Selectiv Recovery of Copper(II) from Incineration Ash Produced from a Municipal Waste Incineration Facility Using a Flow-through Type Electrolysis Method

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Abstract

Recovery of copper was attempted from municipal waste incineration ashes using acid extraction and electrodeposition by a flow-through type electrolysis cell (FE). Efficient extraction of copper from the incineration ash was obtained using 0.5 mol L$^{-1}$ sulfuric acid, i.e., copper extraction rate: 77% from bottom ash and 88% from fly ash. The copper in the 10-fold diluted extractant injected into the FE was quantitatively adsorbed by applying $-0.4$ V and was quantitatively desorbed by eluting with nitric acid.

Keywords Copper, incineration ash, electrolysis, extraction
Introduction

The incineration ash produced from a municipal waste incineration (MWI) facility is reused for roadbed materials and as a concrete aggregate, but the elution of hazardous substances such as heavy metals and dioxins pose an environmental concern. Therefore, most incineration ash is not used and is disposed of in a landfill at high cost. From another point of view, heavy metals are important resources for industry and the economy. However, the depletion of metal resources produced from mines is a concern, along with increased demand of heavy metals from industrial developments. Many researchers have developed methods to recycle heavy metals from industrial wastes. Therefore, incineration ash contains a large amount of heavy metals and is considered to be a useful resource.

In this study, we attempted to collect copper from incineration ash. Copper is an abundant base-metal, but the current production and reserves are concerned to be depleted within several decades due to the rapid increase in demand and economic development in countries such as Brazil, Russia, India and China. Currently, the industrial refining of copper in solution is mainly performed by electrolysis, as copper has less of an ionization tendency compared with other metals and is easily deposited on the electrode in an electrolytic cell.

We used this principle to recover copper using a handheld flow-type electrolysis cell (FE), which is an electrolytic cell with a carbon fiber-packed column as a working electrode. The determination of copper using the flow-through type electrolyte with carbon as a working electrode is relative classical technique. However, because the method has the high selectivity for targeted analyte metals, it has been utilized to the determination of heavy metals in real samples such as natural water or beverages samples even now. Also, this device is used for the electrosynthesis of organic compounds, oxidation of organic compounds with radicals, or as a continuous flow-type electrochemical detector in flow injection analysis. However, there were no reports that applied a flow-through type electrolysis cell to selective recovery of copper from
industrial wastes such as incineration ash.

We investigated whether the FE could selectively recover copper in the eluate of acid-treated MWI ash. This note reports the following: 1) the extraction of heavy metals from incineration ash by a strong acid, 2) the electrodeposition of heavy metal ions onto the FE, and 3) the selective recovery of copper ions eluted from the acid-treated ash by FE.

Experimental

Incineration ash sample

The incineration ash sample was obtained from a waste disposal incineration facility in Gunma Prefecture. Two types of incineration ash samples were used: bottom ash collected from the bottom of the incinerator, and fly ash from the combustion waste collected from the bag filter of the incinerator. The bottom ash sample was uneven in shape and particle size, so it was crushed in a mortar and screened to < 0.1 mm. The fly ash sample had a particle size of 0.1 mm or less and was used without sieving.

Reagents and apparatuses

Special-grade reagents were used as the measurement standards (Wako Pure Chemical Industries, Osaka, Japan). The water used for dissolving the reagent and diluting the solution was obtained from a deionized-distilled water (water) production system (ASK-2DS, Iwaki Co, Ltd., Tokyo). Strong acids (HCl, HNO₃ and H₂SO₄) used to leach heavy metals from the incineration ash sample were diluted to 0.05 to 4 mol L⁻¹ with water.

Heavy metal concentrations in the sample solutions were determined by a polarization-type flame atomic absorption spectrophotometer Z-5310 (AAS; Hitachi, Ltd., Tokyo, Japan). A F-22 pH meter (HORIBA, Ltd., Kyoto, Japan) was used for pH measurement. The composition of the incineration ash samples was measured by energy dispersive X-ray fluorescence spectrometer
EDX-700 (EDX; Shimadzu, Ltd., Kyoto, Japan). Organic elemental analysis in the ash samples was performed by simultaneous determination of hydrogen, carbon and nitrogen with a Micro Corder JM10 (J-Science Lab, Ltd., Kyoto, Japan).

