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Recovery of vanadium and nickel from spent-residue oil hydrotreating catalyst by direct acid leaching−solvent extraction

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Abstract: A process for the selective extraction and separation of vanadium and nickel from spent-residue oil hydrotreating catalysts by a direct acid leaching−solvent extraction method was studied. The extraction and separation of vanadium(IV) and nickel(II) are divided into two stages: acid coleaching of vanadium and nickel and solvent extraction. In the acid coleaching stage, the leaching ratios of vanadium and nickel reach 88.07% and 75.58%, respectively, which can realize highly effective coleaching. In the solvent extraction stage, countercurrent experiments show that the extraction ratio of vanadium can reach 99.21% after a three-stage extraction with P204 as the high-efficiency extractant of vanadium in the acidic environment, while nickel and iron are not extracted. After the anti-extraction solution is pretreated by aluminum precipitation, the extraction ratio of nickel reaches 99.79% after a three-stage extraction with LIX84-I as a high-efficiency extractant of nickel in ammonia medium. A process flow for the recovery of vanadium and nickel is proposed, which not only can realize the separation and recovery of vanadium and nickel but also can realize the recycling of reagents.

Key words: spent-residue oil hydroprocessing catalyst; acid leaching; solvent extraction; vanadium; nickel

1 Introduction

As important rare metals, vanadium and nickel have been widely applied in many fields such as alloy steel, batteries, catalysts and military equipment, which mainly originate from vanadium−titanium magnetite [1], stone coal [2,3], black shale [4,5] and laterite nickel ore [6]. However, with the continuous exploitation of vanadium and nickel-bearing mineral resources, the single production method of extracting nickel and vanadium from mineral resources cannot meet the demand. Spent hydrotreating catalysts contain not only a large number of complex organic compounds, but also many metal impurities such as vanadium [7,8], molybdenum [9,10], nickel, cobalt, aluminum and other metal elements, which are multicomponent secondary resources and are difficult to treat. At the same time, inactivated spent catalysts can bring serious environmental pollution problems [11,12]. Therefore, the development of a process for recovering valuable metals from spent hydrotreating catalysts can not only bring important economic value, but also effectively avoid the waste of resources and environmental pollution.

According to the different types of spent catalysts, the conventional processes can be subdivided into roasting−acid or alkali leaching, pressurized acid or alkali leaching, direct acid or alkali leaching, alkali leaching−acid leaching and so on [13,14]. The process of extracting valuable metals such as vanadium and nickel from spent hydrotreating catalysts is mainly (sodium) roasting−acid or alkali leaching [15,16]. This process has the advantages of mature technology and high metal

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recovery, but there are some drawbacks such as high energy consumption, poor operation conditions and environmental pollution in the roasting process [17,18]. The acid leaching process with sulfuric acid as the leaching agent has the advantages of low cost, simple processing, strong adaptability and low environmental pollution [19,20]. Regardless of which leaching process is adopted, the valuable metals in the leaching solution need to be separated and purified by traditional methods such as precipitation, solvent extraction, ion exchange and activated carbon adsorption [21−23]. As an environmentally friendly hydrometallurgical process, solvent extraction is often used for purification, concentration and separation of valuable metals [24,25]. At present, research on recovering valuable metals such as vanadium or nickel from leaching solutions of different minerals or secondary resources by solvent extraction methods or exploring the extraction mechanism by synthesizing leaching solutions of soluble salts of metals is gradually increasing. Table 1 shows that the above studies on recovering vanadium and nickel from solution by the solvent extraction method mainly focus on the following two aspects. On the one hand, pure vanadium−nickel sulfate is used as a raw material to synthesize leaching solution and explore the extraction mechanism of different extractants or the feasibility of the extraction and separation of vanadium and nickel. On the other hand, a single metal is studied to explore the recovery process for only one metal element. However, there are relatively few studies on extracting and separating nickel and vanadium directly from spent-residue oil hydrotreating catalysts.

In the present work, a direct acid leaching−solvent extraction method was developed to recover vanadium and nickel from spent-residue oil hydrotreating catalysts, which could realize the recycling of the reagents and meet the requirement of clean production.

2 Experimental

2.1 Materials

The spent-residue oil hydrotreating catalyst taken from Zhejiang Province, China, was used as a feedstock in this study. The extractants of P204 (di(2-ethylhexyl) phosphoric acid) and LIX84-I (2-hydroxy-5-nonylacetophenone oxime) were provided by the Institute of Chemistry, Chinese Academy of Science, and the reagents were used without further purification. As a diluent, kerosene was supplied by Shanghai Science and Technology Co., Ltd. (China). Other chemical reagents such sulfuric acid, aqueous ammonia, sodium sulfite and ammonium sulfate were of analytical grade.

