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ORIGINAL ARTICLE

Recycling of Ni from leached spent catalyst residue by H_2SO_4 leaching and solvent extraction: leaching kinetics, purification and product preparation

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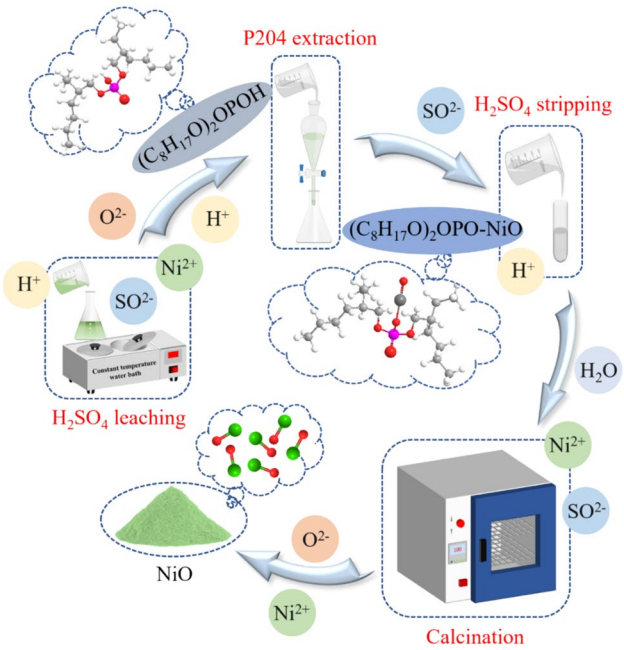
Abstract

Spent hydrodesulfurization catalyst (HDS) is considered as the important secondary resource for Mo and Ni. The separation of Mo from HDS was usually conducted by soda roasting and water leaching, while Ni remained in the leached residue. This study proposed a method to recover Ni from leached residue by H_2SO_4 leaching and solvent extraction, and Ni was recycled in the form of NiO. The results showed that the optimum Ni leaching process were conducted using 30% H_2SO_4 with liquid–solid ratio of 10 at 70 ℃ for 120 min. The optimal extraction was accomplished using 30% di-(2-ethylhexyl) phosphate (P204) saponification at pH value 6.0 with organic/aqueous (O/A ratio) of 1 for 1 min. Additionally, 20% H_2SO_4 could be used to strip Ni from organic phase with O/A ratio of 10. Finally, $NiSO_4$ was calcined at 850 ℃ for 1.0 h to obtain NiO. The Ni leaching kinetic analysis showed that the activation energy of Ni leaching process was 16.10 kJ/mol, which was accorded with the shrinkage unreacted kernel model controlled by internal diffusion. This study provided an alternative method to recycle Ni and given a deeper insight to the leaching mechanism during H_2SO_4 leaching Ni from spent catalyst.

Graphical abstract



Keywords Spent hydrodesulfurization catalyst · Kinetic · H_2SO_4 leaching · Nickel sulfate · Internal diffusion

Extended author information available on the last page of the article

Introduction

Hydrodesulfurization (HDS) catalysts were widely used in the production and processing of petrochemical products [1]. HDS catalysts would be permanently deactivated after long-term use due to thermal aging, heavy metal poisoning and other reasons [2–5]. Environmental Protection Agency in most countries usually listed spent catalysts as hazardous waste, because the random placement and simple treatment of these spent HDS catalysts would bring fatal hazard to the water and soil environment [6, 7]. However, spent HDS catalysts were also valuable secondary resource and contained 10–30% of molybdenum (Mo) and 2–5% of nickel (Ni) with high industrial recycling value [8, 9]. The global resource consumption of Mo and Ni were 0.0254 and 2.4105 million tons in 2019, and the consumption amount continued to increase every year [7]. Therefore, the recovery of Ni, Mo from the spent HDS catalyst had considerable economic and environmental benefits due to the lack of raw ore resources.

There were many research works focused on recovery of valuable metals from spent HDS catalysts. Pyrometallurgy had higher recovery efficiency and little environmental pollution. The spent catalyst was calcinated and smelted reductively at 1800–2400 ℃, and then 99% metal was recovered in the form of alloys [7]. However, the energy consumption and equipment costs of pyrometallurgy method were expensive due to the high temperature [10]. Hydrometallurgy had low treatment cost, simple process flow and low requirements for equipment [11]. Shen et al. leached 89% Mo and 65.7% Ni with 0.1 M citric acid solution [12]. Ni was not leached but remained in the solid leaching residue after soda roasting and water or strong alkali leaching, which resulted in the waste of Ni resources [13]. Gao et al. used soda roasting and water leaching to separated Mo and Ni from spent catalyst, and Ni was leached from the solid residue [14]. Wang et al. used NaOH solution to leach spent catalyst after blank calcination, while NiO was insoluble in strong alkaline solutions and remained in the leaching residue [15]. Therefore, more efforts should be paid to improving Ni leaching efficiency with low cost.

At present, the main method to recover Ni from spent hydrogenation catalyst is hydrometallurgy. Rachit Oza et al. used ultrasonic-assisted leaching to extract 95% Ni from spent Ni-Al_2O_3 catalyst within 50 min at 90 ℃, 40% HNO_3 concentration and solid–liquid ratio of 10. P.K [16]. Parhi et al. leached the spent catalyst at 323 K for 2 h with 1 M HCl, and Ni was selectively leached from the spent catalyst [17]. However, it was not efficient to use HCl and HNO_3 as leaching solvents to recover Ni from spent catalysts. To leach Ni with lower costs and high efficiency, H_2SO_4 directly leaching was the optimal choice to recover Ni because the operation process was more economical, which could avoid exhaust gas generation [18]. When Ni was transferred from the solid phase to the liquid phase, high efficiently recovering Ni from the leaching solution also needed to be considered. Liu et al. adopted $H_2C_2O_4$ and H_2O_2 leaching-chemical precipitation process to recover valuable metals and transformed Ni to NiC_2O_4 precipitate [19]. Cai et al. employed Na_2S precipitation agent to convert Ni^+ into Ni(OH)S precipitate to recover metal Ni [20]. However, the traditional chemical precipitation method produced a large amount of acid and alkali waste liquid, and the purity of the product was not high. To selectively separate Mo and Ni, solvent extraction was a better choice to separate metals selectively. Solvent extraction was highly selective and efficient for the extraction of metals from leaching solution, and the purity of the obtained product was higher than that of the traditional chemical precipitation method. To selectively separate Mo and Ni, solvent extraction was a better choice to separate metals selectively, because it was highly selective and efficient for the extraction of metals from leach solution [18]. In conclusion, H_2SO_4 leaching-solvent extraction was the best method to recover Ni from leaching residue temporarily.

