Extraction of platinum and gold from copper anode slimes by a process of chlorinating roasting followed by chlorinating leaching

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Abstract: A novel process of chlorinating roasting followed by chlorinating leaching to extract platinum and gold from copper anode slimes was proposed in this research. Results of thermodynamic analysis and experimental research show that the platinum is chlorinated into PtCl₂ while the gold exists in the form of metallic Au during the roasting process. With the copper anode slime being directly leached using a traditional process, the Pt recovery rate is low to 80.72%. After roasted with sodium chloride and concentrated sulfuric acid in oxygen atmosphere, the recovery rate of Pt is increased to a value around 95%. Moreover, with excessive addition of concentrated sulfuric acid, more H₂O (g) are generated and the formation of Cl₂ (g) is decreased due to the transition from HCl (g) and Cl₂ (g), as a result of which the Pt recovery rate decreases. In addition, this chlorinating roasting affects little on the Au recovery due to its difficulty to be chlorinated.

Keywords: Copper anode slime; recovery of platinum and gold; chlorinating roasting; chlorinating leaching

1. Introduction

Platinum (Pt) and gold (Au) are costly precious metals with wide applications in the manufacturing of catalysts, electronic devices, space materials, biomedical devices, jewelry and so on, due to their distinct properties, such as chemical inertness, corrosion resistance, catalytic activity, thermoelectric stability and stable electrical properties [1-4]. However, they are limited availability in nature and both the abundance in the earth's crust are below 10μg/g in addition to their mineral ores becoming depleted [5-6]. To meet the future demand, it is necessary to process the secondary platinum and gold containing materials, such as spent catalysts, electronic scraps, anode slimes and so on [7-8].

The copper anode slime, a byproduct of the copper electro-refining process, is a valuable secondary resource containing valuable elements such as Cu, Se, Sb, Ag, Au and platinum group metals [9-11]. Based on the different composition and mineralogy in

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anode slimes, numerous approaches have been made to utilize it following the processes of pyro-, pyrohydro-, hydromyro- and hydrometallurgical methods \textsuperscript{[12-16]}. These processes can be divided into in two steps of the separation and recovery of non-ferrous metals first and then the recovery of target precious metals \textsuperscript{[17]}. The leaching process is mainly used to recover precious metals from the secondary slime using different lixiviants, such as sulfuric acid, nitric acid, hydrochloric acid, chloride or iodide solutions, etc. J. Hait found that the recovery rate of Au was low with sulfuric acid leaching process without any additive \textsuperscript{[18]}. Also in the thiosulfate leaching process, the Au extraction rate was only 88\% \textsuperscript{[19]}. High leaching rates of Au and Pt could be reached using aqua regia; however, it caused an environmental pollution \textsuperscript{[20]}. With the anode slime dissolved with the help of chlorine gas in aqueous medium, a high recovery of gold of 94.4\% could be obtained, but the chlorine gas causes serious corrosion of equipment \textsuperscript{[21]}. Compared with these methods, a chlorinating leaching process using NaCl-H\textsubscript{2}SO\textsubscript{4}NaClO\textsubscript{3} mixed solution has a few advantages, including a higher dissolution rate of gold, lower price of leaching reagents as well as the simplicity of the process itself \textsuperscript{[22]}. However, the leaching rate of platinum is low at the optimal condition favoring Au leaching, which causes a considerable amount of platinum to be distributed in the leaching residue and consequently the recovery rate of platinum difficult to be increased.

In this paper, a novel process of chlorinating roasting followed by a chlorinating leaching to recovery platinum and gold from copper anode slime was investigated. Thermodynamic simulation of the chlorinating roasting procedure was discussed, and the effects of roasting temperature, oxygen flow rate, dosage of sodium chloride and concentrated sulfuric acid on recovery rates of platinum and gold were researched using XRD, SEM and chemical analysis.

