The Recovery of Ca and Zn from the Municipal Solid Waste Incinerator Fly Ash

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Abstract: The treatment and disposal of municipal solid waste incineration (MSWI) fly ash containing significant amounts of dissolvable salts and heavy metals is a seriously challenge. At present, the common treatment method for MSWI fly ash in Taiwan is the cement-based stabilization/solidification (S/S) process. In this work, an integrated hydrometallurgical process for the treatment of MSWI fly ash was evaluated. Ca was first recovered by combining water washing and ion exchange sequentially. Meanwhile, Zn in the water-washed fly ash was recovered by combining acid leaching and ion exchange sequentially. Combining the water washing efficiency of 30% on raw ash and the acid leaching efficiency of 40% on pre-washed ash, a total of 58% mass reduction rate of fly ash was achieved. In addition, an 80% Zn and 58% Ca recovery was achieved.

Keywords: fly ash; washing; leaching; ion exchange; calcium; zinc

1. Introduction

Incineration is one of the efficient methods in current waste treatment techniques and is capable of achieving volume reduction. In Taiwan, there have been 24 municipal solid waste incinerator (MSWI) plants in operation up to now and 6.24 million tons of waste was treated annually. After incineration, one-fifth of the weight of the MSW becomes residues and 23 wt.% of the residues is fly ash. In this manner, 302,000 tons of the MSWI fly ash are produced in Taiwan annually [1]. In recent years, MSWI has also become a popular method to treat MSW in Japan and several European countries due to the merits of volume reduction [2,3] and energy recovery [4,5]. MSWI fly ash contains chloride salts, dioxins, and heavy metals, such as zinc (Zn), lead (Pb), copper (Cu,) and Cadmium (Cd) and is considered as a hazardous waste [6]. CaO or CaCO3 are injected into the furnace to neutralize the emission of acid gases such as HCl and SOx during MSW incineration which led to a high calcium (Ca) content of fly ash. The reported sources of Pb, Cd and Zn in MSW include plastic, food waste, and paper products [7,8]. Zn usually condenses onto the surface of fly ash during incineration due to its low boiling point. Various methods of treating MSWI fly ash such as solidification/stabilization (S/S), acid extraction, vitrification and sintering have been used to treat MSWI fly ash [9–14]. At present, the common treatment method for MSWI fly ash in Taiwan is the cement-based stabilization/solidification (S/S) process. However, the S/S process generally increases the mass of fly ash to 145% of its original mass [1] and consequently limits the landfill capacity. Treatment methods capable of both environmental stabilization and resources’ recovery should be considered. The wet extraction processes using various reagents [15–19] to achieve fly ash stabilized and metals’ recovery have been investigated. However, most of the literatures focuses on the leaching of metals in MSWI fly ash and discusses the effects of experimental conditions such as reaction time, temperature, leaching reagents used, and the liquid-to-solid ratio. In this study, a novel process aiming for the mass reduction and metal recovery of MSWI fly ash was proposed. Firstly, a water-

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A washing process was applied to dissolve soluble salts of potassium (K), sodium (Na), and Ca from fly ash and the wash-out leachate was then treated by ion exchange [20] to recover Ca. Secondly, an acid-leaching process was applied to extract Zn from the residues after water-washing and the leachate was then treated by ion exchange [20] to recover Zn.

