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RECOVERY OF HEAVY METALS IN ELECTROSTATIC PRECIPITATOR ASH BY CARBON DIOXIDE AS A PRE-EXTRACTION REAGENT

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ABSTRACT

This study investigated the efficiency of heavy metal separation and recovery in electrostatic precipitator (ESP) ash from a municipal solid waste incinerator (MSWI) when carbon dioxide is used as the pre-extraction agent. The experiments were conducted at 120°C with pH values of 3–6 and liquid-to-solid (L/S) ratios varying from 10:1 to 40:1. The results indicate that an increase in the L/S ratio enhances the separation and recovery efficiency of heavy metals in the MSWI ash. The separation efficiency of Cd, Cr, and Zn increased significantly with the increased L/S ratio. The pH level was the prominent factor affecting the extraction of heavy metals from ESP ash: at pH 3–4, maximum amounts of Cd and Cr were extracted. However, due to the increased release of ions with increased CO_3^{2-}, Zn was relatively soluble at high pH values. In

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cases with an L/S ratio of 40:1 and pH 3, the Cd, Cr, and Cu extraction amounts were 86.4%, 71.2%, and 34.9%, respectively. Pb and its compounds remained in a stable state under experimental conditions. The above results point toward the feasibility of heavy metal recovery and fly ash reutilization when carbon dioxide is used as the pre-extraction agent. Both greenhouse gas (CO_2) emissions and acid extraction operating costs are reduced with this process.

Key Words: Municipal Solid Waste; Electrostatic precipitator (ESP) ash; Separation; Heavy metal

INTRODUCTION

To cope with increasingly stringent waste disposal regulations and the constantly growing amount of municipal solid waste (MSW), the Taiwanese government plans to install more than 36 municipal solid waste incinerators (MSWI) before 2003. These facilities will be designed to process an estimated 75% of the island's MSW. However, the potential environmental risk from the release of heavy metals through flue gas and incinerator residues has become a primary concern of the island's population. Recently, most studies have focused on the treatment or reutilization of bottom and toxic fly ash. Dry/semi-dry scrubber ashes have been classified primarily as stable and nontoxic materials. However, other studies have shown that the ash leachate concentration of lead, determined by the toxicity characteristic leaching procedure (TCLP), often exceeds the regulatory requirements because of high pH levels. A leaching characteristic assessment for MSWI ashes is necessary for their management and disposal.

Leachability studies on heavy metals from MSWI ashes have been presented in the literature. Metal leachability from these ashes appears to be dependent upon the combustion temperature, pH of the leaching medium, pH after extraction, ash particle size, metal speciation, liquid-solid (L/S) ratio, chemical composition of the ashes and wastes, and the flue-gas cleaning system (1–5). Cernuschi et al. (2) showed that Pb in fly ash collected in dry or semi-dry acid gas-removal systems that used lime were much more soluble than the same metal in fly ash collected without added lime. The fly ash contained some ions and excess alkali, such as calcium and magnesium, which can significantly change the metal leaching characteristics. Buchholz and Landsberger (6) investigated the pH effect on metal leaching characteristics and pointed out that the pH of the resulting leachate was the greatest factor governing the concentration of metals in solution. Alba et al. (7) also demonstrated the effect of adding lime to MSWI ashes in metal speciation and distribution.

