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Kinetics study on cobalt leaching from cobalt-bearing ternary sulfide in sulfuric acid solution under atmospheric pressure

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Abstract: The leaching of cobalt from cobalt-bearing ternary sulfide with sulfuric acid solution under atmospheric pressure was investigated. The influence of stirring speed, leaching temperature, H_2SO_4 concentration, and particle size on the leaching efficiency of cobalt was studied, and the kinetics analysis of cobalt leaching from the cobalt-bearing ternary sulfide was performed. The results showed that cobalt and iron were selectively leached with high efficiency (>99%) under the optimal conditions, while molybdenum and copper were enriched in residues. According to the analysis of the experimental data, the leaching of cobalt conformed to the shrinking core model with a solid product layer and was controlled by internal diffusion. The activation energy of the leaching reaction was 49.86 kJ/mol, and the reaction orders of H_2SO_4 concentration and particle size were 0.57 and −1.4, respectively.

Key words: cobalt white alloy; cobalt-bearing ternary sulfide; cobalt; sulfuric acid; leaching kinetics

1 Introduction

Cobalt is a strategic rare metal with high stability and magnetism. It is widely used in several fields such as machinery manufacturing, electronics, electrical engineering, aerospace, and the chemical industry [1]. In recent years, the consumption of cobalt has greatly increased with the development of lithium-ion battery materials. China is the largest producer and consumer of cobalt but lacks cobalt resources, possessing only 1% of global reserves [2−4]. Most cobalt raw materials are imported from the Democratic Republic of the Congo (DRC) [5,6]. Because of the export policy restrictions of the DRC, cobalt ores must be smelted before being exported. Due to the limitation of the local industries, only the primary smelting process is performed to produce cobalt-containing intermediate products. Therefore, China imports intermediate products such as crude cobalt hydroxide and cobalt white alloy. Cobalt white alloy is obtained from the reduction smelting of copper cobalt oxide ore [7], which contains cobalt, iron, copper, silicon, and low amounts of other impurity elements. Because the alloy is a water-quenched product, all the elements are closely embedded. Therefore, the separation and extraction of valuable metals are difficult [8].

Previous studies have demonstrated the treatment of cobalt white alloy by oxygen pressure leaching and atmospheric pressure leaching processes [9−11]. A high leaching efficiency of cobalt and copper was obtained through the oxygen

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pressure leaching process [12]. However, the leaching process was performed under high temperature and pressure, which introduces severe requirements for the leaching equipment, and resulted in high investment and production cost. Atmospheric pressure leaching has also been used to treat cobalt white alloy [13]. Due to the stable chemical properties of cobalt white alloy, numerous strong oxidants, i.e. nitric acid, chlorine, and sodium hypochlorite were used in the leaching process [14−16]. However, these oxidants form toxic compounds such as NO and Cl_2 in the leaching process, causing environmental problems and economic recycling difficulties.

The leaching of cobalt white alloy is limited by its inert chemical structure, particularly the ferrosilicon component [17−19]. Therefore, the structure conversion of cobalt white alloy may be an alternative way to improve its leaching performance. Calcification or sodium roasting pretreatment was used in previous studies to remove silicon from cobalt white alloy [20,21], improving its leaching performance. Although several issues such as the low recovery rate of cobalt and large consumption of desilication agents occurred in this leaching process, the conversion of the inert structure of cobalt white alloy was achieved. Therefore, this approach has certain significance in the development of a novel cobalt white alloy leaching method.

In our previous study [22], a structure conversion pretreatment was used to enhance the leaching of cobalt white alloy and molybdenite. In this process, cobalt white alloy was converted into cobalt-bearing ternary sulfide through smelting with molybdenite. Compared with cobalt white alloy, the leaching performance of cobalt in ternary sulfide was greatly improved in acid solutions. However, the leaching kinetics of cobalt-bearing ternary sulfide under atmospheric pressure is still unclear.

In this study, the leaching mechanism and kinetics of cobalt in cobalt-bearing ternary sulfide were investigated in H_2SO_4 solution under atmospheric pressure. The effects of stirring speed, leaching temperature, H_2SO_4 concentration, and particle size on the leaching kinetics of cobalt were systematically investigated. The control step, apparent activation energy, and reaction orders of the leaching reaction were determined, and the kinetic equation was established.

2 Experimental

2.1 Materials

The cobalt white alloy used in the study was obtained from the DRC, and its chemical composition was as follows (wt.%): Co 38.72, Fe 39.21, Cu 8.15, Si 5.71, and S 0.25. Molybdenite was provided by Jinduicheng Molybdenum Co., Ltd., (Xi'an, China), and its chemical composition was as follows (wt.%): Mo 43.31, S 26.78, Fe 4.24, Cu 0.47, and Si 2.17. The samples were characterized by X-ray diffraction (XRD) using Cu K_α radiation in a D/Max 2500 Rigaku device. The main phase compositions of cobalt white alloy were $(Fe,Co)_xSi_y$ and Cu metal (Fig. 1(a)), while only the MoS_2 phase was detected in the molybdenite (Fig. 1(b)). The cobalt white alloy and molybdenite before smelting were ground to the required particle size of 106 μm. All the reagents in this leaching process were of analytical grade and used without further purification. Deionized water was used in the experiments.