2.2 Experimental procedure of acid leaching

Leaching experiments were carried out in a 250 mL three-necked flask equipped with a reflux condenser at atmospheric pressure to maintain the concentrations of reactants and products. The reaction mixture was stirred by a magnetic stirrer and heated in a water bath (DF-101S type of Chongqing Electrical Appliance Co., Ltd., China). After the solution was heated to the required temperature, the solid sample was added, and then the experiment was carried out for a predetermined time. After the leaching process was completed, the product was cooled to room temperature and then treated by vacuum filtration. The content of vanadium and nickel in the leaching residue was determined by the ammonium ferrous sulfate titration method and EDTA titration method, and

Table 1 Recovery of valuable metals by solvent extraction method

Researcher	Extractant	Goal
KIM et al [26]	LIX 973N, Alamine 336, Alamine 308, Cyanex 272 and D2EHPA	Extract, separate and recover vanadium
YE et al [27]	N235	Recover vanadium
NOORI et al [28]	D2EHPA and Cyanex 272	Separate vanadium and nickel
REDDY and PRIYA [29]	LIX841	Separate nickel, copper and zinc
SUN et al [30]	2-hydroxy-5-nonylacetophenone oxime mixed with organic acids containing neodecanoic acid and bis(2-ethylhexyl) phosphoric acid	Extract nickel

the dissolution ratios of vanadium and nickel were determined according to the following formula:

$$\varepsilon = 1 - \frac{m_1 \beta}{m \alpha} \tag{1}$$

where ε represents the leaching ratio (%) of vanadium or nickel, m_1 is the mass (g) of leaching residue, β represents the grade (%) of vanadium or nickel in leaching residue, m represents the mass (g) of the raw ore, and α represents the grade (%) of vanadium or nickel in raw ore.

2.3 Experimental procedure of solvent extraction

First, after pretreatment, the pH of the aqueous phase was adjusted to the required value by adding H_2SO_4 or NH_4OH. In addition, different organic phases were prepared by mixing different volumes of P204 or LIX84-I with kerosene, and then the organic and aqueous phases were mixed according to a certain ratio. The extraction experiments were carried out in a separation funnel with continuous mechanical oscillation at room temperature for a specified time. After phase separation, the concentrations of elements in the aqueous phase were analyzed by inductively coupled plasma optical electron spectroscopy (ICP–OES, iCAP Duo6300, Thermo Scientific, UK), and the extraction ratios of vanadium and nickel were determined according to Eq. (2):

$$\eta = 1 - \frac{C V_2}{C_0 V_1} \tag{2}$$

where η is the extraction ratio (%) of vanadium or nickel, C represents the concentration (g/L) of vanadium or nickel in raffinate, C_0 represents the concentration (g/L) of vanadium or nickel in the aqueous phase, V_1 represents the initial volume of the aqueous solution and V_2 represents the final volume of the aqueous solution.

The countercurrent experiments were carried out in a box-type coagulation settling device equipped with six coagulation settling sections, where the mixer volume was 0.5 L and the settler volume is 1.5 L. The stirring speed was set as 400 r/min. The required organic and aqueous phases were prepared in advance. Before the experiment, the flow ratio was adjusted to a certain value. After several hours of the experiment, the aqueous phase and organic phase were separated. ICP–OES technology was used to analyze the content of elements in the aqueous phase, and the concentration of vanadium or nickel in the organic phase was calculated according to mass balance.

3 Results and discussion

3.1 Direct acid leaching

In the acid leaching experiment, sulfuric acid was used as the leaching reagent to extract valuable metals from the spent-residue oil hydrotreating catalyst. To obtain the maximum leaching ratios of valuable metals, condition experiments were carried out for various process parameters, such as the solid-to-liquid ratio, sulfuric acid concentration, leaching time and leaching temperature. The final results show that the maximum leaching ratios of 88.07% and 75.58% for vanadium and nickel can be obtained under the optimum leaching conditions of a liquid-to-solid ratio of 10:1, sulfuric acid concentration of 0.45 mol/L, leaching time of 2 h and leaching temperature of 80 °C. To explore the rationality of the acid leaching process, some comparison experiments were carried out with traditional leaching processes, such as sodium roasting−water leaching and sodium roasting−acid leaching processes, and the experimental results are given in Table 2.

The experimental results show that compared with the other leaching processes, the direct acid leaching process can not only achieve the maximum recovery of vanadium and nickel but also save energy consumption and reduce environmental pollution.

After the acid leaching process was completed, the leaching solution was obtained by filtration and washing. The chemical components in the leaching solution were determined by ICP–OES technology, and the results are given in Table 3. The leaching solution was used in the follow-up experiment for vanadium−nickel extraction.

3.2 Solvent extraction of vanadium(IV)

3.2.1 Pretreatment of leaching solution

Pretreatment of the leaching solution is an important process for solvent extraction. Because phosphorus extractants such as P204 have a strong extraction ability for Fe^{3+} and VO^{2+} in acidic media and Fe^{2+} is difficult to extract by P204, some VO^{2+} and Fe^{2+} ions may be oxidized to VO_2^+ and Fe^{3+}, which affects the extraction efficiency of P204 for

Table 2 Comparisons of recovery ratios of vanadium and nickel under different technical conditions

Method	Experimental condition	Vanadium recovery ratio/%	Nickel recovery ratio/%
Direct acid leaching	Liquid-solid ratio 10:1, sulfuric acid concentration 0.45 mol/L, leaching time 2 h, and leaching temperature 80 °C	88.07	75.58
Sodium roasting−water leaching	Roasting conditions: Roasting temperature 900 °C, roasting time 6 h, and NaCl dosage 10%; Leaching conditions: Liquid-to-solid ratio 10:1, leaching time 2 h, and leaching temperature 80 °C	87.71	13.78
Sodium roasting−acid leaching	Roasting conditions: Roasting temperature 900 °C, roasting time 6 h, and NaCl dosage 10%; Leaching conditions: Liquid-to-solid ratio 10:1, sulfuric acid concentration 0. 50 mol/L, leaching time 2 h, and leaching temperature 80 °C	88.78	53.57

Table 3 Chemical compositions of leaching solution (g/L)

