



HOKKAIDO UNIVERSITY

Title	Recovery of heavy metals from MSW molten fly ash by CIP method
Author(s)	Alorro, Richard Diaz; Hiroyoshi, Naoki; Ito, Mayumi et al.
Citation	Hydrometallurgy, 97(1-2), 8-14 https://doi.org/10.1016/j.hydromet.2008.12.007
Issue Date	2009-06
Doc URL	https://hdl.handle.net/2115/38746
Type	journal article
File Information	97-1-2_p8-14.pdf



Recovery of Heavy Metals from MSW Molten Fly Ash by CIP Method

ALORRO, Richard Diaz ^{a,*}, HIROYOSHI, Naoki ^a, ITO, Mayumi ^a, TSUNEKAWA, Masami ^a

^a*Laboratory of Mineral Processing and Resources Recycling, Division of Solid Waste, Resources and Geo-environmental Engineering, Graduate School of Engineering, Hokkaido University, Kita 13, Nishi 8, Kita-ku, Sapporo, 060-8628 Japan*

ABSTRACT

Molten fly ash (MFA), generated by the melting process of municipal solid waste incineration (MSWI) solid residues in Japan, contains considerable amounts of heavy metals such as Pb, Zn, Cu and Cd. Therefore, MFA is classified as a hazardous waste and needs treatment for detoxification or recovery of heavy metals as secondary sources. Carrier-in-Pulp (CIP) method, which is similar in principle with the Carbon-in-Pulp technology for gold recovery from ores, was proposed to recover these heavy metals from molten fly ash. Unlike the traditional Carbon-in-Pulp process, the carrier or adsorbent in the Carrier-in-Pulp method is not only limited to carbon; other materials such as Fe powder can also be used. Moreover, other physical separation techniques such as magnetic separation can also be employed to harvest the carrier from the leach pulp.

The present study, which can be regarded as a batch mode carbon-in-pulp process, investigated the application of the CIP technique to recover heavy metals from MSW molten fly ash containing 10.2 wt% Zn, 2.78 wt% Pb, 0.14 wt% Cu, and 0.12 wt% Cd. Granular activated carbon (GAC) was utilized as an adsorbent in batch multi- and single-component adsorption tests and experiments involving the CIP method using NaCl as lixiviant. The effects of activated carbon dosage, pH, NaCl concentration, and treatment time were determined. Adsorption tests showed that the competition of metal ions present in a multi-component system suppressed the adsorption of Pb, Zn, Cu and Cd on GAC but the

suppression can be minimized by increasing the GAC dosage. Around 90-100% of Pb, Zn, Cu and Cd were extracted from MFA at various conditions. At the optimum conditions (5 kmol m⁻³ NaCl, 10 g GAC, pH 5-6, and 3 hours treatment time), GAC recovered 57% Zn, 40% Pb, 90% Cu, and 54% Cd. The leaching test confirmed that the extraction of Pb from the CIP-treated residue was below the standard, thus, satisfying the land-filling guidelines in Japan.

* Corresponding author. Tel/fax: +81-011-706-6315

E-mail address: richard@eng.hokudai.ac.jp (Richard Diaz Alorro)

1. INTRODUCTION

Compared to other OECD (Organization for Economic Co-operation and Development) countries, Japan depends heavily on incineration as the primary method to treat and dispose of municipal solid waste (MSW). In 2001, as much as 80% of the 52 million tons generated MSW was incinerated (Okada et al., 2006). Incineration generates solid reaction by-products (bottom ash and fly ash), which require pre-treatment before landfilling, to immobilize the hazardous metals and to decompose the dioxins. These by-products are generally subjected to treatment by any of the four methods as specified by the Japanese Waste Disposal and Public Cleansing Law of 1992, i.e. melting treatment, cement solidification, chemical stabilization, or extraction (Zhang et al., 2006). Among these treatment methods, melting is the most popular and is being used on a large scale in Japan (Nagib et al., 2000).

During the melting of incineration residues (1300-1800°C), metal elements with low boiling point, such as Zn, Pb and metal chlorides, evaporate as flue dust and accumulate in the secondary fly ash or molten fly ash (MFA) collected by the air pollution control system of the melting plants (Jung et al., 2007). According to Japan Waste Research Foundation (2006),

144 melting plants including gasification-melting facilities were in operation as of 2004, generating 0.2 million tons of MFA as well as 0.5 million tons of molten slag annually.

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 a 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 are nearly equal to the quality of raw ore (Japan Waste Research Foundation, 2006). Molten fly ash is actually supplied as a feed material to some non-ferrous pyrometallurgical plants (Nagib et al., 2000). However, the presence of high concentration of chloride ion and other undesirable components such as Si and Sn in the ash, which are detrimental to the smelting process, limits this application. Due to this limitation, the application of hydrometallurgical techniques to recover heavy metals from MFA seems to be the most promising option.

Several studies on the extraction of heavy metals from fly ash using hydrometallurgical techniques have been reported (Hong et al., 2000a; Hong et al., 2000b; Izumikawa, 1996; Katsuura et al., 1996; Nagib et al., 2000; Okada et al., 2006; Wan et al., 2006; Wu et al., 2006; Zhang et al., 2006). In these studies, metal extractions were carried out using acid, alkaline, chelating agents, and saponins as the leaching agents. Filtration was employed to separate the residue from the leachate. The dissolved metals in the pregnant solution were recovered by chemical precipitation. 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. Therefore, washing or stabilizing processes are required before the final disposal of the leaching residue to free the residue from dissolved toxic metals.

Carrier-in-Pulp method (Figure 1) was proposed to address the problem offered by the conventional hydrometallurgical technique to recover heavy metals from molten fly ash. The Carrier-in-Pulp method is similar in principle to the Carbon-in-Pulp (CIP) process, which is widely applied in the recovery of gold and silver from ores. In the CIP process, gold adsorption is carried out by direct contacting of the activated carbon with the leach pulp. The particle size of the carbon (usually granular coconut-shell carbon or peat-based extruded carbon) is sufficiently greater than that of the ore from which it can be simply separated by screening (Ollivier et al., 1982; Jackson, E., 1986; Staunton, W.P., 2005; Acton et al., 1982). The main advantage of CIP is that it avoids the need for solid/liquid separation of the pregnant solution from the leached ore thereby avoiding the high capital cost of a filtration or counter-current decantation system (Michaelis, H., 1982; Jackson, E., 1986; Staunton, W.P., 2005; Fleming, C.A., 1992). Moreover, in the case of molten fly ash, since the carrier or adsorbent removes most of the dissolved toxic metals, the leaching solution becomes free of metals, thereby eliminating the washing or stabilization process of the residue after separation. On the other hand, unlike the traditional Carbon-in-Pulp process, the carrier or adsorbent in the Carrier-in-Pulp method is not only limited to carbon; other materials such as Fe powder can also be used (Alorro et al., 2008). Furthermore, other physical separation techniques such as magnetic separation can also be employed to harvest the carrier from the leach pulp.

