Leaching of Gold and Silver from Anode Slime with Inorganic Reagents

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Abstract

Leaching experiments of anode slime were performed with several inorganic acids (HCl, HNO₃ and H₂SO₄) together with thiourea and thiosulfate solution to recover gold and silver. Gold was not dissolved at all into these inorganic acids in the absence of any oxidizing agents. At the same concentration of inorganic acid, the leaching of percentage of Ag was the highest in the sulfuric acid solution. The leaching percentage of silver increased with the increase of HCl concentration owing to the formation of AgCl₂⁻. Copper, nickel and zinc except tin was almost dissolved in these inorganic acids but no tin was dissolved in nitric acid solution. Most of Au and Ag were dissolved into the mixture of sulfuric acid and thiourea solution. Thiosulfate could dissolve some silver from the anode slime but no gold was dissolved by this agent.

Key words : Anode slime, Leaching, Inorganic acids, Thiourea, Thiosulfate
1. Introduction

Anode slime is considered as an important secondary resource containing some precious metals such as Ag, Au and PGMs (platinum-group metals)\(^1\)-\(^3\). In recent years, extensive studies have been established to dissolve gold and silver from different secondary resources. According to the composition and contents of the elements in resources, either pyrometallurgy or hydrometallurgy is employed to recover the precious metals. Some common reagents, such as chlorine gas, sulfuric acid and nitric acid are used to dissolve anode slimes in the presence of oxidants such as oxygen and \(\text{Fe}^{3+}\) etc. to improve the leaching efficiency of the reagents\(^3\)-\(^5\).

For this purpose, thiosulfate and thiourea have been widely studied\(^6\)-\(^11\). In order to improve the leaching of metals and to reduce the degradation, some complexing or oxidizing agents such as oxygen, \(\text{Fe}^{3+}\), \(\text{H}_2\text{O}_2\), EDTA and sodium citrate etc are investigated\(^12\)-\(^20\). However, during the leaching process, some decomposition was caused due to the presence of oxidants and some new compounds were formed resulting in the high consumption of thiourea and thiosulfate.

In some research, the combination of pyrometallurgy and hydrometallurgy is utilized to treat the anode slime and refractory ores. The common processes are sodium hydroxide roast-acetic acid-thiosulfate leaching\(^21\), alkali fusion-leaching\(^22,23\), sulfatizing roast-thiourea leaching\(^24\). These technologies mainly employ the pyrometallurgical methods to remove the base metals which affect the leaching of precious metals or result in the high consumption of leaching reagents. However, some hazardous gas or slag-rich base metals are formed and lead to the pollution of the environment.

In addition, some physical technologies such as milling, mechanical activation and mechanochemical pretreatment are employed to pretreat the resources, resulting in a change in chemical or physico-chemical properties\(^25\). However these pretreatments give higher dissolution of metals in the leaching process\(^26,27\). Moreover, some researchers combined the ultrasound, microwave, pressure into the leaching process for the dissolution of silver from spent solid materials\(^28,29\). These measures can facilitate the dissolution of metals and increase the diffusion coefficient of soluble species\(^30\). Nevertheless, these techniques demand high investment of instrument and are only utilized in the bench-scale experiments.

In order to investigate the appropriate leaching methods to recover gold and silver from the anode slime, inorganic acids such as hydrochloric acid, nitric acid and sulfuric acid as well as thiosulfate and thiourea were employed in this work. The leaching behavior of gold and silver as well as other metal present in the anode slime was mainly discussed.

2. Experimental

2.1. Material and reagents

The as-received anode slime from the company was dried at 60°C in oven for 24h, and then milled into a particle size less than 100 μm. The chemical composition is indicated in Table 1. The main elements of this anode slime include Cu, Ag, Sn and Au. Mineralogical phases of the anode slime were determined by X-ray diffraction analysis.

The reagents used in the experiments, such as sodium thiosulfate, sodium hydroxide, sulfuric acid, \(\text{H}_2\text{O}_2\), nitric acid and hydrochloric acid were of analytical grade.

2.2. Leaching procedure

All leaching experiments were performed with desired concentration of leaching agents in a 250 mL of three-neck flat bottom beaker. During the leaching experiment, the reactors were kept closed by the covers to avoid evaporation losses. The magnetic stirrer bar was used to mix the reactor solution. After the temperature was set to the required level, the anode slime was added to the leaching solution to maintain a pulp density of 10 g/L unless otherwise stated.

