Oxidation leaching of tin anode slime by controlling potential

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Abstract. The selective leaching of tin anode slime was extremely important in the process of the recovery of tin anode slime. With the successful leaching, the efficiency of value metals recycling was elevated obviously. Hence, the pretreatment of tin anode slime was studied in this paper by using the environmental technology and hydrometallurgical approach to achieve the goal of valuable metal recovery from traditional waste tin anode slime. It is worth noting that there are a large amount of value metals including Sn, Sb, Bi, Cu and Ag in the tin anode slime. The results indicated the optimal conditions of leaching process are 3.0 M HCl with 0.1M NaClO3 and liquid-solid mass ratio of 30 ml/g in 30 minutes at 45 degrees of Celsius and about Sn 85.32%, Sb 96.93%, Bi 97.63%. Meanwhile, silver and copper were all leached out by HCl solution in the leaching of tin anode slime.

1. Introduction
Tin anode slime, the insoluble by-product which is deposited at the bottom of electrolytic refining tank during electrolytic refining belongs to a curial secondary resource owing to the presence of valuable metals and metalloids in the tin anode slime, accounting for Ag, Bi, Cu, Si, Sn, Sb and Pb. Therefore, the research trend will be focus on an effective and environmentally friendly process to recovery tin anode slime [1]. However, the content of antimony markedly declines the amount of tin recycling by the reason of new Stistaite structure combined with the antimony and the tin. Hence, the researchers should pay more attention to recover them due to the great quantity of value metals in the tin anode slime. The main metals in tin anode slime are tin, bismuth, antimony; these metals are valuable metals and widely used in the electronics industry, materials industry and pharmaceutical industry. Additionally, bismuth and antimony have lots of innovative invention gradually.
According to the report of the US Geological Survey [6], not only tin but also bismuth and antimony has low rate of secondary resources; consequently, in order to avoid a lot of industrial waste and environmental issues, using environmental technology such as recycling are important and necessary.

The treatment process of anode slime includes the following sequences: pre-treatment, enriching precious metal(concentration), refining. Particularly, pre-treatment is the most vital to dominate the whole process, which contains the following methods: sulfation-roasting-leaching process[7-8], oxidation-roasting-leaching process[9], and alkaline pressure oxidative leaching process[10-12]. In sulfation-roasting-leaching process states that the thermodynamic calculation and trend analysis of sulfidation roasting process for tin anode slime, focusing on the sulfurized selection; In oxidation-roasting-leaching process, studied at recovery of lead and bismuth by means of beneficiation-metallurgy combination process. Nevertheless, high energy consumption, equipment corrosion and serious environmental pollution limit the recovery efficiency with current methods although there are lots of research on separation of value metals. Besides, with the complex component of tin anode slime and increasingly environmental protection awareness, it is essential to figure out an economical and eco-friendly approach to pretreat tin anode slime, especially for the uncomplicated pretreatment.

The selective leaching of tin anode slime is an important method in hydrometallurgical processes. Nowadays, there are few relevant reports to deal with the tin anode slime, and the leaching agent such as sulfuric acid [13], hydrochloric acid [14], nitrous acid [15], and alkaline fusion-leaching [16] are mentioned in the process. On the other hand, several reports on the pretreatment of copper anode slime has been studied in recent years, which added hydrogen peroxide as an oxidant to dissolve value metals. The mixed solution of NaOH and low carbon polyhydric alcohol was also arranged to dissolve base metals from copper slime. But it is relatively difficult to recover metals from the leaching solution [17].

Owing to the lack of reports on acid-leaching of tin anode slime, the research should focus on finding the most suitable acid concentration, reaction temperature, liquid-solid mass ratio and apposite oxidant added in the solution. The goal of this study is focus on researches the selective leaching condition about valuable metals from tin anode slime. Consequently, the used of different parameters exactly discusses acid leaching efficiency with tin, antimony, bismuth and other metals. The final solution and solid products were analyzed by ICP-OES and XRD for confirming the results. In this study, we will focus on the selective leaching process. In this process, the tin, antimony and bismuth has better leaching efficiency, compared with other papers.

