# Sequential extraction for evaluating the leaching behavior of selected elements in municipal solid waste incineration fly ash

Su-Jeng Huang [a], Cheng-Yuan Chang [a], Do Trong Mui [a], Fang-Chih Chang [b], Ming-Yu Lee [c], Chu-Fang Wang [a,*]

[a] *Department of Biomedical Engineering and Environmental Science, National Tsing Hua University, Hsinchu 30013, Taiwan, ROC*
[b] *Graduate Institute of Environmental Engineering, National Taiwan University, 71 Chou-Shan Road, Taipei 106, Taiwan, ROC*
[c] *Department of Civil Engineering, National Central University, No. 300, Jhongda Road, Jhongli City, Taoyuan County 32001, Taiwan, ROC*

## Abstract

A sequential extraction method has been applied for the determination of binding forms of trace elements in the municipal solid waste incineration (MSWI) fly ash and evaluating their leaching behavior in view of their potential environmental impact. The elemental determinations in the different leachates are performed by ICP-AES and ICP-MS, respectively. The morphology and mineralogical phases after extraction step were performed by scanning electron microscopy (SEM). Total of 20 elements in the samples are investigated. A reference material of city waste incineration fly ash (BCR No. 176) is also tested to examine the applicability as well as accuracy of the proposed method. The sum of most elements present in the individual fractions shows a good agreement with the total elemental concentrations. The extraction efficiencies are generally higher than 80% except for that of Cr and V. The extractable data of most elements give information about the binding forms of various elements in both incineration fly ashes. It was found that the elements such as Ca, K, Na, Pb, Zn, Cd, Cu and Sr have exhibited a remarkable mobility in fly ash. More than half of them would be dissolved or exchanged under a mild leaching condition. The toxic elements such as Pb, Cd, Zn and Cu have a great potential to be released into the environment under normal conditions.
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*Keywords:* Incineration fly ash; Sequential extraction; ICP-AES; ICP-MS

## 1. Introduction

Incineration has been considered an effective management strategy for treating combustible municipal solid waste (MSW) that cannot be recycled in Taiwan recently. The total MSW generated in Taiwan in 2005 was estimated to be about 5.84 million tonnes. In other words, each person produced about 0.71 kg MSW per day in average. Out of the total MSW produced, 57.2% was processed by incineration, 20.2% by landfill and 16.5% by resource recycling [1]. With incineration, the volume of the waste can be reduced and the exothermic energy be recovered after the oxidation of organic materials [2]. However, less volatile inorganic elements in the waste may be concentrated in the bottom ash or captured as fly ash in air pollution con-

trol devices. Availability of these elements to the environment depends greatly on the characteristics of the particle surface, the type and strength of the bond and the properties of the solution in contact with the solid sample [3,4]. In other words, the transformation of the trace element species on fly ash as well as bottom ash particles includes a variety of competing reactions, such as complexation with both organic and inorganic ligands, changes in oxidation state, precipitation, dissolution, ion exchange and metal-particulate association [3–8]. It is known that stable forms contained in the waste residual are unlikely to be released even under weathering conditions. On the other hand, species water soluble and exchangeable under slightly acidic pH are quite mobile. From the viewpoint of the environmental risk, it is thus important to quantify the availability of various elements for further disposal or treatment of these ashes.

The determination of the bulk content of trace elements in fly ash may give information concerning possible enrichment of these fly ash samples with heavy metals, but generally, and for

* Corresponding author. Tel.: +886 3 5715131x34222; fax: +886 3 5727298.
*E-mail address:* cfwang@mx.nthu.edu.tw (C.-F. Wang).

Table 1
Detailed information of the six-step sequential extraction method

| Step | Fraction | Temperature (°C) | Extraction solution | Time (h) |
|---|---|---|---|---|
| 1 | Water soluble ions | 25 | 18.2 MΩ bi-distilled water (pH ∼ 6.2) | 3 |
| 2 | Exchangeable cations | 25 | 0.1 M MgCl$_2$ (pH ∼ 5.8) | 3 |
| 3 | Carbonate | 25 | 0.1N NaOAc/HOAc (pH ∼ 4.9) | 3 |
| 4 | Reducible phase | 60 | 0.1N NH$_2$OH·HCl (pH ∼ 2.2) | 3 |
| 5 | Sulfide | 85 | 2% HNO$_3$/H$_2$O$_2$ (3:7, v/v) | 3 |
| 6 | Residue | 190 | HNO$_3$/H$_2$O$_2$/HF (3:5:2, v/v) | 5 |

most elements, there are no sufficient criteria for estimating their health and ecological effects [9]. In other words, the behavior of various elements in the environment (e.g., bio-availability, toxicity and distribution) cannot be reliably predicted on the basis of their total concentration.

