Selective Extraction Of Silver From Semiconductor Waste

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ABSTRACT

Semiconductor waste can cause a serious problem in term of storage and pollution since it contains high concentration of heavy metals. One possible alternative to treat this waste is to recover the metals especially precious metals such as silver. In this wok, an attempt was made to recover the silver from semiconductor waste obtained from local semiconductor company using leaching and liquid-liquid extraction processes. Characteristics of the waste was investigated initially and found that it contains 21.57 % of water and 14.73 % of organic matter with the density of 2.87 gcm^{-3}. 7.55 % (w/w) of silver was found in the waste and existed mostly in the form of Ag and AgCl. In the leaching experiment, it was found that HCl gives better silver leaching. The extent of silver leaching increases with increasing the chloride concentration which can be achieved by either increasing the HCl concentration or addition of high NaCl concentration. In the extraction studies, dithizone is capable to extract silver selectively at wide range of pH. It was also found that at pH higher than 6, copper and iron precipitation were occurred.

1. INTRODUCTION

Current emphasis on industrialization leads to the development of silver use and increment of silver consumption. In 1916, the world's industrial consumption of silver as 900 MT has increased to 12,900 MT in 1971 [1]. Due to the high demand of silver consumption, the price of silver has increased substantially. For instance, the price from just under US$2 per troy ounce during 1971 went out to US$50 a troy ounce during early 1980 [2].

Semiconductor industry is one of the industries consumes high amount of silver for the plating purpose to improve the electric contact of semiconductor devices. In Malaysia, the performance of this industry during the period of 1988-1994 had been particularly remarkable, registering an output growth of 30.3 % per annum [3]. However, by the rapid growth of this industry, it generates huge amount of waste which cause the waste accumulation and pollution problems. Hayhurst [4] claimed that the production of one wafer generates 17,000 litres wastewater, 12 kg of chemical, 0.6 m^3 hazardous gases and 4 kg of hazardous solid waste. The growth rate of waste generation in electronic and semiconductor sectors in Malaysia was estimated at 5 % per annum out of the total industrial waste generation for the period from 1987-1992 [5]. This waste contains high content of heavy metals and other precious metals. One possible alternative to treat this waste is to recover the metals especially precious metals such as silver.

This paper will present the results of the study on semiconductor waste characterization followed by silver recovery processes which are leaching, precipitation and liquid-liquid extraction.

2. MATERIALS AND METHODS

A. Characterization

Sample of semiconductor waste was obtained from M-SMM Electronics Sdn. Bhd. The waste was heated at 100 °C to achieve constant weight for determination of water content. Whereas, the organic matter content was determined by heating the dry sample, first by means of soft flame and then raised to about 420 °C. Sample density was carried out by using multipycnometer (Quantachrome). In granulometric analysis, the screening process was performed by mechanical shaker (Pascall Engineering) with different sieve sizes (75, 150, 250, 500, 710, 1000 and 2380 μm). X-ray Fluorescence, XRF (Siemens SRS 303), Energy Dispersive X-ray Analysis, EDAX (Philips PV 9900) and X-ray Diffraction, XRD (Siemens Diffraktometer D5000) were used to determine the chemical composition of semiconductor waste.

B. Leaching experiment

The dry sample was added into 500 ml beaker at specified solid/liquid ratio containing 300 ml of leaching agent. The mixture was then stirred at 500 rpm using magnetic stirrer. During the stirring, 5 ml of leaching solution were withdrawn by pipette at selected time intervals. The samples were then separated by centrifuge (Hettich Zentrifuger EBA 12) at 4500 rpm for 15 minutes and the collected supernatants were used for metal determination by using Atomic Absorption Spectroscopy, AAS (Philips PU9200X). The leaching agents used were hydrochloric acid, HCl (37 %), nitric acid, HNO_3 (69.1 %) and sulfuric acid, H_2SO_4 (95-97 %).

C. Liquid-liquid extraction experiment

A series of leaching solution were prepared comprising of different pH that adjusted by NaOH (99.0 %) and HCl. The pHs of the solutions were measured by using pH meter (F series of Horiba). The solutions were then left for overnight and separated by centrifuge at 4500 rpm for 10 minutes. Only the supernatants were used as aqueous phase for liquid-liquid extraction experiment. 0.02 M of dithizone (97 %) in chloroform, $CHCl_3$ was used as organic phase. In the extraction experiment, 10 ml of each aqueous and organic phase were introduced into 50 ml separating funnel and shaken for 20 minutes. The mixture was left for one hour and aqueous phase was then taken for metal analysis using AAS. The metal contents of organic phase were determined by mass balance.