In the treatment and resourcification of heavy metals from MSWI ashes, three different approaches are currently in use. Heavy metals are separated, solidified, or stabilized within the ash matrix. The separation technology comprises physicochemical processes, such as leaching with acids/solvents, ion exchange, crystallization, distillation, and electrochemical processes. Several studies conducted on the separation and recovery of heavy metals from incinerator ash have indicated the application potential of these processes. Vehlow et al. (3) developed a 3R (recover, remove, and return) process for removing the heavy metals from MSWI fly ash on a pilot scale. The 3R process was used to leach the fly ash using acidic flue-gas washing water. After the treatment, the incinerator ashes were reported to satisfy environmental regulations. Katsuura et al. (8) used acid extraction sulfide stabilization (AES) for the treatment of MSWI ashes in a full-scale operation. The soluble heavy metals were extracted easily using acidic agents, and sodium sulfide was added to stabilize the remaining metals. The leaching of the heavy metals from residues was thus prevented during the AES treatment process. Other researchers treated leached MSWI ashes with other solvents and applied flue gas as a means of acid extraction for heavy metal separation (9). In this process, a technique similar to the AES process was applied; only the extraction agent was replaced by flue gas. However, very little information has been documented about this process and its application. In recognition of this, the main objectives of this research were 1) to evaluate the effect of the L/S ratio on heavy metal separation and recovery, 2) to determine the effect of pH on the heavy metal extraction characteristics, and 3) to develop a flue gas neutralizing process for the recovery of heavy metals in incinerator residues.

EXPERIMENTAL

Materials and Analysis Methods

Incinerator ash samples were taken from a MSWI plant located in northern Taiwan to determine the extraction characteristics and recovery amounts of heavy metals. This plant, which began operation in 1995, is a typical mass-burning system capable of processing 1500 tons of MSW per day through four parallel furnaces and flue gas treatment devices (Fig. 1). The air pollution control devices consist of an electrostatic precipitator (ESP) for particulate removal and a wet scrubber for SO_2 and acid gas control. All bottom and ESP ash samples were collected from the ash pit and the ESP under regular incinerator operation. The ash samples from all sampling points were analyzed for their total heavy metal and toxicity concentrations using standard analytical techniques, which included TCLP. The heavy metal concentrations in the ash samples and leachate were mea-

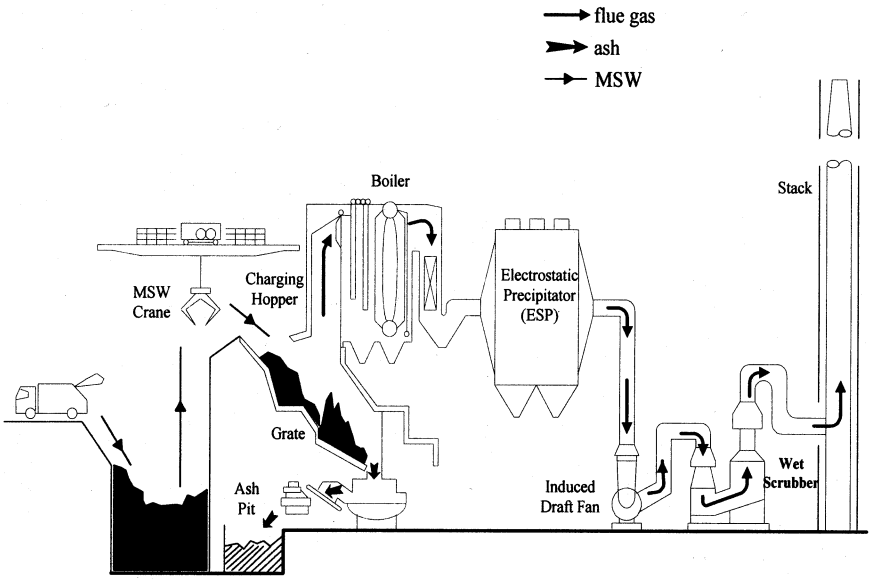

Figure 1. Schematic diagram of MSWI plant.

sured using flame atomic absorption spectroscopy. The methods used for characterization of the samples, based on R.O.C. Environmental Protection Agency (EPA) methods, were as follows:

TCLP Target Metals (Pb, Cd, Cr, Cu, and Zn)	Method 4210.0
Digested Method	Method R 302.20T
Heavy Metal Contents (Pb, Cd, Cr, Cu, and Zn)	Method 4614, 4616, 4618, 4621, 4623

Experimental Apparatus

The experimental apparatus, as shown in Fig. 2, consisted of a stirring reactor and a flue gas absorbing train. The flue gas neutralizing reactor is made of a polypropylene tank, 50 cm long, 30 cm wide, and 25 cm tall, which is a pH controlled and closed system. In this work, CO_2 was used for the simulated flue gas from the MSW incinerator and was injected with nozzles into the stirring tank and dissolved in water, which reduced the extraction pH level. The pH was monitored using a sensor mounted inside the end of the reactor. The pH was adjusted with

1N HCl. A flue gas absorbing train was located downstream from the reactor. The absorbing train was composed of 2 impingers (1 N NaOH) connected in series to prevent flue gas emissions during the experimental procedure.