Conventional method for the identification and evaluation of the availability of heavy metals in ash samples is the leaching of samples by means of chemical extractants. Both single extraction and sequential extraction have been used [10–16]. It is difficult to provide detailed information about the specific chemical species in the ash samples. However, determination of broader defined forms, e.g. so-called 'mobile' or 'carbonated bound' forms, can still be achieved through an operationally defined procedures [17–21].

The aim of the research is the use of a sequential extraction method to determine the speciation of trace elements in MSWI ash to evaluate their leaching potential. A total of 20 elements (Al, Ca, Fe, K, Mg, Na, S, Zn, As, Ba, etc.) in the MSWI ash samples were investigated [22]. A six-step sequential extraction approach was utilized to characterize speciation of various elements in MSW incineration ash separated from flue gas by a bag-house filter, collected from an incinerator unit in Taipei. The partitioning of various elements among the water soluble, exchangeable, carbonate, Fe/Mn oxide, bound to sulfide compounds and residual fractions were established. Total composition and the residual fraction of ash samples were determined by a HNO$_3$/H$_2$O$_2$/HF acid mixture digestion method coupled with ICP-AES or ICP-MS measurement [23,24].

## 2. Experimental

### 2.1. Sample description and preparation

Fly ash samples were collected hourly over a period of 3 days from the Beitou municipal solid waste incineration plant of Taipei, Taiwan. The unit is designed with opposing burners at three levels in the furnace and has a semi-dry scrubber/bag-house filter air pollution emission control system. The type of MSW burned during the sampling period varied from day to day. To obtain a representative ash composition, the collected samples were thoroughly mixed, pulverized and dried before the analyses.

In addition to the collected samples, a BCR reference material No. 176 city waste incineration ash is also analyzed to test the precision and accuracy of the method.

### 2.2. Sequential extraction procedure

A six-step sequential extraction method basically modified from the method proposed by Tessier et al. [9] was adopted, but the residual fraction was particularly digested by HNO$_3$/H$_2$O$_2$/HF acid mixture as proposed in our previous paper [25]. The amounts of elements liberated by each sequential extraction were summed and compared with the certified total values as well as with the total digested data to examine the applicability and accuracy of the proposed method. Table 1 listed the detailed information of each step. The time required for conducting the first five steps (not including elemental determination) was about 15 h. At least five replicates of all ash samples were analyzed with the proposed procedure. The extractions were sequentially performed in 50 ml polyethylene tubes using mechanical shaking. After each extraction, the suspension was centrifuged at 3000 rpm for 10 min. The residual was then rinsed with 10 ml of bi-distilled water followed by another centrifugation for 10 min. Both supernatant and wash solution were collected for the ICP-AES and ICP-MS measurement. The residue was then ready for the next step.

*Step 1*: water-soluble dilution was introduced to the study with a expectation to collect some elements such as Ca, Pb, Na, K, etc. that can be easily extracted from water solution at ambient temperature. In this step, 20 ml bi-distilled water was added to 2 g of pulverized fly ash to leach water-soluble ions.
*Step 2*: to separate soluble part of the heavy metal content (exchangeable cations), 20 g of MgCl$_2$ solution (1 mol/l, pH ∼ 6) were added to the residue of step 1 for second step

Table 2
Instrument operating conditions

| ICP-MS (PE-Sciex Elan 5000) | | ICP-AES (PE ICP Optima 3000) | |
|---|---|---|---|
| RF Power (W) | 1100 | RF Power (W) | 1300 |
| Gas flow rates (l min$^{-1}$) | | Gas flow rates (l min$^{-1}$) | |
| Coolant | 14 | Coolant | 15 |
| Auxiliary | 0.8 | Auxiliary | 0.8 |
| Nebulizer | 0.8 | Nebulizer | – |
| Dwell time | 20 ms | Delay time | 30 s |
| Resolution | Normal | Integral | Peak area |
| Reading/replicate | 50 | | |
| Sweeps/reading | 1 | | |
| Scanning cone | Nickel (1.1 mm) | | |
| Skimmer | Nickel (1.1 mm) | | |

extraction. The experiment was carried out at ambient temperature.

*Step 3*: 10 ml of 0.1N NaOAc/HOAc was added to the residue from step 2 in the centrifuge tube and extracted by shaking for 3 h at ambient temperature. Extraction and solid–liquid separations as well as extract storage were carried out as described above.

*Step 4*: 10 ml of 0.1N $NH_2OH\cdot HCl$ was added to the residue from step 3 in the centrifuge tube and extracted by shaking for 3 h at 60 °C. Extraction and solid–liquid separations as well as extract storage were carried out as described above. At this step, the reducible forms associated with oxides and hydroxides of Al, Mn and Fe.

