Section IV: Discussion

EC Removal

The results from the pickling solution experimentation demonstrated the effects of different concentrations of HNO3 on the efficiency of EC removal. The quickest results were from the solution comprised of 40 vol% nitric acid (HNO3, ACS reagent, 70%, Sigma-Aldrich), 40 g/L ferric nitrate (Fe(NO3)3, purified, Cole-Parmer), five g/L ferric chloride (FeCl3, reagent grade, 97%, Sigma-Aldrich), five g/L sodium chloride (NaCl, ReagentPlus®, ≥99%, Sigma-Aldrich), ten g/L benzotriazole (C6H5N3, analytical standard, Sigma-Aldrich), and five g/L sulfamic acid (NH2SO3H, ACS reagent, 99.3%, Sigma-Aldrich), which completely removed ECs in 38 minutes at room temperature at a S/L ratio of 1g:5ml. The 35% vol HNO3-based pickling solution still provided acceptable effectiveness within a reasonable time of 70 minutes. For industrial implementations, an HNO3 concentration of 35 to 40 vol% is recommended for the pickling solution recipe.

The reaction of HNO3 with metals, including Sn, Pb, and Cu, results in the generation of nitrogen oxide and nitrogen dioxide. Nitrogen oxides are known to damage the human respiratory system and contribute to acid rain. They cannot be released directly into the air. Thus, industrial implementation of this recipe will require a process designed to collect and deal with the products of nitrogen oxides. Since HNO_3-based pickling solutions are widely used in the metal manufacturing industry to remove impurities, such a process has been well-established and can be adapted easily (Dahlgren, 2010).

The alternative recipe with 2.5mol/L fluoroboric acid (HBF_4, 48 wt. % in H_2O, Sigma-Aldrich) and 0.4 mol/L hydrogen peroxide (H_2O_2, 30 % (w/w) in H_2O, contains stabilizer, Sigma-Aldrich) removes EC in 60 minutes at a s/l ration of 1g:5ml. However, due to the high price of fluoroboric acid and hydrogen peroxide, the cost of chemicals needed in this process is estimated to be many times more than that of the pickling solution process. Tables 10 and 11 compare the cost of chemicals needed for 100 L of

solutions for each recipe. The cost of chemicals in the pickling solution is $37.32/100 L, while the cost for the fluoroboric acid-based recipe is $4,136/100 L. Thus, the pickling solution process was determined to be more economically beneficial for large-scale implementation in the industry.

Table 10

Cost of Chemicals Needed for 100 L Pickling Solution

Recipe: 35% (v/v) HNO_3 ,40 g/L $Fe(NO_3)_3$, 5 g/L $FeCl_3$, 5 g/L NaCl, 5 g/L $H_3NSO_3$and 10 g/L $C_6H_5N_3$					
Chemical	Chemical formula	Weight or Volume needed in 100L solution	Market price		Cost in 100L solution
Nitric acid	HNO_3	50L 70vol%	$0.32/kg (Mike, 2023)		$22.4
Iron(III) Nitrate nonahydrates	$Fe(NO_3)_3{\cdot}9HO_2$	6.68kg	$1.2/kg (Ferric Nitrate Nonahydrate, n.d.)		$8.02
Iron(III) chloride	$FeCl_3$	0.5kg	$230/ton (*High-Quality Chemical and Reagents for Sale | Camachem*, n.d.)		$1.15
Sodium chloride	NaCl	0.5kg	$0.1/kg (*Sodium Chloride Price per Kg - Search - IndexBox*, n.d.)		$0.5
Sulfamic acid	H_3NSO_3	0.5kg	$0.508/kg (*Sulfamic Acid Price and Market Analysis - ECHEMI*, n.d.)		$0.25
benzotriazole	$C_6H_5N_3$	1kg	$5,000/ton (*[Hot Item] Hot-Selling High-Quality CAS 95-14-7 Corrosion Inhibitor 99.5% Benzotriazole 1H-Benzotriazole BTA*, n.d.))		$5
Total cost (In 100L pickling solution): $37.32					

Table 11

Cost of Chemicals Needed for 100 L Tetrafluoroboric Acid-based Recipe

Recipe: 2.5M HBF_4 and 0.4M H_2O_2				
Chemical	Chemical formula	Weight or volume needed in 100L solution	Market price	Cost in 100L solution
Tetrafluoroboric acid	HBF_4	32.67L 48w%	$90.1/kg (*Buy Tetrafluoroboric Acid Solution, 4x500 Gram*, n.d.)	$4120.9

Hydrogen peroxide	H_2O_2	38.84L 35w%	$0.36/kg (Mike, 2020a)	$15.8
Total cost (In 100L solution): $4,136.7				

The EDX result in Figure 11 confirms that the precipitates obtained in this step contained Cu, Sn, and Pb. Thus, the precipitates should be collected and further processed to recover the metals.

