Kinetics research on rhenium of the waste platinum-rhenium catalyst under pressure oxygen leaching

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**Abstract:** Experimental material was the waste platinum-rhenium catalyst; the kinetics of rhenium in PT rhenium catalyst failed by pressure oxygen leaching was studied. The effects of leaching pressure, temperature, sulfuric acid acidity, stirring speed and particle size on the kinetics of rhenium leaching were investigated in this paper. The results showed that sulfuric acid, leaching temperature, leaching pressure and particle size had a significant effect on the leaching rate of rhenium; the chemical reaction control model can well describe the rhenium gas liquid-solid reaction process in the waste platinum-rhenium catalyst for pressure oxygen leaching. In the experimental range, the apparent activation energy is determined to be 42.96kJ/mol, which is in agreement with the chemical reaction control model.

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 1.0x10<sup>-8</sup>[1], mainly in molybdenum. It is mainly used in the fields of aerospace, electronics and petrochemical industry, among which the largest use of rhenium is 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 leaching process [3], pressure sodium carbonate leaching [4], mixed acid dissolution [5], total dissolution [6] and ammonium salt roasting [7]. In this paper, the rhenium dynamics in the waste platinum-rhenium catalyst with pressure oxygen leaching rhenium was studied, which provided theoretical basis for efficient extraction of rhenium in the waste platinum-rhenium catalyst.
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: $\text{Al}_2\text{O}_3$ 78.16%, $\text{MgO}$0.012%, $\text{SiO}_2$0.09%, S0.26%, $\text{H}_2\text{O}$14.2%, Pt1780 g/t and Re3600 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 $\text{Al}_2\text{O}_3$.

![Fig.1 XRD patterns of the waste platinum-rhenium catalyst](image)

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 weyie instrument co., LTD.), electronic balance (model: TY5002, Shanghai precision scientific instrument co., LTD.), autoclave (model: GSH - 2, weihai chemical machinery co., LTD.).

Reagent: $\text{FeSO}_4\cdot7\text{H}_2\text{O}$ (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 $\text{ReS}_2$, $\text{Re}_2\text{O}_7$. When materials are leached with pressure under the acid systems, $\text{ReS}_2$ reacts with acid and oxygen, which can be transformed into rhenic acid water and elemental sulphur, and $\text{Re}_2\text{O}_7$ reacts with water to form rhenic acid.

\[
\begin{align*}
2\text{ReS}_2 + \text{H}^+ + \text{O}_2 & = 2\text{HReO}_4 + \text{H}_2\text{O} + 4\text{S} \\
\text{Re}_2\text{O}_7 + \text{H}_2\text{O} & = 2\text{HReO}_4
\end{align*}
\]

2.4 Experimental method
The waste platinum-rhenium catalysts were obtained in different particle size ranges through the process of sample preparation and screening. According to the requirements of the experiment, the waste platinum-rhenium catalyst was weighed and mixed with water and dilute sulfuric acid. The reactor was added to 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℃; 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.

Kinetics description: this reaction is a liquid-solid-gas poly-phase reaction process, which sulfur in rhenium sulfide is oxidized and precipitates elemental sulfur during the reaction. With the extension of leaching reaction time, sulfur increases gradually on the surface of ore particles. Therefore, the kinetic experimental data obtained in this study were processed mathematically with the interfacial chemical reaction control equation (3) and the diffusion control equation (4) of the compact solid product layer to determine which kind of control the multiphase reaction belongs to [8].

\[
1 - (1-a)^{1/3} = k_c t \quad \text{(3)} \\
\text{where}, \quad k_c = \frac{Mk'C}{b\rho\gamma}
\]

In equation (3), \( a \)-the reaction fraction of the waste platinum-rhenium catalyst in the reaction time \( t \); \( t \)-leaching time, min; \( M \)-relative to the atomic(molecular) quantity mass, g; \( C \)-concentration of B in the solution, mol/L; \( b \)-the stoichiometric coefficient \((A(s)+bB(aq))\) to \( P(s) \) of the reactant \( b \); \( \gamma_o \)-initial radius of the grains, cm; \( \rho \)-the density of A, g/cm³; \( K \)-the surface chemical reaction rate constant; \( k_c \)-the chemical control rate constants.

\[
1 - \frac{2}{3} a - \frac{2}{3} (1-a)^{2/3} = k_p t \quad \text{(4)} \\
\text{where}, \quad k_p = \frac{2MDC}{b\rho\gamma_o^2}
\]

In formula (4): D- the diffusion coefficient; \( k_p \)-the diffusion control apparent rate constants.