The application of the carbon-in-pulp method to recover heavy metals from secondary sources, such as molten fly ash, has not been investigated before. Nevertheless, the utilization of activated carbon as adsorbent to recover heavy metals from aqueous solutions has been previously explored. Several studies (Leyva Ramos et al., 2002; Gabaldon et al., 1996; Kobya et al., 2005; Babic et al., 2002; Ferro-Garcia et al., 1988; Mohan et al., 2002; Ricordel et al., 2001; Gercel et al., 2007) have reported the adsorption of heavy metals such as Zn, Hg, Cd,

Pb, Ni and Cu present in single- or binary-component systems from aqueous solutions. Various forms of activated carbon were used; e.g. powders, granular and shaped products.

In an earlier work (Alorro et al., 2008), CIP method using iron powder as the carrier material was applied to recover Pb, Zn, Cu and Cd from molten fly ash. More than 97 wt% of Pb, Zn, Cu, and Cd were extracted from MFA to the solution phase. However, the iron powder, which was harvested from the pulp by magnetic separation, recovered only Pb and Cu (more than 94%) through cementation, leaving behind Zn and Cd ions in the solution phase. Due to this problem, an alternative carrier material that would recover the major heavy metal components from MFA, most especially Zn, was desired.

The present study demonstrated the application of the CIP method to recover the heavy metals from MFA, using granular activated carbon (GAC) as adsorbent. Batch multi- and single-metal adsorption tests were carried-out. The extraction and recovery of the heavy metals from MFA under various conditions and the leaching potential of the treated solid residue were investigated.

2 MATERIALS AND METHODOLOGY

2.1 Materials

The granular activated carbon (GAC) (Wako Chemicals Ltd., Japan) used was of commercial grade with a particle size of about 2-4 mm. The surface area and the pore diameter of the GAC, measured by N₂-BET method using Nova 2200e Surface Area and Pore Analyzer (Yuasa Ionics, Japan), was 1200 m²/g and 2.8 nm, respectively. The MSW molten fly ash utilized was obtained from an ash melting plant in Japan. The average particle size of the MFA was 20 µm and contained about 10.2 wt% Zn, 2.78 wt% Pb, 0.14 wt% Cu, and 0.12 wt% Cd, as the major heavy metal components (Table 1). The elemental components (Si, Al, Na, K, Ca, Fe, Mg, Cu, Zn, Se, As, Cd, Hg, Pb, Cr) of the ash were determined by dissolving the fly ash sample with *aqua regia* (3 HCl:1 HNO₃ v/v) through a microwave-assisted

digestion, filtering using a 0.20 μm nitro-cellulose membrane filter (Sartorius, Germany), and analysing the filtrate for metal components using an Inductively Coupled Plasma-Atomic Emission Spectrometer (ICP-AES) (SPS 7800, Seiko Instruments, Japan).

As a leaching agent, NaCl solution was used. The solutions with different concentrations were prepared by dissolving different amounts of reagent grade NaCl powder (Wako Chemical 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 (Alorro et al., 2008). The effectiveness of NaCl as a lixiviant for extracting heavy metals from fly ash was reported by Hirosyoshi et al. (2004). The study suggested that Pb extraction without the ligand was limited.

2.2 Methodology

Two types of experiments in batch mode were conducted in this study. The first type was adsorption experiments using solutions containing Pb, Zn, Cu and Cd ions in single- and multi-metal system. The second type involved the application of the CIP method to extract and recover Pb, Zn, Cu and Cd from MFA. Both types of experiment utilized granular activated carbon as the metal adsorbent.

2.2.1 Batch Adsorption Tests

Multi-metal and single-metal batch adsorption experiments were conducted. For the multi-metal adsorption experiment, NaCl leaching of molten fly ash was carried out and the leachate was used as the source of heavy metal ions. The leachate, analyzed by ICP-AES, contained around 14 mol m^{-3} Pb, 147 mol m^{-3} Zn, 1.8 mol m^{-3} Cu and 1.2 mol m^{-3} Cd as the major metal components. Other metals such as Hg, As, and Cr were also present in minimal amounts (about 0.03-0.003 mol m^{-3}). The experiment was performed by adding varied amounts of granular activated carbon in a 50 cm^3 Erlenmeyer flask containing 25 cm^3 of the

leachate. The pH of the solution was controlled by adding H_2SO_4 . The flask was placed in a water bath shaker and was shaken for 3 hours at a rate of $120 \text{ strokes min}^{-1}$ and a temperature of 25°C . After the treatment, the mixture was filtered using a 0.84 mm test sieve (Tyler, USA). The filtrate was analysed for metal components using ICP-AES.

For the single-metal adsorption experiment, stock solutions of Pb(II) , Zn(II) , Cu(II) , and Cd(II) were prepared from reagent grade PbCl_2 , ZnCl_2 , $\text{CdCl}_2 \cdot 2\frac{1}{2}\text{H}_2\text{O}$, $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ powders (Wako Pure Chemical Ind., Ltd., Japan) as the source of the individual metal ions. The experiment was performed by adding varied amounts of granular activated carbon into a flask containing 25 cm^3 of 5 kmol m^{-3} NaCl solution and the target metal ion. The heavy metal concentrations were fixed at 14 mol m^{-3} Pb , 147 mol m^{-3} Zn , 1.8 mol m^{-3} Cu , and 1.2 mol m^{-3} Cd , consistent with the metal concentrations of the multi-metal experiment. Other operating conditions, such as treatment time, shaking rate, temperature, and pH control, were the same as the multi-metal experiment.

2.2.2 CIP Experiments

Batch experiments were conducted to demonstrate the effect of the CIP method on the extraction and recovery of Pb , Zn , Cu and Cd from molten fly ash. The CIP experiments consisted of adding varied amount of granular activated carbon (GAC) to 50 cm^3 glass Erlenmeyer flask containing 2.5 g MFA and 25 cm^3 of NaCl solution of different concentrations ($1\text{-}5 \text{ kmol m}^{-3}$) and then shaken in a water bath shaker (ML-10F, Taitec, Japan) for 1- 24 hours at a rate of $120 \text{ strokes min}^{-1}$ and temperature of 25°C . The pH of was varied by adding H_2SO_4 .

After each treatment, the activated carbon granules were harvested from the pulp by sieving using a 0.84 mm Tyler test sieve. An aliquot sample of the leachate was obtained, centrifuged, filtered and set aside for analysis. The activated carbon was dried overnight in a vacuum oven.

The amount of metals adsorbed onto the activated carbon was determined by desorption experiments, which were carried out using 16 kmol m^{-3} HNO_3 for 24 hours. Previous desorption experiments showed that at this HNO_3 concentration and treatment time, almost 100% of Pb, Zn, Cu and Cd were desorbed from GAC. The solutions were analysed for metal contents using ICP-AES.

