

Extraction of metals from municipal solid waste incinerator fly ash by hydrothermal process

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Abstract

This work examined the extraction properties of metallic elements from municipal incinerator fly ash under hydrothermal conditions. The ash was firstly pre-washed by distilled water, then subjected to hydrothermal treatments. The pre-washing process was effective for Na, K, Ca extraction with extraction percentages of 67%, 76% and 48%, respectively. The optimum contact time was 30 min for the pre-washing process. Five types of acids were tested for the extraction experiments and hydrochloric acid was found to be most effective for metal extraction from the ash. Compared to room condition, hydrothermal treatment accelerated the dissolution of the ash, thus promoted the reaction of acid with hazardous metals such as Cr, Cd, Pb, and furthermore, the consumption speed of acid was slowed down under hydrothermal condition. The acid simultaneously reacted with all the metal in the ash under hydrothermal condition but preferentially reacted with Ca at room condition. The optimum hydrothermal treatment temperature, time and liquid/solid ratio were 150 °C, 5 h and 10:1 (ml:g), respectively.

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1. Introduction

Fly ash discharged from municipal solid waste (MSW) incineration plant has been classified as “hazardous waste requiring special control” in many developed countries for several years. In Japan, regulated by 1992 legislation [1], the fly ash is generally subject to treatment by any of the four ways, i.e. melting treatment, chemical stabilization, cement solidification, or extraction. Converting the ash into slag by melting process has been improved in recent years since the melted slag has the potential to be used as construction materials such as aggregates and ceramic linings [2,3]. The only shortcoming of this process is that it is much more costly compared with other methods, which makes it difficult for exact application. In-situ stabilization/solidification of heavy metals inside the fly ash using chelate agents or mixing the ash with Portland cement, on the other hand, is also practicing alternative nowadays for the relatively low treatment

cost and ease of application. However, these processes present some drawbacks, namely slow releasing of heavy metals from the treated ash in a wet environment, which makes it still be hazardous for the environment [4,5]. Moreover, solidification with Portland cement could considerably increase the volume and weight of the residue, since the solidification operation usually adds 15–30 wt.% of cement and 1–3 wt.% of chemical reagent such as carboxylic, thiol or carbamate functional groups with the fly ash [4]. Comparably, extraction of heavy metals from the fly ash is an environmentally preferable method for the ash treatment. This process is actually a hydrometallurgical process as most of the metals may dissolve in the acidic solution.

The recovery of base metals such as Cu, Ni, Co, Zn and Pb from waste ashes provides an opportunity to convert the hazardous waste to innocuous material while at the same time extracting valuable pay-metals. To date, various hydrometallurgical methods using lixiviation reagents for metal extraction from waste ashes have been examined [6–8]. Among the reagents, mineral acids such as HCl, HNO₃, H₂SO₄, and alkaline solutions such as NaOH and aqueous NH₃, are frequently employed. Hydrochloric acid and nitric acid have the advantages of extracting almost all metallic elements, and sulfuric acid could dissolve many of the metals but leave Ca and Pb

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in the residue, while alkaline solutions have the advantages of selective extraction of amphoteric metals such as Zn and Pb and leave other metals in the solid residue. Nevertheless, a large amount of acids or alkaline solutions are generally needed for these processes, and furthermore, the resulting solutions are usually extremely acidic or alkaline with only low concentration of metals in the resulting leachate, which are difficult for recovery. Hence, these processes require high-level wastewater control, and are not suitable for ash disposal plants without wastewater treatment equipments.

Hydrothermal process is a functional way to active reactions whose major mechanism is via dissolution. In recent years, this technique has been applied to waste ash treatment so as to recycle the waste material. Many researchers have employed coal fly ash as a precursor material trying to convert the ash to zeolite-like materials in an alkaline condition. Thus far, many types of zeolite such as phillipsite, analcime, zeolite P, gismondine, and gmelinite have been successfully synthesized using fly ashes [9–11]. Recent reports also indicated that hydrothermal process could significantly increase fly ash pozzolanic reaction [12,13]. The resulting compounds can be used for immobilizing toxic wastes, and also have the potential to be used as the precursors of new kind of low-energy cements called fly ash belite cements. Furthermore, it has reported that hydrothermal treatment of MSW incinerator fly ash with water or alkaline solution could decompose dioxins such as PCDDs and PCDFs through dechlorination, especially at high temperature [14–16].

