio, sulphuric acid at a predetermined concentration was transferred into the reactor, which was then heated to the desired temperature through the digital homoeo-thermic water bath before adding the ore samples. After a certain period of time, the mechanical stirrer and the digital homoeo-thermic water bath were both switched off. The leach slurries were then filtered and washed several times with deionized water. All solutions were collected for subsequent analysis. In the meantime, the leach residues were dried in an oven at 100°C for 6 h, weighed. Finally, Elemental analysis of the residue samples was conducted using X-ray fluorescence spectrometer (XRF, XRF-1800, Shimadzu, Japan) and filtered leaching liquor was conducted using atomic emission spectrometer (ICP-AES, IRIS Intrepid II XSP, Thermo Electron Corporation, USA).

In the leaching tests, all chemicals were of analytical reagent grade and were used as precursors without further purification. The effect of oxidant species, liquid-to-solid ratio, leaching time, oxidizing agent and mineral quality ratio, H_2SO_4 concentration, temperature, and sodium chloride concentration were investigated. Only one of the above parameters was allowed to vary while all others were fixed.

The leaching ratios of metals mean the proportion of the dissolved quantity to the total quantity in the raw material, and it can be calculated as Eq. (1)

$$R_{Me} = \frac{C_{\text{leaching solution}} \times V_{\text{leaching solution}}}{M_{\text{raw material}} \times \omega_{\text{raw material}}} \times 100\% \qquad (1)$$
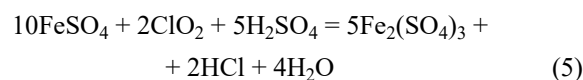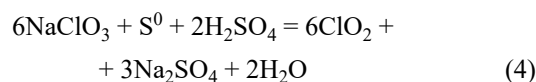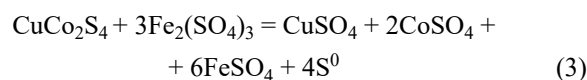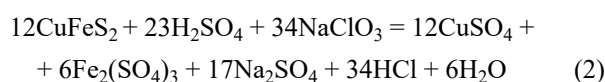
where R_{me} is the leaching ratio (%), $C_{\text{leaching solution}}$ is the concentrations of metals in the leaching solution (g/L). $V_{\text{leaching solution}}$ is the volume of leaching solution (L). $M_{\text{raw material}}$ is the weights of raw material (g). $\omega_{\text{raw material}}$ is the contents of metals in raw material (wt.%).

3. Results and discussion

3.1. Effect of oxidant species

To investigate the effect of oxidant species on the extraction efficiency of Co, leaching experiments on carrollite ore were first carried out by varying the leaching time from 2 h to 10 h with four different oxidants, including sodium chlorate (NaClO₃), ferric sulfate (Fe₂(SO₄)₃), hydrogen peroxide (H₂O₂) and sodium persulfate (Na₂S₂O₈). In these experiments, the particle size, stirring speed, liquid-to-solid ratio, H_2SO_4 concen-

tration, and temperature were fixed at P80-P90 of the sample was d < 0.0074 mm, 400 rpm, 7/1, 2 mol/L, 85°C, respectively. NaClO₃, Fe₂(SO₄)₃, Na₂S₂O₈ and mineral quality ratio were all fixed at 1. The liquid-to-solid ratio of hydrogen peroxide and minerals was fixed at 4/1. Fig. 3 shows the effect of oxidant species on the extraction efficiency of Co. As shown in Fig. 3, the performances of four different oxidants on extracting cobalt rank as follows: NaClO₃ > H₂O₂ > Na₂S₂O₈ > Fe₂(SO₄)₃. And the leaching efficiency of Co increased slightly with leaching time from 2 h to 10 h when using ferric sulfate, hydrogen peroxide, and sodium persulfate as oxidant separately. When using sodium chlorate as the oxidant, the leaching efficiency of Co increased steadily with oxidation time up to 8 h, beyond which it did not change with further increased in the oxidation time. The above phenomenon may be explained by the following leaching principles:

$$12CuFeS_2 + 23H_2SO_4 + 34NaClO_3 = 12CuSO_4 + 6Fe_2(SO_4)_3 + 17Na_2SO_4 + 34HCl + 6H_2O \qquad (2)$$

