



Full length article

Enhanced extraction of copper from electronic waste via induced morphological changes using supercritical CO₂Emily Hsu^{a,b}, Christopher J. Durning^a, Alan C. West^{a,b,c}, Ah-Hyung Alissa Park^{a,b,c,*}^a Department of Chemical Engineering, Columbia University in the City of New York, 10027 NY, United States^b Lenfest Center for Sustainable Energy, Columbia University in the City of New York, 10027 NY, United States^c Department of Earth and Environmental Engineering, Columbia University in the City of New York, 10027 NY, United States

ARTICLE INFO

Keywords:

Electronic wastes
Supercritical CO₂
Metal recovery
Leaching
Copper
Polymer

ABSTRACT

Electronic waste (e-waste) is one of the fastest growing waste segments in the world. This study investigates the use of supercritical CO₂ (scCO₂) and aqueous acid as co-solvent for the treatment of e-waste, specifically for the extraction of copper. Printed circuit board (PCB) was selected as the e-waste of study. In order to perform controlled experiments, melt-pressed Cu foil and polycarbonate sheets were prepared as surrogates for PCBs. It was found that a scCO₂ and acid pre-treatment induced drastic morphological changes in the polymer, creating pores, cracks, and delamination. This finding was translated to the actual waste PCB system. This unique process involved the pre-treatment of the PCB with scCO₂ and aqueous sulfuric acid at 120 °C and 148 atm for 30 min followed by leaching of the treated PCB in a solvent containing 2 M sulfuric acid and 0.2 M hydrogen peroxide at ambient conditions. Experimental results showed that 82% of the copper contained in the PCB was extracted in under 4 h. The characterization of the PCB demonstrated that the pre-treatment with scCO₂ and acid induced the crystallization of the plastics (polymer component), creating pores and weakening the structure of the PCB, thereby enhancing the transport of the solvent to the buried metal interfaces. This novel process using scCO₂ could reduce physical processing (e.g. grinding of the PCB) and acid usage during the extraction of Cu from e-waste, providing a greener alternative for current methods of recycling of metals, which are energy intensive with large environmental footprints.

1. Introduction

The management of waste, particularly electronic waste (e-waste), has become a significant challenge faced by humanity as the globe becomes increasingly connected and automated. Worldwide, the number of discarded computers, phones, and other appliances reached 45 million tons in 2016, and based upon projections, this number could exceed 50 million tons by 2021 (Baldé et al., 2015; Baldé et al., 2017; Robinson, 2009). Presently, the disposal of e-waste encompasses recycling the nontoxic, valuable components and releasing the toxic components into the surroundings, most often via pyrometallurgy (incineration and smelting) (Zhang et al., 2012). The environmental release presents hazards; consequently, much research has been dedicated to developing new recycling methods for e-waste with an emphasis on green metal extraction and recovery. Fig. 1 shows an example of how metals are currently being recovered from electronic scrap.

Electronic waste is an intricate mixture of metals, plastics, and refractory material. The amount of valuable metals in e-waste depends on the type of waste. Printed circuit boards (PCB), a major constituent of e-waste, contains one of the highest concentrations of base and precious metals. The overall composition of PCB is approximately 40% metals, 30% organics, and 30% refractory. Copper is the most abundant metal in PCB, comprising 20% of the metal content, and its recovery has high economic value (Hagelken, 2006; Yamane et al., 2011; Le et al., 2013; Park and Fray, 2009; Goosey and Kellner, 2002; Cui and Zhang, 2008). Other base metals found in PCB include Fe, Al, and Ni, in addition to precious metals, Au and Ag. The organic content of PCB consists of various polymers, such as Polycarbonate (PC) and Polyvinyl chloride (PVC), and the refractory materials are silica and alkaline oxides (Shuey and Taylor, 2014; Stevens and Goosey, 2008). Brominated flame retardants (BFRs) are included in polymers in PCB and are of particular concern due to their toxicity. The BFRs, poly-brominated diphenyl ether (PBDE) and tetrabromo-bisphenol A (TBBA), can react with oxygen to

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Received 31 December 2019; Received in revised form 12 November 2020; Accepted 15 November 2020

Available online 24 November 2020

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form dioxins.

Conventional treatment of PCB generally consists of physical processing and separation followed by metal extraction and recovery. The crushing of PCB to fine particle sizes along with other mechanical methods tends to be energy and labor-intensive. Shredding and grinding processes can produce dangerous dusts and dioxins, and metal losses of up to 40% have been reported during mechanical processing (Jiang et al., 2012). Thermal and chemical treatments, such as pyrolysis and supercritical fluids, are also utilized, particularly to remove the flame-retarding polymeric components and recover the plastics (Hall and Williams, 2006; Jie et al., 2008; Miskolczi et al., 2008; Xing and Zhang, 2013; Wang and Xu, 2014; Sanyal et al., 2013). These processing steps play a critical role in metal separation and recovery, affecting the ultimate amount of metal recovered and the overall efficiency of metal recycling. Two main routes are used for the separation and recovery of metals, namely pyrometallurgy and hydrometallurgy.

Pyrometallurgy, that is incineration and smelting, is the most standard treatment method. Approximately 70% of waste PCBs are treated in smelters, instead of undergoing mechanical processing (Cui and Zhang, 2008). Pyrometallurgy has proven effective and economically viable, but the risks of toxic gas release and dioxin formation combined with the formation of slag waste are limitations. Most pyrometallurgical processes only yield high Cu recovery, losing Al and Fe to the slag. Emission control systems, such as the one installed at the advanced smelter, Umicore plant in Belgium, are costly (Teller, 2006).

