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Experimental research on the pressure oxygen leaching rhenium of waste platinum-rhenium catalyst with low acid

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Abstract: Experimental material was the waste platinum-rhenium catalyst; X diffraction was used to characterize the material, and the results showed that the main phase of the waste platinum-rhenium catalyst was Al_2O_3 . The process of rhenium pressure oxygen leaching in platinum-rhenium catalyst with low acid was put forward. The effects of leaching pressure, leaching temperature, leaching time, initial acidity of sulfuric acid and liquid-solid ratio on the leaching rate of rhenium during leaching were investigated in this paper. The results showed that the initial acidity of sulfuric acid had a significant effect on the leaching rate of platinum and rhenium. As the acidity increased, the leaching rate of platinum and rhenium also increased, and the leaching rate of carrier Al_2O_3 also increased. The experimental results show that the leaching of the optimal process conditions were as follows: leaching pressure 5 MPa, leaching time 3h, leaching temperature 140 °C, the initial sulfuric acid concentration 10%, liquid-solid ratio 4:1, mixing speed 350 rpm. Under these conditions, the leaching rate of rhenium and platinum was 98.11% and 83.59% respectively, and the slag rate was 75.56%. In order to prevent platinum from dispersing, ferrous sulphate was added at the end of the leaching process to reduce the platinum into the leaching residue. This process has the advantages of simple operation, high rhenium leaching rate, less impurity elements in the leaching liquid and low acidity, etc., which can provide reference for rhenium extraction from the waste platinum -rhenium catalyst.

1. Introduction

Rhenium is a kind of silver-white rare high-melting metal, which is hard, wear-resistant and corrosion-resistant. The mass fraction in the crust is 1.0×10^{-8} ^[1], mainly in molybdenum ore. It is mainly used in the fields of aerospace, electronics and petrochemical industry, among which the largest use of rhenium is used as a catalyst in the petrochemical industry. Worldwide, the consumption of rhenium accounts for more than 60% of the total consumption. The platinum-rhenium catalyst loses its activity due to poisoning, coke deposition, structural change of support, aggregation or loss of metal grains during its use. It is necessary to replace periodically. The waste catalyst has become the



important second resources for recovering platinum and rhenium metals ^[2]. Rhenium resources are scarce in China, and a large amount of metal rhenium is needed for aerospace and aviation. Therefore, it is of great practical significance to study the recovery of rhenium from failed platinum rhenium catalysts.

At present, the methods of recovering rhenium from the waste platinum-rhenium catalyst include alkali process ^[3], pressure sodium carbonate leaching ^[4], mixed acid dissolution ^[5], total dissolution process ^[6] and ammonium salt roasting process ^[7]. To efficiently extract the rhenium from the waste platinum-rhenium catalyst, the process of oxygen pressure leaching rhenium of the waste platinum-rhenium catalyst was put forwards. The effects of oxygen pressure, leaching temperature, leaching time, initial acidity of sulfuric acid and liquid/solid ratio on leaching rate of rhenium during leaching were mainly studied. The purpose is to obtain high leaching rate of rhenium under the condition of pressure oxygen leaching with low acid and control platinum into leaching residue. Rhenium was purified from leachate with D296 anion resin ^[8~12], leaching residue was used as raw materials for extraction of platinum with the oxidation leaching.

2. Experiment

2.1 raw materials

The experimental raw materials are from petrochemical refineries, and the waste platinum-rhenium catalyst is analyzed with the fluorescence spectrometer (XRF), which mainly contains aluminum, silicon, iron, magnesium, sulfur and a small amount of platinum and rhenium. According to the qualitative analysis, the results are as follows: Al_2O_3 78.16%, MgO 0.012%, SiO_2 0.09%, SO_2 0.26%, H_2O 14.2%, Pt 1780 g/t and Re 3600 g/t. XRD analysis was used to characterize the dried waste platinum-rhenium catalyst. The results are shown in fig. 1. As can be seen from figure 1, the main phase of material is Al_2O_3 . The main testing equipment is ICP01 and TP03.