Many outstanding advantages have been demonstrated in waste ash recycle by hydrothermal treatment. To the knowledge of the authors, however, the leaching properties of heavy metals from fly ash under hydrothermal condition are less reported in the literature. In the present study, hydrothermal treatments on MSW incinerator fly ash were conducted so as to understand the extraction behaviors of metallic elements from the ash during hydrothermal process. The aim was to extract more metals using less acid. The optimum leaching conditions were established, and the crystalline and morphological properties of the residue were clarified.

2. Experimental

Fly ash was obtained from a MSW incineration plant in Nagoya, Japan. The plant has two 24 h running large-scale PLC based incinerators, and the furnace of each incinerator is design to dispose more than 5-tonne refuse per hour. The furnace room temperature is sustained within 850–1000 °C. The fly ash was captured by a bag-filter and was removed twice every day. The fly ash typically contains metallic elements such as Na 2.91%, Mg 1.08%, Al 2.83%, K 4.11%, Ca 22.5%, Cr 0.18 g kg⁻¹, Mn 0.97 g kg⁻¹, Fe 7.63 g kg⁻¹, Cu 0.90 g kg⁻¹, Zn 17.3 g kg⁻¹, Cd 0.14 g kg⁻¹, Pb 1.00 g kg⁻¹ with variation limits around 0.03–1.23%, and non-metallic elements such as C 7.0%, Si 4.0%, P 0.28%, S 0.84%, Cl 28.3% with variation limits around 0.08–8.17%. Carbon content in the ash was determined using a CHN corder (Yanako, MT-6), and the other non-metallic elements were examined using a scanning electron microscope (SEM, JSM-6330F) coupled with an energy-dispersive X-ray

spectrometer (EDS, JED-2140). The details of the fly ash were presented in a previous report [17].

The fly ash was firstly vacuum dried at 105 °C for 24 h. Then a portion of the ash was pre-washed by distilled water. In the pre-washing process, a liquid/solid ratio of 20:1 (ml:g) was performed. The vibration time varied from 5 min to 20 h, and the temperature was approximately 20 °C. After vacuum filtration, metallic elements in the leachate were determined using inductively coupled plasma atomic emission spectroscopy (ICP-AES, Perkin-Elmer).

After separation, the pre-washed residue was vacuum dried at 105 °C for 24 h and subjected to hydrothermal treatments. A series of autoclaves were employed for the hydrothermal experiments. Each autoclave consists of a 50 ml Teflon interior and a stainless exterior. The pressures inside changes along with the temperature change, which were around 1.2–2.0 MPa. Hydrochloric acid, nitric acid, sulfuric acid, oxalic acid and citric acid were examined to compare their leaching effects. The treatment time varied from 1 to 70 h, and the temperatures varied from 100 to 200 °C. Liquid/solid ratios of 3:1, 5:1, 10:1 and 20:1 (ml:g) were performed. After hydrothermal treatment, the autoclaves were immediately cooled using an electronic fan. Upon cooling, the supernatant solution was filtrated using a vacuum filter. Metallic elements in the leachate were determined by ICP-AES, and the pH of the solution was measured using a HORIBA D-21 pH meter. For comparison, parallel experiments were also conducted at room conditions.

The crystalline properties of the residue and the original ash were examined by a RIGAKU X-ray diffractometer (XRD, Rint 2000) at 50 kV and 100 mA using Cu K α radiation ($\lambda = 1.5418\text{\AA}$), and the surface morphology was examined by SEM. A high performance liquid chromatograph (HPLC, SHIMAZU) was employed for Cl⁻, SO₄²⁻ and NO₃⁻ determination. Oxalic anion in the filtrate was precipitated with calcium chloride and determined by KMnO₄ titration, while citric anion was titrated with sodium methanolate in a 3:1 methanol/dimethylformamide mixture.

The quality and precision of metallic element analysis for the fly ash and other samples were controlled using four reference materials, i.e. coal ash (ZUK-1) from Institute of Geochemistry, Irkutsk (Russia), bone ash (NIST 1400) from National Institute of Standards and Technology (USA), and two sewage sludge (nos. 101 and 102) from National Institute of Agro-Environmental Science, Ministry of Agriculture, Forestry and Fisheries (Japan). The recoveries for the elements were: Na (94–97%), Mg (93–96%), Al (95–103%), K (101–106%), Ca (95–99%), Ti (102–110%), V (97–101%), Cr (106–115%), Mn (91–98%), Fe (102–108%), Co (95–99%), Ni (93–100%), Cu (98–106%), Zn (103–110%), As (99–100%), Sr (100–102%), Cd (101–103%), Ba (96–99%), Pb (99–101%), respectively.