3. Results and discussion

3.1 Influence of the sulphuric acid concentration on the leaching rate of rhenium

Leaching experiments were carried out under the conditions of the leaching temperature 120 °C, oxygen pressure 2 MPa, mixing speed 350 rpm and granularity size 74 ~ 104 µm, the influence of the sulphuric acid concentration on the leaching rate of rhenium was examined, and the experimental results were shown in figure 2.

As can be seen from figure 2, the leaching rates of rhenium increase with the increase of the concentration of sulfuric acid, mainly because the initial concentrations of sulfuric acid increase and the reaction speeds are accelerated. According to the data in fig.2, fig.3 was obtained by drawing the leaching time \( t \) with a plot of \( 1-2/3a-(1-a)^{2/3} \). The straight line did not pass the origin, indicating that the reaction did not conform to the diffusion control through the dense solid product layer. According to the data in fig 2, fig 4 is obtained by plotting leaching time \( t \) with \( 1-(1-a)^{1/3} \). The straight line goes through the origin, indicating the chemical reaction control at the reaction interface. According to fig 4, the chemical control rate constant \( k_c \) for the sulphuric acid concentration of 0.8mol/L, 1.0mol/L and 1.2mol/L was 3.9×10⁻³, 4.7×10⁻³ and 5.3×10⁻³, respectively, and the linear correlation coefficients were 0.9965, 0.9981 and 0.9987, respectively. Fig 5 is obtained by drawing -ln\( k_c \) with –ln\( c \). Thus, the reaction series of the sulphuric acid concentration is 0.7641, and its linear regression correlation coefficient is 0.9961.
Fig. 2 Effect of the concentration of sulfuric acid on rhenium leaching rate

$$y = 0.0018x - 0.0216$$  \(R^2 = 0.9775\)

$$y = 0.0015x - 0.0189$$  \(R^2 = 0.9763\)

$$y = 0.0019x - 0.0078$$  \(R^2 = 0.9871\)

Figure 3 relation between reaction time and 1-2/3a-(1-a)^2/3

$$y = 0.0047x + 0.0006$$  \(R^2 = 0.9981\)

$$y = 0.0039x + 0.0114$$  \(R^2 = 0.9965\)

$$y = 0.0053x + 0.0095$$  \(R^2 = 0.9987\)

Figure 4 relation between reaction time and 1-(1-a)^1/3

$$y = 0.053x + 0.0095$$  \(R^2 = 0.9987\)

$$y = 0.0047x + 0.0006$$  \(R^2 = 0.9991\)

$$y = 0.0039x + 0.0114$$  \(R^2 = 0.9965\)
3. Influence of leaching temperature on rhenium leaching rate

The effect of leaching temperature on rhenium leaching rate was investigated when keeping the sulphuric acid concentration 10%, oxygen pressure 2 MPa, agitation speed 350 rpm and particle size 74-104 µm constant, the results were shown in fig. 6.

It can be seen from fig. 6 that the rhenium leaching rate increases with the increase of leaching temperature. According to the data in fig. 6, fig. 7 can be obtained by plotting 1-(1-a)²/³ of leaching time t, with its straight line passing through the origin. According to fig. 7, the chemical control rate constant k_c at the leaching temperature of 383 K, 393 K and 403 K was obtained for 2.9×10⁻³, 4.7×10⁻³ and 6.0×10⁻³, respectively. The linear correlation coefficients were 0.9983, 0.9981 and 0.9812. Again by 1000 / T to get fig. 8 lnk_c mapping, the linear correlation coefficient is 0.9808, and the straight line of slope is 5166.8. By Arrhenius formula: lnk_c=-E_a/R×1/T + A (E_a=-5166.8=-E_a/R), the apparent activation energy can be obtained within the scope of the corresponding temperature as follows: E_a = 42.96 kJ/mol.
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 °C, the sulphuric acid concentration 10%, agitation speed 350 rpm and particle size 74-104 µm, the results were shown in figure 9.