2. Materials and Methods

2.1. MSWI Fly Ash

The MSWI fly ash used in this study came from an incineration plant in southern Taiwan. Grab samples of the ash were collected from the bag filter. The fly ash sample was mixed with a blender for 30 s in the laboratory to ensure that the samples became homogeneous. The coning and quartering method was used to reduce the sample weight to 2 kg. The fly ash samples were passed through a sieve and the fraction smaller than 0.59 mm in diameter was collected and used in the following experiments. The elemental compositions of the fly ash was determined by acid digestion [21]. A 0.1 g ground sample was digested using aqua regia at 100 °C for 30 min. After cooling and filtration, the composition of the filtrate was determined using an inductively coupled plasma–optical emission spectrometry (ICP–OES) (Optima 8300DV, PerkinElmer, Santa Clara, CA, USA). All the analyses were run in duplicate and the mean values were considered. The results were found to vary within 3%. The mineralogical composition of the fly ash samples were analyzed by an X-ray diffractometer (XRD–RAPID II, Rigaku, Woodlands, TX, USA) to examine the mineral phases of the sample. The morphological images of the fly ash samples were observed by scanning electron microscopy (SEM, JSM-5610LV, Electron Optics Laboratory, Akishima, Tokyo, Japan) after Au coating.

2.2. Water Washing

The original fly ash sample was first washed with distilled water to remove the soluble salts. A dried fly ash sample was mixed with distilled water at different liquid/solid (L/S) ratios of (20–50):1 (in mL:g) and stirred in a beaker at room temperature. Samples of the suspension were taken at different time intervals up to 2.5 h. The sample was vacuum filtrated and Ca in the filtrate was analyzed by the ICP/OES spectrometer. All the filtrates were collected and used in the subsequent ion exchange experiments. The filtration cake was dried to constant weight and analyzed by using X-ray diffractometer.

2.3. Ca Recovery by Ion Exchange

2.3.1. Resin

We examined several commercial resins for their suitability for Ca separation and a commercial weak acid chelating resin, IRC748, produced by Rohm and Haas appears to be very promising for this purpose. This resin is an iminodiacetic acid chelating cation exchange resin with high selectivity for heavy metal cations. The selectivity is achieved by the iminodiacetic acid functionality chemically bound to a macroreticular resin matrix as shown in Figure 1. Metal ions usually bind with one nitrogen and two oxygen atoms. The sodium form of the resin was used as received in this study.

![Molecular structure of the IRC748 resin.](image_url)
2.3.2. Column Experiments

The recovery of Ca using ion exchange was carried out via the column operation. A 10 cm-long and 2.5 cm in diameter glass column was filled with 45 mL of the resin. The feed liquor was added to the top of the column at a constant flow rate and room temperature for column loading. Samples of the column effluent were taken from the bottom of the column periodically and the metal concentrations were analyzed to construe the breakthrough curves. The loaded column was then eluted by passing HCl through the column at a fixed flow rate. The elution curves were constructed in the same way as the breakthrough curves.

2.4. Acid Leaching

Acid leaching was applied to the water-washed fly ash for Zn extraction. Then, 10–40 g dried pre-washed fly ash was mixed with 200 mL solution with a fixed HCl concentration at room temperature. Samples of the suspension were taken after 1 h magnetic stirring. The sample was vacuum filtrated and Zn in the filtrate was analyzed by the ICP/OES spectrometer. All the filtrates were gathered and used in the subsequent column experiments. The filtration cake was dried to constant weight and the percent solid dissolved was calculated.

2.5. Zn Recovery by Ion Exchange

2.5.1. Resin

We examined several commercial resins for their suitability for Zn separation and a commercial weak acid chelating resin, Dow M4195, produced by Rohm and Haas, appears to be very promising for this purpose. Dow M4195 consists of the bispicolylamine ligand supported by a polymeric backbone of styrene cross-linked with divinylbenzene. Bispicolyl amine is a heterocyclic polyamine with three nitrogen donor atoms, as shown in Figure 2. The resin was used as received in this study.

