1. Introduction

Carbon-in-Pulp process has been successfully applied in the recovery of gold from cyanide pulps. In this process, gold adsorption is carried out by direct contacting of the activated carbon with the leach pulp or slurry of finely ground gold ore. The gold bearing carbon is much larger than the processed ore from which it can be simply separated by screening. Adsorbed gold is usually recovered by desorption and electrowinning and the activated carbon is recycled. Since the extracted gold in the solution can be recovered prior to solid-liquid separation (i.e., filtration), gold losses due to operational risks particularly insufficient filtration, can be minimized. Moreover, the employment of the Carbon-in-Pulp technique has offered solutions to problems associated with treating complex and clayey ores, and grinding of ores to fine sizes for the improvement of leaching efficiency and kinetics [1].

The application of the Carbon-in-Pulp process in the recovery of metals from secondary sources has never been explored before. In this study, a modified method called Carrier-in-Pulp (CIP) was proposed (Figure 1) and its application in waste treatment and resource recycling was investigated. Carrier-in-Pulp method follows the same principle with the traditional Carbon-in-Pulp process, i.e. metal recovery is done by direct contacting of the carrier material with the leach pulp. In a vessel containing the leaching solution, the metal source and the carrier are added together. The metals are extracted into the aqueous phase and are recovered by the sorbent. In contrast to the conventional Carbon-in-Pulp process, the carrier (adsorbent) in the Carrier-in-Pulp method is not limited to activated carbon only; other adsorbents, capable of recovering metal ions from the solution can be utilized. Furthermore, to separate the loaded carrier from the leach slurry, other physical separation techniques, such as magnetic separation, can also be employed.

The primary objective of this dissertation, therefore, is to demonstrate and investigate the application of the proposed Carrier-in-Pulp method in the recovery of metals for waste treatment and resources recycling. Specifically, this study aims to (i) examine the effects of different process parameters, such as pH, treatment time, reagent concentration, and amount of sorbent, on the recovery of metals; (ii) evaluate and develop potential or candidate carriers/sorbents for Carrier-in-Pulp method. Different model experiments were conducted and the results of the investigations are presented in two parts.

2. Recovery of heavy metals from MSW Molten fly ash

Molten fly ash (MFA) is generated by the melting process of the municipal solid waste (MSW) incineration residues. MFA contains considerable amounts of heavy metals, such as Pb, Zn, Cu, Cd, and Hg, which pose environmental threats due to their leaching potential in landfill environment. Of particular interests are Zn and Pb, which are highly concentrated in MFA, with a content of 0.75-31.6% and 0.29-3.8%, respectively, which is nearly equal to the quality of raw ore [2,3]. The application of the CIP method in the extraction and recovery of heavy metals from MFA was investigated using NaCl as the leaching agent. Two carrier materials were used: granular activated carbon (GAC) or Fe powder.

![Figure 1. Schematic representation of the Carrier-in-Pulp method.](image-url)
To demonstrate the effect of CIP method, batch-mode shaking flask experiments were conducted. The experiments consisted of adding together varied amounts of the carrier and MFA (2.5 g) to a flask containing 25 cm$^3$ NaCl leaching solution of different concentrations. The pH of the solution was controlled by adding H$_2$SO$_4$. The mixture was shaken for 1-24 h, and the carrier materials were recovered by magnetic separation or screening. The fly ash residue and the solution were then filtered. To determine the amount of metals recovered by the carrier, the loaded Fe powder was dissolved by microwave-assisted digestion, while for GAC, desorption was conducted using 16 kmol/m$^3$ HNO$_3$. The resulting solution and the filtrate were analyzed for metal contents using ICP-AES (SPS 7800, Seiko Instruments, Japan). Japanese Leaching Test No. 13 was performed to determine the leaching potential of the MFA residue [2,3].

2.2. Results and discussion

2.2.1. Granular activated carbon

Carrier-in-Pulp method was applied to recover Pb, Zn, Cu and Cd from molten fly ash using granular-type activated carbon and NaCl as the leaching agent. Single-component adsorption test showed that GAC recovered more than 85% Pb, Zn, Cu and Cd. The amount of Pb, Zn, Cu and Cd recovered by GAC decreased when the heavy metals were present in the multi-component system, suggesting that adsorption was suppressed by the competition among the metal ions for active sites on GAC. However, the suppressive effect on adsorption in a multi-metal system can be minimized by increasing the activated carbon dosage.