### 2. Experimental

#### 2.1 Materials

The copper anode slime used in this work was obtained from a copper smelter which located in Yunnan province of China. As presented in Table 1, the major elements contained in this slime are Cu, Sn, Sb, Ag, As, S, O, and Te, and the contents of Pt and Au are 93.76 g/t and 1812.15 g/t respectively. Fig.1 shows that this copper anode slime is mainly composed phases of SnO\textsubscript{2}, Sn\textsubscript{1.91}Sb\textsubscript{1.09}O\textsubscript{2}, PbSO\textsubscript{4}, Cu\textsubscript{2}S, SbAsO\textsubscript{5} and Ag\textsubscript{2}SO\textsubscript{4}, while Pt and Au phases can’t be detected due to their little contents. Generally, they mainly occur in metallic state \textsuperscript{[23]}. The reagents used in the experiments were all analytical grade, including sodium chloride, sodium chlorate, sodium hydroxide, concentrated sulfuric acid, gold powder and platinum powder. Besides, deionized water was used to prepare solutions in all leaching experiments.

| Element | Pt (g/t) | Au (g/t) | Cu | Sn | Sb | Ag | As | S | Pb | Ni | Zn |
|---------|----------|----------|----|----|----|----|----|---|----|----|----|
| Content | 93.76    | 1812.15  | 12.77 | 13.72 | 9.83 | 4.79 | 6.21 | 8.32 | 3.18 | 3.20 | 0.99 |

| Element | Bi | Se | Te | Si | O | others |
|---------|----|----|----|----|---|---------|
| Content | 3.15 | 3.23 | 4.37 | 0.50 | 23.78 | 1.96 |
2.2 Experimental procedures

The experimental apparatus and process flow sheet investigated for extractions of platinum and gold from copper anode slimes are given in Fig. 2. For the experimental procedure, the copper anode slime was firstly dried at 100 °C for 24 h, ground to below 0.15 mm, and then mixed with a given amount of sodium chloride in a sample boat. After the tube furnace being heated to a proper temperature, a given amount of concentrated sulfuric acid was added to the sample boat, and then was immediately located in the tube furnace and roasted in a certain flow rate of O2. The exhaust gas was absorbed with the saturated sodium hydroxide solution. After a proper roasting time, the O2 was cut off and the roasted samples were cooled down to room temperature before taking out from the tube furnace, and then weighed and stored for analysis and subsequent leaching experiments. In order to study the effects of roasting variables on the leachability of gold and platinum, each roasting product was leached under an identical condition (80 °C; 4h; 3mL/g liquid-solid ratio; 120 g/L sulfuric acid, was taken as the leaching agent; 60 g/L sodium chloride solution, was used to provide Cl-, 18 g/L sodium chlorate solution, was taken as the chlorinating agent). For the leaching procedure, the roasted copper anode slime was firstly ground to below 0.074mm, put into a 400 mL glass conical flask containing the leaching solution, and then the glass conical flask was placed in an oscillation box equipped with a thermostatic water bath. It is noteworthy that the sodium chlorate solution was added per half an hour apart to ensure the high partial pressure of chlorine. After the leaching process finished, the solution was filtrated, and then the filter residue was collected, dried and weighed for analysis.
2.3 Analytical methods

The chemical composition of the copper anode slime was characterized by chemical analysis. The contents of Pt and Au in samples were determined by flame assaying method. Mineralogy of the samples was characterized by scanning electron microscope analysis (SEM-Tecnai G2 TF30, FEI, Netherlands). Phase composition of the sample was detected by X-ray diffraction analysis (XRD, Rigaku, TTR-III), which was carried out using Cu Kα radiation with the scanning rate was 8°/min and the 2θ was varying from 10 to 90°. The leaching rate of platinum and gold was calculated according to:

\[
\varepsilon_p = \left(1 - \frac{m_p w_p}{m_tw_{op}}\right) \times 100\% \quad \text{Eq. 1}
\]

\[
\varepsilon_a = \left(1 - \frac{m_t w_a}{m_tw_{oa}}\right) \times 100\% \quad \text{Eq. 2}
\]

Here, \(\varepsilon_p\) and \(\varepsilon_a\) is the leaching rate of platinum and gold, respectively; \(m_t\) and \(m_r\) are the masses of the original slime and leaching residue in g, respectively; \(w_{op}\) and \(w_{oa}\) are the contents of platinum and gold in the original slime in mass%, respectively; and \(w_p\) and \(w_a\) are the contents of platinum and gold in the leaching residue in mass%, respectively.

