Hydrometallurgy 157 (2015) 184–187

Contents lists available at ScienceDirect

Hydrometallurgy

journal homepage: www.elsevier.com/locate/hydromet

Technical note

Separation of Sn from waste Pb-free Sn–Ag–Cu solder in hydrochloric acid solution with ferric chloride

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ARTICLE INFO

Article history:
Received 22 May 2015
Received in revised form 5 August 2015
Accepted 20 August 2015
Available online 28 August 2015

Keywords:
Lead-free tin solder
Hydrochloric acid leaching
Ferric chloride
Recycling

ABSTRACT

A recycling process consisting of hydrochloric acid leaching with ferric chloride as an oxidant and cementation using Sn powder followed by solvent extraction was proposed to separate Sn from Pb-free solder. Leaching tests showed that the effect of HCl concentration on the leaching efficiency of Sn was negligible in 1.0–2.0 kmol · m^{-3} HCl, and the efficiency was lower at 0.5 kmol · m^{-3} HCl. Higher temperature yielded higher dissolution rates of Sn and Cu in the beginning of leaching; the leaching efficiencies of Sn and Cu increased to more than 99% within 90 min, but Ag was not detected, indicating that Ag could be separated successfully from Sn and Cu. When more than 1 g of Sn powder was added to 100 ml of leach solution containing 98.1 g · m^{-3} Cu, Cu ions could be removed from the leach solution by the cementation reaction. In the solvent extraction test using tri-butyl phosphate (TBP) diluted with kerosene, the extraction efficiency of Sn increased with increasing TBP volume ratio in the organic phase, and 99.9% of Sn was extracted selectively by 3-time solvent extraction with 15% TBP and 1:1 O/A ratio at 30 °C.

1. Introduction

Environmental regulations for the use of Pb in electric home appliances have been tightened due to its toxicity (Kwon et al., 2013; Tsunekawa et al., 2008). Lead-free solder using tin, silver, copper, bismuth, antimony, and zinc have been developed and are being increasingly used in place of tin/lead solders (Ma and Suhling, 2009). The Sn–Ag–Cu series covers approximately 70% of the reflowing Pb-free solder market (Ma and Suhling, 2009). Waste Pb-free solder is also being used as recycled solder bar after simple melting processes, which could cause air pollution due to the gas emission generated from combustion of organic flux in the Pb-free solder (Yoo et al., 2012).

Hydrometallurgical processes have been recognized as alternatives for recycling of waste Pb-free solder. Rhee et al. (1994) and Kim et al. (2012) investigated the leaching behavior of tin under basic conditions. Leaching behaviors of tin in nitric acid leaching tests using Pb-free solder (Yoo et al., 2012) and printed circuit boards (Mecucci and Scott, 2002) have also been studied. Although tin was separated readily from other metals by stannic acid precipitation, there are concerns regarding NOx emission in these processes.

A recycling process using HCl leaching with H_2O_2 was proposed to recover Sn, Ag, and Cu from waste Pb-free solder (Kim et al., 2014). In their study, H_2O_2 oxidized metals, causing AgCl precipitation separately from Sn and Cu ions; subsequently, Cu was removed by cementation with Sn powder in the process. This method does not result in NOx emission but H_2O_2 is unstable and consistently added to the process. The present study is aimed at developing a new recycling process using ferric ions as oxidants instead of H_2O_2 because it was expected that reusing of oxidant could be achieved by oxidizing ferrous ion, which is generated as reaction product in ferric ion leaching process. Cementation and solvent extraction tests were performed to separate Cu and Sn, respectively, from a ferric chloride leach solution. The effects of the parameters such as leaching temperature, HCl concentration, and agitation speed, on the leaching behavior of Sn, Ag, and Cu are discussed here.

