Investigation of accelerated and natural carbonation of MSWI fly ash with a high content of Ca

Lei Wang [a,b,*], Yiying Jin [a], Yongfeng Nie [a]

[a] *Department of Environmental Science and Engineering, Tsinghua University, Beijing 100084, China*
[b] *Key Laboratory of Energy of Liaoning, Shenyang Institute of Aeronautical Engineering, Shenyang 110034, China*

ARTICLE INFO

ABSTRACT

The application of accelerated carbonation and natural carbonation to treat municipal solid waste incinerator (MSWI) fly ash was presented. The influence of reaction time and the liquid-to-solid (L/S) ratio, which both affect the reactivity of CO_2, was evaluated to determine their impact on the quality of carbonation. The optimum carbonation reaction of fly ash was found to occur when an L/S of 0.25 was used. Carbonation decreased the leaching of Pb, Cu, Zn and As, but increased the leaching of Cd and Sb. Based on the leaching of these six heavy metals, the optimum pH of the carbonated fly ash was 9.5–10.5. The release of soluble salts such as SO_4, Cl and F changed little following carbonation, and their release occurred independently of pH. The release potential and leaching behavior of carbonated fly ash were further evaluated using the three-step sequential extraction procedure proposed by the commission of the European Communities Bureau of Reference (BCR). The results of the BCR analyses revealed that carbonation exerted a significant effect on the heavy metal fractions in steps 1 and 2, but little effect on the distribution of heavy metals in step 3 and residue fraction. Physical and chemical changes induced by carbonation were presented and discussed.

1. Introduction

The present strategy of China for waste management favours incineration over direct landfilling, by far the most dominant waste management option. Treatment of MSW by incineration provides mass and volume reduction, disinfection, reduction of organic matter and the possibility of energy recovery [1,2]. While the cleaning of incineration flues gases generates residues equal to 3–5 wt% of incinerated waste. Indeed, there are currently 67 MSW incineration plants in China with a total processing capacity of 33,000 tonnes per day. In such facilities, the flue gas of the incinerators is usually treated with semi-dry lime and activated carbon to remove the acidic gases and dioxins. In China, the fly ash and the Air Pollution Control residues are commonly collected together and named as fly ash. As a result, it has been estimated that approximately 300,000–500,000 tonnes of fly ash are produced in China each year. Due to the high levels of dioxins, soluble salts and heavy metals present in MSWI fly ash, fly ash is classified as hazardous waste in China and must be treated before final disposal. The presence of unreacted lime gives fly ash a high alkalinity, and the fly ash has a high content of chloride (usually 10–20%) which has strong complexing capacity of a number of trace metals. These two factors resulted in an increased potential for leaching of amphoteric heavy metals, which is important when landfill is concerned. Due to the reasons mentioned above, finding new treatment techniques that result in the demobilization of critical heavy metals in MSWI fly ash are necessary.

Recent research on carbonation [3–7] and natural weathering [8,9] of MSWI residues demonstrate these treatment to possibly decrease the leaching behavior of heavy metals, i.e., Pb [8–11], Cr [11], Cd [11], Cu [10] and Zn [8,9,11]. However, some critical heavy metals may still exceed the limit imposed by governmental regulations for non-hazardous waste or for disposal in non-hazardous waste landfills after carbonation [12]. Furthermore, the level of soluble salts in carbonated fly ash has been found to be higher than the landfill acceptance limits for hazardous waste [2]. Additionally, soluble salts often remain mobile following carbonation [6].

In this study, accelerated carbonation and natural carbonation are studied on the MSWI fly ash with a high Ca content to evaluate their potential for decreasing the leaching of heavy metals and soluble salts. From view point of easy engineering operation, experimental parameters including reaction time and the liquid-to-solid (L/S) ratio were chosen. Specifically, we evaluated the leaching of the carbonated fly ash for the following components: Cu, Pb, Cd, Zn, Sb, As, Cl^-, F^- and SO_4^{2-}.

* Corresponding author. Tel.: +86 10 6279 4697; fax: +86 10 6279 4147.
E-mail address: wlei05@mails.tsinghua.edu.cn (L. Wang).

Table 1
Chemical composition in major and trace elements of the MSWI fly ash.

Compound	wt.%	Heavy metal	wt./mg kg^{-1}	Heavy metal	wt./mg kg^{-1}
CaO	53.02	Zn	5278.5	As	20.34
SiO$_2$	4.36	Pb	2251.4	Mo	17.14
Al$_2$O$_3$	0.94	Cu	1426.5	Zr	11.17
Fe$_2$O$_3$	1.75	Sb	650.5	Ag	8.12
Na$_2$O	5.71	Sn	534.85	Bi	6.66
K$_2$O	5.46	Ba	274.9	Nb	5.42
MnO	0.30	Sr	125.65	Hg	2.77
TiO$_2$	0.56	Cr	103.21	Ga	2.46
P$_2$O$_5$	0.26	Cd	96.97	Ce	0.39
Cl	18.88	Ni	73.25	La	0.28
SO$_3$	5.18	W	22.14	Nd	0.08
F	1.15	Co	21.43		