![Figure 2. Molecular structure of the Dow M4195 chelating resin.](image)

2.5.2. Column Experiments

The recovery of Zn using ion exchange was carried out via the column operation. A 10 cm-long and 2.5 cm in diameter glass column was filled with 45 mL of the resin. The feed liquor was added to the top of the column at a fixed flow rate and room temperature for column loading. Samples of the column effluent were taken from the bottom of the column periodically and the metal concentrations were analyzed to construe the breakthrough curves. The loaded column was eluted by passing the first HCl solution, then the NH₄OH solution through the column at a constant flow rate. The elution curves were constructed in the same way as the breakthrough curves.
3. Results

3.1. Characteristics of Fly Ashes

Before starting the study of metal recovery from fly ash, the total content of the elements in the fly ash sample was required. The results for eight major elements are shown in Table 1. The major elements contained in fly ash are: 17.14% Ca, 6.01% Na, 3.22% K, and notably 1.30% of Zn. CaO or CaCO₃ are injected into furnace to neutralize the emission of acid gases such as HCl and SOₓ during MSW incineration which led to a high calcium content and alkalinity of fly ash. Due to the volatile nature of sodium and potassium, fly ash also contains quite a large amount of sodium and potassium chlorides which are enriched in the fly ash during incineration. Considering the large amounts of water soluble Ca, Na and K salts in fly ash, a simple water washing pretreatment to remove the water soluble salts before further treatment is feasible. Table 1 indicates that fly ash contains harmful heavy metal such as Zn, Pb, Cu, and Cd. Figure 3a shows the SEM images of the fly ash before water washing. An agglomerated structure was observed in the SEM image of the original fly ash. The fly ash particles were highly agglomerated and the small particles were coated on the surface of the large particles, forming agglomerates. The XRD diffraction results of the original fly ash was shown in Figure 4. We identified that the main crystal phases of fly ash include Ca₆(SiO₂)(Si₂O₇)(OH)₂ and Na₂Ca₅(SO₄)·3H₂O.

Table 1. Chemical contents of 8 elements in the municipal solid waste incinerator (MSWI) fly ash (%).

| Composition | Wt.% |
|-------------|------|
| Ca          | 17.14|
| Na          | 6.01 |
| K           | 3.22 |
| Mg          | 1.74 |
| Zn          | 1.30 |
| Pb          | 0.31 |
| Cu          | 0.08 |
| Cd          | 0.01 |
3.2. Water Washing

Considering the large amounts of water soluble Ca, Na and K salts in fly ash, a simple water washing pretreatment to remove the water soluble salts before further treatment is feasible. Figure 5 displays the effect of washing time on the solid-dissolved ratio for fly ash washing at the L/S ratio of 30. It was observed that the soluble salts in fly ash dissolves rapidly during water washing and the solubility attained a maximum value of 30% before 0.5 h. Extended washing resulted in a slightly decreased solubility of fly ash, presumably due to the re-precipitation of salts. Figure 3b shows the SEM images of the fly ash after water washing. A de-agglomerated structure was observed in the SEM image of the washed fly ash. The fly ash particles were de-agglomerated due to the dissolution of cementing salts. The XRD diffraction results shown in Figure 4 provide a comparison between the crystal phases identified in the raw fly ash and the water-washed fly ash and showed that some peaks of the water-soluble salts were weakened in the washed ash. The results of fly ash pre-washing using various volumes of water mixed with a fixed amount of fly ash (L/S of 5 to 30 v/w) are displayed in Figure 6. The results indicate that the increase in washing water volume increased the solubility of the salts in fly ash and it was found that a washing efficiency of 30% fly ash dissolved was obtained at a L/S (v/w) of 30. Although a higher L/S ratios is favorable for the dissolution of salts in fly ash, a L/S ratio of 30:1 is recommended, considering both the washing efficiency and water conservation. The Ca released in the wash water could be recovered as a source of CaO and the results of Ca released for pre-washing using different volumes of water are shown in Figure 7. The extraction of Ca generally increases with an increasing L/S ratio and reaches a maximum value (25 wt.%) at a L/S (v/w) of 40. Further increase in the L/S ratio slightly reduces the extraction amount of Ca, presumably because that part of the extracted Ca was re-precipitated in the solution containing 1400 ppm Ca. Based on the above results, water washing with experimental conditions of an L/S of 30 (v/w) and 0.5 h reaction time would give a 30% solid dissolved rate and 23% Ca extraction.
Figure 5. Dissolution of fly ash with water at liquid/solid (L/S) 30 for different time periods.