*Step 5*: 5 ml of 8.8 M $H_2O_2$ (pH 2–3, adjusted with $HNO_3$) solution was added to the residue from step 4. Extraction (digestion) was carried out in a covered vessel at room temperature for 1 h. It was continued with cover being removed for 1 h at 85 °C to reduce the volume to a few ml. Aliquot of 5 ml of 8.8 M $H_2O_2$ solution was added into the cooled down solution and it was heated at 85 °C for another 1 h until the volume was reduced to few ml. Then 25 ml of 1 M $NH_4OAC$ (pH 2, adjusted with $HNO_3$) was added to the cooled residue for 16 h extraction at ambient temperature. The solid residue was separated from the extract by centrifugation and decantation of the supernatant liquid into a 50 ml volumetric flask, which was filled up with de-ionized water.

*Step 6*: This step was called as residues, bound to silicate and aluminosilicate and the residual forms associated with oxides of Al, Na and Si. The final residue was high-pressure bomb digested with 10 ml mixed acid ($HNO_3 + H_2O_2 + HF = 3$ ml: 5 ml: 2 ml, v/v) at 190 °C. After the digestion, the sample solution was transferred into a PTFE beaker and heated gently (<90 °C) on a hot plate to allow the residual acid to evaporate. The residue was diluted to 50 ml for being measured by instrument analysis. A pressure bomb digestion system consisting of a 25 ml Polytetrafluoroethylene (PTFE) vessel and thermostatically controlled heating block supplied by Berghof (Germany) was used for sample digestion. Details regarding the instruments used herein can be found elsewhere.

### 2.3. Containers and reagents

PTFE, polyethylene and polypropylene containers were cleaned by immersing the vessels in concentrated $HNO_3$ overnight, and then washing successively with de-ionized water. All chemicals used were supplied by Merck (pro analysis grade). High-purity water (resistance >16 M$\Omega$ cm) produced by reverse osmosis and demineralization was used. Stock solutions of the elements of interest (1000 $\mu g$ ml$^{-1}$) were prepared from Titrisol concentrations (Merck) by diluting to volume with de-ionized water.

### 2.4. Apparatus

A Perkin-Elmer Optima 3000DV multi-collector type ICP-AES was employed for determining Al, Ca, Fe, K, Mg, Na, S and Zn while a SCIEX Elan Model 5000 ICP-MS manufactured by Perkin-Elmer was employed for determining As, Ba, Cd, Cr, Cu, Mn, Ni, Pb, Sb, Se, Sr and V. Operating details of these instruments are given in Table 2. Morphological investigations were carried out by scanning electron microscopy analyzer (SEM, JEOL JSM-6300F).

Table 3
Bulk content of major and trace elements of the reference material (BCR No. 176) and collected fly ash