The correlation results in Table 4 indicate that the time needed to remove the ECs has a strong correlation with the concentration of nitric acid in the pickling solution recipe. For a recipe with 35 vol% nitric acid, the average time needed to remove ECs is 67.2 minutes with a standard deviation of 4.6 minutes. Thus, in implementation, an immersion time of around 67.2 minutes can be expected, which is a reasonably short time for industry implementation. Having confidence in a reliable operation time is very important for commercial adoption of this process.

Compared with previous studies, this project identified a lower range of nitric acid concentration to effectively remove EC within a short time. It identified the s/l ratio needed for a fluoroboric acid-based recipe to remove ECs. It also compared the cost of two recipes and established the nitric acid-based pickling solution as the more cost-effective recipe.

Solder Mask Removal

The experiments conducted involving etching with the potassium and sodium hydroxide (KOH; NaOH) at 90 °C for 90 minutes resulted in the complete removal of the solder mask using potassium hydroxide and the partial removal with sodium hydroxide. Based on these results, potassium hydroxide was determined to be more effective. The next tests conducted compared the results of potassium hydroxide at concentrations of 2M and 1M with different S/L ratios. Figure 6 shows that at a concentration of 2M, an s/l ratio of 1g:1ml was sufficient to remove the solder masks fully. Figure 5

shows that at a concentration of 1M, the solder masks were only partially removed at all tested S/L ratios. Thus, 2M KOH at an S/L ratio of 1g:1ml was used for further studies.

The most cost-effective NaOH-based recipe that was suggested in previous studies requires 3M NaOH at 70 °C for 2 h (Kang et al., 2021). In this project, a new recipe with 2M KOH and a s/l ratio of 1g:1ml at 90°C for 90 min was identified. Compared with previous studies, this new recipe saves both cost and time.

Mechanical Shredding and Dense Medium Separation

Figure 8 shows that mechanical shredding was effective in breaking PWBs without solder masks into small pieces.

Dense medium separation experiments compared different TBE to acetone ratios ranging from 10ml:2ml to 10ml:10ml and showed that only 10ml:6ml to 10ml:8ml ratios resulted in satisfactory separation of shredded pieces with Cu foils from laminated polymer pieces. In these two solutions, pieces with Cu foils all sank to the bottom, while laminated polymer pieces all floated to the surface of the solutions. Ratios of 10ml:2ml to 10ml:4ml resulted in pieces with Cu foils floating together with laminated polymer pieces. The ratio of 10ml:10ml resulted in all pieces sinking to the bottom. Thus, a ratio in the range of 10ml:6ml to 10ml:8ml is determined to be effective in separating Cu foils from the laminated polymer pieces.

A bromoform and acetone mixture solution has been previously shown to be effective in separating metal-enriched pieces and metal-depleted pieces after milling of waste PCBs (with ECs) (Nekouei et al., 2018). However, due to the concern of bromoform being more hazardous with higher vapor pressure (5.9 mm Hg at 25oC) compared with tetrabromoethane (TBE) (Hauff & Airey, 1980), in this study, a TBE-based recipe was developed for density separation. TBE has a density of 2.95 g/mL and

a low vapor pressure (0.02 mm Hg at 25oC). It is widely used in mineral separations and is safer than bromoform.

Reuse of Chemicals

The reuse of spent chemicals in this developed process, including picking solution, KOH, and dense medium, was studied. Results summarized in Table 3 in the Results section show that the pickling solution was only effective for three cycles of EC removal. In the third cycle, the time needed to remove ECs was already too long to be feasible for large-scale implementation.

ICP results in Table 6 confirmed that after each round of using the pickling solution to remove ECs, the concentrations of metal elements increased. At the end of the reuse experiments of the pickling solution, adding KOH effectively precipitated the metals out of the solution. There was no residual metal in the solution after KOH treatment. It was noted that the Fe concentration was high in the fresh solution due to the fact that the additives in the recipe contained Fe.