V(IV)	Ni	Al	Fe	P	Mg	Si	Na
0.76	0.98	2.06	0.07	1.18	0.03	0.01	0.23

vanadium. Therefore, sodium sulfite was added according to 1.2 times of the theoretical calculation to the leaching solution as a reducing agent to remove Fe^{3+} and to reduce oxidized VO^{2+}. Possible reactions in the pretreatment process of the leaching solution are shown in the following equations:

$$2VO_2^+ + SO_3^{2-} + 2H^+ = 2VO^{2+} + SO_4^{2-} + H_2O \quad (3)$$

$$2Fe^{3+} + SO_3^{2-} + H_2O = 2Fe^{2+} + SO_4^{2-} + 2H^+ \quad (4)$$

3.2.2 Effect of initial aqueous phase pH, extractant P204 concentration and phase ratio (O/A)

In solution, the pH value has a significant effect on the existing form of metal ions. By controlling the pH value of the solution, some metal ions can exist in ideal ionic form, which is beneficial to the extraction and separation of different metals. The effects of the pH value of the initial aqueous phase on the extraction ratios and separation efficiency of vanadium, nickel and iron were investigated. The extraction experiments were performed at an extraction temperature of 25 °C, extraction time of 8 min, O/A ratio of 2:1 and P204 content of 20 vol.%, and the results are illustrated in Fig. 1(a). The effects of the extractant P204 content on the extraction ratios and separation efficiency of vanadium, nickel and iron were studied. The extraction experiments were carried out under the following conditions: pH value of initial aqueous phase of 2.0, extraction temperature of 25 °C, extraction time of 8 min and O/A of 2:1. The experimental results are presented in Fig. 1(b). The effects of O/A on the extraction ratios and separation efficiency of vanadium, nickel and iron were investigated under the following conditions: initial pH value of leaching solution of 2.0, extraction temperature of 25 °C, extraction time of 8 min and P204 content of 20 vol.%. The experimental results are shown in Fig. 1(c).

Figure 1(a) shows that the pH value of the initial aqueous phase has an important effect on solvent extraction. As the pH value increases from 0.5 to 2.0, the extraction ratio of vanadium and the separation ratios of vanadium, nickel and iron rapidly increase. As the pH value of the initial aqueous phase increases further, the extraction ratio of vanadium is stable at approximately 93%. However, when the pH value increases to 2.0, the extraction ratio of nickel increases significantly, and the separation efficiency of vanadium and nickel decreases. Therefore, it is reasonable that the pH value of the initial aqueous phase in this experiment is determined to be 2.

Figure 1(b) shows that the extraction ratio of nickel and iron is obviously lower than that of vanadium, indicating that P204 has a stronger extraction ability for vanadium than nickel and iron. The extraction ratio of vanadium continuously increases with increasing P204 content from 5 to 20 vol.%. When the P204 content reaches 20 vol.%, the extraction ratio of vanadium is 93.47%. With continuing to increase the P204 content, the extraction ratio of vanadium remains basically unchanged, while the values of iron and nickel increase significantly, which is not conducive to the

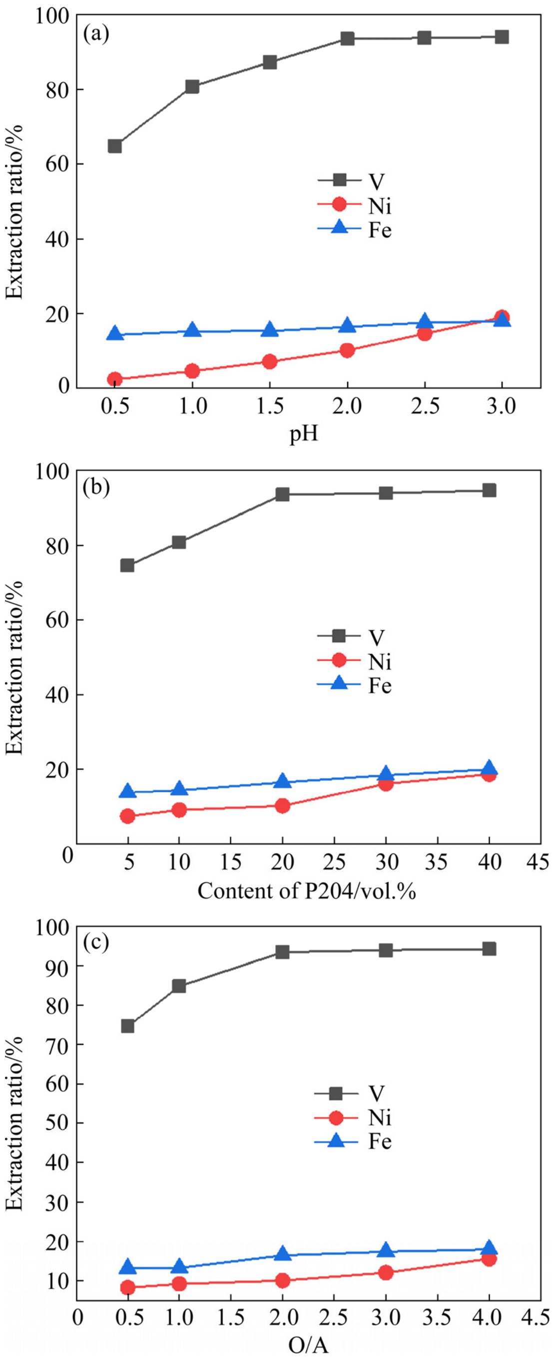

Fig. 1 Effects of pH value of initial aqueous phase (a), extractant P204 content (b) and O/A (c) on extraction ratios of vanadium, nickel and iron

selective extraction of vanadium. At the same time, as the P204 content increases, the viscosity of the organic phase also increases, which is not beneficial to the mixing and separation of the two phases. Therefore, the optimum extraction content of P204 is determined to be 20 vol.%.