$$CuCo_2S_4 + 3Fe_2(SO_4)_3 = CuSO_4 + 2CoSO_4 + 6FeSO_4 + 4S^0 \qquad (3)$$

$$6NaClO_3 + S^0 + 2H_2SO_4 = 6ClO_2 + 3Na_2SO_4 + 2H_2O \qquad (4)$$

$$10FeSO_4 + 2ClO_2 + 5H_2SO_4 = 5Fe_2(SO_4)_3 + 2HCl + 4H_2O \qquad (5)$$

According to the above reaction equation, it can be seen that the reducing agent is Fe^{2+}, which is obtained by reacting Fe^{3+} with S^{2-} [29]. Sodium chlorate and chlorine dioxide (internationally recognized as a safe, non-toxic green disinfectant) can oxidize most of the sulfur to sulfate, which can avoid the formation of a passivation layer on the mineral surface by a large amount of sulfur. In contrast, ferric sulfate, hydrogen peroxide, and sodium persulfate can only oxidize small amount of the sul-
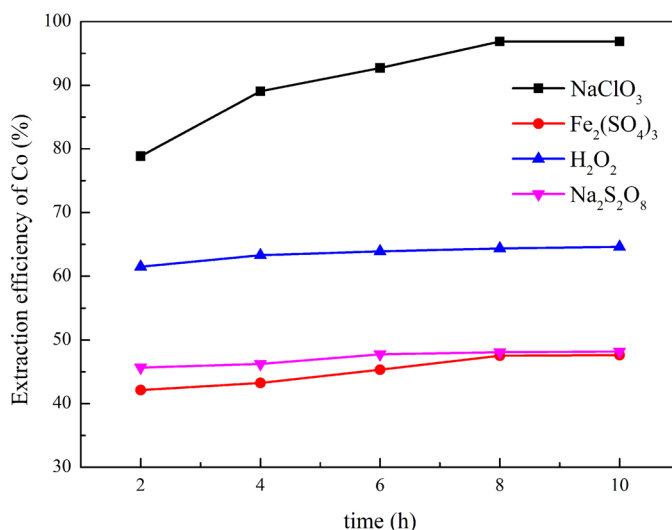

Fig. 3. Effect of oxidant species on the extraction efficiency of Co

fur to sulfate. Chloride ion also enhances the anodic oxidation of mineral sulfides and the dispersion of molten sulfur [30,31]. In addition, the chalcopyrite may also promote carrollite dissolution in sulfuric acid due to the galvanic effect [32-34]. Based on these results and analysis, sodium chlorate was selected as the oxidant for further leaching experiments of the carrollite concentrate.

3.2. Effect of liquid-to-solid ratio

Fig 4 shows the effect of liquid-to-solid ratio on the extraction efficiency of Co, Cu, Fe. There was a significant effect on the extraction efficiency of Co, Cu, and Fe. When the liquid-to-solid ratio was increased from 3:1 to 7:1, the extraction efficiency of Co, Cu and Fe increased from 81.31 to 92.18%, 87.47 to 100%, 72.67 to 94.98%, respectively, with no further change as per further increments of liquid-to-solid ratio up to 11:1. The above phenomenon can be explained by the following reason: significant amounts of silica within the samples and sulfur created a diffusion layer on the particle surfaces, which restricts H^+ and ClO_3^-, etc access to the un-reacted surfaces. Increasing liquid-to-solid ratio can reduce pulp viscosity and allow silica and sulfur to disperse in solution. But continuing to increase the liquid-to-solid ratio will influence the subsequent process. Therefore, the optimum liquid-to-solid ratio was determined to be 7/1.
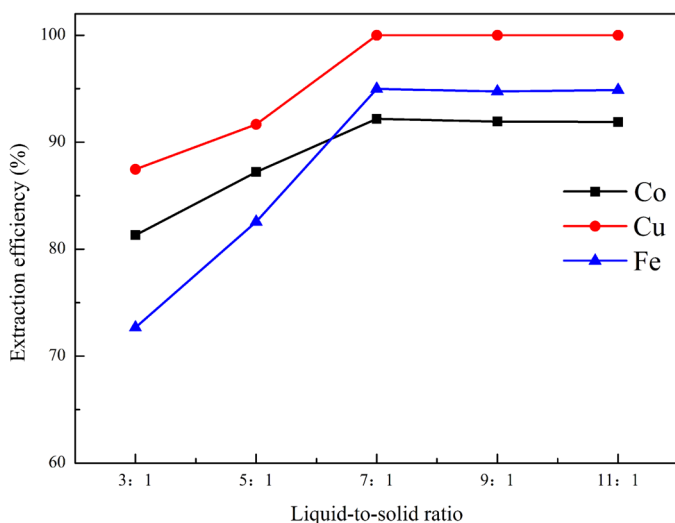