3. Results and discussion

3.1. Pre-washing effects

In the metal extraction processes, the most economic approach is simply washing the fly ash with water to separate

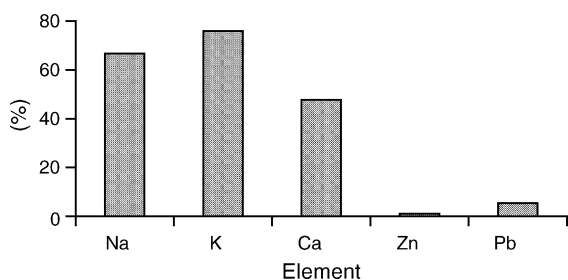


Fig. 1. Leaching percentage of metals by distilled water in the pre-treatment process. Liquid/solid = 20 ml/g, contact time = 30 min, temperature = 20 °C.

insoluble minerals from water-soluble compound. In this way, a large amount of liquor can be saved in the subsequent acid washing process. Fig. 1 illustrates that a large amount of Na, K, Ca were washed out from the ash during the pre-washing treatment, with leaching percentages of 67%, 76% and 48%, respectively. Furthermore, approximate 1% Zn and 5% Pb were also leached out into the leachate. Though in low concentrations, 32% Sr and 38% Ba were also leached out into the solution, which were not shown in Fig. 1. XRD diffraction pattern of the fly ash indicates that some of the Na and K in the ash are in the crystal forms of NaCl and KCl, which are easy to dissolve into water, but no crystalline peaks for Ca are found, implying that Ca in the ash exists in its amorphous form (Fig. 2). Calcium is mainly introduced into the ash from exterior since a solution suspension of lime is used as the neutralizer for treating the flue acid gas from the incinerator. Thereby, Ca in the ash is supposed to be in the forms of CaCl₂, Ca(OH)₂, CaS, Ca(HS)₂, CaSO₄, etc.

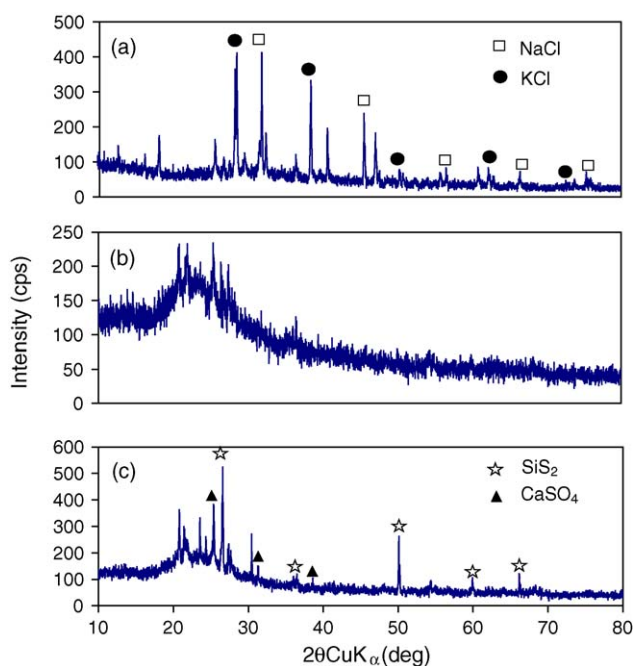


Fig. 2. XRD patterns of untreated and hydrothermal treated IFA. (a) Original IFA; (b) 5 h treated IFA; (c) 40 h treated IFA. Hydrothermal conditions: liquid/solid = 10, temperature = 150 °C.

Table 1

Leaching of elements from the fly ash by distilled water in the pre-treatment process (mg l⁻¹)

	5 min	10 min	30 min	1 h	5 h	10 h	20 h
Na	832	842	889	894	832	837	837
Mg	0.03	0.01	2.91	0.14	0.07	0.08	0.01
Al	0.21	0.24	0.54	0.75	0.33	0.14	0.14
K	1498	1492	1544	1487	1425	1555	1482
Ca	5512	5512	5668	5408	5106	5408	5356
Cu	1.55	1.08	0.85	0.65	0.08	0.06	0.32
Zn	20.2	9.72	8.62	6.64	5.23	6.53	5.40
As	4.14	0.31	0.08	0.04	0.07	0.08	0.07
Sr	5.77	4.33	4.49	4.40	4.24	4.79	4.70
Ba	1.26	1.33	1.39	1.38	1.26	1.46	1.41
Pb	3.48	2.88	2.56	2.19	1.47	1.72	1.87

Liquid/solid = 20 ml/g.