As seen from Fig. 1(c), the extraction ratio of vanadium continuously increases with increasing O/A from 0.5 to 2, and the value remains basically unchanged as the phase ratio increases further. During the whole extraction process, the extraction ratios of nickel and iron are less affected by the change in the phase ratio, and the extraction ratios remain basically unchanged. Therefore, the optimum O/A is determined as 2.

3.2.3 Countercurrent extraction simulation of vanadium

The McCabe−Thiele equilibrium isotherm is commonly used to predict the number of stages required for countercurrent extraction [31−33]. To determine the number of stages required for countercurrent extraction, the McCabe−Thiele plot for vanadium extraction was established by changing the O/A under the conditions of P204 content of 20 vol.%, pH value of initial aqueous phase of 2.0 and extraction time of 8 min. The experimental results illustrated in Fig. 2 show that when the O/A is 2, two theoretical stages are needed to extract vanadium. However, for actual operation, an extra stage is usually needed. Therefore, three stages are required in the countercurrent extraction process.

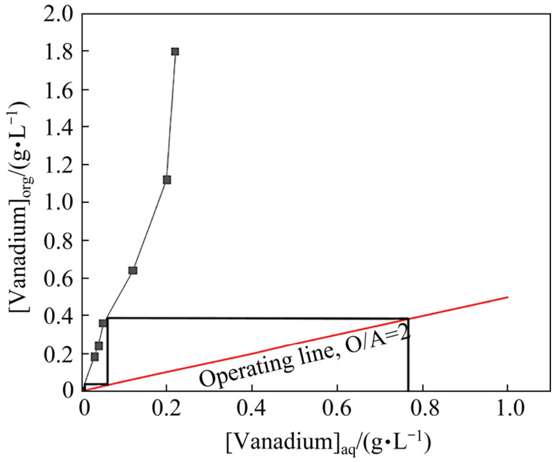

Fig. 2 McCabe−Thiele plot for vanadium(IV) extraction

To confirm the prediction of the McCabe−Thiele method, three-stage countercurrent extraction experiments were carried out in a box-type coagulation settler under the conditions of a P204 content of 20 vol.% and an O/A of 2. The final results show that the vanadium contents in the raffinate and loaded organic phases are 0.006 and 0.377 g/L, respectively, the extraction ratio of vanadium is 99.21%, and nickel and iron are hardly extracted.

3.2.4 Vanadium removal

Vanadium removal experiments for the loaded organic phase with a vanadium concentration of 0.377 g/L were carried out by changing the sulfuric acid concentration under an O/A of 2 and a stripping time of 8 min, and the results are presented in Fig. 3. The results show that the removal ratio of vanadium increases from 79.56% to 94.49% with increasing sulfuric acid concentration from 0.5 to 2 mol/L, and the value remains unchanged as the sulfuric acid concentration further increases. Therefore, the optimum concentration of sulfuric acid is determined to be 2 mol/L.

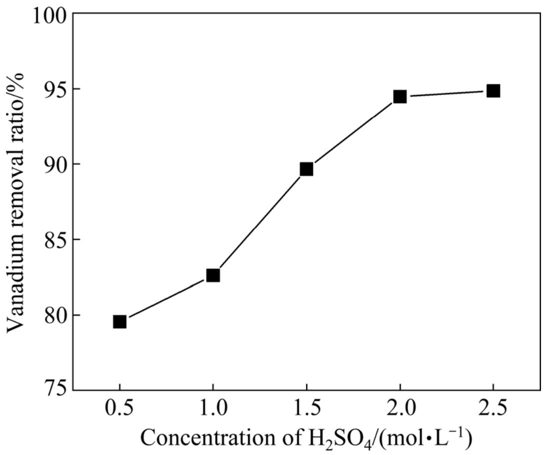

Fig. 3 Effect of sulfuric acid concentration on vanadium removal

The McCabe−Thiele plot of vanadium removal for loaded organic phase with the vanadium concentration of 0.377 g/L was established with different phase ratios (O/A) under the condition of sulfuric acid concentration of 2 mol/L. The results illustrated in Fig. 4 show that when the O/A is 2, two theoretical stages of vanadium removal are needed. For practical operation, an additional stage is usually required. Therefore, a three-stage countercurrent vanadium removal for the loaded organic phase is needed under the conditions of sulfuric acid concentration of 2 mol/L and O/A of 2. To confirm the prediction of the McCabe−Thiele method, three-stage countercurrent vanadium removal experiments were carried out in a box-type coagulation settling device with a sulfuric acid concentration of 2 mol/L and an O/A of 2. The final experimental results show that the vanadium content in the aqueous phase is 0.75 g/L, indicating that the vanadium in the loaded organic phase is basically removed.

