Copper Recycling Technique Using Electrochemical Processes

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The recent growing awareness of the environment and interest in resource saving have raised the importance of metal recycling. As an electric wire maker that handles a large quantity of copper, we strive to promote copper recycling proactively and have developed a copper recycling technique using electrochemical processes for small-scale operations. We made the process as eco-friendly as possible and succeeded in continuously recycling electric wire scrap into high-purity copper.

Keywords: electrical wire scrap, copper, recycling, electrochemical, closed system

1. Introduction

With the rise in concern about the environment and upsurge of resource nationalism in recent years, metal recycling has become increasingly important. Copper is a common material we use in everyday life. The Japanese 10-yen coin and various types of cables are made of copper. However, the reserves-to-production ratio of copper is estimated to be 40 years. Therefore, copper is a natural resource of which there are concerns about depletion. In addition, the quality of copper concentrate extracted from copper mines has been declining over the years, which has boosted the load on the extraction and smelting processes.(1)

Scrapped electronic devices, such as printed wiring boards (PWBs), contain a large amount of useful elements including precious metals, which are mostly recycled at copper refineries using the non-electrochemical method.*1 However, it takes much energy and cost to transport copper scraps from cities, where they are collected, to refineries, which are often far from cities. And some components in the scrap can produce toxic gases in the recycling process.(2),(3) As mentioned above, the load on non-electrochemical refineries has been increasing. And, based on the principle of local production for local consumption, the need for distributed recycling has been growing. However, as the name suggests, distributed recycling tends to be operated on a small scale, which often restricts efficiency and cost reduction. On the other hand, the electrochemical method*2 is suitable for small-scale operations with relatively high efficiency, despite some problems including effluent treatment.

Electrical wires, which have been our mainstay for a long time, are often made of high-purity copper because of its excellent electrical conductivity. An electrical wire consists of a copper core covered with resign to provide insulation and corrosion resistance. The life of an electrical wire is mainly determined by the life of the outer covering(4) and the core can be recycled to copper material. Scrapped electrical wires are collected and the outer covering and inner cores are separated, which are recycled or disposed of Sumitomo Electric Industries, Ltd. and its group companies have been actively committed to recovering copper from scraped electrical wires. We collect the wire scrap, separate the outer covering from the inner core with a stripping machine, and recycle the copper as a raw material for electrical wires. Thin wires, which cannot be processed by the stripping machine, are fed to a process, generally called a "nugget process," which cuts the wires into small pieces and sorts them into covering and copper metal by a physical method (e.g. gravity separation).(5) However, separation is not perfect and a small amount of mixed resin and copper pieces is left. It is thought that such sludge, which we call a "crushed sample" here, is also used as a recycling material at non-electrochemical refineries. Since the crushed sample, the target of this research, has a simple composition mainly consisting of resin covering and copper metal, we thought they can be processed with a straightforward electrochemical method. As a model case of distributed recycling, we have developed an electrochemical recycling technology that is suitable for crushed samples.

2. Concept of Recycling

The crushed sample, which is the target of this research, is a mixture of small pieces of covering resin and copper metal that cannot be sorted by a physical method. The concept of our recycling method is to dissolve only the copper metal in a solvent and remove the remaining resin, then recover the copper. Specifically, copper metal is dissolved chemically and recovered by electrodeposition, a process called "electrowinning."

Waste liquid is a significant issue in the electrochemical method. To cope with this, a closed system was designed that minimizes waste liquid. In electrowinning in an aqueous solvent, an oxygen-generating reaction by electrolysis of water generally occurs at the anode, which consumes relatively a large amount of electricity. Therefore, a reaction with minimum electric power cost was used. In addition, with consideration given to the cost, ease of handling, and reusability of the chemical liquid, a trivalent iron ion (Fe^{3+}) was used for dissolving copper metal (Cu), which was regenerated at the opposite electrode during electrodeposition (Fig. 1). This technique requires a two-liquid electrolytic bath with a diaphragm that prevents re-dissolution of the recovered copper into the liquid flown from the opposite electrode where it has been regenerated. Sulfuric acid was added to the liquid to maintain stability.