2. Materials and methods

2.1. Fly ash description

The fly ash samples used in this study were taken from a MSWI facility located in Suzhou (China). The incinerator, capable of processing 1000 tonnes of local municipal solid waste per day, is equipped with air pollution control devices consisting of a cyclone, a semi-dry flue gas cleaning tower, an activated carbon absorption reactor, and a fabric baghouse filter. The fly ash was homogenized, oven dried at 105 °C for 24 h, and then its chemical composition characterized. The major components in the fly ash are shown in Table 1, with CaO and SiO$_2$ comprising 53.02% (w/w), 4.36% (w/w) of the total, respectively. The fly ash has a high chloride and SO$_3$ content, contributing about 18.8% (w/w) and 5.18% (w/w) of the total, respectively. Table 1 also shows the trace metal concentrations in the fly ash, which were determined by inductively coupled plasma and mass spectrometry (ICP-MS, SERIES) following microwave digestion. The results revealed that Zn, Pb, Cu, Sb, Sn and Ba were the most abundant trace metals in the MSWI fly ash, Cd and As were present in concentrations of 96.97 mg kg^{-1} and 20.34 mg kg^{-1}, respectively. The accuracy of the ICP-MS was less than 1.5%RSD.

2.2. Accelerated carbonation of fly ash

All experiments were conducted at room temperature in a glass cylinder with an internal volume of approximately 1000 mL that was connected to an analytical grade CO$_2$ container. Prior to carbonation, the MSWI fly ash was dried at 105 °C for 24 h to a constant weight, after which 200 g were mixed with water at various liquid-to-solid (L/S) ratios and then placed into the reactor. The air in the chamber was then removed, after which it was filled with CO$_2$. After the determined reaction time, the fly ash was removed and weighed. Next, 10% of the fly ash was removed, dried at 105 °C for 24 h and then utilized for further analysis. The remaining fly ash was reintroduced into the cylinder, after which the cylinder was rapidly sealed and subjected to carbonation as described above. The weight gain of the dried fly ash was measured in triplicate.

The following two parameters were evaluated to characterize carbonation efficiency:

- L/S ratio: it has been reported that the optimum L/S ratio is 0.2 for the carbonation of cement-solidified wastes [13,14]; therefore, L/S ratios of 0.1, 0.25 and 0.5 were evaluated in this study.
- Reaction time: the reaction time ranged from 2 h to 240 h to characterize the change in the pH of the fly ash that occurred.

2.3. Natural carbonation of fly ash

To evaluate the carbonation efficiency, the products formed by natural carbonation (NC) were compared to those formed by accelerated carbonation. To accomplish this, fly ash samples were placed uniformly in the bottom of a round flat-bottomed pallet with a thickness of approximately 2 mm while leaving the upper part of the pallet open to the atmosphere. Every 4 d, samples were removed and prepared for further analysis. The experiment last for 2 months.

2.4. Leaching tests

Leaching tests were performed at an initial water-to-carbonated fly ash ratio (w/s) of 10 L kg^{-1} using distilled water and following the Solid Waste Extraction Procedure for Leaching Toxicity (GB/5086.2-1997). The pH of the solution was analyzed immediately, after which the metal concentrations in the leachates were evaluated by ICP-MS. The Cl$^-$, sulphate and F$^-$ concentrations were determined by Ionic Chromatography (Dionex-100).

2.5. Water washing test of the carbonated fly ash

A water washing test was conducted at different w/s ratios using deionized water and following the same experimental procedure that was used for the leaching test.

2.6. BCR sequential extraction

2.6.1. Reagents and apparatus

The extractant solution was prepared from analytical grade regents and was checked for possible trace metal contamination. Sulfuric acid, nitric acid and hydrogen peroxide were analytical reagent grade. The elements concentration in all extracts were analyzed by ICP-MS. Blank extractions (without sample) were carried out throughout the complete procedure.

The sequential extraction procedure has already been described in more detail elsewhere and the four steps was given in Table 2 [15].

3. Results and discussion

3.1. Carbonation

3.1.1. Weight gain

The carbonation mechanism is often described as a process comprised of at least two steps that includes a prior CO$_2$ absorption in water followed by the actual carbonation reaction in aqueous medium [7,11]. The primary reaction is known to be the Ca(OH)$_2$ carbonation in aqueous medium, which corresponds to
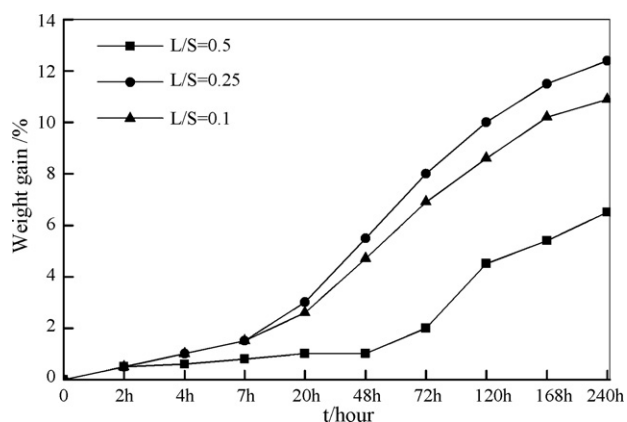
Table 2
Sequential extraction procedure.

