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Influence of ligands on metals leachability from landfilling bottom ashes

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Abstract

After municipal solid waste is incinerated, its bottom ash used to be disposed by landfill. Although the leachate quality is less polluted, some heavy metals in the bottom ashes are affected by ligands, which raise their release potential. Concerned by the bottom ashes landfilling, this research explored the influence strengths of ligands in leaching heavy metals, by rotary extraction and lysimeter leaching test. The results from extraction proved that with the rising concentration of extraction solutions of HCO_3^-, CO_3^{2-} and NH_3, the released amount of Cu was most likely to exceed the local effluent standard in Taiwan. The lysimeter leaching test achieved the same results as those of extraction and it proved that the results of extractive process could be applied to the landfill site. The results from these experiments confirmed that the extraction could simulate the release of Cu and predict the accumulation of released amounts of Cu in the leachate from landfill of bottom ashes. The statistic regression formulas obtained from this research were feasible, since they could highlight the release trend of Cu concentration, although they were unable to predict the trend precisely. © 1998 Elsevier Science B.V.

Keywords: Incinerator bottom ashes; Heavy metal leachability; Ligands; TCLP; Lysimeter leaching test

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1. Introduction

Incinerated residuals weigh only one fifth of raw refuse. However, heavy metals (after undergoing gasification, oxidation, chlorination, condensation, coagulation, and nuclearation), which come from raw wastes, are condensed into incinerated residues that cause more potential harm to the environment [1,2]. Since the characteristics of incinerated residues are distinctly different from those of raw refuses, researchers have

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taken much interest in studying the composition and recycle techniques of incinerated residues. According to their results, fly ashes proved to be harmful [3,4], while bottom ashes used to be landfilled directly or recycled after some treatment. Although there have been many studies and instances of recycling of bottom ashes, the techniques are yet to mature and need to be elevated. As a result, most countries still treat bottom ashes by landfill. When bottom ashes are in the process of landfilling (though the leachate quality is less polluted), some heavy metals are affected by their ligands and leachate, which consequently increase their hazard potential to the environment [5]. Focusing on the incinerated bottom ashes as well as co-disposal with the raw MSW, we designed a series of experiments in order to explore the influence strengths of ligands on the leaching of heavy metals, and obtain the factors that affect the release potential of heavy metals. We also hope to suggest the optimal conditions for on-site operations.

2. Experimental

This research carried out rotary extraction and lysimeter leaching test in three stages to gradually explore how ligands affect the release of heavy metals from bottom ash landfill. The rotary extraction was operated according to the toxicity characteristic leaching procedure (TCLP), but the extraction solutions were changed to suit the designed formulas.

2.1. Preliminary extraction experiments

Rotary extraction was first applied to evaluate the heavy metals' leaching strengths as influenced by various ligands in the extraction solutions (shown in Table 1). The results showed that the order of influence strengths of ligands on Cu leachability were $NH_3 > HCO_3^- > CO_3^{2-} > SO_4^{2-} > CL^-$. Since the first three ligands had much greater influence than the last two, the first three were applied in the continued experiments.

2.2. Rotary extraction experiments

The following extraction procedures adopted extraction solutions for both single and mixed ligands to explore the relationship between the release of heavy metals and the

Table 1
The designed concentrations of extraction solutions for the preliminary experiments

Extraction solutions	Concentrations of the salts in the solutions (M)		
NaCl	0.1	1.0	2.0
Na_2SO_4	0.1	1.0	2.0
Na_2CO_3	0.1	1.0	2.0
$NaHCO_3$	0.1	1.0	2.0
NH_3	0.025	0.25	0.5

concentrations of ligands in it. Though the extracting method in this stage were the same as that in the previous stage, the formulated concentrations of the extraction solutions were expanded to eight categories. These were 0.004 to 0.5 M for both HCO_3^- and CO_3^{2-}, and 0.002 to 0.25 M for NH_3. Not only the single ligand was prepared in the extraction solutions, but also two or three ligands were prepared in the mixed solutions to extract bottom ash. A total of 66 combinations were executed in this stage of experiments. By means of the statistic multi-linear regression, correlation formulas were obtained to discuss the relationships between the extraction solutions concentrations of NH_3, HCO_3^-, CO_3^{2-}, and the release of heavy metals. A comparison among these coefficients of formulas indicated the influence of the three ligands on leaching potential of heavy metals from ashes.