2. Experimental

2.1. Materials

Waste Sn–Ag–Cu series Pb-free solder powder from fabricating processes of printed circuit boards for electronic home appliances was obtained from a recycling company in Korea. The solder was ground and dry-sieved with 150-μm (100 mesh) sieve after removing unwanted materials such as granular resin particles and papers. The remaining solder contained 90.2% Sn, 4.11% Ag, and 0.65% Cu as main components and 0.022% Bi and 0.021% Pb as minor components. In the previous

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http://dx.doi.org/10.1016/j.hydromet.2015.08.016
0304-386X/

study (Kim et al., 2014), the peaks of Sn and Ag_3Sn were observed in the XRD results. All the chemicals used in this study are of reagent-grade.

2.2. Leaching

Leaching tests were performed in a 500 cm^3 three-necked Pyrex glass reactor using a heating mantle to maintain temperature. The reactor was fitted with a stirrer and a reflux condenser to avoid solution loss at high temperatures. A 200 cm^3 of solution consisting of 0.5 kmol · m^{-3} ferric chloride and 0.5–2 kmol · m^{-3} HCl was placed in the reactor and allowed to reach thermal equilibrium (30–90 °C) at which point 3 g of solder powder was added and the solution was agitated at 200–600 rpm. During the tests, 3 cm^3 of the solution sample was withdrawn periodically at a desired time interval (15–90 min).

2.3. Cementation testing

Cementation tests for removing Cu from the leach solution were performed by adding Sn powder (Junsei Chemical Co. Ltd.; assay, min 99%). The leach liquor was obtained under the following leaching conditions: 400 rpm agitation speed, 1 kmol · m^{-3} HCl concentration, 0.5 kmol · m^{-3} $FeCl_3$ concentration, 50 °C temperature and 1.5% pulp density. The prepared leach solution contains 98.1 g · m^{-3} Cu. The tests were conducted in a 250 cm^3 Pyrex reactor, which was equipped with a water jacket for temperature control. Tin powders (0.1 to 2.0 g) were added to 100 cm^3 of the leach solution at 400 rpm and 30 °C.

2.4. Solvent extraction testing

Leach solutions with Sn and Fe concentrations of 14,970 g · m^{-3} and 26,688 g · m^{-3}, respectively, were collected from the cementation tests. An extractant was prepared by mixing tri-butyl phosphate (TBP) and kerosene and the volume ratios of TBP in the extractant were adjusted from 5% to 30%. The leach solution and extractant mixture was placed in a separatory funnel (O/A ratio = 1) and shaken mechanically for 30 min at 30 °C. The aqueous phase was then separated after settling the mixture for 6 h.

2.5. Analytical methods

The samples were filtered with a 0.45-μm membrane filter and then diluted with 5% HNO_3 solution for Cu and Ag analyses and 15% HCl solution for Sn analysis. Metal concentrations were then measured with atomic absorption spectrometry (AA7000, Shimadzu Co. Ltd.) and inductively coupled plasma-atomic emission spectrometry (ICP-AES, JY-38 plus, Jobin Yvon Ltd.).

3. Results and discussion

Ferric ion (Fe^{3+}) has been found to be a strong oxidant. The oxidation of Cu and Sn occurs according to the following reactions:

$$2Fe^{3+} + Cu = 2Fe^{2+} + Cu^{2+} \quad (1)$$

$$4Fe^{3+} + Sn = 4Fe^{2+} + Sn^{4+}. \quad (2)$$

The standard electrode potentials of Eqs. (1) and (2) have been calculated as 0.43 V and 0.76 V (Brett and Brett, 1993), respectively. Since only the reactants exist in the leaching system at the beginning of leaching, it could be expected that the reactions are spontaneous.

The leaching tests of waste Pb-free solder at agitation speeds in the range 200–600 rpm were carried out to examine the effect of liquid film boundary diffusion surrounding the solid particles on the leaching efficiency in 1 kmol · m^{-3} HCl with 0.5 kmol · m^{-3} Fe^{3+} at 50 °C. The leaching efficiencies of Sn and Cu are independent of the agitation speeds (data not shown). Therefore, in all subsequent leaching tests, a working agitation speed of 400 rpm was selected to ensure effective particle suspension in the solution.