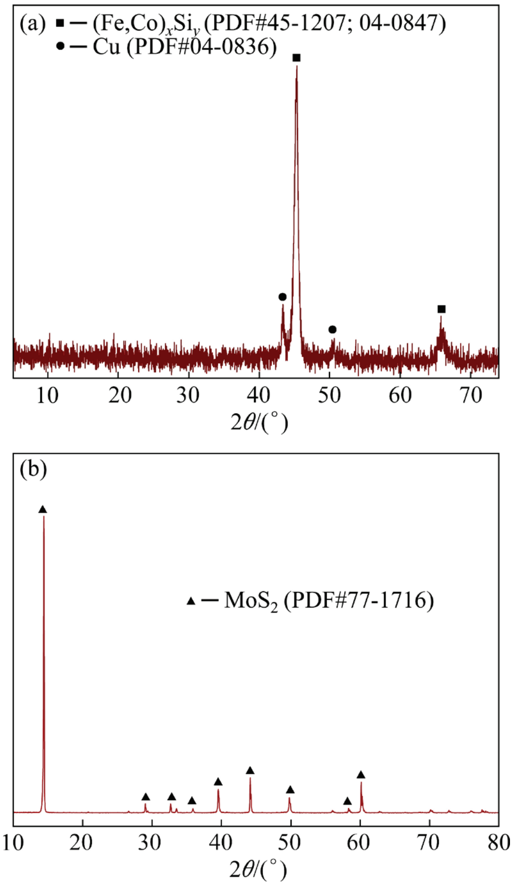

Fig. 1 XRD patterns of cobalt white alloy (a) and molybdenite (b)

2.2 Preparation of cobalt-bearing ternary sulfide

The cobalt-bearing ternary sulfide was obtained using a structure conversion pretreatment. In this process, cobalt white alloy and molybdenite (with a certain mass ratio of cobalt alloy to molybdenite being 1:2) were mixed and poured into a corundum crucible, which was then inserted into a carbon crucible. Afterwards, the crucible was put in a vacuum induction furnace and heated to a preset temperature of 1050 °C. After smelting for 90 min, it was cooled to room temperature using the water-cooling system. The cobalt-bearing ternary sulfide was crushed and milled into powder samples of different size fractions: 75−106, 58−75, and 48−58 μm. For the determination of the chemical composition of cobalt-bearing ternary sulfide with different particle sizes, a 0.15 g sample was weighed and added into a corundum crucible with Na_2O_2 (1 g) at the bottom, and Na_2O_2 (1.2 g) was then laid on the top. The corundum crucible was further baked at 700 °C for 25 min in a muffle furnace, and then naturally cooled to room temperature. Afterwards, the samples in the crucible were dissolved with HCl solution (6 mol/L), and the content of the elements in the solution was detected by an inductively coupled plasma optical emission spectrometer (ICP-OES, ICAP 7000). The cobalt-bearing ternary sulfide was analyzed by XRD.

2.3 Leaching with sulfuric acid under atmospheric pressure

The leaching of cobalt-bearing ternary sulfide was investigated in sulfuric acid solution under atmospheric pressure. The experimental process was as follows. 700 mL of sulfuric acid solution was placed in a three necked flask with adjustable mechanical stirring system, which was then heated in a water bath. After the sulfuric acid solution was heated to the preset temperature and stabilized, the product (2 g) was added. At preset interval, a 2 mL aliquot of leaching solution was taken out and quickly diluted to 100 mL. Afterwards, the diluted solution was analyzed by ICP-OES. In order to understand the leaching behavior of the conversion product, the phases and morphologies were characterized by XRD and scanning electron microscopy (SEM) on a JEOL JSM−5600 scanning electron microscope (JEOL Ltd., Tokyo, Japan). The extraction efficiencies of cobalt, iron, copper, and molybdenum (x) were calculated as follows:

$$x=(Vc)/(mw) \tag{1}$$

where c is the concentration of cobalt, iron, copper, and molybdenum in the leaching solution (g/L), respectively; V is the volume of the leaching solution (L); m is the mass of the added cobalt-bearing ternary sulfide (g); w is the mass fraction of cobalt, iron, copper, and molybdenum in cobalt-bearing ternary sulfide, respectively.

3 Results and discussion

3.1 Leaching behavior of cobalt-bearing ternary sulfide under atmospheric pressure

The phase compositions of cobalt-bearing ternary sulfide were characterized by XRD. The results are shown in Fig. 2. The main phase of the cobalt-bearing ternary sulfide was $M_xMo_6S_8$ (M=Co, Fe, Cu; x=0−4). By comparing Figs. 1(a) and 1(b), it can be deduced that a complete phase conversion of cobalt-bearing compound took place, and the inert structure of cobalt white alloy was no longer maintained. The chemical compositions of cobalt-bearing ternary sulfide are shown in Table 1.

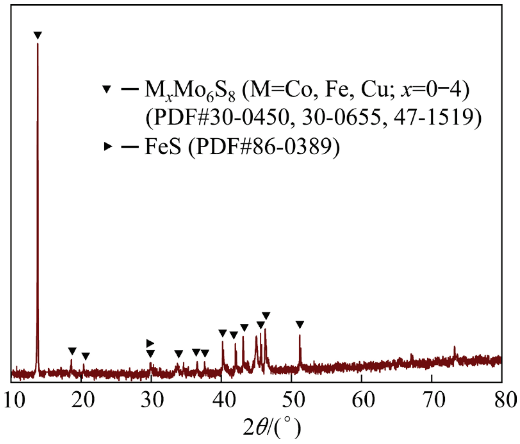

Fig. 2 XRD pattern of cobalt-bearing ternary sulfide

Table 1 Chemical compositions of cobalt-bearing ternary sulfide in different size ranges (wt.%)

Size range/μm	Mo	S	Fe	Co	Cu	Si
75−106	36.2	24.3	17.7	9.21	2.92	1.75
58−75	36.1	24.6	17.5	9.17	2.79	1.81
48−58	36.4	24.9	17.1	9.24	2.84	1.78

To study the influence of the structure conversion pretreatment on cobalt leaching, a comparison between the leaching of cobalt white alloy and cobalt-bearing ternary sulfide in sulfuric acid solution under the same condition was conducted. The obtained results are shown in Fig. 3.

It can be seen from Fig. 3(a) that the leaching efficiency of cobalt and iron increased with prolonging time, while copper was hardly leached. When the leaching time was 30 min, the leaching efficiencies of cobalt and iron rapidly increased to 19.5% and 22.3%, respectively. However, when the reaction time was prolonged to 210 min, the leaching efficiencies of cobalt and iron slowly increased to the maximum, which were only 39.4% and 42.7%, respectively. Due to the inclusion of insoluble copper and ferrosilicon, cobalt cannot be completely leached from cobalt white alloy [23]. The leaching performance of cobalt was greatly improved by using the structure conversion pretreatment. It can be observed from Fig. 3(b) that the leaching efficiencies of cobalt and iron quickly increased with prolonging time, while copper and molybdenum were not leached. When the leaching time was increased to 95 min, the leaching efficiencies of cobalt and iron were greater than 99%, which indicated that cobalt and iron were completely leached at this time.