When the leaching tests were completed, the residues

| Table 1. Chemical composition of the anode slime employed in this work |
|-----------------------------|-----------------|-----------------|----------------|-----------------|-----------------|-----------------|
| Metal | Cu | Au | Ag | Sn | Ni | Zn |
| Content, % | 41.14 | 1.5 | 4.59 | 5.75 | 0.32 | 0.18 |
were separated on the Bucher filter using a vacuum pump and then dried in an oven. The leaching percentage was calculated on the basis of the metal concentration of the solution. An ICP-atomic emission spectrometer (OPTIMA 8300, Perkin Elmer) was used to determine the concentration of all the metals in the leaching solutions.

3. Results and Discussion

3.1. Leaching with hydrogen chloride

Fig. 1 shows the effect of HCl concentration on the leaching of Au and Ag as well as other metals from the anode slime. The experimental conditions employed were: stirring speed, 200 rpm; temperature, 75°C; particle size, 100 µm; reaction time, 2 h. It is seen that all metals except Au were dissolved into the solution. Increasing the HCl concentration from 4 to 8 M led to a significant enhancement in the leaching percentage of Ag from 2% to 8% over 2 h.

The solubility of AgCl is very small. Therefore, the dissolved silver ion form precipitates AgCl with the chloride ion in the solution. When there are excess chloride ions in the solution, the precipitated AgCl can be dissolved by forming anionic complex AgCl$^-$ with chloride ion, which can be represented as

$$\text{AgCl}_\text{(s)} + \text{Cl}^- = \text{AgCl}^- \quad K_{sp} = 2.88 \times 10^{-5}$$ (1)

The effect of HCl concentration on the solubility of silver was considered by calculating the concentration of AgCl$^-$ in the above equation and the results are shown in Fig. 2. According to this figure, the maximum solubility of silver in 8 M HCl solution is 15 ppm. Therefore, the increase in the leaching percentage of Ag with HCl concentration is related to the complex formation of AgCl$^-$, which is represented by Eq. (1). However, it was found that some precipitates were observed after keeping the leaching solution for several days.

When Cu$^{2+}$ is present in the leaching solution, Ag can be oxidized by Cu$^{2+}$ and the reaction of which is represented in Eq. (2) together with the standard free energy change at 20°C and 80°C. Although the reaction can be spontaneous at 80°C, the equilibrium constant is very small$^{31,32}$.

$$\text{Ag} + \text{Cu}^{2+} + 4\text{Cl}^- = \text{AgCl}_2^- + \text{CuCl}_2^-$$

$$\Delta G_{(20^\circ C)}^{0} = 2.2 \text{ kJ/mol}; \Delta G_{(80^\circ C)}^{0} = -9 \text{ kJ/mol}$$ (2)

3.2. Leaching with nitric acid

Table 2 shows effect of HNO$_3$ concentration on the leaching of anode slimes. The results were obtained at the following experimental conditions: temperature, 75°C;
reaction time, 2 h; pulp density, 10 g/L; stirring speed, 200 rpm; particle size, 100 μm; HNO$_3$ concentration, 6 M. Table 2 indicates that some Ag was dissolved by nitric acid solution but no Au was dissolved. Eqs. (3) and (4) represent the leaching reaction of silver by HNO$_3$. Cu, Ni and Zn were completely dissolved into the nitric acid solution within the experimental conditions. However, no Sn was dissolved into the nitric acid solution owing to the formation of SnO$_2$, for which Eqs. (5) and (6) are responsible$^{33}$. With nitric acid solution alone, Au and Sn were not dissolved and just a small amount of Ag was dissolved.

$$3\text{Ag} + 4\text{HNO}_3 = 3\text{AgNO}_3 + 2\text{H}_2\text{O} + \text{NO}$$

(3)

$$\text{Ag} + 2\text{HNO}_3 = \text{AgNO}_3 + \text{H}_2\text{O} + \text{NO}_2$$

(4)

$$3\text{Sn} + 4\text{HNO}_3 + \text{H}_2\text{O} = 3\text{SnO}_2\cdot\text{H}_2\text{O} + 4\text{NO}$$

(5)

$$\text{Sn} + 4\text{HNO}_3 = \text{SnO}_2\cdot\text{H}_2\text{O} + 4\text{NO}_2 + \text{H}_2\text{O}$$

(6)

Fig. 3 shows the effect of reaction time on the leaching percentage of the metals from the anode slime under the following experimental conditions: temperature, 95 °C; pulp density, 10 g/L; stirring speed, 200 rpm; particle size, 100 μm; HNO$_3$ concentration, 6 M. This figure indicates that Cu, Ag, Ni, and Zn were completely dissolved into the nitric acid solution. However, the leaching percentage of all metals remained the same and was not affected as the reaction time increased from 1 to 8 h. In addition, no Sn and Au were dissolved in the range of reaction time employed here.