Extraction step	Reagents	Extraction conditions (nominal target phases)
1	Acetic acid (0.11 mol L^{-1})	Exchangeable, water and acid-soluble (carbonates)
2	Hydroxylammonium chloride (0.1 mol L^{-1}) adjusted to pH 2 with HNO$_3$	Easily reduced (iron/manganese oxyhydroxides)
3	Hydrogen peroxide (8.8 mol L^{-1}), ammonium acetate (1 mol L^{-1}) adjusted to pH 2 with HNO$_3$	Oxidizable (organic matter and sulfides)
4	Aqua regia, hydrofluoric acid, nitric acid	Residual fraction

Fig. 1. Weight gains of fly ash following carbonation at different L/S ratios.

the following expression [7,11,16]:

$$Ca(OH)_2(aq) + CO_2(aq) \rightarrow CaCO_3(s) + H_2O(I) \qquad (1)$$
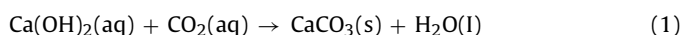
The formation of calcite ($CaCO_3$) induces an increase in sample mass. Fig. 1 shows the weight gain of samples with different L/S ratios. The maximum weight gain occurred at an L/S ratio of 0.25, while the minimum weight gain occurred at an L/S ratio of 0.5. This occurred because water is required for the carbonation reaction to proceed, but too much water hinders the diffusion of CO_2 into the pores of a solid. Pore water hydrates and dissolves the CO_2 and the Ca^{2+} ions from the solid phase so that they can react to form calcium carbonate. Although it has been reported that the optimum L/S ratio is between 0.06 and 0.20, successful carbonation using samples with L/S ratios as high as 0.35 has been reported [13,14].

3.1.2. pH of the fly ash after accelerated and natural carbonation

Carbonation is expected to reduce the alkalinity of the fly ash as the unreacted lime is transformed to calcium carbonate. The original pH of the fly ash was 12.1, which is very close to the pH of a solution saturated with $Ca(OH)_2$. Fig. 2 shows the change in pH that occurred following carbonation. Indeed, the carbonation process could be divided into two stages, an early stage, in which the pH of the fly ash changed only slightly until the $Ca(OH)_2$ was depleted, and a later phase that occurred after the depletion of the $Ca(OH)_2$. During the later phase, the pH of the leachates of samples subjected to accelerated carbonation decreased from 11.5 to 9 within a very short period. Given a long enough carbonation time, the final pH of the fly ash decreased to approximately 7.

3.1.3. Particle size distribution

The particle size distribution of the fly ash before and after carbonation was evaluated using a Laser Particle Size Analyzer (Mastersizer 2000) and the results are shown in Fig. 3. The volume percentage of small particles decreased and that of large particles increased after carbonation. The change in the specific surface area as well as in the mean diameter of the particles is shown in Table 3. The specific surface area of the original fly ash was 0.938 $m^2 g^{-1}$, while that of the fly ash with an L/S ratio of 0.25 that was subjected to accelerated carbonation for 240 h was only 0.216 $m^2 g^{-1}$, which
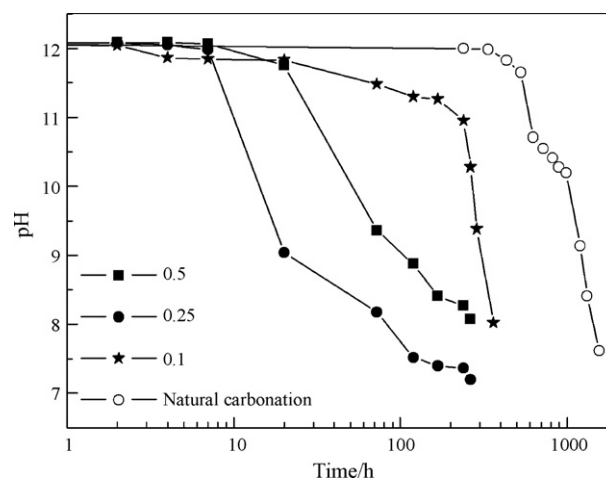