Figure 6. Effect of liquid/solid ratio on dissolution efficiency during water washing.

Figure 7. Effect of liquid/solid ratio on Ca extraction during water washing.

3.3. Ca Recovery Using Ion Exchange

The filtrate collected from water washing containing 1300 ppm Ca (pH 12) was adjusted to pH 7 by adding 5N HCl solution. In the column experiments, the feed solutions with pH 7 and 12 were
added to the top of the column filled with the IRC748 resins at a fixed flow rate and room temperature. The Ca concentration in the column effluent (C) was compared to the Ca concentration in the feed (C₀). The C/C₀ ratio versus the dimensionless effluent volume (bed volume, BV) were used to construct the breakthrough curves. Figure 8 shows the breakthrough curves for Ca at pH 7 and 12. It is observed that the chelating resin IRC748 shows a high affinity for Ca ions at basic conditions. The breakthrough volume changed from 12 BV to 20 BV when the pH was varied from 7 to 12. Due to the presence of carboxylate groups, the dissociation of iminodiacetate functional groups of IRC748 is dictated by pH. At pH = 12, all carboxylate groups are deprotonated, therefore, Ca²⁺ was adsorbed preferentially by IRC748 and separated from the coexisting Na⁺, K⁺ ions. The amount of Ca adsorbed in the IRC748 resin column from feed containing 1300 mg/L Ca before the breakthrough of Ca was found to be 39 g/L resin. The column elution was immediately conducted after the completion of the column loading. Figure 9 shows the elution curves for Ca loaded IRC748 resin using 1N and 3N HCl respectively. Results indicated that Ca loaded IRC748 resin was well eluted with 3N HCl solution at a fixed flow rate of 0.1 mL/min, and complete elution was achieved when around 9 BV of eluent was applied. The maximum measured concentration of Ca in the eluted solution was 22 g/L and a concentration ratio of 17 was achieved from feed containing 1300 ppm Ca.

![Figure 8](image1.png)  
**Figure 8.** Breakthrough curves (C/C₀ versus BV) for Ca loading on IRC748 resin.

![Figure 9](image2.png)  
**Figure 9.** The elution curves for Ca eluted from the IRC748 resin.
3.4. Acid Leaching

The results of the acid leaching using different S/L ratio (10 to 40 g/200 mL) and HCl concentrations (1, 3, 5, 7 N) are presented in Figure 10. The results reveal that the decrease in S/L ratio increased the solubility rate of the pre-washed ash and it was found that a solubility rate of 40% was achieved at S/L (g/200 mL) of 30. Although the lower S/L (g/200 mL) ratios are favorable for the dissolution of pre-washed ash, an S/L (g/200 mL) of 30 is recommended, considering both the washing efficiency and water conservation. The effect of acid concentration on dissolution efficiency was examined at a S/L of 10 to 40 (g/200mL), and a reaction time of 60 min at room temperature. It is found from Figure 10 that the dissolution ratio of pre-washed ash decreased with decreasing acid concentration at the highest S/L ratio of 40 (g/200mL), presumably because that the amount of acid is limited at the condition of high solid loading. However, for lower S/L ratios (10–30), the amount of solid becomes the limited factor and no significant effects of acid concentration on the dissolution ratio were observed. Combining a water washing efficiency of 30% on raw ash and an acid leaching efficiency of 40% on pre-washed ash, a total of 58% mass reduction rate of fly ash was achieved. The effect of acid concentration (1, 3, 5, 7 N HCl) on Zn dissolution from the pre-washed ash was examined at S/L of 10 to 40 and a reaction time of 60 min at room temperature. It was found from Figure 11 that the dissolution rate for Zn generally decreased with the increasing S/L ratio. For example, the Zn dissolution rates at the S/L ratio of 10 and 30 were found to be 100% and 80%, respectively. Although the high acid concentrations are favorable for the Zn dissolution at an S/L ratio of 30, 1N HCl solution is recommended, considering both the dissolution efficiency (80%) and acid conservation.