The amount of metals extracted and recovered from MFA was calculated according to the following equations

$$\text{Extraction (\%)} = \frac{C_{\text{GAC}} + C_s}{C_{\text{MFA}}} \times 100 \quad (1)$$

$$\text{Recovery (\%)} = \frac{C_{\text{GAC}}}{C_{\text{MFA}}} \times 100 \quad (2)$$

where C_{GAC} is the amount of metal in GAC, C_s the amount of metal in the solution phase, and C_{MFA} the amount of metal in molten fly ash.

2.2.3 Japanese Leaching Test No. 13

The residues obtained from the CIP treatment were subjected to the leaching test specified in the Notification No. 13 of the Environmental Agency of Japan (Environmental Agency of Japan, 1973). In the leaching test, 1 g of the dried residue was leached with 10 cm^3 distilled water in a 50 cm^3 Erlenmeyer flask for 6 hours. The filtered solution was analysed for hazardous metals using ICP-AES.

3 RESULTS AND DISCUSSION

3.1 Batch Adsorption Tests

Molten fly ash contains various metal ions; hence, an adsorption experiment involving more than three metal ions was conducted as preliminary work in order to assess the ability of GAC to adsorb metals present in multi-component system. A single-metal adsorption experiment was also conducted for comparison.

Figure 2(a-d) shows the adsorption of Pb, Zn, Cu and Cd in multi- and single- metal systems as a function of carbon dosage. In all cases, the adsorption of Pb, Zn, Cu and Cd increased with increasing activated carbon dosage, due to the increase in the available adsorption sites offered by the higher amount of GAC added. The adsorption amount of Pb, Cu and Cd (Figures 2a-2c) in the the multi-metal system was smaller than that in the single-metal system, indicating that adsorption was suppressed in the presence of other metal ions. The suppressive effect was also observed in Zn adsorption, but the degree of the suppression seemed to be less significant in comparison with other metals. It should also be noted that the degree of suppression in the adsorption of Pb, Cu, and Cd was apparently high when the activated carbon dosage was smaller and became low with large carbon dosage.

The suppressive effect mentioned above may be interpreted by assuming the competition of metals ions in the adsorption process. In the batch adsorption experiments, the Zn concentration was 147 mol m^{-3} ; much higher than the concentrations of the other metals (Pb 13.9 mol m^{-3} , Cu 1.8 mol m^{-3} , and Cd 1.2 mol m^{-3}). For simplicity, let us consider the effect of competition in the adsorption of a dominant metal ion A and minor metal ion B. If the number of the adsorption sites for the metal ions is limited, the adsorption amount of each ion would be affected by the presence of the other, and the adsorption of both ions would be suppressed. But the degree of suppression is not the same for both ions; the suppressive effect would be stronger for minor species than the dominant species. This is in agreement with the observed result, i.e., the adsorption of Pb, Cu and Cd (minor species) was strongly suppressed in multi-metal system, while the degree of suppression of the adsorption of Zn (dominant species) was less. When the number of adsorption sites is sufficient to accommodate all the ions involved in the system, competition will not occur. This may be the reason why the suppressive effect on the adsorption of Pb, Cu, and Cd decreased in the presence of large activated carbon dosages.

As discussed above, granular activated carbon can recover Pb, Zn, Cu and Cd present in single- and multi-metal system. Adsorption was suppressed when the metal ions are present in a multi-phase system due to competition. However, the suppressive effect can be minimized by adding large dosages of activated carbon. This suggests that GAC can be utilized as a carrier material (adsorbent) to recover Pb, Zn, Cu and Cd from molten fly ash.

3.2 CIP Method

The adsorption of heavy metals in CIP method was carried out by the direct contact between the carrier and the slurry. In this study, the Pb, Zn, Cu and Cd from the MSW molten fly ash were extracted to the solution phase and then adsorbed on activated carbon. The metals were distributed into three fractions: fly ash residue, GAC, and solution. The effects of activated carbon dosage, NaCl concentration, treatment time, and solution pH on the extraction and recovery of Pb, Zn, Cu and Cd from MFA were investigated.

3.2.1 Effect of Activated Carbon Dosage

Figure 3 shows the effect of activated carbon dosage on the extraction of Pb, Zn, Cu and Cd from molten fly ash. The addition of activated carbon enhanced the extraction of the heavy metals from fly ash. It should be noted that without activated carbon, the extraction of Pb was about 60%, 69% for Zn, 20% for Cu, and 90% for Cd. The extraction of Pb, Zn, Cu and Cd from MFA improved to 90-100% upon the addition of activated carbon. Similar effects were also observed when Fe powder was used as a carrier to recover Pb, Zn, Cu and Cd from MFA by CIP method (Alorro et al., 2008). These observations agreed with the findings of Reese, K.L. et al. (2000) in the case of gold extraction from ores in the presence of activated carbon.

The effect of activated carbon dosage on the recovery of Pb, Zn, Cu and Cd is displayed in Figure 4. With increasing activated carbon dosage, the amount of heavy metals

recovered increased. The recovery of Pb, Zn, and Cd were less than 10%, and around 28% for Cu at 1 g GAC addition. At 15 g activated carbon addition, the recovery increased to 100% for Cu, 60% for Zn and Cd, and about 40% for Pb. The increase in the metal recovery can be attributed to the larger surface area available for adsorption, which was offered by the higher amount of activated carbon added. It is worthy to note that in the CIP method using Fe powder as carrier (Alorro et al., 2008), negligible amounts of Zn were recovered.

Figure 5 shows the amount of metals remaining in the solution phase at different activated carbon dosages. The amount of Pb, Zn, Cu and Cd remaining in the solution phase decreased with increasing activated carbon amounts. About 5% Cu, 30% Zn and Cd, and 60% Pb were left in the solution phase at 15 g GAC addition.

3.2.2. Effect of pH

The pH dependence of the extraction of Pb, Zn, Cu and Cd from fly ash is illustrated in Figure 6. About 90-100% of the heavy metals were extracted at the acidic pH range. The amount of metals extracted started to decrease at the neutral pH range. At pH 8-11 the extraction values were less than 5%. This result means that the extraction of the heavy metals from fly ash is favored at lower pH.

Figure 7 exhibits the effects of pH on the recovery of heavy metals from molten fly ash. At pH 1-6, around 90% Cu, 60% Zn and Cd, and 40% Pb were recovered. The recovery values started to decrease at the neutral pH range and became negligible at the alkaline region. It should be noted that at the acidic region, 90-100% of Pb, Zn, Cd and Cu were extracted to aqueous phase. The presence of high amount of metal ions in the solution phase at lower pH range could be the reason why recovery was at a maximum in this pH region.