The study reported a reliable method to high-efficiency recovery of Ni from spent HDS catalyst with H_2SO_4 leaching and P204 extraction. The leaching process of Ni from spent catalyst was studied, and influence factors, including H_2SO_4 volume, liquid–solid ratio, temperature and time, were determined. The oxidation leaching process of NiS to Ni(II) in H_2SO_4 solution was studied, including reaction mechanism, kinetics and phase transition. The solvent extraction of Ni from leaching solution with P204 was studied, and influence factors, including pH, extraction solution concentration, temperature, time and O/A, on the extraction of Ni were analyzed. This study could provide a reference method to recycling Ni from leached spent catalyst residue, and a deeper insight to the leaching mechanism during H_2SO_4 leaching Ni from spent catalyst.

Materials and methods

Materials and chemical reagents

The spent HDS catalyst was from a petroleum refinery plant in Dongying City, Shandong Province, China. The raw materials used in this experiment involved the powdered leaching residue of the spent HDS catalyst after water leaching for separating Mo. The results of XRF analysis of the leaching residue were shown in Table 1, which showed that it contained 64.624% NiO, 34.2% Al_2O_3 and trace amounts of

Table 1 Main composition of water leaching residue analyzed by XRF

Compounds	Al_2O_3	MoO_3	SO_2	P_2O_5	NiO	SiO_2	Fe_2O_3	CoO
Mass fraction (%)	34.2	0.51	0.204	0.15	64.624	0.13	0.118	0.064

Mo. H_2SO_4 solution, which was diluted with 98% concentrated H_2SO_4, was used as leaching and stripping agent in this study, and the desired pH of leachate was adjusted with NaOH solutions. The extractant of P204 [21] was used for nickel extraction. Sulfonated kerosene was used as a diluent. Aluminum standard solution and nickel standard solution were used to examine the concentration of Al and Ni. All chemical reagents were analytically pure and purchased from Sinopharm Chemical Reagent Co., Ltd.

Experimental procedures

The leaching residue whose weight was 10 g was put into a thermostatic mixer and was leached by 15–55% H_2SO_4 at 50–100 ℃ for 60–210 min with a liquid–solid ratio of 7:1–12:1. And the mixing speed of the thermostatic mixer was 300 r/min. H_2SO_4 and NaOH were used to adjust the pH value of the leaching solution to 5–6. The precipitation of $Al(OH)_3$ was produced using the difference of the precipitation interval of Ni and Al. The leaching solution after separating Al was placed in a beaker.

The extraction process was carried out by the mixture solution in a separation funnel. The used organic phase was composed of P204 and sulfonated kerosene. The organic phase and aqueous phase were put into a 1 L jacketed glass reactor with desirable ratio and then stirred for 1–5 min. H_2SO_4 and NaOH were added to adjust pH at 4.5–6. A pear-shaped funnel was used to separate the mixed phase. Ni in the organic phase was stripped with 10–35% H_2SO_4 for 1–6 min, then filtered and evaporated processes. The crystallization obtained by evaporation was recovered in the form of NiO. A schematic flow process diagram for the leaching and recovery of Ni from spent catalyst leaching residue is given in Fig. 1. Each single-factor experiment was repeated three times.

Analysis and characterization

The content of compounds in solid leaching residue was determined by X-ray fluorescence spectrometer (XRF, BrukerS8Tiger, Germany). X-ray diffraction (XRD, BrukerD-2Phaser, Germany) was used to examine the mineralogical

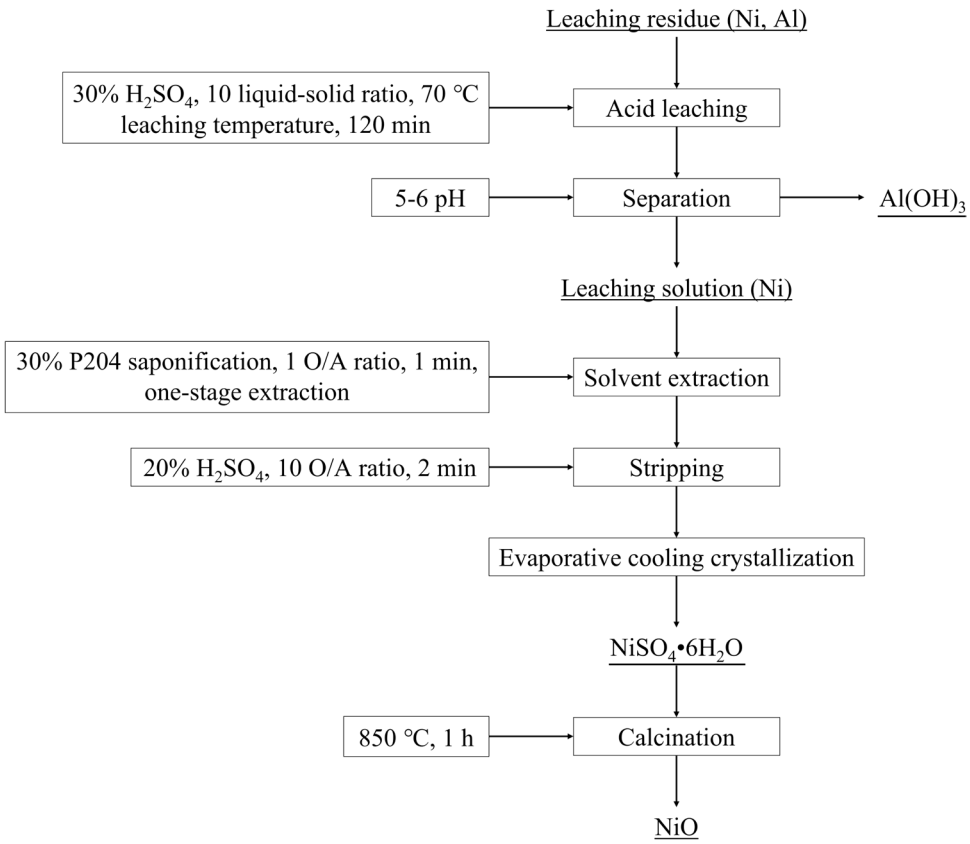


Fig. 1 A schematic flow process diagram for recovering of Ni from leached spent catalyst residue

phase of solid leaching residue. The flame atomic absorption spectrometer (AAS, novAA-300, America) was used to determine the concentration of Ni ions in solutions.

