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Recovery of Heavy Metals from MSW Molten Fly Ash by Carrier-in-Pulp Method: Fe Powder as Carrier

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ABSTRACT

Municipal solid waste (MSW) molten fly ash is classified as a hazardous waste because it contains considerable amount of heavy metals, which pose environmental concern due to their leaching potential in landfill environments. This study proposes Carrier-in-Pulp (CIP) method as a new hydrometallurgical route to extract and recover Pb, Zn, Cu, and Cd from molten fly ash before landfilling. In this method, a carrier material, which recovers the extracted metals, is added simultaneously with fly ash to a leaching solution and is harvested from the pulp by physical separation method, such as magnetic separation or sieving.

To demonstrate the effect of the CIP method, shaking flask experiments were conducted under various conditions using NaCl solution, iron powder as carrier, and molten fly ash. More than 99 wt% Pb, Zn, and Cd, and 97 wt% Cu were extracted from the ash. However, only Pb and Cu were recovered (96.3 wt% Pb and 94.3 wt% Cu) by the iron powder through cementation, leaving behind Zn and Cd ions in the solution phase. The leaching test conducted on the treated fly ash residue revealed that the CIP method suppressed the solubilization of Pb to values below the landfill disposal guideline.

Keywords: *Hydrometallurgy, Leaching, Cementation, Magnetic Separation, Waste Processing*

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1. INTRODUCTION

Incineration has been increasingly adopted as a major waste management technology in Japan due to the increasing amount of generated municipal solid waste (MSW) and the decreasing available area for landfill. In 2001, as much as 80% of the 52 million tons of generated MSW was incinerated (Okada et al., 2006). Although the process is very effective in reducing the volume of waste by about 80–90%, it suffers from a disadvantage of generating solid reaction byproducts (fly ash and bottom ash) which require pretreatment before landfilling to immobilize the hazardous metals and to decompose the dioxins in the ash. To decompose the dioxins, ash melting process is frequently used. In this process, the ash is heated at high temperatures (1300-1800°C) in a furnace to convert the materials into slag (Jung et al, 2007). It generates a newly formed fly ash known as MSW molten fly ash (MFA) or secondary fly ash (Nagib et al., 2000).

The melting process of MSW incineration residue produces about 6-10% MFA of the total input (Sakai et al., 2000). As of 2004, 144 melting plants were in operation in Japan, generating about 0.2 million tons of MFA annually (Japan Waste Research Foundation, 2006). Molten fly ash is a regulated hazardous waste because it 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 environments. Some of these metals are present at concentrations that allow an economic recovery. Extraction and recovery of these metals seem to be more environmentally and economically attractive than disposing the ash to landfill after immobilization process.

Hydrometallurgical method is one of the many possible ways to extract and recover metals from fly ash. It is gaining popularity nowadays due to its simple operation and low-energy requirement. Various methods using different leaching reagents have been investigated (Nagib et al., 2000; Okada et al., 2006; Hong et al., 2000; Hong et al, 2007;

Izumikawa, 1996; Wu et al., 2006; Wan et al., 2006; Zhang et al., 2006; Katsuura et al, 1996). These methods usually employ leaching, using acid, alkaline or other reagents, filtration and then chemical precipitation to recover the dissolved metals in the pregnant solution. The major drawback of this conventional route is that a significant amount of leaching solution containing high concentrations of toxic metals is discharged together with the solid residue due to incomplete filtration. Because of this, washing or stabilizing processes are required before the final disposal of the leaching residue.

This study proposes Carrier-in-Pulp (CIP) method (Figure 1) as a new hydrometallurgical route to extract and recover heavy metals from MFA before landfilling. In this method, a carrier powder, which recovers extracted metals from the aqueous phase, is added simultaneously with fly ash to leaching solutions and is harvested from the pulp by physical separation method, such as magnetic separation or sieving. The solid residues can be discharged into landfill after filtration. Because most metals are adsorbed on the carrier and the solution becomes free of metals, this method offers the great advantage of not requiring washing or stabilization process for the discharge. In this paper, the CIP method using iron powder as the carrier was applied for MSW molten fly ash. The extraction and recovery of the heavy metals from MFA and the leaching potential of the treated solid residue were investigated.

