Recycling of Electronic Waste II, Proceedings of the Second Symposium
Edited by: Lifeng Zhang and Gregory K. Krumdick
TMS (The Minerals, Metals & Materials Society), 2011

LEACHING OF LEAD FROM SOLDER MATERIAL USED IN ELECTRICAL AND ELECTRONIC EQUIPMENT

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Keywords: Lead, Tin, Solder, Leaching

Abstract

Present work is a part of developing novel recycling technique for waste printed circuit boards (PCBs) i.e. the liberation of metals from PCBs by organic swelling followed by the treatment of resin to remove/ recover hazardous soldering materials. In order to recover the hazardous metallic constituent lead from the liberated resin, initially the leaching studies were made using fresh solder containing 63.9% Pb and remaining tin. Experimental results obtained in different conditions viz. time, temperature and acidity showed ~97.20% of lead dissolution with 6M HNO_3 at solid to liquid (S:L) ratio 1:10 (g/mL) and temperature 90^oC in 75 minutes. The result of the studies validated with crushed PCBs shows that almost total lead and tin was leached out with 6M HNO_3 and 6M HCl respectively at S:L ratio 1:10 (g/mL) and temperature 90^oC within 50 minutes. The results will be useful for the treatment and safe disposal of PCBs resin.

Introduction

Global economical growth and technological advancement resulted in the incredible increase in the volume of electrical and electronic equipments (EEE) being procured by the consumers with replacement of used EEE [1]. Therefore, huge amount of waste EEEs generation takes place globally, specially in industrialized countries such as India, China, Greece etc. India is one of the fastest growing economies countries of the world and the growth in PC ownership per capita during the period 1993 - 2000 increased to the extent of 604%, compared to a world's average of 181% [2]. As India is the second most populous country with over 1 billion population, the quantity of e-waste generation is also high, respectively. These electronic products are made up of variety of components. Printed Circuit Boards (PCBs) are essential component in advanced EEE, and its recycling is one of the major challenges. The surface of the PCBs mainly contains the Cu metal circuits which is usually covered by a layer of epoxy resin and solder material, which is an alloy of lead and tin. Direct leaching of metallic fractions encapsulated with plastics, reinforced resins and ceramic rarely accomplishes effective extraction of metals from these waste PCBs [3]. Metal recovery using hydrometallurgical technique readily involves the leaching process in order to reduce the volume of the waste material and to recover selectively valuable as well as the perilous metals. In pyrometallurgical recycling processes, traditional methods such as incineration, melting etc are employed to recover precious and non ferrous metals from e-waste

at high temperature. In this process a considerable amount of metals loss takes place with high energy consumption, therefore it is not suitable for the recycling of valuable, noble, rare metals etc. In other hand, PCBs components also contain plastic and brominated flame retardants, which produce toxic gases and carcinogenic compounds during incineration. Therefore, it is necessary to develop an environmental and economically feasible technique for recovery of metals from electronic scrap. Among the several extraction processes, hydrometallurgy is a suitable route for recycling of valuable metals of high commercial value following leaching, solvent extraction, ion-exchange etc. Therefore, sincere efforts have been made world wide to develop an eco-friendly process using mechanical pretreatment in combination with hydrometallurgical technique [4]. Lee et al. [5] have reported that the metal liberation from these waste PCBs could be achieved up to 95-100% using swing hammer type impact mill or stamp mill, but those pretreatment processes are not applied in the commercial plant yet. Liberation of metals from PCBs is difficult due to its complex material of construction and lack of appropriate grinding/ mechanical pre-treatment processes. A series of hydrometallurgical processes, including leaching, separation and recovery has been employed for the recovery of valuable metals from the metallic concentrate. Some technologies are under lab scale investigation for leaching of the valuable metals from waste PCBs using electro-generated chlorine leaching [6, 7], ammoniacal leaching [8, 9] and bacterial leaching [10, 11]. The development of individual process or hybrid processes, including precipitation, cementation, solvent extraction, ion exchange and supported liquid membrane is underway. Developments of eco- friendly and energy-saving processes are necessary to comply with stringent environmental regulations.