The extraction of metallic elements, such as Na, K, Ca, from the ash rapidly reached maximum value, and longer time contact of the ash with water could only reduce the extraction amount of some of the hazardous heavy metals (Table 1). For example, the extraction amount of Zn and Pb at 5 min was 20.2 and 3.48 mg l⁻¹, compared to the amount of 5.40 and 1.87 mg l⁻¹ at 20 h. During the pre-washing process, the pH value of the suspension rapidly changed from around 5.5 to around 12.5 within 5 min, and was almost changeless during the 20 h vibration. Hence, it is supposed that part of the previously extracted metals precipitated in the alkaline solution along with the contact time.

Moreover, it is noted from Table 1 that the extraction amount of As and Pb at 5 min was 4.14 and 3.48 mg l⁻¹, respectively, which surpassed the standard value of 0.1 mg l⁻¹ for wastewater treatment regulated by many developed countries including Japan [18]. However, the concentration of As at 30 min reduced to 0.08 mg l⁻¹ along with the contact time, which could attribute to the formation of Ca(HAsO₃)₂·nH₂O and Ca₃(AsO₄)₂·nH₂O [18]. Accordingly, it is suggested that the optimum contact time is 30 min for the pre-washing process. In this case, the washing solution could be simply drained off after Pb disposal.

3.2. Acid selection

In this section, extraction experiments at room condition and under hydrothermal treatment were simultaneously carried out. Similar trends for the five types of tested acids were obtained for the two conditions, thus only the results of hydrothermal treatment were presented in Table 2.

Organic acids are known to selectively extract metals from various materials. In this study, Oxalic acid and citric acid were tested for the extraction experiments. Generally, metal extraction effects from fly ash by organic acids are lower than those of mineral acids. The two types of organic acids are generally effective for Na, Mg, K, Mn, Sr extraction. Oxalic acid has the least extraction effect for many of the heavy metals compared with other acids, especially for Ca, Ti, Zn, Cd, Pb extraction. Additionally, considering the high cost of organic acids comparing with mineral acids, we do not recommend organic acids as metal leaching reagent for fly ashes. On the other hand, it was

Table 2
Comparison of element leaching effects by different acids under hydrothermal treatment (%)

	HCl	H ₂ SO ₄	HNO ₃	Oxalic acid	Citric acid
Final pH	2.63	2.41	2.63	3.52	4.61
Na	62.1	23.2	54.9	78.9	62.0
Mg	50.0	48.1	49.7	50.9	29.9
Al	28.9	28.8	28.5	7.79	6.83
K	56.8	52.1	54.3	49.2	52.5
Ca	77.7	7.85	76.5	1.84	48.8
Ti	6.80	8.18	6.70	1.03	3.80
V	13.1	43.6	2.94	8.48	6.69
Cr	13.6	19.3	7.59	16.6	8.17
Mn	35.6	38.1	35.3	36.6	32.4
Fe	10.1	11.1	10.1	6.85	8.63
Co	13.0	11.2	12.9	5.90	6.12
Ni	18.2	10.3	13.5	3.51	2.87
Cu	25.8	25.5	24.2	0.48	0.96
Zn	47.8	47.5	47.6	9.23	41.9
As	36.5	45.8	35.7	63.0	7.58
Sr	89.6	83.2	88.5	56.9	36.1
Cd	99.8	97.3	99.5	16.6	34.6
Ba	10.5	6.54	9.24	6.50	3.11
Pb	58.6	2.82	58.6	12.2	44.4

Acid concentration = 1 M, liquid/solid = 5 ml/g, temperature = 150 °C, treatment time = 5.

found that not all the organic anions remain in the solution after the extraction process, e.g. the concentrations of oxalic and citric anions in the filtrate were 0.75 and 0.89 mol l⁻¹, respectively.

Comparatively, mineral acids are much more effective for metal extraction from the ash. H₂SO₄ is not efficient for Ca and Pb extraction because of the formation of CaSO₄ and PbSO₄, e.g. the extraction percentages of Ca and Pb by H₂SO₄ were 7.85% and 2.82%, compared to those of around 77% and 58% by HCl and HNO₃, respectively. Similar extraction effects for HCl and HNO₃ were found with the exception of the lower extraction percentages for V, Cr and Ni by HNO₃. In addition, it is understood that hydrochloric acid is easy to handle at low cost, hence we recommend this acid as extraction reagent for fly ash. After the extraction process, no significant change of Cl⁻ and NO₃⁻ concentrations were found, but the concentration of SO₄²⁻ in the filtrate reduced to 0.72 mol l⁻¹, indicating that part of SO₄²⁻ ion was transferred into the residue as precipitates such as CaSO₄ and BaSO₄. Furthermore, distilled water was also tested for metal extraction under hydrothermal treatment, but no significant amount of elements was extracted.

