ABSTRACT

Advanced Technology Materials, Inc. (ATMI) has developed a novel process based on green chemistry and green engineering methodologies for reclaiming valuable materials from waste electronics. We have demonstrated that we can recover metals and valuable components from end-of-life products using cost-effective, sustainable, and scalable methods (e.g., systems that are closed-loop, energy efficient and environmentally benign). This includes both chemical desoldering and precious metal reclaim from printed wiring boards (PWBs) and integrated circuits (ICs) near room temperature with all metals recovered and resold. Our current system is processing approximately 400 lbs. per hour of high value printed wiring boards.

Keywords: e-waste, gold fingers, non-toxic, aqua regia, green chemistry

INTRODUCTION

Globally more than 50 million metric tons of electronic waste (e-waste) was disposed of in 2009 (1). This is expected to grow to over 72 million metric tons by 2014. Less than 20% of all e-waste is recycled with the majority ending up in China, India and other developing countries. While <2% of the mass in US landfills, e-waste accounts for 70% of the heavy metals (2). In addition to the environmental insult, e-waste contains large quantities of valuable metals. For example, one ton of used mobile phones (~6000 handsets – a small fraction of the nearly 1 billion annual production) contains 340 g of gold, ~3.5 kg of silver, 140 g of palladium and 130 kg of copper (3) with a combined value of $15,000 (~$2.5 billion total). Global revenues for e-waste recovery are expected to grow to $14.6 billion by 2014 (1).

From a mass and volume standpoint, the majority of electronic waste is metal, plastic and glass – much of which can be recycled using conventional technologies. Approximately 5% by weight of e-waste consists of printed wiring boards (PWBs). Although some are repaired and resold, most are sent abroad for disposal. Those with high metal value are sold to overseas smelters and those with low value are sent to Asia or Africa where the chips are manually desoldered and the trace precious metals are collected either by open burning or from chemical leaching with toxic chemicals such as hot aqua regia or cyanide. These standard hydrometallurgical processes dissolve all components in, for example, a strong acid and then selectively remove the specific elements of interest. While the dissolution step is simple, selectively removing each component from the mixture in high yield is a complex and time consuming challenge.

Alternatively, one may use more complex chemical formulations to selectively dissolve individual metals from waste PWBs and integrated circuits (ICs) thereby simplifying the overall process. Building on its 25-year knowledge-base of developing chemistries for the fabrication of semiconductors, ATMI has chosen this latter approach. Using the principles of Green Chemistry and Green Engineering (4, 5), we have demonstrated a proprietary (patent pending) process to extract maximum value from waste PWBs and ICs in a safe, environmentally sound and economic manner. A schematic diagram of the process is shown in Figure 1. Note that no shredding or grinding is required at this point which may lead to the loss of up to 40% of precious metals and/or to the formation of dangerous metal fines, dust containing brominated flame retardants, and dioxins (6).
After rinsing the boards to remove surface dirt, dust, etc., all chips and components (capacitors, resistors, heat sinks, connectors, etc.) are chemically desoldered. This step requires less than 20 min in an acidic solution at a temperature between 30 and 40 °C (see Figure 2).

The solder is collected as a salt and resold while the resulting chips are still fully functional. Note that the gold connectors remain intact on the board demonstrating the selectivity of the desoldering chemistry.

The chemistry is highly selective towards both Pb/Sn and Sn/Ag solders leaving copper, gold, etc. on the board and base metal components intact. Lead, tin and silver salts (typically oxides) are recovered in high purity (>95% recovery) and are resold. The bath chemistry can be loaded to over 250 g per liter and both this chemistry and the rinse water are recycled multiple times. Tests of the desoldered chips show that they are still operational and thus may be reused. Given that manufacturing a single 2 g chip uses 1.6 kg of fossil fuels, 72 g of chemicals, 32 kg of water and 700 g of gases, this is a tremendous environmental savings (7).

Alternatively, the ICs may be ground and the trace precious metals extracted using the chemistry summarized below. Base metal components (primarily steel and aluminum) are also collected and resold.