The paper is a part of novel recycling technique, which is going to be developed under joint collaboration of NML, India and KIGAM, South Korea. The process consists of 1) organic swelling of waste PCBs, 2) liberation of thin layer of metals, 3) removal of solder material from epoxy resin for its safe utilization. Waste PCBs consist of several layers of resin, thin glass fiber, reinforced epoxy resins and interconnecting metal wires and plates. Aim of the study is to optimize the leaching parameters for recovery of lead and tin from the solder materials used in PCBs. The data will be useful to recover lead and tin from the liberated epoxy resin obtained after the separation of metals from the organic swelled PCBs. The data will also be useful to develop and simulate the leaching process in continuous mode.

Experimental

Solder material purchased from local market was used for the experimental purposes. Solder wire of diameter 0.7 mm was cut to 25.4 mm length. The solder contained 63.89% Pb and remaining Sn. The leaching experiment was carried out in a temperature controlled leaching reactor. The samples were taken at particular interval of time to see the leaching behavior of the metals for particular acid. After leaching the residue was dried in oven and weighed to see the material balance. Good material balance was obtained for each set of experiment. Lead and tin present in the leach solution were analyzed using Atomic Absorption Spectrophotometer instrument. Based on the result of leaching of the solder, the removal of lead and tin from waste printed circuit boards were also validated. The crushed PCBs of size ~7 mm used for experimental purposes contained 1.5% Pb and 1.23% Sn. The obtained leaching result for lead and tin from PCBs was validated with its leaching from solder wire. Good validation was

observed between both the results. All the reagents used were of AnalaR/LR grade chemical without any further purification.

Results and Discussion

Leaching studies were carried out for the extraction and separation of the lead/ tin from the solder material of PCBs. Initially, some batch experiments were carried out with freshly purchased solder. The solder contained 63.89% lead and remaining tin. The effect of process parameters viz. time and acid concentration was studied to examine the leaching behavior of lead and tin. After getting the data from solder leaching, the experiments were carried out to leach lead and tin from crushed PCBs.

Leaching of Pb and Sn from solder in HNO_3 medium

Leaching experiments were carried out by taking 25 grams of solder wire (diameter 0.7 mm and size ~25.4 mm) in 250 mL of dilute HNO_3 (1-6 M) at solid to liquid ratio 1: 10 i.e. pulp density 100 g/L and temperature 90^{o}C. The leaching of lead was found to increase with increase in reaction time. The Fig. 1 indicates that in 75 minutes the maximum percentage leaching of lead obtained was 51.93, 55.98, 84.98 and 97.20 with 1M, 2M, 4M and 6M nitric acid, respectively. In all cases the leaching of tin was found very poor. Fig. 2 indicates that the percentage leaching of lead with 6M HNO_3 was increased from 85.64 to 97.20 with increase in time from 10 to 75 minutes at pulp density 100 g/L and temperature 90^{o}C, however in same set of experiment very little amount of tin was found to be leached out due to salt formation.

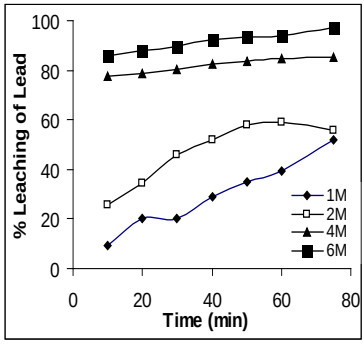

Fig. 1. Leaching of lead from solder with different nitric acid concentration [Pulp density = 100 g/L, Temp. = 90^{o}C]

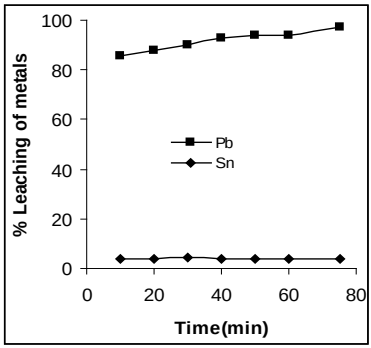

Fig. 2. Leaching of metals from solder with 6M HNO_3 [Pulp density = 100 g/L, Temp. = 90^{o}C]