Experimental Procedures

The effects of the liquid-solid (L/S) ratio and pH level on heavy metal separation and recovery during the carbon dioxide extraction process were investigated by performing a series of experiments at different L/S ratios with varied pH values. First, 0.5–1.0 kg of the ESP ashes were completely mixed with water at different L/S ratios, and simulated flue gas (CO_2) was used for treatment. Afterwards, the excess carbon dioxide was driven out and absorbed by impingers. For each batch, the extraction time was 2 hours. After the extraction of each batch, the residues and the extraction liquid in the stirring tank were analyzed separately. Finally, the normalized metal separation and recovery was calculated as the mass of metal in the extraction liquid divided by the total mass of metal measured in the ESP ash residues and the extraction liquid.

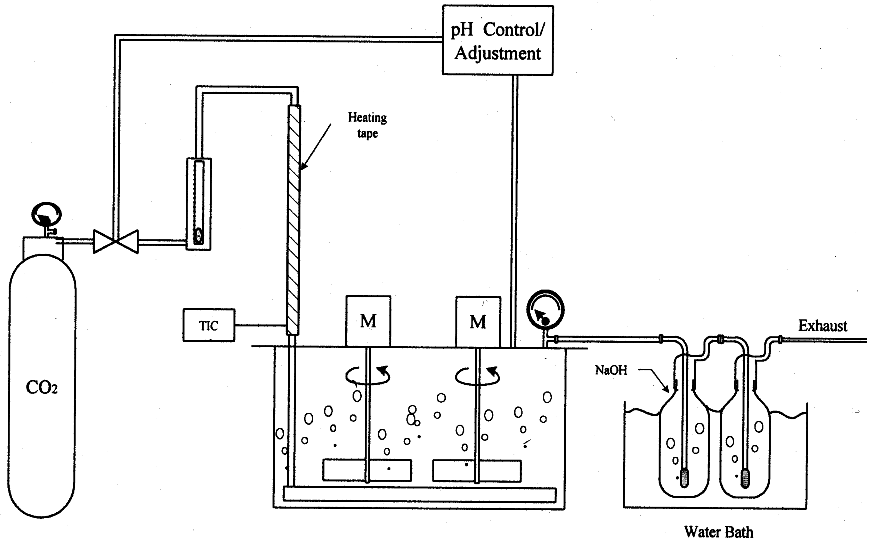

Figure 2. Schematic diagram of flue gas neutralization facilities. TIC = temperature indicated control.

