# Effective Metal Recovery in the Mobile Phone Waste by Chemical and Biological Treatments

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**Abstract** Recycling electronic waste is an important subject not only from the point of view of waste treatment, but also regarding the recovery of valuable metals. This research examined the stepwise recovery of metals in mobile phone waste using chemical treatment via pH swing and biological method using biomineralization. In chemical treatment, the metal fraction attached to the printed circuit board (PCB) and camera parts were separated from the mobile phone waste and were then pulverized into particles with a size less than ~ 2 mm. The metal fraction was dissolved in aqua regia, and the pH of the solution was increased to 10.5 by adding $NH_4OH$. The first precipitate was iron oxide, produced by raising the pH to 3.1~4.2 with $NH_4OH$. Sequentially, copper chloride and rare earth-metal complex were produced at pH 5.7~7.7 and 8.3~10.5, respectively. In the biological method, the filtrate at pH 7.7 was added to a metal-reducing bacteria growth medium as precursor. After two weeks of incubation, rhodochrosite and calcite were precipitated as nano-sized minerals. The results indicate that effective metal recovery of mobile phone waste is feasible using chemical and biological treatments, and the recovered metals and rare earth metals can be recycled into raw materials for various industries.

**Keywords:** Metal recovery, Electronic waste, Urban mining, pH swing process, Biomineralization

## 1. Introduction

The amount of generated waste of electrical and electronic equipment (WEEE) has been growing due to rapid economic growth and technological advances all over the world. In the EU, 9 million tonnes of WEEE were generated in 2005, and this figure is expected to grow to more than 12 million tonnes by 2020 (EU). Recycling WEEEs may provide a substantial source of both (non) ferrous and precious metals. Although most metals are base metals such as copper, iron, nickel, tin, lead, aluminum and zinc, a significant amount of attention has been expended on the recovery of precious metals, including gold, silver and palladium (Sheng and Etsell, 2007). Waste mobile phones usually consists of a body, printed circuit board (PCB), liquid crystal display (LCD), camera, key board, etc. Since the PCBs contain a great amount of useful and precious metals, including gold, silver, and palladium, researchers have focused on PCBs for precious metal recovery (Park *et al*., 2009; Kim *et al*., 2011). However, camera parts including neodymium magnets ($NdFeB_{48}H$) have rarely been studied despite the high need for neodymium recovery. In previous studies, hydrometallurgical processes using various reagents (e.g., cyanide, thiosulfate, aqua regia etc.) have shown high efficiency in metal recovery, but the high cost and toxic byproducts remain to be addressed. To solve these cost-related and environmental disadvantages, some microbiological processes have recentely been proposed as alternatives to chemical methods. Some microbes, such as *C. violaceum, A. ferrooxidansm, Chromobacterium violaceum,* and *Aspergillus* sp. increased Au and Cu leaching/recovery from mobile phone PCBs waste (Pham and Ting, 2009; Chi *et al*., 2011; Brandl and Faramarzi, 2006; Madrigal-Arias *et al*., 2015). Also, Brandl *et al*. (2001) reported that bacteria such as *Thiobacillus ferrooxidans* and *T. thiooxidans*and fungi such as *Aspergillus niger* and *Penicillium simplicissimum* were able to mobilize high percentages of Cu, Sn, Al, Ni, Pb and Zn particles from WEEE. Therefore, the combination of chemical and biological methods can increase the efficiency of metal recovery from mobile phone waste and achieve the effect of an environmentally-friendly treatment. Thus, the objectives of this study were to investigate the stepwise separation and recovery of metals including both (non) ferrous and precious metals from mobile phone waste by combining chemical and biological methods.

## 2. Experimental

### 2.1. Preparation of the metal solution using aqua regia

First, the camera parts and PCB parts attached to the mobile phone waste were separated and collected for the experiment (Fig. 1). The process of separating and recovering metals, including both ferrous and non-ferrous metals, as well as precious metals from the mobile phone waste are shown in Fig.2.

