Environmentally friendly hydrometallurgical recovery of tin and lead from waste printed circuit boards: Thermodynamic and kinetics studies

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ABSTRACT

The aim of this research was to develop an environmentally friendly flowsheet to recover Sn and Pb, which are two well-known hazardous elements, from waste printed circuit boards (PCBs), resulting in solving an environmental issue besides reproducing high-value metals. In the leaching process, the highest Sn and Pb recoveries of 88% and 99% were achieved by using 2 M hydrochloric acid (HCl) at an agitation rate of 500 RPM at 75 °C. Thermodynamic evaluations were employed successfully to confirm the leaching results. The kinetics studies indicated that the reaction mechanism shifted from a mixed control model (surface reaction control and diffusion through product layer) to the diffusion control, by increasing the agitation rate. The temperature and acid concentration controlled the dissolution by the diffusion mechanism. Production of an ash layer on the particle surface suppressed Sn and Pb dissolution as a result of enhancing both the temperature and acid concentration. The results of the kinetics modeling have been validated by scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS) studies. The activation energies for Sn and Pb were found to be 39.49 and 50.60 kJ/mol, respectively. The Fourier-transform infrared spectroscopy (FTIR) indicated the presence of alkyne and alkyl halides, as well as carboxylic and aromatic components, in the pregnant leach solution. The metallic Sn–Pb product was obtained by using Al-based heat sink scrap separated from the same PCBs via the cementation method. The SEM and X-ray mapping studies were carried out to characterize this product. The selectivity of the cementation method for Sn and Pb was confirmed by the above-mentioned methods.

1. Introduction

“The number of transistors used in a densely integrated circuit doubles approximately every two years”. Gordon Moore (1965) stated this sentence to indicate the rapid pace of electronic equipment development. The time for this doubling has decreased to few months during recent years and will decrease to a few days in the future (Kaku, 2011). This means that new electronic devices are being introduced to the market faster today as compared to the past. The exponential demand growth for these products has led to increased productions of electronic wastes. Therefore, it is essential to develop new and environmentally friendly techniques for recycling these hazardous wastes.

Printed circuit board (PCB) is the main unit of all electronic devices. Land-filling of PCBs can create serious environmental concerns because of releasing hazardous metals, e.g., Pb, Cd, Hg, As, and Sb (Ghosh et al., 2015; Khan et al., 2013), and brominated flame retardants (Wang et al., 2018). Landfill, informal recycling, or improper management systems can cause releasing of heavy metals to the environment, which can adversely affect human, animal, and plant health (Ikhlayel, 2018; Yao et al., 2018). For instance, Pb can make detrimental impacts on human health, including cancer, anemia, muscle and joint pain, kidney problems, and high blood pressure (Ahmaruzzaman, 2011; Ma et al., 2018).

Besides, due to the high concentrations of precious metals (Au, Ag, and Pd) and base metals (Sn, Pb, Cu, Zn, Al, Fe, and Ni), these wastes can be categorized as an economic resource for metal
production (Habib Al Razi, 2016; Nekouei et al., 2018). The existence of various elements in PCBs has led to naming them as multi-metal urban mines. Recycling of PCBs has become an attractive topic for researchers for providing the following advantages: 1) conservation of primary resources; 2) reduction of solid waste volumes; 3) consumption of lower energies for recycling compared to mining activities; 4) prevention of environmental pollution resulted from the released heavy metals, fire-retardant solvents, and plastics (Akcil et al., 2015; Hadi et al., 2015).

Sn and Pb are widely used in the form of solder in the electronics industry. Regarding the approximate prices of 20,225 and 1,965 $/t (featured London Metal Exchange (LME) prices), recycling of Sn and Pb is essential both to save the environment and have economic benefits. There are few numbers of researches in this area; therefore, Pb and Sn recycling from PCBs need deeper studies. Havlik et al. (2010) investigated the effects of thermal pretreatment on Sn and Cu dissolutions. Their research revealed that metallic Sn or Sn(OH)3 at a high concentration of HNO3 (Mecucci and Scott, 2002). Sn precipitated in the form of metastannic acid with a high recovery, while leaving Sn as SnO2 in the residue (Jha et al., 2012b). Sn precipitated in the form of metastannic acid (H2O2Sn) at a high concentration of HNO3 (Mecucci and Scott, 2002).