| | BCR No. 176 | | | Collected samples | |
| --- | --- | --- | --- | --- | --- |
| | Certified value | Total digestion | *S/T* | Total digestion | *S/T* |
| Major element (mg/kg) | | | | | |
| Al | 101,600 | 86,400 ± 1200 | 0.63 | 14,500 ± 500 | 0.99 |
| Ca | 88,000 | 89,800 ± 900 | 0.95 | 243,000 ± 14,000 | 1.02 |
| Fe | 21,300 | 21,500 ± 400 | 0.90 | 3700 ± 900 | 1.04 |
| K | 450,000 | 35,100 ± 400 | 0.75 | 37,300 ± 4600 | 0.93 |
| Mg | 218,000 | 19,600 ± 200 | – | 7900 ± 300 | – |
| Na | 430,000 | 41,700 ± 1200 | – | 43,000 ± 3100 | – |
| Pb | 109,000 | 10,600 ± 100 | 0.97 | 29,500 ± 1500 | 0.95 |
| S | 446,000 | 37,900 ± 1400 | 0.74 | 3900 ± 600 | 1.01 |
| Zn | 258,000 | 25,000 ± 300 | 0.95 | 8800 ± 500 | 0.98 |
| Trace element (mg/kg) | | | | | |
| As | 93 | 87.4 ± 0.8 | 0.92 | 61.3 ± 41.0 | 0.82 |
| Ba | 3910 | 3830 ± 30 | 0.98 | 390 ± 70 | 1.13 |
| Cd | 470 | 400 ± 21 | 0.84 | 160 ± 41 | 0.96 |
| Cr | 863 | 423 ± 8 | 0.42 | 70.3 ± 29.2 | 1.10 |
| Cu | 1302 | 1250 ± 40 | 1.05 | 610 ± 50 | 1.02 |
| Mn | 1390 | 1430 ± 40 | 0.97 | 310 ± 23 | 0.96 |
| Ni | 124 | 118 ± 3 | 0.92 | 310 ± 16 | 0.93 |
| Sb | 412 | 342 ± 13 | 0.84 | 480 ± 33 | 0.89 |
| Se | 41 | 35.3 ± 4.8 | 0.78 | 160 ± 32 | 0.85 |
| Sr | 462 | 379 ± 8 | 0.80 | 430 ± 17 | 0.91 |
| V | 100 | 43 ± 3 | 0.40 | 10.3 ± 3.2 | 0.37 |
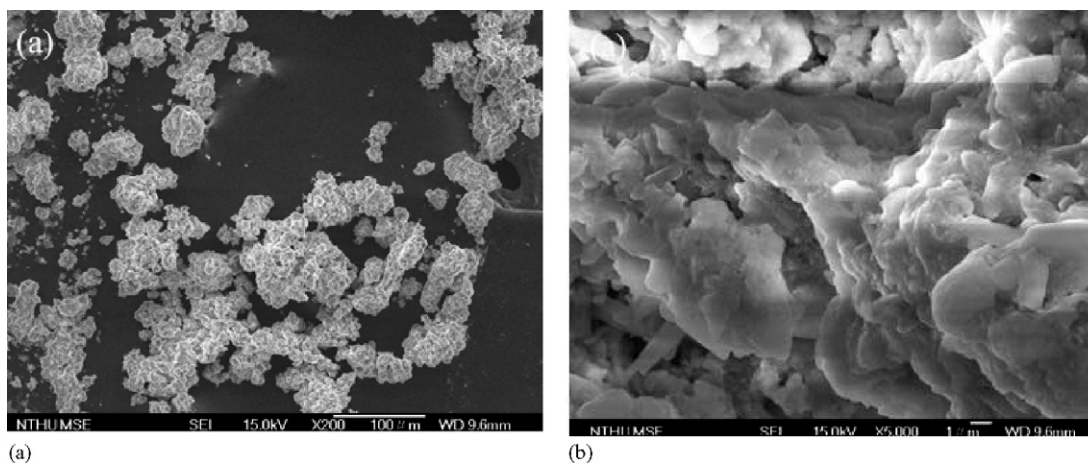
Fig. 1. SEM micrographs of fly ash before water-leached: (a) SEM 200× and (b) SEM 5000×.

The environmental impact from disposal or treatment of MSWI fly ash can be evaluated from the sequential extraction data. The accuracy and repeatability of the analyses are thus critical. It was observed that the utilization of ICP-MS should be very careful in analyzing some of the elements in fly ash samples. For instance, huge dilutions may vitiate the results of Ca determination to a certain extent. It was learned that ICP-MS is a useful but not a magic tool to analyze the matrix-complicated fly ash samples for sequential extraction process. Interference problems due to reagent-derived background ions, formed during the ion-extraction process, may significantly degrade the analytical abilities for many elements. It is known that the formed $^{12}C^{12}C^+$, $^{13}C^{14}N^+$, $^{16}O^{16}O^+$, and $^{38}Ar^1H^+$ may inhibit their respective detection of $^{24}Mg^+$ (79%), $^{27}Al^+$ (100%), $^{32}S^+$ (95%) and $^{39}K^+$ (93%), even if these elements are abundant in fly ash samples. Highly concentrated major cations (e.g., calcium and sodium) and in some cases chloride in the leachate may also deteriorate the accurate determination of many trace elements. For instance, in the ICP-MS measurement, the peaks of major nickel isotopes, $^{58}Ni^+$ (abundance 68%) and $^{60}Ni^+$ (26%), can be interfered with $^{58}Fe^+$ and $^{44}CaO^+$, respectively. Since both iron and calcium are major elements in incineration fly ashes, only minor peaks of nickel isotopes can be used for analysis. To extend the scope of elemental determination, a synchronous measurement of ICP-AES is thus suggested as an alternative method of analysis for elements such as Al, Ca, Fe, K, S and As.