### 3.3. Comparison of different acids

Sulfuric acid is a good reagent for leaching and has a strong oxidizing power at high temperature. Therefore, sulfuric acid was used for leaching of the anode slime. In Table 3, a comparison of the leaching percentage of metals in HCl, H$_2$SO$_4$ and HNO$_3$ solution was made at the same experimental conditions: temperature, 75°C; reaction time, 2 h; pulp density, 10 g/L; stirring speed, 200 rpm; particle size, 100 μm; HCl concentration, 4 M; HNO$_3$ concentration, 4 M; H$_2$SO$_4$ concentration, 4 M. It is seen in Table 3 that Au cannot be dissolved into HCl, H$_2$SO$_4$ and HNO$_3$ solution. Meanwhile, the leaching percentage of Cu was relatively consistent for the three inorganic acids. Sn was completely dissolved into HCl solution from the anode slime under the current work. However, Sn cannot be dissolved into the nitric acid solution owing to the formation of SnO$_2$·H$_2$O and only 34.7% of Sn was dissolved into H$_2$SO$_4$ solution. In contrast, in HCl solution, Cu, Ni, Zn and Sn could be

![Fig. 3. Effect of reaction time on the leaching of metals in the anode slime by 6 M HNO$_3$ solution. (temperature, 95°C; pulp density, 10 g/L; stirring rate, 200 rpm; particle size, 100 μm)](image)

| Acids    | Cu   | Au   | Ag   | Ni   | Zn   | Sn   |
|----------|------|------|------|------|------|------|
| HCl      | 99.38| 0    | 20.62| 100  | 100  | 100  |
| H$_2$SO$_4$ | 100  | 0    | 56.44| 34.69| 100  | 100  |
| HNO$_3$  | 97.98| 0    | 19.4 | 0    | 100  | 100  |

Table 2. Effect of HNO$_3$ concentration on the leaching of metals. (temperature, 75°C; reaction time, 2 h; pulp density, 10 g/L; stirring speed, 200 rpm; particle size, 100 μm)

| HNO$_3$, M | Leaching percentage, % |
|------------|------------------------|
| Cu | Au | Ag | Ni | Zn | Sn |
| 4 | 97.98 | 0 | 19.4 | 100 | 100 | 0 |
| 6 | 100 | 0 | 100 | 100 | 100 | 0 |

Table 3. Effect of the nature of an inorganic acid on the leaching of the metals. (temperature, 75°C; reaction time, 2 h; pulp density, 10 g/L; stirring rate, 200 rpm; particle size, 100 μm; HNO$_3$ concentration, 4 M; H$_2$SO$_4$ concentration, 4 M; HCl concentration, 4 M)
completely dissolved. In addition, a small amount of Ag was dissolved into the solution by the formation of AgCl$_2^–$.

### 3.4. Leaching with thiourea

Since thiourea is unstable in alkaline solution, the experiments should be performed in acidic solution and thus the experiments were done in sulfuric acid solution. Table 4 displays the effect of thiourea concentration on the leaching of the metals at the following conditions: H$_2$SO$_4$ concentration, 4 M; pulp density, 10 g/L; reaction temperature, 25°C; stirring speed, 200 rpm; particle size, 100 μm; reaction time, 2 h; H$_2$O$_2$ concentration, 0.3 M. The Au and Ag in the anode slime were completely dissolved by thiourea solution and the leaching reactions can be represented as Eqs. (7) ~ (9).

\[
\text{Au} + 2\text{CS(NH}_2\text{)}_2 = 4\text{Au[CS(NH}_2\text{)]}_2 + e^- \quad (7)
\]

\[
2\text{SC(NH}_2\text{)}_2 + \text{H}_2\text{O} = [\text{SC(NH}_3\text{)}_2]^+ + 2\text{H}_2\text{O} \quad (8)
\]

\[
\text{Ag} + 3\text{CS(NH}_2\text{)}_2 = \text{Ag[CS(NH}_2\text{)]}_3 + \quad (9)
\]

Except Cu, all the metals in the anode slime were dissolved in the mixture of thiourea and sulfuric acid solution. After keeping the leaching solution for several hours, the formation of elemental sulfur was observed in the solution, indicating that some oxidation-reduction reaction would continuously occur and there should be aging effect on the leaching solution.$^{18}$ The formation of sulfur from thiourea solution can be represented as

\[
[\text{SC(NH}_3\text{)}_2]^2 = \text{CS(NH}_2\text{)}_2 + \text{NH}_2\text{CN} + \text{S} \quad (10)
\]