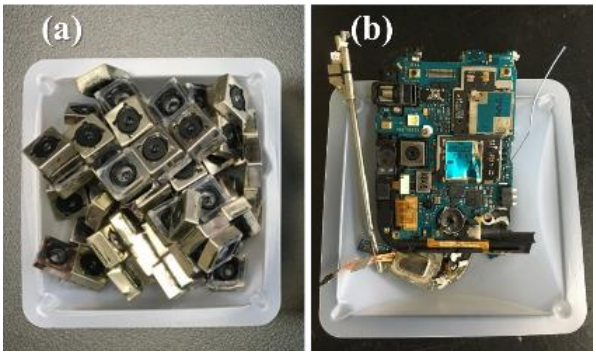

**Figure 1.** Camera and PCB parts separated from mobile phone waste

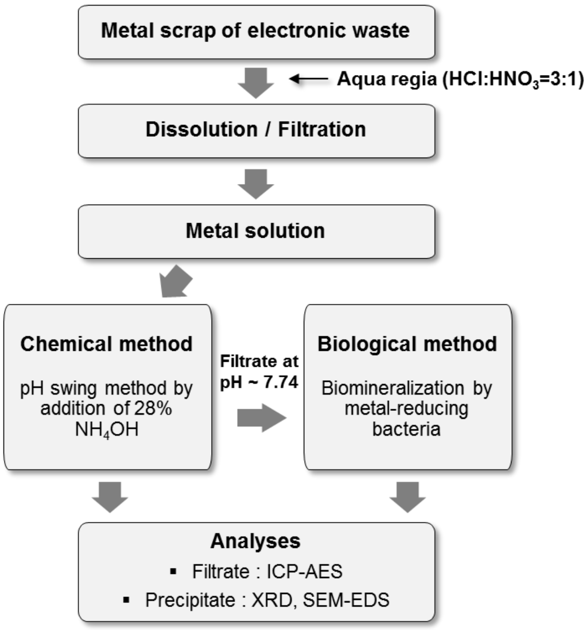

**Figure 2.** The process to separate and recover metals including Fe, Cu, and rare earth-metal complex from mobile phone waste by combining chemical and biological methods.

The metal fraction attached to the PCB and camera parts was pulverized to less than ~ 2 mm in size to prepare metal powders that can be easily dissolved. As a metal solvent, aqua regia was freshly prepared at a 3:1 mixture of hydrochloric acid: nitric acid. The prepared aqua regia was poured into metal powders in glass beakers and remained at room temperature for 48 h. In this reaction, the mixing volume ratio of the solvent to the metal powder was approximately 10: 1. The metal concentration dissolved in aqua regia was analyzed via inductively coupled plasma-atomic emission spectroscopy (ICP-AES).

### *2.2. Chemical method for metal recovery*

The metal solution dissolved in aqua regia was a very strong acid. Ammonium hydroxide ($NH_4OH$) solution (28%) was slowly added into the acidic metal solution to precipitate ferrous, non-ferrous, and precious metals with gravity only and with rapid stirring. The increase in pH with the addition of $NH_4OH$ induced the formation of precipitates, and when a certain pH is reached, precipitates are formed with change in color. When the precipitate had formed at a certain pH, the addition of $NH_4OH$ into the suspension stopped, but stirring continued for a sufficient time. The suspension was centrifuged to separate into a precipitate and a supernatant. The precipitate was washed with distilled water three times and then dried for mineralogical analyses. The supernatant was filtered with a syringe filter (0.45 μm), and then the filtrate was analyzed in the change in the concentration of metal ions via ICP-AES. The remaining supernatant was used to recover the other metal ions, and the experiment was continuously carried out in the same process.

### *2.3. Biological method for metal recovery*

Metal-reducing bacteria (Hwapo-1) were enriched from intertidal flat sediments of Suncheon in the Jeonnam province of South Korea. The medium for the bacterial growth and microbial synthesis of magnetite contained the following ingredients (g/L): 2.5 $NaHCO_3$, 0.08 $CaCl_2 \cdot 2H_2O$, 1.0 $NH_4Cl$, 0.2 $MgCl_2 \cdot 6H_2O$, 10 NaCl, 0.5 yeast extract, 7.2 HEPES (hydroxyethylpiperazine-N'-2-ethanesulfonic acid), 10 ml trace mineral, 1 ml vitamin. The medium was pre-reduced by boiling and purging with nitrogen gas and dispensing into 125 ml serum bottles. The bottles were sealed with butyl rubber stoppers and autoclaved for 20 min. at 121°C and 1.2 kgf/cm$^2$. The final pH of the medium was about 8.0 (Kim *et al.*, 2011). To produce biogenic metal- precipitates, 2 ml of the filtrate at pH 7.7 was added to the medium containing 10 mM of glucose ($C_6H_{12}O_6$) and 2 ml of enriched metal-reducing bacteria. The bacteria were cultivated in a shaking incubator at 25°C under an anoxic atmosphere for 2 weeks.