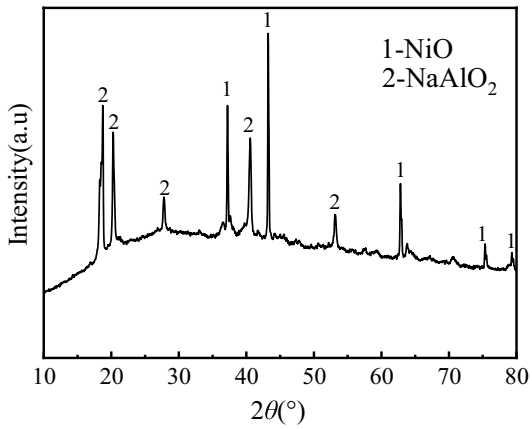


Fig. 2 XRD of leaching residue

Results and discussion

Leaching Ni and Al from leaching residue by H_2SO_4

The spent catalyst residue after separation of Mo by soda roasting and water leaching was dried and analyzed by XRD, and the results are shown in Fig. 2. XRD analysis showed that the leaching residue mainly contains NiO and $NaAlO_2$ phases.

Figure 3 shows effects of H_2SO_4 on the leaching efficiencies of Ni and Al from leaching residue. Ni and Al leaching efficiencies increased from 88.12% and 91.24% to 98.52% and 99.03% when H_2SO_4 concentration gradually increased from 15 to 30% (Fig. 3a). With the increase of sulfuric acid concentration, the active ingredients in the system increased, and the contact chance between nickel and aluminum in the leaching residue and sulfuric acid increased. The concentration of H^+ in the unit volume increased, resulting in a large concentration difference between the particles and the acid

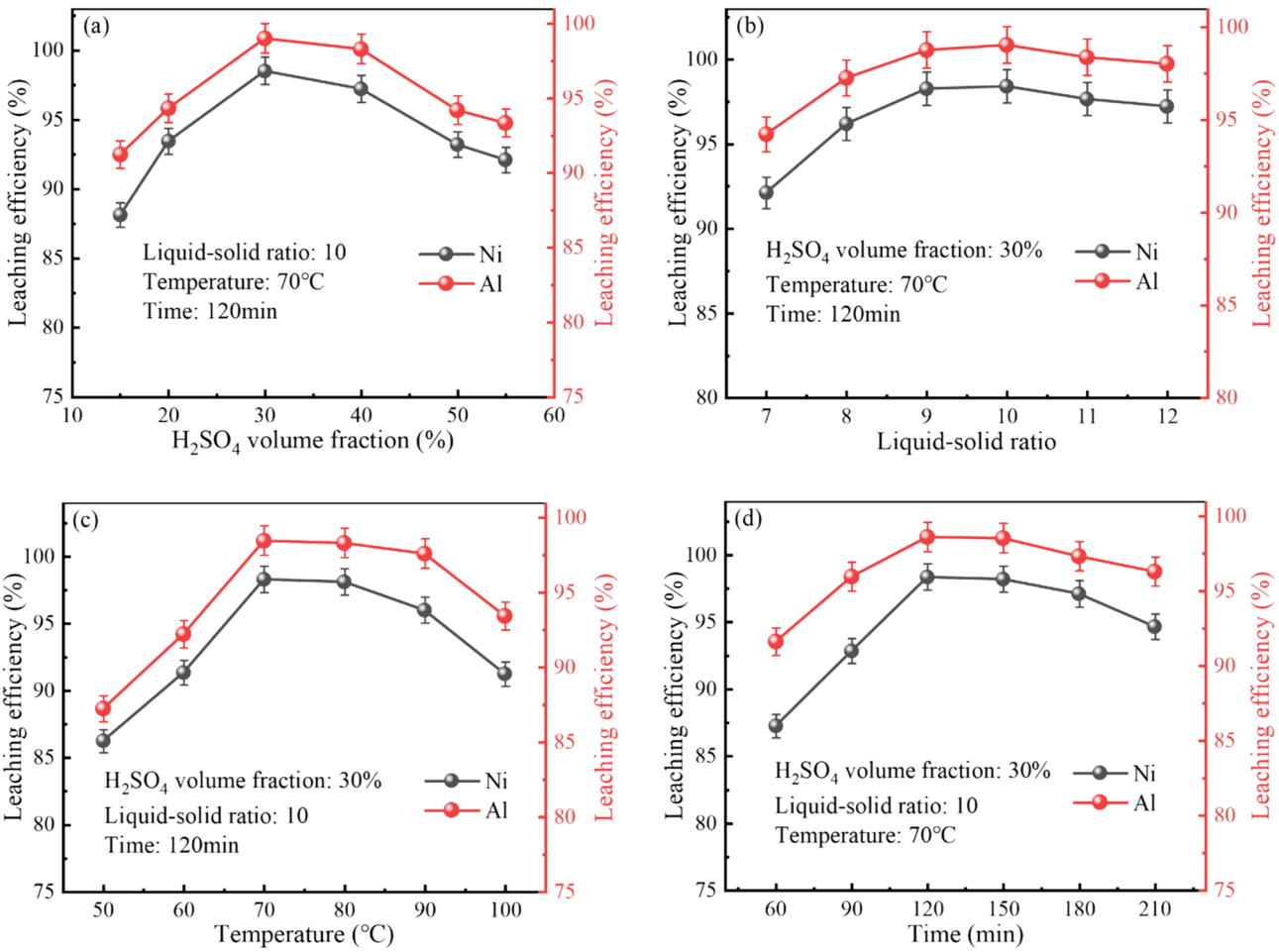


Fig. 3 Effects of **a** H_2SO_4 volume fraction, **b** liquid–solid ratio, **c** leaching temperature and **d** time on the leaching efficiencies of Ni and Al