Hydrometallurgy is an alternative method involving chemical leaching with acids, such as nitric acid and sulfuric acid, followed by metal recovery from the leached solutions via techniques such as cementation and solvent extraction (Cui and Zhang, 2008; Mecucci and Scott, 2002; Pant et al., 2012; Oh et al., 2012; Zhang and Xu, 2016; Awasthi and Li, 2017). A recent development in hydrometallurgy is bioleaching, which uses acidophilic groups of bacteria to leach metals from PCB (Zhang and Xu, 2016; Hong and Valix, 2014). In recent years, hydrometallurgy has become the more prominent method for the benefits it affords, compared to pyrometallurgy. Hydrometallurgical techniques are more controllable, environmentally-friendly, and precise. There are four conventional techniques, consisting of acid leaching, cyanide leaching, thiosulfate leaching, and thiourea leaching.

Acid leaching, the most popular route, results in high leaching rates and allows for metal-specific leaching, but is corrosive, especially when used in large amounts. Some examples of acid systems include nitric acid, which is commonly used to leach Cu, but cannot be used directly for electroplating, and sulfuric acid and hydrogen peroxide, which is

highly effective for leaching of Cu, but can be corrosive at high concentrations. Aqua regia, the most effective solvent for leaching of metals, yields the highest Cu extraction; yet, it is the most corrosive leaching agent and presents hazards when used in large amounts.

Cyanide leaching was traditionally used for gold mining, but has begun to be disregarded due to its toxicity. Thiosulfate and thiourea leaching, on the other hand, are greener processes used for precious metal extraction, particularly in the leaching of Au and Ag. Ammoniacal thiosulfate solutions have been demonstrated to yield 95% Au and 100% Ag extracted from PCBs of mobile phones (Oh et al., 2012). However, this reaction is time-consuming, lasting from 24 to 48 h in total (Oh et al., 2012). Additionally, the presence of Cu and Al can cause low Au extraction efficiencies in thiosulfate solutions because of the re-deposition of extracted Au ions. Researchers have investigated different combinations of physical pre-treatment schemes to overcome these challenges regarding Au extraction in ammonium thiosulfate media (Jeon et al., 2019). Thiourea leaching with ferric ion as an oxidant has been shown to yield 86% Au and 71% Ag extraction, but is quite costly and requires a large amount of solvent for a small amount of solid (Behnamfard et al., 2013; Birloaga et al., 2013). There are drawbacks associated with each of the different leaching chemistries, and thus, research efforts in hydrometallurgy, particularly metal extraction, have focused on reducing the amount of corrosive acids used and developing greener solvent systems for chemical leaching.

Supercritical fluids present an interesting, greener alternative to acid leaching, and have been increasingly studied by researchers. Processes with supercritical H₂O have been shown to be effective for the removal of BFRs (Xing and Zhang, 2013; Wang and Xu, 2014; Hadi et al., 2015; Wang and Zhang, 2012). Researchers have shown that treatment with supercritical water results in 97.6% debromination efficiency (Wang and Zhang, 2012). Supercritical water has even been combined with acid leaching for metal extraction from PCBs (Xiu et al., 2013; Xiu et al., 2015; Liu et al., 2016). Two pre-treatment processes, supercritical water oxidation (SCWO) and supercritical water depolymerization (SCWD), together with HCl leaching, proved effective for the recovery of Cu, reaching 99.8% Cu recovery [Xiu et al. 2013].

Other solvents, beyond supercritical water, have also been utilized for the debromination of waste PCBs. Recently, a low temperature near-critical aqueous ammonia (NCAA) process was demonstrated to yield 100% Br removal at 300 °C with a reaction time of 60 min (F.R. Xiu et al., 2019). The NCAA treatment was tested at varying temperatures of 200–350 °C, reaction times of 30–90 min, and ammonia concentrations of 1.7–7.4 M. High debromination efficiencies were only achieved at

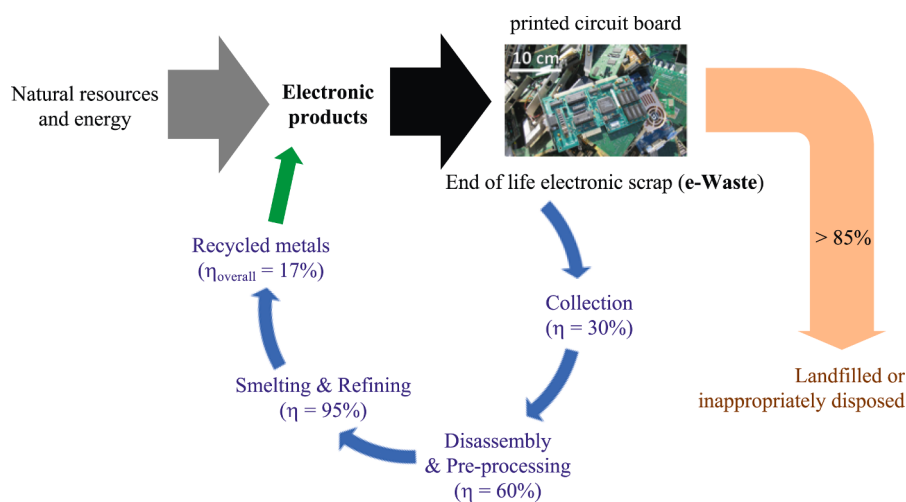


Fig. 1. Recycling sequence for gold recovery in EU with associated efficiencies of each unit processing (adapted from ref (Hageluken, 2006)).

high concentrations of ammonia, specifically 4.1 mol/L and 7.4 mol/L.