3.2.3 Effect of NaCl Concentration

The effect of NaCl concentration on the extraction of heavy metals from MSW molten fly ash can be seen in Figure 8. The extraction of Zn, Cd and Cu was not significantly affected by the increase in NaCl concentration. Almost 100% of Zn, Cd and Cu were extracted even at low NaCl concentration. On the other hand, the extraction of Pb from molten fly ash showed a very strong dependence on NaCl concentration. The extraction of Pb increased with increasing NaCl concentration. At 0.1 kmol m^{-3} NaCl, only around 8% of Pb was extracted from fly ash, while at 5.0 kmol m^{-3} NaCl almost 100% of the metal was extracted.

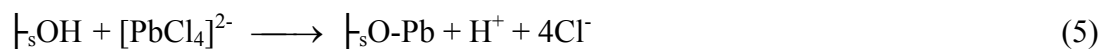
Figure 9 presents the effect of NaCl concentration on the recovery of heavy metals from MSW molten fly ash. At different NaCl concentration, about 90% of Cu was recovered, signifying that its recovery was not affected by the changes in the NaCl concentration. At $0.1\text{-}2.0 \text{ kmol m}^{-3}$ NaCl, the recovery of Zn and Cd increased and became constant at around 60% thereafter. At increasing NaCl concentration, the recovery of Pb from fly ash increased. Around 50% of Pb was recovered at 5.0 kmol m^{-3} NaCl.

Changes in the ionic strength due to the presence of complexing ligands such as Cl^- , may alter the metal's aqueous chemistry and the electric double layer surrounding the carbon surface. At high ionic strengths, the carbon surface is swarmed by the electrolyte, and access to the surface is made more difficult (Reed, 2002). If we assume that Pb in fly ash is present as PbO , its extraction can be hypothesized to obey the following chemical reactions:



At very low NaCl concentration, some amount of Pb can be extracted as Pb^{2+} with H^+ as the main extractant (Equation 3). At higher NaCl concentration, Pb forms soluble chloride complexes with Cl^- , such as $[\text{PbCl}_4]^{2-}$ (Equation 4). During adsorption, the lead-chloride complex may react with the OH^- on the surface of the activated carbon (Equation 5),

returning H^+ and Cl^- ions into the solution phase to extract more metals. This is assumed to be the operating mechanism for the adsorption of Pb onto GAC.



3.2.4. Effect of Treatment Time

Figure 10 shows the effect of treatment time on the extraction of heavy metals from MSW molten fly ash. The extraction of Zn, Cu and Cd increased during the first 2 hours and reached equilibrium after 3 hours with metal extraction of about 90-100%. The extraction of Pb at increasing treatment time displayed a different trend; it peaked at 3 hours and started to decrease thereafter. From an almost 100% extraction at 3 hours, it decreased to about 70% after 24 hours.

With increasing treatment time, the recovery of Zn, Cu and Cd increased (Figure 11). After 24 hours, 100% Cu, 79% Cd and 75% Zn were recovered by the activated carbon. In the case of Pb, the recovery exhibited a similar pattern with its extraction behavior. Recovery for Pb peaked (42%) at 3 hours and decreased thereafter. After 24 hours, only around 30% Pb was recovered. The reason for the decrease is unclear to the authors; further investigation is required to confirm this behavior. One possible reason is that at a longer treatment time, CO_2 may have penetrated and dissolved into the solution forming CO_3^{2-} , which may have reacted with Pb, forming an insoluble and less absorbable $PbCO_3$.

3.3 Leaching Test of Treated Fly Ash Residue

In Japan, fly ash is disposed either in a controlled or a special-type landfill. Special-type landfills accept fly ash which has leaching potentials of hazardous materials. The landfill type is determined by the leaching test specified by the Environmental Agency (Environmental Agency of Japan, 1973).

In this study, the residues recovered from the CIP treatment of molten fly ash at optimum condition (10 g GAC, 5 kmol m⁻³ NaCl, pH 5-6, 3 hours treatment time) were examined by the leaching test. The results of the test in comparison with other treatment methods are shown in Table 2. No Pb was detected from the leachate of the CIP-GAC treated residue (Figure 12). The results are comparable to that of the CIP method using iron powder (Alorro et al, 2008). The Cu, Hg and Cr extraction from the fly ash residue was also below the set guidelines in Japan. The amount of Zn and Cd ions detected from the leachate was higher compared to other methods. The Cd amount detected was beyond the set standard for landfill materials in Japan. The standard for Zn is not yet set in Japan. 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. This means that the CIP method was able to treat the alkalinity of the molten fly ash.

4. CONCLUSION

Municipal solid waste (MSW) molten fly ash contains heavy metals such as Pb, Zn, Cu and Cd which pose environmental threats due to their leaching potential in landfill environment. Molten fly ash must be treated for detoxification or recovery of these heavy metals as secondary sources. The CIP method was applied to recover Pb, Zn, Cu and Cd from MFA 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.

It was found that the 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. Increasing the GAC dosage also increased the amount of heavy metals recovered from MFA. 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 favoured 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. The leaching test confirmed that the Pb extraction from the CIP-treated residue was below the standard, thus, satisfying the land-filling guidelines in Japan.

REFERENCES

- Acton, C. F., Charles, W. D., 1982. Current gold and silver recovery practice. In: Maltby, P.D.R. (Ed), Proceedings of the XIV International Mineral Processing Congress. CIM, Toronto, Canada, Session II, pp II-2.1-2.19
- Alorro, R.D., Mitani, S., Hiroyoshi, N. Ito, M., Tsunekawa, M., 2008. Recovery of heavy metals from MSW molten fly ash by Carrier-in-Pulp Method: Fe powder as carrier. *Minerals Engineering*, 21 (15), 1094-1101
- Babic, B.M, Milonjic, S.K., Polovina, M.J., Cupic, S., Kaludjerovic, B.V., 2002. Adsorption of zinc, cadmium and mercury ions from aqueous solutions on an activated carbon cloth. *Carbon*, 40, pp. 1109-1115
- Environmental Agency Japan, February 17, 1973. Testing methods for metals in industrial wastes, Notification No. 13 of the Environmental Agency, Japan (in Japanese)

Ferro-Garcia, M.A., Rivera-Utrilla, J., Rodriguez-Gordillo, J., Bautista-Toledo, I., 1988. Adsorption of zinc, cadmium, and copper on activated carbons obtained from agricultural by-products. *Carbon*, 26(3), pp. 363-373

Fleming, C.A., 1992. Hydrometallurgy of precious metals recovery. *Hydrometallurgy*, 30, 127-162

Gabaldon, C., Marzal, P., Ferrer, J., Seco, A., 1996. Single and competitive Adsorption of Cd and Zn onto granular activated carbon. *Water Research*, 30(12), pp. 3050-3060

Gercel, Ozgul, Gercel, H. Ferdi, 2007. Adsorption of lead (II) ions from aqueous solutions by activated carbon prepared from biomass plant material of *Euphorbia rigida*. *Chemical Engineering Journal*, 132, pp. 289-297