3.3. Comparison of metal extraction effects under hydrothermal treatment and at room condition

Metal extraction effects under hydrothermal and room conditions at liquid/solid ratios of 3:1, 5:1, 10:1 (ml:g) were examined. Only the results of 5:1 were illustrated in Fig. 3 since similar trends for the three cases were found. Hydrothermal treatment is much more effective for metal extraction compared to room condition. For example, at room condition, the extraction of Al, V, Cr, Fe, Cu and As could not be detected, but around 10–35% of

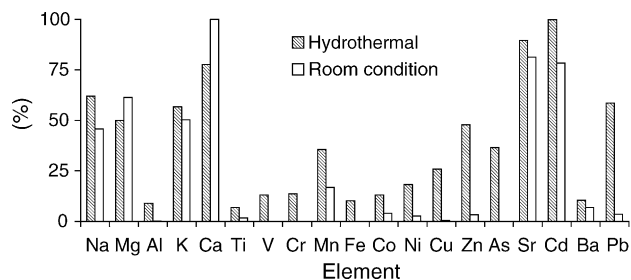


Fig. 3. Element leaching percentages by 1 M HCl solution under hydrothermal treatment and room condition. Hydrothermal conditions: liquid/solid = 5 ml/g, temperature = 150 °C, treatment time = 5 h; room conditions: liquid/solid = 5, temperature = 20 °C, treatment time = 5 h.

these elements could be leached out under hydrothermal condition. As one of the environmentally concerned hazardous metals, approximately 60% of Pb could be leached out compared to 3% at room condition. One interesting result from Fig. 3 is that almost 100% of Ca could be leached out at room condition, while 77% of Ca was leached out under hydrothermal treatment. This could attribute to the special forms of the acid and the mechanisms of hydrothermal process. It has been reported that hydrochloric acid is almost completely ionized at room temperature, but aqueous molecular HCl dominates at high temperature such as above 250 °C [19]. Accordingly, it is supposed the hydrochloric acid was partly ionized under the hydrothermal conditions in the present study. This state could restrain the consumption of the acid by Ca. On the other hand, it is understood that one of the main mechanisms of hydrothermal process is via dissolution, i.e. accelerate the dissolution of the ash into the liquor. Thus, it is concluded that hydrochloric acid preferentially reacts with Ca at room condition, but simultaneously react with all the metal in the ash under hydrothermal condition. Hydrothermal treatment promoted the reaction of acid with hazardous metals such as Cr, Cd, Pb, and furthermore, slowed down the consumption speed of the acid. This was well explained by the pH changes during the extraction processes. Fig. 4 depicts the pH changes under hydrothermal treatment and at room condition. The pH of the leachate increased from 0.17 (pH of the original liquor) to around 5 within 30 min at room condition,

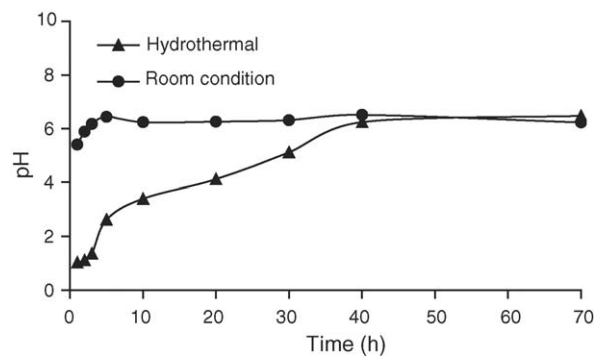


Fig. 4. pH changes during metal leaching process by 1 M HCl solution. Liquid/solid = 5 ml/g, hydrothermal temperature = 150 °C, room temperature = 20 °C.

Table 3
Element leaching percentages by 1 M HCl solution along with hydrothermal treatment time (%)