Fig. 2. pH of the fly ash after accelerated and natural carbonation for different lengths of time. Accelerated carbonation was performed at different L/S ratios (0.1, 0.25, 0.5).
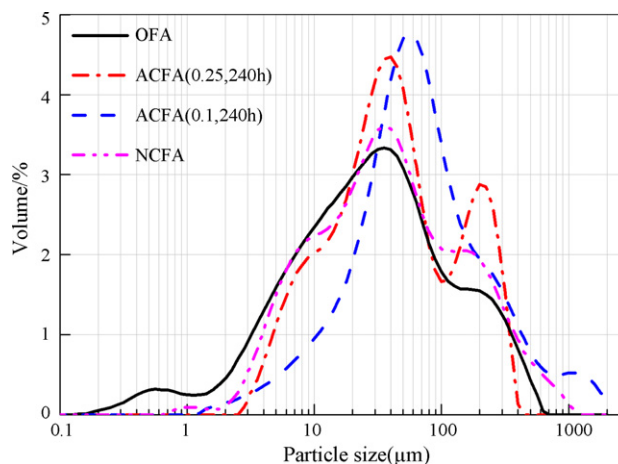

Fig. 3. Particle size of the fly ash before and after carbonation (OFA: original fly ash; ACFA: accelerated carbonated fly ash with different L/S ratios (0.25, 0.1) and with a carbonation time of 240 h; NCFA: natural carbonated fly ash with a carbonation time of 41 d).

was the minimum value observed after accelerated and natural carbonation.

3.1.4. Morphology

The morphology of the fly ash before and after carbonation was examined using an Ultra-high Resolution Scanning Electron Microscope (S-5500) and the results are shown in Fig. 4. Specifically, the original fly ash showed sheet morphology and contained more pores (Fig. 4(a)), whereas carbonation caused the sheet to become larger and irregular in shape, although no crystalline reaction products were identified. In addition, the L/S ratio had a strong effect on the particle morphology of the samples. As shown in Fig. 4(b), carbonation of samples with an L/S ratio of 0.5 and a carbonation time of 240 h resulted in the formation of loose particles. However, when

Table 3
Changes in particle size, the specific surface area and volume weight mean diameter.

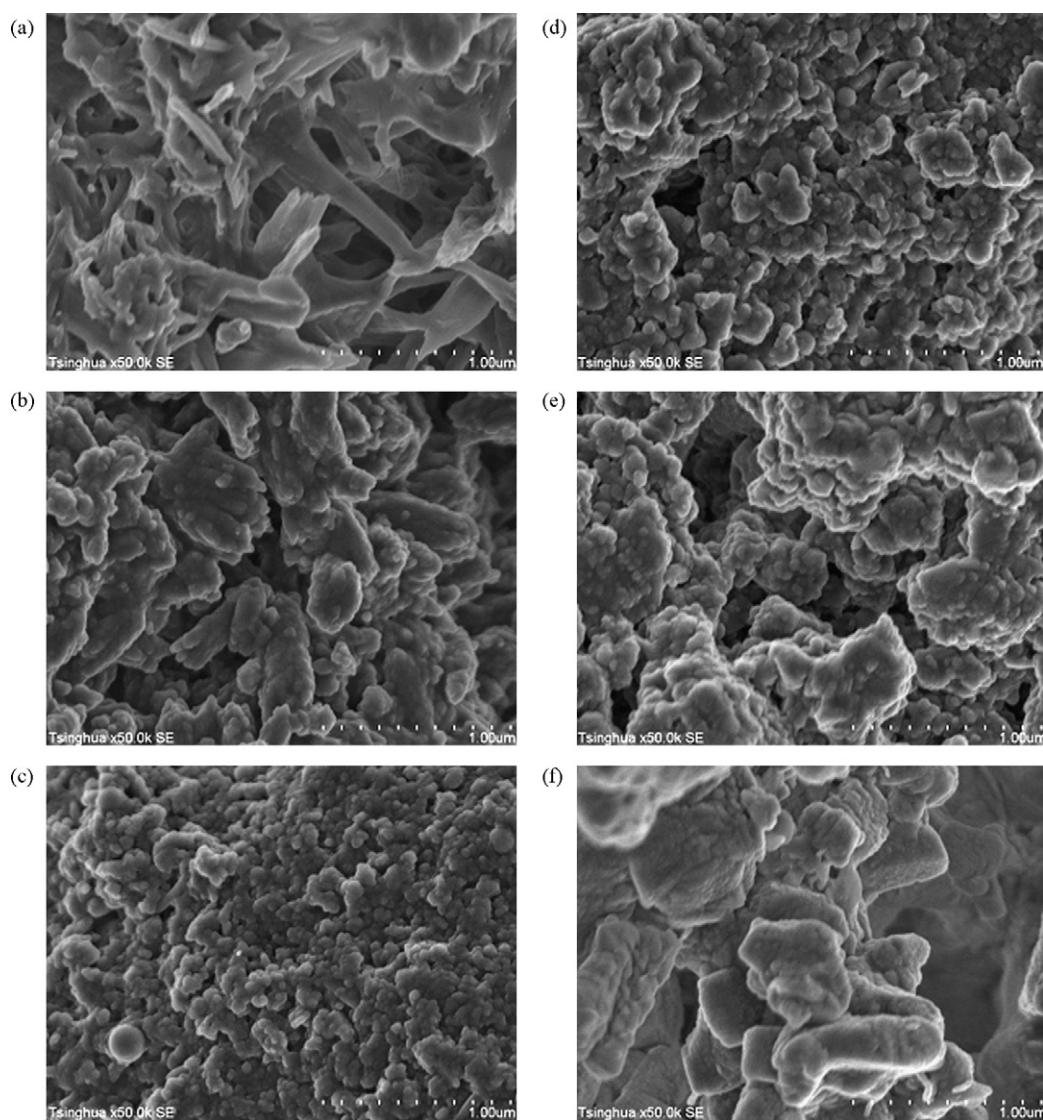| Ash	Particle size/μm	Specific surface area/$m^2 g^{-1}$	Volume weight mean diameter/μm
OFA	0.142–632.5	0.938	61.862
ACFA (L/S = 0.25, t = 240 h)	1.262–2000	0.216	136.993
ACFA (L/S = 0.1, t = 240 h)	2.825–399	0.288	70.342
NCFA (t = 41 d)	0.71–1261.9	0.34	94.622