Cementation is a key reaction to recover metals from a pregnant leach solution (PLS) (Artamonov et al., 2012; Yuan et al., 2014) and is widely used in the minerals industry (Demirkiran et al., 2007). Some researchers investigated the cementation processes of Pb and Sn from chloride solution by using Al (Artamonov and Shchetinina, 1990). The high performance and rate of this process, simplicity of the treatment equipment, and recovery of metals ions in the metallic form are the interesting advantages of this process (Farahmand et al., 2009).

The current paper investigated the effects of the 3 different parameters of agitation rate, hydrochloric acid concentration, and temperature on Sn and Pb recoveries from PCBs. The PCBs were ground for size reduction following the manual separation of Al-based heat sinks, without any physical separations or thermal treatments for removing plastic particles. Furthermore, a thermodynamic study was performed to anticipate metals behaviors in an aqueous solution due to the complex processes of metals leaching from PCBs. Also, a kinetics study was comprehensively carried out to determine the leaching mechanisms. Finally, the possibility of Pb and Sn recoveries from PLS by using a heat sink scrap as a cementation agent was studied to obtain a valuable product that can diminish environmental concerns.

2. Materials and methods

2.1. PCB preparation

Several wastes of personal computer motherboards from different brands were collected. From now on, a motherboard is referred to PCB. All the heat sinks were disassembled manually and then; the PCBs were cut to the approximate size of 1 cm with an industrial shredder. A cutting mill equipped with the various screen-opening sizes of 8, 4, 2, and 1 mm was employed to grind the PCB pieces into a size of 1 cm. Finally, a ring mill was used to reduce the particle sizes and obtain a size fraction between 250 and 354 μm.

1 g of the representative PCB powder was digested in aqua regia at 200 °C to fully dissolve the metals. Sn and Pb concentrations in the digested PCBs were analyzed by atomic absorption spectroscopy (AA240 Varian) and the contents of other metals were analyzed with coupled plasma optical emission spectrometry (Vista-Pro Varian, Australia). The contents of the metals in the PCBs are shown in Table 1.

### 2.2. Leaching experiments

Ground particles were used for leaching experiments without any chemical or thermal pre-treatment. One-factor-at-a-time method was used to study the effects of impeller speed, acid concentration, and temperature. For this purpose, 3 tests with the different agitation rates of 400, 500, and 600 RPM were performed in the first step, while the other two parameters were fixed (temperature = 60 °C and HCl concentration = 2 M). In the 2nd and 3rd steps, the effects of acid concentration (at 2, 2.5, and 3 M) and temperature (at 45, 60, 75, and 90 °C) were investigated. All the leaching tests were carried out in a 0.5-L glass reactor, which was connected to an oil bath in a closed circuit to control the temperature (Fig. 1). The reactor was equipped with a reflux condenser to cool down and recycle the leaching medium to avoid any mass loss. A mixer was used to agitate the pulp and a port was embedded for sampling and temperature monitoring. For each test, the reactor contained 200 mL of the leaching reagent and 20 g of PCBs. The experiment was continued for 240 min. The leaching time was chosen based on the preliminary tests in order to obtain maximum recovery. Hydrochloric acid (Merck-Germany) was selected as a leaching reagent.

2 mL of PLS was withdrawn at the selected intervals and diluted with a HCl solution of the same molarity as PLS in a 25-mL volumetric flask to analyze Sn and Pb concentrations. All the tests were repeated twice, unless the difference between the results was more than 5%, which urged a third repetition and reporting of the average of the results. Also, PLS was analyzed for the experiment by using inductively coupled plasma-optical emission spectrometry under optimum processing conditions and the elemental analysis of the final PLS was determined. The solid residue obtained from this experiment was also used for the SEM and EDS (VEGA-TESCAN, Czech Republic) studies. Finally, the PLS was analyzed via Fourier-transform infrared spectroscopy (FTIR) (Bruker, Alpha II) to determine the organic component in the solution.

### 2.3. Cementation experiments

Cementation was done for Sn and Pb recoveries from the PLS achieved from the test under optimum leaching conditions. The separated Al-based heat sinks (Habib Al Razi, 2016) were used as a reductant agent in order to cement Pb and Sn. The calculated weight of a separated tooth of a heat sink was added to 50 mL of the
were observed at lower temperatures. Again, increasing the temperature caused the extraction of Au, and Sb. Fe and Zn were leached out partially; however, Ni reactions at those conditions, while no extractions were detected for Cu, Ag, Al, and Pb concentrations in the leaching residual were negligible due to the dissolutions of these metals, while the concentrations of Ni, Sb, Cu, and Cl were high. It should be noted that Ni was probably dissolved at the first minutes and then precipitated and adsorbed on the solid phase due to the metal reduction (Karlfeldt Fedje et al., 2010; Mishra et al., 2008). For instance, Ni reaction with oxygen might contribute to the formation of insoluble NiO at the surface, which could stop further dissolution (Füchtjohann et al., 2000).