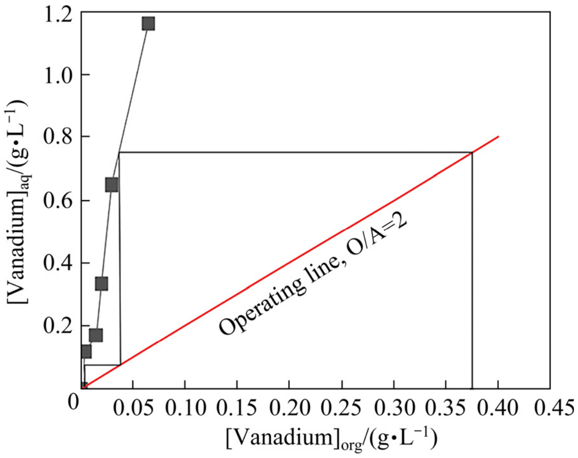

Fig. 4 McCabe−Thiele plot for vanadium(IV) stripping

3.3 Solvent extraction of nickel

3.3.1 Solution pretreatment

In an alkaline environment, most metals exist as hydroxide precipitates, and nickel hydroxides can react with excess NH^{4+} to form soluble substances. The pH value of the solution was adjusted to be 8.5 with aqueous ammonia, and ammonium sulfate was subsequently added to adjust its concentration to be 50 g/L. A large amount of aluminum ions and iron ions in the solution precipitated as precipitates, and nickel complexed with NH^{4+} to form new soluble substances. After filtration, the nickel concentration in the solution was 0.96 g/L, and the nickel loss ratio was 2%. The optimum extraction conditions for nickel were investigated by using this solution.

3.3.2 Effect of different factors on nickel extraction rate

Nickel extraction experiments were carried out with different ammonium sulfate concentrations under the following conditions: pH value of initial leaching solution of 8.5, extraction temperature of 25 °C, extraction time of 3 min, LIX84-I content of 15 vol.% and O/A of 1. The results are shown in Fig. 5(a). Nickel extraction experiments were carried out with different pH values under the following conditions: extraction temperature of 25 °C, extraction time of 3 min, LIX84-I content of 15 vol.%, ammonium sulfate concentration of 100 g/L and O/A of 1, and the results are illustrated in Fig. 5(b). Nickel extraction experiments were carried out with different LIX84-I contents at an extraction temperature of 25 °C, extraction time of 3 min, pH value of 8.5, ammonium sulfate concentration of 100 g/L and O/A of 1, and the

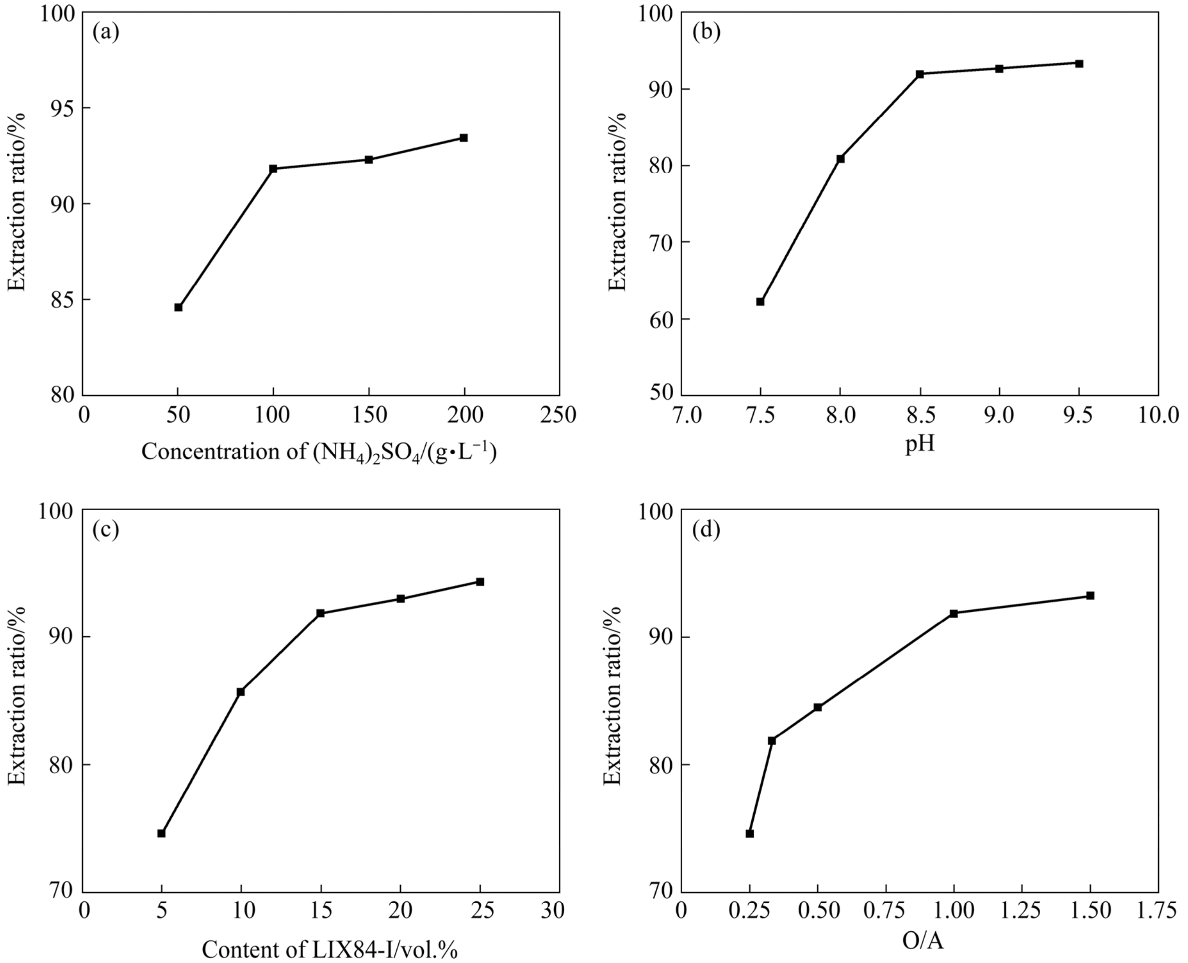

Fig. 5 Effect of ammonium sulfate concentration (a), pH value of initial aqueous phase (b), LIX84-I content (c) and O/A (d) on nickel extraction ratio