Fig. 4. SEM of the fly ash before and after carbonation. (a) Original fly ash; (b) carbonated fly ash (L/S = 0.5, t = 240 h); (c) carbonated fly ash (L/S = 0.25, t = 240 h); (d) carbonated fly ash (L/S = 0.1, t = 240 h); (e) natural carbonated fly ash (t = 41 d); (f) carbonated fly ash after the leaching test (L/S = 0.1, t = 240 h).

the L/S decreased to 0.25 (Fig. 4(c)), newly precipitated solids were observed and the particles became more compact. Furthermore, when the L/S ratio decreased to only 0.1 (Fig. 4(d)), the particles were looser than those formed when the L/S ratio was 0.25, but were still more compact than those formed when the L/S ratio was 0.5. These results clearly demonstrate that the best carbonation conditions for the fly ash evaluated in this study were obtained when the L/S ratio was 0.25.

For natural carbonation, the pH of the fly ash decreased much slower than the accelerated carbonated fly ashes using as L/S of 0.25, 0.1 or 0.5. For example, the pH of a natural carbonated fly ash with a carbonation time of 41 d was only 10.19. Yet only under this pH ash carbonation had already occurred. As shown in Fig. 4(e), natural carbonated fly ash also became compact, but was less compact than that of accelerated carbonated fly ash produced using an L/S of 0.25 or 0.1. These findings are supported by the results of a study conducted by Ecke, who stressed that stabilization through carbonation occurred due to changes in pH as well as chemical composition [10]. Finally, the results of a leaching test of the carbonated fly ash revealed that the fly ash became more porous. Because the fly ash contained large amounts of soluble salts, during the leaching test, the soluble salts would enter into the solution (Fig. 4(f)).

3.1.5. Mineralogy

The crystalline minerals present in the solid residues were identified using X-ray powder diffraction (TTR-III diffractometer). Scans were conducted from 10.00° to 100.00° at a rate of 4°2θ/min. The X-ray diffraction analysis of the fly ash and carbonated fly ashes (Fig. 5) revealed that they were comprised of a mixture of predominantly Ca-rich compounds, amorphous glass and silicates. The fly ash was also rich in chloride compounds (NaCl, KCl, CaClOH). CaClOH is an intermediate phase formed during the absorption of HCl, which is described in reaction (2)–(4) [17]. Pb_2O_5 was identified in the original fly ash; the presence of calcite in the original fly ash may have been caused by partial, earlier weathering of the ash [8]. Table 4 lists the mineral changes in the fly ash that occurred as a result of carbonation. Following carbonation, the $Ca(OH)_2$ and CaClOH peaks disappeared, while many $CaCO_3$ peaks appeared in the carbonated samples. It is very likely that the peak corresponding to $Ca(OH)_2$ was no longer present due to reaction (1), whereas it is likely that the peak corresponding to CaClOH was no longer present due to reactions (5) and (6) [17]. According to reaction (6) the $CaCl_2$ was newly formed following the carbonation reaction. Yet no peak corresponding to $CaCl_2$ was identified in the diffractogram of the carbonated fly ashes, rather a peak of $KCaCl_3$ appeared. Maybe a
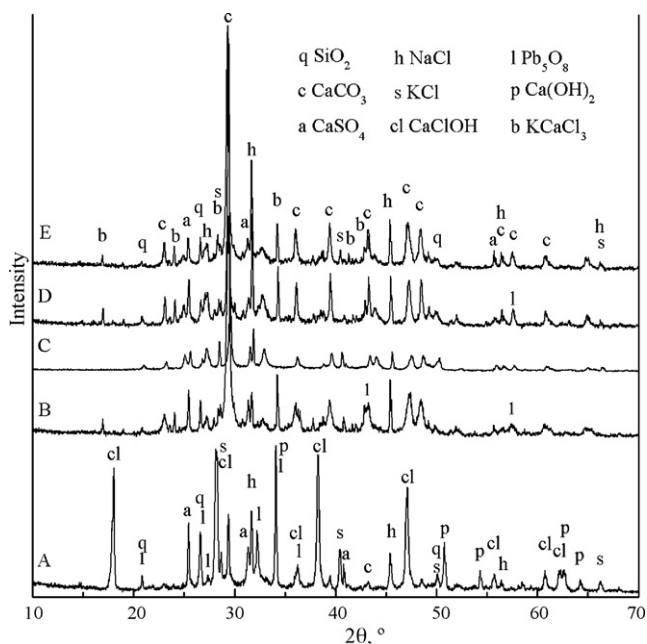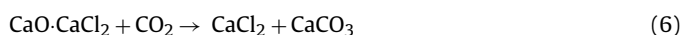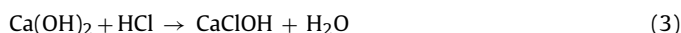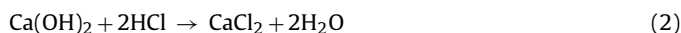
Fig. 5. Diffractogram of original fly ash and carbonated fly ash (A: original fly ash; B: accelerated carbonated fly ash with an L/S ratio of 0.5 and a carbonation time of 10 d; C: accelerated carbonated fly ash with an L/S ratio of 0.25 and a carbonation time of 10 d; D: accelerated carbonated fly ash with an L/S ratio of 0.1 and a carbonation time of 10 d; E: natural carbonated fly ash with a carbonation time of 41 d).