	Liquid/solid = 5					Liquid/solid = 10				
	3 h	5 h	10 h	40 h	70 h	3 h	5 h	10 h	40 h	70 h
Final pH	1.36	2.63	3.41	6.24	6.48	0.92	1.32	2.41	5.96	6.13
Na	30.1	62.1	53.0	49.8	47.7	55.4	102	66.1	68.1	96.3
Mg	36.6	50.0	27.7	20.2	10.2	75.8	103	103	107	105
Al	20.2	28.9	4.59	0.34	0.10	50.3	74.6	32.8	25.2	9.81
K	30.8	56.8	45.0	48.7	69.7	49.3	89.2	57.8	55.1	69.6
Ca	61.6	77.7	81.6	87.7	86.6	69.8	98.9	101	100	102
Ti	0.56	6.85	2.25	1.28	1.34	2.89	65.8	19.0	6.61	6.54
V	2.21	13.1	8.25	6.35	5.98	26.4	76.8	29.2	28.6	54.9
Cr	12.0	13.6	11.5	12.6	12.8	21.4	27.3	28.7	27.8	22.4
Mn	24.9	35.6	18.9	9.82	5.99	72.2	91.4	80.4	106	103
Fe	14.0	10.1	7.16	0.13	0.21	35.2	62.9	63.7	60.5	65.7
Co	1.35	13.0	4.21	3.18	1.24	60.6	85.7	48.2	36.4	62.0
Ni	17.5	18.2	5.66	2.49	0.04	41.0	105	104	104	105
Cu	37.4	25.8	10.4	6.86	0.49	42.6	51.0	24.2	3.38	5.93
Zn	37.2	47.8	25.6	11.5	2.04	71.8	109	67.4	86.6	20.8
As	28.3	36.5	29.1	18.8	9.06	39.6	88.1	63.9	32.0	58.3
Sr	40.5	89.6	52.0	57.6	69.4	76.0	102	82.5	58.2	32.5
Cd	102	99.8	79.2	75.3	73.0	102	105	103	103	102
Ba	6.59	10.5	4.54	41.9	45.6	7.57	88.6	70.1	76.1	79.9
Pb	40.5	58.6	14.0	8.95	2.00	47.0	96.5	33.8	10.1	7.36

Hydrothermal temperature = 150 °C.

indicating that the acid was rapidly consumed by Ca. However, under hydrothermal condition, the solution pH changed very slowly, e.g. changed to around 1 within 1 h and around 2.5 within 5 h. The acid was almost completely consumed after 40 h hydrothermal treatment.

3.4. Effect of hydrothermal treatment time on metal extraction

The effect of hydrothermal treatment time on metal extraction from the ash was examined at liquid/solid ratios of 5:1 and 10:1 (ml:g). Table 3 shows that almost the same trends for the two ratios were found. The maximum metal extraction percentages were obtained at 5 h, and further hydrothermal treatment conversely reduced the extraction effect. For example, at a liquid/solid ratio of 5:1 (ml:g), 99.8% Cd and 58.6% Pb could be extracted into the leachate at a period of 5 h hydrothermal treatment, but the extraction percentages reduced to 73% and 2% respectively after 40 h treatment. Under hydrothermal condition, the behaviors of metallic elements in the ash follow the two ways, i.e. hydrothermal leaching firstly and then hydrothermal precipitation along with the treatment time. This viewpoint is strongly supported by the XRD patterns and SEM photographs of the ash obtained at different hydrothermal treatment times. Fig. 2 depicts that many of the crystalline components were destroyed after 5 h hydrothermal treatment, indicating that metallic elements were leached out from the ash into the leachate. However, many new peaks appeared after 40 h hydrothermal treatment. These peaks are mainly the crystalline peaks of SiS₂ and CaSO₄. It is of concern how the SiS₂ crystal was formed under the condition of the present study. The ash used in this study typically contains about 4% Si and 1% S, part of both elements might be

firstly leached out in the hydrochloric acid solution and gradually crystallized along with the hydrothermal treatment. The *d*-space values for the SiS₂ crystal were about 2.22–3.59 Å calculated by Bragg's equation ($n\lambda = 2d \sin \theta$). These data reflect the average intersegmental distance of the SiS₂ crystals. SEM images (Fig. 5) of the ashes under various treatments indicate that metal leaching mechanisms are quite different under these conditions.

Table 4
Element extraction percentages by 1 M HCl solution at different hydrothermal treatment temperatures (%)

	100 °C	120 °C	150 °C	180 °C	200 °C
Final pH	1.57	1.26	2.63	1.74	1.71
Na	31.2	31.3	62.1	40.8	8.31
Mg	35.5	34.9	50.0	33.1	25.6
Al	18.9	20.2	28.9	15.0	0.19
K	32.2	33.2	56.8	42.9	47.6
Ca	59.8	55.3	77.7	57.6	65.7
Ti	0.36	0.58	6.80	0.28	0.11
V	29.5	31.0	13.1	19.5	1.65
Cr	6.65	6.85	13.6	3.67	0.65
Mn	23.9	24.9	35.6	25.2	20.7
Fe	12.2	13.0	10.1	11.7	4.65
Co	11.2	9.29	13.0	9.26	5.55
Ni	22.4	24.8	18.2	15.6	14.5
Cu	27.8	27.6	25.8	18.9	3.58
Zn	37.1	35.6	47.8	31.8	24.6
As	36.9	38.9	36.5	67.2	17.1
Sr	45.3	43.8	89.6	48.8	55.1
Cd	94.9	97.9	99.8	89.4	62.0
Ba	2.50	2.88	10.5	4.04	5.59
Pb	30.8	31.5	58.6	23.0	2.06

Liquid/solid = 5 ml/g, treatment time = 5 h.