### *2.3. Analytical methods*

The mineralogical characteristics of the precipitates formed during experiments were examined using X-ray diffraction (XRD) and scanning electron microscopy (SEM) with energy dispersive X-ray (EDS) analyses. The X-ray diffraction analysis was performed using an X'Pert PRO (PANalytical, Netherlands) equipped with Cu Kα radiation (40 kV, 20 mA) at a scan speed of 5 θ/min. An SEM analysis was done on a JSM-7500F (JEOL, Japan) with an accelerating voltage of 200 kV to determine the morphology and elemental composition of the synthesized biogenic precipitates. The metal concentrations were measured using inductively coupled plasma atomic emission spectroscopy (ICP-AES) on an Optima 8300 (Perkin-Elmer, USA) following the standard method. Every experiment was run in triplicate, and the average values were used in the graph. The minimum detection limit for the ICP-AES of the metals was about 0.004 mg/L.

## 3. Results and discussion

### *3.1. Dissolution of metals in aqua regia*

The concentration of the metal leaching in aqua regia was determined via ICP-AES. The major metals (over 800 mg/L) leached from the camera parts were Cu (4,610 mg/L), Fe (3,380 mg/L), Zn (1,930 mg/L), Ni (1,690 mg/L) and Nd (874 mg/L), whereas minor metals (less than 200 mg/L) were Pr (200 mg/L), Cr (168 mg/L), Sn (114 mg/L), Dy (38 mg/L) and Tb (34 mg/L). In the case of the PCB parts, the major leached metals (over 2,500 mg/L) were Cu (23,600 mg/L), Fe (22,200 mg/L), Cr (4,460 mg/L), Ni (4,120 mg/L) and Zn (2,800 mg/L) whereas the minor metals (less than 500 mg/L) were Nd (425 mg/L), Pr (152 mg/L), Ag (63.6 mg/L), Mg (30.7 mg/L) and Au (20.9 mg/L). Thus, the types of leached metals showed similar trends, and the concentrations of Cu and Fe were the highest in both the camera and the PCB parts. However, the leaching rate of Nd was relatively high in the camera due to the Nd-magnet attached to the part. Also, the concentrations of all leached metals in the PCB were higher than those of the camera parts, and precious metals such as Ag and Au were leached out from the PCB.

### *3.2. Chemical recovery of copper, iron and rare earth-metal complex*

The pH of the metal solution, which is a strong acidic solution, slowly increased by injecting the ammonia solution dropwise. The solution of the camera metal was dark green at the initial pH of 0.4. As the pH increased, the color became darker, and a brown precipitate was formed at pH 4.2. The precipitate was separated by centrifugation, and the supernatant was filtered using a syringe filter (0.45 μm). The filtrate was reacted with the ammonia solution in the same manner. The pH of the filtrate gradually increased to pH 7.7, and it then transformed into a light blue precipitate. The precipitate was also separated by centrifugation. The pH of the supernatant was increased using the same method, and it turned to dark blue with the formation of a light gray precipitate at pH 10.5. The mineralogical characteristics of the precipitate were investigated via XRD analysis. In the results, the brown precipitate formed at pH 4.2 was difficult to identify in terms of the mineral type due to the low crystallinity, but ICP-AES analysis confirmed that the poorly crystalline minerals were composed of Fe, Cu, Cr and Sn (Fig. 4(a,b)). In particular, Fe, which was present at a high concentration in the metal solution, was found to have completely precipitated near 100% removal from the solution at pH 4.2. The light blue precipitate formed at pH 7.7 was mainly crystalline copper chloride hydroxides (Fig. 3(b)). The elemental analysis also showed that the concentration of Cu in the supernatant had been greatly reduced (Fig. 4(a)). Finally, a small amount of gray precipitate that formed at pH 10.5 showed no peak in the XRD analysis and was considered to be an amorphous mineral (data not shown). However, the presence of rare earth mixed minerals composed of Cu, Nd, Pr, Dy and Tb were confirmed via ICP analysis (Fig. 4(a,b).