3. Results and discussion

3.1. Leaching studies

Fig. 2 shows the effect of the mentioned parameters on Sn and Pb recoveries from PCBs. The highest Sn and Pb recoveries (80% and 87%, respectively) were achieved at an agitation rate of 500 RPM (Fig. 2a and b). The Sn and Pb extractions decreased from 80 to 79% and 87 to 78% by increasing the agitation rate from 500 to 600 RPM. It meant that the agitation rate increase led to an enhanced energy consumption without any significant improvements in the recoveries of the metals.

The acid concentration influence was examined with 2, 2.5, and 3 M HCl. Sn extractions with 2 and 2.5 M HCl (80% and 79%, respectively) were almost similar after 240 min of leaching. The highest Pb recovery (87%) was achieved at 2 M HCl concentration. Therefore, it could be concluded that the optimum HCl concentration was 2 M. The lowest Sn and Pb recoveries (69% and 63%, respectively) occurred at 3 M HCl. Finally, the highest dissolutions of Sn and Pb (88% and 99%, respectively) occurred at 75 °C, while their very low recoveries were observed at lower temperatures. Again, increasing the temperature to 90 °C had negligible effects on their extractions. The Sn and Pb recoveries at 90 °C were 88% and 98%, respectively. To summarize, the optimum processing conditions for Sn and Pb extractions from PCBs were chosen at an agitation rate of 500 RPM, HCl concentration of 2 M, and temperature of 75 °C.

The concentrations and recoveries of different metals in PLS which was obtained from test under the optimum conditions were shown in Table 2. High percentages of Sn, Pb, and Al were dissolved at those conditions, while no extractions were detected for Cu, Ag, Au, and Sb. Fe and Zn were leached out partially; however, Ni recovery was very low. Therefore, an efficient and selective extraction was obtained for Sn and Pb. Dissolutions of other major metals, including Al, Fe, and Zn occurred through the mentioned process to some extent, but they essentially imposed no further interferences on the recycling process based on thermodynamic assessments as will be discussed in the section of cementation studies.

The surface morphology studies were also performed for the different metallic particles using SEM before and after leaching (Fig. 3). The surfaces of the particles were smooth before processing, while the corrosion tracks were observable on the surfaces after leaching (especially at the particle edges). The EDS analysis showed that the non-metallic particle (fiber particle) contained high concentrations of carbon, oxygen, silicon, and calcium (the data are shown in a supplementary file). The EDS analysis was carried out to determine changes to the elemental compositions during leaching. The Al, Pb, and Sn concentrations in the leaching residual were negligible due to the dissolutions of these metals, while the concentrations of Ni, Sb, Cu, and Cl were high. It should be noted that Ni was probably dissolved at the first minutes and then precipitated and adsorbed on the solid phase due to the metal reduction (Karlfeldt Fedje et al., 2010; Mishra et al., 2008). For instance, Ni reaction with oxygen might contribute to the formation of insoluble NiO at the surface, which could stop further dissolution (Füchtjohann et al., 2000).

3.2. Thermodynamic studies

Fig. 4 represents the Eh-pH diagrams for the metals in the aqueous solution to analyze the thermodynamic possibility of providing a condition for the presence of various metal ion species as calculated by HSC 6.0 chemistry software. The metal-H2O systems were superimposed for the better comparison of the solubility areas and consolidation (Fig. 4a–c). All the metal concentrations used for the construction of Eh-pH graphs were chosen from Table 1, considering the actual amounts of the metals.

As can be seen from Fig. 4 (a), Ni2+, Zn2+, and Al3+ ions are the stable species of their metals at the lower pH levels of 5 (A), 6.4 (B), and 3 (C), respectively. It should be reminded that the determined points with capital letters indicated the potential and acid concentration in which the metals spontaneously started to dissolve (Asadi et al., 2018). Fig. 4 (b and c) also shows the oxidation regions for Sn, Fe, Pb, and Cu, elucidating that Cu leaching is almost impossible in the Eh-pH range of this study. The diagrams for Ni, Zn, Al, Sn, Fe, and Pb represent a competitive relationship for solubility in the aqueous solution. Nevertheless, some conditions, including an efficient agitation rate, proper potential, and adequate concentration of the dissolution agent, needed to be provided for metal extraction.