3. RESULTS AND DISCUSSION

A. Characterization

The sample of semiconductor waste was collected from wastewater treatment plant as metal hydroxide sludge which falls under classification no. N151 of the Environmental Quality (Scheduled Waste) Regulation 1989 [6]. The sample in the form of dry solid comprises of various sizes, green brownish and odorless. By continued excessive contact with the waste might cause dermal irritation [7]. The waste contains 21.57 % and 14.73 % of water and organic matter respectively. The particle density is found to be 2.87 gcm^{-3}. The organic matter in the waste might probably come from the organic solvent used for precleaning process in plating system. From the granulometric analysis (Table 1), it is found that most of the particle sizes distributed below 500 μm. In order to determine the chemical composition of the waste, a systematically study using XRF, EDAX ad XRD was carried out. The elemental composition of the waste which shown in Table 2 indicates that the silver content is 7.55 %. Most of the silver compounds exist in the form of Ag and AgCl which identified by XRD analysis.

Table 1: Particle size distribution of the semiconductor waste

Particle size (μm)	% w/w
0-75	16.03
75-150	19.91
150-250	16.69
250-500	19.19
500-710	8.80
710-1000	8.44
1000-2380	10.94

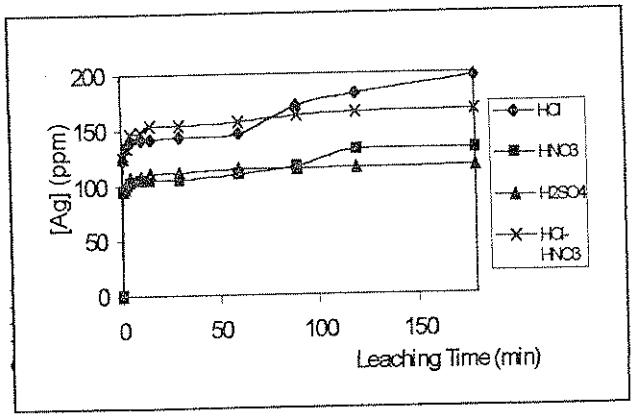
Table 2: Elemental compositions in semiconductor waste determined by EDAX.

Element	% w/w	Element	% w/w
O	21.05	S	1.37
Al	3.15	Cl	1.64
Si	0.19	Ag	7.55
Ca	3.44	P	2.07
Fe	5.15	Sn	17.83
Ni	1.59	Cu	34.96

B. Leaching Process

Effect of leaching agent types

Figure 1 shows the effect of leaching agent types on silver leaching from semiconductor-waste. It indicates that, at similar leaching agent concentration, HCl shows a highest silver leaching capacity followed by the HCl-HNO_3, HNO_3 and H_2SO_4. HCl provides free chloride ions which form the soluble silver chloro complexes with Ag and AgCl, and therefore increases the leaching of the silver from the waste. However, for the HNO_3 and H_2SO_4 medium, the leaching of the silver is limited. But, still the formation of $AgNO_3$ from HNO_3 medium gives a silver recovery value of 132 ppm.



Effect of chloride ions concentration

The presence of Cl^- ions is essentially to increase the solubility of AgCl. It is proved in the Figure 2 which shows the increment of leached silver concentration is proportional to the increasing of HCl concentration. The equilibrium constants involved in the progressive formation of silver chloro complexes are very low [8], therefore, it found that the silver leaching increases fairly gradually to about 2.0 M HCl, and thereafter rises rapidly with increasing acid concentration.

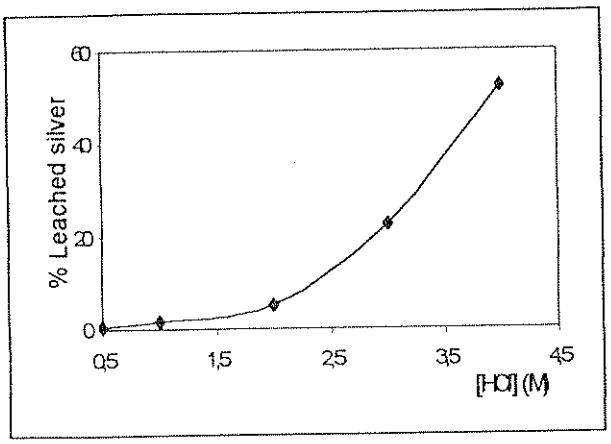


Figure 2: Effect of HCl concentration for silver leaching at 29.5 °C, 500 rpm and 1.5 g of solid in 200 ml HCl.