2. MATERIALS AND METHOD

2.1 Materials

The fly ash used in this study was obtained from an ash melting plant in Japan. The average particle size of the ash sample was found to be less than 20 μm by Microtrac Size Analyzer (MT3300SX, USA). To determine the elemental composition, an ash sample was dissolved with *aqua regia* (3 HCl:1 HNO₃ v/v) through a microwave-assisted digestion. The

solution was filtered using a 0.20 μm nitro-cellulose membrane filter (Sartorius, Germany) and the filtrate was analyzed for Si, Al, Na, K, Ca, Fe, Mg, Cu, Zn, Se, As, Cd, Hg, Pb, and Cr using an Inductively Coupled Plasma-Atomic Emission Spectrometer (ICP-AES) (SPS 7800, Seiko Instruments, Japan). Table 1 shows the elemental composition of the ash. The major heavy metal components, which consist of about 14 w/w% of the fly ash sample, are Zn, Pb, Cu, and Cd. A reagent grade electrolytic iron powder (Wako Pure Chemical Ind., Ltd., Japan) was chosen as the carrier due to its magnetic property, which can be exploited by magnetic separation. The particle size of the powder as provided by the company was less than 150 μm (95%).

As a leaching agent, NaCl solution was used. The solution of different concentrations were prepared by dissolving different amounts of reagent grade NaCl powder (Wako Pure Chemical Ind., Ltd., Japan) in distilled water. The choice of NaCl as the leaching solution, apart from being a mild reagent, was due to its high affinity to Pb; chloride ion serves as a ligand to extract Pb from MFA. A study done by the other co-authors (Hirosoyoshi et al, 2004) reported that Pb extraction without the ligand was limited.

Table 1: Representative fly ash composition

Metals	Composition (mg/g ash)
Si	2.76
Al	4.87
Na	81.52
K	89.98
Ca	69.81
Fe	3.29
Mg	0.99
Cu	1.43
Zn	102.10
Se	0.05
As	1.19
Cd	1.20
Hg	0.07
Pb	27.82
Cr	0.06

2.2 Method

The shaking flask experiments consisted of adding varied amounts of molten fly ash and iron powder to a 50 cm³ glass Erlenmeyer flasks containing 25 cm³ of NaCl solution of different concentrations (1-5 kmol/m³) and then shaking in a water bath shaker (ML-10F, Taitec, Japan) for 1-6 hours at a rate of 120 rpm and at 25°C. The molten fly ash contains around 70 wt% Ca in the form of Ca(OH)₂ or CaO as an alkaline component. To neutralize and obtain acidic pH values, H₂SO₄ was added to the leaching system.

After each treatment, the iron particles were harvested from the pulp using a magnet. To determine the total metal content for each fly ash sample, three fractions of the leaching system (fly ash residue, leaching solution, Fe carrier) were analyzed. Aliquot sample of the leaching solution was obtained, centrifuged (IEC 6101010-2-020 Centrifuge Machine, Kubota, Japan), and then filtered using a 0.20 µm nitro-cellulose membrane filter. The fly ash residue and Fe powder were vacuum-dried, digested with *aqua regia* in a microwave station, and then membrane filtered. The solutions were analyzed for metal contents using ICP-AES.

To determine the leaching potential of the treated fly ash residue, Japanese Leaching Test No. 13 (Environmental Agency of Japan, 1973) was conducted. One gram of the dried residue was leached with 10 cm³ distilled water for 6 hours. The filtered solution was analyzed for hazardous metals using ICP-AES.

3. RESULTS AND DISCUSSION

3.1 Removal and recovery of metals

In the CIP method, the metals in MSW molten fly ash are extracted to solution phase and then adsorbed onto the carrier, so that the metals are distributed into the solution, the carrier, and the solid residue of the ash after treatment. The effects of NaCl concentration,

carrier/fly ash ratio, treatment time, and final pH on the metal distribution in the CIP treatment using Fe powder as carrier were investigated.

Figure 2 shows the effects of NaCl concentration, Fe carrier/fly ash ratio, treatment time, and pH on Pb distribution. The Pb distribution was significantly affected by the four parameters considered. The treatment time showed a significant effect at the first 2 hours. No significant effect was seen after 2 hours (Fig. 2d) with Pb recovery of about 85%. Increasing concentrations of NaCl enhanced the Pb extraction from fly ash and Pb recovery by the carrier. Solution pH was also an important factor: Pb recovery by the carrier was more than 80% at pH 1 to 7, but the recovery decreased at pH higher than 7 and lower than 1.

With increasing Fe to fly ash ratio, Pb recovery by the carrier increased. It should be noted that the addition of Fe powder promoted the Pb extraction from fly ash. The Pb extracted from the ash, for instance, was more than 80% when the Fe carrier/ash ratio was over 1 w/w%; but it was only about 30% without Fe powder.