Leaching kinetics of lead from solder

An attempt has been made to study the kinetics of dissolution of lead from solder material using shrinking core models. All standard equations of the shrinking core models were tested for reaction kinetics [12, 13]. The calculated data was tested to fit with all standard kinetics core equation but these value most suitably fitted with "Chemical reaction control dense constant size cylindrical particles, $1-(1-X)^{1/2} = Kct$", where Kc = reaction rate constant (min^{-1}), t = time (min) and X = fraction reacted of lead (% extraction/100) kinetics rate equation. The kinetics model (Fig. 3) is selected on the basis of constant value of Kc and regression coefficient i.e. higher the regression coefficient close to 1 among all kinetics core equation.

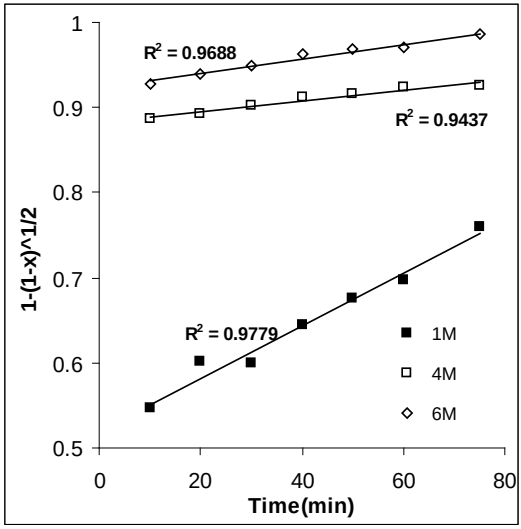

Fig. 3. Kinetics of leaching of lead from solder with HNO_3

Leaching of Pb and Sn from solder in HCl medium

The leaching studies were carried out with HCl to study the leaching behavior of lead and tin from solder having diameter 0.7 mm and size ~25.4 mm. The solder wire (25g) was leached with HCl (1-6 M) at solid to liquid ratio 1: 10, pulp density 100 g/L and temperature 90^{o}C in 500 mL flask. The leaching was found to be increased with increase in reaction time. Fig. 4 indicates that maximum leaching of tin could be achieved up to 26.97% with 6M HCl in 75 minutes. As the acid concentration increases from 1 to 6M, the leaching of tin also increases from 7.77 to 26.97% in 75 minutes. The results of leaching studies for lead and tin from solder using 6M hydrochloric acid are presented in Fig. 5. As the leaching time increases from 10 to 75 minutes the percentage leaching of lead and tin also increases from 2.51 to 9.13 and 9.86 to 26.97, respectively.

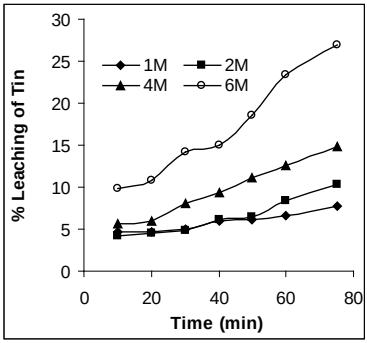

Fig. 4. Leaching of tin from solder with different hydrochloric acid concentration [Pulp density = 100 g/L, Temp. = 90^{o}C]

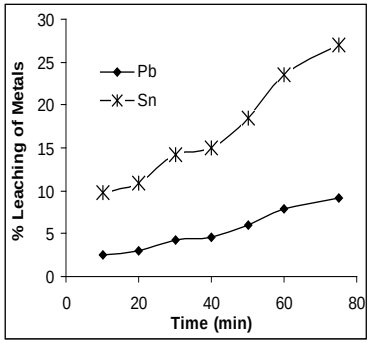

Fig. 5. Leaching of metals from solder with 6M HCl [Pulp density = 100 g/L, Temp. = 90^{o}C]

Leaching results of solder with HCl and HNO_3, show that nitric acid is suitable leachant for lead recovery whereas hydrochloric acid is effective for tin. Therefore, the leaching experiments for the removal and recovery of lead and tin from PCBs were carried out with both the acids using crushed PCBs of size 7 mm containing 1.5% lead and 1.23% tin. The result for the leaching of lead from PCBs in nitric acid medium at S:L ratio 1:10 i.e. pulp density 100 g/L is presented in Fig.6.