Table 1. Characterization of MSWI Ashes

	ESP Ash				Bottom Ash			
Items	Sample No.	Max.	Min.	Ave. ± S.D.	Sample No.	Max.	Min.	Ave. ± S.D.
pH (in water)	10	7.61	6.18	6.91 ± 0.34	10	12.31	12.27	12.29 ± 0.01
Moisture (%)	10	1.49	0.91	1.08 ± 0.17	10	23.66	19.92	22.21 ± 1.39
Ignition loss (%)	10	4.75	4.07	4.31 ± 0.27	10	7.92	5.10	6.54 ± 1.05
Cl^- (mg/kg)	10	150 940	142 940	147 550 ± 902	10	2699	1799	2369 ± 355
SO_4^{2-} (mg/kg)	10	45 680	34 430	38 920 ± 454	10	N.D.	N.D.	N.D.
Metals total concentration (mg/kg)								
Pb	10	7251	6397	6806 ± 304.8	10	4950	1225	3348 ± 1256
Cd	10	2400	322	1050 ± 107.2	10	12	7	9.40 ± 1.78
Cr	10	211	185	198 ± 30.1	10	56	15	33.0 ± 13.8
Cu	10	2165	1991	2064 ± 164.3	10	8260	1440	3494 ± 2248
Zn	10	7840	7320	7580 ± 182	10	5600	2700	3590 ± 930.1
Metals toxicity characteristic leaching procedure concentration (mg/L)								
Pb	10	9.26	8.05	8.53 ± 0.37	10	2.06	0.57	1.21 ± 0.50
Cd	10	36.2	33.9	35.1 ± 0.77	10	0.07	0.05	0.06 ± 0.01
Cr	10	0.49	N.D.	0.12 ± 0.16	10	0.05	N.D.	0.06 ± 0.01
Cu	10	0.22	0.11	0.17 ± 0.03	10	3.52	2.34	2.74 ± 0.34
Zn	10	25.2	11.4	15.8 ± 3.93	10	2.05	0.27	1.12 ± 0.56

N.D. Not Detected.

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RESULTS AND DISCUSSION

Characterization of MSWI Ashes

In this work, the physical and chemical properties of the MSWI ashes were characterized: 1) pH in water was 6.91 ± 0.34 for ESP ash and 12.29 ± 0.01 for bottom ash; 2) moisture content was 1.08 ± 0.17% for ESP ash and 22.21 ± 1.39% for bottom ash; 3) ignition loss was 4.31 ± 0.27% for ESP ash and 6.54 ± 1.05% for bottom ash; 4) Cl^- content was 147 550 ± 902 mg/kg for ESP ash and 2 369 ± 355 mg/kg for bottom ash; and 5) SO_4^{2-} content was 38 920 ± 454 mg/kg for ESP ash. The average concentrations of Pb, Cd, Cr, Cu, and Zn in the MSWI ashes are shown in Table 1. Typically, the bottom ashes were found to contain high concentrations of Cu (up to 8 260 mg/kg and an average of 3494 mg/kg), Pb (up to 4,950 mg/kg and an average of 3 348 mg/kg), and Zn (up to 5,600 mg/kg and an average of 3 590 mg/kg). The Cd and Cr average concentrations were low to moderate in the bottom ash, ranging from 9.40 ± 1.78 mg/kg for Cd to 33.0 ± 13.8 mg/kg for Cr. In ESP ashes, high concentrations of Zn (average of 7 580 ± 182 mg/kg), Pb (average of 6 806 ± 304.8 mg/kg), and Cd (average of 1 050 ± 107.2 mg/kg). The results show that Zn, Pb, and Cd might absorb onto the surfaces of the fly ash particles and be captured in the ESP. In addition, in Taiwan, the MSWI ashes contain higher concentrations of heavy metals than they do in other developed countries. These relatively high metal concentrations are the result of mixing and incinerating industrial wastes and the lack of integrated separation and resource recycling systems prior to the implementation of MSWI.

The results of TCLP analysis for the incinerator ashes are listed in Table 1. The average TCLP leachate concentrations of Pb, Cd, Cr, Cu, and Zn in the bottom ash were nearly in compliance with R.O.C. EPA regulatory thresholds 2001. In the case of ESP ashes, the TCLP leachate Pb and Cd concentrations often exceeded the regulation requirements, meanwhile other metals mostly fell under R.O.C. EPA standard limits.

Effects of the L/S Ratio on Metals Separation

Laboratory experiments have shown that the extractability of heavy metals depends on the L/S ratio. The extraction levels of nearly all selected heavy metals, especially for Cd, Cr, and Zn, showed a tendency to increase significantly as the L/S ratio increased. Figure 3 shows the L/S ratio effect on Cd separation and recovery efficiency. The separation and recovery efficiency for Cd increased when the L/S ratio ranged from 10:1 to 40:1. A maximum of a 86.4% extraction level occurs at an L/S ratio of 40:1 and pH 3.

