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Hydrometallurgical Recovery of Metals from Waste Solders

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ABSTRACT

Solders are predominantly used in electronic products. The use of Pb solders in electronic products is restricted because of its inherent toxicity, which has prompted the development and enhanced the use of Pb-free solders. However, the waste Pb-free solders are also comprised of many base metals. Their recycling is essential in viewpoint of economy as well as environment. Various pyro-, hydro- and biohydrometallurgical methods are reported for the recycling of waste solders. The present paper reviews the methods used for recovery of metals from waste solders, with special attention to the hydrometallurgical techniques.

Keywords: Solder, Lead-free solder, Hydrometallurgy, Metal recovery

INTRODUCTION

Electronic products are indispensable parts of day-to-day life and solders are the cornerstone technology of electronic interconnections [1]. Sn-Pb solders have been most successful in all electronic products for many decades because of its outstanding solderability and reliability [2-4]. However, its use is restricted due the health and environmental concerns associated with the toxicity of Pb [5-7]. Therefore, there is a rising demand for Pb-free solders, which include tin-silver (Sn-Ag), tin-zinc (Sn-Zn), and tin–copper (Sn-Cu) solder alloys [8-13]. The market share of Sn-Ag-Cu series increased to approximately 70% for reflowing Pb-free solder [14,15].

Although the Pb-free solders avoid the release of toxic Pb in nature, their excessive use eventually releases other metals such as Ag, Cu, and Zn, thus risking health and ecosystem [16]. Hence, it is necessary to reclaim these metals from the waste solders. This mini-review aims to explore various recycling processes for recovery of metals from waste solders and emphasizes on the hydrometallurgical techniques.

METAL RECOVERY

Pyrometallurgical process

A Pb refining process comprising of melting and re-powdering was applied for recycling of waste Sn-Pb solders [17]. Similar melting processes have been applied to Pb-free solders as well. Melting of solder at 220-230°C followed by the separation of the organic flux and metal components by specific gravity was applied for the recycling of waste Pb-free cream solder. But these pyrometallurgical processes consume high energy and emit various harmful gases causing air pollution. Also, it is difficult to recover individual metals using these process [18,19].

Hydrometallurgical process

Hydrometallurgical processes are recognized as the alternative methods for reclamation of metals from waste solders. These treatment processes are low cost, require low energy, have a less environmental impact and are easily managed as compared with the pyrometallurgy [20,21]. **Table 1** shows the comparison of various leaching agents of Sn-Pb and Pb-free solders. **Table 2** shows the comparison of pyro and hydrometallurgical processes.

Sn-Pb Solders

Waste PCBs consist of multiple metals and the Sn and Pb from solder material hinder the recovery of other base and valuable metals. Moreover, direct leaching of waste PCBs results in poor metal extraction efficiency due to the presence of plastics, ceramics, resins, etc. Researchers were

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able to release the soldering material present on the outer epoxy resin layer of waste PCBs through a novel pre-treatment technique of organic swelling using n-methyl-2-pyrrolidone [22]. Further, they investigated the leaching of Pb from solders using different leaching agents such as sulfuric acid, hydrochloric acid, and nitric acid. Various process parameters were optimized and 99.99% Pb was leached using 0.2 M HNO_3 at S:L ratio 1:100 (g/ml), at 90°C in 120 min. Kinetic studies revealed the chemically controlled reaction model with activation energy 26.94 kJ/mol. Application of the process for solder leaching of the liberated epoxy resin of swelled PCBs resulted in 99.99% leaching of Pb with 0.2 M HNO_3 at 90°C in 45 min. Further, Sn in the residue was leached to obtain 98.74% recovery with 3.5 M HCl at 90°C for 120 min at S:L ratio 1:20 (g/ml).

Table 1. Comparison of leaching agents of Sn-Pb and Pb-free solders.