A Scanning Electron Microscope (SEM-EDX) image of an iron particle recovered after the treatment (Figure 3) revealed the presence of Pb on the surface of Fe powder. This result qualitatively confirmed the recovery of Pb by the iron powder. The XRD analysis of the recovered Fe powder indicates that Pb on the powder was present as an elemental Pb (data not shown).

The results shown in Figures 2 and 3 may be interpreted by assuming that the Pb extraction from the ash was due to the formation of a soluble lead chloride complex like PbCl_4^{2-} (Equation 1) and the subsequent Pb cementation onto Fe powder (Equation 2).



As shown in Equation 1, 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 (Figures 2a and 2c). At excessively low pH, however, low Pb recovery was observed (Fig. 2d). Other recent studies reported that the presence of the abundant supply of H^+ ions at highly acidic solution, and the corrosion of Fe affects the deposition of metal on the iron surface. For some substrates, such as iron (Fe), cementation rate decreases at high solution acidity due to the adsorption of H_2 formed at the metal surface (Equation 3), or the continuous coating of the iron surface with layers of secondary corrosion products (Equation 4) which causes the decrease in the available reduction sites for metal ions present in the solution phase (Djoudi et al, 2007; Komnitsas et al, 2007). This could be the reason why low Pb recovery was obtained at pH less than 1.



In the absence of Fe, Equation 1 may reach the equilibrium state when PbCl_4^{2-} accumulated in the solution phase. Upon the addition of Fe powder, Fe consumes PbCl_4^{2-} from the solution phase and causes the enhancement of Pb extraction (Eq 1). This enhancement effect can be confirmed using Fig. 2b: amount of Pb remaining in the residue decreased with increasing Fe carrier additions.

As discussed above, it was confirmed that the CIP method using Fe carrier is effective to extract and recover Pb from MSW molten fly ash, which is a major toxic metal component of the ash. Aside from Pb, the effect of CIP method on the extraction and recovery of Cu, Zn, and Cd were also investigated, and the results are shown in Figures 4 to 6.

As shown in Figures 4-6, Cu, Zn, and Cd contents in the solution, residue, and carrier were not extensively affected by NaCl concentrations. The figures also show that the Cu content in the carrier and the Zn and Cd content in the solution were higher in weak acid

region than in alkaline region. This indicates that these metals did not form chloride complex and that they can be extracted by an acid. When assuming MO as a metal component in the fly ash, the acid extraction of M^{2+} (Cu^{2+} , Zn^{2+} or Cd^{2+}) can be described by



Maximum recovery of Cu by the Fe powder was 95.6% at pH 4, and more than 80% of Zn and Cd were extracted to solution phase in the acidic region. However, the Fe powder was not able to recover the extracted Zn and Cd from the solution.

The possible removal reaction mechanisms of the heavy metal ions by the iron powder include the direct reaction with Fe which results in the electrochemical reduction of the metal ions to Fe onto the iron surface or cementation, and the adsorption onto the surface of iron particles or onto iron corrosion products (iron oxides and hydroxides) formed on the non-reacted metal surface (Bartzas et al, 2005; Shokes and Moller, 1999; Furukawa et al, 2002). The XRD (not shown) of the iron particle after treatment did not detect the presence of iron oxide or hydroxide. The formed corrosion products on the non-reacted surface of the iron particle may have been detached due to the solid-solid interaction or interparticle rubbing (MFA particles and Fe powder), and the agitation due to the shaking movement imparted to the leaching system. Another possible reason could be the limitation of the XRD to positively identify amorphous phases or a phase consisting of a minor weight fraction of the total sample mass (Furukawa et al, 2002). Therefore, in this study, cementation was considered as the primary removal mechanism.

Cementation involves precipitation of one ion in the presence of another one. To obtain the reduction of an ion from aqueous solution, the potential of the reducing system must be more negative than the potential of the ion system undergoing reduction (Jackson, 1986). The standard potentials of Fe, Pb, Cu, Zn, and Cd are shown in Table 2.

As seen in Table 2, the potential of Fe is more negative than Cu and Pb which made these metals easily recoverable by cementation. The chemical reactions involved for these two metals are given by Equations 6 and 7, respectively.