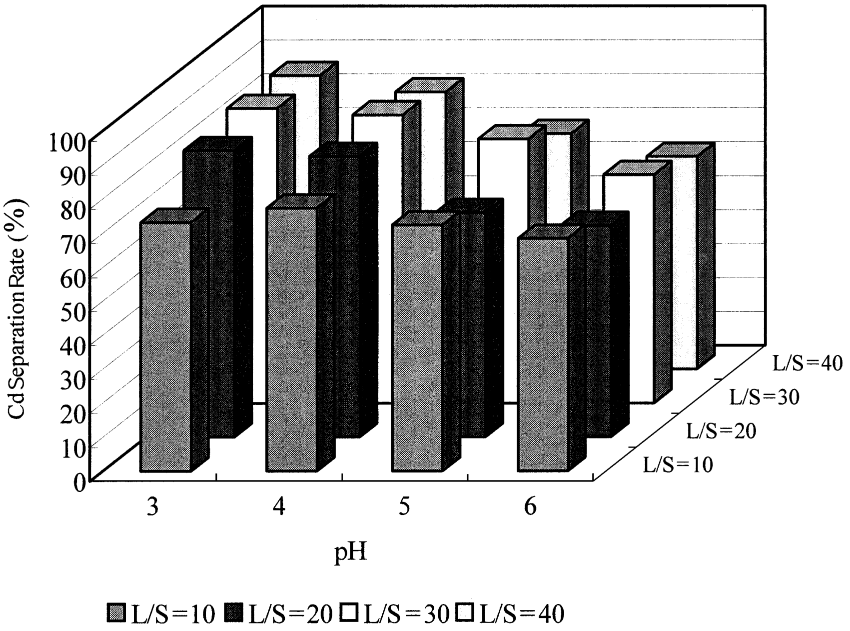

Figure 3. The effect of L/S and pH on Cd separation.

The effects of varying the L/S ratio on the extraction of Cr, Zn, Cu, and Pb were also examined. As Figs. 4 and 5 reveal, an increased L/S ratio of 40:1 was related to increased extraction levels of Cr and Zn due to the effect of water extraction changes. Figure 6 also indicates that the Cu separation rate increased with an increased L/S ratio. In addition, an increased separation rate was related to an increase in the amount of heavy metal recovery from ESP ash and an increased opportunity for ESP ash recycling and reutilization. However, a higher L/S ratio may provide insufficient extractability for a large amount of Pb. As shown in Fig. 7, the maximum extraction amount was around 10% at a L/S ratio of 20:1 and pH 3. As indicated by a previous study (10), it was unclear whether solid-phase solubility or surface adsorption controls Pb concentrations. That is, neither the L/S ratio nor the pH were clearly related to Pb concentrations.

In a previous study, we demonstrated that the L/S ratio and alkaline nature of the semi-dry scrubber (SDS) ash enhanced the efficiency of Pb separation. Meanwhile, other tested heavy metals (e.g., Cd, Cr, Cu, and Zn) and/or compounds still remained in a stable state under operating conditions (11). A major difference was found between the MSWI ashes treated by lime injection and those that were not. That is, the amount of Pb separation is slightly higher due to the higher pH level and alkalinity in the lime-treated SDS ash.

Effects of pH Level on Metal Separation

To compare pH level effects on heavy metal separation changes, experiments were conducted at pH values ranging from 3 to 6. The results, as shown in Figs. 3 and 4, indicate that more Cd and Cr were extracted at lower pH ranges. However, Fig. 5 shows that at higher pH values (pH 6) resulted in significantly higher Zn concentrations in the extraction solutions. The result, due to the release of Zn^{2+} increased with the CO_3^{2-} increased, indicated greater effectiveness at high pH values. Consequently, the maximum 50% extraction amount occurs at pH 6 and an L/S ratio of 40:1. In addition, as Fig. 6 indicates, when the pH values were decreased to 3, the Cu extraction amounts increased significantly. Herein, the maximum extraction levels for Cu is around 30% at pH 3 and an L/S ratio of 40:1. Pb was found to be the most insoluble in ESP ash; as shown in Fig. 7, only 10% of its content was extracted under the experimental conditions in our study. The findings illustrate that the observed, related metals separation generally agrees with variations in L/S ratio and pH values. Furthermore, in this study, the separation and recovery effectiveness of the targeted metals was found in decreasing order as: Cd, Cr, Zn, Cu, and Pb.