The results showed that CIP method extracted around 90-100% of Pb, Zn, Cu and Cd from MFA at various conditions. The addition of activated carbon enhanced the extraction of heavy metals from molten fly ash (Figure 2). Increasing the GAC dosage also increased the amount of heavy metals recovered from MFA (Figure 3). The extraction and the recovery of Pb from MFA were greatly influenced by the NaCl concentration; Pb extraction and recovery increased with increasing NaCl concentration. Moreover, the extraction and recovery of Pb, Zn, Cu and Cd were determined to be favored at lower pH region. The optimum conditions were determined to be 5 kmol/m$^3$ NaCl, 10 g GAC, pH 5-6, and 3 hours treatment time. At these conditions, around 90% Cu, 57% Zn, 54% Cd, and 40% Pb were recovered from MFA through adsorption [2].

2.2.2. Iron powder

As discussed above, granular activated carbon was used as a sorbent to recover heavy metals from MFA and experimental studies showed that the addition of GAC enhanced the extraction of heavy metals from molten fly ash. However, due to the competition of the extracted metal ions present in the solution, the recoveries of Pb, Zn, Cu and Cd were suppressed to limited values. The competition of heavy metal ions for active sites on the surface of carbon can be minimized by increasing the surface area of activated carbon either by adding high dosages of granular activated carbon or utilizing powdered forms of activated carbon. Both forms of activated carbon, however, suffered from problems associated with crowding of the pulp due to very high solid-liquid ratio, or difficulty of solid-solid separation due to the very small particle size differences between MFA and the powdered carbon. Due to this problem, iron powder, with combined ability to recover heavy metals and to be easily separated from the mixture, was considered as an alternative carrier.

![Figure 2](image2.png)

**Figure 2. Effect of activated carbon dosage on the extraction of Pb, Zn, Cu and Cd from MFA (5 kmol/m$^3$ NaCl, pH 5-6, 3 h treatment time).**

![Figure 3](image3.png)

**Figure 3. Effect of activated carbon dosage on the recovery of Pb, Zn, Cu and Cd from MFA (5 kmol/m$^3$ NaCl, pH 5-6, 3 h treatment time).**

Similar to the CIP method using GAC, the extraction of Pb, Zn, Cu and Cd from MFA was also enhanced by the addition of the iron powder. Significant amounts of the heavy metals were extracted from MFA at various conditions. The iron powder recovered Pb and Cu through cementation. At optimum conditions (NaCl concentration, 5 kmol/m$^3$; pH 5-6; Fe powder/fly ash ratio, 2; and treatment time, 3 hours), as much as 96.3% Pb and 95.6% Cu were recovered by the Fe powder. Figure 4 shows the extraction and recovery results for Pb.
In the case of Pb, the extraction and recovery mechanism can be interpreted by assuming that the Pb extraction from the ash was due to the formation of a soluble lead chloride complex like PbCl$_2$ (Equation 1) and the subsequent Pb cementation onto Fe powder (Equation 2). Both Cl$^-$ and H$^+$ are the reactants to extract Pb from PbO in fly ash. This was the reason why high NaCl concentrations and low pH values were required for extracting and recovering Pb

\[
PbO + 4Cl^- + 2H^+ \rightarrow [PbCl]_2^2+ + H_2O \quad (1) \\
[PbCl]_2^2+ + Fe \rightarrow Pb + Fe^{2+} + 4Cl^- \quad (2)
\]

The reacted iron particles were examined under Scanning Electron Microscope-Energy Dispersive X-ray (SEM-EDX). The SEM micrograph revealed the presence of Pb on the surface of Fe powder (Figure 5). This result qualitatively confirmed the recovery of Pb by the iron powder [3].

![Figure 4. Effect of (a) NaCl concentration, (b) Fly ash ratio, (c) final pH, and (d) treatment time on Pb content in Fe carrier, residue, and solution.](image)

![Figure 5. SEM micrograph, EDX mapping and spectra of an iron particle after CIP treatment.](image)

### 2.2.3. Leaching test

The residues recovered from the CIP treatment of molten fly ash at optimum conditions were examined by leaching test in accordance with Notification No. 13 of the Environmental Agency of Japan for materials to be disposed in landfill. The results of the test in comparison with other treatment methods are shown in Table 1. No Pb was detected from the leachate of the CIP-treated residues. On the other hand, the leachate registered a pH value of 6.50 which falls within the standard pH of 5.8-8.3 for effluent. Collectively, these results suggest that the CIP method sufficiently suppressed the extraction of Pb and other heavy metals from fly ash indicating that the material was successfully detoxified to meet landfilling guideline. There is no regulation standard yet for Zn and Cu in Japan [2,3].