![Figure 10. Effect of solid/liquid ratio and acid concentration on dissolution efficiency for water-washed fly ash.](chart.png)
Figure 11. Effect of solid/liquid ratio and acid concentration on Zn extraction from water-washed fly ash.

3.5. Zn Recovery Using Ion Exchange

The filtrate collected from acid leaching containing 8200 ppm Ca and 1000 ppm Zn at pH 2 was used in the ion exchange experiments to recover Zn. In the column experiments, the feed solution with pH 2 was added to the top of the column filled with the Dow M4195 resin at a fixed flow rate of 1.7 BV/h and room temperature. The C/C₀ ratio of Ca and Zn concentrations versus the dimensionless effluent volume (bed volume, BV) were used to construct the breakthrough curves. Figure 12 shows the breakthrough curves for Ca and Zn. It can be seen that the breakthrough of Ca appeared at 5 BV, while the breakthrough of Zn did not happen until the volume of effluent reached 14 BV. Apparently, the affinity order of metals for Dow M4195 resin is Zn > Ca. In addition, the breakthrough curve for Ca indicates that a small portion (10%) of Ca in the feed was continuously adsorbed by Dow M4195 during the column loading. Thus, the separation of Zn from Ca was not completed by Dow M4195 resin under the experimental conditions of column loading used in this study. The column elution was immediately conducted after the completion of the column loading. The difference in the affinities of Ca and Zn on Dow M4195 resin was utilized to separate the adsorbed Ca and Zn by conducting a chromatographic elution. Figure 13 shows the elution curves for Ca and Zn loaded Dow M4195 resin using 4N HCl and 4M NH₄OH. The 4N HCl first eluted the adsorbed Ca, and subsequent elution with 4M NH₄OH successfully eluted Zn from Dow M4195 resin. A Ca elution efficiency of 98% was achieved when around 8 BV of eluent was applied. The maximum measured Ca concentration in the eluted solution was 10 g/L with a purity of 97.5%. The loaded Zn was well eluted with 4M NH₄OH solution by using 7 BV solutions. An elution efficiency of 98% was achieved and the maximum concentration of Zn in the eluted solution was 6 g/L with a purity of 98.7%. 
3.6. Recommended Process for Recovery of Ca and Zn

A proposed process for the washing of Ca and acid leaching of Zn from MSWI fly ash and the recovery of Ca and Zn from the leached solution using ion exchange is summarized in Figure 14. A water washing with an L/S of 30 v/w and 0.5 h reaction time gives about 30% solid dissolved rate and 23% Ca extraction. The filtrate was then treated by ion exchange to adsorb Ca. The loaded Ca is eluted with 3 N HCl and the concentrated Ca solution is collected. The washed fly ash was further leached with 1N HCl at an S/L ratio of 30 and 0.5 h reaction time. A 40% solid dissolved rate and 80% Zn dissolution were achieved. The filtrate was then treated by ion exchange to adsorb Zn. The Ca and Zn loaded column was firstly eluted with 3 N HCl to collect the concentrated Ca solution and secondly eluted with 4M NH₄OH to collect the concentrated Zn solution.
4. Conclusions

This study indicated that Ca can be effectively and selectively recovered using a water washing and ion exchange process. Under optimum conditions, the 23% Ca was recovered and a 30% fly ash mass reduction rate was achieved in this stage. Zn in the water-washed fly ash was recovered using an acid leaching and ion exchange process. Under optimum conditions, 80% Zn and an additional 35% Ca were recovered, and together with a further 28% fly ash mass reduction rate was achieved in this stage. The findings of this study demonstrated that this process integrating water washing, acid leaching and ion exchange can provide an alternative solution for MSWI fly ash treatment.

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