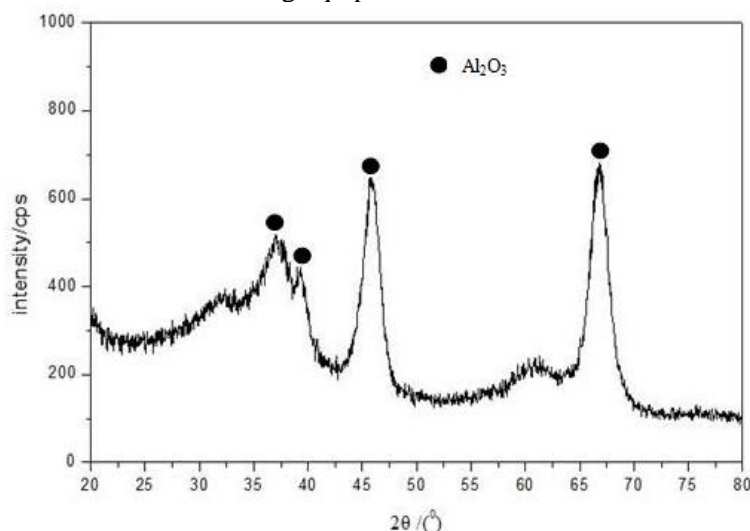


Fig.1 XRD patterns of waste platinum-rhenium catalyst

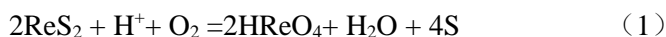
2.2 Instruments and agents

Instrument: digital constant temperature water-bath water (model: XMTD - 204, the jintan city precision instrument manufacturing co., LTD), precision Ceng Li electric mixer (model: JJ - 1, the jintan city east new instrument factory), circulating water vacuum pump (model: SHB - IIIA, Beijing zhongxing weiye instrument co., LTD.), electronic balance (model: TY5002, Shanghai precision scientific instrument co., LTD.), autoclave (model: GSH - 2, Weihai chemical machinery co., LTD.).

Reagent: $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (pure analysis, made in China tianjin fengchuan chemical reagent science co., LTD.), sulfuric acid (pure analysis, made in China Xilong chemical co., LTD.).

2.3 Experimental principle

The literature indicates that the main rhenium phases of the waste platinum-rhenium catalyst are ReS_2 , Re_2O_7 . When materials are leached with pressure under the acid systems, ReS_2 reacts with acid and oxygen, which can be transformed into rhenic acid water and elemental sulphur, and Re_2O_7 reacts with water to form rhenic acid.



2.4 Experimental method

The waste platinum-rhenium catalysts were obtained in different particle size range through the process of sample preparation and screening. According to the requirements of the experiment, the waste platinum-rhenium catalysts was weighed and mixed with water and sulfuric acid slurry. The reactor was put into the autoclave. The cap of the autoclave was sealed and the screws were tightened. When the leaching experiment ended, oxygen be turn off, agitator stop mixing, reactor stop heating; the reactor is cooled by cooling water until the reactant in the reactor was cooled to about 40°C ; the kettle cover be opened after the reactant in the reactor was cooled to about 40°C , the reactants were removed from the reactor and filtered and washed to obtain leach liquor and leaching residue.

$$\eta = \frac{c \times v}{m \times \alpha} \times 100\% \quad (3)$$

η - leaching rate of rhenium, %;

c - Rhenium content in leaching solution, g/L;

v - leach liquid, L;

m - mass of the waste platinum-rhenium catalyst, g;

α - rhenium content in the waste platinum-rhenium catalyst, %.

3. Results and discussion

3.1 Influence of initial sulfuric acid concentration on the leaching rate and slag rate of rhenium

Leaching was carried out under the conditions of the leaching temperature 120°C , oxygen pressure 5 MPa, mixing speed 350 rpm, liquid-solid ratio 4:1 and granularity size $74 \sim 104 \mu\text{m}$, the influences of the initial sulfuric acid concentration on the leaching rate were shown in figure 2.

