Recovery of tin from copper dross by acid leaching

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Abstract. Copper dross (CD) is a waste product formed during copper doping where sulphur was added to the tin metal during refining process to remove copper in the form of copper sulphide. CD was found to contain significant amount of tin and other valuable metal such as copper that could be trapped during copper doping process. The main objective of this work is to assess the potential of CD as a secondary resource for tin product and the applicability of hydrometallurgical process to extract tin and copper. Two main parts involves in this work are CD characterization and recovery of tin by acid leaching. From elemental composition analysis by XRF, in CD sample, amount of SnO₂ present is about 63% followed by SO₃ with 14%, Fe₂O₃ is 9% and CuO with 2.5%. Cassiterite and magnetite is the main phases found by XRD analysis. From the leaching study, it was found that almost 60% of tin has been dissolved in acid solution at condition of 80 °C, 2 M HCl with 8 hours leaching time.

1 Introduction

The increasing demand and resource depletion for tin in the world has required intensive studies for the recovery and extraction of this metal from different source. There are more than 50 kinds of tin bearing minerals on Earth; among them, cassiterite (SnO₂) is the only natural mineral from which tin metal can be economically extracted. According to the Minerals Commodity Summaries 2017 issued by Geological Survey of the United States, the proven global reserve of tin resources are 4.7 Mts, and they are mainly concentrated in China (110 kt), Indonesia (80 kt), Brazil (70 kt) and Malaysia (25 kt). Tin reserves was reported to decrease sharply from 9.6 Mts down to 4.7 Mts from the year 1999 to 2016. Since tin mine production cannot meet the demand for global tin consumption, tin-bearing secondary resources become important alternative sources for tin production. During the traditional tin extraction process, tin bearing by-products are generated with different tin contents which includes tin-bearing tailing, tin middlings, tin slag, hardhead and tin anode slime. In addition tin bearing solid waste, such as tin plates, tin alloys and electronic waste (E-waste) are also recyclable [1].

In this case, copper dross (CD) is the example of by-products from tin processing that is underutilize as when the copper dross were produced from the copper doping in refining process, it is treated as a waste or by-product. The product of CD has become a problem for the industry to store it and it also does not yield a convincing profit. Some of other industries

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will be interested to buy the copper dross at very low price. For that reason, the industry has made the effort to utilize the presence of copper dross but could not make a clear methodology in searching for the suitable parameters to extract the copper and also tin from the copper dross. There was also still lack of research or study on tin recovery from CD that has been reported particularly.

Apart from that, there are few published works on extraction of copper from slag [2], recovery of tin from tin soldering dross [3] and extraction of zinc and copper from brass slag [4]. All of these published works were using either hydrometallurgical or pyrometallurgical process for metal extraction from slag or dross. However, there are limitation where some of the metal oxides that formed during roasting or refining process will have resistant to the acid/lixiviants that most commonly used for hydrometallurgical treatment [2]. For that reason, an extensive work has to be done on development of tin extraction process from secondary resources that has been produced by tin industry particularly in Malaysia. In order to study the feasibility of tin recovery from CD, a few stage of research work has to be implemented such as characterization of CD, statistical evaluation for process optimization and development of mineral/metal processing circuit. In this work, the preliminary work has been initiated with characterization and leaching studied.

2 Experimental Work

2.1 Sample Preparation

10 kg of copper dross (CD) received from Malaysian Smelting Corporation (MSC) were used in this work. The cone and quartering method was performed on received sample until achieved the representative sample size. This representative sample then were crushed and ground to reduce the particle size until achieved 80% passing 75μm. Then the samples were divided into few sub sample for characterization analysis and leaching experiment.

2.2 Characterization Studies

The representative samples have been undergo characterization analysis such as X-Ray Diffraction (XRD) and X-Ray Fluorescence (XRF). The objective of characterization is to understand the composition of sample, percentage of elements, physical and chemical characteristics of the sample.