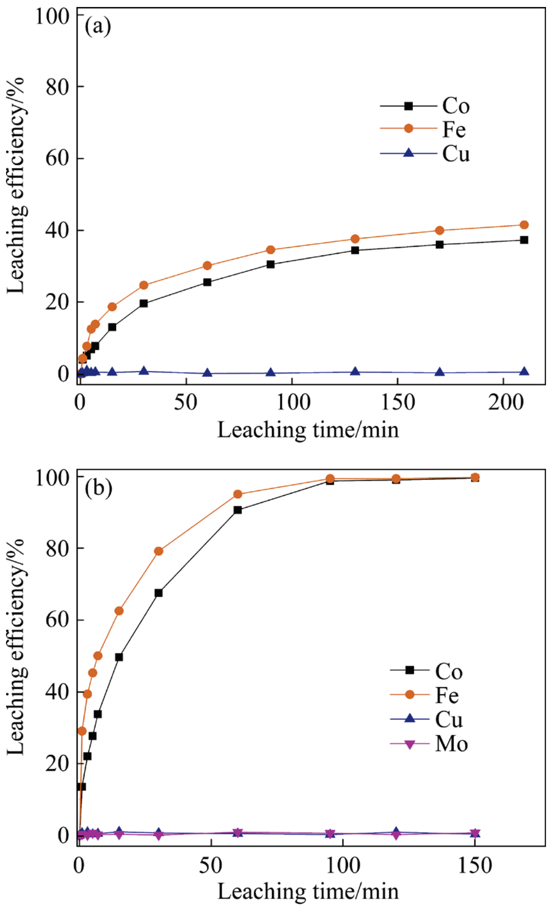

Fig. 3 Influence of time on Co and Fe leaching from cobalt white alloy (a) and cobalt-bearing ternary sulfide (b) (stirring speed 500 r/min; $c(H_2SO_4)$= 2.5 mol/L; 353 K; particle size 48−58 μm)

In general, due to the conversion of cobalt white alloy into cobalt-bearing ternary sulfide with high leaching performance, the inert structure of cobalt white alloy was broken, and the leaching efficiencies of cobalt and iron were greatly improved.

3.2 Influence of several factors on cobalt leaching efficiency

The leaching of cobalt in cobalt-bearing ternary sulfide was carried out under different conditions to explore the effects of stirring speed, temperature, sulfuric acid concentration, and particle size. In addition, the leaching mechanism of cobalt-bearing ternary sulfide was studied by analyzing the characteristics of leaching residues at different time.

3.2.1 Effect of stirring speed and leaching temperature

The influence of the stirring speed on the efficiency of cobalt leaching from cobalt-bearing ternary sulfide was studied in the range of 400−500 r/min, with a temperature of 348 K, a sulfuric acid concentration of 1.2 mol/L, a solid/liquid (S/L) ratio of 1/350, a duration of 185 min, and a particle size in the range of 58−75 μm. The stirring speed has a large influence on the liquid−solid leaching reaction when the leaching is controlled by the liquid film diffusion [24,25]. Increasing the stirring speed was conductive to the dispersion of solid particles in the leaching solution, which clearly contributed to the increase of the dissolution efficiency. Increasing the stirring speed in the range of 400−500 r/min had no effect on the leaching of cobalt as shown in Fig. 4(a). It can then be concluded that the solid particles were fully dispersed in the leaching solution homogeneously, and the thickness of the liquid film boundary of the particle remained constant. This indicated that the leaching reaction of cobalt was not affected by the liquid film around the cobalt-bearing ternary sulfide particles, which was consistent with previous studies [26]. Therefore, 450 r/min was applied in the subsequent experiments.

The leaching of cobalt was performed by varying the temperature from 328 to 358 K with a stirring speed of 450 r/min, a H_2SO_4 concentration of 1.2 mol/L, and a particle size in the range of 58−75 μm. The obtained results are shown in Fig. 4(b). It can be seen that the reaction temperature had a significant effect on the leaching of cobalt. By increasing the temperature from 328 to 358 K for 150 min, the leaching efficiency increased from 62.1% to 99.6%. Increasing the temperature could reduce the viscosity of the leaching solution and increase the mass transfer, which was conductive to the increase of the diffusion rate [27]. The higher the leaching temperature is, the faster the diffusion rate is.

3.2.2 Effect of H_2SO_4 concentration and particle size

The leaching of cobalt was studied by varying the H_2SO_4 concentration in the range of 0.4−2.0 mol/L while the other parameters were fixed as follows: stirring speed of 450 r/min, temperature of 348 K, and particle size in the range of 58−75 μm. The obtained results are shown in Fig. 5(a). After leaching for 150 min, when the H_2SO_4 concentration increased from 0.4 to 1.6 mol/L, the efficiency increased from 85.5% to 99.7%. This indicated that increasing the H_2SO_4 concentration increased the leaching efficiency within this concentration range. By further increasing the H_2SO_4 concentration, the leaching efficiency of cobalt was not significantly improved. According to the previous study [28], the leaching of cobalt-bearing ternary sulfide ($M_xMo_6S_8$) is a consuming acid reaction. Therefore, it is conductive to leach cobalt from the conversion product by appropriately increasing the initial H_2SO_4 concentration.