As can be seen from figure 2, the leaching rate of rhenium increases with the initial concentration of sulfuric acid increasing, mainly because the reaction speed is accelerated when the initial concentration of sulfuric acid increases and. When the initial sulfuric acid concentration is 2%, the rhenium leaching rate is 84.00%, and the leaching residue rate is 95.70%. When the initial sulfuric acid concentration is 10%, the leaching rate of rhenium is 98.11%, and the leaching slag rate is 75.56%, further increasing the initial sulfuric acid concentration to 12%, the leaching rate of rhenium can reach 99.37%, compared with the initial sulfuric acid concentration of 10%. Although the leaching rate of rhenium can increase by 1.26%, the leaching slag rate decreased by 4.83%, that is, by 4.83% Al_2O_3 dissolution into leaching solution which causes difficulty in subsequent extraction of rhenium from leaching solution. Therefore, it is reasonable to determine the initial sulfuric acid concentration of 10%.

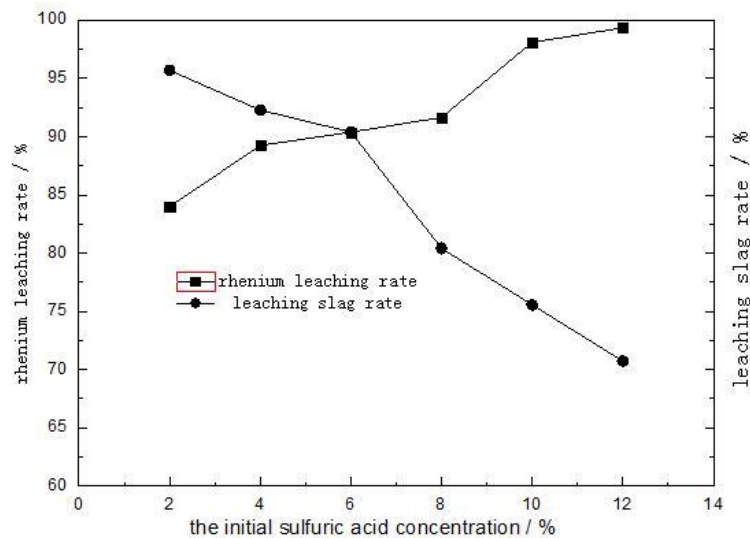


Fig.2 Effect of the initial sulfuric acid concentration on rhenium leaching rate and leaching slag rate

3.2 Effect of leaching temperature on rhenium leaching rate

The effect of leaching temperature on rhenium leaching rate was investigated when keeping the initial sulfuric acid concentration 10%, oxygen pressure 5 MPa, agitation speed 350rpm, liquid-solid ratio 4:1 and particle size of 74-104 μm constant, the results were shown in figure 3.

It can be seen from the figure 3, the leaching rate of rhenium were improved when the leaching temperature rises, and when the leaching temperature is 100 $^{\circ}\text{C}$, rhenium leaching rate was 81.28%. The leaching temperature has significant influence on the leaching rate of rhenium when leaching temperature range from 100 to 140 $^{\circ}\text{C}$, and leaching temperature was over 140 $^{\circ}\text{C}$, the leaching rate of rhenium increase at slow speed with leaching temperature increasing. When leaching temperature is 150 $^{\circ}\text{C}$, the leaching rate of rhenium than leaching temperature at 140 $^{\circ}\text{C}$ only increased by 0.67%. Therefore, it is determined that the leaching temperature is 140 $^{\circ}\text{C}$.