Subcritical methanol (subCM) was explored for the removal of PBDE from waste PCBs. In this process with subCM, the minimum reaction temperature was 200 °C and minimum reaction time was 60 min. For the complete removal of PBDE, a temperature of 300 °C was deemed necessary when using subCM alone, and a slightly lower temperature of 250 °C was required when using subCM with NaOH (F.R. Xiu et al., 2019). The main disadvantage of supercritical water, NCAA, and subCM treatments is the high temperature requirement. Supercritical water processes require temperatures of 420–440 °C, while NCAA and subCM processes require temperatures greater than 200 °C. Supercritical CO₂, on the other hand, is less toxic and has a lower critical temperature, and thus, presents a greener alternative.

This study aims at developing a novel process to leach Cu and other metals in separate streams from pieces of waste PCB with supercritical CO₂ (scCO₂) and aqueous acid. Through the synthesis of metal and polymer laminates as “model PCB” to reduce the complexity of PCB samples, the effects of scCO₂ with various co-solvents were investigated in a high-pressure, high-temperature reactor. The results of this fundamental study suggest that the role of scCO₂ is not in the direct extraction of metal from the PCB, but rather to induce physical changes to the polymer. From this key finding, a pre-treatment process with scCO₂ was investigated using small pieces of actual waste PCB and different co-solvents (water and sulfuric acid). The total amount of solvent was maintained at a low volume to reduce the amount of acid in the system. After pre-treatment with scCO₂/co-solvent, the PCB was leached in sulfuric acid and hydrogen peroxide (2 M H₂SO₄: 0.2 M H₂O₂) with the same volume, but at ambient conditions, to evaluate the extraction of Cu from the waste. The results demonstrate that pre-treatment with scCO₂ and acid was most effective, yielding pure 80% Cu extraction from the waste PCB in the subsequent ambient leaching process. Pre-treatments with scCO₂ and water, and with N₂ and acid (i.e. in the absence of CO₂) at the same temperature and pressure proved inferior, indicating the importance of pre-treatment with scCO₂ combined with acid. Detailed physical characterization of the PCB using Differential Scanning Calorimetry (DSC) and Scanning Electron Microscopy (SEM) was performed to explain why this combination enhanced the extraction of Cu from waste PCBs.

The proposed scheme utilizing a supercritical CO₂ + acid pre-treatment shows promise for metal extraction from e-waste with improved environmental sustainability. Currently, the majority of reported hydrometallurgical techniques use finely-crushed PCB as the starting feedstock and the role of scCO₂ in e-waste treatment is poorly understood (Calgaro et al., 2015). With the technology proposed in this study, vigorous mechanical pre-processing may be minimized, while reducing the amount of acid, for the effective extraction of Cu from e-waste.

2. Materials and methods

2.1. Preparation and characterization of waste PCB

Printed circuit board scrap was collected from waste computers in a local scrap collection. The waste PCB was cut into small pieces ranging in size between 0.2–1 cm² lateral area. A portion of the waste PCB was ground into fine particles (<1 mm in size) in a Blendtec Designer 725 blender. The metal composition of the PCB was determined in two ways: 1) dissolving the finely crushed waste PCB in concentrated, heated H₂SO₄ solution (Certified ACS Plus, Fisher Chemical) and H₂O₂ (30 wt% w/inhibitor, Sigma-Aldrich) for >24 h and 2) pyrolyzing the small pieces of waste PCB at 500 °C and then dissolving the char in concentrated, heated acidic solution for >24 h. From the results, the metal component of the PCB samples was determined to consist of the following base metals: Cu 20%, Al 2%, Fe 2%, and Ni 3%.

2.2. Preparation of model PCB

Model PCB laminate samples were prepared using Cu foil (0.1 mm thick, Puratronic®, 99.999% (metals basis), Alfa-Aesar) and polycarbonate (sheets of 1.0 mm thickness, Goodfellow). The laminated, layered composites (polymer/metal/polymer) were made on a hot press (Carver Model 4122) at a temperature of 166 °C, above the glass transition temperature, T_g, of the polycarbonate. 8 mm-diameter disks of Cu foil were cut out and sandwiched between two (4 cm x 7.5 cm) sheets of polycarbonate, and a load of 1.6 t was applied to press the sheets together, encapsulating the Cu disks. The desired thickness of the model PCB samples was 1.1–1.3 mm, comparable with the thickness of real PCB waste. Once the desired thickness was achieved in the hot press, the sample was removed for cool-down and individual samples were punched out as 12 mm-diameter disks. The Cu foil was completely encased between the two polycarbonate layers, and the average thickness of the model PCB samples was 1.2 mm.

2.3. Reaction of PCB and analysis of leached solutions and treated solid samples

The model PCB samples and small pieces of actual waste PCB were treated with supercritical CO₂ in a high-pressure, high-temperature (P, T) reactor (Model 4597 Micro Reactor, max pressure = 340 atm, max temperature = 350 °C, Parr Co.) connected to a syringe pump (Model 500D syringe pump, Teledyne ISCO). Fig. 2 shows a schematic of the setup. The treatment with scCO₂ was conducted at a temperature of 120 °C and a pressure of 148 atm with a stirring rate of 600 rpm.