2.3. Lysimeter leaching experiments

The lysimeter leaching experiments were implemented to verify the results of the rotary extractions. Three ligands were individually formulated at three concentration categories to get nine leachants, and distilled water was treated for the 'blank'. The formulation of leachant and the lysimeters design were shown in Table 2 and Fig. 1, respectively. The lysimeters were designed in semi-aerobic condition, and leachant were added once every 3 days at the volume of 128 ml/time, which was the average annual precipitation of Taipei City in 10 years to be multiplied by the area of the cross section of the lysimeter. The leachates were collected once every 3 days in the initial 21 days, and once every 6 days in the latter stage. The whole period of landfilling was 93 days.

The quantity and concentrations of NH_3, HCO_3^-, CO_3^{2-}, and heavy metals of leachate were surveyed for each sample. The results were compared with the regression formulas of the rotary extraction in order to determine whether the empirical regression formulas could predict the heavy metals release from landfilled bottom ashes.

2.4. Sampling and analyzing

The bottom ash samples in this research were taken from two municipal solid waste incinerators with mechanical grate mass burning type. The amount of ashes for each extraction was 40 g, and for lysimeter leaching experiment, it was 4.5 kg/column.

The extraction solutions and leachant were prepared with analytical grade chemicals (NaCl, Na_2SO_4, Na_2CO_3, $NaHCO_3$, and NH_3), and de-ionized distilled water. The quantities of extraction solutions were twenty times the weight of solid in the bottom ash samples.

Table 2
Designed concentration of leachant for each lysimeter

Ligand in the leachant	HCO_3^-			CO_3^{2-}			NH_3			Distilled Water
Lysimeter number	#1	#2	#3	#4	#5	#6	#7	#8	#9	#10
Ligand concentration (M)	0.004	0.008	0.016	0.004	0.008	0.016	0.004	0.032	0.125	–

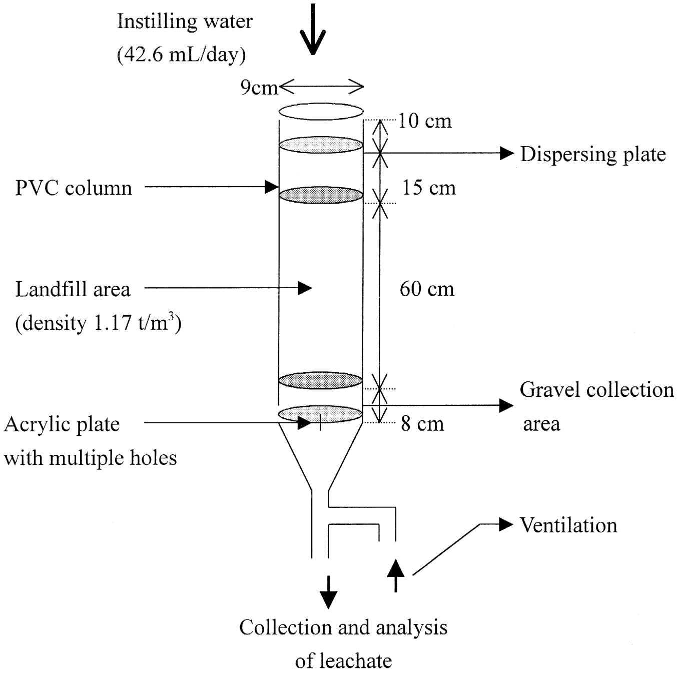

Fig. 1. The lysimeter configuration.

The basic characteristics of bottom ashes that were analyzed include ignition loss, moisture contents and pH value, Cu, Cd, Pb, Zn, for both TCLP and the total content. The qualities of extract and leachate that were analyzed include pH value (electrode method). CL^- (mercuric nitrate titration), SO_4^{2-} (turbidity method), NH_3–N (nesseler tube), alkanility (titration), and the above-mentioned heavy metals (flame atomic absorption). The rotary extractor (Danger, USA) was fixed at 30 rpm for an 18-h extraction.

3. Results and discussions

3.1. Basic characteristics of bottom ashes

The pH of bottom ashes studied in this research was between 11.54 and 12.02, while the percentage of ignition loss was 2.5–3.9%. Among the measured concentration of ligands (by extraction from distilled water), CO_3^{2-} (11,330 mg/kg) and CL^- (4128 to 6680 mg/kg) were the largest. The content of heavy metals (by acidic digestion), Cu (4560 to 4620 mg/kg), Pb (4380 to 4620 mg/kg), and Zn (3410 to 650 mg/kg) were larger. Among the heavy metal release concentrations of TCLP, only Pb exceeded the local regulation (5.0 mg/l).