2. Experiment

2.1. Materials

The sample of tin anode slime used in the experiment was provided from a technology materials company. The original tin anode slime was washed with dilute nitric acid and dried at 100 °C, and then sieved with 200 mesh(0.074mm) to eliminate large particle. The content of dried tin anode slime was shown in Table 1 by inductively coupled plasma
optical emission spectrometry (ICP-OES, Varian, Vista-MPX) with dissolving in aqua regia and hydrofluoric acid (3:1:1 HCl: HNO3: HF ratio) at liquid-solid mass ratio of 1:50, 80 °C for 3 hours. Besides, the whole chemical reagents of HCl, HNO3 and H2SO4 are of analytical grade, and so are hydrogen peroxide and Sodium chlorate.

### Table 1. The chemical compositions of tin anode slime.

| Composition | Sn  | Sb  | Bi  | Cu  | Si  | Ag  |
|-------------|-----|-----|-----|-----|-----|-----|
| Wt. %       | 52  | 10  | 7.88| 16.74| 8.8 | 0.64|

2.2. Equipment

The materials were analysed by energy-dispersive X-ray spectroscopy (EDS; XFlash6110, Bruker, Billerica, MA, USA), X-ray diffraction (XRD; DX-2700, Dangdong City, Liaoning, China), scanning electron microscopy (SEM; S-3000N, Hitachi, Tokyo, Japan), X-ray fluorescence analyser (XRF, Spectro XEPOS), and inductively coupled plasma optical emission spectrometry (ICP-OES; Varian, Vista-MPX, PerkinElmer, Waltham, MA, USA).

2.3. Experiment procedures

2.3.1. Selective Leaching

Selective Leaching procedures were carried out in standard laboratory leaching equipment. The tin anode slime was leached by three kinds of chemical reagents as acids like nitric acid, sulfuric acid, and hydrochloric acid. Furthermore, the leaching parameters such as acid concentration, reaction temperature, reaction time and liquid-solid mass ratio were investigated. Leaching efficiency were calculated according to Eq.1. Acidity was set from 0.25 to 8 M (mole/L) with liquid-solid ratio from 10 to 50 (g/mL). The effect of temperature was set from 20 °C to 50 °C and the reaction time was set from 2 mins to 1024 mins to get optimal selective leaching efficiency of tin anode slime.

where \( X_A \) is leaching rate, \( n_1 \) is the actual quantity of metal leaching, \( n_2 \) is the metal quantity of raw material

\[
X_A = \left( \frac{n_1}{n_2} \right) \times 100\% \quad (1)
\]

2.3.2. Selective leaching through different oxidant

The Metal-H2O systems were used as a guide in pH and Eh values of the leaching situation. Figure. 1 gives[20] the Eh-pH diagrams of system Sn-O-H, Sb-O-H and Bi-O-H. Note that the concentrations of related metallic ions are fixed at 1 M, and both of partial pressures of oxygen and hydrogen are at the standard atmospheric pressure of 10^5 Pa. Figure. 1(a) indicates that increasing in potential would lead to the conversion of SbO\(^{\text{II}}\), which can exist soluble species in the leaching solution. Based on our knowledge, it is crucial to enhance the redox potential, hence, the research would focus on adding the suitable oxidant to increase the leaching efficiency of the value metals in tin anode slime.
3. Results and discussion

3.1. Analysis methods

The raw material was analyzed by various instruments. As the Table 1 shown, Sn, Sb, Bi, Cu, Ag, Si and the low contents of Pb and Ag were analyzed by inductively coupled plasma optical emission spectrometry (ICP-OES, Varian, Vista-MPX) with dissolving in aqua regia and hydrofluoric acid. In addition, the microstructure analysis by scanning electronic microscope (SEM) and the energy dispersive X-ray spectrometry (EDS) image of tin anode slime were shown in the Figure. 2. The crystal symbiosis of the tin and the antimony was confirmed in the Figure. 2 and Figure. 3. The tin and antimony would be intergrowth in heavy mineral concentrates from placer deposits [18-21].