The solid to liquid ratio in the reactor was controlled at 25 g PCB/1 L of solution, where the total volume of solution in the reactor was maintained at 10 mL. This loading was selected based on the conventional PCB treatment processes found in literature to make comparisons. Sulfuric acid solution with a concentration of 2 M H₂SO₄ was prepared using deionized water and H₂SO₄ (Certified ACS Plus, Fisher Chemical). The concentrations of solvents were chosen from previously reported leaching systems, which yielded high metal extraction rates (Oh et al., 2012). For the subsequent leaching process, experiments were conducted at ambient temperature and pressure in a 100 mL beaker on a digital, magnetic stirring plate with stir speed set to 300 rpm. The leaching solution was prepared using 2 M H₂SO₄ solution and 0.2 M H₂O₂ prepared from hydrogen peroxide solution (30 wt% w/inhibitor, Sigma-Aldrich). The total volume of leaching solution was controlled at 10 mL and the solid to liquid ratio was kept at 25 g PCB/1 L consistent with the experimental conditions in the reactor. Once leaching was completed, the solution was collected using a 10 mL syringe connected to a 2.5 µm filter to ensure the leached solution was free of sample

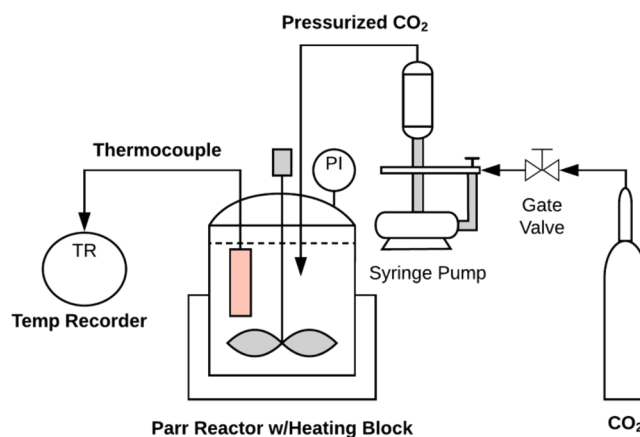


Fig. 2. Schematic of the high-pressure, high-temperature reactor system for e-waste pre-treatment with scCO₂.

residue. The leached solutions were then analyzed using Inductively Coupled Plasma-Optical Emission Spectrometry ICP-OES (Agilent 720) to determine the fractions of Cu, Fe, Al, and Ni extraction. Characterization of the model and actual waste PCB was performed using Differential Scanning Calorimetry, DSC (TA Instruments DSC250), and Scanning Electron Microscopy, SEM (Zeiss Sigma VP).

3. Results and discussion

3.1. Evolution of unique morphological structures during the treatment of model PCB in the presence of supercritical CO₂

The heterogeneity of real PCB complicates the understanding of the main interactions of PCB with supercritical CO₂ and co-solvents. As discussed earlier, PCB is a composite of plastics (polycarbonate, polyvinyl chloride, polyethylene, polypropylene, acrylonitrile butadiene styrene, epoxy resin, and BFRs) and metals. In order to develop a fundamental understanding of the effect of supercritical CO₂ on real PCB, one plastic and one metal component were used to construct model PCB samples. Specifically, polycarbonate (PC) and Cu metal were chosen for the model samples.

Previously, it was shown that supercritical CO₂ in sulfuric acid and hydrogen peroxide swells the polymer and induces a permanent, physical change (no chemical change) (Hsu et al., 2019). Building upon this work, more detailed studies on the morphological changes of the polymer (polycarbonate) during exposure to scCO₂ and co-solvent were conducted. Various contact times, ranging from 30 min to 5 h, and different solvent and scCO₂ combinations were tested. The sample treatments were performed in the high P, T reactor at 148 atm and 120 °C for a maximum reaction time of 5 h. These conditions were selected based upon prior studies of the crystallization behavior of amorphous polycarbonate treated with scCO₂ alone (Liao et al., 2003; Sun et al., 2014; Beckman and Porter, 1987). It has been reported that supercritical CO₂ enables the crystallization of initially amorphous PC at relatively low temperatures and that the effect depends on the temperature and pressure of the scCO₂ contact. In particular, researchers found a larger effect with increasing scCO₂ temperatures in the range of 100–140 °C at constant pressure, and with increasing scCO₂ pressures up to a threshold pressure. For example, this threshold pressure was approximately 158 atm at a temperature of 120 °C (Liao et al., 2003). Thus, from these reported results, 148 atm and 120 °C were selected as the scCO₂ pressure and temperature for the pre-treatment of samples with scCO₂ and co-solvents, since these conditions appeared to induce significant crystallization of amorphous PC when exposed to scCO₂ alone.

Two baseline experiments were then conducted: the exposure of the PC and Cu model samples to dry scCO₂ and to scCO₂ and water, for a maximum time of 5 h. Substantial porosity and cracking were not observed in these two cases, indicating that sulfuric acid and hydrogen peroxide together create porosity, cracking, and delamination in the samples. When evaluating the effects of sulfuric acid and hydrogen peroxide as the co-solvents, the role of hydrogen peroxide became clear. Hydrogen peroxide is an oxidizing agent that leaches the Cu metal and is more costly than sulfuric acid from the economic standpoint. Removing hydrogen peroxide from the exposure to scCO₂ could be favorable, especially if sulfuric acid alone could induce porosity, cracking, and delamination in the sample. The PC and Cu samples were reacted with sulfuric acid (2 M H₂SO₄) and scCO₂ only at various reaction times (30 min, 2 h, 3 h, and 5 h) to assess this hypothesis. Fig. 3 displays the effects on the model samples. Beyond contact times of two hours, the samples showed no further difference in appearance.

In just 30 min, the sample undergoes a change in opacity and swells, the surface roughens, and pores form. Permanent morphological changes are observed. At 2 h, the sample has broken apart and the PC becomes fragmented, likely due to the well-mixed, rapid stirring in the reactor. It is evident that hydrogen peroxide (H₂O₂) is not necessary to induce the physical changes in the model PCB samples. DSC



Fig. 3. Photos of model Printed Circuit Board samples before and after the pre-treatment with scCO₂ and H₂SO₄.

measurements show that these changes are accompanied by the crystallization of the initially amorphous PC on much shorter timescales than typical for scCO₂ exposure alone (on the order of 4–6 h) (Liao et al., 2003; Beckman and Porter, 1987). This study demonstrates that the exposure of model PCB, PC and Cu laminates, to scCO₂ and 2 M H₂SO₄ at elevated temperature and pressure for just 30 min results in significant morphological changes, including delamination. The combination of scCO₂ and sulfuric acid induces crystallization of PC in a notably reduced timescale, opening up the structure of the sample and allowing for enhanced transport of the leaching solvent to the metal.