complex reaction involving KCl occurred during carbonation.

$$Ca(OH)_2 + 2HCl \rightarrow CaCl_2 + 2H_2O \tag{2}$$

$$Ca(OH)_2 + HCl \rightarrow CaClOH + H_2O \tag{3}$$

$$Ca(OH)_2 + CaCl_2 \rightarrow 2CaClOH \tag{4}$$

$$2CaClOH \rightarrow CaO \cdot CaCl_2 + H_2O \tag{5}$$

$$CaO \cdot CaCl_2 + CO_2 \rightarrow CaCl_2 + CaCO_3 \tag{6}$$

Carbonation also changed the mineralogy of heavy metals in the fly ash samples. For example, lead was identified as Pb_5O_8 in the original fly ash and as complex lead compounds in the carbonated samples. Owing to the low concentration of these species and the overlapping of peaks of complex lead compounds usually overlap with the main phases of the carbonated fly ash, the accurate evaluation of Pb or other heavy metal compounds in the carbonated fly ashes were difficult.

3.2. Leaching test

3.2.1. Heavy metals release

The effect of the accelerated carbonation treatment was also evaluated on the mobilization of some hazardous heavy metals (Cu,

Table 4
Inorganic compounds identified in original fly ash and carbonated fly ash.

Mineral	Formula	A	B	C	D	E
Quartz	SiO_2	√	√	√	√	√
Calcite	$CaCO_3$	√	√	√	√	√
Anhydrite	$CaSO_4$	√	√	√	√	√
Halite	NaCl	√	√	√	√	√
Sylvite	KCl	√	√		√	√
	CaClOH	√				
Portlandite	$Ca(OH)_2$	√				
	Pb_5O_8	√	√		√	√
	$KCaCl_3$		√		√	√

Pb, Cd, Zn, As, and Sb) in the leachates at their natural pH (Fig. 6). Plots describing the leaching of Pb, Zn and Cu revealed amphoteric behavior (Fig. 6(a–c)). Specifically, the metals were found to be soluble at low and high pH values and relatively insoluble at neutral pH values. A plot of the leaching of As also revealed amphoteric behavior to a certain degree (Fig. 6(d)). The pH dependent leaching of heavy metals observed in this study agree with the results of a study conducted by Meima et al. [3]. Indeed, the minimum solubility of Pb was found to occur between pH 8 and 10, whereas that of Cu and Zn occurred between pH 9 and 11 and that of As occurred at a pH of approximately 10.5. In addition, Cd and Sb were more soluble in carbonated than in un-carbonated samples (Fig. 6(e and f)), possibly due to the transition from $Cd(OH)_2$ to $CdCl_2$ [18].

The amount of Pb released from the samples decreased dramatically with carbonation (Fig. 6(a)). Indeed, although the Pb concentration in the leachate of the untreated fly ash was very high, after carbonation it was reduced by 3 orders of magnitudes to less than 10 μg/L. However, when the pH of the fly ash was less than 8.5, the concentration of Pb increased. Pb is the best retained species when compared with other metals because the leaching concentration of Pb was mostly decreased following carbonation.