## 3. Results and discussion

### 3.1. Characterization of the MSWI ash

#### 3.1.1. Chemical characterization

For quality control, a certified reference material of BCR 176 was analyzed simultaneously with the collected incineration fly ash samples. The bulk content of major and trace elements of the reference material (BCR No. 176) and collected fly ash are included in Table 3. A total of 20 major and trace elements were determined. The accuracy and precession of the analytical method for each element were thus examined by comparing the data of both standard and collected samples. The *S/T* values are the ratio between the sum of sequential extraction and total digestion concentrations. Good results were obtained for most of
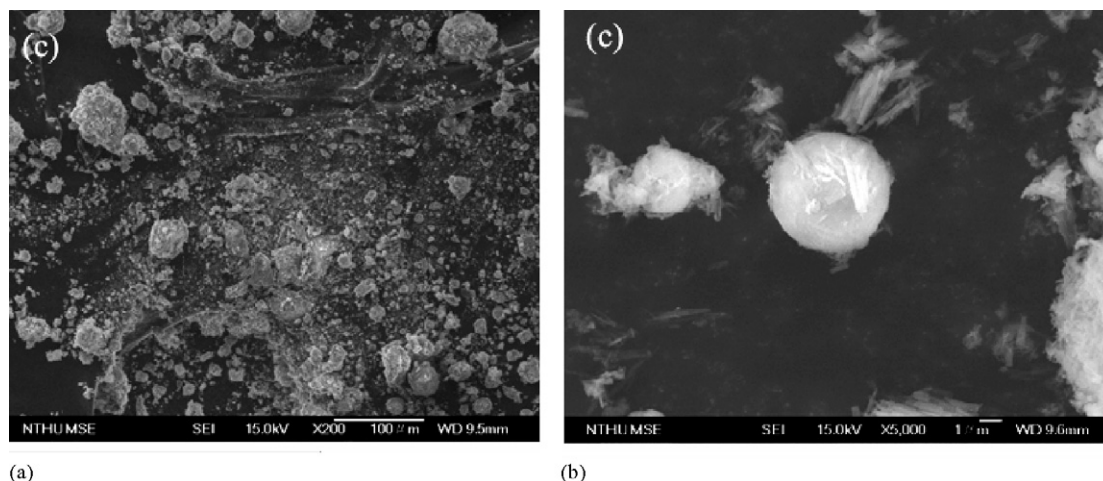


Fig. 2. SEM micrographs of fly ash after water-leached: (a) SEM 200× and (b) SEM 5000×.

elements except for that of Cr, V, Mg and Na. Concentrations of Cr and V in BCR 176 were significantly underestimated, which can be attributed to chemical loss during the extraction or digestion process. It is reasonable to expect a lower total recovery for these elements in highly chlorinated fly ash samples. The concentrations of Cl in BCR 176 and collected samples are about 4.1 and 5.0%, respectively. Due to the influence of added reagent in the extraction steps, only the first one or two fractions of Mg and Na can be determined. However, 49% of Na can still be verified with the proposed method. It was also observed that significant difference occurred between the sum of sequential extraction and total digestion data for some elements. We believed that contamination as well as the chemical loss during the laborious extraction steps is the reason for these variations, which can be simply improved by increasing the amount of sample analyzed. As a result, the measured values of these elements in the studied ash samples should be made with care. A repetition of five experiments was performed and the relative standard deviation (R.S.D.) of $S/T$ ranged from 4% (for Mn) to 18% (for As).

### 3.1.2. Morphological characterization

Scanning electron microscopy (SEM) was taken on the origin and solvent leaching samples. Fig. 1 illustrates the microscopy phases of fly ash for initial samples. SEM pictures indicated that fly ash consists largely of agglomerated particles of a wide range (Fig. 1a and b). Along with some roughly hollow sphere in the size ranges 5–100 μm size, the samples are highly agglomerated, smaller particles adhere to the larger ones

**Table 4**
Recoveries (%) of sequential extraction steps for BCR No. 176 reference material ($n = 5$).

|  | Step 1 | Step 2 | Step 3 | Step 4 | Step 5 | Step 6 |
|---|---|---|---|---|---|---|
| **Major element (mg/kg)** | | | | | | |
| Al | 1 (1)[1] | 1 (1) | 2 (1) | 1 (1) | 27 (1) | 31 (1) |
| Ca | 29 (1) | 8 (1) | 18 (1) | 8 (1) | 28 (2) | 4 (1) |
| Fe | 1 (1) | 1 (1) | 1 (1) | 3 (1) | 28 (1) | 56 (3) |
| K | 41 (1) | 3 (1) | 4 (1) | 1 (1) | 15 (1) | 12 (1) |
| Mg | 3 (1) | — | — | — | — | — |
| Na | 46 (1) | 3 (1) | — | — | — | — |
| Pb | 4 (1) | 2 (1) | 58 (1) | 6 (1) | 23 (1) | 4 (1) |
| S | 58 (2) | 9 (1) | 5 (1) | 1 (1) | 2 (1) | 1 (1) |
| Zn | 3 (1) | 3 (1) | 37 (1) | 7 (1) | 17 (2) | 14 (1) |
| **Trace element (mg/kg)** | | | | | | |
| As | 6 (1) | — | 42 (2) | 7 (1) | 30 (2) | 8 (1) |
| Ba | 4 (1) | 10 (1) | 6 (1) | 13 (3) | 57 (4) | 8 (1) |
| Cd | 26 (2) | 12 (1) | 38 (1) | 4 (1) | 5 (1) | — |
| Cr | — | — | 1 (1) | — | 8 (3) | 33 (1) |
| Cu | 3 (3) | 3 (1) | 55 (1) | 10 (1) | 23 (2) | 11 (2) |
| Mn | 1 (1) | 1 (1) | 7 (1) | 11 (1) | 61 (4) | 17 (1) |
| Ni | — | — | 3 (1) | 1 (2) | 21 (1) | 67 (5) |
| Sb | 4 (1) | 3 (1) | 6 (1) | 4 (1) | 15 (4) | 52 (4) |
| Se | 10 (1) | — | 34 (2) | — | 28 (1) | 3 (1) |
| Sr | 16 (1) | 9 (1) | 10 (1) | 8 (1) | 32 (2) | 6 (1) |
| V | 1 (1) | — | 2 (1) | 3 (1) | 22 (1) | 13 (1) |