The thermodynamic data of species were given by FactSage 7.2 thermochemical software.

3. Results and discussion

3.1 Thermodynamic analysis

Gold and platinum, as precious metals, have a low chemical activity and show a high ability of resistance to dissolution. Traditionally, a chlorination leaching method is directly used to extract Pt and Au from copper anode slimes, in which the Pt and Au are chlorinated and transferred to acidsoluble \(\text{PtCl}_6^{2-}\) and \(\text{AuCl}_4^-\) through reactions (1)-
(2) in a solution of NaCl-H$_2$SO$_4$-NaClO$_3$. The stability Eh-pH diagrams for systems of Au-Cl-H$_2$O and Pt-Cl-H$_2$O at 80 °C are presented in Figs.3 (a) and (b) respectively. The potential for Au leachable ranges from 0.96 V to 1.32 V with the pH from -2 to 5.45 seen from Fig.3 (a), and that for Pt ranges from 0.75 V to 1.58 V with the pH from -2 to 9.69 as shown in Fig.3 (b). To achieve these high potentials for obtaining high leaching rates of Au and Pt, much NaClO$_3$ should be employed in the leaching process. However, it causes the utilization efficiency of chlorine to be decreased due to the more emission of Cl$_2$ during the leaching process.

$$3\text{Pt} + 2\text{ClO}_3^- + 16\text{Cl}^- + 12\text{H}^+ = 3\text{PtCl}_6^{2-} + 6\text{H}_2\text{O} \quad (1)$$

$$2\text{Au} + \text{ClO}_3^- + 7\text{Cl}^- + 6\text{H}^+ = 2\text{AuCl}_4^- + 3\text{H}_2\text{O} \quad (2)$$

An innovative process of copper anode slimes roasted with NaCl and H$_2$SO$_4$ in O$_2$ atmosphere was proposed in this research to convert Pt and Au to acid-soluble chlorides [24]. The equilibrium compositions of systems of Pt-NaCl-H$_2$SO$_4$-O$_2$ and Au-NaCl-H$_2$SO$_4$-O$_2$ were firstly calculated with Equilib Module of Factsage 7.2, in which some certain species which originated from 40g copper anode slimes (Table 2). 4.00E-02mol H$_2$SO$_4$, 1.61mol O$_2$ and 6.84E-3mol (or 3.42E-02 mol) NaCl were used.

| Table 2 | Species amounts used in the calculation for equilibrium composition of 40 g copper anode slimes roasted with H$_2$SO$_4$ and NaCl in O$_2$ |
|---------|--------------------------------------------------------------------------------------------------|
| Reagent | Pt | Au | SnO$_2$ | Cu$_2$S | PbSO$_4$ |
| mol     | 1.92E-07 | 3.68E-06 | 4.61E-02 | 4.02E-02 | 6.14E-03 |
| Reagent | SbAsO$_5$ | Ag$_2$SO$_4$ | NiO | SiO$_2$ | ZnO |
| mol     | 3.31E-02 | 8.88E-03 | 2.17E-02 | 7.14E-03 | 6.15E-03 |

The results in Table 3 indicate that the chlorination of Pt proceeds through a progressive phase transformation process as the temperature rises as described in Eq. (3) through reactions (4) to (6). Compared to that with 1% NaCl addition, the partial pressure of Cl$_2$ is higher at 5% NaCl added seen from Table 3, which increases the phase transition temperature of both PtCl$_4$ to PtCl$_3$ and PtCl$_3$ to PtCl$_2$ as shown in Table 3 from the viewpoint of chemical equilibrium. In addition, with the temperature increase, the partial pressure of Cl$_2$ corresponding to the PtCl$_x$ (x=2, 3, 4) stable region increases seen from the predominance area diagram of Pt-Cl-O system at 50 °C, 250 °C.
and 450 °C respectively as shown in Fig.4.