3.2. Rotational extraction with single ligand

HCO_3^-, CO_3^{2-} and NH_3 were individually formulated to get eight single-ligand extraction solutions for this extraction experiment. The results of metals release were plugged into the optimal regression formula for evaluation.

Within the range of extraction solution concentrations, the release of Cu was enhanced with the rising concentrations of HCO_3^-, CO_3^{2-} and NH_3, and the three ligands exerted different influence strengths. At the same extraction solution concentration, their relative influence strength were $NH_3 > CO_3^{2-} > HCO_3^-$.

The release of Pb decreased as the concentration of extraction solutions of HCO_3^- and CO_3^{2-} rose, yet, there was no remarkable relationship with NH_3. The rising concentration of HCO_3^- lowered the release of Zn, whereas the increasing of NH_3 raised the Zn release. An increase of CO_3^{2-} at a lower concentration would reduce the release of Zn, but pose an opposite effect at higher concentrations.

The results from the extraction were analyzed by regression as shown in Table 3, and Figs. 2–5. A comparison among the effects of ligands indicated that if bottom ashes and raw refuse were landfilled together and the leachant concentrations of the three ligands are increased, the release of Cu would most likely exceed the effluent standard of 3.0 mg/l in Taiwan.

3.3. Rotational extraction with mixed ligands

The results from extracting bottom ashes with mixed ligands as well as with single ligands were plugged into the multiple linear regression formula to analyze the relationship between the extract concentrations and the release of heavy metals.

3.4. Multiple linear regression

Suppose all individual ligand concentrations maintained a linear relation with the release of heavy metals. A multiple linear regression formula was used for the analysis on the three ligands, the release concentrations of heavy metals and their release amounts. The results showed that, t-test and F-test were passed for the initial hypothesis, while the relative coefficients were only 0.65, 0.17, and 0.78 for Cu, Pb, and Zn, respectively.

A comparison among the coefficients of factors in each regression formula indicated that the release amounts of Cu and Zn could be sharply raised by NH_3 extraction solution, whereas Pb could be lowered by both HCO_3^- and CO_3^{2-}. When bottom ashes were extracted by mixed ligands, only the Cu release had a simple multi-linear relation with the three ligands, and the relation was highly reliable. On the other hand, the release of Pb and Zn could not concurrently maintain a linear relation with the three ligands.

3.5. Nonlinear multiple regression

Suppose all individual ligand concentrations had a nonlinear relation with the release of heavy metals. The regression formula from the previous single ligand extraction

Table 3
The regression formulas of heavy metals release in single and mixed ligand extraction

Ligands	Release of Cu		Release of Pb		Release of Zn	
	Regressions formulas	R^2	Regression formulas	R^2	Regression formulas	R^2
	$Y = 0.50 f_1(X) + 1.05 f_2(X) + 0.99 f_3(X) - 45.86$	0.98	$Y = 1.00 f_1(X) + 0.28 f_2(X) + 0.23 f_3(X) - 122.4$	0.26	$Y = 1.68 f_1(X) + 1.18 f_2(X) + 0.89 f_3(X) - 60.56$	0.97
HCO_3^-	$f_1(X) = 1.28\ln(X) + 45.4$	0.97	$f_1(X) = 37.31 X^{-0.12}$	0.53	$f_1(X) = 0.613\ln(X) + 11.12$	0.43
CO_3^{2-}	$f_2(X) = 2.53 X^{0.38}$	0.96	$f_2(X) = 31636 X^{-0.70}$	0.60	$f_2(X) = 6E - 0.8 X^2 - 0.0018 X + 24.4$	0.51
NH_3	$f_3(X) = 27.69 e^{0.0007X}$	0.98	$f_3(X) = -0.0002 X^2 + 0.786 X + 264$	0.65	$f_3(X) = 32.08 e^{0.0006 X}$	0.97

Y, Release of heavy metals (mg/kg).
R^2, Relative coefficient.
Confidence interval: 95%
X, Concentration of ligands in the extraction solutions (mg/l).
$f_1(X)$ $f_2(X)$ $f_3(X)$, Metals release achieved by HCO_3^-, CO_3^{2-}, NH_3.