3.2. Leaching behaviors of metals from waste PCB samples pre-treated using supercritical CO₂

In the development of a treatment process for the real waste PCB, the energy-intensive conditions of the reactor with supercritical CO₂ (high pressure and high temperature) and the total processing time are major factors for consideration. Drawing from the results of the model PCB study, supercritical CO₂ treatment and leaching solution (2 M H₂SO₄: 0.2 M H₂O₂) were decoupled in a two-step process. Fig. 4 illustrates this process: 1) scCO₂ and sulfuric acid pre-treatment at 120 °C and 148 atm for 30 min to induce morphological change and extract the metals, Al, Ni, and Fe and 2) acid/oxidizing agent leaching at ambient T, P for 3 hrs to extract Cu solely.

This two-step treatment scheme was applied to the small pieces of actual waste PCB and investigated for metal extraction efficacy. While cracking and delamination of the PCB chips were not observed as in the study with model PC and Cu laminates, notable morphological differences were observed on the surface of the waste PCB after the novel treatment. Pores formed and appeared to penetrate deep into the PCB structure and some final degradation and fragmentation of the plastics were noted. Most importantly, ICP analysis of the leached solutions revealed a major enhancement in Cu leaching from the pieces of actual waste PCB via the scCO₂ and acid pre-treatment process.

Three variations of the pre-treatment step were investigated, keeping the pre-treatment temperature and pressure conditions constant at 120 °C and 148 atm. The leaching step to extract Cu was kept consistent in all three cases. In the first case, only water was used as the co-solvent in the

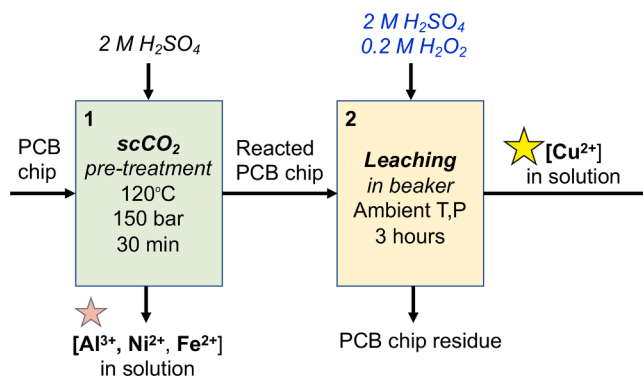


Fig. 4. Proposed scheme for the extraction of metals from PCB chips utilizing scCO₂ as a pre-treatment medium.

exposure to scCO_2 , and the total volume of solution, 10 mL, was maintained. After this treatment, no visible changes were seen on the PCB, the plastics appeared intact, and the surface appeared smooth and seemingly unaffected. The extent of Cu extraction obtained from ICP analysis was only 17% in this first case. In the second case, CO_2 was removed from the pre-treatment and replaced with N_2 at the same temperature and pressure conditions. The solvent system contained 2 M H_2SO_4 . ICP analysis revealed a marginal improvement over the pre-treatment with scCO_2 and water, yielding 31% Cu extracted. Finally, the proposed pre-treatment of scCO_2 and 2 M H_2SO_4 was investigated. The leached solution from the novel treatment was analyzed and 82% Cu was extracted. Fig. 5 summarizes the Cu, Al, Fe, and Ni leaching results for these three cases and depicts a representative PCB sample before and after the pre-treatment of scCO_2 and acid. The initial compositions of Cu, Al, Fe, Ni, and other metals in the small pieces of PCB are also presented. Recall from Fig. 4 that Al, Fe, and Ni are extracted in a separate stream from the Cu; Cu is purely extracted after the 3-hour leaching process and Al, Fe, and Ni are extracted only after the pre-treatment with scCO_2 .

Clearly, the proposed methodology with supercritical CO_2 and acid pre-treatment significantly enhances the extraction of Cu. 80% Cu extraction is achieved after leaching along with 58% Ni and 34% Al extraction after pre-treatment with scCO_2 and acid. It is important to highlight that when small pieces of actual waste PCB are leached without pre-treatment (3 hrs in sulfuric acid and peroxide only), only 12% Cu is extracted, and no Ni, Al, or Fe is extracted. This corresponds closely to the results from pre-treatment with scCO_2 and water. The combination of scCO_2 and acid in the pre-treatment is clearly key to enhancing Cu extraction. In assessing the sustainability of the leaching solvent consisting of sulfuric acid and hydrogen peroxide, alternative oxidizing agents, beyond hydrogen peroxide, were considered. Specifically, the ferric ion, $\text{Fe}_2(\text{SO}_4)_3$, was investigated as an oxidant (Yazici and Deveci, 2014). The concentration of oxidant in the leaching solvent was maintained at 0.2 M $\text{Fe}_2(\text{SO}_4)_3$ in 2 M H_2SO_4 . After pre-treating the small pieces of PCB in scCO_2 and acid and leaching the pre-treated PCB in the ferric salt solution, ICP analysis revealed that only 50% Cu was extracted. These results mainly indicated that the 2 M H_2SO_4 : 0.2 M H_2O_2 leaching solution was significantly more effective but also suggested that the solvent may not be solely limited to the usage of hydrogen peroxide as the oxidant. The other base metals, Ni, Al, and Fe,

were leached in lower amounts likely due to the fact that Cu is evenly dispersed within the board as the main conductive element in PCB. Additionally, the differences in leaching may have been attributed to galvanic interactions between Cu and Al in solution (Jeon et al., 2018).