\[
\begin{align*}
\text{Pt} &\rightarrow \text{PtCl}_4 \rightarrow \text{PtCl}_3 \rightarrow \text{PtCl}_2 \\
\text{Pt} + 2\text{Cl}_2 (g) &\rightarrow \text{PtCl}_4 \\
2\text{PtCl}_4 &\rightarrow 2\text{PtCl}_3 + \text{Cl}_2 (g) \\
2\text{PtCl}_3 &\rightarrow 2\text{PtCl}_2 + \text{Cl}_2 (g)
\end{align*}
\]

Table 3 Equilibrium composition of Pt-containing phases in Pt-Cl₂ system calculated by Factsage 7.2

| T (°C) | P(Cl₂) (atm) | Pt phase equilibrium composition (mol) |
|-------|--------------|--------------------------------------|
|       |              | PtCl₄ | PtCl₃ | PtCl₂ |
| NaCl amount: 6.84E-3 mol (NaCl addition: Copper anode slimes = 1%, mass %) |
| 50    | 2.06E-03     | 1.92E-07 | 0 | 0 |
| 250*  | 1.79E-03     | 0 | 1.92E-07 | 0 |
| 305*  | 1.61E-03     | 0 | 0 | 1.92E-07 |
| 450   | 9.54E-04     | 0 | 0 | 1.92E-07 |
| 500   | 7.42E-04     | 0 | 0 | 1.92E-07 |
| NaCl amount: 3.42E-02 mol (NaCl addition: Copper anode slimes = 5%, mass %) |
| 50    | 1.05E-02     | 1.92E-07 | 0 | 0 |
| 283*  | 9.48E-03     | 0 | 1.92E-07 | 0 |
| 352*  | 8.78E-03     | 0 | 0 | 1.92E-07 |
| 450   | 7.43E-03     | 0 | 0 | 1.92E-07 |
| 500   | 6.62E-03     | 0 | 0 | 1.92E-07 |

*The temperature data corresponding to the Pt phase transition temperature.

Table 4 Equilibrium composition of Au-containing phases in Au-Cl₂ system calculated by Factsage 7.2

| T (°C) | P(Cl₂) (atm) | Au phase equilibrium composition (mol) |
|-------|--------------|--------------------------------------|
|       |              | AuCl₃ | Au |
| 50    | 2.06E-03     | 3.68E-06 | 0 |
| 106*  | 2.05E-03     | 0 | 3.68E-06 |
| 300   | 1.61E-03     | 0 | 3.68E-06 |
| 450   | 9.54E-04     | 0 | 3.68E-06 |
| 500   | 7.42E-04     | 0 | 3.68E-06 |

*The temperature data corresponding to the Au phase transition temperature.

Table 4 shows that the chlorination of Au can only be carried out at a low temperature, and then the AuCl₃ will be transformed to Au completely at temperature higher than 106 °C. Also as shown in Fig.5, the Au exists stably in a high partial pressure of Cl₂, and the temperature rise increases the upper limit of Cl₂ partial pressure for Au stable region.
Fig. 5. Predominance area diagrams for the Au-Cl-O system at 50, 300 and 450 °C

The thermodynamic analysis above supports a conclusion that the platinum is more easily to be chlorinated than that for gold. Then an experiment was designed to verify this, in which 10 g copper anode slime mixed with 4 g concentrated sulfuric acid, 0.5 g NaCl, powders of 0.5 g Pt and 0.5 g Au, were roasted at 450 °C for 180 min in O₂ atmosphere and the X-ray diffraction pattern of the corresponding roasted residue is presented in Fig. 6. The presence of PtCl₂ peak and Au peak in Fig. 6 validates the thermodynamic analysis.