<table>
<thead>
<tr>
<th>Metals</th>
<th>UA</th>
<th>S</th>
<th>NL</th>
<th>GAC</th>
<th>Fe</th>
<th>Std</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb</td>
<td>2.18</td>
<td>0.35</td>
<td>0.50</td>
<td>0.00</td>
<td>0.00</td>
<td>0.30</td>
</tr>
<tr>
<td>Cu</td>
<td>0.08</td>
<td>0.11</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>-</td>
</tr>
<tr>
<td>Zn</td>
<td>1.38</td>
<td>0.05</td>
<td>17.56</td>
<td>22.60</td>
<td>13.80</td>
<td>-</td>
</tr>
<tr>
<td>Cd</td>
<td>0.03</td>
<td>0.03</td>
<td>0.71</td>
<td>1.40</td>
<td>0.15</td>
<td>0.30</td>
</tr>
</tbody>
</table>

UA-untreated ash; S-sulfurization; NL-NaCl Leaching

### 3. Recovery of gold from chloride solution by magnetite

The recovery of gold from secondary sources has gained significant attention in the past few years due to the declining available resources and the increasing amount of gold-containing waste materials generated and stockpiled in urban mines. The development of environmental-friendly lixiviants as alternatives to cyanide and the increasing recycling activities to recover gold from waste materials have prompted researchers to find efficient methods of recovering gold from aqueous solutions or to search for alternative sorbents. This study explored the use of magnetite (Fe$_3$O$_4$) as a sorbent to recover gold from chloride solutions. Magnetite is a semiconductor and has the capability of transferring electrons both within the solid state and across the solid-liquid interface and has the ability to reduce metal species at the surfaces, particularly Au [4].

The premise of this study is that gold chloride complexes are redox sensitive species in solution and can be reduced to metallic state on the surface of an electro-conductive material. The sorption of gold from chloride solution on different types of magnetite (synthetic, natural, and slag magnetite) was studied under various conditions. Batch sorption experiments were carried out to evaluate the capability of magnetite as a sorbent for gold in the Carrier-in-Pulp method.

### 3.1. Materials and methodology

Reagent grade gold (HAuCl$_4$ in 1 kmol/m$^3$ HCl) standard solution (Wako Chemicals, Japan) was used as the source of gold ions. The commercial grade synthetic magnetite powder was purchased from Wako Chemicals Japan. The natural magnetite sample,
crushed and sieved to the desired particle sizes, was obtained from Iron County, Utah, USA. The slag magnetite sample was provided by a metal smelting plant from Japan. The magnetite samples were characterized using different analytical techniques to determine the composition, surface area, and other properties. The rest of the chemicals involved in this experiment, such as NaCl, HCl, and NaOH, were all of reagent grade.

Batch sorption experiments were performed to demonstrate the ability of Fe₃O₄ to recover gold from chloride solution. The experiments were carried out by adding 0.1 gram of Fe₃O₄ powder to a 50 cm³ flask containing 10 cm³ of NaCl solution (0.001-1.0 M) with HAuCl₄ at varied concentrations. The pH of the solution was adjusted by adding HCl or NaOH solutions. The mixture was shaken in a water bath at a specified time interval. After shaking, the mixture was centrifuged and then membrane filtered. The gold content in the aqueous phase was determined by ICP-AES.

The nature of the deposited gold on magnetite was examined by electrochemical experiments. The working electrode was prepared from a natural magnetite sample. A conventional three-electrode cell (Figure 6) was used in the experiment: prepared magnetite electrode as the working electrode; Pt electrode as the counter electrode; and a KCl saturated Ag/AgCl electrode (Silver Chloride Electrode, SCE) as the reference electrode. The electrodes were inserted in a cell containing 1.0 kmol/m³ NaCl solution. Prior to each measurement, the cell was purged with a N₂ gas for 15 min. to exclude O₂ from the system. Cyclic voltammetric (CV) measurements were performed using a Solartron Electrochemical Measurement Unit (England) supported by a Corrware Version 2.3 Electrochemistry Software (USA). All experiments were performed at room temperature, and all the recorded data were compared against SCE electrode. Potential sweeps were initiated from the open circuit potential of the working electrode towards a positive direction.