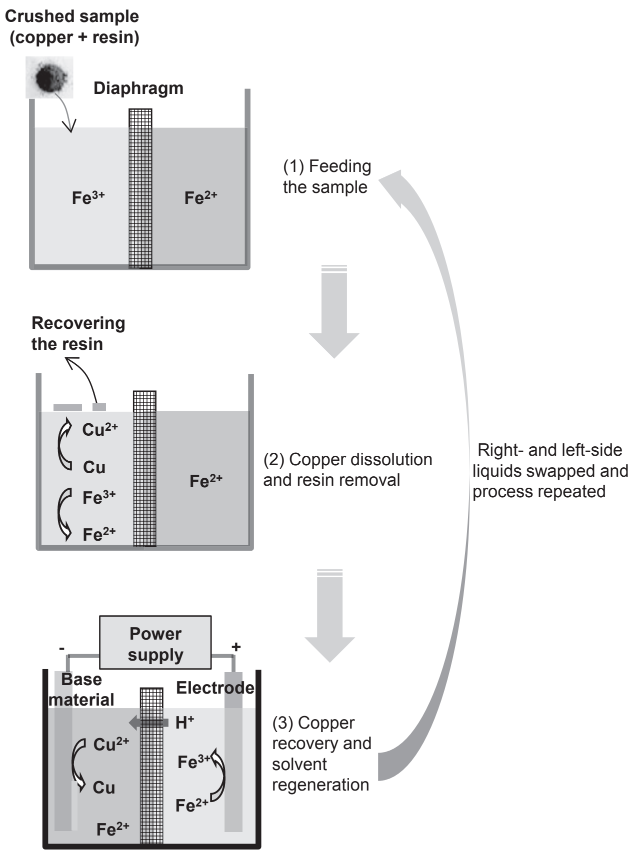

Fig. 1. Concept of this process

3. Element Experiment

To evaluate the feasibility of this concept, we built a mini plant with 80 L of liquid per electrode, and conducted experimental recovery of copper metal from a crushed sample, which is illustrated in Fig. 1.

3-1 Copper dissolving process

Copper metal is dissolved with a trivalent iron ion according to reaction Eq. (1).

$$2Fe^{3+} + Cu \rightarrow 2Fe^{2+} + Cu^{2+} \quad \cdots\cdots (1)$$

In this reaction, the standard free energy change*3 is negative. Therefore, the reaction should progress spontaneously according to thermodynamics. However, the speed of the reaction is affected by various parameters including the surface area of the copper to be dissolved, the concentration, and the temperature of the dissolvent. We measured how long it took for the copper to be dissolved using the crushed sample, and the copper could be dissolved in several hours.

A reaction, which is essentially the same as the above equation, is sometimes used to etch copper on PWBs. This suggests that developing and applying this process might make it possible to recover copper from waste etching liquid.

3-2 Resin removal process

The copper solution contained covering resin in powder form, which was removed by passing the solution through a general-purpose filter.

3-3 Electrowinning and liquid regeneration process

The solution with the resin removed was poured into a vessel with two sections separated by a diaphragm, such as an ion-exchange membrane, and the positive and negative electrodes were plunged into the solution in each section. When the electrodes were connected to a power source, copper metal was deposited on the negative electrode, the cathode according to the electroplating principle. At the positive electrode, the anode, an oxidation of iron ions from bivalent to trivalent occurred, which results in regenerating the solution so it can dissolve copper again. These reactions are expressed in the following equations:

$$\text{Cathode: } Cu^{2+} + 2e^- \rightarrow Cu \qquad E^0 = 0.340\text{ V} \cdots (2)$$

$$\text{Anode: } Fe^{2+} \rightarrow Fe^{3+} + e^- \qquad E^0 = 0.771\text{ V} \cdots (3)$$

where, e^- indicates an electron and E^0 the standard electrode potential.(6) At the cathode, if the potential is lower than E^0, the reaction in Eq. (2) moves from left to right. If the potential of the anode is higher than E^0, the reaction in Eq. (3) moves from left to right. Since an aqueous solvent is being used, electrolysis of water occurs as a side reaction,*4 which is represented in the following equations:

$$\text{Cathode: } 2H^+ + 2e^- \rightarrow H_2 \qquad E^0 = 0.000\text{ V} \cdots (4)$$

$$\text{Anode: } 2H_2O \rightarrow 4H^+ + O_2 + 4e^- \qquad E^0 = 1.229\text{ V} \cdots (5)$$

E^0 in Eq. (2) is higher than that in Eq. (4), and E^0 in Eq. (3) is lower than that in Eq. (5). This follows that the standard electrode potentials of the reactions of this copper recovery process are inside the standard electrode potentials of the electrolysis of water at both the cathode and anode. Therefore, in principle, it is possible to promote the copper recovery reaction without involving electrolysis of water.