Fig. 6. X-ray diffraction pattern of the roasted residue of copper anode slime mixed with powders of Pt and Au

During the roasting process, the partial pressures of Cl₂ and O₂ determine the chlorination behavior of Pt and Au [25]. The equilibrium composition of NaCl-H₂SO₄-O₂ system was calculated by Equilib Module in Factsage 7.2 and the results are shown in Fig. 7.

Fig. 7 (a) indicates that with the increase in NaCl dosage, Cl₂ (g), HCl (g) and Na₂SO₄ amounts increase along with the obvious reduction of SO₃ (g) at 450°C. Thus, the release of chlorine from NaCl might be carried out through reactions (7) - (9). Fig. 7 (b) shows that with increasing H₂SO₄ amount, the Cl₂ (g) amount firstly increases and then decreases slightly while coupled with an always increase of HCl (g) amount, which might be due to the translation between HCl (g) and Cl₂ (g) according to Eq. (10). More H₂O (g) will be generated through reaction (7) with more H₂SO₄ added, and consequently the generation of HCl (g) is promoted in reaction (10). Meanwhile, the reaction (10) is a reversible exothermic reaction, due to which more Cl₂ (g) will also be transformed to HCl (g) with the temperature increase as shown in Fig. 7 (c). The increase in O₂ (g) amount enhances Cl₂ (g) formation obviously seen from Fig. 7 (d),
and the NaCl is almost transferred to Cl$_2$ (g) and HCl (g) at O$_2$ (g) amount of 0.2 mol. Increasing O$_2$ (g) amount further, the amounts of Cl$_2$ (g) and HCl (g) changes slightly while the partial pressures of them decrease. An appropriate NaCl amount, roasting temperature and O$_2$ (g) amount is important for the Cl$_2$ (g) generation and Pt chlorination.

\[
\begin{align*}
H_2SO_4 &= SO_3(g) + H_2O(g) \\
2NaCl + SO_3(g) + H_2O(g) &= Na_2SO_4 + 2HCl(g) \\
2NaCl + SO_3(g) + 0.5O_2(g) &= Na_2SO_4 + Cl_2(g) \\
4HCl(g) + O_2(g) &\rightleftharpoons 2Cl_2(g) + 2H_2O(g)
\end{align*}
\]

![Equilibrium amount vs NaCl amount](image1) ![Equilibrium amount vs H$_2$SO$_4$ amount](image2)

**3.2 Results**

This process consists of two main stages named chlorination roasting first and chlorination leaching followed respectively, and the leaching procedure was carried out with the same condition as described in Section of “2.2 Experimental procedures”. The parameters of roasting temperature, oxygen flow rate, addition amounts of concentrated sulfuric acid and sodium chloride were focused to study the effect of the roasting variables on leachability of gold and platinum, and the results are shown in Table 5.

| Temperature (°C) | n(NaCl): 6.84E-3 mol | n(O$_2$): 1.61 mol |
|------------------|----------------------|-------------------|
| n(Cl$_2$)        | n(HCl)               | Partial pressure (atm) |
| n(H$_2$SO$_4$): 0.04 mol | n(O$_2$): 0.04 mol |

![Equilibrium amount vs Temperature](image3) ![Equilibrium amount vs O$_2$ amount](image4)

Table 5 Effects of the roasting variables on recovery of gold and platinum
| T (°C) | NaCl addition (wt%) | H₂SO₄ addition (wt%) | O₂ flow rate (mL/min) | Time (min) | Pt recovery (%) | Au recovery (%) |
|-------|---------------------|----------------------|-----------------------|------------|----------------|----------------|
| 400   | 1                   | 40                   | 200                   | 120        | 95.09          | 98.68          |
| 425   | 1                   | 40                   | 200                   | 120        | 97.52          | 98.84          |
| 450   | 1                   | 40                   | 200                   | 120        | 98.37          | 98.76          |
| 475   | 1                   | 40                   | 200                   | 120        | 98.25          | 98.46          |
| 500   | 1                   | 40                   | 200                   | 120        | 97.17          | 98.36          |
| 525   | 1                   | 40                   | 200                   | 120        | 94.61          | 98.08          |