Zinc is more electronegative than Fe. Cadmium, on the other hand, although is more positive than Fe, was present in the fly ash at a minimal amount (around 0.12 wt%). Its standard potential doesn't vary much from that of Fe. For a cationic system (i.e, Pb, Zn, Cu, Cd), the potential is a function of the metal ion activity in the solution in accordance with the Nernst equation (Equation 8) where E^o_{aq} is the standard potential of the cationic system (Jackson, 1986). The more negative redox potential of Zn and the lower potential of Cd due to minimum concentration could have been the reasons why these metals were not recovered from the solution.

$$E = E^o_{aq} + \frac{RT}{zF} \ln a_M^{z+} \quad (8)$$

Table 2: Standard potentials of some metal systems (Jackson, 1986)

Electrode System	E^0/V
$\text{Cu}^{2+} + 2\text{e} = \text{Cu}$	+0.337
$\text{Pb}^{2+} + 2\text{e} = \text{Pb}$	-0.126
$\text{Cd}^{2+} + 2\text{e} = \text{Cd}$	-0.402
$\text{Fe}^{2+} + 2\text{e} = \text{Fe}$	-0.440
$\text{Zn}^{2+} + 2\text{e} = \text{Zn}$	-0.763

3.2 Metal extraction from the CIP treated residue

Table 3 shows the result of the leaching test conducted on the treated fly ash in accordance with the Japanese leaching test for materials to be disposed in landfills. The result was compared to the leaching test of the residues from other treatment methods. Only 0.001 mg L⁻¹ of Pb and 0.147 mg L⁻¹ of Cd were extracted from the residues which were way below

the regulation standards. The CIP-Fe method sufficiently suppressed the extraction of Pb 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.

Table 3: Leaching test results (mg L⁻¹)

Metals	Untreated Ash	Sulfurization	NaCl Leaching	CIP-Fe	Standard
Pb	2.182	0.348	0.502	0.001	0.300
Cu	0.078	0.113	0.001	0.030	-
Zn	1.378	0.049	17.560	13.796	-
Cd	0.028	0.028	0.712	0.147	0.300

4. CONCLUSION

Fly ash produced by the melting of MSW incineration residues contains considerable amount of heavy metals which can be recovered and recycled. A Carrier-in-Pulp method using iron powder was proposed as a new method to recover these heavy metals from fly ash. The extraction of Pb, Zn, Cu and Cd from MFA was enhanced by the addition of Fe powder and more than 80% extraction was achieved at various conditions. However, Fe powder recovered only Pb and Cu through cementation, leaving behind the extracted Zn and Cd in the solution phase. At optimum conditions (NaCl concentration, 5 kmol/m³; 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. The leaching test conducted on the treated fly ash residue revealed that the solubilization of Pb was suppressed to a value way below the standard indicating the safe disposal of the residue to landfills.

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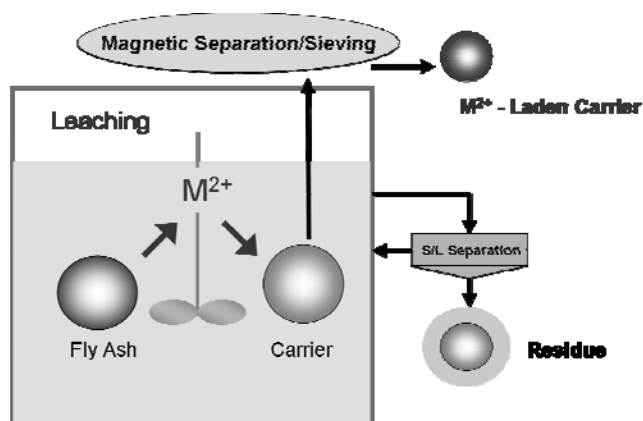