Contents of heavy metals in incineration ash

The incineration ash sample was weighed (1.00 ± 0.05 g) into a Teflon beaker, and 10 mL of hydrofluoric acid (46%, 23 mol L⁻¹) and 2 mL of perchloric acid (60%, 9.2 mol L⁻¹) were added and evaporated to dryness at 105 °C. Then, 10 mL of hydrofluoric acid and 1 mL of perchloric acid were added into the Teflon beaker and again evaporated to dryness at 105 °C. The residue was completely dissolved in 1 mL hydrochloric acid and the volume was fixed at 25 mL with water containing 0.5% nitric acid. The concentration of heavy metal in the solution was quantified by AAS.

Extraction of heavy metals in incineration ash using strong acids

The incineration ash sample (7.5 g) was added to 100 mL of a strong acid solution (HCl, HNO₃, or H₂SO₄), which was prepared in the range of 0.05–4 mol L⁻¹. The sample solution was stirred for 1 h at 200 rpm using a magnetic stirrer (RS-1DN, AsOne, Osaka) at 25 °C. The suspension was filtered through a disposable PTFE syringe filter (0.2 µm, Advantec Japan, Tokyo), and the concentration of heavy metal ions in the eluate was quantified by AAS.

Flow-type electrolysis cell (FE)

As shown in Fig. 1, the FE used in this study was an electrolytic cell HX-301 (Hokuto-Denko, Ltd., Saitama, Japan), consisting of a Ag/AgCl reference electrode, a platinum wire counter electrode, and a carbon fiber working electrode (effective volume: 2 mL, effective surface area: 3000 cm²) packed in a porous vycor glass tube (10 mm o.d., 7.8 mm i.d., 50 mm length). The voltage was applied to the FE with a potentiostat HA-151B (Hokuto-Denko, Ltd.). Sample
solutions introduced into the FE and 0.1 mol L\(^{-1}\) HNO\(_3\) used to desorb metal ions from the FE were introduced using a peristaltic pump (POT-100N; Iwaki).

Prior to the experiments, bubbles were removed from the working electrode in the FE by placing it vertically and passing methanol over the electrode for 1 h followed by pure water for 30 min. Next, 10 mL of a heavy metal solution in 0.05 mol L\(^{-1}\) H\(_2\)SO\(_4\) was introduced into the FE at a flow rate of 2.5 mL min\(^{-1}\) at constant voltage (−1.0 V to +0.2 V). The initial concentrations of metal ions were as follows: [Cu\(^{2+}\)] = [Zn\(^{2+}\)] = 6.0 × 10\(^{-5}\) mol L\(^{-1}\), and [Cd\(^{2+}\)] = 6.0 × 10\(^{-6}\) mol L\(^{-1}\). Heavy metals non-adsorbed to electrode in the FE or those in the piping connected in the FE were flushed out with 10 mL of 10 mmol L\(^{-1}\) HNO\(_3\). The solutions that were flushed out were collected and the heavy metals were quantified by AAS. The electrodeposition and desorption of heavy metal in the FE was performed at 25 °C.

When desorbing heavy metal ions adsorbed onto the working electrode of the FE, 10 mL of 0.1 mmol L\(^{-1}\) HNO\(_3\) was flowed through at 2.5 mL min\(^{-1}\) at a voltage of +0.4 V, which was the minimum positive potential at which metals adsorbed in the FE could be desorbed quantitatively (Fig. S1 in Supporting information). The heavy metals in the eluates collected from the FE were quantified by AAS.

**Influence of the flow rate**

10 mL of 6.0 × 10\(^{-5}\) mol L\(^{-1}\) Cu\(^{2+}\) solution in 0.05 mol L\(^{-1}\) H\(_2\)SO\(_4\) was flowed into the FE at a flow rate of 0.5–3.5 mL min\(^{-1}\) at a voltage of −0.4 V. The flow rate when introducing eluent (0.1 mol L\(^{-1}\) HNO\(_3\)) into the FE was the same as that when flowing the sample solution. The other procedures were performed as described in the previous section (*Flow-type electrolysis cell*).