Fig. 4. Effect of liquid-to-solid ratio on the extraction efficiency of Co, Cu, Fe (conditions: The particle size = –0.074 mm (80%~90%), stirring speed = 400 rpm, t = 6 h, sodium chlorate (NaClO$_3$) and mineral quality ratio = 0.75, H$_2$SO$_4$ concentration = 2 mol/L, T = 85°C)

3.3. Effect of leaching time

The effect of the leaching time on the extraction efficiency of Co, Cu, Fe was examined by varying time from 6 h to 10 h. The results are shown in Fig. 5. It can be seen from Fig. 5 that the leaching efficiency of Co increased gradually from 92.18% to 96.35% in the leaching time of 6-8 h and was stable at the time more than 8 h. The leaching efficiency of Cu and Fe are almost

unchanged with the leaching time from 6 h to 10 h. The above phenomenon can be explained by the following reason: it takes a certain time for the reaction of Fe^{3+} and S^{2-} to generate Fe^{2+}. Therefore, the leaching efficiency of Co increased steadily with increasing the leaching time until all Fe^{2+} were consumed in the solution. Based on these results, the optimum leaching time was determined to be 8 h.
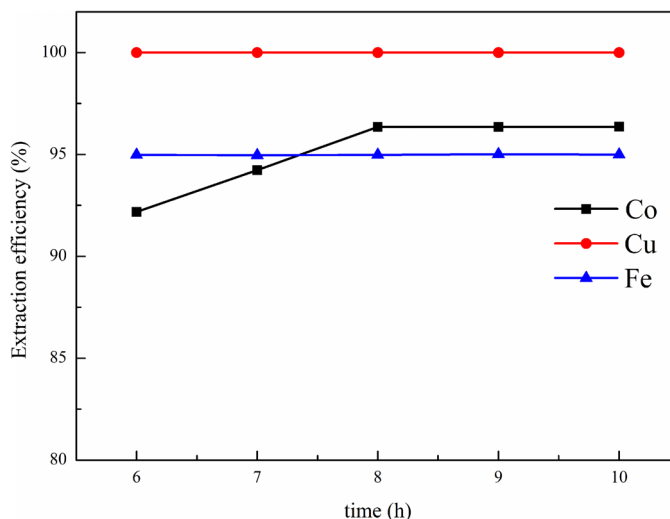

Fig. 5. Effect of leaching time on the extraction efficiency of Co, Cu, Fe (conditions: The particle size = –0.074 mm (80%~90%), stirring speed = 400 rpm, liquid-to-solid ratio = 7:1, sodium chlorate (NaClO$_3$) and mineral quality ratio = 0.75, H$_2$SO$_4$ concentration = 2 mol/L, T = 85°C)

3.4. Effect of sodium chlorate (NaClO$_3$) and mineral quality ratio

The effect of sodium chlorate and mineral quality ratio on the extraction efficiency of Co, Cu, and Fe are shown in Fig. 6. The leaching efficiency of Co, Cu, and Fe increased consider-
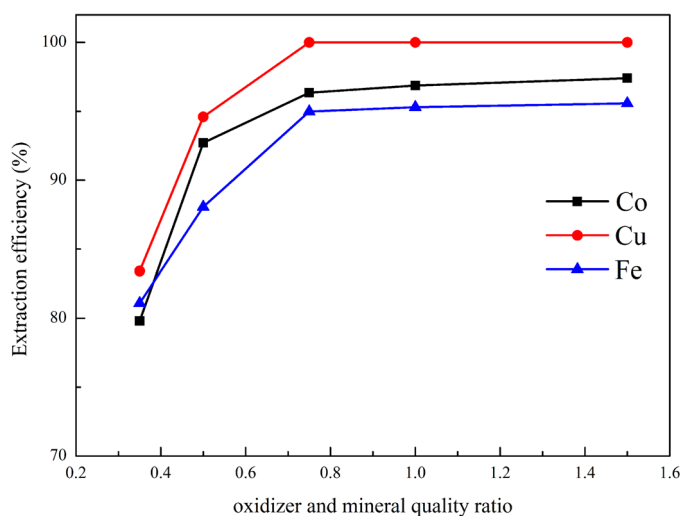

Fig. 6. Effect of sodium chlorate and mineral quality ratio on the extraction efficiency of Co, Cu, Fe (conditions: The particle size = –0.074 mm (80%~90%), stirring speed = 400 rpm, liquid-to-solid ratio = 7:1, t = 8 h, H$_2$SO$_4$ concentration = 2 mol/L, T = 85°C)

ably with the sodium chlorate and mineral quality ratio up to 0.75, beyond which they increased slightly. From the perspective of production costs, the optimum sodium chlorate and mineral quality ratio were determined to be 0.75.