Leaching agent	**Acetic acid**	**HNO_3**	**Flouroboric acid with hydrogen peroxide**	**Flouroboric acid with Ti+4**	**NaOH**	**HCl**	**HNO_3**	**HCl with H_2O_2**
Advantages	Highly efficient	Effective recovery of metals from Pb-free solders	Highly efficient	Highly efficient	Dissolves all metals from Sn-Pb and Pb free solders	Effective for recovery of Pb and Sn	Effective for recovery of Pb and Sn from Sn-Pb solders	Effective recovery of metals from Pb-free solders
Disadvantages		Release of NO or NO_2 gases causing sir pollution	Co-dissolution of copper with the solders	High operating costs hinders it applications	Precipitation of metal hydroxides from Sn-Pb solders	Precipitates AgCl resulting in loss of Ag	Results in oxidation of Sn to an insoluble form	Process is difficult to manage due to unstable H_2O_2
References	[13]	[19]	[23]	[23]	[24]	[24]	[24]	[25]

Table 2. Comparison between pyrometallurgical and hydrometallurgical processes

Process	**Pyrometallurgical process**	**Hydrometallurgical process**
Principal	Use of heat to separate the metals from other materials, employing the differences between oxidation potentials, melting points, vapor pressures, densities and/or miscibility of the ore components when melted. Includes different treatments at high temperatures: incineration, smelting in plasma arc furnace or blast furnace, drossing, sintering, melting, etc.	Use of leaching agents- acids or halides for metal leaching followed by purification using solvent extraction, adsorption or ion exchange and metal recovery from solution by electrorefining, chemical reduction or crystallization
Objective	Recover maximum amounts of metals	Recover maximum amounts of metals
Advantages	Easy commercialization; Almost all metals are recovered	Low capital cost; Simple and easy operation; Relative low environmental damage; Almost all metals are recovered
Disadvantages	High cost for investment; High energy consumption; Environmental pollution; Partial recovery of metals with impurities which need further processing; Difficult to recover precious metals	High cost of some chemicals; Generates some hazardous gases along with huge amounts of waste and polluted water; Some leaching agents employed for the process are dangerous and thus need high safety standards

The fluoroboric acid containing an oxidizing agent was used for the selective dissolution of solder [23]. Use of hydrogen peroxide as oxidizing agent resulted in co-dissolution of copper with the solder. Hence, Ti^{4+} ions were used as an oxidizing agent to obtain selective recovery. Though the process is highly efficient, high operating costs hinders it application for wastes enriched in Sn and Pb content.

The use of cost-effective leaching agents for Pb and Sn recovery was investigated by Ranitovic et al. [24]. NaOH was not effective as leaching agent due to the dissolution and precipitation of metal hydroxides. 2 M HNO_3 and 2 M

HCl were found effective for recovery of Pb and Sn respectively. However, further studies revealed the adverse interactions of leaching agents, making it incompatible for integrated hydrometallurgical recovery. HNO_3 resulted in oxidation of Sn to an insoluble form, whereas use of HCl precipitated AgCl resulting in loss of Ag.

Pb-free solders

The leaching behavior of heavy metals from Sn-Ag-Cu, Sn-Zn and Sn-Pb solders using H_2SO_4, NaCl and NaOH solutions was observed by Cheng et al. [6]. Most of the Sn was leached from the Sn-Cu solder joint than from solder alloys in the NaCl solution as compared to that with NaOH and H_2SO_4 solutions. The surface corrosion products on the solder and their joints were composed of oxide, oxide hydroxide or oxychloride of the component element [6].

Nitric acid leaching was studied for recycling of waste Pb-free solders by Yoo et al. [19]. In the process, 99% of Ag and Cu were dissolved in 2 kmol/m^3 HNO_3 at 75°C, 100 kg/m^3 pulp density and 400 rpm for 120 min. Also, the XRD results showed that tin was converted into stannic oxide (SnO_2) which is sparingly soluble in the HNO_3 solution. Further, precipitation or cementation was used to separate Ag and Cu by addition of NaCl or Cu powder.3755g/m^3 Ag was recovered with the addition of 2 kg/m^3 of NaCl or 125 kg/m^3 of Cu powder to the leaching solution at 30°C. However, NO or NO_2 gases generation during HNO_3 leaching results in air pollution. Thus, Kim et al. [25] developed the recycling process for waste Pb-free solders utilizing hydrochloric acid and hydrogen peroxide and separate Sn, Ag and Cu as an individual component. Oxidants are required to dissolve metals into metal ions during e-waste leaching procedures. Many such studies are reported. Increase in temperature and HCl concentration increased Sn dissolution. 27090 g/m^3 Sn and 191 g/m^3 Cu were leached with 1 kmol/m^3 HCl, 0.8 kmol/g^3 H_2O_2 at 50°C and 400 rpm for 120 min. Ag was not detected in the leaching tests, suggesting its separation from Sn and Cu in the process. Further Cu ions were selectively precipitated by cementation process with Sn powder, while Sn could be recovered by electrowining from the Cu free solution. The Cu was re-dissolved as a result of the oxidation of remaining cupric ion and subsequent re-oxidation of a cuprous ion by oxygen, which was prevented by introducing the nitrogen gas during cementation. 92.8 g/m^3 Cu was recovered with 0.1 g Sn powder at 30°C, 400 rpm, 0.3 ml/min N_2 flow. However, such a process is difficult to manage as hydrogen peroxide is relatively unstable.