The particle size is also an important factor in the cobalt leaching process. Three particle sizes (75−106, 58−75, and 48−58 μm) were considered in the experiments that were conducted in sulfuric acid solution at a concentration of 1.2 mol/L, while the other parameters remained unchanged. The leaching efficiency of cobalt at different particle sizes is shown in Fig. 5(b). It can be observed that, when the particle size decreased from 75−106 to 48−58 μm at 155 min, the leaching efficiency of

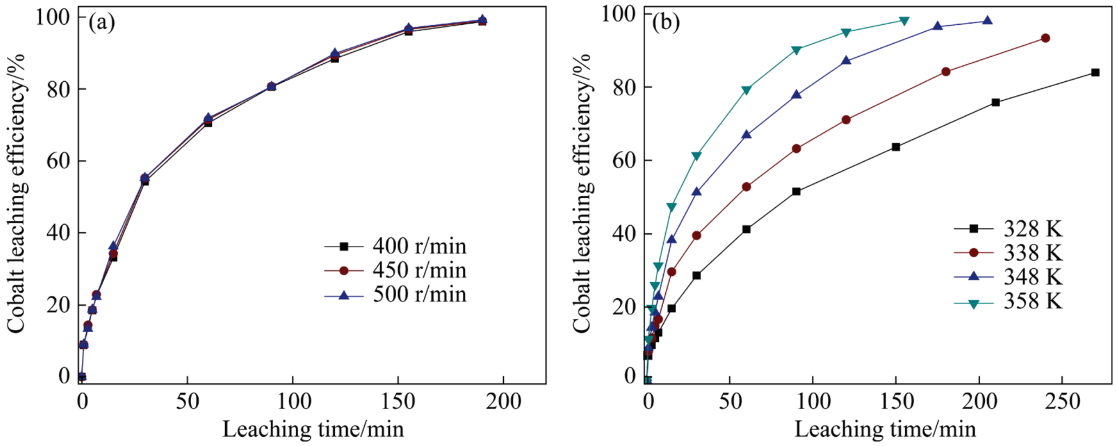

Fig. 4 Influence of stirring speed (a) and leaching temperature (b) on leaching efficiency of cobalt

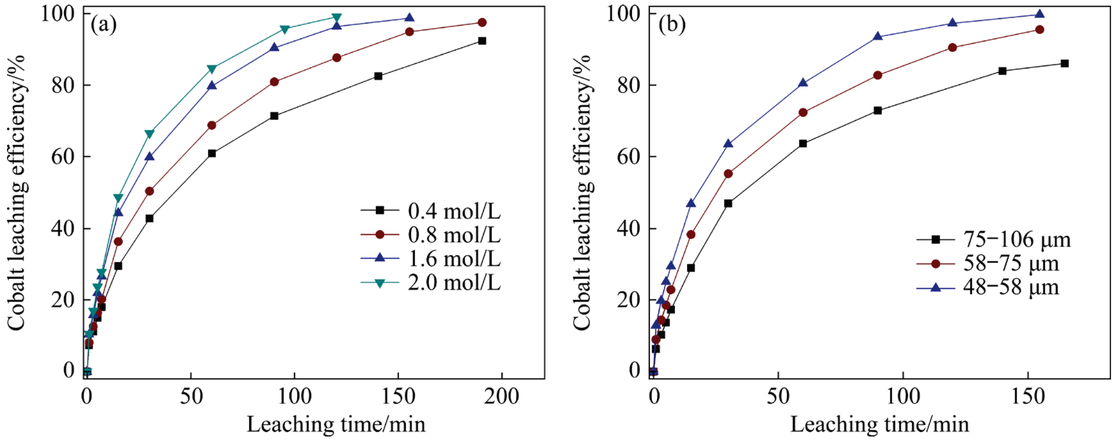

Fig. 5 Influence of H_2SO_4 concentration (a) and particle size (b) on leaching efficiency of cobalt

cobalt increased from 87.4% to 99.5%. According to this result, the leaching efficiency of cobalt was higher at smaller particle size. Reducing the particle size can significantly increase the surface area, which may improve the contact between the active site of the particle and the leaching agent. In addition, when the particle size decreased, the internal diffusion resistance also decreased, which was conductive to speed up the leaching rate of cobalt.

The impact of several factors on the leaching of iron was also studied. The results are shown in Fig. 6. The experimental conditions applied in the leaching process were similar to those of the cobalt leaching. It can be seen that the leaching behavior of iron was similar to that of cobalt. After leaching, cobalt and iron were selectively leached into sulfuric acid solution, while molybdenum, sulfur, and copper were maintained in leaching residue.

3.3 Characterization of leaching residues

The leaching residues obtained at different leaching time were identified by XRD. The results are presented in Fig. 7. When the leaching time increased from 15 to 90 min, the peaks of $M_xMo_6S_8$ gradually disappeared, while new peaks of Mo_3S_4 and $Cu_{0.5}Mo_3S_4$ (Mo_6S_8 is the three-dimensional stack of Mo_3S_4) were detected. As the leaching reaction further continued, the diffraction intensities of Mo_3S_4 and $Cu_{0.5}Mo_3S_4$ increased. At 150 min, only Mo_3S_4 and $Cu_{0.5}Mo_3S_4$ were detected in the residue, which indicated that the leaching reaction was already completed. It can be clearly deduced that the $M_xMo_6S_8$ phase was gradually decomposed with the increase of the reaction time, which was consistent with previous studies, indicating that cobalt and iron were easily dissolved from the cobalt-bearing ternary sulfide in acidic solution [29].

To further investigate the microstructure transformation in the leaching process, the residues obtained at different time were identified by SEM. The results are shown in Fig. 8. It can be seen that the particle size did not significantly change with the increase of the reaction time, which was due to