3.5. Effect of H_2SO_4 concentration

Fig. 7 shows the effect of H_2SO_4 concentration on the extraction efficiency of Co, Cu, and Fe. It can be seen from Fig. 7 that the leaching efficiency of Co and Cu increased gradually with H_2SO_4 concentration up to 1 mol/L. Then they increased slowly with H_2SO_4 concentration up to 2 mol/L, beyond which they did not change with further increased in the H_2SO_4 concentration. According to the Reaction (5), although a certain amount of hydrogen ions is consumed during the reaction, they are also generated at the same time. Therefore, H_2SO_4 concentration shows a small effect on the extractions of Co and Cu. However, the sulfuric acid concentration will influence the extraction efficiency of Fe significantly. The leaching efficiency of Fe increased considerably with H_2SO_4 concentration from 0.5 mol/L to 2.5 mol/L. However, silica gel will be formed from silica with higher H_2SO_4 concentration, which will affect the filtration performance of leaching pulp. Therefore, the optimum H_2SO_4 concentration was determined to be 2 mol/L.
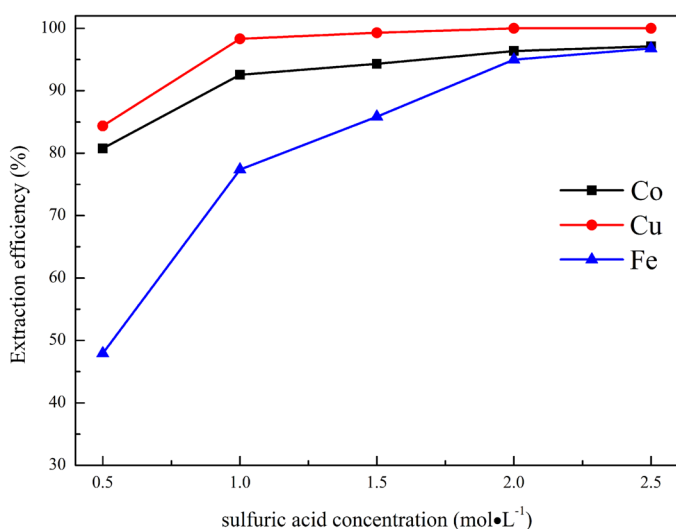

Fig. 7. Effect of H_2SO_4 concentration on the extraction efficiency of Co, Cu, Fe (conditions: The particle size = –0.074 mm (80%~90%), stirring speed = 400 rpm, liquid-to-solid ratio = 7:1, t = 8 h, sodium chlorate (NaClO$_3$) and mineral quality ratio = 0.75, T = 85°C)

3.6. Effect of leaching temperature

Fig. 8. shows the effect of leaching temperature on the extraction efficiency of Co, Cu, and Fe. It can be seen that the leaching efficiency of Co increased gradually with temperature up to 90°C, beyond which they remained stable with further increasing the temperature. The leaching efficiency of Cu increased gradually with temperature up to 80°C, beyond which

they did not change with further increasing the temperature. However, the extraction efficiency of Fe decreased gradually on increasing the temperature from 75°C to 95°C due to the formation of precipitates such as ferric oxide. Based on these results, the optimum leaching temperature was determined to be 90°C. Under this condition, 97.06%, 100% and 92.45% of Co, Cu, and Fe were recovered, respectively.
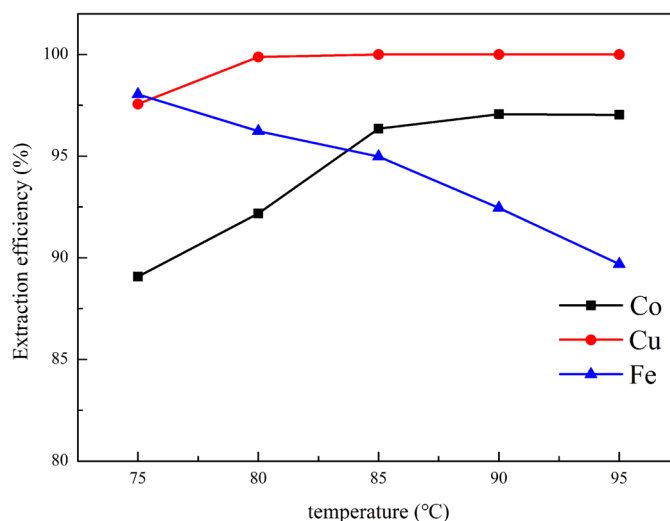