In continuation of this study, Lee et al. [26] studied a process utilizing ferric ions instead of H_2O_2 as an oxidant. Ferrous ions produced during the leaching process could be oxidized to get ferric ions and thus reuse the oxidant. The difference in Sn leaching was insignificant at 1.0-2.0 kmol/m^3 HCl and was found to be independent of agitation speed. In the beginning, higher recovery rates were obtained for Sn and Cu at a higher temperature. Ag was not detected in the solution, suggesting its separation from Sn and Cu. Cu and Sn were separated from the ferric chloride leach solution by cementation and solvent extraction, respectively. Cu ions were removed by cementation using >1 g Sn powder in 100 ml leach solution containing 98.1 g/m^3 Cu. The extraction efficiency of Sn increased with increasing tri-butyl phosphate (TBP) (diluted with kerosene) volume ratio in the organic phase. 99.9% of Sn was extracted selectively by 3-time solvent extraction with 15% TBP and 1:1 O/A ratio at 30°C.

In another study, Kim et al. [27] investigated the use of HCl and Stannic chloride for recycling of Pb-free solders, where Sn^{4+} was used as an oxidant. At the beginning of leaching process, Sn leaching increased rapidly with increasing agitation speed, HCl concentration, and temperature. However, it remained unaffected after 90 min at 1-3 kmol/m^3 HCl, 300-600 rpm at 50-70°C. The increase in pulp density to 2% did not result in the Sn dissolution due to the unavailability of the oxidant. 99% Sn leaching was achieved in 90 min with 1 kmol/m^3 HCl, 10500 g/m^3 Sn^{4+} at 50 °C and 400 rpm with 1.5% pulp density. Ag was not detected in the process. Cu (24.5 g/m^3) was precipitated by cementation using Sn powder.

Effects of temperature and agitation speed during nitric acid leaching of Sn and Bi from spent Pb-free solders were studied by Jeon et al. [28]. In the Eh-pH diagrams of Bi-H_2O and Sn-H_2O systems, bismuth, and tin exist as Bi^{3+} and SnO_2, respectively, under the oxidizing and acidic conditions, so nitric acid was selected to separate Bi and Sn. The rapid increase in Bi leaching was observed with increase in agitation speed and temperature. 97.8% Bi was leached using 1 kmol/m^3 HNO_3 at 90°C, 400 rpm and 1% pulp density in one hour. The leaching efficiency was increased initially and then decreased in case of Sn, followed by formation of white precipitate of stannic acid ($SnO_2.H_2O$) as revealed by XRD.

In further studies, Jeon et al. [29] reported the recycling of Pb-free Sn-Bi-Cu solder paste employing a multi-step process consisting of swelling, ammonia leaching followed by hydrochloric acid leaching with cupric and stannic acids as oxidants, respectively. Sn-Bi-Cu solder paste contains a resin which affects the leaching efficiency. This resin was successfully separated by swelling the solder paste in methyl ethyl ketone at 30°C, 200 rpm and 5% pulp density. Further, the resin was precipitated by addition of distilled water and was confirmed to be an epoxy resin by FT-IR analysis. Complete recovery of Cu was obtained in 15 min using ammonia solution with cupric ions as 5 M NH_3 solution, 1 M $(NH_4)_2CO_3$, 0.1 M $CuCO_3$, 50°C and 1% pulp density. Sn and Bi were recovered as leach residue in this step. Further, Sn was selectively leached using 0.5 M HCl solution with 10,000 mg/L Sn^{4+} and 1% pulp density at 50°C and 400 rpm. However, Bi was not detected in the leach solution. Thus, the process could successfully separate Sn, Cu, Bi and resins from Pb-free solder paste.