results are presented in Fig. 5(c). Nickel extraction experiments were carried out with different phase ratios (O/A) under the following conditions: extraction temperature of 25 °C, extraction time of 3 min, pH value of 8.5, ammonium sulfate concentration of 100 g/L and LIX84-I content of 15 vol.%. The results are shown in Fig. 5(d).

As seen from Fig. 5(a), the ammonium sulfate concentration has a significant effect on the extraction ratio of nickel. The extraction ratio of nickel reaches 91.83% as the ammonium sulfate increases to 100 g/L, and the value basically remains unchanged as the ammonium sulfate increases further. However, as the ammonium sulfate concentration increases to 200 g/L, the extraction rate of nickel decreases. This indicates that ammonium sulfate can promote the extraction of nickel in a certain concentration range and can inhibit the extraction of nickel when its concentration is too high. Therefore, the optimum ammonium sulfate concentration for nickel extraction is 100 g/L.

Figure 5(b) shows that the pH value of the initial aqueous phase has an important effect on solvent extraction. As the pH value increases from 7.5 to 8.5, the extraction ratio of nickel increases rapidly. With continuing to increase the pH value, the extraction ratio of nickel is stable between 91% and 93%. Therefore, the pH value of the initial aqueous phase should not be less than 8.5. Comprehensively, the pH value of the initial aqueous phase for nickel extraction is determined to be 8.5.

As shown in Fig. 5(c), LIX84-I has a strong extraction ability for nickel in an alkaline ammonia medium. During the whole experiment, the extraction ratio of nickel increases with increasing LIX84-I content in the organic phase. When the LIX84-I content is less than 15 vol.%, the extraction ratio of nickel increases significantly. When the content is 15 vol.%, the value is 91.83%. With continuously increasing the LIX84-I content, the extraction ratio of nickel remains basically unchanged, and the visocosity of the organic phase also increases, which is detrimental to the mixing of the two phases and increases the difficulty of separation. Therefore, the optimum LIX84-I content for nickel extraction is determined to be 15 vol.%.

Figure 5(d) shows that the extraction ratio of nickel increases continuously with increasing O/A value from 0.2 to 1, and the value remains basically unchanged as the O/A increases further. Therefore, the optimum O/A for nickel extraction is determined to be 1.

3.3.3 Countercurrent extraction simulation of nickel

To determine the number of stages required for countercurrent extraction, the McCabe−Thiele plot for nickel extraction was established with different O/A values under the conditions of LIX84-I content of 15 vol.%, pH value of initial aqueous phase of 8.5, extraction time of 3 min and ammonium sulfate concentration of 100 g/L, and the results are illustrated in Fig. 6. The results show that when the O/A is 1, two theoretical extraction stages are needed. For actual operation, an extra stage is usually required. Therefore, a three-stage countercurrent extraction process is needed.

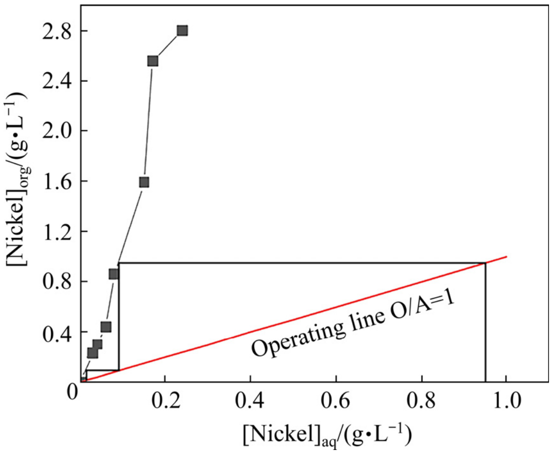

Fig. 6 McCabe−Thiele plot for nickel extraction

To confirm the prediction of the McCabe−Thiele method, the three-stage countercurrent extraction experiments were carried out in a box-type coagulation settling device under the conditions of an LIX84-I content of 15 vol.% and an O/A of 1. The final experimental results show that the nickel content in the raffinate and loaded organic phase is 0.002 and 0.958 g/L, respectively, and the extraction ratio of nickel is 99.79%.

3.3.4 Nickel removal

Nickel removal experiments for the loaded organic phase with a nickel concentration of 0.958 g/L were carried out with different sulfuric acid concentrations under an O/A ratio of 1 and a stripping time of 4 min, and the results are illustrated in Fig. 7. The results show that the nickel removal ratio increases from 79.56% to 92.05% with increasing sulfuric acid concentration from 0.5 to 1 mol/L, and the value remains basically unchanged with further increases in sulfuric acid concentration. Therefore, the optimum sulfuric acid concentration for nickel extraction is determined to be 1 mol/L.