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Figure 1. Eh-pH diagrams of system, (a) Sb-O-H, (b) Sn-O-H and (c) Bi-O-H

Figure 2. (a) Microstructure analysis of tin anode slime by scanning electron microscope (SEM); (b) Characteristic Analysis of tin anode slime by energy dispersive X-ray spectrometry (EDS)
3.2. Effect of H₂SO₄, HCl, and HNO₃ leaching

This section discussed the leaching efficiency of tin anode slime by sulfuric acid, hydrochloric acid and nitric acid respectively. The pre-treated tin anode slime was reacted with three hours with concentration of 5M (mole/L) at liquid-solid ratio 50 (ml/g) at 25°C. Requiring the analysis of leaching efficiency in three kinds of acid reagents by ICP-OES.

As Table 2. shown, three value metals, antimony, bismuth and tin, were all reacted with hydrochloric acid merely. Therefore, hydrochloric acid was selected as leaching reagent. However, the leaching efficiency of tin anode slime was still low for the reason of the low solubility of antimony in leaching solution.
Table 2. The leaching efficiency of tin anode slime by sulfuric acid, hydrochloric acid and nitric acid with concentration of 5M at liquid-solid ratio 50 at 25°C.

| Value Metals | Sn  | Sb  | Bi  | Cu  | Ag  |
|--------------|-----|-----|-----|-----|-----|
| Leaching Efficiency in H2SO4 (%) | 25.3 | 38.3 | 0.02 | 0.03 | 0.01 |
| Leaching Efficiency in HCl (%) | 73.6 | 21.7 | 60.3 | 49  | 20.6 |
| Leaching Efficiency HNO3 (%) | 3.07 | 10  | 67.8 | 42.5 | 95.5 |

3.3. Elevating the Redox potential through oxidant
When the concentration of HCl was varied from 0.25 to 8 M for liquid-solid ratio of 50 at 25°C, Sn and Bi were extraordinary increased in the condition of HCl up to 3.0M instead of Sb, the leaching percentage of Sb kept constant at 21.12%. The results indicated that antimony did not convert into the soluble species like SbO$^{+1}$, therefore, Redox potential played a vital role in the acid leaching of tin anode slime.

Figure 5. Effect of leaching percentage on HCl. L/S = 50 at 25°C
Figure 6. Effect of adding hydrogen peroxide as oxidant. L/S = 50, at 25°C

3.3.1. Effect of adding hydrogen peroxide as oxidant
The effect of H$_2$O$_2$ was investigated by using HCl with liquid-solid mass ratio of 50 for three hours at 25°C as shown in Figure. 6. The results observed that adding H$_2$O$_2$(10% in solution) was effective in tin anode slime leaching process. With the reaction time increased, tin and bismuth were dissolved 80.17% and 89.86% in the leaching solution respectively. However, the leaching efficiency of antimony would deeply decrease as antimony first reacted with oxide and then antimony oxide was reacted with hydrogen peroxide for generating the new species of antimony pentoxide, which belonged to a kind of colloidal dispersion and was insoluble in liquor. The equation of chemical reaction was shown in Eq. 2 and Eq. 3 [22].
3.3.2. Effect of adding Sodium chlorate as oxidant. As Figure 7 shown, the leaching percentage of antimony and bismuth in tin anode slime were all apparently elevated by HCl with 0.1M Sodium chlorate, liquid-solid mass ratio of 50 and 500 rpm for three hours at 25°C. The leaching efficiency of Sn and Sb significantly increased as HCl concentration was increased from 2.0 to 3.0 M. Thereafter, it tended to slowly increase and then keeping constant when the concentration was higher than 3.0M. To obtain good leaching efficiency both in Sn, Sb and Bi, the concentration of HCl was therefore chosen as 3.0 M, and all further experiments were carried out at this concentration and sodium chlorate as oxidant to increase leaching percentage.