Figure 1 Carrier-in-Pulp Method

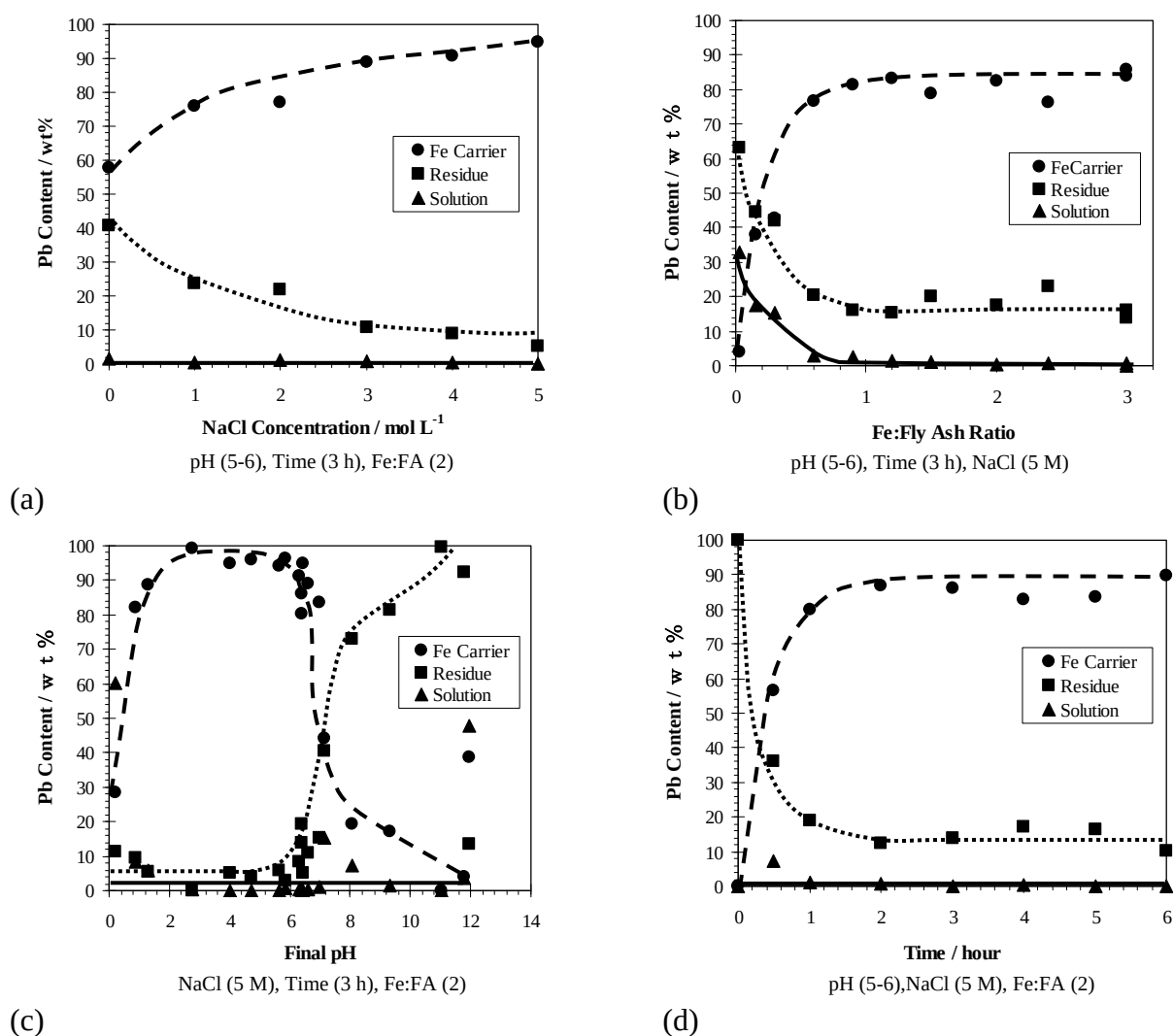


Figure 2 Effect of (a) NaCl concentration, (b) Fe:fly ash ratio, (c) final pH, and (d) treatment time on Pb content in Fe carrier, residue, and solution.