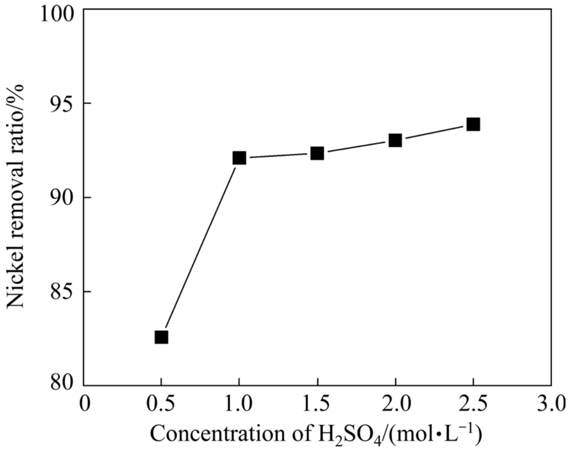

Fig. 7 Effect of sulfuric acid concentration on nickel removal ratio

The McCabe−Thiele plot of nickel removal for the loaded organic phase with a nickel concentration of 0.958 g/L was established by changing the O/A ratio at a sulfuric acid concentration of 1 mol/L, and the results are shown in Fig. 8. The results show that when the O/A is 1, two theoretical stages are needed. For practical operation, an additional stage is usually required. Therefore, the loaded phase needs three-stage countercurrent nickel removal under the conditions of sulfuric acid concentration of 1 mol/L and O/A of 1. To confirm the prediction of the McCabe−Thiele method, three-stage countercurrent nickel removal experiments were carried out in a box-type coagulation settling device under the conditions of a sulfuric acid concentration of 1 mol/L and an O/A value of 1. The final experimental results show that the nickel concentration in the aqueous phase is 0.95 g/L, indicating that nickel removal in the loaded organic phase is basically completed.

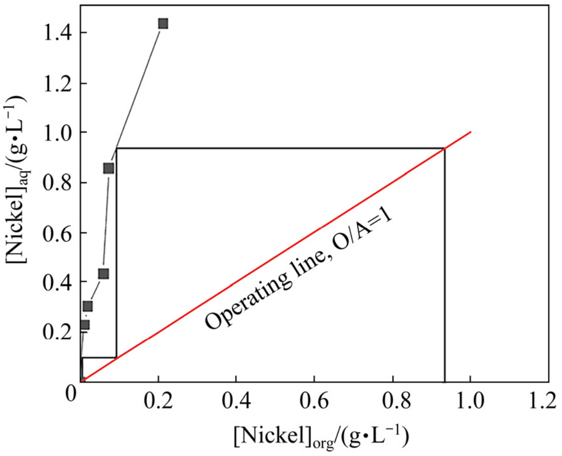

Fig. 8 McCabe−Thiele plot for nickel(II) stripping

3.4 Process flow for recovering valuable metals from spent catalyst

On the basis of the above research and discussion, a clean production process for selective separation and recovery of vanadium(IV) and nickel(II) from spent-residue oil hydrotreating catalysts by acid leaching−solvent extraction was proposed, and the process flow chart is shown in Fig. 9. In the acid leaching process, vanadium and nickel in the spent-residue oil hydrotreating catalyst can be leached together under the conditions of liquid-to-solid ratio of 10:1, sulfuric acid concentration of 0.45 mol/L, leaching time of 2 h and leaching temperature of 80 °C, and their leaching ratios are 88.07% and 75.58%, respectively. The leaching solution containing 0.76 g/L vanadium, 0.98 g/L nickel, 2.06 g/L aluminum and 0.07 g/L iron was obtained by filtration and washing.

In the solvent extraction process of the leaching solution, the organic loaded phase with a vanadium concentration of 0.377 g/L can be obtained under the conditions of a P204 content of 20 vol.%, O/A of 2:1 and pH value of 2 by using a three-stage countercurrent extraction, and the extraction ratio of vanadium is 99.21%, while nickel and iron are not extracted. For the organic loaded phase containing vanadium, vanadium can be completely removed from the loaded organic phase under the conditions of sulfuric acid concentration of 2 mol/L and O/A of 2 by using a three-stage countercurrent vanadium removal process, and a solution with vanadium concentration of 0.75 g/L can be obtained.