As a result of the experiment, a high current efficiency*5 of 95% or more was obtained. The oxidation of iron ions, represented in Eq. (3), occurred at near 100% efficiency, which indicates that electrowinning with minimal side reaction was achieved.

4. Purity of Recovered Copper

Since high-quality copper is required as a raw material of electrical wires, the purity of the recovered copper was measured. Using copper foil with a thickness of 20 μm as a starting material, copper several mm thick was deposited onto the foil by electrodeposition. The recovered copper was melted and formed into an ingot and then analyzed with a quantometer.*6 Table 1 shows a summary of one sample. The contamination of iron, the main component of the solvent, was not so high. The amount of impure elements did not exceed several ppm, which indicates 99.99% or higher purity was obtained. Due to restrictions of the measurement method, oxygen could not be checked.

Table 1. Sample result of impurity analysis on recovered copper

Concentration	Impurity elements
> 10 ppm	None
10-6 ppm	Co, Sn
5-3 ppm	Fe, Ag, Zn, Si
< 3 ppm	Pb, S, Al, etc.

5. Repetition Stability

For a copper recovery system to be closed and generate little waste liquid, which is the concept behind this technology, the iron ions need to be reused repeatedly. Using the mini plant with 80 L of liquid per electrode, which was used in the element experiment, and the crushed sample, the repletion stability of this process was evaluated.

Assuming the series of processes described in Section 3 as a single cycle, we conducted a long-term test with 50 cycles, in which each of the two liquids is used as the cathode liquid and anode liquid, alternately. Approximately 1 kg of copper was dissolved or recovered in a single cycle, and the cycle time was around 8 hours. These parameters are independently adjustable by specifying the amount of solution and areas of the electrodes. Therefore, a full-scale facility can be designed according to the operation mode.

Figure 2 shows the changes in the current efficiency over 50 cycles. The behavior is stable, showing that the solution is reusable. It was not necessary to refill the iron and copper in the solution, and almost no waste liquid was discharged during operation. The sulfuric acid component, which is an additive, indicated slight reduction and needs regular refilling. We believe that the feasibility of our concept was demonstrated in a limited number of 50 cycles.

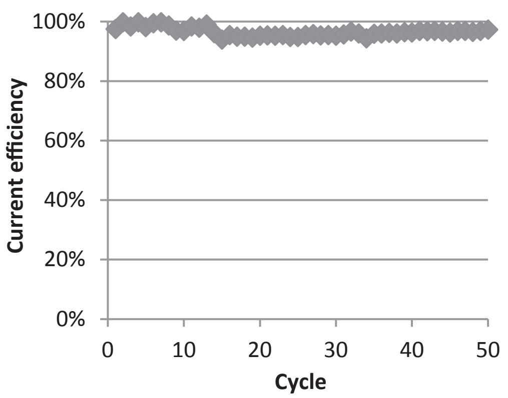

Fig. 2. Change in current efficiency

6. Conclusion

Since environmental problems, such as diminishing natural resources and global warming, have become more serious, the importance of recycling technology for small-scale operations will increase. As an electrical wire manufacturer, we have taken full recovery of copper from scrapped electrical wires, which was impossible with the conventional method, as a model case, developed a copper recycling technology, and demonstrated that high-purity copper metal can be recovered. The process of the equipment for demonstrating the principle consumes a relatively large amount of electricity. However, we believe that this can be reduced by improving the equipment design.

Aiming for expansion into fields with applications such as recycling more complicated electronic devices, etching waste liquid, and plating sludge, we strive to contribute to saving precious metal resources.

Technical Terms

*1 Non-electrochemical method: Contrary to the electrochemical method, which uses an aqueous solution, this process mainly treats materials with heat without a solution.

*2 Electrochemical method: Unlike the non-electrochemical method, which does not use an aqueous solution, this process is based on a solution, and uses electrolysis and chemical reactions occurring in the solution.

*3 Standard free energy change: The change in energy between before and after a reaction. If the change is negative, the energy decreases after the reaction, moving towards the more stable state.

*4 Side reaction: Unexpected and unavoidable reaction in addition to the main reaction, which is often not desired.

*5 Current efficiency: An index indicating the amount of electricity used to deposit copper. 100% indicates an ideal deposition.

*6 Quantometer: Multi-element simultaneous quantitative analysis device using the emission spectrum, etc.

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