Hiroyoshi, N., Kishimoto, N., Tsunekawa, M., Hirajima, T., Mishima, H., 2004. Recovery of metals from melting furnace fly ash by ammonia/chloride leaching. In: *Proceedings of the 29th Spring Annual Meeting of the Mining and Materials Processing Institute of Japan*, pp. 31-32 (in Japanese)

Hong, K., Tokunaga, S., Kajiuchi, T., 2000. Extraction of heavy metals from MSW incinerator fly ashes by chelating agents. *Journal of Hazardous Materials*, B75, pp. 57-73

Hong, K.J., Tokunaga, S., Ishigami, Y., Kajiuchi, T., 2000. Extraction of heavy metals from MSW incinerator fly ash using saponins. *Chemosphere*, 41, pp. 345-352

Izumikawa, Chiaki, 1996. Metal recovery from fly ash generated from vitrification process for MSW ash. *Waste Management*, 16 (5/6), pp. 501-507

Jackson, E., 1986. *Hydrometallurgical Extraction and Reclamation*. Ellis Horwood Limited, England, pp. 106-108

Japan Waste Research Foundation, 2006. *Research on Technology of Separation/Concentration/Recovery of Metals in Residues Generated in Waste Treatment (in Japanese)*

Jung, C.H., Osako, M., 2007. Thermodynamic behaviour of rare metals in the melting process of municipal solid waste (MSW) incineration residues. *Chemosphere*, 69, pp. 279-288

Katsuura, H., Inoue, T., Hiraoka, M., Sakai, S., 1996. Full-scale plant study on fly ash treatment by the acid extraction process. *Waste Management*, 16 (5/6), pp. 491-499

Kobya, M., Demirbas, E., Senturk, E., Ince, M., 2005. Adsorption of heavy metal ions from aqueous solutions by activated carbon prepared from apricot stone. *Bioresource Technology*, 96, pp. 1518-1521

Leyva Ramos, R., Bernal Jacome, L.A., Mendoza Barron, J., Fuentes Rubio, L., Guerrero Coronado, R.M., 2002. Adsorption of zinc (II) from an aqueous solution onto activated carbon. *Journal of Hazardous Materials*, B90, pp. 27-37

Michaelis, H.V., 1982. Innovations in gold and silver recovery. In: Maltby, P.D.R. (Ed), Proceedings of the XIV International Mineral Processing Congress. CIM, Toronto, Canada, Session II, pp II-1.1-1.25

Mohan, Dinesh, Singh, Kunwar P., 2002. Single- and multi-component adsorption of cadmium and zinc using activated carbon derived from bagasse-an agricultural waste. Water Research, 36, pp. 2304-2318

Nagib, S., Inoue, K., 2000. Recovery of lead and zinc from fly ash generated from municipal incineration plants by means of acid and/or alkaline leaching. Hydrometallurgy, 56, pp. 269-292

Okada, T., Tojo, Y., Tanaka, N., Matsuto, T., 2006. Recovery of zinc and lead from fly ash from ash-melting and gasification-melting processes of MSW—Comparison and applicability of chemical leaching methods. Waste Management, 27, pp. 69-80

Ollivier, P., Barberry, G., 1982. Development of a carbon-in-pulp process for clayey gold ores. In: Maltby, P.D.R. (Ed), Proceedings of the XIV International Mineral Processing Congress. CIM, Toronto, Canada, Session II, pp II-4.1-4.27

Reese, K.L. Van Deventer, J.S.J., 2000. The mechanism of enhanced gold extraction from ores in the presence of activated carbon. Hydrometallurgy, 58, pp. 151-167

Ricordel, S., Taha, S., Cisse, I., Dorange, G., 2001. Heavy metals removal by adsorption onto peanut husks carbon: characterization, kinetic study and modelling. *Separation and purification Technology*, 24, pp. 389-401

Staunton, William P., 2005. Carbon-in-pulp. In: Adams, Mike D. (Ed.), *Developments in Mineral Processing*, Vol. 15: *Advances in Gold Ore Processing*. Elsevier B.V., The Netherlands, pp562-586

Wan, X., Wang, W., Ye, T., Guo, Y., Gao, X., 2006. A study on the chemical and mineralogical characterization of MSWI fly ash using a sequential extraction procedure. *Journal of Hazardous Materials*, B134, pp. 197-201

Wu, H.Y., Ting, Y.P., 2006. Metal extraction from municipal solid waste (MSW) incinerator fly ash-Chemical leaching and fungal bioleaching. *Enzyme and Microbial Technology*, 38 pp. 839-847

Zhang, F.S., Itoh, H., 2006. Extraction of metals from municipal solid waste incinerator fly ash by hydrothermal process. *Journal of Hazardous Materials*, B136, pp. 663-670

Table 1: Representative fly ash composition

<i>Metals</i>	<i>Composition (mg/g ash)</i>
Si	2.76
Al	4.87
Na	81.5
K	90.0
Ca	69.8
Fe	3.29
Mg	0.99
Cu	1.43
Zn	102
Se	0.05
As	1.19
Cd	1.20
Hg	0.07
Pb	27.8
Cr	0.06

Table 2 Leaching Test: Analysis of the leachate of CIP-GAC treated fly ash residue in comparison with other treatment methods

Method	Metals, mg L ⁻¹						pH
	Cu	Zn	Cd	Hg	Pb	Cr	
Standard	-	-	0.30	0.01	0.30	1.50	5.8 - 8.3
Untreated Ash	0.08	1.38	0.03	0.16	2.18	0.04	-
Sulfurization	0.11	0.05	0.03	0.00	0.35	0.00	-
NaCl leaching	0.00	17.56	0.71	0.00	0.50	0.00	-
CIP-Fe	0.03	13.80	0.15	0.00	0.00	0.00	7.2
CIP-GAC	0.00	22.60	1.40	0.00	0.00	0.60	6.5

Figure 1. Carrier-in-Pulp (CIP) Method

Figure 2. Multi- and single-metal adsorption of (a) Pb, (b) Cu, (c) Cd and (d) Zn on granular activated carbon ($5 \text{ kmol m}^{-3} \text{ NaCl}$, pH 5-6, 3 hours treatment time)

Figure 3. Effect of activated carbon dosage on the extraction of Pb, Zn, Cu and Cd from MFA ($5 \text{ kmol m}^{-3} \text{ NaCl}$, pH 5-6, 3 hours treatment time)

Figure 4. Effect of activated carbon dosage on the recovery of Pb, Zn, Cu and Cd from MFA ($5 \text{ kmol m}^{-3} \text{ NaCl}$, pH 5-6, 3 hours treatment time)

Figure 5. Amount of Pb, Zn, Cu and Cd in the solution phase at different activated carbon dosage ($5 \text{ kmol m}^{-3} \text{ NaCl}$, pH 5-6, 3 hours treatment time)