The magnetite electrode was first treated with gold before the voltammetry measurement. The experiment consisted of dipping the magnetite electrode in a 50 mL of 0.1 kmol/m³ NaCl solution containing 0.3 mol/m³ AuCl₄⁻ at pH 6-7 and then shaken for 24 h in a water bath shaker at a rate of 120 strokes per minute at 25°C. The treated magnetite electrode was rinsed with distilled water before inserting into the electrochemical cell.

3.2 Results and discussion

3.2.1 Synthetic and natural magnetite

Synthetic and natural magnetite particles were utilized as sorbents to recover gold from chloride solution. Sorption experiments involving various metal ions demonstrated that synthetic magnetite exhibited selectivity towards Au, Pt, Pd, Cu and Ni at varying degrees, while the natural magnetite exhibited selectivity towards Au only (Figure 7).

The pH dependence of Au sorption on both types of magnetite (Figure 8) showed similar patterns with maximum peaks at pH 6-7. At this pH range, maximum gold uptake values of 4.4 µmol/g and 5.0 µmol/g were obtained for synthetic and natural magnetite, respectively. Investigation on the effects of contact time and residual Au concentration on Au recovery revealed that natural magnetite can uptake more gold at 24 h contact time compared to the synthetic magnetite. High chloride concentration decreased the Au uptake capacity of both types of magnetite. The SEM-EDX and BSE analyses confirmed the presence of gold concentrated on some areas of the synthetic and natural magnetite’s surfaces. The detected gold appeared as a cluster of Au precipitates suggesting the reduction of AuCl₄⁻ to metallic Au on the surface of magnetite (Figure 9).
chloride solution can be heterogeneously reduced on the surface of magnetite. The cyclic voltammetry, shown in Figure 10, measured for the magnetite electrode dipped in a gold chloride solution recorded an anodic peak which was in agreement with the current generated for the anodic dissolution of metallic gold. From these results, a possible uptake mechanism was proposed. The uptake of AuCl₄⁻ by magnetite follows a four-stage reaction which includes the transport of AuCl₄⁻ from the bulk solution to the magnetite surface, adsorption of AuCl₄⁻ ions on magnetite surface through electrostatic attraction, electrochemical reduction of AuCl₄⁻ to metallic Au, and finally the transport of soluble species to the solution phase. The over-all reaction is given by:

$$\text{AuCl}_4^- + 3\text{Fe}_2\text{O}_3 + \frac{3}{2} \text{H}_2\text{O} \leftrightarrow \text{Au}^0 + \frac{9}{2} \text{Fe}_2\text{O}_3 + 4\text{Cl}^- + 3\text{H}^+ \quad (3)$$

**Figure 8.** Effect of solution pH on Au uptake by synthetic and natural magnetite. Initial Au concentration: 0.05 mol/m³; contact time: 24 h; NaCl concentration: 0.1 kmol/m³; Fe₂O₃ amount: 0.1 g; temperature: 298K.

**Figure 9.** SEM-EDX and BSE micrograph, mapping and spectra for natural magnetite containing Au (2000x magnification).

Based on the proposed model and the results of auxiliary experiments (zeta potential measurements and adsorption experiments under different conditions), the pH dependence of Au recovery was explained. At acidic pH regions, the surface charge of magnetite is positive which is favorable for electrostatic adsorption of AuCl₄⁻ ions. However, at very low pH values, Fe³⁺ ions are extracted into solution and provide competition for electrons with the AuCl₄⁻ complex. At near neutral pH range (pH 4-7), the zeta potential of magnetite is unstable and very minimal Fe³⁺ ions are present in the solution. These conditions offer a favorable environment for AuCl₄⁻ to approach the magnetite surface and adsorb by virtue of electrostatic attraction. The contact between AuCl₄⁻ ions and the magnetite surface through adsorption would initiate the transfer of electrons for the subsequent reduction. Finally, at alkaline pH region, magnetite has a negative surface charge which renders the AuCl₄⁻ approach towards the oxide’s surface difficult due to electrostatic repulsion.

**Figure 10.** Cyclic voltammogram (0.0 V to 1.5 V, 20 mV/s) recorded for a gold-plated magnetite electrode in 1.0 kmol/m³ NaCl at room temperature. (Gold plating conditions: 0.3 mol/m³ AuCl₄⁻, pH 6-7, 24 h, 0.1 kmol/m³ NaCl, 298 K).