during the reaction process, which promoted the progress of diffusion. At the same time, a large amount of H^+ broke the balance of elements in the system, which was more conducive to the leaching of nickel and aluminum. However, Ni leaching efficiency decreased to 92.10% when H_2SO_4 concentration increased to 55%. Too high concentration of sulfuric acid would increase the difficulty of subsequent waste liquid treatment, and the liquid after the leaching reaction was thicker when H_2SO_4 concentration continued to increase, which was not conducive to solid–liquid separation. Therefore, the suitable concentration of H_2SO_4 was 30% in volume fraction. The leaching efficiencies of Ni and Al were 98.42% and 99.05%, respectively when the liquid–solid ratio was 10 (Fig. 3b) because more dilute H_2SO_4 were easier to leach Ni and Al. The content of acid in the solution increased and the liquid fluidity enhanced due to the increase of liquid–solid ratio, and the leaching reaction was more adequate. However, the leaching efficiencies of Ni and Al decreased 6% slightly when the liquid–solid ratio decreased from 10 to 7. Moreover, the change of leaching efficiency was not obvious when the liquid–solid ratio was increased. Considering that the leaching reaction time was long, the liquid volatilization loss was relatively serious. Therefore, an appropriate leaching liquid–solid ratio of 10 was selected. Ni leaching time was long and the liquid volatilization was relative intense. The appropriate leaching liquid–solid ratio was 10. The leaching efficiencies of Ni and Al increased from 86.25% and 87.24% to 98.31% and 98.48% when the leaching temperature increased from 50 ℃ to 70 ℃ (Fig. 3c). The high temperature accelerated the molecular thermal movement of each substance component in the solution and improved the solid–liquid contact, which could accelerate the leaching reaction. However, the leaching efficiencies of Ni decreased to 91.25% when leaching temperature increased to 100 ℃. The reason was that H_2SO_4 was lost due to the evaporation when the temperature was too high, and it was not conducive to the leaching reaction. Therefore, 70 ℃ was set as the optimal temperature to leach Ni and Al. The leaching efficiencies of Ni and Al increased from 87.25% and 91.63% to 98.37% and 98.63% when the leaching time increased from 60 to 120 min (Fig. 3d). The leaching process of Ni in H_2SO_4 solution was relatively slow in a short time, resulting in a lower leaching efficiency of Ni. The leaching efficiency increased because of the proper extension of leaching time, which made the leaching residue dissolve more fully. However, Ni leaching efficiency decreased to 94.67% when the time increased to 210 min. Most of Ni and Al in the leached residue had been leached after a period. However, the leaching solution was exposed to the air for a long time under heating conditions, which caused evaporation of leaching solution. Additionally, Ni and Al formed a small amount of $NiAlO_2$ during the roasting process, which was insoluble in H_2SO_4. Therefore, 120 min was the optimal time for the leaching Ni and Al from the residue. Wu et al. conducted a study on sulfuric acid leaching of serpentine ore from Inner Mongolia to effectively recover valuable metals such as Ni [22]. The results showed that the optimal leaching parameters were sulfuric acid concentration of 5 mol/L, liquid–solid ratio of 4 and leaching temperature of 100 ℃. The sulfuric acid concentration was basically the same as that used in this study. The large liquid–solid ratio in this study may be due to different raw materials, and the phase of Ni was not exactly the same. In this study, the leaching temperature was lower and the leaching efficiency was higher, which saved energy consumption to a certain extent.

Ni leaching kinetic analysis

The leaching process of valuable metals from leaching reside with H_2SO_4 involved multiphase reactions between liquid and solid phases. The reaction between metals and acid solutions firstly occurred on the metal particle surface and gradually shrank to the particle center with the process of reaction, which caused the unreacted nuclei to shrink in size [23]. Therefore, it was assumed that Ni leaching process might be consistent with the shrinkage core model. The leaching process regulated by the shrinking core model was therefore controlled by liquid phase mass transfer, solid film diffusion and apparent chemical reaction or by mixing [24]. However, the influence of liquid mass transfer could be ignored under high-speed agitation. The leaching reaction rate was thus controlled by solid film diffusion, chemical reaction, or the mixture of both. The equations for the three types of reaction models were followed as equations and the corresponding apparent activation energies range from 4 to 12, 40 to 300 and 12 to 40 kJ/mol, respectively [25–27]:

Kinetics equation controlled by external diffusion:

$$a = kt. \tag{1}$$

Leaching kinetics equation controlled by chemical reaction:

$$1 - (1 - a)^{1/3} = kt. \tag{2}$$

Leaching kinetics equation controlled by internal diffusion:

$$1 - 2/3a - (1 - a)^{2/3} = kt, \tag{3}$$

where k was the kinetic constant of the leaching reaction model; a was Ni leaching efficiency; t was the leaching time, min.

Figure 4 shows the change of Ni leaching efficiency with different times. Ni leaching efficiency increased with the elevating of temperature (Fig. 4). However, the relationship between Ni leaching efficiency and time was not a one-time