3.3. Thermal properties of waste PCB samples before and after the scCO_2 + H_2SO_4 pre-treatment

Further investigation into why there is an improvement in Cu leaching when supercritical CO_2 is combined with acid as a pre-treatment was conducted through characterization of the actual waste PCB. Differential thermal analysis was performed using DSC. Fig. 6 shows the thermal scans for untreated PCB and treated PCB, where the treated PCB represents PCB that underwent pre-treatment with scCO_2 and acid.

Two heating and cooling scans were performed with isothermal dwell times of 30 min following each scan. The heating rate was controlled at 1 °C/min, and the maximum temperature was fixed at 250 °C. The scan for untreated PCB, shown in dashed lines, exhibited unremarkable thermal transitions, but a small baseline shift can be seen during the first temperature ramp to 250 °C (heat 1 in Fig. 6), at a temperature of approximately 150 °C. This shift likely represents the glass transition of PC. The sharp endotherm at 225 °C, observed during both temperature ramps to 250 °C (heats 1 and 2 in Fig. 6), corresponds to the melting temperature of tin, as tin is found in the solder material on the surface of the PCB. On the other hand, the thermal scan of the treated PCB, shown in continuous lines, does not exhibit this sharp melting peak and shows no sign of a glass transition during the first heat. Rather, there is a decrease in heat flow during heat 1, likely due to the volatilization of residual acid, H_2SO_4 , from the PCB. Sulfuric acid has a boiling point that exceeds the temperature at which this transition occurred, but recall the solvent in the system was diluted sulfuric acid (2 M H_2SO_4), not pure sulfuric acid. Since sulfuric acid is hydrophilic, it is reasonable to speculate that the vapor released was rich in H_2O , thus lowering the boiling point of H_2SO_4 .

3.4. Visual observation of morphological changes of waste PCBs pre-treated with scCO_2 + H_2SO_4

SEM microscopy provided telling evidence as to why the process

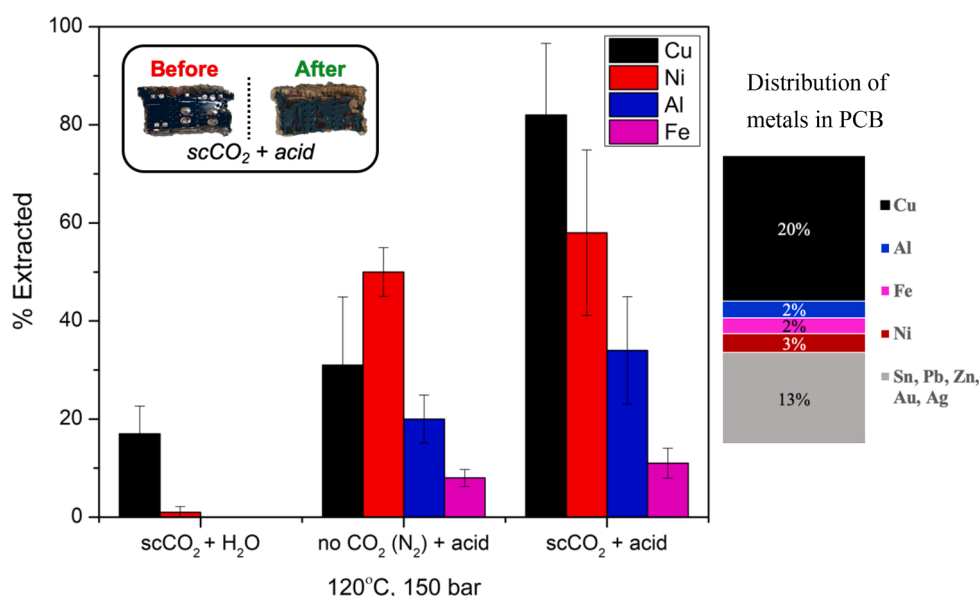


Fig. 5. Leaching behaviors of different metals from PCB in three different pre-treatment media illustrating the effect of scCO_2 and H_2SO_4 . The same leaching process was used for all 3 cases (ambient temperature and pressure conditions, 3 hrs, 2 M H_2SO_4 and 0.2 M H_2O_2), in which only Cu was extracted. Al, Fe, and Ni were extracted during pre-treatment. The distribution of metals in the PCB is given on the right as a reference.

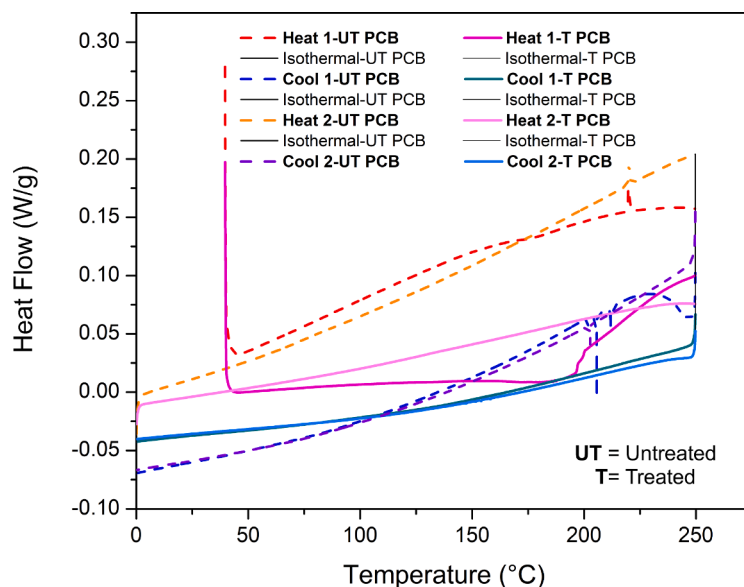


Fig. 6. DSC curves for the untreated and treated Printed Circuit Board samples (two heating and cooling scans).