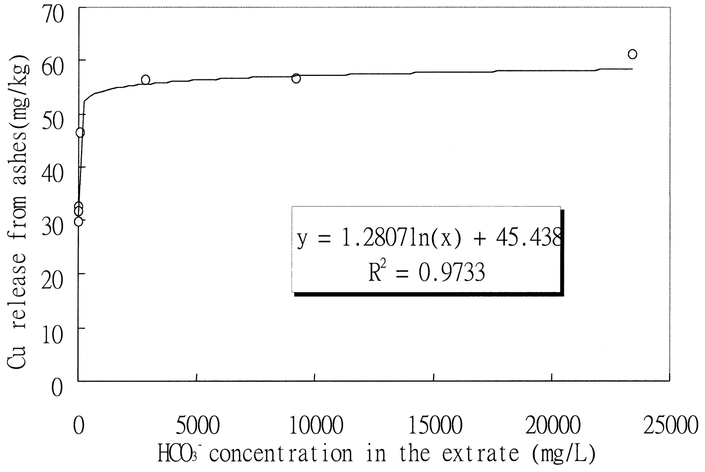

Fig. 2. The influence of HCO_3^- on Cu released from ashes.

(shown in Table 3) were plugged into the nonlinear relation to get the release amounts of heavy metals affected by different ligands. The results together with the total of actual release amount were analyzed by the multiple linear formula. Among the regression formulas and statistic parameters from the statistic analysis, also shown in Table 3, the relative coefficients (R^2) of the Cu and Zn release formulas were up to 0.98 and 0.97, respectively.

3.6. Lysimeter leaching test

The concentration variation diagram indicated that for more than 90 days the concentrations in Cu release from all lysimeters had tremendously exceeded the effluent

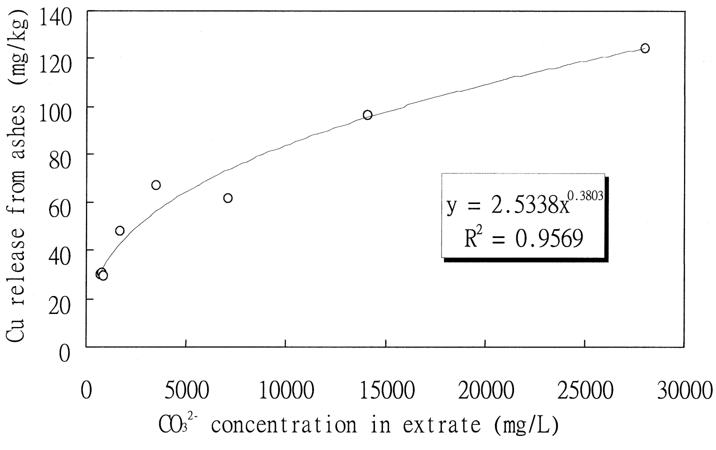

Fig. 3. The influence of CO_3^{2-} on Cu released from ashes.

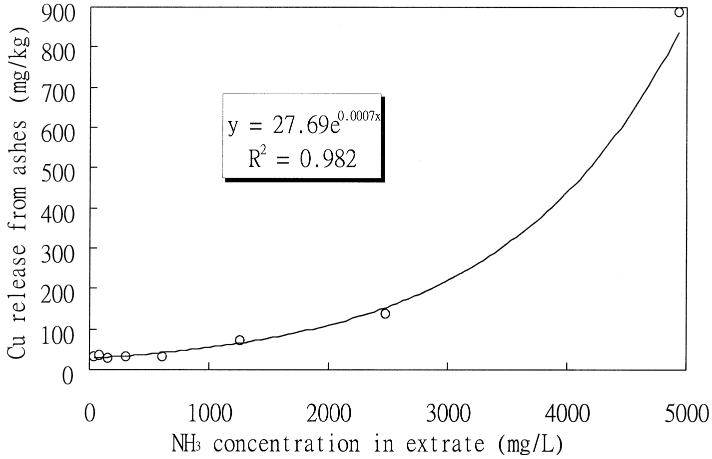

Fig. 4. The influence of NH_3 on Cu released from ashes.

standard (3 mg/l). Judging from the cumulative release and the concentrations of leaching liquids, including the leachant and the leachate, we discovered that the cumulative Cu release increased as the concentrations of HCO_{3-}, CO_3^{2-} and NH_3 rose.