Figure 6. Effect of pH on the extraction of Pb, Zn, Cu and Cd from MFA ($5 \text{ kmol m}^{-3} \text{ NaCl}$, 10 g GAC, 3 hours treatment time)

Figure 7. Effect of pH on the recovery of Pb, Zn, Cu and Cd from MFA ($5 \text{ kmol m}^{-3} \text{ NaCl}$, 10 g GAC, 3 hours treatment time)

Figure 8. Effect of NaCl concentration on the extraction of Pb, Zn, Cu and Cd from MFA (pH 5-6, 10 g GAC, 3 hours treatment time)

Figure 9. Effect of NaCl concentration on the recovery of Pb, Zn, Cu and Cd from MFA (pH 5-6, 10 g GAC, 3 hours treatment time)

Figure 10. Effect of treatment time on the extraction of Pb, Zn, Cu and Cd from MFA (pH 5-6, 10 g GAC, 5 kmol m^{-3})

Figure 11. Effect of treatment time on the recovery of Pb, Zn, Cu and Cd from MFA (pH 5-6, 10 g GAC, 5 kmol m^{-3})

Figure 12. Pb extraction from the CIP-GAC treated fly ash residue in comparison with other treatment methods

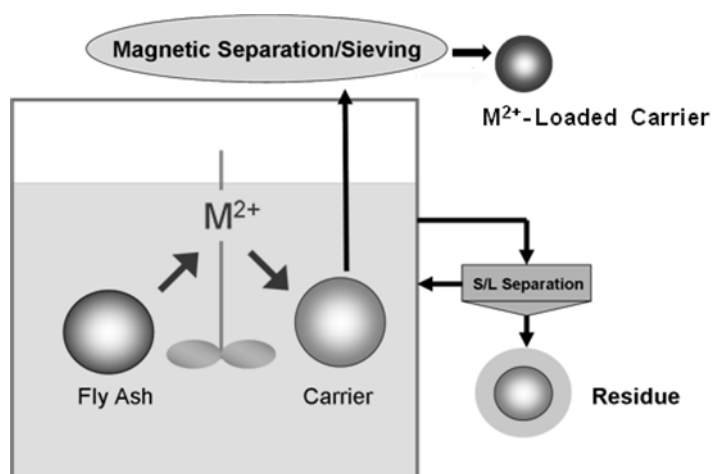


Figure 1

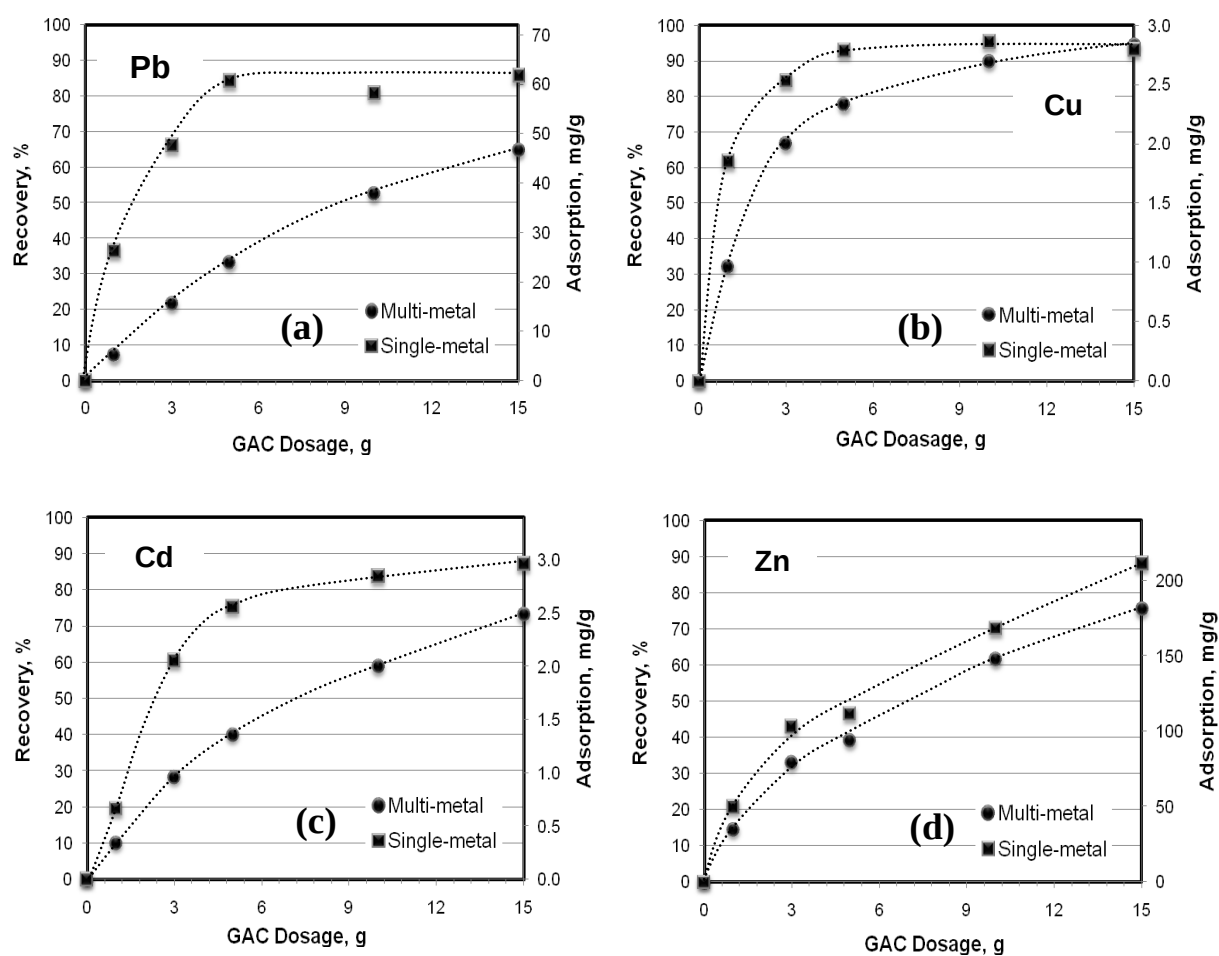


Figure 2