Fig. 5 shows the Eh-pH diagrams of the metal species represented in Table 2 (calculated by Medusa software, Ver. 16 Dec. 2010) in the presence of 2 M Cl ligand. For the known complexes without the equilibrium constant values in the Medusa software database, the solubility constants of Log K were recalculated using their standard Gibbs free energies (Soltani et al., 2018). As can be seen from Fig. 5 (a–f), the complexes of Al, Ni, Zn, Sn, Fe, and Pb are formed with Cl ligand at acidic pH and a moderate potential. However, in the same conditions, Cu (Fig. 5 g) did not form any soluble species. In the presence of chlorine, Cu and Ag formed CuCl(s) (Kim et al., 2011) and AgCl(s), respectively (Kim et al., 2014; Naseri Joda and Rashchi, 2012), which could act as passive layers and prevent metal dissolutions.

The FTIR analysis was performed for a 2 M HCl solution before the leaching experiment and PLS which was achieved from the test under the optimum conditions. The spectrum for the first sample was subtracted from the second spectrum to determine changes to the solution after leaching (Fig. 6). 4 main peaks were detected from the spectra at ~620, ~1250, ~1650, and ~3250 cm⁻¹. The peak
at 620 cm\(^{-1}\) could occur due to the presence of the compositions of alkynes or alkyl halides in the sample. Alkyl halides have the general formula of XR, where R is an alkyl or substituted alkyl group and X is a halogen. Due to the high concentration of Cl\(^-\) in the leaching environment, chloroethane formation was possible (Milligan and Jacox, 1971). The formations of \((\text{C}_2\text{H}_5)_2\text{PbCl}_n\) (\(n = 1-4\)) and \((\text{C}_2\text{H}_5)_3\text{PbCl}_{n-1}\) (\(n = 0-3\)) complexes were also reported (Giustiniani et al., 1964), indicating that Pb dissolution had occurred due to the formations of both chloro complex and organolead cations. The peak at \(-1250 \text{ cm}^{-1}\) indicated the presence of alkyl halide, carboxylic acid, and aromatic components. The bonds for carboxylic acid and aromatic component were also repeated at \(-1600 \text{ cm}^{-1}\). The general formula for carboxylic acid is R–COOH. R is the rest of the molecule, which could be the aromatic components in the current environment. Carboxylic acids are a wide category of organic acids, such as acetic acid and formic acid. Sn\(^{2+}\) has a great tendency to react with acetate and form a solid compound (Donaldson and Knifton, 1966, 1964). Finally, the peak at 3250 cm\(^{-1}\) could reflect the presence of carboxylic acid too. The alkene bands could be also detected from the peaks at 1650 and

<table>
<thead>
<tr>
<th>Table 2</th>
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<tbody>
<tr>
<td>The elemental analysis of PLS and corresponding metals recoveries at the optimum processing conditions of leaching process.</td>
</tr>
<tr>
<td>Metal</td>
</tr>
<tr>
<td>---</td>
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<tr>
<td>Concentration (mg/L)</td>
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<tr>
<td>Recovery (%)</td>
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Fig. 2. Effect of agitation rate (a & d), HCl concentration (b & e), and temperature (c & f) on Sn and Pb recoveries.
Therefore, it could be concluded that the dissolutions of organic materials in the PCBs occurred during the leaching experiments. Sn and Pb were evidenced to be dissolved in the forms of both chloride and organic complexes.

3.3. Kinetics studies

3.3.1. Agitation rate effect

Different models (Table 3) were fitted to the fraction reacted achieved from the tests at different agitation speeds. All of these models were defined for spherical reacting particles. The microscopic studies indicated that more than 90% of the metallic particles had a spherical shape (Fig. 7). According to Fig. 8, from among all the fitted models, Equation 1 was best fitted to the data at the agitation speeds of 400 and 500 RPM (with $R^2 = 0.99$ and 0.97 for Sn and $R^2 = 0.96$ and 0.97 for Pb). This model demonstrates that the reaction mechanism is the surface chemical reaction by shrinking core model (Padilla et al., 2008). On the other hand, Equation 2 was best fitted to the data for 600 RPM with $R^2 = 0.94$ and 0.91 for Sn and Pb, respectively. According to this model, at the current conditions, the reaction is controlled by a mixed control model (surface

3250 cm$^{-1}$ (Gauglitz and Moore, 2014).