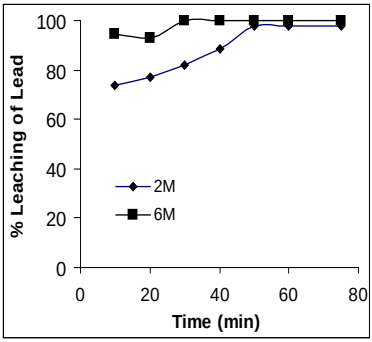

Fig. 6. Leaching of lead from crushed PCBs with different concentration of nitric acid [Pulp density = 100 g/L, Temp. = 90^{o}C]

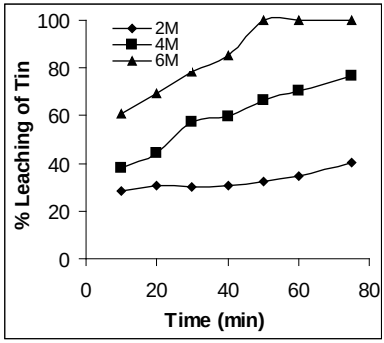

Fig. 7. Leaching of tin from crushed PCBs using different hydrochloric acid concentration [Pulp density = 100 g/L, Temp. = 90^{o}C]

The result indicates that 99.99% lead could be leached with 6M nitric acid at 90^{o}C in 30 minutes maintaining the above experimental condition. The NO_x gas generated during nitric acid leaching can be scrubbed in suitable scrubbing solution. After recovery of lead from PCBs the effort were made to leach out the tin from the waste PCBs. The experiments were carried out by varying the acid concentration from 2M to 6M. As the concentration of hydrochloric acid increases, the leaching efficiency of tin also increases. The results presented in Fig. 7 indicates that 32.31%, 66.33% and 99.99% of tin could be recovered with 2M, 4M and 6M HCl, respectively in 50 minutes at solid to liquid ratio 1:10, pulp density 100 g/L and temperature 90^{o}C. Further leach liquor can be purified by solvent extraction process, and from the purified solution salt/ pure novel, valuable and precious metal can be obtained using suitable hydrometallurgical techniques.

Conclusions

Leaching of lead and tin from solder / crushed PCBs were performed using hydrochloric and nitric acid. Nitric acid is suitable leachant for dissolution of lead from solder as well as PCBs. The leaching of lead increases with the increase in the nitric acid concentration. Maximum leaching of lead from solder was found to be 97.20% with 6M HNO_3 at pulp density 100 g/L and temperature 90^{o}C. In nitric acid medium tin dissolved significantly but precipitated due to the salt formation. The recovery/ leaching of tin was found very poor with HNO_3. Kinetics of the leaching of lead from solder follows the model "Chemical reaction control dense constant size cylindrical particles, $1-(1-X)^{1/2} = Kct$" in all concentration of nitric acid. The experimental results for the leaching of lead from PCBs in nitric acid medium at S:L ratio 1:10, pulp density 100 g/L indicates that 99.99% of lead could be leached with 6M nitric acid. The recovery of tin could be obtained 99.99% with 6M HCl in 50 minutes time at solid to liquid ratio 1:10, pulp density 100 g/L and temperature 90^{o}C. The NO_x gas generated during nitric acid leaching can be scrubbed in suitable scrubbing solution. Further leach liquor can be purified by solvent extraction, and from the purified solution salt/ pure novel, valuable and precious metal can be obtained using suitable hydrometallurgical techniques.

Acknowledgement

This paper is based on the sponsored work supported by Resources Recycling R&D Centre, South Korea under collaboration between National Metallurgical Laboratory (CSIR), Jamshedpur, India and Korea Institute of Geosciences & Mineral Resources (KIGAM), South Korea. Authors are also thankful to Mr. Abhishek, 3rd Year B. Tech. Chemical Engineering, student of AISSMS College of engineering, Pune for his contribution during the research work.

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