The use of strong acid leachates releases toxic gases as well as generate an acidic waste solution which consequently is harmful to nature. To avoid this problem, Jadhav et al. [13] proposed the use of acetic acid as a leaching agent for recovery of metals from solders. Acetic acid was more efficient in leaching of Sn-Cu solder as compared to the Sn-Cu-Ag solder. Optimization of process parameters resulted in complete recovery of Sn and Cu in 30 h. Metal recovery increased with increase in acid concentration, resulting in complete metal recovery at 80% acid concentration. However, metal leaching decreased with an increase in temperature as well as particle size. Further, the authors compared the acetic acid leaching efficiency with the biologically produced acetic acid using Acetobacter. 39 and 54% of Cu and Sn were recovered using culture supernatant of Acetobacter, respectively. Although the leaching efficiency of Acetobacter supernatant was less as compared to acetic acid, it was still fairly good and can be applied to the bioleaching process.

Biohydrometallurgical process

Biohydrometallurgical methods are clean, low cost highly efficient and most promising environmentally friendly technology [30]. Biohydrometallurgical processes involve the use of microorganisms, wherein the metabolic products of microbes such as inorganic and organic acids and ferric ions play a vital role in the leaching of metals [31]. Such a process for recovery of metals from solders was investigated by Hocheng et al. [32]. Two-step bioleaching process was investigated employing the culture supernatant of *Aspergillus niger* and *Acidithiobacillus ferroxidans* for recovery of metals from various solders like Sn-Pb, Sn-Cu, Sn-Cu-Ag. *A. niger* supernatant was found to be more efficient in leaching of metals as compared to *A. ferroxidans*. *A. niger* metal leaching from Sn-Cu-Ag solders was faster as compared to others, with 99% metal dissolution at 30°C, 200 rpm in 60 h. *A. ferroxidans* displayed good bioleachability for Sn-Cu and Sn-Cu-Ag solders as compared to Sn-Pb solders. Bioleaching by *A. niger* involves the acidolysis/complexolysis process driven by produced organic acids. *A. niger* produces citric acid using sucrose as a carbon source (Eq. 1). The produced citric acid creates an acidic environment favoring metal dissolution (Eq. 2) and formation of soluble metal complexes (Eq. 3).

$$C_6H_{12}O_6 + 1.5\,O_2 \rightarrow C_6H_8O_7 + 2H_2O \quad (1)$$

$$C_6H_8O_7 \leftrightarrow (C_6H_7O_7)^- + H^+ \quad (2)$$

$$(C_6H_7O_7)^- + M^+ \rightarrow Metal\ citrate\ complex \quad (3)$$

However, *A. ferroxidans* bioleaching involves the oxidation mechanism. *A. ferroxidans* uses Fe^{2+} as an energy source to produce Fe^{3+} (Eq. 4), which acts as an oxidising agent for metal solubilization (Eq. 5).

$$2Fe^{2+} + 2H^+ + 0.5O_2 \rightarrow 2Fe^{3+} + H_2O$$

$$Fe^{3+} + e^- \rightarrow Fe^{2+} \quad (4)$$

$$M_{(s)} - e^- \rightarrow M^+{}_{(aq)} \quad (5)$$

Further 85% Sn and 80% Ag were precipitated from Sn-Cu-Ag bioleached solution by addition of NaOH and NaCl, respectively. 57% Pb was precipitated from Sn-Pb bioleached solution by passing H_2S gas at pH 8.1. This process provides an alternative technology for metal waste recycling. However, further studies are essential to make the process fast and more economical for its application on large scale.

CONCLUSION

Waste solders can cause environmental hazards if not treated properly. However, they are comprised of metals, which if recycled properly are of great significance in viewpoint of economy as well as environment. Many recycling technologies are available while certain drawbacks hamper their use. The disadvantages must be looked upon and improved in order to develop a cost-effective and an environmentally friendly method. Application of a method for metal recycling depends mainly on the type and composition of waste being treated and further on technical and economic analysis. The possible solution for recycling of heterogeneous waste lies in the use of combined technologies. Thus, disadvantages of individual technologies could be neutralized by developing integrated technologies to attain a sustainable and environmentally friendly metal recycling.

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