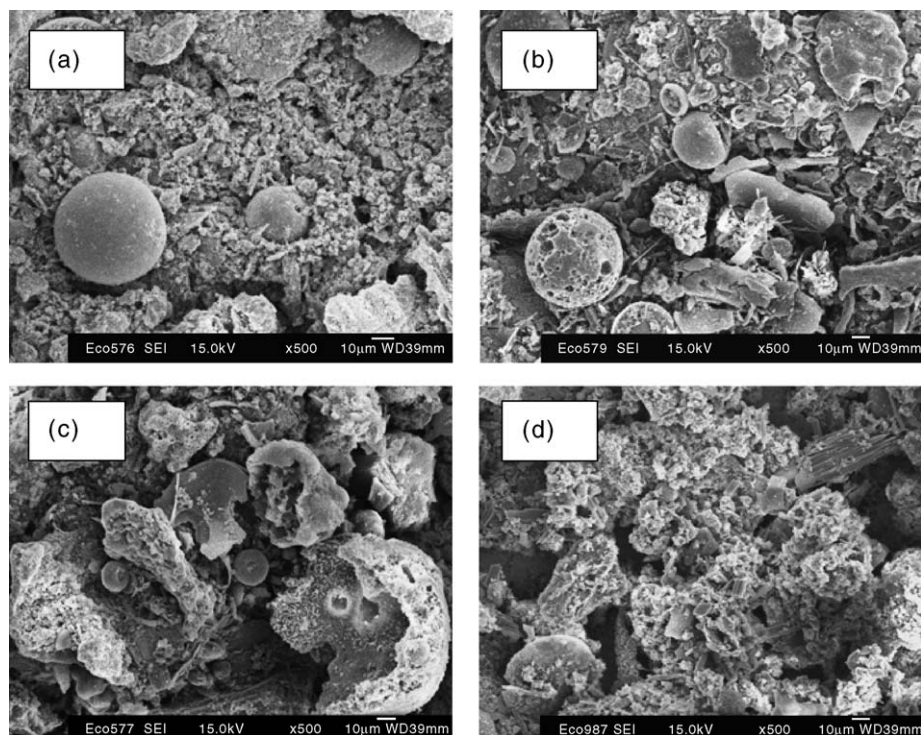


Fig. 5. SEM images of (a) pre-treated fly ash, (b) 1 M HCl treated fly ash at room condition, (c) hydrothermal treated fly ash by 1 M HCl for 5 h, (d) hydrothermal treated fly ash by 1 M HCl for 40 h. Room conditions: temperature = 20 °C, liquid/solid = 10, contact time = 5 h; hydrothermal conditions: temperature 150 °C, liquid/solid = 10.

At room temperature, the leaching is a surface controlled process (Fig. 5b), but under hydrothermal condition, the subcritical acidic solution could diffuse into the ash particles thus split them into fragments (Fig. 5c). This process could greatly accelerate

the leaching effect of metals inside the particle into the liquor. Furthermore, the crystals such as SiS_2 and CaSO_4 after long time hydrothermal treatment were also confirmed in SEM image (Fig. 5d).

Table 5
Effect of liquid/solid ratio on element leaching by 1 M HCl solution under hydrothermal treatment

	Liquid/solid ratio							
	3:1		5:1		10:1		20:1	
	mg l ⁻¹	%	mg l ⁻¹	%	mg l ⁻¹	%	mg l ⁻¹	%
Final pH	6.77		2.63		1.32		0.52	
Na	1484	45.6	1204	62.1	1004	102	520	99.8
Mg	603	16.5	1085	50.0	1136	103	592	101
Al	275	2.90	1637	28.9	2142	74.6	1592	105
K	1507	45.4	1121	56.8	894	89.2	544	103
Ca	13720	32.8	19376	77.7	12516	98.9	6844	102
Ti	18.9	1.18	65.2	6.82	319	65.8	230	89.5
V	0.32	9.51	0.26	13.1	0.78	76.8	0.53	98.6
Cr	1.73	2.90	4.85	13.6	4.94	27.3	7.11	74.2
Mn	12.1	3.75	68.8	35.6	89.7	91.4	54.7	105
Fe	164	6.40	155	10.1	487	62.9	425	104
Co	0.03	0.46	0.42	13.0	1.42	85.7	0.87	99.5
Ni	0.10	0.78	1.34	18.2	3.89	104	2.01	101
Cu	0.93	0.31	46.4	25.8	46.5	51.0	49.6	103
Zn	164	2.86	1636	47.8	1894	109	906	98.5
As	0.91	12.6	1.57	36.5	1.93	88.1	1.12	96.7
Sr	34.5	52.3	35.2	89.6	20.1	101	10.5	99.7
Cd	37.0	78.6	28.0	99.8	14.9	105	7.88	105
Ba	3.19	24.3	0.82	10.5	3.51	88.6	2.03	96.8
Pb	12.8	4.03	111	58.6	92.7	96.5	52.7	104