2.3 Leaching study

For leaching study, hydrochloric acid (HCl) as leaching reagents and millipore water was used throughout the experiments. Batch leaching test was carried out using 500 cm³ glass reactor provided with a reflux condenser and magnetic stirrer. The desired volume of HCl of the required concentration was poured in the reactor and about 10 g of CD was added. The reactor was heated to the desired temperature using a thermostatically controlled water bath. The leachate were taken from the reactor using syringe at various time intervals and filtered through Whatman Cellulose Nitrate membrane filters with pore size of 0.45 μm. Leachate samples was analysed using Inductively coupled plasma atomic emission spectroscopy (ICP-AES) to determine tin content in solution.
3 Results and Discussion

3.1 Chemical compositions and Phases

Chemical analysis and X-ray diffraction data for CD sample are shown in Table 1 and Fig. 1 respectively. From Table 1 it is revealed that SnO$_2$ is the major component of the dross (62.7%) followed by SO$_3$ (14.3%), Fe$_2$O$_3$ (9.4%), As$_2$O$_3$ (6.01%) and CuO (2.5%). XRD characterization of CD indicated that the major crystalline phases are cassiterite (SnO$_2$), quarzt (SiO$_2$), corundum (Al$_2$O$_3$), chalcocite (CuS) and magnetite (Fe$_3$O$_4$). Due to complexity of the materials, thorough XRD analysis should be done to identify each of mineral phases that present in the materials.

| Composition | Mass (%) |
|-------------|----------|
| SnO$_2$     | 62.7     |
| SO$_3$      | 14.3     |
| Fe$_2$O$_3$ | 9.4      |
| As$_2$O$_3$ | 6.01     |
| CuO         | 2.5      |
| SiO$_2$     | 2.1      |
| Al$_2$O$_3$ | 1.7      |
| MnO         | 0.02     |
| Co$_3$O$_4$ | 0.32     |
| NiO         | 0.033    |
| ZnO         | 0.12     |

Table 1. Chemical composition of CD sample at -75 μm before leaching.

Fig. 1. X-ray diffractogram for CD sample.

The morphological surface of CD was also observed under SEM and analyzed using EDX as shown in Fig. 2. Different morphologies were observed on the sample revealed that the sample contain different types of minerals due to different shapes and variation of brightness. EDX analysis indicated that Sn and sulphur was the main elements consists in the samples.
For the tin recovery from CD sample, leaching method using HCl as a leaching reagent has been accomplished. Parameters such as temperature (60 – 80°C), acid concentration (1.0 M -2M), stirring rate (350rpm) and leaching time (8 hours) was studied. It can be observed from the results obtained in Table 2, the recovery of tin depends strongly on acid concentration and leaching temperature. The highest recovery of tin (63%) achieved at 80°C in 2.0 M HCl. SnO₂ is reported to be refractory materials, therefore it is not soluble in acid or in bases [3]. This is explained why the recovery of Sn was low even at high leaching temperature. Therefore, CD maybe need to undergo pre-treatment process to convert insoluble SnO₂ to soluble Sn.

Table 2. Sn recovery (%) from selected leaching experiments.

| Exp | T/(°C) | [HCl]/(M) | Stirring rate(rpm) | Leaching Time (hours) | Sn Recovery (%) |
|-----|--------|-----------|--------------------|-----------------------|----------------|
| 1   | 60     | 1.0       | 350                | 8                     | 13.56          |
| 2   | 60     | 2.0       | 350                | 8                     | 50.20          |
| 3   | 70     | 1.5       | 350                | 8                     | 50.21          |
| 4   | 80     | 1.0       | 350                | 8                     | 18.08          |
| 5   | 80     | 2.0       | 350                | 8                     | 63.03          |
3.3 Proposed process flowsheet

A simplified process flowsheet for the recovery of tin from copper dross using roasting and acid leaching process is shown in Fig. 3. Copper dross sample can produced two different types of product which are tin oxide powder and tin metal through precipitation and electrowinning process. This work need further studies on solubility of Sn from CD in acid solution and also separation process.

![Diagram of process flowsheet](image)

**Fig.3.** Proposed process flowsheet for SnO$_2$ and Sn metal product.

4 Conclusion

Copper dross is highly potential to become a secondary resources for tin industry. With significant amount of tin in CD samples it is crucial to recover tin from the waste product. It is also promote sustainable route for production of tin at the same time reduce the waste stockpiles. Successful extraction of tin will upgrade the application of this by-product and value added to the industry.

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