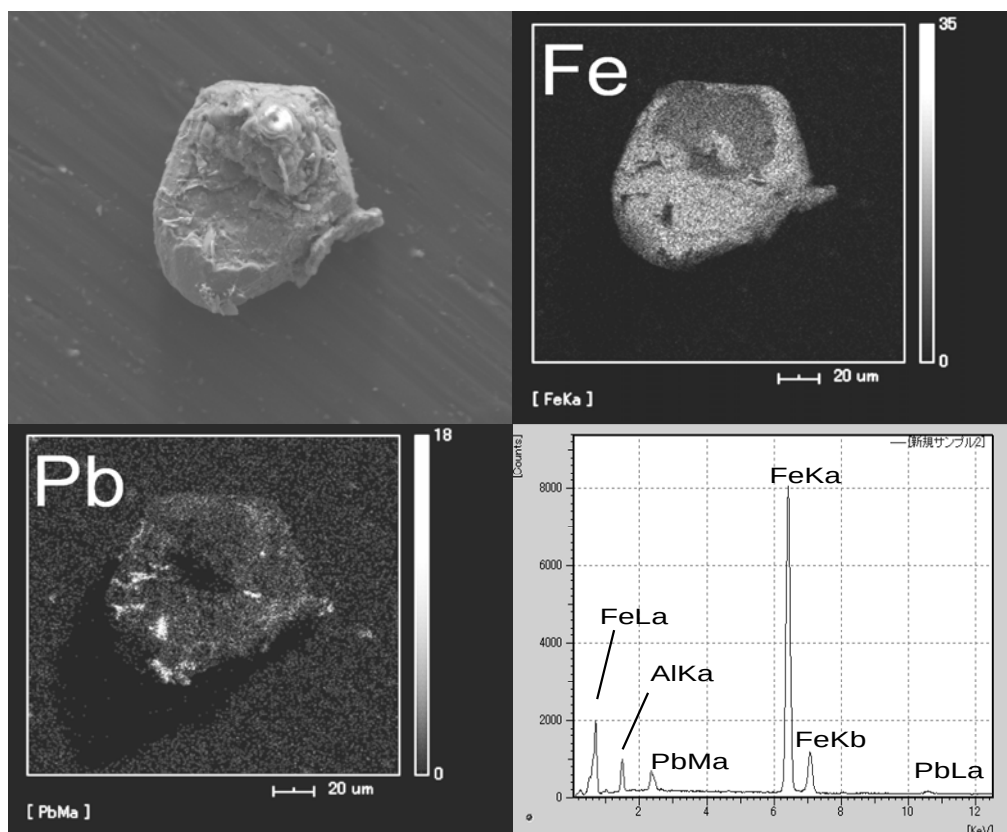
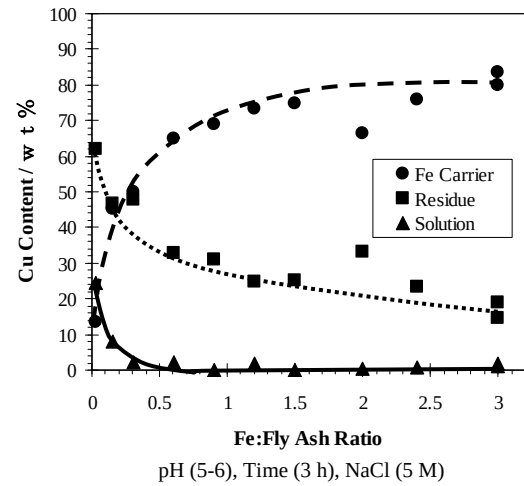
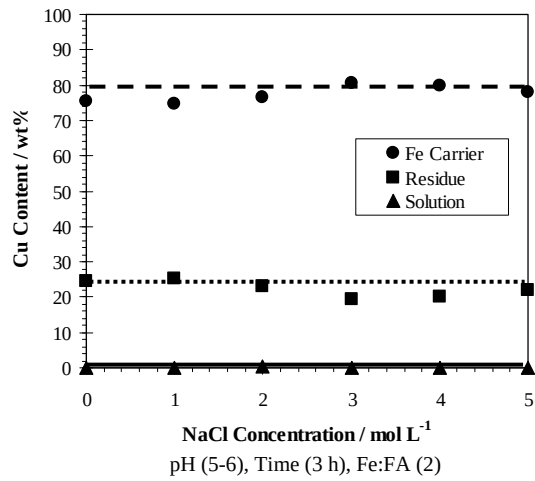
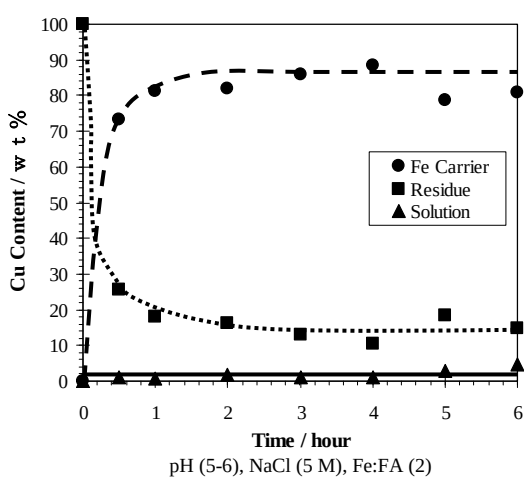
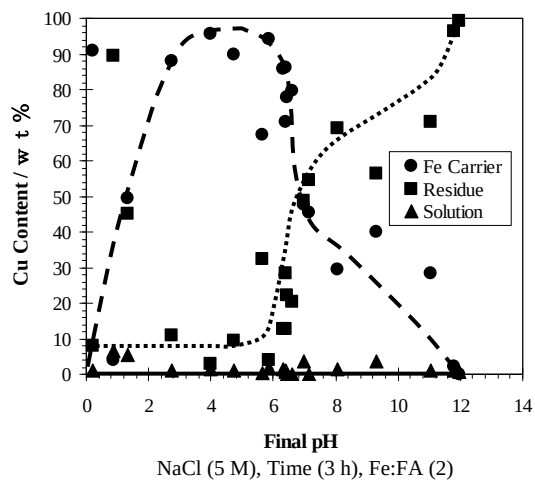


Figure 3 SEM-EDX image of an iron particle after CIP treatment.