Temperature = 150 °C, treatment time = 5 h.

3.5. Effects of hydrothermal temperature and liquid/solid ratio on metal extraction

The ionization state of hydrochloric acid under hydrothermal condition relates closely to temperature, hence the leaching speed of metals from the ash was greatly affected by the hydrothermal temperatures. Table 4 indicates that the optimum hydrothermal treatment temperature is 150 °C. At lower temperature, the ash particles could not split, and conversely, at higher temperature, the acid is not effectively ionized, both of which restrict the chemical reactions of metal extraction. Metal extraction from ash sample under hydrothermal condition is a complicated process, including competition among dissolution, neo-formation and precipitation.

The effect of liquid/solid ratio on metal leaching efficiency was examined with the ratios change from 3:1 to 20:1 (ml:g) (Table 5). At lower liquid/solid ratio, such as 3:1 and 5:1 (ml:g), only limited amount of metals was leached out. Over addition of hydrochloric acid into the reaction system could sufficiently extract metals from the ash, but the resulting residue and the leachate were extremely acidic, requiring high-level wastewater and residue control, e.g. the pHs of the leachates at liquid/solid ratios of 10:1 and 20:1 (ml:g) were 1.32 and 0.52, respectively. For liquid/solid ratio of 5:1 (ml:g), the final pH of the leachate was 2.63, indicating that there was enough acid available, but low metal leaching ratios were still obtained since the reaction solution was close to saturation due to the lack of liquid. According to the results in Table 5, a suitable liquid/solid ratio of 10:1 (ml:g) is recommended. In this case, most of the major metals, such as Na, Mg, Al, K, Ca are leached out, and the leaching percentages for environmental concern metals, such as Cd and Pb, are 100% and 97%, respectively.

It can be seen from Table 5 that Cr was difficult to be extracted, e.g. only 27% and 74% of Cr were leached out at liquid/solid ratios of 10:1 and 20:1 (ml:g), respectively. The effective extraction method of Cr from the ash will be a new theme for future study.

4. Conclusions

An effective process for metal extraction from MSW incinerator fly ash was established in the present work. The process consists of two steps, i.e. pre-washing and hydrothermal extraction. Pre-washing could extract 67% Na, 76% K, 48% Ca, 5% Pb and 1% Zn from the ash, respectively. The optimum pre-washing time is 30 min. Longer time washing will reduce the extraction effect for some of the hazardous heavy metals. XRD patterns indicate that some of the Na and K in the ash are in the forms of crystalline of NaCl and KCl, but Ca exists in its amorphous form.

Hydrochloric acid is the most effective extraction reagent among the five types of tested acids. Under hydrothermal condition, hydrochloric acid simultaneously reacts with all the metals in the ash, but the acid preferentially reacts with Ca under room condition. SEM images indicate that hydrothermal treatment could split the ash particles into fragments hence promotes the reaction of the acid with hazardous metals such as Cr,

Cd, Pb, and furthermore, slows down the consumption of the acid.

The maximum metal extraction percentages were obtained at 5 h, and longer hydrothermal treatment conversely reduced the extraction effect. Therefore, it is suggested that the behaviors of metallic elements in the ash follow the two ways under hydrothermal condition, i.e. hydrothermal leaching and hydrothermal precipitation. This viewpoint was supported by the formation of crystals such as SiS₂ and CaSO₄ after 40 h hydrothermal treatment. The optimum hydrothermal treatment temperature and liquid/solid ratio were found to be 150 °C and 10:1 (ml:g), respectively. After hydrothermal treatment at optimum conditions, the residue mainly contains Si, S, C, P and O with a little amount of Cr, thus has the potential to be used for silicon and sulfur fertilizer manufacture after further removal of Cr.

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