### Table 4. Effect of thiourea concentration on the leaching of metals. (H$_2$SO$_4$, 4 M; pulp density, 10 g/L; temperature, 25°C; stirring speed, 200 rpm; particle size, 100 μm; reaction time, 2 h)

| [CS(NH$_2$)$_2$] g/L | Cu    | Au   | Ag   | Ni   | Zn   | Sn   |
|---------------------|-------|------|------|------|------|------|
| 10                  | 95.77 | 79.67| 100  | 100  | 100  | 61.94|
| 20                  | 95.50 | 100  | 100  | 100  | 100  | 97.75|
| 30                  | 96.83 | 63.49| 100  | 100  | 100  | 100  |
| 40                  | 91.37 | 100  | 100  | 100  | 100  | 100  |
| 50                  | 94.97 | 100  | 100  | 100  | 100  | 100  |

3.5. Leaching with sodium thiosulfate

The effect of sodium thiosulfate concentration on the leaching of anode slime from alkaline solution was investigated at the experimental conditions: pulp density, 10 g/L; temperature, 95°C; stirring speed, 200 rpm; particle size, 100 μm; reaction time, 2 h; H$_2$O$_2$ concentration, 0.3 M. In the presence of oxidants, the reaction of gold and silver with thiosulfate can be expressed as Eqs. (12) and (13). Table 5 presents the leaching percentage of all the metals in the thiosulfate solution. In the presence of oxygen, parts of S$_2$O$_3^{2−}$ would decompose into S$_3$O$_6^{2−}$ and SO$_4^{2−}$.$^7$ S$_3$O$_6^{2−}$ is generally stable in solution in the absence of ammonia and has a negative effect on the leaching of Au. Therefore, Au cannot be completely dissolved into the solution. Moreover, the leaching percentage of Ag was low owing to the possibility of the formation of the Ag$_2$S in the absence of ammonia$^{2,34}$. Meanwhile, high content of Cu brings about more consumption of thiosulfate.

\[
4\text{Au} + 8\text{S}_2\text{O}_3^{2−} + 2\text{O}_2 + 2\text{H}_2\text{O} = 4\text{Au(S}_2\text{O}_3)_2^{3−} + 4\text{OH}^- \quad (12)
\]

\[
2\text{Ag} + 0.5\text{O}_2 + 4\text{S}_2\text{O}_3^{2−} + \text{H}_2\text{O} = 2\text{Ag(S}_2\text{O}_3)_2^{3−} + 2\text{OH}^- \quad (13)
\]

### Table 5. Effect of thiosulfate concentration on the leaching of metals. (pulp density, 10 g/L; temperature, 95°C; stirring speed, 200 rpm; particle size, 100 μm; reaction time, 2 h)

| [Na$_2$S$_2$O$_3$] g/L | Leaching percentage, % |
|-----------------------|------------------------|
| Cu    | Ag | Ni | Zn | Sn | Au |
| 10 | 2.96 | 3.9 | 0 | 0 | 100 | 0 |
| 20 | 6.27 | 22.52 | 0 | 100 | 100 | 0 |
| 30 | 3.02 | 0 | 0 | 100 | 100 | 0 |
| 40 | 24.15 | 100 | 0 | 100 | 100 | 0 |
| 50 | 46.35 | 60.68 | 0 | 100 | 6.10 | 0 |

### 4. Conclusion

In order to develop a hydrometallurgical process to
recover gold and silver from anode slime containing copper, tin, nickel and zinc, leaching experiments were done at atmospheric pressure by employing several inorganic acids (HCl, HNO₃ and H₂SO₄) together with thiourea and thiosulfate solution. First, no gold was dissolved into the above inorganic acids in the absence of any oxidizing agents. Tin was not dissolved at all into the nitric acid solution. When the concentration of inorganic acid was the same, the highest leaching percentage of silver was obtained by sulfuric acid but it was difficult to dissolve all the silver present in the anode slime. In the leaching with HCl, the leaching percentage of silver increased with the increase of HCl concentration owing to the formation of AgCl₂⁻. Except tin, copper, nickel and zinc was almost dissolved by the above inorganic acids at 75°C. Most of the gold and silver was dissolved into the mixture of sulfuric acid and thiourea solution. However, the formation of sulfur was observed after keeping the mixture for several days, indicating the instability of this mixture. Thiosulfate could dissolve some silver from the anode slime but no gold was dissolved by this agent. Moreover, the high content of copper in the anode slime would lead to the high consumption of thiosulfate, which makes the employment of this reagent less attractive.

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