### 3.2.2 Slag magnetite

The converting stage of copper smelting process generates slag as a by-product which contains significant amounts of magnetite. The magnetite from this slag was collected and was utilized as a sorbent to recover gold from chloride solution. The mineral components of the slag magnetite are shown in Table 2.

Batch sorption experiments were performed to evaluate the effects of pH, contact time, chloride concentration, and initial Au concentration on the amount of Au uptake. The results showed that slag magnetite can effectively recover gold from chloride solution. More than 99% recovery was obtained at acidic and near-neutral pH ranges (Figure 11). The Au sorption rate was relatively fast and over 98% recovery was achieved even at 15 min contact time. Increasing the chloride concentration did not influence the Au uptake.

The perceived Au uptake mechanism was reductive precipitation or cementation. Parameter studies and spectrometric analyses suggested that chalcopyrite (Cu₉S₈) and metallic Cu present in the slag magnetite reduced the gold chloride complex to metallic Au. The chemical reactions involved in the cementation process are summarized in Tables 3 and 4. The SEM-EDX and BSE analyses of the reacted slag magnetite particles (Figure 12) revealed that gold accumulated on the area where the copper sulfide was present.
The study also demonstrated that the slag magnetite was selective only towards precious metals, such as Au, Pt and Pd due to the differences in the reduction potentials. The converter slag magnetite can be used as an economical and effective sorbent to recover gold from secondary sources. The gold-loaded slag magnetite can be returned to the smelting stage of copper processing to recover the deposited gold and other precious metals.

Table 2. Mineral components of the Cu converter slag magnetite determined by Point Counting Method.

<table>
<thead>
<tr>
<th>Mineral Component</th>
<th>Unit %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Metallic Cu</td>
<td>1.3</td>
</tr>
<tr>
<td>Chalcocite (Cu₂S)</td>
<td>3.3</td>
</tr>
<tr>
<td>Bornite (Cu₅FeS₄)</td>
<td>0.1</td>
</tr>
<tr>
<td>Magnetite (Fe₃O₄)</td>
<td>35.8</td>
</tr>
<tr>
<td>Fayalite (Fe₂SiO₄)</td>
<td>50.6</td>
</tr>
<tr>
<td>Glass</td>
<td>8.9</td>
</tr>
</tbody>
</table>

Figure 11. Effect of solution pH on Au uptake by magnetite from copper converter slag. Initial Au concentration: 0.05 mol/m³; contact time: 24 h; NaCl concentration: 0.1 kmol/m³; Fe₃O₄ amount: 0.1 g; temperature: 298K.

Table 3. Reduction of AuCl₄⁻ by Cu₂S.

<table>
<thead>
<tr>
<th>Reaction Zones</th>
<th>Chemical Reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anodic:</td>
<td>Cu₂S ↔ 2Cu²⁺ + S⁰ + 2e⁻</td>
</tr>
<tr>
<td>Cathodic:</td>
<td>AuCl⁻ + 3e⁻ ↔ Au⁰ + 4Cl⁻</td>
</tr>
<tr>
<td>Over-all Reaction:</td>
<td>AuCl⁻ + 3/4 Cu₂S ↔ Au⁰ + 3/2 Cu²⁺ + 3/4 S⁰ + 4Cl⁻</td>
</tr>
</tbody>
</table>

Table 4. Reduction of AuCl₄⁻ by Cu

<table>
<thead>
<tr>
<th>Reaction Zones</th>
<th>Chemical Reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anodic:</td>
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<td>AuCl⁻ + 3/2 Cu ↔ Au⁰ + 3/2 Cu²⁺ + 4Cl⁻</td>
</tr>
</tbody>
</table>

3. Conclusion

Carrier-in-Pulp method was proposed and was applied in the recovery of metals for waste treatment and resources recycling. In the first part of this study, CIP method was employed to recover heavy metals from MSW molten fly ash. In the second part, experimental investigations to evaluate magnetite as a sorbent/carrier to recover gold from chloride solution were conducted. The experimental results have demonstrated that CIP method could provide an alternative solution to problems associated with the treatment and recovery of metals from secondary sources. The utility of selective sorbents/carriers plays a very important role in the recovery of desired metals for resources recycling where metal ions usually co-exist in the solutions or leach liquors.

References