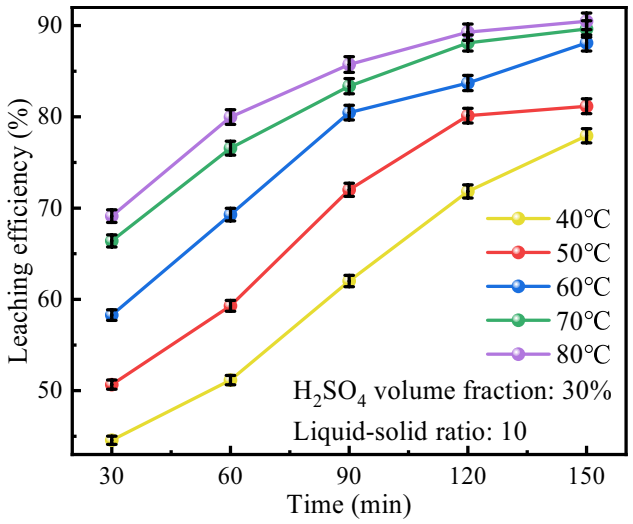


Fig. 4 Effect of leaching temperature on Ni leaching efficiency

function, which ruled out the possibility that Ni leaching was an external diffusion control model [28]. Ni leaching efficiency at different thermodynamic temperatures were substituted into the control equations of diffusion reaction and chemical reaction, respectively, and the kinetic constant k could be calculated. Then the Arrhenius equation was used to calculate the apparent activation energy of the leaching reaction and it could compare whether the result was within the corresponding range of the apparent activation energy of diffusion model. The Arrhenius equation is expressed as [29]:

$$k = A * exp\left(-E_a/RT\right), \tag{4}$$

$$\ln k = \ln A - E_a/RT, \tag{5}$$

where k was the reaction rate constant; E_a was the apparent activation energy, kJ/mol; T was the thermodynamic temperature, K; R was the ideal gas constant, 8.314 J/(mol·K); A was a pre-factor.

The slope of each fitted line in Fig. 5(a) and 6(a) was the reaction rate constant k at different temperatures. The fitting relationship between ln$k$ and 1/T at different thermodynamic temperatures were obtained by plugging the data into Eq. (1), and the results are shown in Fig. 5(b) and 6(b). Then the apparent activation energy of the leaching reaction was calculated according to the slope of the fitted curve. As can be seen from Fig. 5(b), the equation of the fitted line was $y = 1.307x + 1.5386$. It was calculated that the leaching activation energy of Ni was 10.87 kJ/mol, while the activation energy range of chemical reaction controlled was at range of 40 to 300 kJ/mol. Thus, it could rule out the possibility that the acid leaching process of Ni was a model controlled by chemical reaction. Similarly, as can be seen from Fig. 6(b), the equation of the fitted line was $y = 1.937x + 2.738$. The

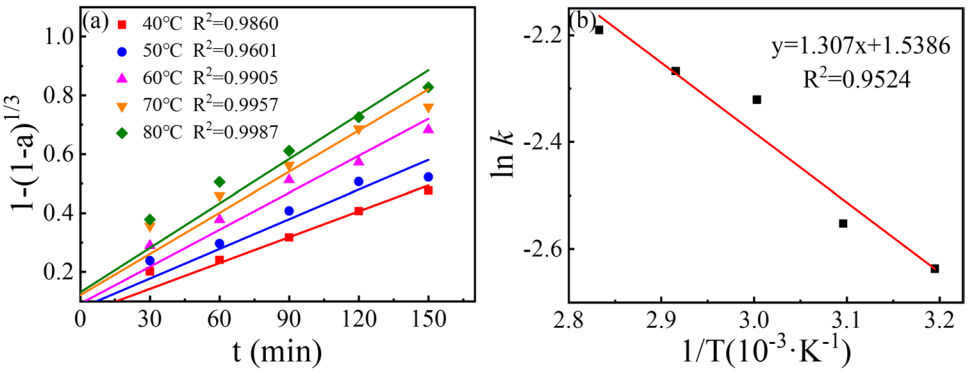


Fig. 5 **a** relationship between 1-(1-a)$^{1/3}$and t at different temperatures **b** relationship between 1-(1-a)$^{1/3}$model ln$k$ and 1000/T

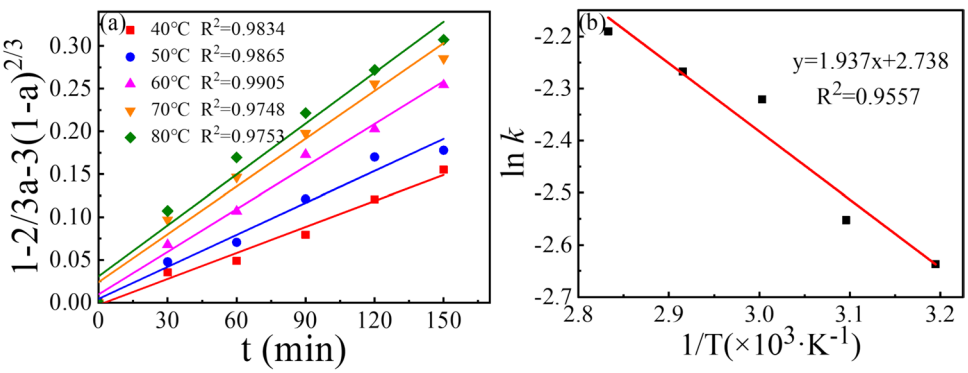


Fig. 6 **a** relationship between 1–2/3a-(1-a)$^{2/3}$ and t at different temperatures **b** relationship between ln$k$ and 1000/T ln1-2/3a-(1-a)$^{2/3}$ model

calculated leaching activation energy of Ni was 16.10 kJ/mol, which was within the range of activation energy controlled by diffusion reaction, and Ni leaching process was mainly controlled by the internal diffusion process. The contact ratio could be increased by reducing the particle size of leaching slag. At the same time, the reaction rate could be accelerated by reducing the thickness of the fixed film and shortening the leaching time.

Solvent extraction and stripping of Ni

P204 is an acid phosphine extractant, and the saponified P204 can extract Co, Ni and Mg from the solutions [30]. The mechanism of extracting metal ions by P204 belongs to the cation exchange reaction. The hydrogen on the hydroxyl group (-OH) of P204 is exchanged with the extracted metal cation. The reaction formula of extracting Ni^{2+} by P204 in H_2SO_4 solution is followed as [31]:

$$Ni^{2+} + 4HA = NiA_2\left(H_2A_2\right) + 2H^+. \quad (6)$$

It can be seen from the reaction formula (Eq. 6) that P204 will release H^+ during the extraction process, increasing the acidity of the solution. However, the reaction reaches equilibrium quickly, which poses a certain adverse effect on the extraction effect. P204 is usually saponified to avoid this adverse effect. Adding alkaline solution in acidic extractant is aimed to proton exchange, then the content of H^+ decreases to avoid premature equilibrium before complete extraction and eliminate the influence of H^+ on extraction. Figure 7 shows the molecular structure diagram of extracting Ni^{2+} by P204. The hydrogen on the –OH of P204 is exchanged with NiO.