**Selective recovery of Cu\(^{2+}\) eluted from incineration ash with sulfuric acid**

After adding 7.5 g of the incineration ash into 100 mL of 0.5 mol L\(^{-1}\) H\(_2\)SO\(_4\) and stirring for 1 h at 200 rpm using a magnetic stirrer at 25 °C, the solution was filtered through a disposable
PTFE syringe filter (0.2 µm, Advantec). The filtrates were diluted 10-fold with water and were
introduced into the FE at a flow rate of 3.5 mL min⁻¹. The eluent (0.1 mol L⁻¹ HNO₃) to desorb
Cu²⁺ from the FE was flowed in the FE at a flow rate of 3.5 mL min⁻¹. The other procedures were
performed as described in the previous section (Flow-type electrolysis cell).

Results and discussion

Chemical component analysis of incineration ash

Prior to the recovery of copper from incineration ash, the components of the incineration ash
(bottom ash and fly ash) were analyzed by EDX. As summarized in Table S1 in Supporting
information, calcium was the highest in both ash samples, followed by silicon. The high calcium
content is related to the input of lime (CaCO₃, Ca(OH)₂) as a neutralizing agent in the furnace,
and a dust collector in the waste incineration plant, to suppress the generation of acid gas (HCl or
SOx) in the incineration facilities.¹⁸

In addition, the silicon, iron, and aluminum content in the bottom ash were higher than those
in the fly ash, and the chlorine content was lower in bottom ash than in fly ash. This is because
their salts and oxides were not volatilized and remained in the bottom ash, while volatile
substances such as chlorine are removed into the fly ash with the flue gas.

The concentration of heavy metals in the incineration ash samples is summarized in Table
S2 in Supporting information. The targeted elements (Cu, Zn, Cd and Pb) were all present at high
concentrations, much higher than the average values found in paddy topsoil from Japan (Cu: 21
mg kg⁻¹; Zn: 75 mg kg⁻¹; Cd: 0.59 mg kg⁻¹; and Pb: 21 mg kg⁻¹; data from 2004).¹⁹ These results
may contribute to the development of recycling technologies for heavy metals in incineration ash.

Heavy metal extraction from incineration ash by strong acids

Extraction of Cu²⁺ from the incineration ash samples was performed with strong acids, HCl,
HNO₃, and H₂SO₄. The extraction rates of Cu²⁺ were estimated by comparing the copper
concentration in each acid extraction to the content in the original ash sample (Table S2).

The concentration of Cu\(^{2+}\) extracted from the ash samples were dependent on the concentration of the acid eluents, as shown in Fig. 2. There were no large differences in the extraction of Cu\(^{2+}\) with the different acids at concentrations above 1 mol L\(^{-1}\). In comparison, more than 80% of the Zn\(^{2+}\) and Cd\(^{2+}\) were extracted from both ash samples using 0.5–4 mol L\(^{-1}\) HNO\(_3\) and H\(_2\)SO\(_4\), and 1–4 mol L\(^{-1}\) HCl. Pb\(^{2+}\) was not extracted from incineration ash with H\(_2\)SO\(_4\) but 40–50% of Pb\(^{2+}\) was extracted with 1–2 mmol L\(^{-1}\) HNO\(_3\) and > 90% of Pb\(^{2+}\) from fly ash with 1–3 mmol L\(^{-1}\) HNO\(_3\). The Pb was not eluted from the incineration ash with sulfuric acid, because of the generation of insoluble PbSO\(_4\).\(^{20}\) The low solubility of lead in H\(_2\)SO\(_4\) is advantageous for the selective extraction of Cu\(^{2+}\) from ash samples using the FE.

The maximum extraction rate of Cu\(^{2+}\) was obtained using at least 0.5 mol L\(^{-1}\) H\(_2\)SO\(_4\). This result is similar to the results obtained by Tang et al.,\(^{21}\) who found that an H\(_2\)SO\(_4\) concentration of 0.5 mol L\(^{-1}\) or higher effectively stripped Cu\(^{2+}\) from fly ash. This concentration extracted 76 ± 5% of the Cu\(^{2+}\) from bottom ash and approximately 88 ± 10% of the Cu\(^{2+}\) from fly ash. The lower extraction efficiency of copper from bottom ash might be because bottom ash contains more silica and alumina as low-solubility silicate or alumina silicate forms, which are not easily eluted with sulfuric acid.\(^{22}\)

Initially, we expected that the precipitation of calcium sulfate was formed by high concentrations of calcium in the ash and was inhibited for the extraction of Cu\(^{2+}\). However, the influence of calcium in the ash samples on the extraction rate of Cu\(^{2+}\) was lower than expected.