Results summarized in Table 4 in the Results section show that KOH can be reused. There was a noticeable loss of volume of KOH solution after each cycle of solder mask removal. For a start volume of 300 ml of 2M KOH, after each round of solder mask removal, 40-50 ml of fresh 2M KOH was added to the spent solution to keep the volume of KOH consistent for the next round of the experiment. After four cycles, there was no sign of decreased effectiveness of the mixed KOH in removing solder masks.

Results summarized in Table 5 in the Results section show that dense medium can be reused. There was a noticeable loss of volume of dense medium solution after each cycle of separation. With a starting volume of 18 ml of the mixed solution, a loss ranging from 2.1 to 3.3 ml was observed after each round of separation experiment. Due to the high evaporation rate of acetone, the loss in acetone was expected to be more significant than the loss of TBE. Thus, even though the starting ratio of TBE to

acetone was 10ml:8ml, with a starting volume of 18 ml of the mixed solution, after each round of separation experiment, about 1ml of TBE and 1.7 ml of acetone were added to maintain the total volume of the liquid consistent for the next round of separation. After ten cycles, there was no sign of decreased effectiveness in the separation of Cu foil pieces from laminated polymer pieces.

Reusing spent solutions is a field that previous studies did not cover. Reusing spent solutions in this process is unique and contributes to improving sustainability, lowering cost, and minimizing the disposal of waste chemicals in the process.

Implications and Applications

These findings are applicable as a practical method for the recycling of PCBs. With this novel, sustainable process, the practices can be used to ensure that the recycling of PCBs is done sustainably and without exhausting many resources. Compared with pyrometallurgical methods that are currently used to recycle a small portion of waste PCBs, this method requires a very low capital investment and a small cost for chemicals, as shown in Table 1. The potential for reusing chemical solutions in this process leads to an even lower operational cost and a great reduction in the need to dispose of waste chemicals from the solder mask removal and density separation steps. With the increasing presence of e-waste and its scarcity of being recycled, this project offers an inexpensive, easily scalable, and reliable alternative to current unsustainable recycling methods; its application provides an impactful solution to this worldwide crisis.

Future Research

The experimental results strongly suggest that KOH and the dense medium can be reused and may not require any disposal process. Removing or minimizing the need to dispose of waste, KOH and the dense medium solutions are very desirable from both a cost and an environmental perspective.

More cycles of experiments will be conducted to confirm the effective reuse of these solutions after many rounds. Because of this project's strong desire for sustainability, reusing chemicals would be very beneficial.

For industrial implementation, tests to scale up each step in this process will be conducted. A lab set-up for large-scale experiments has been created and is shown in Figure 3. Processing conditions determined with small samples may need to be adjusted to be effective in large-scale experiments. For example, using the set-up shown in Figure 3, it was found that the s/l ratio for the solder mask removal step must be changed from 1g:1ml to 1g:3ml to ensure the complete immersion of the whole piece of PWB within the liquid solution for effective processing. Thus, scale-up tests are necessary as a next step.

Section V: Conclusion

In conclusion, this project has successfully developed and demonstrated a scalable, effective, and environmentally sustainable method for recycling printed circuit boards (PCBs), a critical component of electronic waste. Through the innovative combination of mechanical and hydrometallurgical techniques, including wet chemical dissolution, mechanical milling, and dense medium separation, the study has identified optimal conditions for extracting valuable metals from PCBs. The use of 40% vol nitric acid for electronic component removal, 2M potassium hydroxide for solder mask removal, and a 10:8 tetrabromethane and acetone mixture for dense medium separation highlights an improved process to advance standard e-waste recycling. The potential for further improvement in metal recovery from electronic components and the reuse of all solutions involved in this multistep process opens new avenues for research. By focusing on improving the ease of implementation, reducing operational costs, and minimizing the environmental impact of the recycling procedure, this project lays the groundwork for future initiatives aimed at addressing the escalating problem of electronic waste. As the demand for metals continues to rise and the accumulation of e-waste becomes increasingly problematic, the

development of sustainable recycling methods such as this becomes ever more critical. This research not only contributes to the field of waste management and recycling but also aligns with global efforts towards sustainable development and the conservation of natural resources.