Fig. 8. Effect of leaching temperature on the extraction efficiency of Co, Cu, Fe (conditions: The particle size = –0.074 mm (80%~90%), stirring speed = 400 rpm, liquid-to-solid ratio = 7:1, t = 8 h, sodium chlorate (NaClO$_3$) and mineral quality ratio = 0.75, H_2SO_4 concentration = 2 mol/L)

3.7. Effect of sodium chloride concentration

In order to reduce production costs, the effect of sodium chloride concentration on the extraction of Co was initially explored. A series of experiments were carried out by varying sodium chloride concentration from 0 mol/L to 4 mol/L while keeping the other variables constant. In these experiments, the particle size, stirring speed, liquid-to-solid ratio, leaching time, H_2SO_4 concentration and temperature were fixed at P80-P90 of the sample was d < 0.0074 mm, 400 rpm, 7/1, 8 h, 2 mol/L, 90°C, respectively. Fig. 9 shows the effect of sodium chloride concentration on the extraction efficiency of Co. As shown in Fig. 9, the performances of five different sodium chloride concentrations on extracting cobalt rank as follows: 4 mol/L > 3 mol/L > 0 mol/L > 2 mol/L > 1 mol/L. It can be explained by the Reaction (6):

$$2NaClO_3 + 2NaCl + 2H_2SO_4 = 2ClO_2 + 2Na_2SO_4 + 2H_2O + Cl_2 \qquad (6)$$
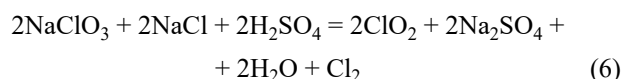
According to the above reaction equation, when sodium chloride was added to the solution, chlorine dioxide and chlorine become main oxidants. However, when the concentration of chloride ions in the solution is low, the oxidation of the sulfur will be reduced to some extent, so that the formation of a thicker passivation layer on the mineral surface by a large amount of sulfur.

Therefore, it is necessary to add an excess of sodium chloride in order to achieve the desired cobalt leaching rate. As long as the amount of sodium chloride added is properly controlled, the amount of sodium chlorate can be reduced while ensuring a high leaching rate, thereby reducing production costs. Based on these results and analysis, the optimum sodium chloride concentration and sodium chlorate and mineral quality ratio were determined to be 4 mol/L and 0.5, respectively. Under this condition, 97.21% of Co was recovered.
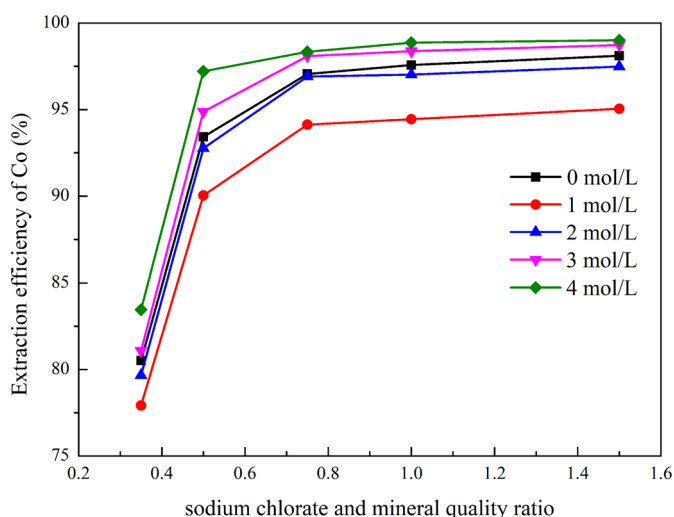

Fig. 9. Effect of sodium chloride concentration on the extraction efficiency of Co