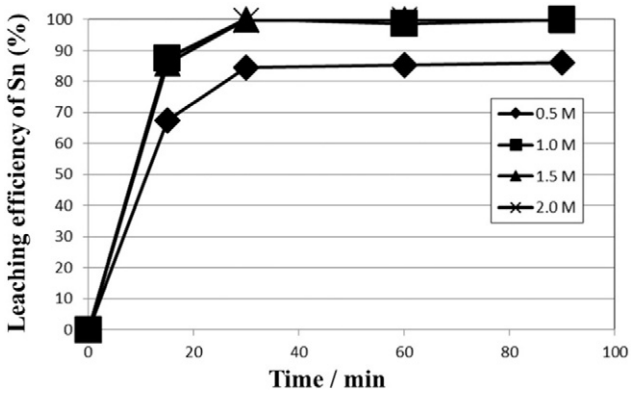

Fig. 1. Effect of hydrochloric acid concentration on the dissolution of Sn from the Pb-free solder at 400 rpm and 50 °C in HCl solution with 0.5 kmol · m^{-3} Fe^{3+} and 1.5% pulp density.

The solubility of tin is higher in hydrochloric acid than in sulfuric acid or nitric acid (Scott et al., 1997), and Harrison (1989) reported that tin(IV) makes complex ion with chloride ion. Therefore, the effect of hydrochloric acid concentration on the dissolution of Sn from the waste solder was investigated in HCl solution with 0.5 kmol · m^{-3} Fe^{3+} at 50 °C and 400 rpm and the results are shown in Fig. 1. The Sn concentration increased to more than 13,000 g · m^{-3} within 30 min in the 1–2 kmol · m^{-3} HCl solution and to 11,500 g · m^{-3} in the 0.5 kmol · m^{-3} HCl solution. Kim et al. (2014) reported that the lower leaching efficiency was observed in the lower HCl solution, and the results would indicate that the HCl concentration plays an important role in the Sn leaching. Fig. 2 shows the effect of temperature on the dissolution of Sn from the waste solder in 1 kmol · m^{-3} HCl solution with 0.5 kmol · m^{-3} Fe^{3+} at 30–90 °C. As can be seen, higher temperatures yielded higher dissolution rates of Sn from the solder in the beginning of leaching. Leaching efficiencies increased to more than 99% at all temperature except 30 °C after 60 min, and the difference in the efficiencies became negligible at 90 min. The ORP (vs Ag/AgCl) decreased from 683 mV to 46.6 mV at 30 min in the leaching test at 90 °C indicating the generation of Fe^{2+}.

In all leaching tests, Ag was not detected (data not shown) because ferric ion cannot oxidize silver and the solubility of AgCl is extremely low ($K_{sp} = 10^{-9.82}$) (Kim et al., 2014; Yoo et al., 2012). Fig. 3 shows that the copper concentration increased with increasing temperature in the beginning of leaching, and the leaching efficiencies increased to more than 99% within 90 min at all temperatures. These results indicate

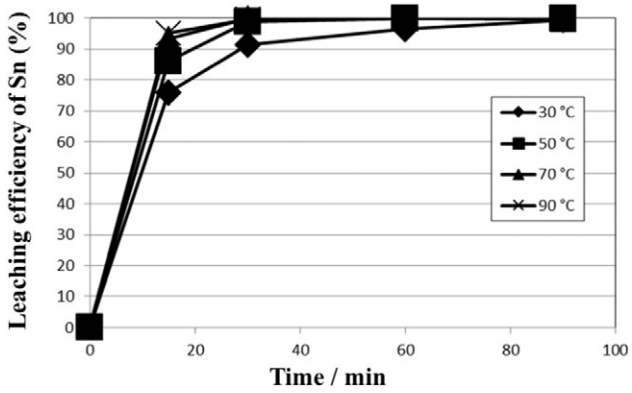

Fig. 2. Effect of temperature on the dissolution of Sn from the Pb-free solder in 1 kmol · m^{-3} HCl at 400 rpm with 1.5% pulp density and 0.5 kmol · m^{-3} Fe^{3+}.