As can be seen from fig.9, rhenium leaching rate increases linearly with the increase of oxygen pressure from 1 MPa to 5 MPa. According to the data in fig.9, the leaching time \( t \) is plotted by \( 1-(1-a)^{1/3} \). According to fig.10, the chemical control rate constant \( k_c \) at the leaching pressure of 1MPa, 2MPa and 3MPa is \( 4.8\times10^{-3} \), \( 4.7\times10^{-3} \), and \( 3.3\times10^{-3} \), respectively. The linear correlation coefficients are 0.9942, 0.9981, and 0.9972, respectively.
40 50 60 70 80 90 100
rhenium leaching rate/%

60 90 120 150 180 210
t/min

Fig.9 Effect of the leaching oxygen pressure on rhenium leaching rate

$y = 0.0047x + 0.0006$
$R^2 = 0.9981$

$y = 0.0033x + 0.0076$
$R^2 = 0.9972$

$y = 0.0048x + 0.0129$
$R^2 = 0.9942$

3.4 Influence of grain size on rhenium leaching rate

The experiments were carried out for the materilas grain size 104~124µm, 74~104µm and 53~74µm, respectively, keeping the leaching temperature 140 °C, oxygen pressure 2 MPa, 10% sulfuric acid concentration and stirring speed 350 rpm constant, the influences of grain size on rhenium leaching rate are shown in figure 11.

It can be seen from fig.11 that the extraction rate of rhenium increases linearly with the increase of grain size. According to the data in fig.11, the leaching time $t$ is plotted by $1-(1-a)^{1/3}$, and figure 12 is obtained. The straight line passes through the origin. The apparent rate constants $k_c$ at the particle size of 104-124, 74-104, 53-74 and 53-74 were obtained as $3.6 \times 10^3$, $4.7 \times 10^3$ and $5.0 \times 10^3$, respectively.

The linear correlation coefficients were 0.9966, 0.9981 and 0.9962, respectively. According to the interfacial chemical reaction control, the chemical control rate constant $k_c$ is inversely proportional to the particle radius. Fig.13 is obtained by plotting $r^{-2}$ with $k_c$. Fig.13 shows that $k_c$ is linear with a linear regression correlation coefficient of 0.9894, which further confirms that the leaching reaction is controlled by chemistry.
Fig. 11 Effect of the grain size on rhenium leaching rate

\[ y = 0.0047x + 0.0006 \quad R^2 = 0.9981 \]
\[ y = 0.0043x - 0.0089 \quad R^2 = 0.9976 \]

Figure 12 relation between reaction time and \(1-(1-a)^{1/3}\)
3.5 Influence of stirring speed on rhenium leaching rate

Leaching temperature of 120 °C and oxygen pressure 2 MPa, concentration of sulfuric acid 1.0 mol/L, particle size 74 ~ 104µm remains the same, the influence of the leaching rate of rhenium of the results are shown in figure 14. It can be seen from fig.14 that rhenium leaching rate is less affected by variation of stirring speed. According to the data in figure 14, the leaching time t is plotted by $1-(1-a)^{1/3}$, and figure 15 is obtained. It can be seen from fig.15 that the straight line passes through the origin. Thus, the apparent rate constant $k_c$ at the stirring speed of 250rpm, 350rpm and 450rpm was obtained, $3.9 \times 10^{-3}$, $4.7 \times 10^{-3}$ and $4.9 \times 10^{-3}$, respectively. The linear correlation coefficients were 0.9966, 0.9981 and 0.9962, respectively.
4. Conclusions
The kinetics of rhenium in the waste spent platinum-rhenium catalyst by pressurized oxygen leaching was studied. The results showed that the chemical reaction control model could be used to describe the process of rhenium gas-liquid-solid reaction in the waste platinum-rhenium catalyst with pressure oxygen leaching. In the experimental range, the apparent activation energy of 42.96 kJ/mol was determined, which was consistent with the chemical reaction control model, indicating that the reaction was controlled by chemical diffusion.

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