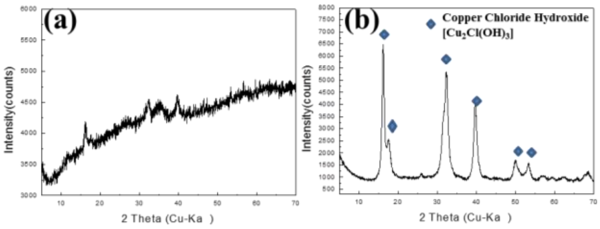

**Figure 3.** XRD patterns of the precipitate separated from the camera metal solution at pH 4.2 (a) and pH 7.7 (b).

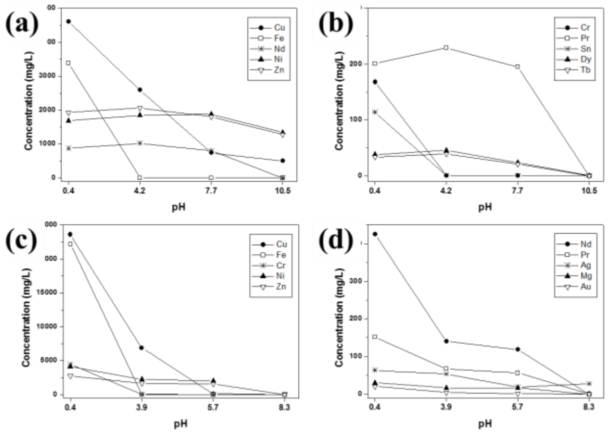

**Figure 4.** ICP-AES analysis of the supernatant at different pHs : (a) camera-major elements, (b) camera-minor, (c) PCB-major elements, (d) PCB-minor elements

The chemical metal recovery experiments using PCB part were conducted in the same manner as above. The PCB metal solution was also dark green at the initial pH of 0.4. As the pH increased, the color became darker, and a brown precipitate was formed at pH 3.9. The precipitate was separated via centrifugation, and the supernatant was filtered using a syringe filter (0.45 μm). Subsequently, the pH of the filtrate gradually increased to pH 5.7 by injecting the ammonia solution, and then a light blue precipitate formed. The precipitate was also separated via by centrifugation. The pH of the supernatant was increased using the same method, and it turned dark blue with the formation of light gray precipitates at pH 8.3. The mineralogical characteristics of the precipitate were investigated via XRD and SEM-EDS analyses. The results of the EDS analysis indicate that the brown precipitate consisted of amorphous iron oxides mainly composed of Fe and O, and a small amount of Cu, Cr and Sn together (Fig. 5(a,b)). The ICP-AES analysis confirmed that the dissolved metals in the solution became precipitated as minerals through the reduction of the element concentration in the supernatant (Fig. 4(c,d)). The light blue precipitate is identified as mainly crystalline copper chloride hydroxides, and the minerals are observed in the form of agglomerated particles of about 100 nm in size (Fig. 5(c,d)). The elemental analysis also showed that the concentration of Cu in the supernatant had been greatly reduced (Fig. 4(c)). Finally, a minor amount of gray precipitate that formed at pH 8.3 made it difficult to identify the mineral due to the low crystallinity. However, it was found that the metal-rare earth mixed minerals composed of Ni, Zn, Nd, Pr, Au and Ag were confirmed through EDS and ICP analyses (Fig. 5(e,f) and Fig. 4(a,b)).

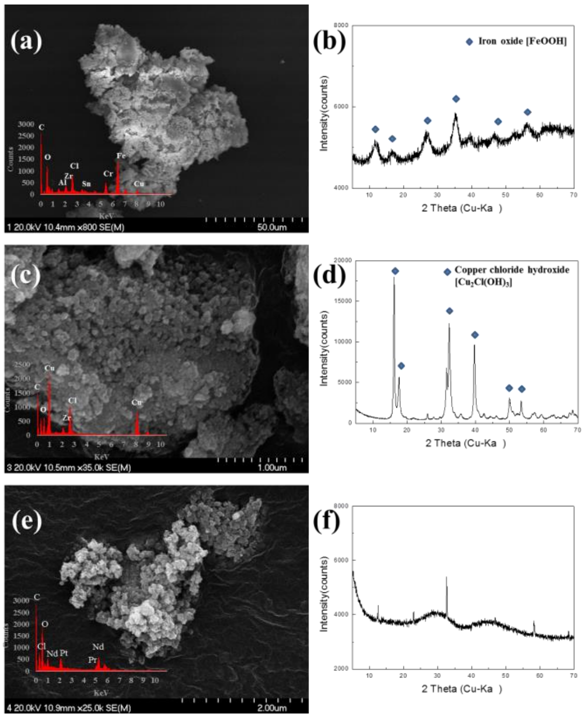

**Figure 5.** SEM-EDS images and XRD patterns of precipitate separated from the PCB metal solution at pH 3.9 (a,b), pH 5.7 (c,d) and pH 8.3 (e,f).