[a] Values presented in parentheses are the relative standard deviations.

forming agglomeration even at a size >100 μm. This speculates many particles of 500–1000 Å intertwined with together to the bigger round of 0.1–10 μm, and accumulated on the surface of the sphere. Mostly the Ca, K, Mg, Na and Cl accumulated containing compounds are enriched on the surface. Fig. 2 depicts the water-leached fly ash, where agglomerated matters on the surface observed in Fig. 2a and b, parts disappeared on the SEM micrograph. It is clearly seen in Fig. 2a and b that the salts aggregated on the origin fly ash surface has been washed with water. Table 3 showed that the incineration fly ash produced in Taiwan is very similar to the fly ash produced elsewhere, and for most toxic elements, may present big potential danger to the environment. The significantly low contents for elements of Al, Fe, Mn and Ba have been observed

in our collected fly ash samples, which is mainly due to the least contribution from crustal materials. On the other hand, much higher concentrations of Ca and Pb were indeed observed. It is thus interested to know whether these elements contained in the residues will be easily released into the environment or not.

### 3.2. Speciation of elements in MSWI ash

Tables 4 and 5 give the results of the sequential extraction procedure for various elements in BCR 176 and collected samples, respectively. The results are given as the fraction of the total amount of various elements (%) found in each step. Values presented in parentheses are their relative standard deviations. The most dominant fraction which can be dissolved during the

Table 5
Recoveries (%) of sequential extraction steps for collected incineration fly ashes (n = 5)

|  | Step 1 | Step 2 | Step 3 | Step 4 | Step 5 | Step 6 |
|---|---|---|---|---|---|---|
| **Major element (mg/kg)** | | | | | | |
| Al | 1 (1)[1] | 1 (1) | 2 (1) | 18 (1) | 65 (1) | 23 (1) |
| Ca | 70 (3) | 12 (1) | 9 (1) | 6 (1) | 4 (2) | 1 (1) |
| Fe | 1 (1) | 1 (1) | 1 (1) | 3 (1) | 28 (1) | 56 (3) |
| K | 85 (2) | 4 (1) | 1 (1) | 1 (1) | 2 (1) | 1 (1) |
| Mg | 1 (1) | — | — | — | — | — |
| Na | 86 (2) | 4 (1) | — | — | — | — |
| Pb | 61 (3) | 18 (1) | 10 (1) | 4 (1) | 1 (1) | 1 (1) |
| S | 60 (2) | 2 (1) | 15 (1) | 14 (1) | 9 (1) | 1 (1) |
| Zn | 18 (1) | 2 (1) | 37 (2) | 36 (1) | 12 (2) | 5 (1) |
| **Trace element (mg/kg)** | | | | | | |
| As | 5 (1) | 3 (1) | 40 ( 2) | 11 (1) | 20 (2) | 3 (1) |
| Ba | 29 (2) | 6 (1) | 6 (1) | 24 (3) | 38 (4) | 10 (1) |
| Cd | 2 (2) | 15 (1) | 39 (1) | 33 (1) | 5 (1) | 2 (1) |
| Cr | 12 (1) | 9 (2) | 17 (1) | 24 (1) | 28 (3) | 30 (1) |
| Cu | 7 (1) | 2 (1) | 61 (3) | 31 (1) | 15 (2) | 6 (2) |
| Mn | 1 (1) | 1 (1) | 10 (1) | 39 (1) | 63 (4) | 12 (1) |
| Ni | 1 (1) | 1 (1) | 1 (1) | 1 (2) | 25 (1) | 64 (5) |
| Sb | 1 (1) | 9 (1) | 13 (1) | 41 (1) | 23 (4) | 32 (4) |
| Se | 7 (1) | 6 (1) | 12 (2) | 8 (1) | 2 (1) | 14 (1) |
| Sr | 28 (1) | 14 (1) | 26 (1) | 14 (1) | 8 (2) | 1 (1) |
| V | — | — | 14 (1) | 1 (1) | 18 (3) | 4 (2) |

[a] Values presented in parentheses are the relative standard deviations.

sequential extraction process is presented in Tables 4 and 5 with shaded background. Fraction data exceeding 10% of total extraction amount are marked with bold type numerical numbers.