(a)

(b)



(c)

(d)

Figure 4 Effect of (a) NaCl concentration, (b) Fe:fly ash ratio, (c) final pH, and (d) treatment time on Cu content in Fe carrier, residue, and solution.

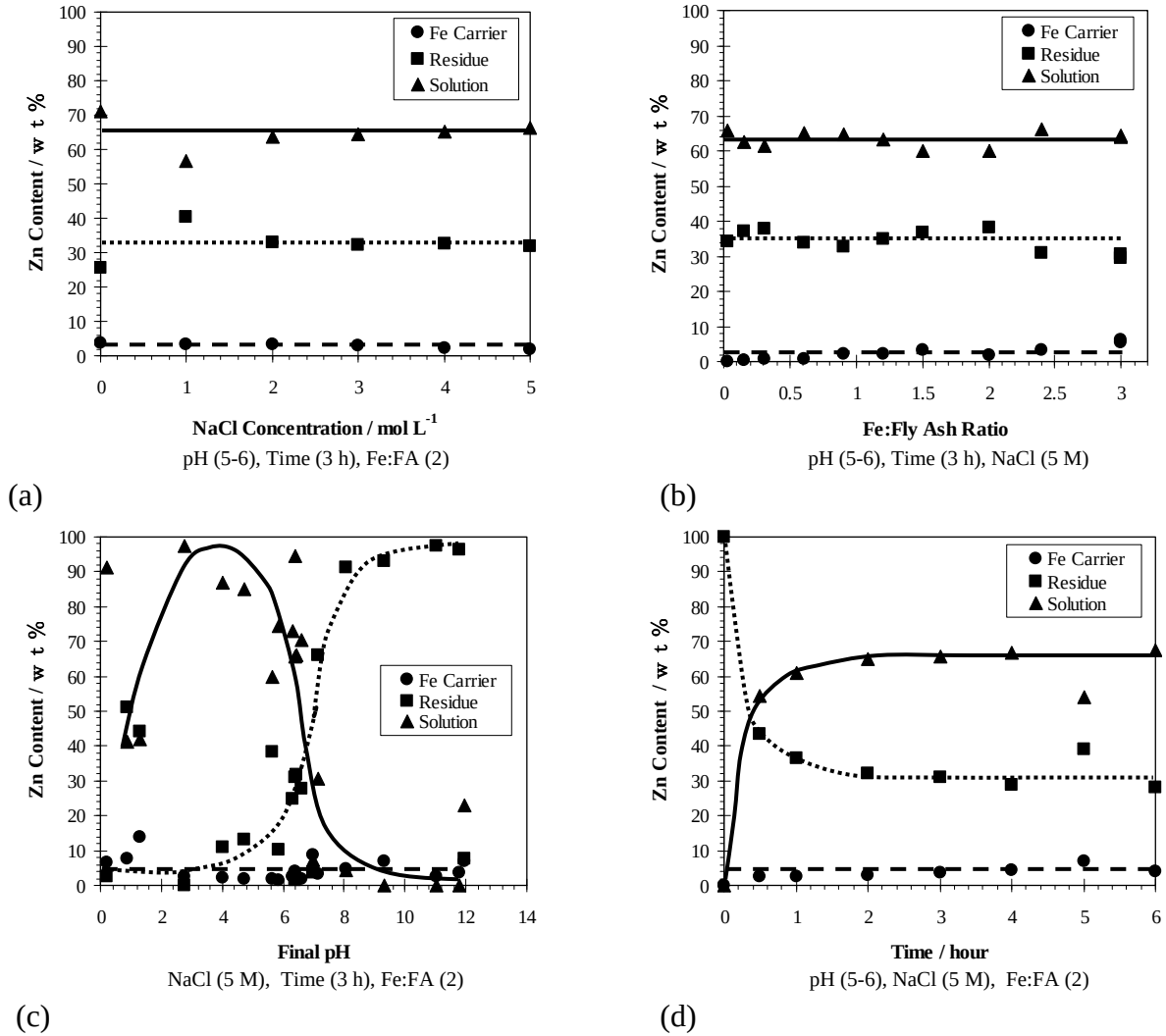


Figure 5 Effect of (a) NaCl concentration, (b) Fe:fly ash ratio, (c) final pH, and (d) treatment time on Zn content in Fe carrier, residue, and solution.