![SEM images with 200X magnification before (a) and after (b) leaching which show smooth surface before leaching and corroded surface after the process.](image)

![Superimposed Eh-pH diagrams of Al (0.22 M)/Ni (0.01 M)/Zn (0.08 M)–$H_2O$ (a), Sn (0.02 M)/Fe (0.08 M)–$H_2O$ (b), and Pb (0.01 M)/Cu (0.66 M)–$H_2O$ (c) systems at 25°C (drawn by HSC 6.0 chemistry software, Outokumpu Research, Finland).](image)
Fig. 5. Eh-pH diagrams of Al (0.22 M) (a), Ni (0.01 M) (b), Fe (0.08 M) (c), Sn (0.02 M) (d), Zn (0.08 M) (e), Pb (0.01 M) (f), and Cu (0.66 M) (g) chloro-complexes systems at 25 °C, calculated by Medusa software (Royal Institute of Technology, Sweden).
reaction control and diffusion through the product layer) (Sokić et al., 2009). Although the diffusion control had no limiting effect on the reaction at lower agitation rates, increasing this parameter might decrease the leaching reagent diffusion to the surfaces of the solid particles. This phenomenon could occur because of the increase in turbulency and formation of vortex flows, which decreases the reagent diffusion onto the surfaces of particles. By the vortex formation in the leaching environment, the particles aggregate around the air column and the liquid diffusion to the surfaces of the particles decreases (Ting and Klein, 1991). As mentioned at Section 3.1, the agitation rate increase from 500 to 600 RPM had negligible effects on the recoveries of the metals, which was confirmed and explained by the kinetics studies.

3.3.2. HCl concentration effect

The mentioned models were examined to study HCl concentration effects on the leaching kinetics of the PCBs. The results indicated that the chemical control mechanism (Equation 3) was a rate-limiting step when 2 M HCl was used for both Sn and Pb leaching (Fig. 9). This might occur due to the limitation of the leaching reagent as a chemical parameter at low HCl concentration. The diffusion control model was best fitted to the data for the tests of Pb leaching with 2.5 M and 3 M hydrochloric acid. Contrarily, the kinetics mechanism for Sn was different from that of Pb. The curve fitting indicated that the interfacial transfer and diffusion across the product layer (Equation 4) mechanism controlled the Sn leaching process at the HCl concentrations of 2.5 M and 3 M. In fact, both for Pb and Sn, lack of the reagent diffusion onto the particle surface can limit the reaction. The kinetics modeling indicated that Sn dissolution at 3 M HCl followed a two-step mechanism (both with the interfacial transfer and diffusion across the product layer mechanism), with different $k_{exp}$ (the reaction rate coefficients for the 1st and 2nd parts of the reaction are 0.0111 and 0.0002, respectively). This change could occur due to the production of an ash layer on the surfaces of the particles. All of the models in this section fitted to the data with a correlation coefficient of higher than 0.93.

3.3.3. Temperature effect

Fitting different models to the fraction reacted at different

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**Table 3**

<table>
<thead>
<tr>
<th>Eq.</th>
<th>Model</th>
<th>Mechanism</th>
<th>References</th>
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<tbody>
<tr>
<td>(1)</td>
<td>$k_t = 1 - (1 - 0.45X)^{1/3}$</td>
<td>Surface chemical reaction by shrinking core model</td>
<td>Padilla et al. (2008)</td>
</tr>
<tr>
<td>(2)</td>
<td>$k_t = -\ln(1 - X)$</td>
<td>Mixed control model (surface reaction control; and diffusion through product layer)</td>
<td>Sokić et al. (2009)</td>
</tr>
<tr>
<td>(3)</td>
<td>$k_t = 1 - (1 - X)^{1/3}$</td>
<td>Chemical reaction control</td>
<td>Levenspiel (1999)</td>
</tr>
<tr>
<td>(4)</td>
<td>$k_t = \frac{1}{3}\ln(1 - X) + \left(1 - X^{2/3} - 1\right)$</td>
<td>Interfacial transfer and diffusion across the product layer</td>
<td>Dickinson and Heal (1999)</td>
</tr>
<tr>
<td>(5)</td>
<td>$k_t = 1 - \frac{2}{3}X - (1 - X^{2/3})$</td>
<td>Diffusion control</td>
<td>Levenspiel (1999)</td>
</tr>
<tr>
<td>(6)</td>
<td>$k_t = [1 - (1 - X)^{2/3}]^{1/2}$</td>
<td>Diffusion through product layer</td>
<td>Ikiz et al. (2006)</td>
</tr>
<tr>
<td>(7)</td>
<td>$k_t = 1 - (1 - X)^{1/3}$</td>
<td>Mixed control model by shrinking core model (diffusion control; chemical reaction control)</td>
<td>Gao et al. (2009)</td>
</tr>
</tbody>
</table>