As seen in Tables 4 and 5, significant amounts of Ca, K, Na, Pb, S and Zn can be located in the fractions I, II and III. The largest contingent of these elements in examined samples was found in the water-soluble fraction. It was found that, nearly 70% of Ca, 85% of K, 86% of Na, 61% of Pb and 60% of S were released from this step. The final leaching solution in the "water soluble" step reaches a pH of 8.5 for BCR 176 and 11.7 for the collected fly ash samples. A more basic characteristic of the collected fly ash samples may be attributed to the existence of significant amount of Ca, which is considered as one of the most important marker elements in fly ashes for incinerators with semi-dry scrubber system. It is known that, in the investigated incinerator, a large amount of CaO was added in the semi-dry scrubber system to remove the $SO_2$ gas. Significantly high Ca and low S contents observed in the collected fly ash as well as in the flue gas are thus expected. It was also found that higher water soluble Ba and Sr existed in collected fly ash samples, which can also be attributed to the utilization of CaO.

Transition metals such as Zn, Cd and Cu showed the highest proportion (37%, 39% and 61%) and appeared significantly in the fraction III, which may indicate that these elements are existing mostly in the carbonate or oxide phase. They were quite high in the step 4 with their proportion of 36%, 33% and 31%. As seems to be the highest in proportion, of 40% in step 3 and lower, of 11% in step 4 and 20% in step 5. The pH of leaching solution for both BCR 176 and collected fly ash samples in step 3 only reached about 7.5 after 3 h shaking. It is thus doubtful that for more basic fly ash samples, a complete extraction of carbonate compound can be achieved by the proposed step 3.

Trace element such as As showed the highest proportions (40%) in step 3, and significant proportions in step 5 (20%) and step 4 (11%). Also noticed the high proportions of As in the step 3 (carbonates), As could not occur as a carbonate, probably As occurred as soluble arsenates at pH 7.5 (for example Zn, Cr or Cu arsenates).

The fractions of Al, Fe as well as Mn in the reducible steps (steps 4 and 5) are large and considerable amount of these elements remains in the residue fraction. This indicates that the existence of soil-originated aluminosilicates in the fly ash. As also revealed in Tables 4 and 5, the alkaline earth originated Ba and Sr are not only owing to the addition of CaO, but also to the contribution of crustal material in the MSW. As shown in Table 5, a much higher Pb content was determined, most of which can be leachated into the environment under the normal condition. Lacking of selectively recovery of Pb-related MSW in Taiwan should be the major reason to cause this.

### 3.3. Potential environmental impact of MSWI ash

However, total elemental concentrations of waste incineration residues indicate only the potential risk of disposal them

Table 6

Comparisons between the sums of first three extraction fractions for various elements in analyzed fly ash samples and the TCLP limits

| | BCR No. 176 (I + II + III) | Collected samples (I + II + III) | TCLP limits |
|---|---|---|---|
| Major element (mg/kg) | | | |
| Al | 4.6 ± 1.2 (4)[a] | 0.6 ± 0.4 (4) | – |
| Ca | 49.2 ± 8.8 (56) | 197 ± 12 (81) | – |
| Fe | 0.6 ± 0.1 (3) | 0.1 ± 0.1 (3) | – |
| K | 21.6 ± 0.5 (48) | 33.6 ± 1.5 (90) | – |
| Mg | 0.6 ± 0.2 (3) | 0.1 ± 0.1 (1) | – |
| Na | 20.3 ± 4.0 (49) | 36.2 ± 1.3 (90) | – |
| Pb | 7.0 ± 1.0 (64) | 26.3 ± 1.2 (89) | 0.05 |
| S | 32.1 ± 1.3 (73) | 3.1 ± 0.2 (77) | – |
| Zn | 11.1 ± 0.5 (43) | 5.0 ± 0.4 (57) | 0.25 |
| Trace element (mg/kg) | | | |
| As | 44 ± 1 (48) | 17 ± 2 (28) | 50 |
| Ba | 782 ± 39 (20) | 160 ± 16 (41) | 1000 |
| Cd | 353 ± 9 (75) | 90 ± 6 (56) | 10 |
| Cr | 9 ± 9 (1) | 27 ± 2 (38) | 50 |
| Cu | 793 ± 39 (81) | 427 ± 31 (70) | 250 |
| Mn | 122 ± 13 (9) | 37 ± 9 (12) | – |
| Ni | 4 ± 1 (3) | 10 ± 10 (3) | 250 |
| Sb | 54 ± 4 (13) | 110 ± 3 (23) | 150 |
| Se | 18 ± 1 (44) | 40 ± 6 (25) | – |
| Sr | 158 ± 5 (4) | 292 ± 17 (68) | 1 |
| V | 3 ± 1 (3) | 1 ± 1 (14) | 250 |