The release of Zn from fly ash was reduced by 1 order of magnitude in response to carbonation (Fig. 6(b)). In addition, when the pH of the fly ash was decreased to <8.5, the Zn concentration increased slightly. As shown in Fig. 6(c), the Cu concentrations were reduced by approximately 90% in response to carbonation. It is interesting to note that the leaching of Cu and Zn from the carbonated fly ash produced using a very short carbonation time was greatly reduced when compared to the leaching from un-carbonated fly ash. In addition, when the carbonation time increased, the leaching of Cu and Zn in the carbonated fly ash decreased slowly. The work of Chimenos et al. shows marked changes in the leaching of elements from short-term weathered MSWI bottom ash were observed, even though a significant change in pH did not occur [19].

Acceleration carbonation had then a positive effect on the leaching of Pb, Zn, Cu and As while had a negative effect on the leaching of Cd and Sb. Taken together, based on the demobilization of heavy metals in integration, the optimum final pH of the carbonated fly ash produced in this study was 9.5–10.5.

The observed reduction in heavy metal leaching may be explained with three combined reasons. First, pH is a dominant parameter in metal leaching. Before carbonation, the original pH of the fly ash is 12.1 and at this pH the leaching concentration of heavy metals were very high, especially Pb, Zn and Cu. After carbonation the pH of fly ash was decreased to between 9.5 and 10.5. V-shaped leaching vs. pH curve for Pb, Zn have their minimum solubility at pH in the range of 9–10 and 9–11, respectively [6,20,21]. So the leaching concentration of Pb and Zn of carbonated fly ash was much lower than the original fly ash. The decrease of pH may cause the precipitation of metal carbonates. In the MSWI fly ash, these metals were probably present in the form of oxides and/or hydroxides [e.g. CdO, $Pb(OH)_2$] due to the combustion process. During the carbonation process, oxides and/or hydroxides were probably converted to carbonates (e.g. $CdCO_3$, $PbCO_3$), which are more insoluble than oxides and/or hydroxides [22]. Furthermore, it has been shown that the leaching of trace elements (Pb, Cd, Cu, Zn, etc.) is probably reduced by sorption onto $CaCO_3$ leading to coprecipitation: Pb, Zn and Cu have a strong affinity with calcite [10,23–27]. This is a possible explanation for the reduced availability of Cu, Zn and Pb. Several other newly formed minerals containing metals have also been observed in weathered bottom ash such as oxides, phosphates and sulphates of Zn and Pb [7,8,11,16,28]. A reduction in leachable As is attributable to an increased sorption by iron oxides at lower pH [22]. Finally, physical retention following carbonation is another reason for the reduction of heavy metal leaching. Carbonation results in decreased porosity of monolithic samples
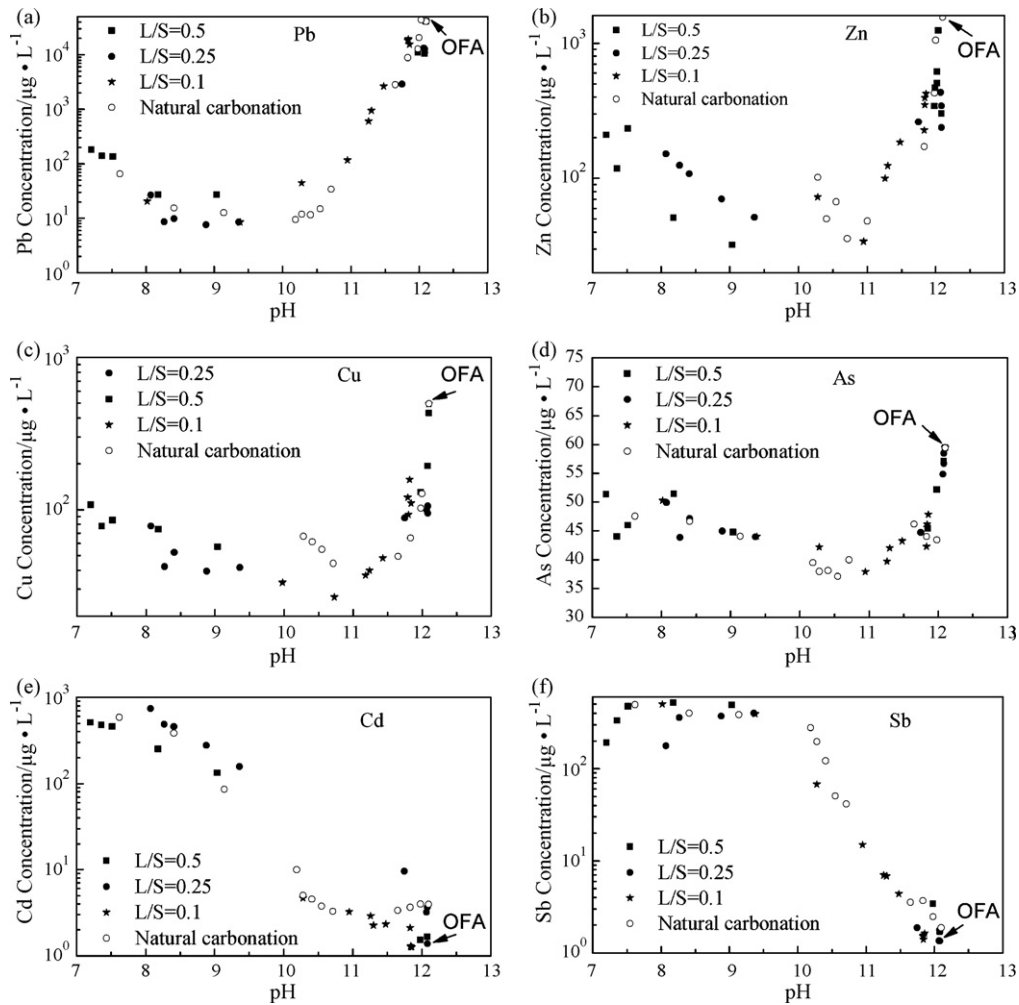
Fig. 6. Heavy metal concentration in the GB leachate at different pHs.