These results show that the PCB and camera from mobile phone waste can be separated using a simple chemical method. The results indicate that the degree of acidity influences the order of the precipitation in this study. Fe precipitated in an acidic condition (pH 3.9~4.2), Cu precipitated in a slightly acidic to neutral condition (pH 5.7~7.7), and the rare earth-metal complex precipitated in an alkaline condition (pH 8.3~10.5). In particular, the presence of various elements showed a tendency to form precipitates at lower pH conditions.

### *3.3. Biological recovery of manganese and calcium*

In the experiment using camera parts, the filtrate (pH 7.7) removed Fe and Cu precipitates and the metal-reducing bacteria were reacted for 2 weeks. As a result, a small amount of white precipitate was formed (Fig. 6(a)) and was identified as rhodochrosite ($MnCO_3$) and calcite ($CaCO_3$) via XRD (Fig. 6(b)) and SEM-EDS analyses (Fig. 6(c-e)). The calcite and manganese carbonate were observed as cubic and spherical particles, respectively, and the particle size varied from 1 to 5 μm (Fig. 6(c-e)). The morphology of these minerals was similar to those of previously reported the microbial synthesized carbonate minerals (Li *et al.*, 2011; Kim *et al.*, 2014).

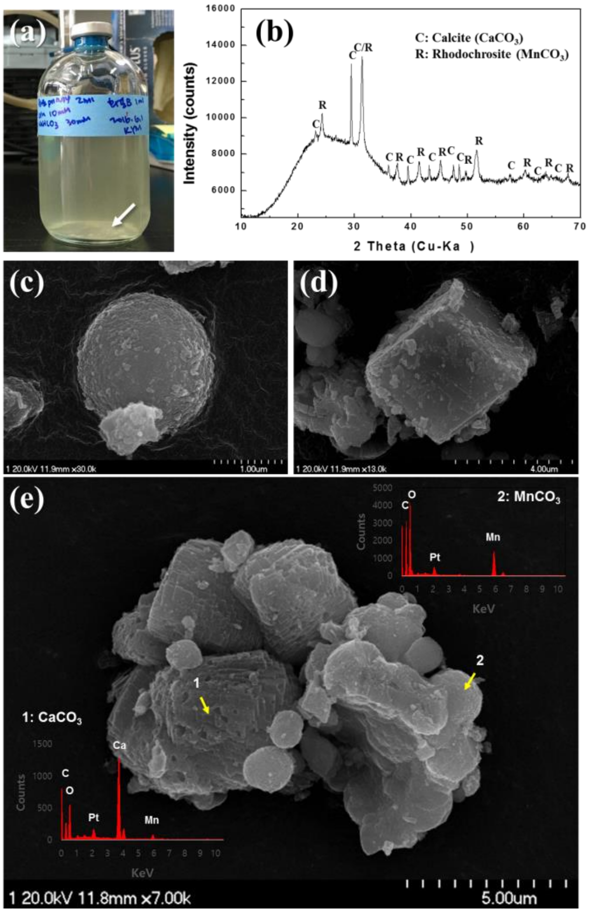

**Figure 6**. A picture showing the white settled precipitate (a), XRD patterns (b), SEM-EDS images of biogenic carbonate minerals (c-e).

The results of the ICP-AES analysis confirmed that the concentrations of Mn, Ca, Co, Cu, Ni, Zn and B present in trace amounts in the filtrate were slightly reduced (data not shown). Therefore, Mn and Ca were used to synthesize microbial carbonate minerals, and other trace elements were not observed because they were below the analytical level of detection even when coprecipitated or precipitated in the minerals. Therefore, the metal ions remaining in the filtrate could be mineralized by the metal-reducing bacteria. At the same time, the mineralization of the carbonate is effective in carbon dioxide sequestration.

## *4.* **Conclusion**

These results showed that the metals dissolved in aqua regia could be recovered using a simple chemical method, such as a pH swing. In particular, Fe showed a tendency to precipitate in an acidic condition (pH 3.9~4.2), Cu precipitated in a slightly acidic to neutral condition (pH 5.7~7.7), and rare earth-metal complex precipitated in an alkaline condition (pH 8.3~10.5), respectively. In addition, the presence of various metal ions in the PCB metal solution influenced the formation of the precipitate at a slightly lower pH compared to the simple mixing state in camera metal solution. Therefore, these results indicate that simple and effective metal recovery of the mobile phone waste might be feasible via chemical and biological treatments, and the recovered metals such as Fe, Cu, and rare earth-metal complex can be recycled as raw materials for diverse industries.

## Acknowledgement

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