*a Eq. = Equation.*
temperatures, indicating that both Sn and Pb dissolutions followed the surface chemical reaction by shrinking the core model mechanism at 45 °C and 60 °C, respectively (according to Equation 1). This model was fitted to the data in the time range of 0–240 min (with $R^2 = 0.91$ and $R^2 = 0.94$ for Sn and Pb at 45 °C, respectively, and $R^2 = 0.99$ for both metals at 60 °C). However, no model was suitably fitted to the data in this time range at 75 °C and 90 °C. Therefore, the models were fitted in other time ranges for these temperatures. Applying different models in different time ranges showed that Sn and Pb leaching followed two different mechanisms in the first and last minutes of the reaction. Equations 1 and 5 were best fitted to the data in the initial and final minutes, respectively (Fig. 10). This meant that the leaching mechanism changed from the surface chemical reaction by shrinking core model to the diffusion control. The diffusion mechanism could control the reaction by forming an ash layer on the surfaces of the particles. A SEM image from the solid residue of the optimum test confirmed the ash layer formation on the surfaces (Fig. 11) (Ghassa et al., 2017a). The EDS analysis for this sample showed high concentrations of Ni, Cu, Sb, Cl, O, and Fe on the surfaces as well. According to this elemental analysis, there was no Sn or Pb available in the surfaces for leaching. This layer could be produced by the metal precipitations due to the reactions of organic and inorganic components with the metals. For instance, Ni ions could easily react with CO to form solid Ni(CO)$_4$ (Keim, 1990). Sb$^{3+}$ and Sb$^{5+}$ could react with the organic components and make an ash layer in the form of R$_n$SbX$_2$ or R$_2$SbX, where R could be an aromatic radical and X was a halogen. The presence of aromatic components was confirmed by the FTIR analysis (Fedeyev et al., 1985). The reagent had to diffuse through this layer to get access to the surfaces of the particles, while this could limit dissolutions of the metals. The value of $k_{exp}$ was higher at 75 °C compared to 90 °C for the second part of the kinetics, which meant that the product layer was thicker and harder to get access to the reagent, at higher temperature. Therefore, although increasing the temperature could improve the dissolution process in the initial minutes by improving the chemical parameters, it would limit the process at the last minutes by restricting the surface accessibility due to producing an ash layer.

The Activation Energies (AEs) for Sn and Pb dissolutions were calculated based on the Arrhenius equation (Ghassa et al., 2017b). It should be pointed out that the AEs were calculated at 75 °C and 90 °C for the first part of the mechanism since it provides the minimum energy required for starting a reaction based on its definition (Naoversnik and Jurecic, 2016). For this purpose, the graphs of ln ($k_{exp}$) vs. $\frac{1}{T}$ were drawn both for Sn and Pb (Fig. 12). The AEs could be calculated from the slopes of the lines (Fig. 12) using the Arrhenius equation. The AEs for Sn and Pb leaching were found to be 39.49 and 50.60 kJ/mol, respectively. The AEs of greater than 42 kJ/mol reflected the chemical control reaction, while those between 13 and 42 kJ/mol indicated a mixed control reaction (Habashi, 1969). Therefore, it could be concluded that the diffusion mechanism could control Sn dissolution more than Pb because AE.
for Sn leaching was lower than that for Pb.

3.4. Cementation studies

Cementation is the process of extracting metals from solutions based on the electrochemical reaction between a cementing metal and a cemented metal ion. The thermodynamic possibility of cementation was evaluated by comparison of electrode potential values. The electrode potential of the replacing metal should be more negative than that of the replaced metal. Metal cementation is remarkably accompanied by a change in the metal concentration on the solution and its consequent potential. The process would be suspended after reaching the equilibrium values (Havlík, 2008).

Equations (8) and (9) describe the overall reactions of Sn$^{2+}$ and Pb$^{2+}$ cementations in the presence of Al.

3 $Sn^{2+} + 2Al \rightarrow 3 Sn + 2Al^{3+}$

3 $Pb^{2+} + 2Al \rightarrow 3 Pb + 2Al^{3+}$

The half-reactions for Sn$^{2+}$ and Pb$^{2+}$ reduction to their metals and half-reactions for metallic Al oxidation to Al$^{3+}$ are defined by the following reactions:

$Sn^{2+} + 2e^- \rightarrow Sn; \quad E_{Sn^{2+}/Sn} = -0.1375 \text{ V}$ (10)

$Pb^{2+} + 2e^- \rightarrow Pb; \quad E_{Pb^{2+}/Pb} = -0.126 \text{ V}$ (11)

$Al^{3+} + 3e^- \rightarrow Al; \quad E_{Al^{3+}/Al} = -1.676 \text{ V}$ (12)

Since the reduction potentials of Sn and Pb (Equations (10) and (11), respectively) are higher than Al (Equation (12)), they can be substituted by Al.