with scCO_2 and acid pre-treatment was effective in the leaching of copper from PCB. Fig. 7 highlights four representative SEM images indicating the surface topology and internal porosity of the pre-treated PCB. Figs. 7a and 7b portray the main difference in surface topology between PCB pre-treated with N_2 (no CO_2) and acid and PCB pre-treated with scCO_2 and sulfuric acid. The surface of the PCB that was treated with scCO_2 and acid is roughened and fractured and contains large voids. Figs. 7c and 7d depict the material on edge fracture surfaces and deep inside the sample. The structures of these materials resemble

polymers having undergone solvent-induced crystallization (Durning et al., 1986). The large pores shown in the SEM images weakens the structural integrity of the plastics and enables access by leaching agent to the buried metal interfaces within the PCB. The creation of pores and openings on the PCB enhances transport of the leaching solvent to the metal, leading to the major improvement in Cu leaching. Fig. 8 illustrates the mechanism of crystallization induced by the pre-treatment with scCO_2 and acid. The crystallization is a purely physical change, in which the polymer chains in the plastic rearrange from a disordered

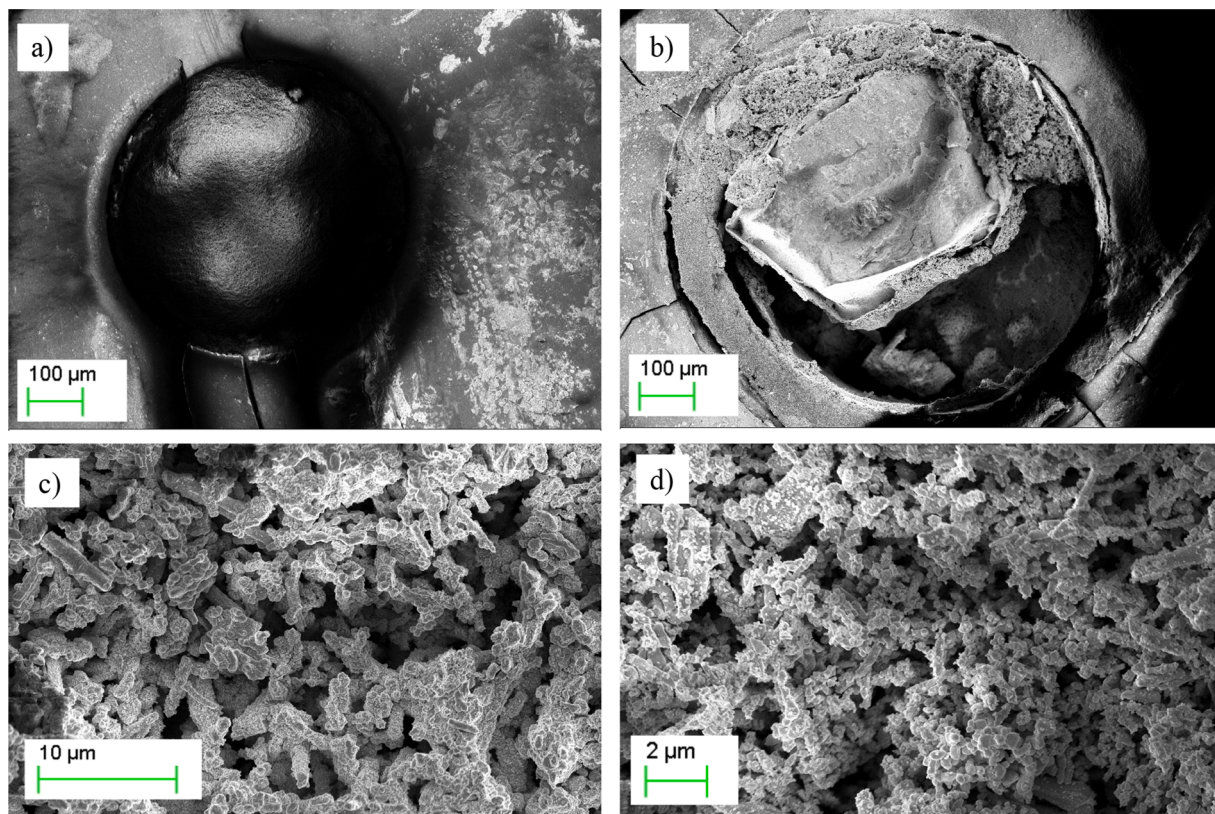


Fig. 7. Morphological changes of Printed Circuit Board after different pre-treatments: surface topology of samples treated in (a) $\text{N}_2 + \text{H}_2\text{SO}_4$ and (b) $\text{scCO}_2 + \text{H}_2\text{SO}_4$. Edge fracture surface (c) and internal pore structure (d) are also shown for the Printed Circuit Board sample treated in the medium containing $\text{scCO}_2 + \text{H}_2\text{SO}_4$.

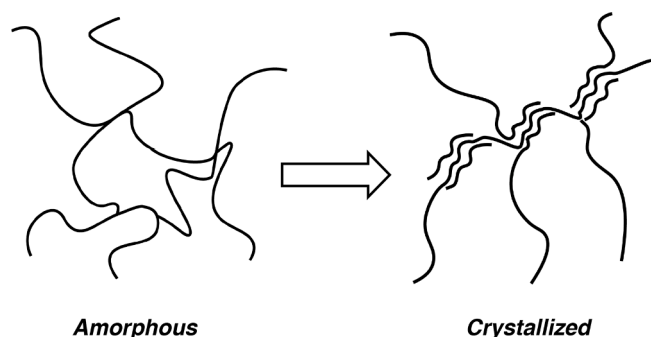


Fig. 8. Mechanism of scCO_2 and acid-induced crystallization of the polymeric component of waste PCB (from amorphous to crystallized).

amorphous state to an organized crystalline state.