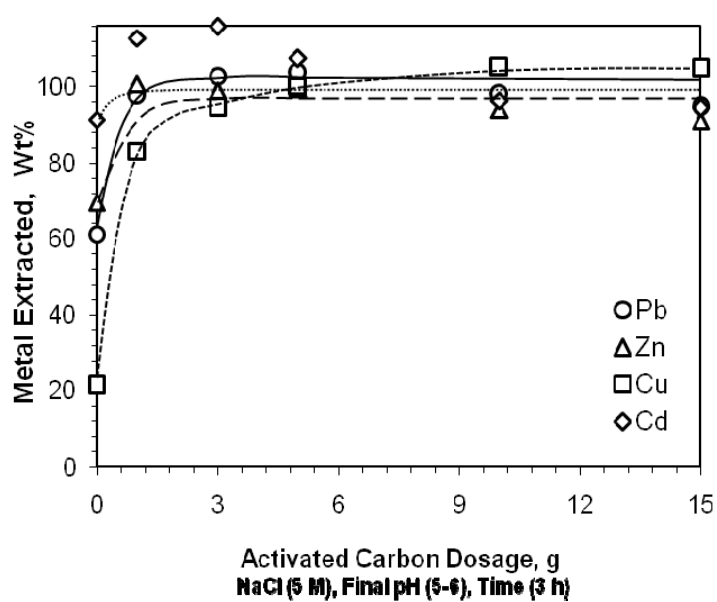


Figure 3

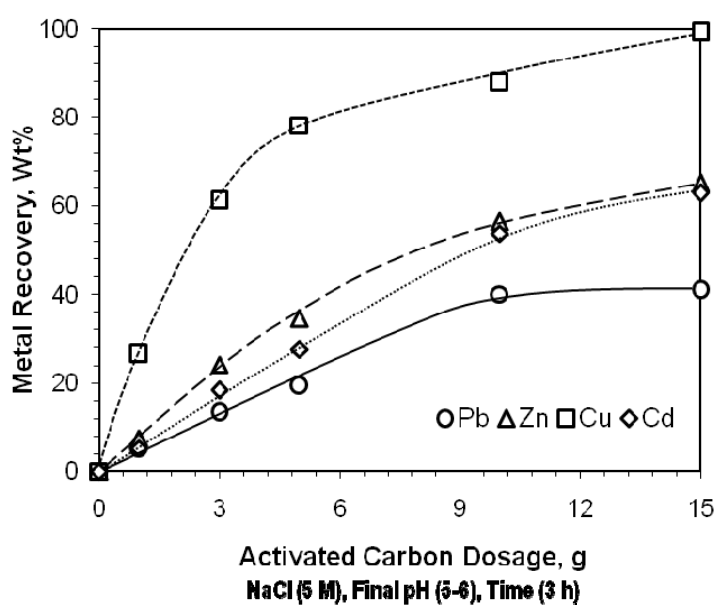


Figure 4

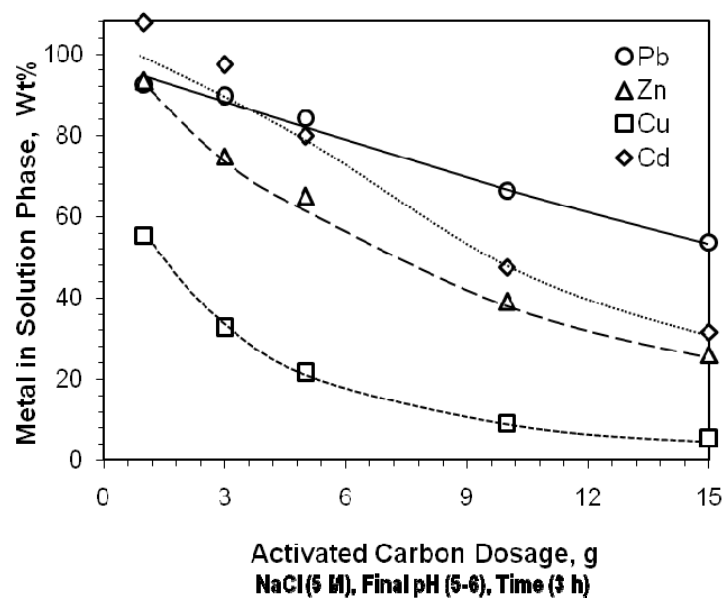


Figure 5

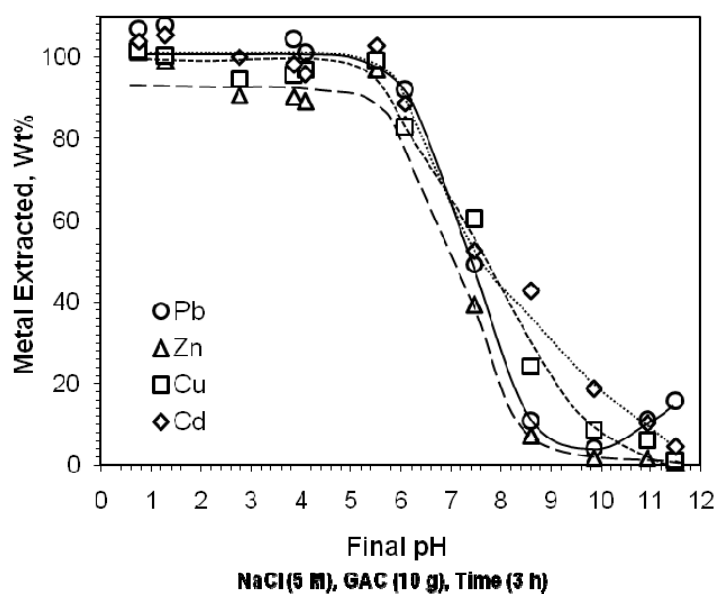


Figure 6

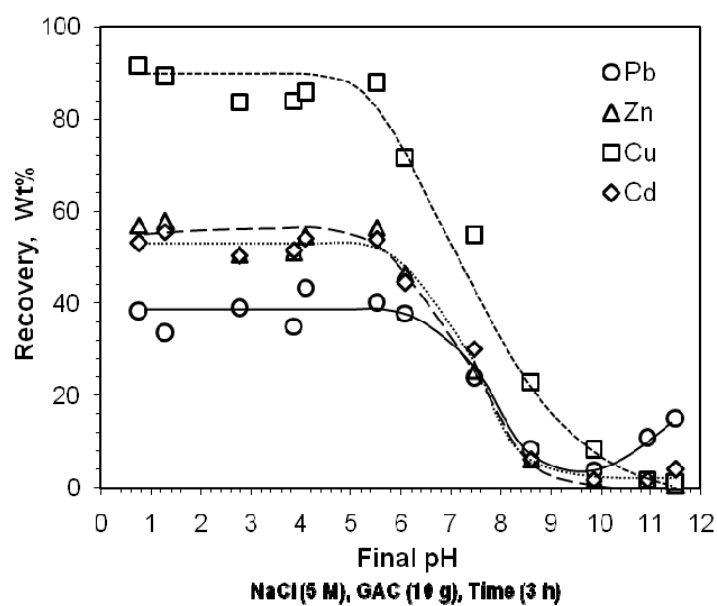


Figure 7

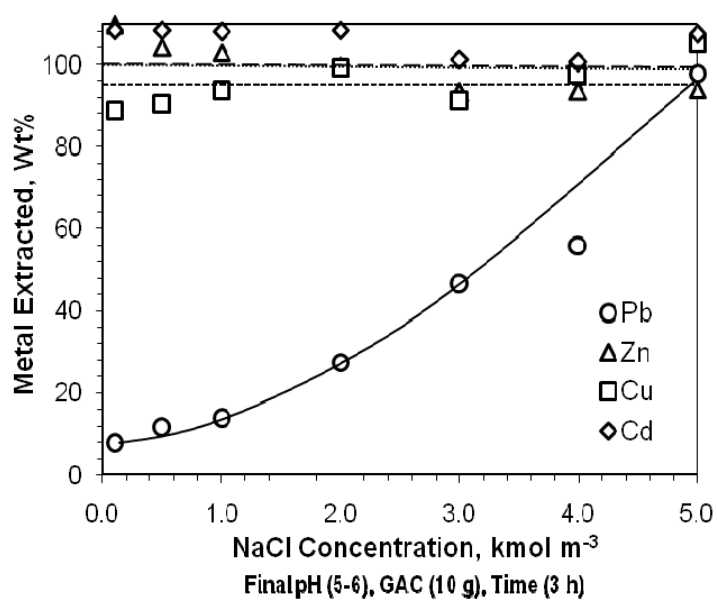


Figure 8

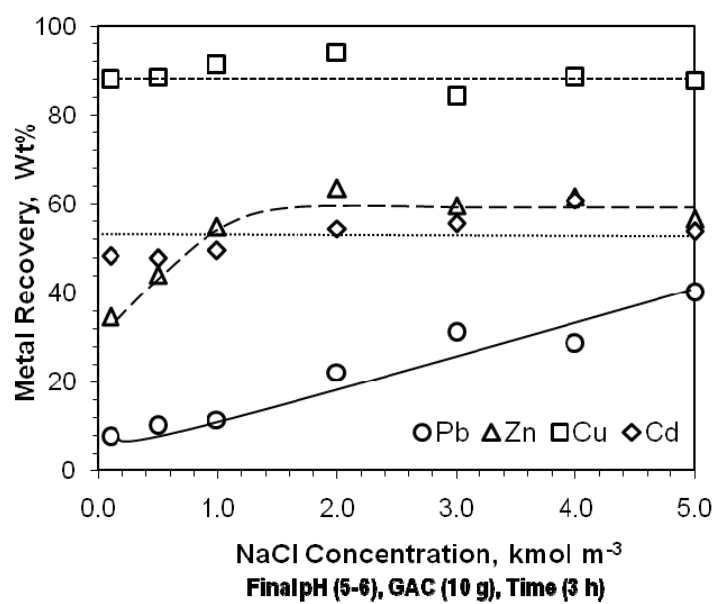


Figure 9

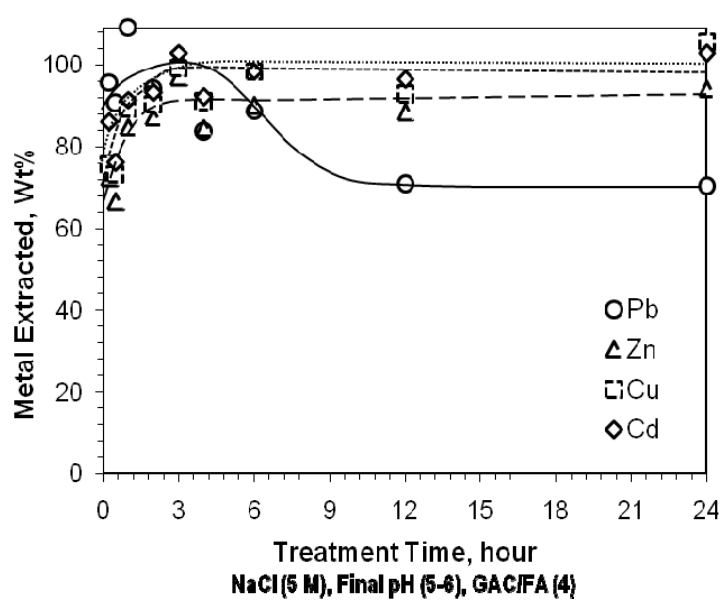


Figure 10

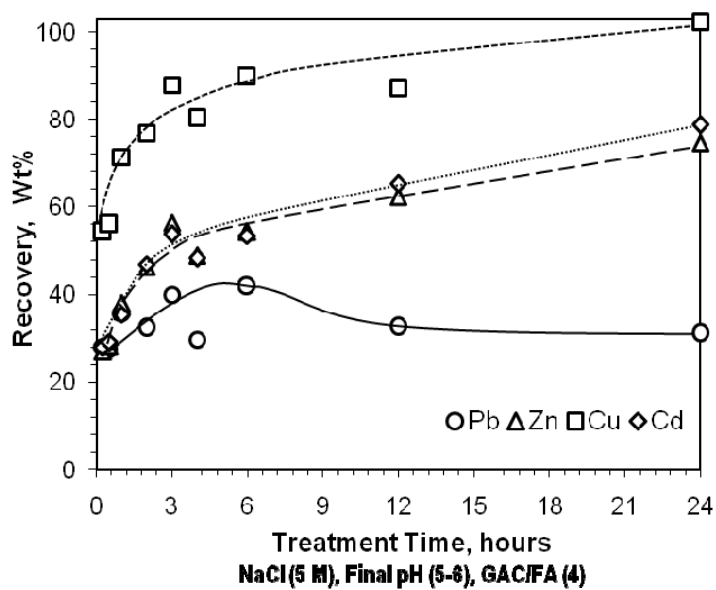


Figure 11

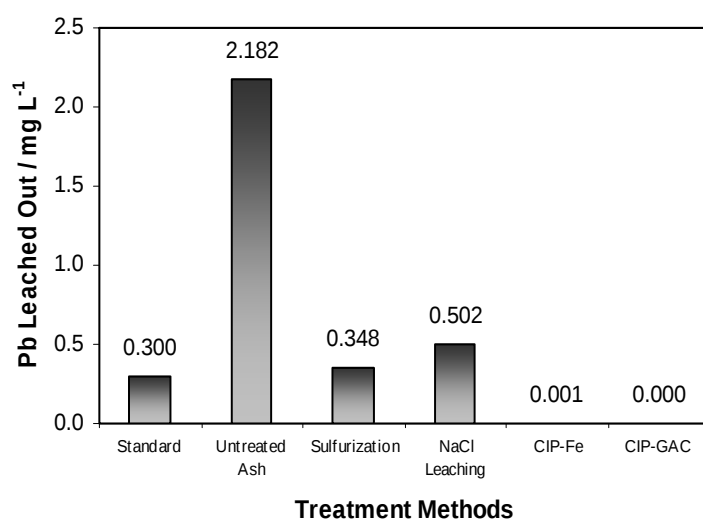


Figure 12