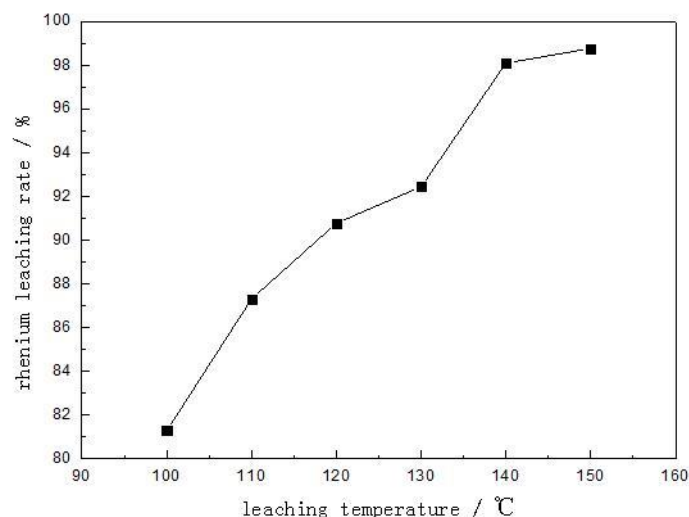


Fig.3 Effect of the leaching temperature on rhenium leaching rate

3.3 Effect of oxygen pressure on rhenium leaching rate

The effect of leaching temperature on rhenium leaching rate was investigated under the leaching conditions of leaching temperature 120 $^{\circ}\text{C}$, sulfuric acid concentration 10%, agitation speed 350 rpm,

liquid-solid ratio 4:1 and particle size 74-104 μm , the results were shown in figure 4.

It can be seen from the figure 4 that leaching rate of rhenium with oxygen pressure increases sharply rise oxygen pressure ranging from 1 MPa to 5 MPa, when the oxygen pressure is 1 MPa, the leaching rate of rhenium reaches 78.99%. When oxygen pressure is increased to 5 MPa, rhenium leaching rate reaches 98.11%, which rhenium leaching rate increased by 19.12% more than that of oxygen pressure being 1 MP. However, when oxygen pressure was more than 5 MPa, rhenium leaching rate increase slowly, and the oxygen pressure is increased further to 6 MPa, rhenium leaching rate can reach 99.05%, which the leaching rate of rhenium increased only 0.94% more than that of the oxygen pressure being 5 MPa. Therefore, oxygen pressure was determined to be 5 MPa.

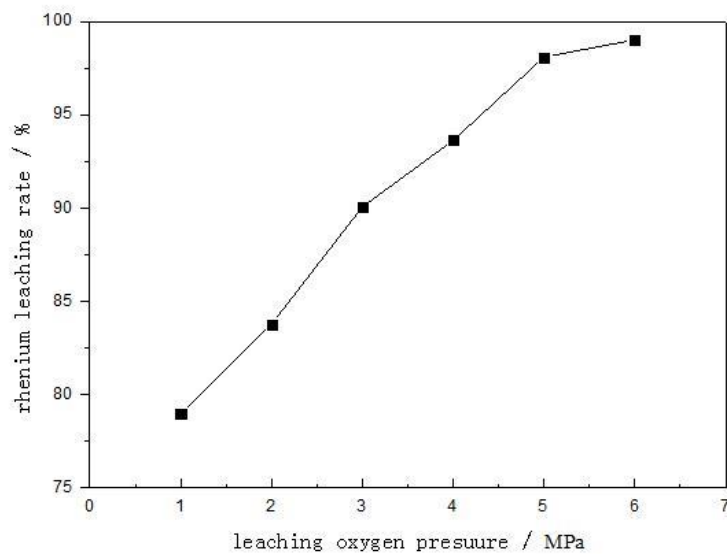


Fig.4 Effect of the leaching oxygen pressure on rhenium leaching rate

3.4 Effects of leaching time on rhenium leaching rate

The experiments were carried out when keeping the leaching temperature 140 $^{\circ}\text{C}$, oxygen pressure 5 MPa, 10% sulfuric acid concentration, liquid-solid ratio 4:1 and stirring speed 350 rpm constant, the results are shown in figure 5.