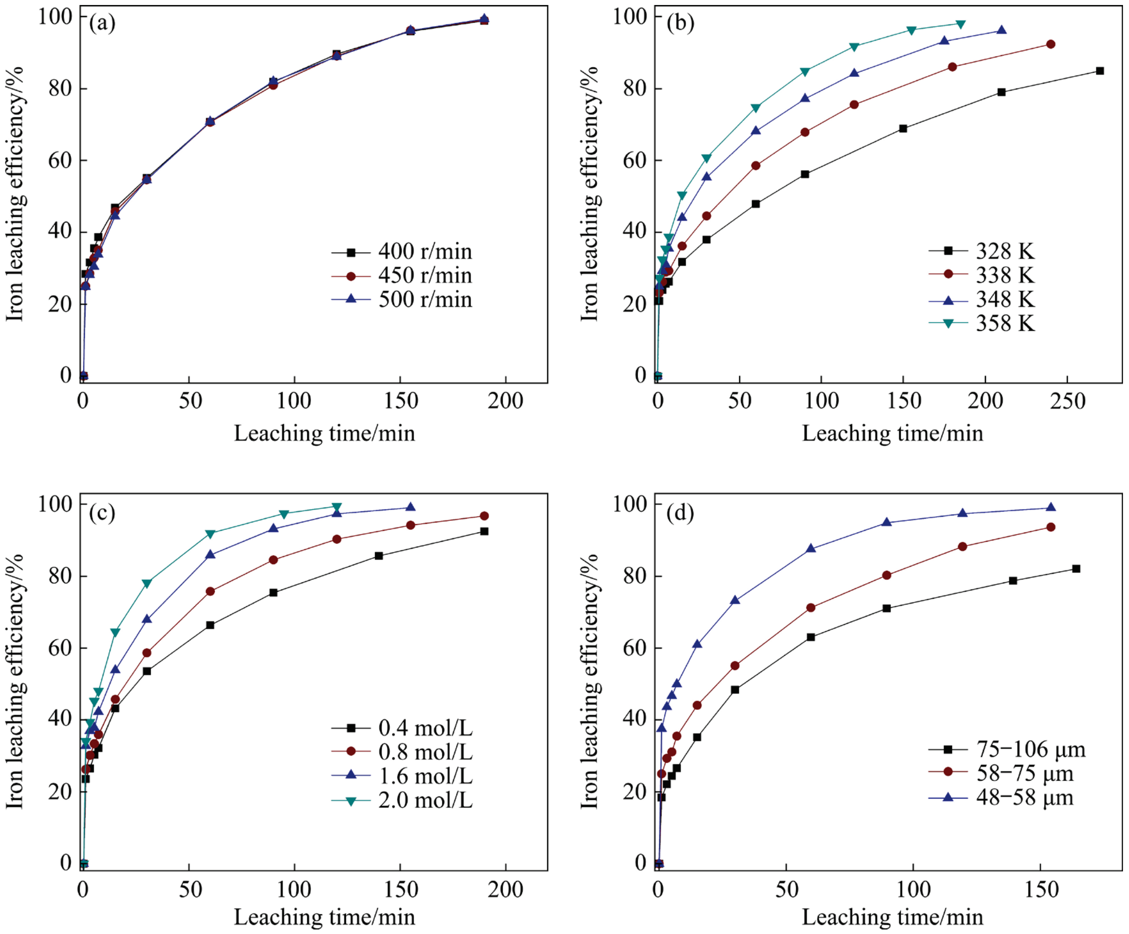

Fig. 6 Influence of stirring speed (a), leaching temperature (b), H_2SO_4 concentration (c) and particle size (d) on leaching efficiency of iron

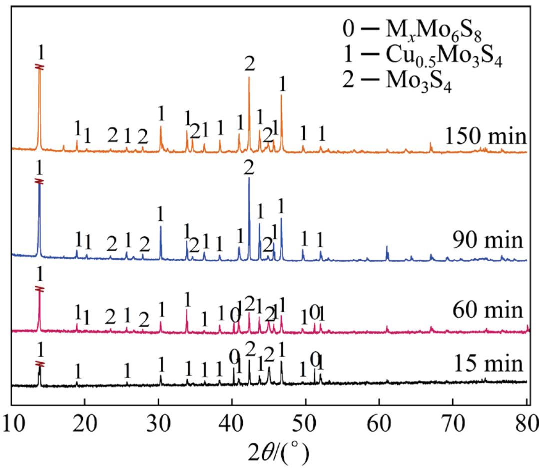

Fig. 7 XRD patterns of leaching residues obtained at different time intervals (stirring speed of 450 r/min, leaching temperature of 348 K, H_2SO_4 concentration of 1.2 mol/L, and particle size of 58−75 μm)

the unreacted particle wrapped by the reaction product. This indicated that the leaching agent only passing through the thicker solid production layer to reach the reaction interface could participate in the leaching reaction. Therefore, the internal diffusion had a significant impact on the leaching of cobalt. When the reaction time was greater than 90 min, many cracks were found on the surface of particles, which may be conductive to the internal mass transfer of the leaching agent, so as to promote the leaching reaction.

In addition, the element contents on the surface of the leaching residue particles, obtained at different time intervals, were obtained by EDS (Table 2). With the extension of the leaching time, the contents of cobalt and iron rapidly decreased, while those of molybdenum, sulfur, and copper gradually increased. After leaching for 150 min, the contents of molybdenum, sulfur, and copper were respectively 62.2%, 27.9%, and 4.65% while those of cobalt and iron were less than 1%, which indicated that the leaching of cobalt and iron was completed.

After leaching, the slurry was filtered to obtain the leaching solution and residue. Cobalt can be extracted by solvent extraction from the leaching solution after removing iron. The residue (Mo_3S_4 and $Cu_{0.5}Mo_3S_4$) can be used to recover molybdenum, copper, and sulfur. In addition, compared with molybdenite, molybdenum in the leaching residue was enriched, and its leaching performance was greatly improved by converting it into ternary sulfide [22,30,31], which was conducive to the subsequent extraction process of molybdenum.