Figure 8 shows the effects of P204 on the extraction ability of Ni from leaching solution. Ni extraction efficiency increased from 75.23% to 99.21% when the pH of the solution increased from 4.5 to 6.0 (Fig. 8a). The reduction of solution acidity was conducive to the extraction reaction. However, Ni in the solution would form $Ni(OH)_2$ precipitation as the pH of the solution continued to increase. Therefore, it was more appropriate that the pH of solution was set at 6.0 during the extraction reaction.

Ni extraction efficiency increased from 85.12% to 99.32% when the saponification rate of P204 increased from 10 to 30% (Fig. 8b). Thus, it could be seen that the extraction effect was improved when the extractant was saponified. However, the viscosity of the extraction system would become larger with the increase of saponification rate, and the fluidity of the liquid would decrease, which resulted in a long two-phase separation time after extraction. Therefore, excessive saponification rate would have adverse effects on the extraction reaction. The suitable saponification rate of P204 was 30%.

Ni extraction efficiency increased from 89.03% to 99.34% when the phase ratio increased from 0.33 to 1 (Fig. 8c). The content of Ni in aqueous phase was relatively high while the extractant content was not enough to extract Ni completely with a low O/A ratio, which resulted in a low extraction efficiency. The content of P204 extractant in the solution was high when the phase ratio lifted, and the extraction efficiency of Ni increased obviously. Thus, lifting ratio was conducive to the extraction reaction. However, Ni extraction efficiency decreased to 95.71% as the phase ratio increased to 4. The solution became viscous due to the increase of organic phase, resulting in difficult separation. Therefore, 1 was considered as the optimal O/A ratio to extract Ni.

The extraction efficiency of Ni decreased from 99.23% to 96.37% when the extraction time increased from 1 to 5 min (Fig. 8d). Therefore, the extraction process could be completed in a short time. The oil phase and aqueous phase would emulsify, resulting in the difficult phase separation after prolonging the reaction time. Therefore, it was suitable that the extraction time was kept for 1 min. The corresponding extraction efficiencies of Ni decreased slightly from 99.24% to 98.98% when the extraction stage increased from 1 to 3 (Fig. 8e). The increase of extraction stage had little effect on the extraction efficiency of Ni. Therefore, the extraction stage was selected as one-stage