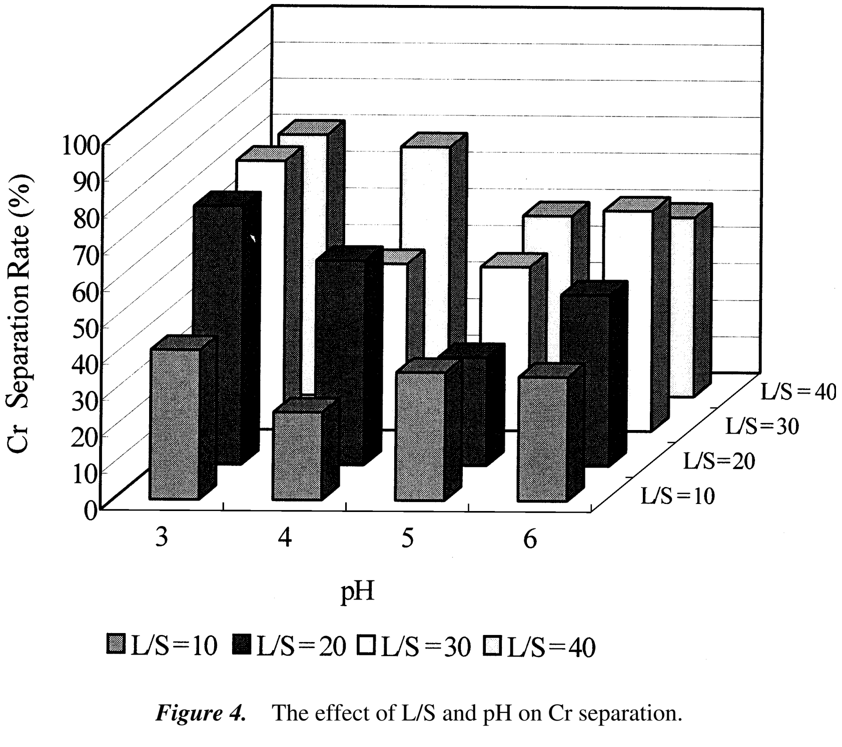

Figure 4. The effect of L/S and pH on Cr separation.

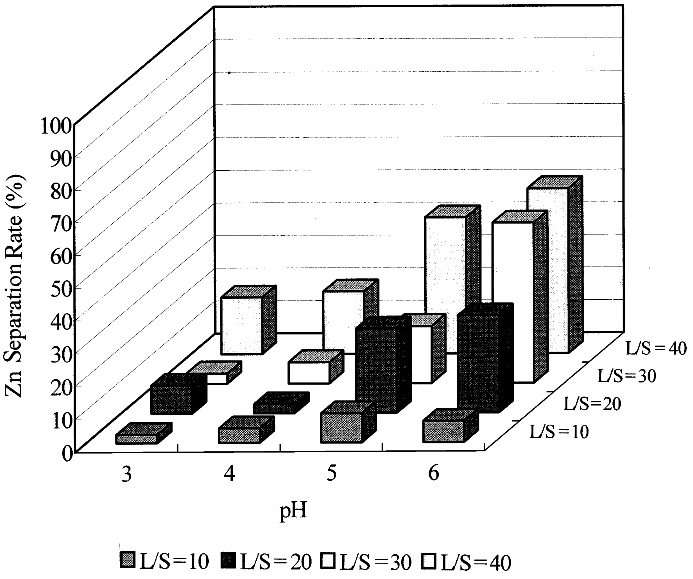

Figure 5. The effect of L/S and pH on Zn separation.