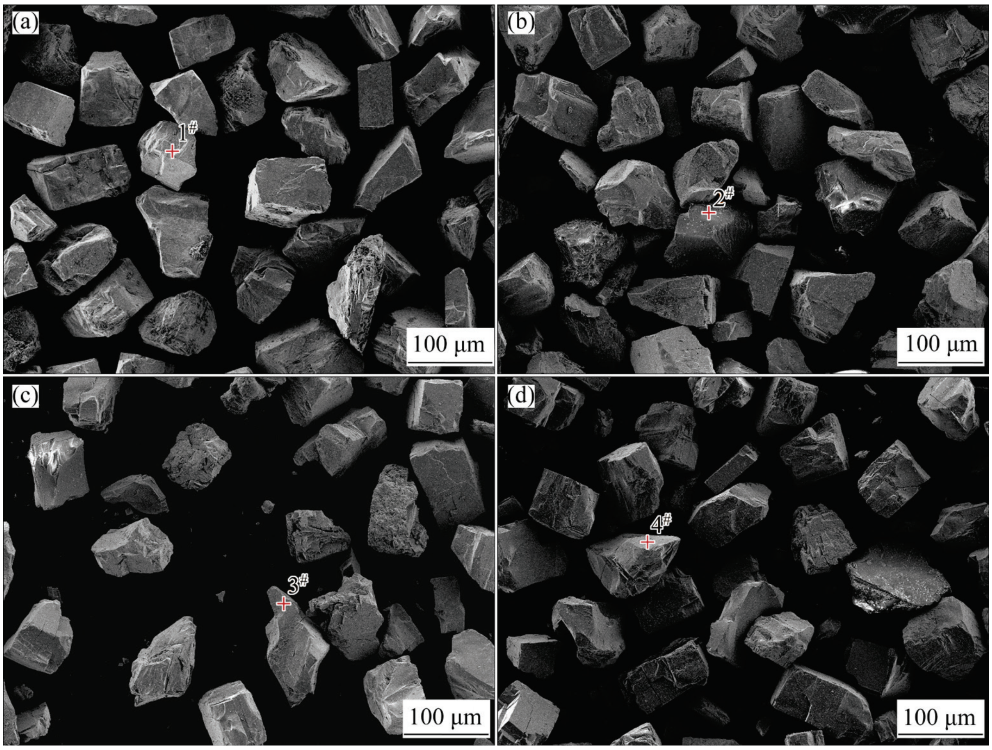

Fig. 8 SEM images and EDS analysis spots of leaching residues at different time: (a) 15 min; (b) 60 min; (c) 90 min; (d) 150 min

Table 2 Chemical compositions of selected particles shown in Fig. 8 (wt.%)

Spot No.	Mo	S	Cu	Fe	Co	Others
1#	48.3	21.6	3.84	14.6	7.97	3.69
2#	51.7	23.9	4.32	7.74	5.39	6.95
3#	56.7	25.8	4.42	3.84	3.61	5.63
4#	62.2	27.9	4.65	0.67	0.05	4.53

3.4 Kinetics of cobalt leaching

The selective leaching of cobalt from cobalt-bearing ternary sulfide in sulfuric acid solution was a solid−liquid heterogeneous reaction. The cobalt-bearing ternary sulfide used in the leaching process had a particle size of <75 μm, which can be considered a ball. The size of the particles remained unchanged during the leaching process (Fig. 8) owing to the production of the dense product layer surrounding the surface of the unreacted core. Therefore, the leaching process conforms to the shrinking core model with a solid product layer.

According to previous studies [32−34], the leaching of the solid particle mainly comprised external diffusion, internal diffusion and chemical reaction. The curves of the cobalt leaching remained unchanged with increasing stirring speed (Fig. 4(a)), indicating that the external diffusion reached equilibrium and could not control the cobalt leaching. Therefore, the leaching of cobalt is controlled by chemical reaction and internal diffusion, which are expressed in Eqs. (2) and (3), respectively [35−38].

$$1-(1-x)^{1/3}=k_a t \tag{2}$$

$$1-3(1-x)^{2/3}+2(1-x)=kt \tag{3}$$

where x is the leaching efficiency of cobalt; k_a and k are the apparent reaction rate constant of different control models (s^{-1}); t is the leaching time (s).

To determine the controlled steps for the cobalt leaching, the data shown in Fig. 4(b) were plotted based on Eqs. (2) and (3), and the results are shown in Fig. 9. The data were not linear with the chemical reaction control model (Fig. 9(a)), while they were linear with the internal diffusion control model (Fig. 9(b)). The leaching of cobalt from ternary sulfide ($M_xMo_6S_8$) was controlled by the internal diffusion, which was different from the direct leaching of cobalt white alloy controlled by a chemical reaction in traditional hydrometallurgical process [39]. Owing to its conversion into cobalt-bearing ternary sulfide with high leaching performance, the inert structure of cobalt white alloy was broken, and its leaching was no longer controlled by the chemical reaction.

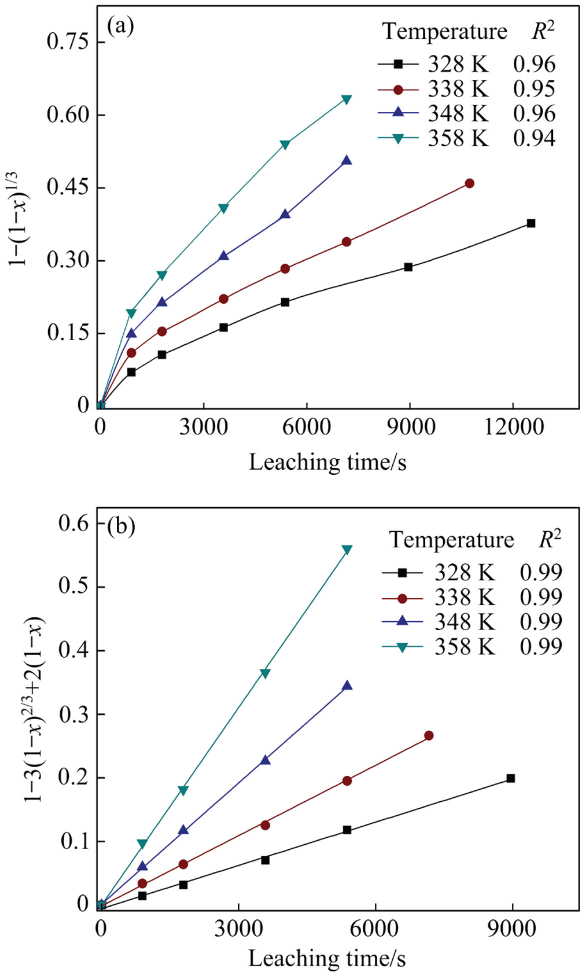

Fig. 9 Linear relationship between $1-(1-x)^{1/3}$ (a) and $1-3(1-x)^{2/3}+2(1-x)$ (b) versus reaction time for leaching of cobalt from cobalt-bearing ternary sulfide at different temperatures

The apparent rate constants (k) at different temperatures (T) obtained from the slope lines (Fig. 9(b)) are shown in Table 3. The apparent activation energy (E_a) was determined by substituting k and T into the Arrhenius equation (Eq. (4)). The result is shown in Fig. 10. The calculated E_a was 49.86 kJ/mol. This was consistent with the value in previous studies that the apparent activation energies were in the range of 34−90 kJ/mol [40].

$$k=A\exp[-E_a/(RT)] \tag{4}$$

where A is the pre-exponential factor, and R is the molar gas constant.