[a] Data in parentheses are the relative percentage (%) of total concentrations by sequential extraction process.

in the environment. The real danger part of the fly ash is the amount of readily soluble constitutes which is best represented by the first three extraction fractions in our experiment. Table 6 lists the sum of first three extraction fractions for various elemental concentrations in analyzed fly ashes to indicate their availabilities on the environment for further disposal or treatment of them in Taiwan. The obtained data was also compared with the TCLP limits of several toxic elements for solid wastes as well as contaminated soils regulated by EPA of Taiwan. As revealed in Table 6, elements such as Ca, K, Na, Pb, Zn, Cd, Cu, and Sr have exhibited a remarkable mobility in fly ashes. More than half of them would be dissolved or exchanged under a mild leaching condition. It was found that the extracted concentrations of toxic elements, such as Pb, Zn, Cd, Cu and Sr, in the real fly ash samples through the first three steps are much higher than the regulated TCLP limits of them. The non-recycle policy of MSW before the incineration may be the reason to cause the high contents of Pb, Cd, Zn and Cu in Taiwan. It was estimated that over 500 million pieces of various kind of batteries has been exhausted during the year of 2001, and only less than 10% of them being recovered. Many toxic elements are left in the ash part with various chemical forms after an incineration process. For example, as shown in Tables 3 and 5, nearly 3% of fly ashes are composed of Pb and 2.4% of it will be easily dissolved by the water extraction only. On the other hand, significant amount of Zn, Cd or Cu can only be extracted under steps of 3 and 4. Since the stabilities of different chemical species in the residue determine the successive disposal or treatment strategy significantly, it is thus important to understand the
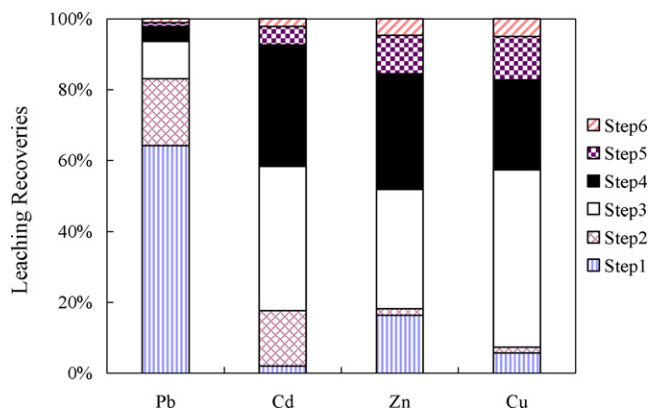
Fig. 3. Distribution of Pb, Cd, Zn, and Cu in collected samples.

leaching trends of toxic substance inside. Fig. 3 shows the accumulated leaching amounts of Pb, Cd, Zn and Cu in collected samples after various extraction steps. The unit of vertical coordinate has been represented by the regulated TCLP limits listed in Table 6. Various leaching behavior was observed, however, most of them would be leaching out after first three steps and exceed the TCLP limits easily. As a result, the obtained data in this study may further help us to evaluate the actual impact of these elements on the environment in the final disposal treatment process.

## 4. Conclusions

A modified sequential extraction method has been proposed and successfully demonstrated as an effective tool to investigate various binding forms of different elements in the MSW incineration fly ash. Using the combined ICP-AES and ICP-MS analytical techniques to determine elemental concentrations in different leachates are performed. Total of 20 elements in the samples can be accurately determined. To examine the applicability as well as accuracy of the proposed method, a certified reference material of city waste incineration fly ash (BCR No. 176) is also analyzed. Both the results of total digestion and the sum of most elements present in the individual fractions show a quite good agreement with the certified values. The extraction efficiencies are generally higher than 80% except for that of Cr and V. The analytical results showed that the major elements such as Ca, Na, K and S can be easily released under natural conditions during an utilization of fly ash in civil engineering. The extractable data of most elements may provide critical information about the binding forms of various elements in both standard and collected incineration fly ashes, which can certainly help us to estimate the potential environmental risk during the disposal or treatment of produced incineration fly ashes.

## Acknowledgements

collection fly ash samples from Beito municipal solid waste incineration plant of Taipei, Taiwan.

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