Cell reduction potential and change in Gibbs free energy can be calculated as follows:

$E_{Cell} = E_{Cathode} - E_{Anode}$ (13)

$\Delta G = -nFE_{Cell}$ (14)

where $E_{Cell}$, $E_{Cathode}$, and $E_{Anode}$ are the reduction potentials of the
cell, cathode, and anode at the standard state; \( \Delta G \) is Gibbs free energy at the standard state; \( n \) is the number of transferred electrons in the reaction cell; and \( F \) is Faraday constant. Therefore, the cell reduction potential and Gibbs free energy of Sn and Pb can be represented by:

\[
E_{\text{Cell, }\text{Sn}^{2+}/\text{Sn}} = -0.1375 - (-1.676) = 1.5358 \text{ V} \tag{15}
\]

\[
E_{\text{Cell, }\text{Pb}^{2+}/\text{Pb}} = -0.126 - (-1.676) = 1.55 \text{ V} \tag{16}
\]

\[
\Delta G^\circ_{\text{Sn}^{2+}/\text{Sn}} = -6 \times 96.485 \times 1.5358 = -889.08 \text{ kJ/mol} \tag{17}
\]

\[
\Delta G^\circ_{\text{Pb}^{2+}/\text{Pb}} = -6 \times 96.485 \times 1.55 = -897.31 \text{ kJ/mol} \tag{18}
\]

The Gibbs free energies of \(-889.08\) and \(-897.31\) kJ/mol for the overall cementation reactions (Equations (8) and (9), respectively) indicate that the mentioned reactions have occurred spontaneously, i.e., without any supplied voltage.

The reduction potentials of the electrochemical reactions can be calculated by Nernst’s law based on the following equation:

\[
E_{\text{cell}} = E_{\text{Cell}} - 2.303 \frac{RT}{nF} \log K \tag{19}
\]

where \( E_{\text{cell}} \) is the cell reduction potential; \( R \) is the gas constant; \( T \) is the temperature (K); and \( K \) is the reaction constant at equilibrium. Based on the Nernst equation at the equilibrium state, Equation (20) is given:

\[
E_{\text{Sn}^{2+}/\text{Sn}} - 2.303 \frac{RT}{nF} \log K = E_{\text{Al}^{3+}/\text{Al}} - 2.303 \frac{RT}{nF} \log K \tag{20}
\]

\[
[\text{Sn}^{2+}] = 10^{-52.63} M \tag{21}
\]

Equation (21) shows that only \( 10^{-52.63} M \) of Sn\(^{2+} \) would remain in the solution if 0.1 M Al is added to it. In other words, cementation of Sn\(^{2+} \) in the presence of Al can be completed. Similarly, the following equations can be written for Pb:

\[
E_{\text{Pb}^{2+}/\text{Pb}} - 2.303 \frac{RT}{nF} \log K = E_{\text{Al}^{3+}/\text{Al}} - 2.303 \frac{RT}{nF} \log K \tag{22}
\]

\[
[\text{Pb}^{2+}] = 10^{-53.11} M \tag{23}
\]

By adding 0.1 M Al to the solution, almost all Pb\(^{2+} \) can be deposited on Al.

As discussed above, the spontaneous dissolution of Al with simultaneous Sn and Pb depositions were thermodynamically possible. Hence, an Al-based tooth of a waste heat sink, which was separated from PCB, was sunk in 50 mL of the PLS achieved from the test under optimum conditions. Hydrogen evolution occurred simultaneously with Sn and Pb depositions based on Equation (24) when Al was used as the cementing metal in chloride solution. Hydrogen evolution vigorously agitated the solution, which could have screening and/or turbulence effects on Pb to eliminate concentration limitations to the electrochemical reactions occurring at the electrodes of contact electrolyte couples (Makhloifi et al., 2000).

\[
2H^+ + 2e^- = H_2 \tag{24}
\]

SEM-EDS analysis and X-ray mapping were conducted on the cemented deposits in order to characterize the final product. Fig. 13(a and b) shows SEM micrographs and the related Sn–Pb mapping. Pb was precipitated in the form of rod-shape crystals with the length size of around 150–200 \( \mu \text{m} \), while Sn was cemented in the form of dendritic structures with the particle size of 1–10 \( \mu \text{m} \). The EDS studies showed that the final product had high concentrations of Sn and Pb (more than 98%). It should be mentioned that other metal ions, such as Fe and Zn, remained in the solution based on their reduction potentials. Therefore, heat sink scrap could be used efficiently as a secondary resource metal to recover Sn–Pb mixture from PLS.