Table 3 Apparent rate constants at different temperatures

Temperature/K	$k/10^{-5}\ \mathrm{s}^{-1}$
328	2.25
338	3.67
348	6.33
358	10.31

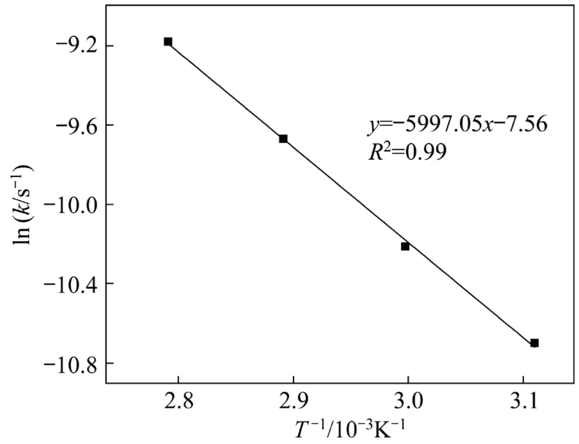

Fig. 10 Arrhenius plot of ln k versus $1/T$

The results of the leaching experiments (Fig. 5) showed that the H_2SO_4 concentration and particle size significantly affected the leaching rate of cobalt, and the Arrhenius equation could also be expanded (Eq. (5)). The cobalt leaching kinetic equation is expressed in Eq. (6) by substituting Eq. (5) into Eq. (3).

$$k=A_0 c_0^a r_0^b \exp(-5997.05/T) \tag{5}$$

$$1-3(1-x)^{2/3}+2(1-x)=A_0 c_0^a r_0^b \exp(-5997.05/T)\cdot t \tag{6}$$

where A_0 is the pre-exponential factor; c_0 is the initial H_2SO_4 concentration; r_0 is the radius of cobalt-bearing ternary sulfide; a and b are the influence indexes of initial H_2SO_4 concentration and radius of cobalt-bearing ternary sulfide, respectively.

The plots of $1-3(1-x)^{2/3}+2(1-x)$ versus the leaching time at different H_2SO_4 concentrations obtained from Fig. 5(a) are shown in Fig. 11(a). The k values obtained from the slopes are shown in Table 4. The k values increased with increasing H_2SO_4 concentrations, indicating that the cobalt leaching was controlled by internal diffusion. The influence index (a) of the initial H_2SO_4 concentration was determined from the slope of the ln k versus ln c straight line (0.57), as shown in Fig. 11(b).

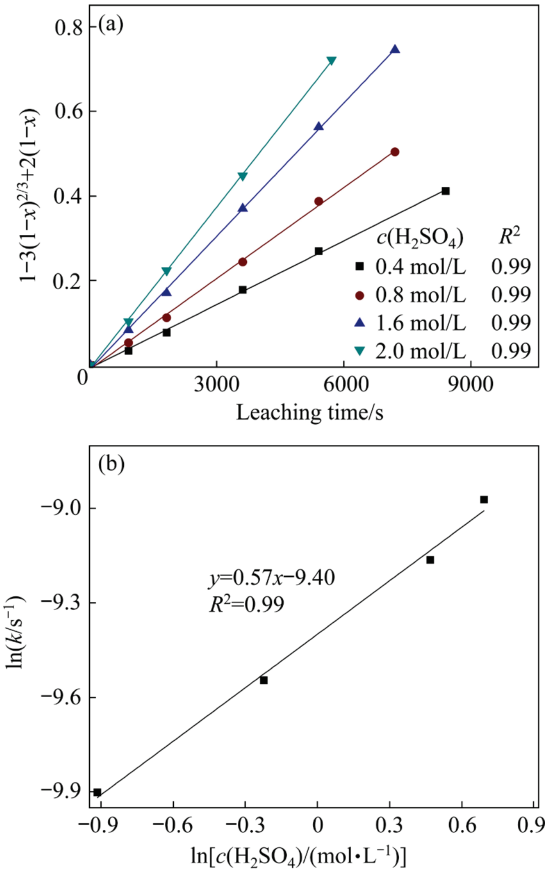

Fig. 11 Plots of $1-3(1-x)^{2/3}+2(1-x)$ versus leaching time for leaching of cobalt in H_2SO_4 solution at different concentrations (a), and relationship between ln k and ln $c(H_2SO_4)$ (b)

Table 4 Apparent rate constants at different H_2SO_4 concentrations

$c(H_2SO_4)/(\mathrm{mol\cdot L^{-1}})$	$k/10^{-5}\ \mathrm{s}^{-1}$
0.4	5.00
0.8	7.15
1.6	10.48
2.0	12.70

The k values, for the leaching of cobalt determined from the slopes of the linear relationships, increased with decreasing the particle size of cobalt-bearing ternary sulfide (Fig. 12(a)). The slope values (k) are shown in Table 5. The plot of ln k versus ln r_0 showed a linear relationship with a slope of −1.40 and a correlation coefficient of 0.99 (Fig. 12(b)). The linear relationship between the rate constant and the inverse particle size also indicated that the cobalt leaching was controlled by the internal diffusion, and the influence index (b) of the particle size was −1.40.