In industrial application, the high acid concentration is not preferable since it contributes to the corrosion problems. Therefore, the source of chloride ions is replaced by using NaCl. A similar observation of silver leaching behaviour with HCl system is also found for the HCl-NaCl system. This suggests that the basic mechanism of the formation of soluble silver chloro complexes is not influenced by the addition of cation from chloride salt, but only depends on chloride ion. Moreover, the use of HCl-NaCl system provides more selective leaching on silver compare to HCl alone. The 4.0 M HCl providing the percent leaching of Ag, Cu, Fe, Sn and Ca as 52.18 %, 51.77 %, 68.35 %, 23.58 % and 8.56 % respectively. The HCl-NaCl system, however, provides the 54.89 % of silver, 47.31 % of Cu, 44.66 % of Fe, 14.10 % of Sn and 0.60 % of Ca.

C. Precipitation process

Metal hydroxide sludge of semiconductor waste is generated during the pH adjustment in wastewater treatment plant. Therefore, the precipitation method is applicable to remove most of the heavy metal from leaching solution. And it is readily proved in the Figure 3 which shows that almost 100 % of Cu and Fe removal are achieved at pH more than 6. It is great appreciable that the silver removal is not much affected by the pH especially at pH 12 where the maximum solubility of silver chloro complex occurs. This is due to the existence of high stability of silver chloro complex in excessive chloride medium.

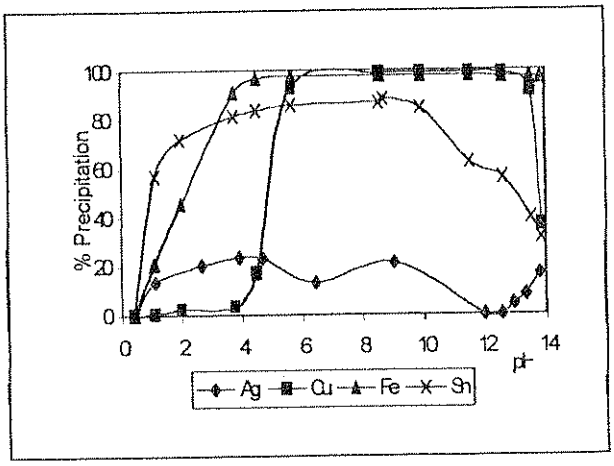


Figure 3: Metal precipitation at different pHs.

D. Liquid-liquid extraction process

Solvent extraction is widely used in metal recovery due to its high selectivity. In this study, dithizone was used as extractant which readily performs a very selective extraction for silver from leaching solution as shown in Figure 4. Based on HSAB principles [9], atom sulfur of dithizone should show great affinity to bind with soft acid such as silver. Therefore, as expected, the silver extraction achieves more than 90 % and leaves behind the unextracted hard acid, stanum in aqueous phase. The high silver extraction is also achieved even at very low pH. It is because the low pK_a value of dithizone (4.55) provides an acidic medium for silver extraction [10]. However, at pH lower than 1, the silver extraction is very low (should be high theoretically). This is observed most probably due to the coextracted soft acid, copper from the leaching solution. At this pH, the presence of high copper content (more than 800 ppm) competes with silver ion to react with the limited amount of dithizone.

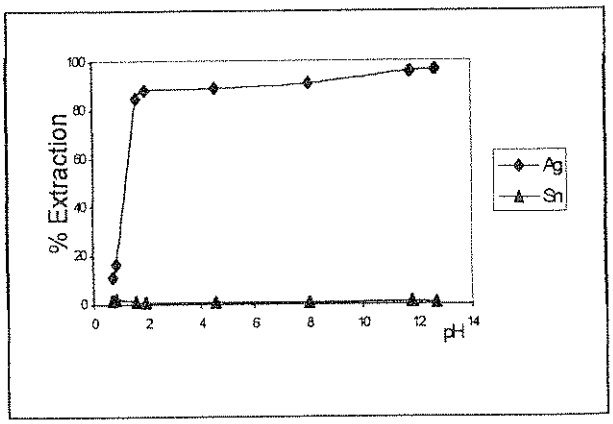


Figure 4: Silver and stanum extraction by 0.02 M dithizone in $CHCl_3$ at 29.5 °C and stirring speed of 250 rpm.

4. CONCLUSION

The semiconductor waste was characterized and found that the silver content is 7.55 % existed mostly in the form of Ag and AgCl. The silver leaching depends on leaching agent types and chloride ion concentration. The extent of silver precipitation is less than 20 % and does not depend on pH due to high stability of silver chloro complexes. The extraction using dithizone, however, capable to recover silver more than 90 %. Overall, the laboratory-scale of leaching, precipitation and liquid-liquid extraction procedures make it possible to recover silver more than 50 % from semiconductor waste.

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