3.5. Application potential

A flowsheet (Fig. 14) was developed for reproducing the Sn–Pb mixture from the waste PCBs based on the results obtained from the explained experiments. Generally, this flowsheet contained 3 main steps: 1) grinding; 2) leaching; and 3) cementation. After separating the heat sinks, a set of shredder, cutting mill, and ring mill was employed in combination with a screen in a closed circuit to grind the PCBs. The ground particles were then leached in a mixer-reactor containing 2 M HCl at an agitation rate of 500 RPM and a temperature of 75 °C. The leaching process was operated at the liquid/solid ratio of 10:1 (wt/wt). Therefore, assuming processing of 1 ton of PCBs, a leaching reactor with an efficient volume of 10 m\(^3\) was required. The PCBs did not need any pretreatment.
which was one of the most important advantages of the proposed flowsheet. The solid-liquid separation was carried out after 2 h of leaching and the obtained PLS was used for cementation by adding the waste heat sink teeth. The Sn–Pb spongy nodules (a porous and compressible product) precipitated onto the heat sink surfaces, which could be readily separated from the liquid. After melting, this product could be sold either directly as an Sn–Pb alloy solder or indirectly as a precursor for the solder alloy with different metal compositions.

1-ton PCBs contained 37.9 kg of Pb and Sn (according to Table 1). Based on the metal recoveries in the current proposed process, 34.67 kg (Sn = 22.79 kg and Pb = 11.88 kg) of Sn–Pb alloy was reproduced. Based on London Metals Exchange prices (1,965 $/t for Pb and 20,225 $/t for Sn), processing of 1 ton of PCB led to a revenue of 466.8 $. The costs including the waste PCB price, maintenance of the equipment, energy consumption, and labor vary in different countries (Xiao et al., 2019).

The high recoveries of Sn and Pb through the proposed flowsheet could resolve the growing concern of heavy metals pollution in the environment, besides recycling valuable metals from the waste PCBs. In addition, elimination of destructive impurities (i.e., Pb and Sn) from PCBs could provide easier recycling of other metals, especially in electrowinning step. Hence, Cu leaching in the following hydrometallurgical process dealt with less complicated waste and waste quantities. The current research proposed an environmentally friendly and economical flowsheet for Sn–Pb reproduction.

4. Conclusions

The present work introduced an environmentally friendly flowsheet for recovering Sn and Pb from waste PCBs. A leaching process was employed to extract Sn and Pb selectively. The results of the leaching process indicated that under the optimum processing conditions of 500 RPM agitation rate, concentration of 2 M HCl, and temperature of 75 °C, Sn and Pb recoveries were 88% and 99%, respectively. Based on the thermodynamic studies, Cu did not form soluble species, while Sn, Pb, Al, Ni, Zn, and Fe formed complexes with Cl− ligand to some extent under the optimum conditions. This finding was in good agreement with the results of the dissolution experiments. Furthermore, the FTIR studies indicated that Sn and Pb dissolutions occurred due to the formation of chemical bonds between both chloride and organic compounds (most probably caused by the partial leaching of organic materials in the PCBs).

The kinetics modeling was carried out to determine the effects of the mentioned parameters on the Sn and Pb leaching mechanism. The results indicated that increasing the agitation rate decreased the reagent diffusion to the surfaces of the particles. The chemical reaction was a rate-limiting step at low HCl concentration, while the diffusion control was a rate-limiting step at high acid content for Pb dissolution. On the other hand, interfacial transfer and diffusion across the product layer mechanism controlled Sn leaching at all HCl concentrations. The kinetics modeling along with SEM studies indicated that an increase in the temperature limited the reagent diffusion to the particle surface due to ash layer formation. The activation energies for Sn and Pb leaching were determined to be 39.49 and 50.60 kJ/mol, respectively. Sn and Pb were recovered from PLS by adding an Al-based heat sink scrap as a secondary metal resource. The final product contained Sn and Pb crystals with a purity of more than 98% based on SEM-EDS analysis and X-ray mapping.

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Appendix A. Supplementary data

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References