3.8. Optimum conditions and residue characterization

Based on the results determined in the previous tests, the optimum conditions are determined as follow: The particle size, stirring speed, leaching time, sodium chlorate ($NaClO_3$) and mineral quality ratio, H_2SO_4 concentration, liquid-to-solid ratio, leaching temperature, and sodium chloride concentration were determined at P80-P90 of the sample was d < 0.0074 mm, 400 rpm, 8 h, 0.5, 2 mol/L, 7/1, 90°C, 4 mol/L, respectively. Three experiments were carried out under optimum conditions. Table 2 shows the leaching efficiencies of Co, Cu, Fe under optimum conditions. The main chemical analysis of carrollite leach solution is given in Table 3. Based on the results of the leaching experiment and the type and content of metals in the leachate, a flow sheet was proposed for recovery of copper and cobalt from carrollite ore. The main feature of this flowsheet is the three-sequential solvent extraction steps. In the first step, the extraction of Cu(II) use Lix984 as an extractant, the loaded organic phase were scrubbed using diluted sulphuric acid solution and stripped by sulfuric acid solution. In the second step, the removal of Fe, Zn, Ca and Mg use P204 as an extractant, the loaded organic phase were scrubbed using diluted sulphuric acid solution and stripped by sulfuric acid solution. In the third step, the extraction and concentration of Co(II) use P507 as an extractant, the loaded organic phase were scrubbed using diluted

sulphuric acid solution and stripped by sulfuric acid solution. The wastewater produced by this process is purified and returned to the leaching stage.

TABLE 2

The leaching efficiency of Co, Cu, Fe under optimum conditions

Experiment number	1	2	3	Average value
Co/%	96.97	97.18	97.09	97.08
Cu/%	100	100	100	100
Fe/%	92.37	92.50	92.48	92.45

TABLE 3

The main chemical analysis of carrollite leach solution

Element	Co	Cu	Ni	Zn	Fe	Ca	Mg
Concentration (g/L)	16.839	12.415	0.067	0.022	6.03	0.363	1.102

The chemical compositions of the 2nd residue obtained in acid oxidative leaching process under optimum conditions are shown in Table. 4. The 2nd residue was also characterized by XRD technique and the result is shown in Fig. 10. From Table 4, it can be observed that the content of cobalt, copper, and iron in 2nd leaching residue is 0.38%, 0.33%, and 2.45%, respectively. It can be seen from Fig. 10 that the dominant phase in 2nd leaching residue is silica.

TABLE 4

The main chemical analysis of 2nd residue

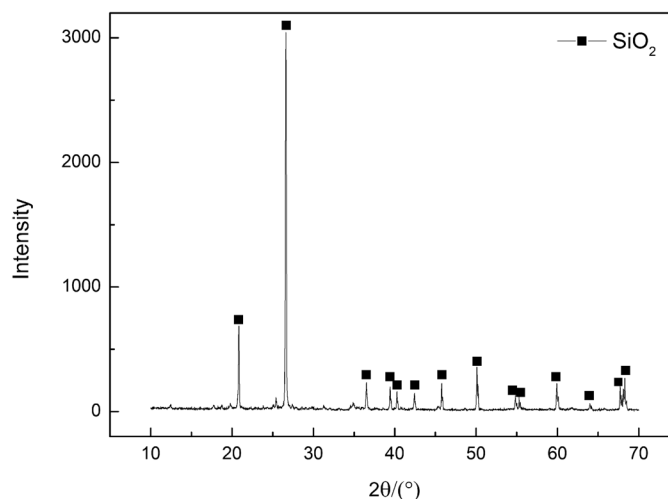| Element	Co	Cu	Fe	S	Si	O
wt.%	0.38	0.33	2.45	2.55	43.01	38.41

Fig. 10. The X-ray diffraction pattern of 2nd residue

4. Conclusions

A new extraction process suitable for treating refractory carrollite ore at atmospheric pressure was proposed. The effect

of the different variables involved in the leaching processes on the extraction efficiency of Co, Cu, and Fe from carrollite ore was studied and the optimal conditions were identified. The optimal conditions include P80-P90 of the sample was d < 0.0074 mm , a stirring speed of 400 rpm, a leaching time of 8 h, sodium chlorate ($NaClO_3$) and mineral quality ratio of 0.5, 2 mol/L H_2SO_4, 7/1 liquid-to-solid ratio, leaching temperature of 90°C and 4 mol/L sodium chloride. Under these conditions, The leaching efficiency of Co, Cu, and Fe were found to be approximately 97.08%, 100%, and 92.45%, respectively. Furthermore, the contents of cobalt and copper in leaching residue were all less than 0.4 wt.%, which satisfies the requirements of industrial production.

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