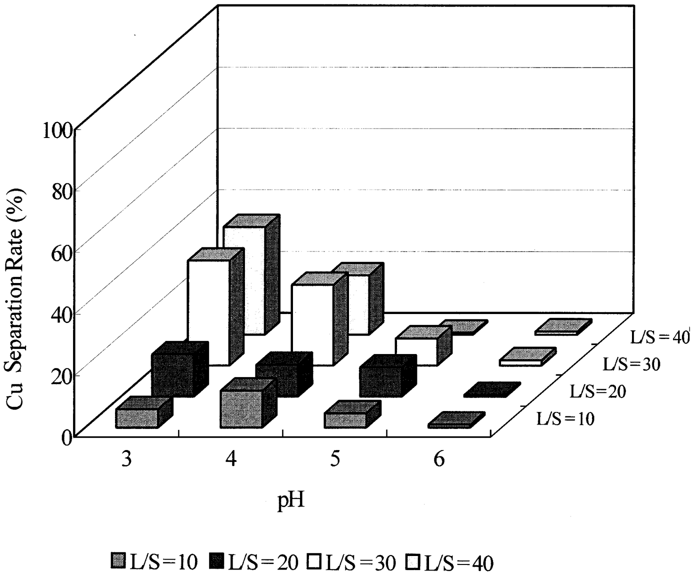

Figure 6. The effect of L/S and pH on Cu separation.

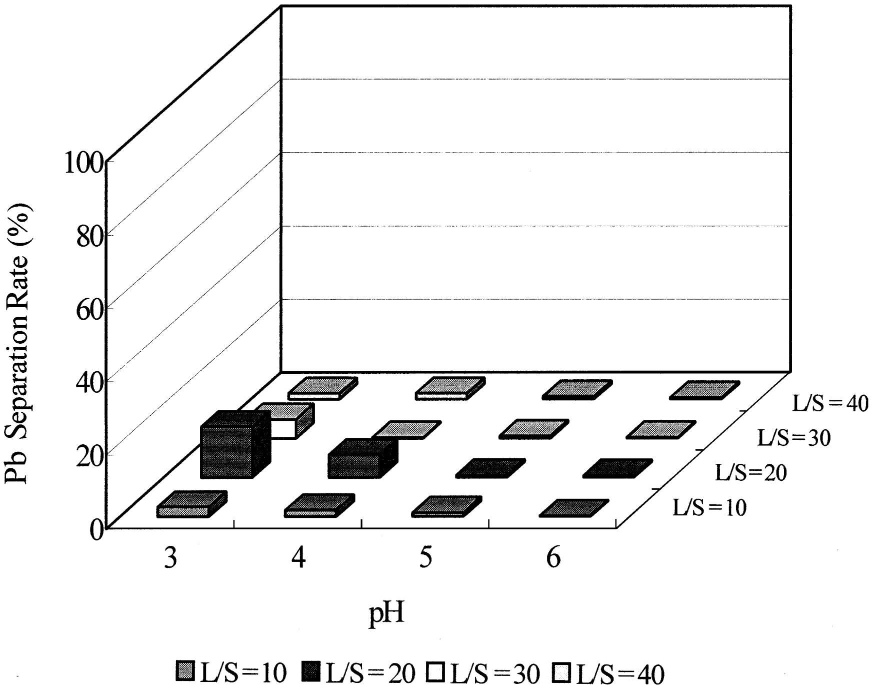

Figure 7. The effect of L/S and pH on Pb separation.

CONCLUSION

This study has demonstrated a combined flue gas neutralization and acid extraction process that will enhance the extractability of heavy metals by injecting CO_2 into the stirring tank and adjusting the L/S ratios and pH values during the separation and recovery of heavy metals in the ESP ash. Some of the significant findings are summarized in the subsequent paragraphs.

The analysis of TCLP leachate concentrations for Pb and Cd in ESP ash denotes a high concentration that exceeded the current R.O.C. EPA regulation thresholds. However, other tested metals still remained in the stable phase and nearly all fulfilled the regulation requirements. Therefore, further treatment of this ash is essential prior to final disposal in landfills.