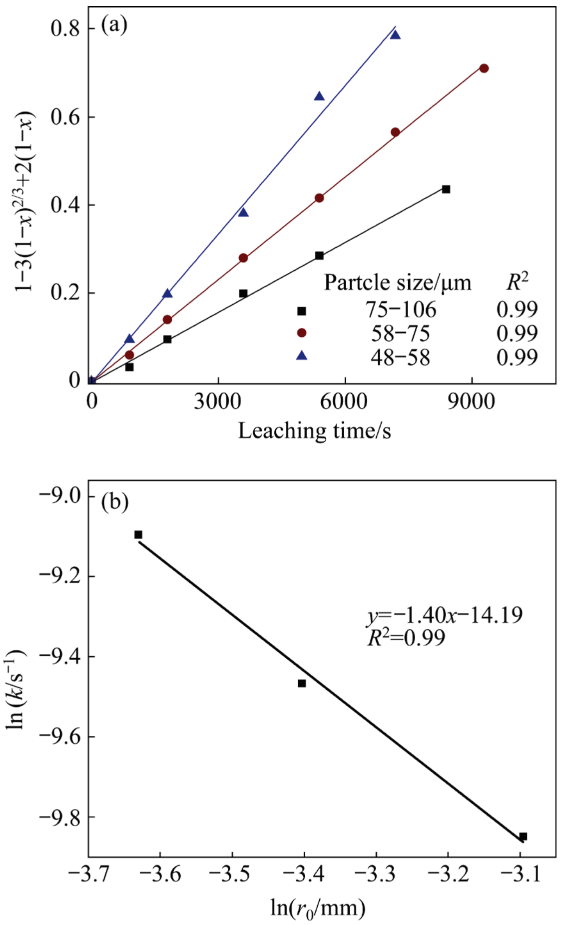

Fig. 12 Linear relationship between $1-3(1-x)^{2/3}+2(1-x)$ and leaching time for leaching of cobalt from cobalt-bearing ternary sulfide with different particle sizes (a), and relationship between ln k and ln r_0 (b)

Table 5 Apparent rate constant (k) versus particle size

r_0/mm	k/10^{-5} s^{-1}
0.04525	5.28
0.03325	7.74
0.02575	11.22

To derive the general kinetic equation, the leaching data of cobalt obtained under different conditions such as the reaction temperature, sulfuric acid concentration, and solid particle size were substituted into Eq. (6). The plot of $1-3(1-x)^{2/3}+2(1-x)$ versus $A_0 c_0^{0.57} r_0^{-1.40}\exp(-5997.05/T)\cdot t$ showed a linear relationship for all leaching data with a correlation coefficient of 0.98 (Fig. 13). This demonstrated that the general kinetic equation and kinetic parameters were reliable. The pre-exponential factor (A_0) of the general kinetic equation obtained from the linear slope was 18.05. The kinetic equation of the leaching of cobalt from the cobalt-bearing ternary sulfide in sulfuric acid solution can be expressed as follows:

$$1-3(1-x)^{2/3}+2(1-x)=18.05c_0^{0.57}r_0^{-1.40}\exp(-5997.05/T)\cdot t \tag{7}$$

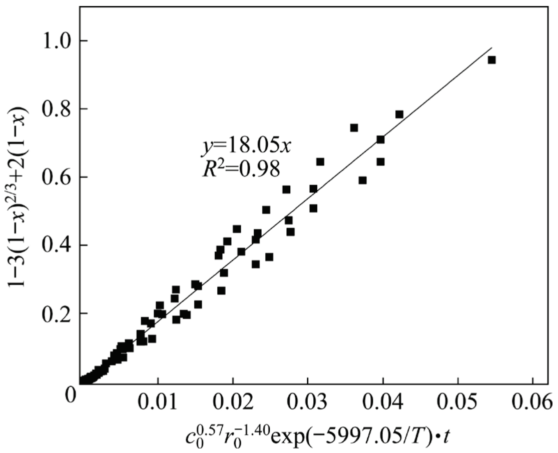

Fig. 13 Relationship between $1-3(1-x)^{2/3}+2(1-x)$ and $c_0^{0.57} r_0^{-1.40}\exp(-5997.05/T)\cdot t$

4 Conclusions

(1) The leaching kinetics of cobalt-bearing ternary sulfide was investigated in sulfuric acid solution under atmospheric pressure. The results showed that cobalt and iron were selectively leached, and the leaching efficiencies increased with increasing reaction temperature and sulfuric acid concentration but decreased with increasing particle size.

(2) Under optimal conditions, the leaching efficiencies of cobalt and iron were greater than 99%. Analysis of the leaching residues via XRD and SEM−EDS demonstrated that solid product layers (Mo_3S_4, $Cu_{0.5}Mo_3S_4$) were formed during the leaching process.

(3) According to the leaching kinetics analysis, the leaching of cobalt conformed to the shrinking core model and was controlled by internal diffusion. The apparent activation energy was 49.86 kJ/mol. The reaction orders of sulfuric acid and particle size were 0.57 and −1.40, respectively. Finally, the kinetic equation was obtained.

CRediT authorship contribution statement

Ding-chuan ZHANG: Conceptualization, Methodology, Formal analysis, Investigation, Visualization, Writing − Original draft; **Feng-long SUN:** Data curation, Writing − Original draft; **Zhong-wei ZHAO:**

Conceptualization, Funding acquisition, Writing − Review & editing, Resources, Supervision; **Xu-heng LIU:** Data curation, Supervision; **Xing-yu CHEN:** Writing − Review & editing; **Jiang-tao LI:** Software, Validation; **Li-hua HE:** Project administration.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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含钴三元硫化物常压硫酸浸出钴的动力学研究

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摘 要：开展含钴三元硫化物常压硫酸浸出的实验研究。考察搅拌速度、浸出温度、硫酸浓度和粒度对钴浸出率的影响，并分析从含钴三元硫化物中浸出钴的动力学。结果表明，在最佳条件下，钴和铁被选择性浸出，且浸出率均大于 99%，而钼和铜则富集于浸出渣。通过对实验数据的分析可知，钴的浸出符合由固体产物层产生的收缩核模型，且浸出过程受内扩散控制。浸出反应的活化能为 49.86 kJ/mol，硫酸浓度和粒度的反应级数分别为 0.57 和−1.4。

关键词：钴白合金；含钴三元硫化物；钴；硫酸；浸出动力学

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