The now solder-free bare boards are subjected to a non-toxic, environmentally benign gold leaching chemistry at 30 °C for approximately 5-10 min (depending on composition and thickness of surface gold), which selectively removes all precious metals (gold, silver, palladium, etc.). See Figure 3. These metals are collected with >99% efficiency and >99.9% purity via chemical reduction or electrowinning and are sold.
These results have now been confirmed by an independent testing laboratory. After rinsing, the clean printed wiring boards may be chopped and the copper collected and sold. We have demonstrated >99% copper recovery with >99.5% purity. Because no solder or base metals are present, the value of these boards is far higher than with competing technologies. The remaining chopped fiberglass may be used as filler in, for example, cement.

Figure 3. Selective removal of gold from gold “fingers” cut from printed wiring boards near room temperature using a non-toxic, environmentally benign formulation. Note that the underlying copper is still present after processing demonstrating the selectivity of the gold leaching chemistry.

The entire process flow has been validated by reclaiming metals from several tons of waste PWBs (TV, computer, cell phone, etc.) in an automated system that is closed so that no vapors escape (Figure 4). Boards pass on a conveyer system from a desoldering (foreground) module to a gold leaching (background) module. IC’s are collected in the bins on the left. Clean boards emerge at the far end of the system. This pilot system has been scaled to handle up to 400 lbs per hour of high value printed wiring boards and all of the chemistry and the rinse water are recycled for reuse in the process. To date the gold leaching chemistry has been recycled nine times with no loss of performance. This system is being used to further optimize both the chemistry and the process flow for various types of PWBs and to refine the process economic models. Water discharged is neutralized, has less than part-per-million trace metals (by ICP analysis) and no organics (see Table 1).

Figure 4. ATMI automated PWB recycling pilot line

| Process | Before Treatment | Before Final Discharge |
|---------|------------------|------------------------|
| Rinse Water | Trace metals (ppm) | Trace metals (ppm) |
|          | pH               | Ag  | Cu  | Fe | Ni | Pb  | Sn  | Zn  | pH | Ag  | Cu  | Fe | Ni | Pb  | Sn  | Zn  |
| Desolder | 2.6              | 0   | 0.3 | 1.4 | 0.56 | 1.3 | 0.09 | 0.09 | 8.6 | 0   | 0   | 0.18 | 0.02 | 0.02 | 0  | 0  |
| Gold Leach | 1.9              | 0.35 | 1   | 5.4 | 0.89 | 0.8 | 0.62 | 5.5 | 0.17 | 0   | 0.19 | 0.03 | 0.06 | 0  | 0  | 0.01 |

Table 1. ICP analysis of process rinse water both before and after treatment showing only trace metals (<<1 ppm) present.

### SUMMARY

ATMI has developed the first cost-effective, all-chemical process for the recovery of metals from waste printed wiring boards and integrated circuits eliminating the need for using cyanide or aqua regia, both traditional methods for precious metal extraction. Metal recovery is >99% with >99% purity; metal salts from solders are recovered at >95%. Our closed process eliminates human exposure to lead, tin, hazardous chemicals, etc. In addition, the non-toxic chemistry is recycled with no toxic byproducts or hazardous air, water or solid waste discharge. All of the process steps are efficient (low volumes of chemicals required), low-energy with a low carbon footprint (near room temperature operation) and low-cost. Formulations have high loading capability (meaning fewer change-outs) and are optimized to reduce cost. The concept is scalable and thus can be sited near sources of e-waste (minimizing transportation costs). Finally, all waste streams are converted to inputs for other processes.

While alternatives exist to the ATMI process, they all have significant drawbacks. For example, smelting only recovers copper and precious metals in moderate yield (no solder) – chips and boards are burned. While many of the pollutants may be scrubbed in the exhaust of sophisticated smelters,
most are simple “backyard” operations (open burning) leading to significant air, water and ground pollution. Thermal (manual) desoldering of PWBs leads to contaminated copper, non-functioning chips and components (not to mention dangerous working conditions due to lead and organic vapors) and no precious metal recovery. Chemical reclamation of gold using aqua regia or cyanide is effective, but has a tremendous environmental burden due to the formation of toxic by-products and to the low selectivity of the process. In addition, these chemistries are not readily recycled.

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