3.3.3. Liquid-solid (L/S) ratio. Liquid-solid ratio (L/S) is an important factor on the leaching of Sn, Sb and Bi. The effect of L/S was therefore investigated by using 3.0 M HCl with 0.1M Sodium chlorate and 500 rpm for three hours at 25°C, and the results are presented in Figure 8. As shown in the graph, both the leaching percentage of Sn, Sb and Bi gradually elevated when the L/S was increased from 20 to 30 mL/g. On the other hand, as the L/S was more than 30 mL/g, leaching rate of Sn and Sb kept constant or having no significant increased. Consequently, the optimal L/S was considered as 30 mL/g.

3.3.4. Leaching temperature. Temperature is the correlation parameter which is related to leaching rate. The higher temperature could raise the speed of molecular motion and enlarge the energy of the particle collision. To investigate the effect of leaching temperature, a series of experiments were conducted from 25 to 85 °C, and the results are shown in Figure 9. It indicates that increasing temperature can contribute to the leaching rate. According to the results obtained, the optimal temperature was about 45 °C, at which

\[
4\text{Sb} + 3\text{O}_2 \rightarrow 2\text{Sb}_2\text{O}_3
\]

\[
2\text{Sb}_2\text{O}_3 + 4\text{H}_2\text{O} \rightarrow 2\text{Sb}_2\text{O}_5 + 4\text{H}_2\text{O}
\]

**Figure 7.** Effect of adding hydrogen peroxide as oxidant. L/S = 50, at 25 o C with [NaClO3] = 0.1M

**Figure 8.** Effect of Liquid-Solid (L/S) ratio. [HCl] = 3M, at 25 o C with [NaClO3] = 0.1M
the leaching rates of Sn, Sb and Bi were 84.79%, 94.89% and 95.3%, respectively. All further experiments were carried out at 45 °C accurately.

Figure 9. Effect of leaching temperature [HCl] = 3M, L/S = 30, with [NaClO3] = 0.1M
Figure 10. Effect of reaction time [HCl] = 3M, L/S = 30, at 45 °C with [NaClO3] = 0.1M

3.3.5. reaction time. Figure 10 shows the effect of leaching rate with reaction time utilizing 3.0M HCl with liquid-solid ratio 30(ml/g) at 45 °C. The leaching efficiency of tin anode slime rises dramatically from 16 minutes to 32 minutes. The reason is that with the increase of leaching time, more and more surface of unreacted particle core would react with HCl. The leaching efficiency of tin anode slime was in balance and stopped increasing after about 32 min. Consequently, the optimal leaching time was carried out about 32 minutes.

4. Conclusions
This study was based on conducive to environmental technology and issues by hydrometallurgy methods. Besides, the tin anode slime was analyzed about containing 52.17% Sn, 16.74% Cu, 10.89% Sb, 8.8% Si, 7.88% Bi, and 0.64% Ag by characteristic analysis. Based on thermodynamic calculation and experiments results, confirming that although hydrogen peroxide was the most common oxidant in the world, there was by-products which deeply reduced the leaching percentage of antimony during the pretreatment leaching of tin anode slime the optimal conditions of leaching process are 3.0 M HCl with 0.1M NaClO3 and liquid-solid mass ratio of 30 ml/g in 30mins at 45 degrees of Celsius and about Sn 85.32%, Sb 96.93%, Bi 97.63%. Meanwhile, silver and copper were all leached into the HCl solution in the pretreatment of tin anode slime. Compared with previous studies, selectively separate tin, antimony and bismuth from tin anode slime by controlling Oxidation-Reduction Potential was the most efficient method of Sn, Sb, Bi recycling.

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