For more than 90 days, the concentrations of Pb release from all lysimeters had enormously exceeded the effluent standard (1 mg/l). It was likely that the amount of Pb in bottom ashes was large (which could be discerned from the TCLP data) while the variation of concentrations was considerably great. An analysis revealed that the cumulative Pb release increased with the rising leachant concentration of HCO_3^-. However, it was hard to tell whether the Pb release had any relation with CO_3^{2-} or NH_3.

The concentrations in Zn release form each lysimeter did not exceed the effluent standard (5.0 mg/l). An analysis between the cumulative release amounts and the

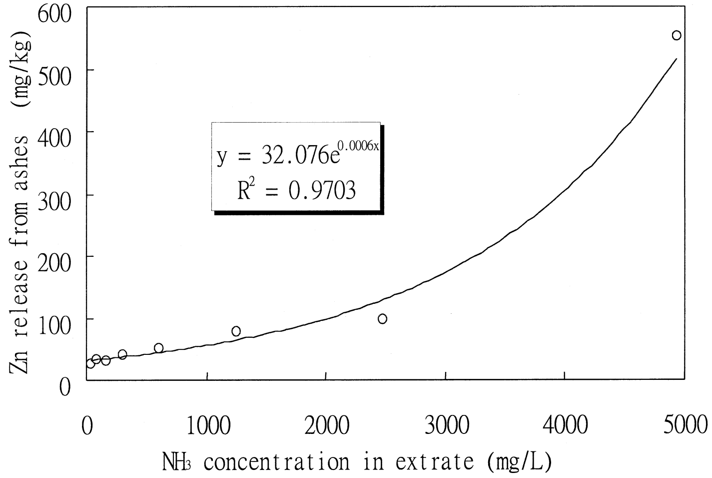

Fig. 5. The influence of NH_3 on Zn released from ashes.

Table 4
The relationship between the heavy metals cumulative release and the concentrations of extraction solutions

Release of heavy metals	Ligands in the extraction solution	Relative concentration of extraction solution	Relative concentration of extract	Relative leachate cumulative release	Relationship between leachate release and concentration of extraction solution	Relationship between leachate release and concentration of extraction
Cu	HCO_3^-	#3 > #2 > #1	#2 > #1 > #3	#3 > #2 > #1	Positive	No
	CO_3^{2-}	#6 > #5 > #4	#5 > #6 > #4	#5 > #6 > #4	No	Positive
	NH_3	#9 > #8 > #7	#9 > #8 > #7	#9 > #7 > #8	No	No
Pb	HCO_3^-	#3 > #2 > #1	#2 > #1 > #3	#3 > #2 > #1	Positive	No
	CO_3^{2-}	#6 > #5 > #4	#5 > #6 > #4	#5 > #4 > #6	No	No
	NH_3	#9 > #8 > #7	#9 > #8 > #7	#7 > #9 > #8	No	No
Zn	HCO_3^-	#3 > #2 > #1	#2 > #1 > #3	#1 > #2 > #3	Negative	No
	CO_3^{2-}	#6 > #5 > #4	#5 > #6 > #4	#4 > #5 > #6	Negative	No
	NH_3	#9 > #8 > #7	#9 > #8 > #7	#9 > #8 > #7	Positive	Positive

concentrations of leachant or leachate showed that the Zn release amounts increased as NH_3 rose, but decreased as HCO_3^- and CO_3^{2-} dropped. These results were shown in Table 4.

3.7. Relation between lysimeter leaching test and extraction

In the extractive process, the amounts of release from long-term leaching of bottom ashes were estimated by batch test, while the lysimeter leaching test emphasized the consecutive concentrations in daily release. Consequently, the resultant amount of release from extraction was much larger than the amount of daily release from the leaching test. On the other hand, because of accumulation, the release concentration form the leaching test was, certainly, larger than the concentration of extrate that came from the extractive process.

3.8. Comparison among released amounts

Since the amount of Cu released from extraction would be the equal to the total leached amount, it could be compared with the cumulative release which was obtained from the leaching test (when the volume of leachate reached 20 times the solid matters in the lysimeter, i.e. in the leaching period of 1720 days). The cumulative Cu release from each lysimeter was analyzed by logarithmic regression to obtain a regression formula, into which the number of days was plugged to derive the coefficients of daily leaching from each lysimeter. The coefficients were then compared with those achieved from extraction (shown in Table 5).