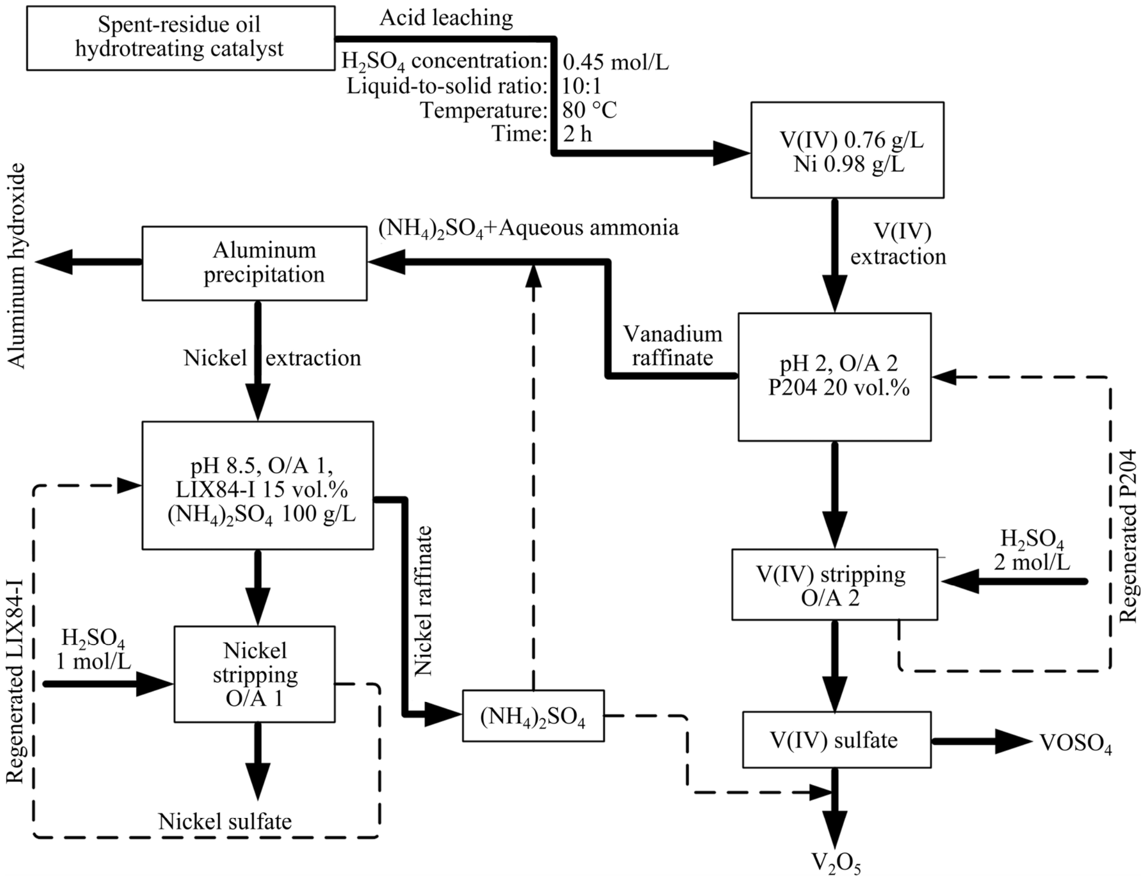

Fig. 9 Process flow chart of polymetallic recovery from spent-residue oil hydrotreating catalyst

A solution with a nickel concentration of 0.96 g/L can be obtained by pretreating vanadium raffinate with aqueous ammonia−ammonium sulfate solution to precipitate aluminum. The organic loaded phase with nickel concentration of 0.958 g/L can be obtained under the conditions of LIX84-I content of 15 vol.%, O/A of 1, pH value of 8.5, ammonium sulfate concentration of 100 g/L by a three-stage countercurrent extraction, and the extraction ratio of vanadium is 99.79%. For the organic loaded phase containing vanadium, nickel can be completely removed from the loaded organic phase under the conditions of sulfuric acid concentration of 1 mol/L and O/A of 1 by a three-stage countercurrent nickel removal process, and a solution with nickel concentration of 0.95 g/L can be obtained.

The vanadium-loaded organic phase (P204) can be recycled after vanadium removal. The as-obtained V(IV) sulfate solution ($VOSO_4$) was treated by precipitating vanadium with ammonium salt and calcination to obtain the V_2O_5 product or directly used as a stock solution for an all-vanadium liquid battery. The nickel-loaded organic phase (LIX84-I) can be recycled to the extraction stage after nickel removal, and the as-obtained nickel sulfate can be treated to obtain various nickel-containing products. The ammonium sulfate product can be obtained from nickel raffinate after crystallization treatment. The as-obtained ammonium sulfate can be returned to the aluminum precipitation stage or used as ammonium salt in the precipitation vanadium process from V(IV) sulfate solution. The whole process can realize the comprehensive recovery of polymetals as well as the recycling of reagents, which meets the requirements of clean production.

4 Conclusions

(1) The process of selective separation and recovery of vanadium(IV) and nickel(II) from spent-residue oil hydrotreating catalysts by the direct acid leaching−solvent extraction method was proposed.

(2) The maximum leaching ratios of 88.07% and 75.58% for vanadium and nickel can be obtained under the conditions of a liquid-to-solid ratio of 10:1, sulfuric acid concentration of 0.45 mol/L, leaching time of 2 h and leaching temperature of 80 °C.

(3) Vanadium with an extraction ratio of 99.21% can be obtained under the conditions of an extractant P204 content of 20 vol.%, pH value of the initial aqueous phase of 2.0, and O/A of 2 by a three-stage countercurrent extraction.

(4) Nickel with an extraction ratio of 99.79% can be obtained under the conditions of an extractant LIX84-I content of 15 vol.%, pH value of the initial aqueous phase of 8.5, O/A of 1 and ammonium sulfate concentration of 100 g/L by a three-stage countercurrent extraction.

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直接酸浸−溶剂萃取法从废油加氢催化剂中回收钒和镍

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摘 要：采用直接酸浸−溶剂萃取法从废油加氢催化剂中选择性萃取分离钒和镍。钒(IV)和镍(II)的萃取分离分为两步：钒和镍的酸浸以及溶剂萃取。首先，通过酸浸实现钒和镍的高效浸取，浸出率分别为 88.07%和 75.58%。其次，逆流萃取实验表明，在酸性环境下以 P204 作为钒的高效萃取剂进行三段萃取，钒的萃取率为 99.21%，而镍和铁则不萃取。钒萃取余液经氨水−硫酸铵脱铝预处理后，在氨介质中以 LIX84-I 作为镍的高效萃取剂进行三段萃取，镍的萃取率为 99.79%。这种钒镍回收的工艺流程不仅可以实现钒和镍的分离回收，而且可以实现试剂的循环利用。

关键词：废油加氢催化剂；酸浸；溶剂萃取；钒；镍

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