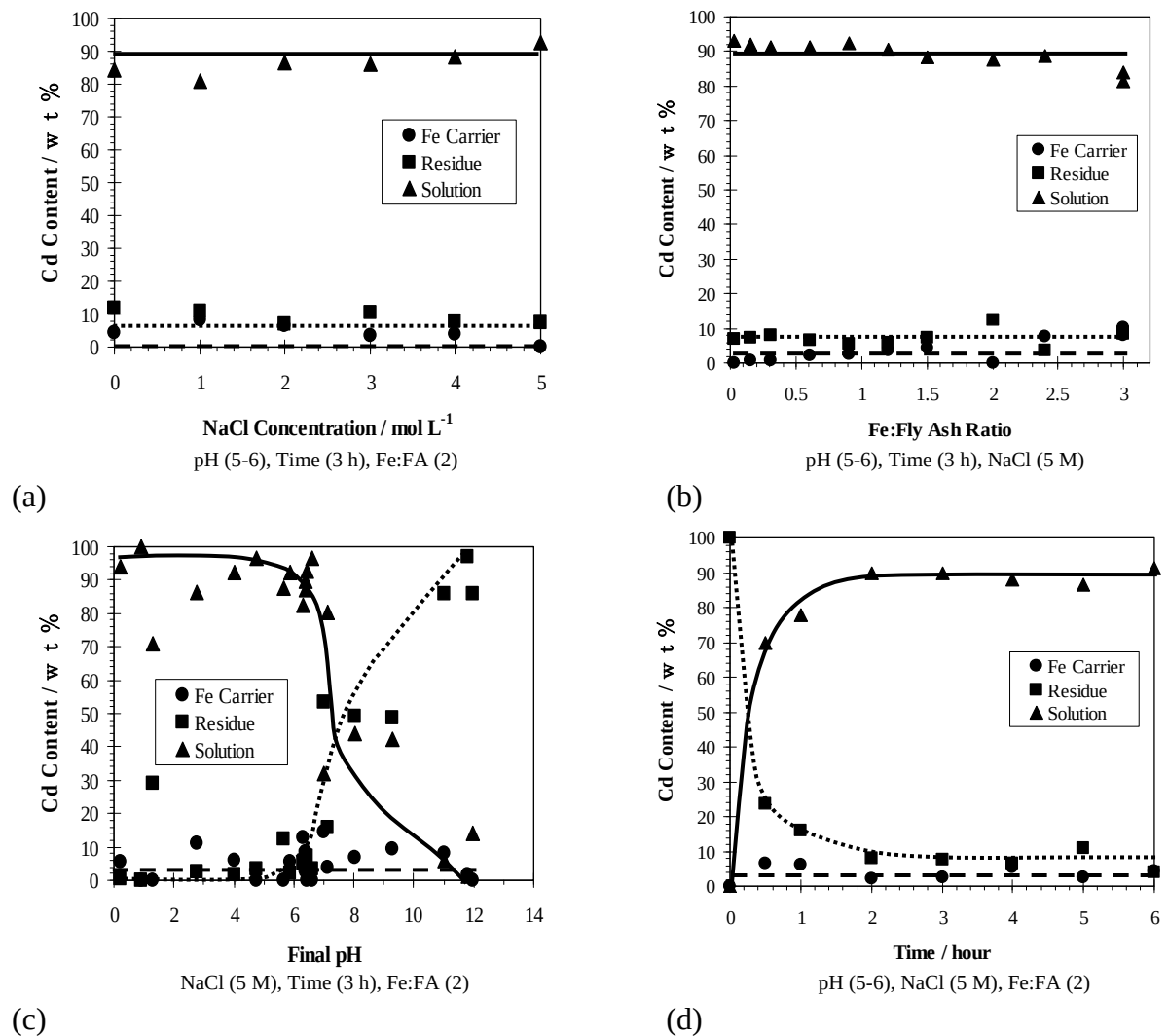


Figure 6 Effect of (a) NaCl concentration, (b) Fe:fly ash ratio, (c) final pH, and (d) treatment time on Cd content in Fe carrier, residue, and solution.