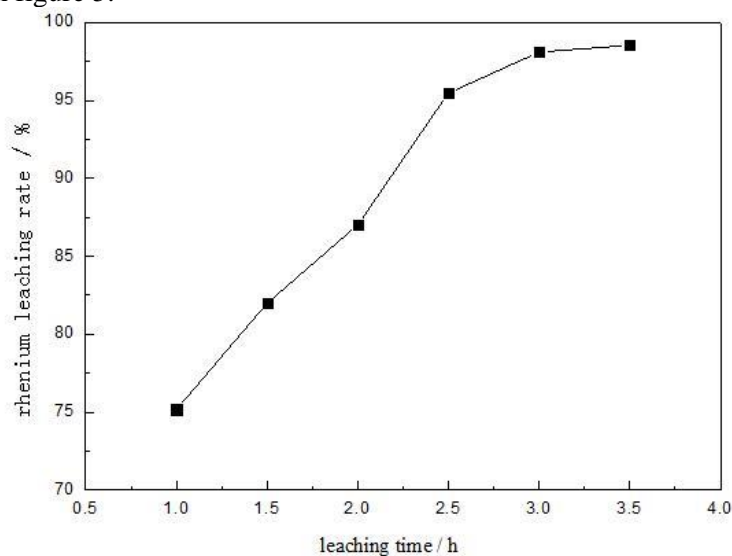


Fig.5 Effect of the leaching time on rhenium leaching rate

The figure 5 shows that within the scope of 0.5 to 3.0 h in leaching time, leaching rate of rhenium and in a straight line rise with the leaching time extended. The leaching rate of rhenium reaches 75.17% when the leaching time is 1.0 h. And then the leaching time is increased to 2.0 h, the leaching rate of rhenium increased by 11.85% compared with that of leaching time of 1 h. However, rhenium leaching rate increase slowly with the leaching time exceeding 3.0 h, and when the leaching time is 3.5 h, the leaching rate of rhenium increased by 0.44% compared with that of the leaching time for 3.0 h. Furthermore, extending the leaching time not only increase energy consumption, but also it reduces equipment processing efficiency during production. Therefore, the appropriate leaching time was determined to be 3.0h.

3.5 Influence of liquid- solid ratio on rhenium leaching rate

Under the fixed leaching conditions: oxygen leaching temperature 140 °C, oxygen pressure 5 MPa, the initial sulfuric acid concentration 10%, leaching time 3.0 h and mixing speed 350 rpm, the influences of liquid - solid ratio on rhenium leaching rate are shown in figure 6.

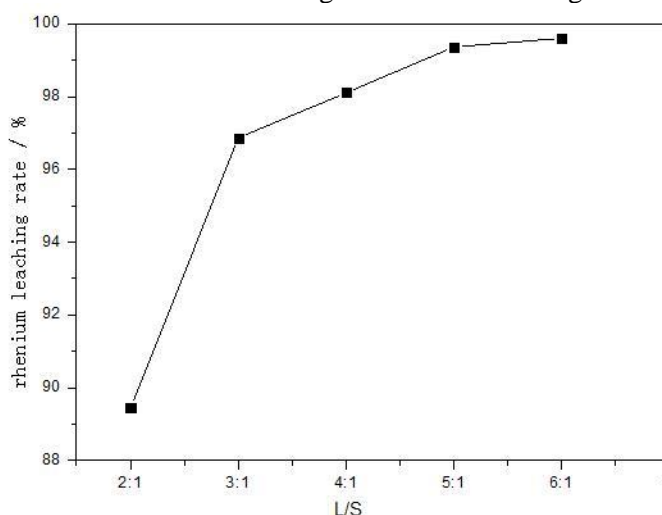


Fig.6 Effect of the ratio of liquid-solid ratio on rhenium leaching rate

As can be seen from the figure 6, rhenium leaching rate improve with liquid-solid ratio increasing gradually, the liquid-solid ratio is small, in the leaching system of viscosity is larger, leaching agent diffusion is slow. The leaching rate of rhenium reaches 89.44% when liquid-solid ratio is 2:1, but rhenium leaching rate reaches 96.87% when the liquid to solid ratio is 3:1, which rhenium leaching rate increased significantly. Furthermore, the liquid-solid ratio is more than 4:1, rhenium leaching rate increase slowly. If the liquid-solid ratio increased, it caused to increase leaching liquid and reduce the rhenium content of leaching liquid during product, which produce the high cost of waste liquid treatment during the subsequent extraction of rhenium. The liquid-solid ratio is determined to be 4:1.