Because the relative coefficient (R^2) in each regression formula was very large (> 0.95), its reliability was relatively high. The comparison also revealed that the relative difference (R_i) between the extractive process and the leaching test was rather

Table 5
The comparison between lysimeter and extraction of Cu release

Ligands	Lysimeter leaching test				Results of rotary extraction		Relative difference (R_i)(%)
	Ligand concentration in leachant (M)	Regression formula of cumulative Cu release	R^2	Y_1 (mg/kg)	Ligand in extraction solution (M)	Cu release Y_2 (mg/kg)	
HCO_3^-	0.004	$y = 3.35\ln(X) - 5.77$	0.91	19.20	0.004	32.53	51.5
	0.008	$y = 4.31\ln(X) - 6.50$	0.97	25.64	0.008	31.80	18.3
	0.016	$y = 4.63\ln(X) - 7.28$	0.96	27.20	0.016	29.77	9.0
CO_3^{2-}	0.004	$y = 4.37\ln(X) - 6.81$	0.96	25.71	0.004	30.16	15.9
	0.008	$y = 5.20\ln(X) - 7.65$	0.97	31.12	0.008	30.53	1.9
	0.016	$y = 4.95\ln(X) - 7.31$	0.95	26.89	0.016	29.46	9.2
NH_3	0.004	$y = 4.81\ln(X) - 6.85$	0.97	28.99	0.002	31.33	7.8
	0.032	$y = 4.00\ln(X) - 5.71$	0.97	24.08	0.004	37.86	44.5
	0.125	$y = 5.04\ln(X) - 8.17$	0.95	29.37	0.008	28.26	3.9
Distilled water	–	$y = 4.28\ln(X) - 6.2$	0.97	25.72	–	25.90	0.7

y, Cumulative release of Cu (mg/kg).
X, Time (day).
Y_1, Estimated y value at 1720 days.
$R_i = |y - Y_2|/(Y_1 + Y_2)/2$.

low, which proved that the extractive process could simulate the release of Cu in a landfill condition and was rather reliable to a certain degree.

3.9. Comparison among released concentrations

For the comparison of Cu release concentrations, the leachate concentrations of HCO_3^-, CO_3^{2-} and NH_3 were plugged into the nonlinear multiple regression formula to derive the corresponding Cu release concentrations. However, owing to the large solid–liquid-ratio, the resultant concentrations tended to be lower and needed modifying.

As for the modification, the resultant Cu release from the regression formula were multiplied by the solid–liquid-ratio modifying coefficient K_{SL}, the detention time K_t (according to the experiment, the hydraulic detention time of lysimeter was 9 days), and the empirical modification coefficient k.

The modifying formula is detailed as follows:

$$Y = Y_1 \times K_{SL} \times K_1 \times k \tag{1}$$

where Y is the modified Cu release concentration (mg/l); Y_1 is the Cu release concentration obtained from the statistic regression formula (mg/l); K_{SL} is the solid–liquid-ratio modifying coefficient (volume of extraction solution/volume of leachant per time = 5.086); K_t is the detention time modifying coefficient = hydraulic detention time of lysimeter/extraction time = $9 \times 24/20 = 10.8$; k is the empirical modifying coefficient = 0.3.