Adsorption behaviors of heavy metals in the FE

The adsorption to the FE was investigated with the addition of standard solutions of Cu\(^{2+}\), Zn\(^{2+}\), and Cd\(^{2+}\) applying a voltage of −1.0 V to +0.2 V. The adsorption rate (\(E_{\text{ad}}\)) of a heavy metal was calculated using Eq. (1).
where [M]_{int} is the concentration of heavy metal before introducing the sample solution into the FE, and [M]_{elut} is the concentration of heavy metal in the sample eluted from the FE (i.e., the amount of heavy metal that was not adsorbed in the FE).

As shown in Fig. 3, Cu^{2+} was quantitatively adsorbed to the FE at an applied voltage of −1.0 V to −0.4 V. The quantitative adsorption of Cd^{2+} occurred at −1.0 V to −0.8 V. However, Zn^{2+} was not completely adsorbed even at an applied voltage of −1.0 V. A metal with a higher reduction potential is more efficiently reduced and adsorbed on the working electrode of the FE. In addition, the application of −1.0 V or more to the FE caused a decrease in the adsorption efficiency because of hydrogen gas generated from the working electrode.

The applied voltage of −0.4 V was optimal to selectively adsorb Cu^{2+} onto the FE. In addition, no electrodeposition of other major heavy metals (Cr, Fe, Mn, Ni, Ca, Mg) was observed when −0.4 V was applied to the FE.

Influence of flow rate

The effect of flow rate on the electrodeposition rate of Cu^{2+} contained in 0.05 mol L^{-1} H_{2}SO_{4} was investigated. We examined flow rates in the range of 0.5 to 3.5 mL min^{-1} where the sample solution was fed to the FE at a constant flow rate by a peristaltic pump and found that Cu^{2+} was quantitatively adsorbed into the FE over this range (Fig. S2 in Supporting information). Subsequent experiments were performed at the maximum flow rate used in this study (3.5 mL min^{-1}).

Recovery of Cu^{2+} eluted from incineration ash with sulfuric acid

The selective collection of Cu^{2+} extracted from the incineration ash sample extracted with 0.5 mol L^{-1} H_{2}SO_{4} for 1 h was tested under the optimized conditions as described above. The
concentration of Cu$^{2+}$, Zn$^{2+}$ and Cd$^{2+}$ in the extract sample introduced into the FE are summarized in Table S3 in Supporting information. The Zn$^{2+}$ and Cd$^{2+}$ in the extract from both ashes passed through the FE at an applied voltage of −0.4 V, while Cu$^{2+}$ was quantitatively deposited. The Cu$^{2+}$ was collected in the eluant by passing 0.1 mol L$^{-1}$ HNO$_3$ as eluent applying a voltage of +0.4 V at a flow rate of 3.5 mL/min to desorb Cu$^{2+}$ from the FE.

When this procedure was repeated four times, the relative standard deviations (RSDs) of recovered Cu$^{2+}$ from average and standard deviation summarized in Table 1 was 27% for eluate for bottom ash and 3% for fly ash extracted with H$_2$SO$_4$. The higher RSD of the recovered Cu$^{2+}$ in the eluate from the bottom ash compared with that of fly ash might be caused by unidentified organic compounds, based on the fact that the organic carbon content in bottom ash (3.39 wt.%) was higher than fly ash (0.66 wt.%) (Table S4 in Supporting information). Alternatively, Cu$^{2+}$ might be accumulated on the working electrode.

Therefore, we further flowed 20 mL of 0.1 mol L$^{-1}$ HNO$_3$ applying +0.4 V to remove the Cu$^{2+}$ accumulated in the FE after the desorption process. The total recoveries of Cu$^{2+}$ were 91.3 ± 2.8% ($n = 4$) in bottom ash, and of 98.7 ± 0.7% ($n = 4$) in fly ash. To completely remove the Cu$^{2+}$ should consider any influences of matrices coexisted in real sample.