In this work, the L/S ratio is a significant parameter for the separation and recovery of the tested heavy metals. Increases in L/S ratio resulted in increased separation efficiency for Cd, Cr, and Zn. However, increases in the L/S ratio had no significant effect on the extraction of Pb. According to the relationship between changes in the separation efficiency and L/S ratio, the effectiveness of the tested metal separation was found in decreasing order as Cd, Cr, Zn, Cu, and Pb.

In the acidic pH range, the heavy metals Cd, Cr, and Cu were separated/extracted more effectively than Zn and Pb from the ESP ashes; 86.4% of the Cd was separated from ESP ashes at pH 3. The separation of Cd, Cr, and Cu increased with decreased pH values.

In this research, separation and recovery of Cd, Cr, and Zn in the ESP ash was performed using carbon dioxide as a pre-extraction agent. This process provided important information about the separation and recovery of the heavy metals in the toxic ESP ash and about the reduction of greenhouse gas (CO_2) emissions from MSW incinerators.

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REFERENCES

1. Sawell, S.E.; Bridle, T.R.; Constable, T.W. Heavy Metal Leachability from Solid Waste Incinerator Ashes. Waste Man. and Res. **1988,** *6* (3), 227– 238.
2. Cernuschi, S.; Giugliano, M.; Paoli, deI. Leaching of Residues from MSW Incineration. Waste Man. and Res. **1990,** *8* (4), 419–427.
3. Vehlow, J.; Braun, H.; Horch, K.; Merz, A.; Schneider, J.; Stieglitz, L.; Vogg, H. Semi-Technical Demonstration of the 3R Process. Waste Man. and Res. **1990,** *8* (4), 461–472.
4. Buchholz, B.A.; Landsberger, S. Trace Metal Analysis of Size-Fractioned Municipal Solid Waste Incinerator Fly Ash and Its Leachates. J. Environ. Sci. Health **1993,** *A28* (2), 423–441.
5. Gong, Y.; Kirk, D.W. Behaviour of Municipal Solid Waste Incinerator Fly-ash I: General Leaching Study. J. of Haz. Mat. **1994,** *36* (2), 249–264.
6. Buchholz, B.A.; Landsberger, S. Leaching Dynamics Studies of Municipal Solid Waste Incinerator Ash. J. of the Air and Waste Man. Assoc. **1995,** *45* (8), 579–590.
7. Alba, N.; Gasso, T.; Lacorte, T.; Baldasano, J.M. Characterization of Municipal Solid Waste Incineration Residues from Facilities with Different Air Pollution Control Systems 1997. J. of the Air and Waste Man. Assoc. **1997,** *47* (11), 1170–1179.

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8. Katsuura, H.; Inoue, T.; Hiraoka, M.; Sakai, S. Full-Scale Plant Study on Fly Ash Treatment by the Acid Extraction Process. Waste Man. **1996,** *16* (5–6), 491– 499.
9. Ecke, H.; Sakanakura, H.; Matsuto, T.; Tanaka, N.; Lagerkvist, A. State-of-the-Art Treatment Processes for Municipal Solid Waste Incineration Residues in Japan. Waste Man. and Res. **2000,** *18* (1), 41–51.
10. Kirby, C.S.; Rimstidt, J.D. Interaction of Municipal Solid Waste Ash with Water. Environ. Sci. Tech. **1994,** *28,* 443–451.
11. Chiang, K.Y.; Chang, C.N.; Chien, T.Y.; Wang, K.S. *Feasibility of Lead Separation in Semi-Dry Scrubber Ash from MSW Incinerator Using Flue Gas Neutralizing Process*, Proceedings of the Sixth Mainland-Taiwan Environmental Protection Conference, Taiwan, R.O.C., December 7–11, 1999; National Sun Yat-sen University: Taiwan, R.O.C.; 1102–1106. (in Chinese)

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