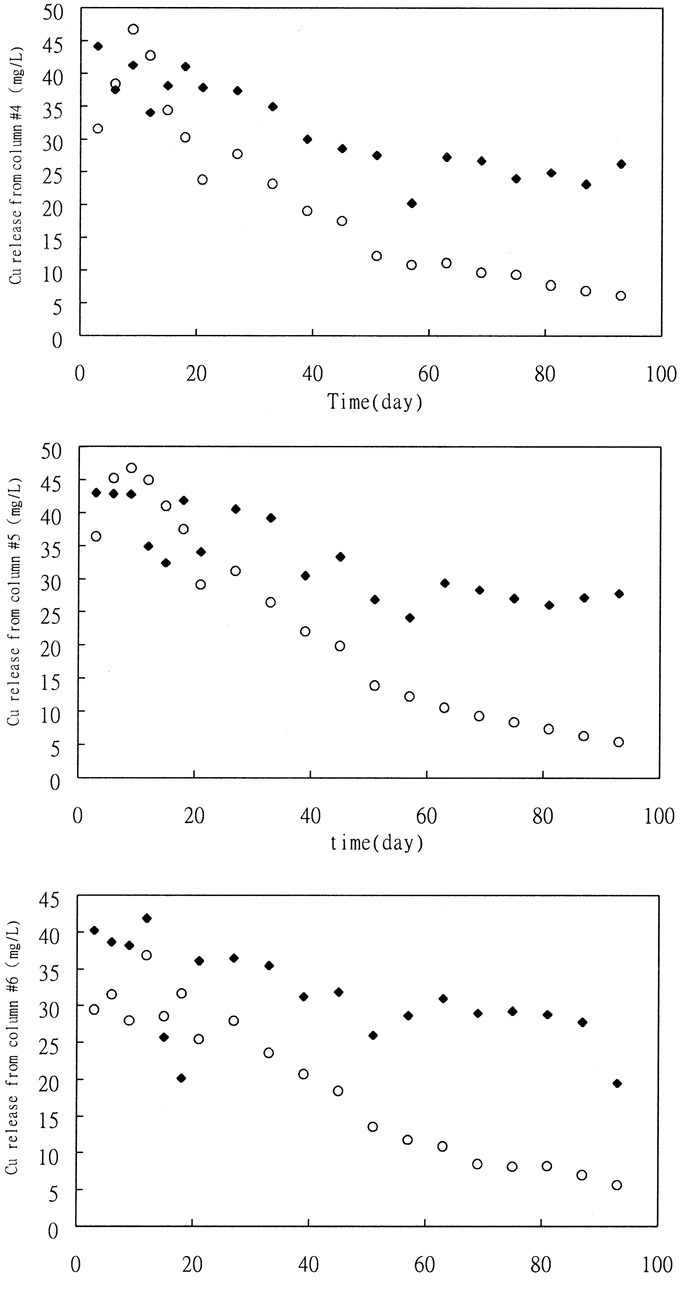

Fig. 6. The estimated and measured concentration of Cu release from lysimeter leaching test (○, measured; ◆, estimated).

The above coefficients are plugged into the formula to get the following formulas:

$$Y = 16.469 \times Y_1 \tag{2}$$

The applied statistic regression formula is:

$$Y_1 = 0.030 f_1(x) + 0.062 f_2(x) + 0.059 f_3(x) - 2.72 \tag{3}$$

in which $f_1(x)$, $f_2(x)$ and $f_3(x)$ represented the release amounts of metals affected by HCO_3^-, CO_3^{2-} and NH_3, respectively.

Eqs. (2) and (3) were employed to achieve the modified concentrations in Cu release from each lysimeter, which were then compared with the measured data as shown in Fig. 6. According to the figure, the estimated values by the formula in Cu release during the period of landfilling almost corresponded to the measured value in the initial stage, but were larger than that in the latter stage.

Nevertheless, the potential trend of Cu release concentrations obtained from this regression formula met the actual conditions. In other words, though the statistic regression formula achieved through extraction could not predict the concentration in Cu release precisely, it was still very feasible since it could estimate precisely the variation of concentrations.

4. Conclusions

From this series of research, we achieved the following results.

Ligands had the most direct influence on the behavior of Cu. The ligands that affected the release of Cu, Pb and Zn included NH_3, HCO_3^- and CO_3^{2-}. Among them, NH_3 had the strongest influence. The rising concentration of extraction solution of NH_3 raised the release amounts of Cu and Zn, while the rising concentration of CO_3^{2-} or HCO_3^- lowered the release amounts of Pb and Zn, but raised that of Cu.

The results from extraction were analyzed by multiple linear regression, the most remarkable linear relation was found in the Cu release with the extract concentrations of ligands. The release amounts of Cu and Zn could be sharply raised by NH_3 in the extraction solution, while the release of Pb could be lowered by the concentration of extraction solution of HCO_3^- and CO_3^-.

From the lysimeter leaching test, the release of Cu was raised with the rising leaching concentrations of HCO_3^-, CO_3^{2-} and NH_3, while Zn release was raised with the rising of NH_3, but lowered with the rising of HCO_3^- and CO_3^{2-}, these results were the same as those from extraction.

The extractive process could appropriately simulate the release of Cu from the landfill of bottom ashes, and could predict precisely the cumulative Cu release till the stable stage of leachate. In addition, the statistic regression formula achieved from extraction was very feasible because it could highlight the potential trends of concentrations in Cu release, though unable to predict it precisely.

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