To investigate the purity of Cu$^{2+}$ in the eluate recovered from the FE, Mg, Al, Ca, Cr, Mn, Fe, Co, Ni, Zn, Sr, Cd, and Ba, which coexist with Cu$^{2+}$ in the solution, were measured by AAS, and were below the quantification limit. However, to confirm the higher purity of copper, high-sensitivity detectors such as inductively coupled plasma mass spectrometry should be used.

In conclusion, the selective recovery of Cu$^{2+}$ from incineration ash with sulfuric acid was obtained by FE with a low negative applied voltage (−0.4 V) at flow rate of 3.5 mL min$^{-1}$. The procedure described in this study is advantageous due to its high speed. For example, when a 20 mL solution is introduced into the FE at a flow rate of 3.5 mL min$^{-1}$, the adsorption process of a targeted metal is completed in approximately 6 min. The reuse of the incineration ash residue after eluting the heavy metals with acid will be studied in our future experiments.
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Supporting Information

Table S1 summarizes the components in the incineration ash as determined by EDX. Table S2 summarized the heavy metal contents in incineration ash samples. Table S3 summarizes concentrations of heavy metal ions in the extract sample obtained from ash samples by the sulfuric acid solution. Table S4 summarizes the elemental analyses in incineration ash samples. Fig. S1 shows relationship of applied voltage and Cu²⁺ concentration eluted from the FE. Fig. S2 shows relationship of electrodeposition of Cu²⁺ and flow rate into the FE. This material is available free of charge on the Web at http://www.jsac.or.jp/analsci/.

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Table 1 Recovery of copper eluted from bottom ash and fly ash samples with 0.5 mol L⁻¹ sulfuric acid (n = 4).

| Type of ash | $C_{\text{dep}}^{a}$/ mmol L⁻¹ | $C_{\text{elut}}^{b}$/ mmol L⁻¹ | Recovery / % |
|-------------|-----------------|-----------------|-------------|
| Bottom ash  | 2.41 ± 0.21c     | 1.88 ± 0.09     | 78.0 ± 21.1 |
| Fly ash     | 0.500 ± 0.023    | 0.441 ± 0.050   | 88.0 ± 2.6  |

$^{a}$ $C_{\text{dep}}$: Cu²⁺ concentration of copper deposited in the FE.

$^{b}$ $C_{\text{elut}}$: Cu²⁺ concentration in acid solution eluted from FE with applied voltage of +0.4 V.

$^{c}$ average ± standard deviation at four-time repeated experiments.

Experimental conditions are described in Experimental section (Selective recovery of Cu²⁺ eluted from incineration ash with sulfuric acid).
Figure Captions

Fig. 1 Acid treatment of incineration ash and the flow-type electrodialysis device used in this study.

Fig. 2 Extraction rate of Cu$^{2+}$ from bottom and fly ashes as functions of acid concentration of the eluent. Experimental conditions: A 7.5 g of ash sample washed with pure water and mixed with 100 mL of an acidic solution for 1 h at 25°C. The acidic solutions used were HNO$_3$, H$_2$SO$_4$, and HCl (0.050 to 4.0 mol L$^{-1}$). Each plot indicates the average and standard errors of four repeated measurements.

Fig. 3 Changes in the electrodeposition ability of heavy metals as a function of the applied potential. Reference electrode (Ag/AgCl) potential: +0.199 V vs. SHE at 298 K. Injected sample: 0.5 mol L$^{-1}$ H$_2$SO$_4$ with heavy metal (10 mL); concentration: [Cu$^{2+}$] = [Zn$^{2+}$] = 6.0 × 10$^{-5}$ mol L$^{-1}$, and [Cd$^{2+}$] = 6.0 × 10$^{-6}$ mol L$^{-1}$; eluent: 0.1 mol L$^{-1}$ HNO$_3$ (10 mL) flow rate of sample solution and eluent: 3.5 mL min$^{-1}$; and measurement: AAS. Each plot indicates the average and standard errors in four repeated measurements.
Fig. 1 Acid treatment of incineration ash and the flow-through type electrodialysis device used in this study.
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Fig. 3 Changes in the electrodeposition ability of heavy metals as a function of the applied potential.
Incineration ash
Sulfuric acid
Cu$^{2+}$
Column flow type electrolysis cell
Selective recovery