| T (°C) | NaCl addition (wt%) | H₂SO₄ addition (wt%) | O₂ flow rate (mL/min) | Time (min) | Pt recovery (%) | Au recovery (%) |
|-------|---------------------|----------------------|-----------------------|------------|----------------|----------------|
| 450   | 0                   | 40                   | 200                   | 120        | 93.85          | 98.63          |
| 450   | 0.5                 | 40                   | 200                   | 120        | 96.56          | 98.67          |
| 450   | 0.75                | 40                   | 200                   | 120        | 97.63          | 98.27          |
| 450   | 1                   | 40                   | 200                   | 120        | 98.37          | 98.76          |
| 450   | 1.25                | 40                   | 200                   | 120        | 97.70          | 98.44          |
| 450   | 1.5                 | 40                   | 200                   | 120        | 96.52          | 98.32          |

| T (°C) | NaCl addition (wt%) | H₂SO₄ addition (wt%) | O₂ flow rate (mL/min) | Time (min) | Pt recovery (%) | Au recovery (%) |
|-------|---------------------|----------------------|-----------------------|------------|----------------|----------------|
| 450   | 1                   | 30                   | 200                   | 120        | 97.10          | 98.69          |
| 450   | 1                   | 35                   | 200                   | 120        | 97.80          | 98.78          |
| 450   | 1                   | 40                   | 200                   | 120        | 98.37          | 98.76          |
| 450   | 1                   | 45                   | 200                   | 120        | 96.87          | 98.58          |
| 450   | 1                   | 50                   | 200                   | 120        | 96.26          | 98.65          |
| 450   | 1                   | 55                   | 200                   | 120        | 96.10          | 98.76          |

| T (°C) | NaCl addition (wt%) | H₂SO₄ addition (wt%) | O₂ flow rate (mL/min) | Time (min) | Pt recovery (%) | Au recovery (%) |
|-------|---------------------|----------------------|-----------------------|------------|----------------|----------------|
| 450   | 1                   | 40                   | 50                    | 120        | 94.73          | 98.99          |
| 450   | 1                   | 40                   | 100                   | 120        | 94.88          | 99.22          |
| 450   | 1                   | 40                   | 150                   | 120        | 95.76          | 98.66          |
| 450   | 1                   | 40                   | 200                   | 120        | 98.37          | 98.76          |
| 450   | 1                   | 40                   | 250                   | 120        | 97.93          | 99.10          |
| 450   | 1                   | 40                   | 300                   | 120        | 96.57          | 98.71          |

### 3.3 Discussion

*Effect of roasting temperature*

First in the blank test, with the copper anode slime being directly treated through a traditional leaching process using the parameters described in Section of “2.2 Experimental procedures”, the Pt recovery rate is low to 80.72% causing the massive waste of Pt resources.
In Table 5, a significant improvement is observed in the recovery of platinum from 95.09% to 98.37% with the temperature increasing from 400 °C to 450 °C. As the roasting temperature over 450 °C, the recovery rate of platinum decreases. It might be attributed to the decrease of \( \text{Cl}_2 \) (g) formation and further the Pt chlorination deduced from Fig.7 (c). In addition, the massive volatilization of \( \text{SO}_3 \) (g) caused by the quick decomposition of concentrated sulfuric acid at higher temperatures also results in a small portion of it available to participate in \( \text{Cl}_2 \) (g) formation. Meanwhile, it is noteworthy that the sintering degree is increased at higher temperatures seen from Fig.8, which slows down the diffusion of \( \text{SO}_3 \) (g) and \( \text{O}_2 \) (g) to the surface of NaCl as well as diffusion of the generated \( \text{Cl}_2 \) (g) to the surface of platinum, thereby inhibiting the Pt chlorination. Obviously, roasting at 450 °C results in a good leaching performance for Pt. In addition, though the Pt can be chlorinated to \( \text{PtCl}_2 \) at 450 °C based on the result in Fig.6, it cannot be detected in Fig.9 due to the small concentration of Pt in the roasted residue.