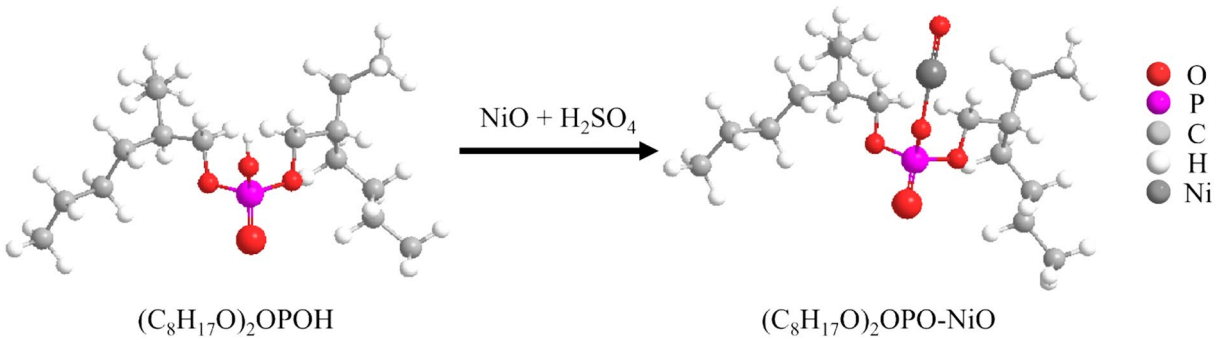


Fig. 7 Molecular structure diagram

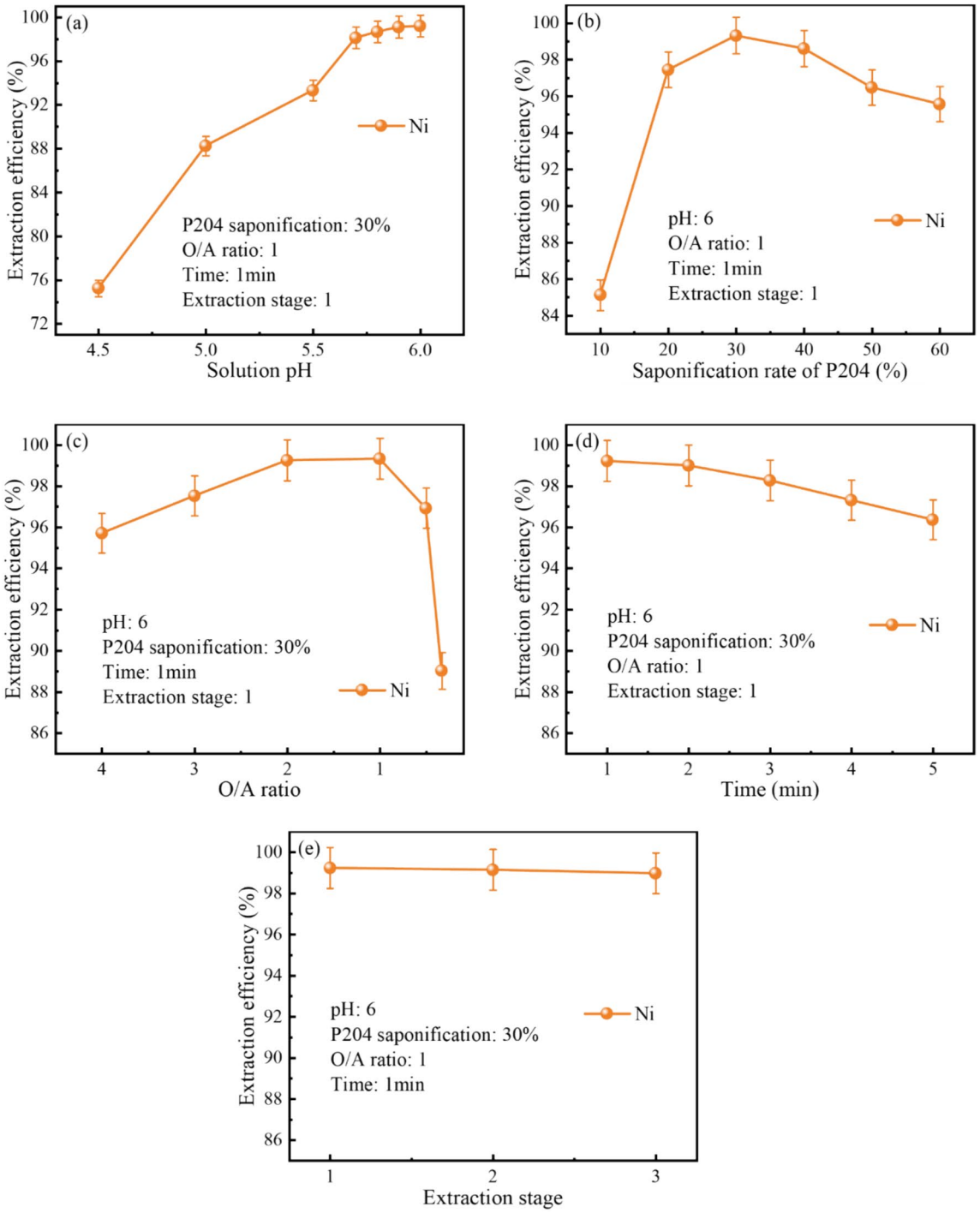


Fig. 8 Effects of **a** solution pH, **b** P204 saponification rate, **c** O/A ratio, **d** extraction time and **e** extraction stage on extraction efficiency of Ni

extraction considering the production cost comprehensively. Zhang et al. proposed a β-dione solvent extraction method to extract Co, Ni and Li from mixed solution [32]. The optimum conditions for Ni extraction were 70% saponification rate, 1:1 O/A ratio and 5 min extraction time. However, in this study, lower saponification rate and less extraction time were used to obtain a slightly higher extraction efficiency, which saved a certain cost.

Figure 9 shows the influence of H_2SO_4 concentration on Ni stripping efficiency. The effect of H_2SO_4 concentration on the stripping of Ni was studied using different concentrations at the range 10–35%. The results shown in Fig. 9a

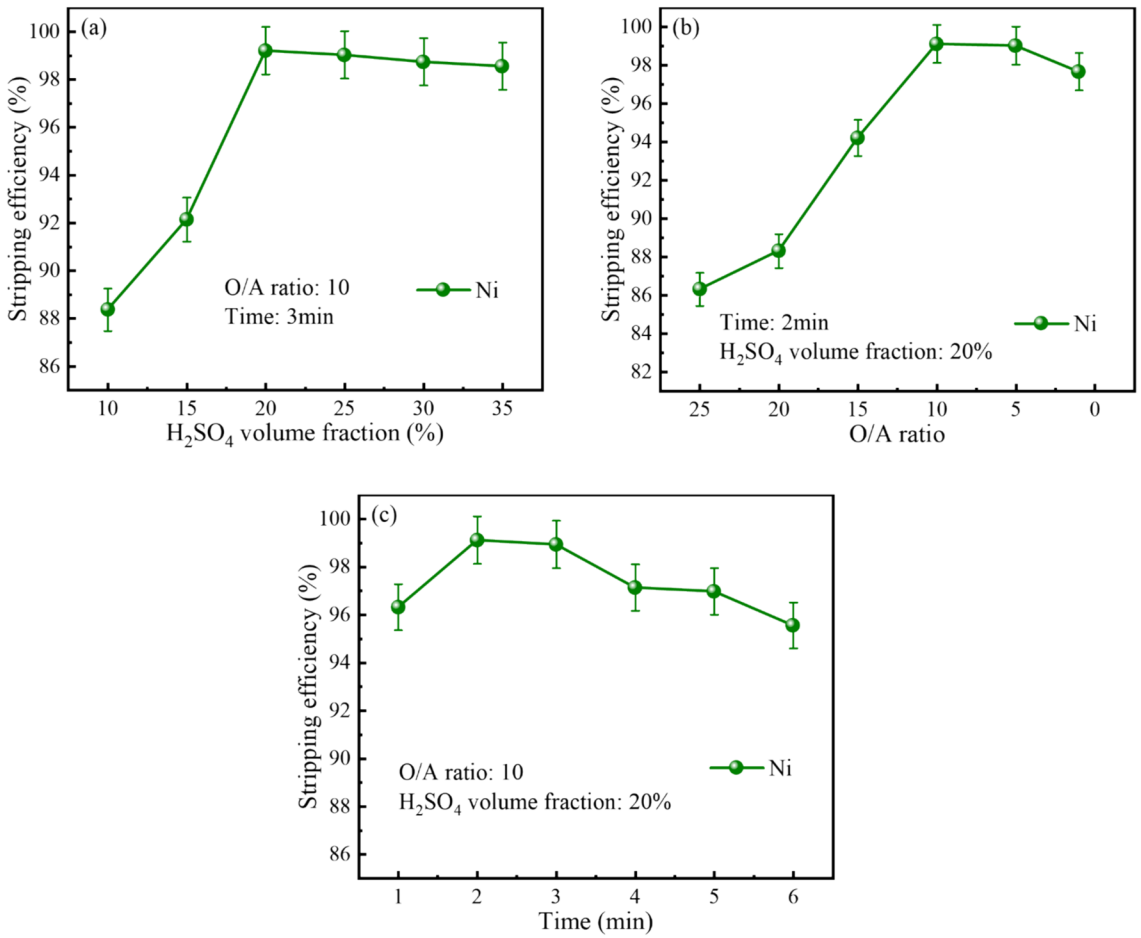


Fig. 9 Effects of **a** H_2SO_4 volume fraction, **b** O/A ratio and **c** stripping time on stripping efficiency of Ni

represent that Ni stripping efficiency increased from 88.37% to 99.21% when the concentration of dilute H_2SO_4 increased from 10 to 20%. Ni stripping efficiency did not increase significantly with the increase of dilute H_2SO_4 concentration sequentially. Therefore, the suitable concentration of H_2SO_4 was 20%. Ni stripping efficiency increased from 97.67% to 99.12% when the ratio increased from 1 to 10 (Fig. 9b). The reaction needed enough and moderate content of H_2SO_4 to carry out. The content of H_2SO_4 was not enough when the ratio was low, and Ni in the organic phase cannot be completely extracted. However, Ni stripping efficiency decreased to 86.31% as the ratio increased to 25. The H_2SO_4 content was insufficient when the ratio was too large, resulting in a low stripping efficiency. Therefore, it was more suitable that the ratio was 10 in the stripping process.