The process utilizing supercritical CO_2 as a pre-treatment proved to be effective in the leaching of Cu from small pieces of actual waste PCB. Nearly 100% copper extraction is obtained in under 4 hrs without energy-intensive physical processing. Thus, the proposed scCO_2 -based treatment process eliminates the grinding and separation steps required in the processing of e-waste, specifically PCBs. When scaled-up, the shredded waste PCBs can be placed directly inside of a large reactor. Existing leaching methods for small pieces of waste PCB require at least 8 hrs of leaching in the same solvent, sulfuric acid and hydrogen peroxide, at an elevated temperature of 85°C (Oh et al., 2012). The pre-treatment time of only 30 min in the high-temperature and high-pressure reactor is significant, as the residence time has been substantially decreased from the 3–6-hour residence time of conventional schemes with supercritical CO_2 . Delamination processes using scCO_2 and water require a minimum of 3 hrs and require further processing steps afterwards (Sanyal et al., 2013). This process shortens the residence time and keeps the PCB structure intact, with only the metals leached out from the board. There is no toxic release of flame retardants and hazardous gasses and there is no generation of byproducts. The separation of PCB into the plastic, metal, and glass fiber components is bypassed entirely. From the materials perspective, an intact PCB could simplify recycling. Furthermore, since Cu is nearly fully leached out, there may be increased access to precious metals in the waste and therefore the extraction of Au and Ag could be improved. Gold could be extracted in a secondary leaching process using solvents such as thio-sulfate solution, thiourea, hydrochloric acid, or aqua regia. Optimally, Au would be separated physically since the PCB was structurally weakened by the pre-treatment with scCO_2 and acid. This type of sustainable, physical separation could be optimized by locating the Au-containing sections of the PCB for a targeted approach to precious metal recovery.

In terms of the corrosivity and toxicity of the solvent, the volume of acid required in the process is relatively small, with a lower solid to liquid ratio compared to that of current processes (Oh et al., 2012). The pre-treatment of pieces of waste PCB with supercritical CO_2 is also advantageous because it does not require special additives. Recently reported pre-treatments utilize expensive and potentially hazardous additives, such as NaOH and citric acid, in sizable amounts (Jadhav and Hocheng, 2015; Jadhav et al., 2016). Specifically, the pre-treatment method with citric acid involves a large amount of concentrated hydrogen peroxide, $1.76\text{ M H}_2\text{O}_2$, which is highly reactive and quite hazardous (Jadhav et al., 2016).

Lastly, by incorporating supercritical CO_2 as a green solvent and eliminating the intensive mechanical processing steps, opportunities towards sustainability are created. With respect to the economic and energy benefits of minimizing mechanical processing, a study conducted on an e-waste recycling facility in California showed that size reduction, dismantling, and separation account for approximately 25% of the operating costs associated with processing e-waste. Energy makes up

roughly 20% of the operating costs from size reduction, and labor and equipment make up the rest of those costs (Kang and Schoenung, 2006). From these estimates, the proposed process has the potential to reduce up to 25% of the operating costs at an e-waste recycling facility, and in turn save energy and reduce labor and equipment costs.

4. Conclusion

A pre-treatment process with supercritical CO_2 and sulfuric acid followed by acid leaching was developed and tested on small pieces of waste PCB. The conventional leaching solvent, 20 wt% sulfuric acid and 2 wt% hydrogen peroxide, was sufficient to leach nearly all of the Cu contained in waste PCB after pre-treatment with scCO_2 and 2 M H_2SO_4 . For the pre-treatment, the temperature and pressure conditions were 120°C and 148 atm and the total reaction time was 30 min. After the pre-treatment, leaching of the PCB pieces was performed in sulfuric acid and hydrogen peroxide, 2 M H_2SO_4 :0.2 M H_2O_2 , at ambient conditions for 3 hrs. Leaching of the pieces of PCB pre-treated with scCO_2 and acid resulted in 82% Cu extracted, much higher than 31% Cu extracted from PCB pre-treated with N_2 and acid and 17% Cu extracted from PCB pre-treated with scCO_2 and water respectively. Characterization of the PCB pieces, especially by Scanning Electron Microscopy, demonstrated why the pre-treatment of scCO_2 and acid was effective. The SEM images showed the creation of pores and openings inside and on the surface of the PCB, allowing the solvent to penetrate into the PCB and thereby react with the metals, leaching out copper. The resulting porosity weakens the robust and flexible structure of the polymers and thus opens up channels in the PCB. Detailed examination of the morphologies in the obtained images suggested evidence of solvent-induced crystallization, a solely physical change, in the polymeric components. During the scCO_2 pre-treatment-induced crystallization, the initially amorphous polymers reordered into organized, crystallized structures. Overall, the major advantages of the proposed process include the reduction of acid, shortened reaction time of less than 4 hrs compared to 8–12 hrs, and lack of intensive mechanical processing, particularly grinding and physical separation techniques that are conventionally necessary to yield > 80% Cu extraction. High-value precious metals could potentially be recovered from the PCB residue after Cu extraction via secondary leaching or physical separation, since the PCB is weakened and brittle from the pre-treatment with scCO_2 . This study demonstrates that the proposed two-step process involving pre-treatment with supercritical CO_2 is a promising treatment scheme for metal extraction from e-waste towards sustainability.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgement

The authors acknowledge NSF (CBET 1706905) for financially supporting this work.

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at [doi:10.1016/j.resconrec.2020.105296](https://doi.org/10.1016/j.resconrec.2020.105296).

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