![Fig.8. SEM images of roasted residues with additions of 1% NaCl and 40% H\textsubscript{2}SO\textsubscript{4} at different temperatures](image)

![Fig.9 X-ray diffraction pattern of roasted residue with additions of 1% NaCl and 40% H\textsubscript{2}SO\textsubscript{4} at 450 °C](image)

**Effect of sodium chloride and concentrated sulfuric acid amounts**

Roasted at 450 °C, the data in Table 5 shows that the Pt recovery rate increases obviously from 93.85% to 98.37% with NaCl amount from 0 to 1%. Then with NaCl amount beyond 1%, the sample will be sintered (Fig.10) and the gas-solid chlorination of Pt will be hindered, as a result of which the Pt recovery rate decreases slightly. In Fig.11, the foundation of \( \text{Ag}_2\text{SO}_4 \) peak in the X-ray diffraction pattern of the roasted residue at 1.5% NaCl addition indicates the lower level of chlorination of the sample compared to that with 1% NaCl added seen from Fig.8. In Fig.8, the \( \text{Ag}_2\text{SO}_4 \) in the
copper anode slime has been transformed to AgCl. Thus, the suitable sodium chloride amount is 1%.

Fig.10. SEM images of the roasted residues with additions of 1% NaCl and 1.5% NaCl respectively at 450 °C and 40% H$_2$SO$_4$

The concentrated sulfuric acid has a complicated effect on the Pt chlorination. With its amount ranging from 30% to 40%, the Pt recovery increases as shown in Table 5. However, more H$_2$O (g) will be generated through reaction (7) when more concentrated sulfuric acid is added, and the formation of Cl$_2$ (g) might be decreased according to reaction (10) and Fig.7 (b), as a result of which the Pt chlorination and recovery decreases (Table 5). The concentrated sulfuric acid amount should be fixed at 40%.

Effect of oxygen flow rate

With the copper anode slimes roasted with 1% NaCl and 40% concentrated sulfuric acid at 450 °C, more Cl$_2$ (g) could be formed with the O$_2$ flow rate increasing from 50 to 200 mL/min, and correspondingly the recovery rate of Pt increases from 94.73% to 98.37%. However, it then decreases slightly with a further increase of O$_2$ flow rate, which might be attributed to the decrease in Cl$_2$ partial pressure at a higher O$_2$ flow rate obtained from Fig.7 (d) which goes against the Pt chlorination.

Besides, this chlorination roasting process affects little on the Au recovery based on the results in Table 5, which is related to the fact that the Au is difficult to be
chlorinated under the roasting conditions and it exists stably in the form of metallic Au after roasted confirmed by Fig.6.

4. Conclusions
The effective recovery of Pt and Au from the copper anode slime through the process of chlorination roasting first and chlorination leaching followed is feasible. The factors, including roasting temperature, oxygen flow rate, sodium chloride and concentrated sulfuric acid amounts play important roles on the Pt recovery, while they affect little on the Au recovery due to it difficult to be chlorinated.

The thermodynamic analysis shows that the chlorination of platinum proceeds through a progressive phase transformation process presented as Pt → PtCl₄ → PtCl₃ → PtCl₂ with the temperature increase, and the transition temperature increases with the increase of Cl₂ partial pressure. With the copper anode slime being directly treated through a traditional leaching process, the Pt recovery rate is low to 80.72%. After roasted with sodium chloride and concentrated sulfuric acid in oxygen atmosphere, the recovery rate of Pt is increased to a value around 95%. However, with excessive concentrated sulfuric acid added, a massive amount of H₂O(g) is generated and the formation of Cl₂ (g) is decreased due to the transition from HCl (g) and Cl₂ (g), as a result of which the Pt recovery rate decreases. Besides, the excessive addition of sodium chloride leads to the sample sintered and the Pt recovery rate also decreases.

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