The volume difference between the two phases was large under the condition that the ratio (O/A) was 10. Therefore, the reaction needed sufficient time to carry out. Ni stripping efficiency increased from 96.32% to 99.12% when the stripping time increased from 1 to 2 min, and Ni stripping reached equilibrium in a short time (Fig. 9c). However, the stripping efficiency of Ni decreased to 95.56% when the time increased to 6 min. The reason was that part of the solvent was lost due to volatilization when the extraction time continued to increase. The density of aqueous phase and organic phase was similar. It was difficult to separate two phases after prolonging reaction time, which was easy to produce emulsification. Therefore, 2 min was considered to be the optimal time to strip $NiSO_4$ from the organic phase. The study of Zhang et al. showed that the O/A ratio at the Ni stripping stage was 30 [32], while in this study, the O/A ratio at this stage was only 10, saving reagent consumption.

Preparation of $NiSO_4$ product

$NiSO_4$ solution was obtained through the above steps, and then $NiSO_4 \bullet 6H_2O$ was obtained through evaporation, cooling and crystallization. Finally, $NiSO_4$ was calcined to prepare NiO. It had been reported that $NiSO_4 \bullet 6H_2O$ would completely decompose to NiO at 600 ~ 850 ℃. Figure 10 shows the product analysis of thermal decomposition of $NiSO_4$ at 600–850 ℃. $NiSO_4 \bullet 6H_2O$ had lost its crystal

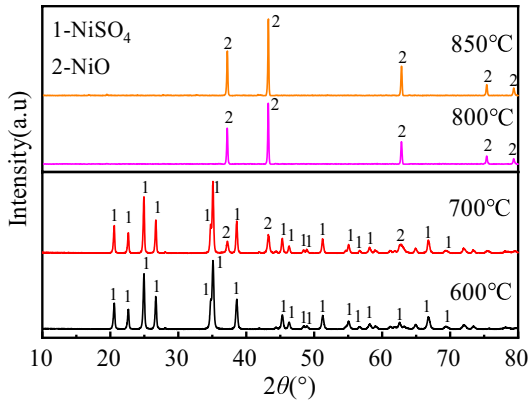


Fig. 10 Product analysis of $NiSO_4$ calcined at different temperatures for 1 h

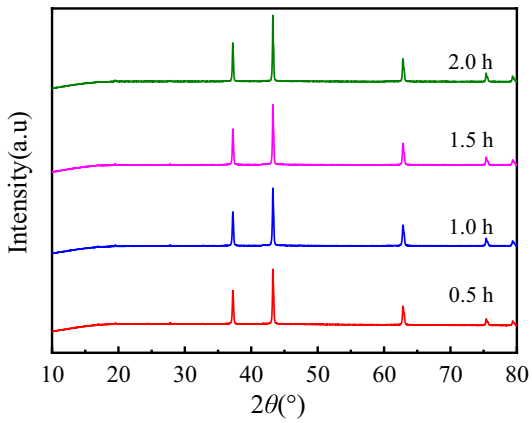


Fig. 11 Product analysis of $NiSO_4$ calcined at 850 ℃ for different time

water at 600 ℃ and became anhydrous $NiSO_4$. Part of the sulfur trioxide in $NiSO_4$ was lost and NiO peak had appeared at 700 ℃. $NiSO_4$ lost sulfur trioxide and was calcined into NiO completely when the temperatures were 800 ℃ and 850 ℃. The peak of NiO at 850 ℃ was sharper, indicating that $NiSO_4$ was calcined more completely at 850 ℃. Therefore, 850 ℃ was set as the superlative temperature to sinter $NiSO_4 \bullet 6H_2O$.

Figure 11 shows the relationship between thermal decomposition and calcination time of $NiSO_4$ at 850 ℃. $NiSO_4$ had been decomposed into NiO when calcined at 850 ℃ for 0.5 h. The peak of NiO was more obvious when the calcination time was extended to 1.0 h. However, the peak of NiO was almost unchanged when the calcination time was extended to 1.5 and 2.0 h. This showed that $NiSO_4$ could be completely decomposed into NiO when calcined at 850 ℃ for 1.0 h. In conclusion, the optimum decomposition procedure of $NiSO_4$ was sintered at 850 ℃ for 1.0 h.

Conclusion

In this study, an efficient method for recovering Ni from the leaching residue was proposed by H_2SO_4 leaching and P204 extraction. The main results were presented as:

1. Over 98.0% Al and Ni were leached from the leaching reside by 30% dilute H_2SO_4 at 70 ℃ for 120 min. The leaching efficiencies of Al and Ni by H_2SO_4 leaching process were higher by 23.05% and 4.52% than that by normal H_2SO_4 leaching methods without heating treatment.
2. 99.34% Ni was extracted from leaching solution by 30% P204 saponification rate at pH value of 6.0 for 1 min with one-stage extraction. Therefore, 99.21% Ni was recycled by 20% dilute H_2SO_4 for 2 min.
3. The kinetic analysis of Ni leaching showed that the activation energy of Ni leaching was 16.10 kJ/mol, which accorded with the shrinkage unreacted kernel model controlled by internal diffusion. The kinetic equation was expressed as $1 - 2/3a - (1 - a)^{2/3} = kt$.
4. 4 $NiSO_4 \bullet 6H_2O$ was obtained through evaporation and cooling crystallization. NiO was obtain by $NiSO_4 \bullet 6H_2O$ which calcined at 850 ℃ for 1 h.

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