3.6 comprehensive leaching conditions

Through single factor leaching experiment results can be obtained by the optimum leaching process conditions: leaching temperature 140 °C, oxygen pressure 5 MPa, the initial sulfuric acid concentration 10%, leaching time 3.0 h, stirring speed 350 rpm, liquid-solid ratio 4:1. Repeated experiments were conducted under these conditions, the leaching rate of rhenium reached 98.15%, the leaching rate of platinum reached 83.12%, and the leaching residue rate was 75.81%, which was consistent with the single factor leaching experimental results. When leaching experiment ended, ferrous sulfate was added to leaching system to react with platinum ions in leaching solution to form platinum for 1 h and then platinum was discharged into the leaching residue through filtration, which can prevent platinum diffusion ^[12]. During the experiment, the addition of ferrous sulfate was 2% of

the mass ratio of the waste platinum-rhenium catalyst, and the leaching rate of platinum was 0.6%. Leached slag contains Al_2O_3 96.74%, sulfur 0.31%, pt 2346.81g /t and re 87.26g /t. XRD analysis was used to characterize the leaching slag. It can be seen from figure 7 that the main phase of the leaching slag is Al_2O_3 , which is consistent with the diffraction peak of the material. The leaching solution contained rhenium 0.63g/L, platinum less than 0.001g/L and aluminum 21.25g/L. The experimental results show that platinum was not dispersed.

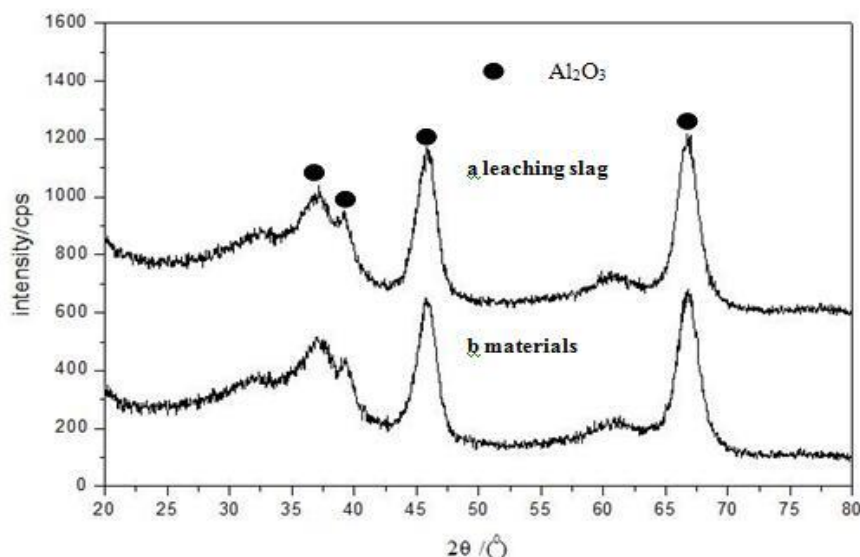


Fig.7 XRD patterns of leaching slag(a: leaching slag; b: materials)

4. Conclusions

(1) The waste platinum-rhenium catalyst was characterized by X diffraction. The results showed that the waste platinum-rhenium catalyst was mainly Al_2O_3 , and the process of selective leaching rhenium in the waste platinum-rhenium catalyst under low acid pressure was feasible.

(2) Through the experimental study, the optimal extraction processes were obtained as follows: leaching temperature 140 °C, oxygen pressure 5 MPa, the initial sulfuric acid concentration 10%, leaching time 3.0 h, stirring speed 350 rpm, liquid-solid ratio 4:1. Under these conditions, rhenium and platinum leaching rates were 98.11%, 83.59% and 75.56%, respectively.

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