and this phenomenon is more evident for samples with an L/S ratio of 0.25.

These experiments concerning both pH and trace elements leaching confirm that accelerated carbonation treatment has the same positive effects as natural carbonation. Consequently, accelerated carbonation could improve some properties of fly ash [14,29].

3.2.2. Soluble salts in leachate

The effect of the accelerated carbonation treatment was also evaluated on the leaching of soluble salts. Fig. 7 shows the leaching of Cl^-, sulphate and F^- during the leaching test (GB/5086.2-1997). Based on the mineralogical analysis of the fly ash, the chloride ions occurred as NaCl, KCl and CaClOH, which are all highly soluble. It has been shown that the leaching of Cl^- is independent of pH, relatively rapid and not controlled by solubility limitations [6]. Of the chloride minerals present in the fly ash evaluated in the present study, only CaClOH reacted with CO_2 during carbonation, as shown in reaction (6). However, $CaCl_2$, the product of reaction (6), is also highly soluble. As a result, 131,000–179,900 mg kg^{-1} of Cl^- which accounts for 73.17–95.29% of the total chloride was released from the carbonated fly ash. Currently, China does not regulate the concentration of soluble salts in products that are disposed of in landfills; therefore, we compared the concentration of soluble salts in the leachate to the EC standard [30]. As shown in Table 5, the results revealed that the level of Cl^- released from the fly ash was much higher than the EC standard for non-hazardous material.

5700–9000 mg kg^{-1} of sulphate which accounts for 11.02–17.49% of the total sulphate was released from the carbonated fly ash, which is under the limit for non-hazardous wastes. According to the diffractogram of the original fly ash (Fig. 5), $CaSO_4$ was the only SO_4^{2-} related compound, other authors' works have also shown that $CaSO_4$ was the major SO_4^{2-} related compound. So it can be concluded that the presence of sulphate in the leachate was primarily due to the partial dissolution of $CaSO_4$. In addition there was no obvious correlation between reactivity during
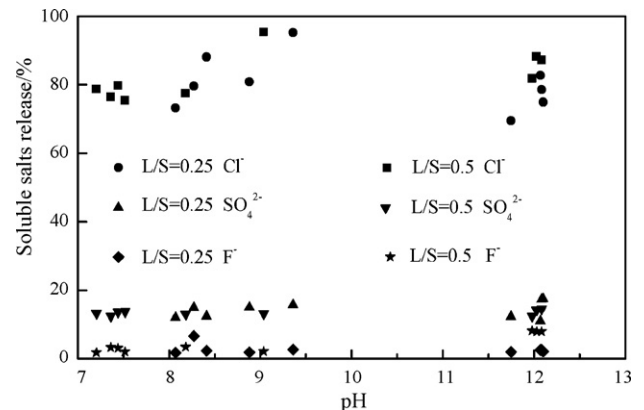

Fig. 7. Cl, sulphate and F released in the GB leachate at different pH.

Table 5
Cl, sulphate and F released in the GB leachate at different pHs and the EC limits (2002) for inert waste or non-hazardous waste prior to landfill (mg kg^{-1} dry substance).

Component	Symbol	This study		EC, 2002	
		Minimum value of soluble salts released at different pH	Maximum value of soluble salts released at different pH	Inert waste	Non-hazardous waste
				L/S = 10 L/kg	L/S = >10 L/kg
Chloride	Cl$^-$	131,000	179,900	800	15,000
Sulphate	SO$_4{}^{2-}$	5,700	9,000	1000	20,000
Fluoride	F$^-$	200	940	10	150

the carbonation of fly ash and the concentration of leachable sulphate.

As shown in Table 1, the fly ash evaluated in this study contained 1.15% F. Although the amount of F is relatively small when compared to the amount of Cl or sulphate that was present in the fly ash, the EC standard has regulated the concentration of F in products that are disposed of in landfills. Therefore, it is necessary to evaluate the leaching behavior of F before and after carbonation. As shown in Fig. 7, 200–940 mg kg^{-1} of F$^-$ which accounts for 1.79–8.18% of the total fluoride was released from the carbonated fly ash. The leaching amounts is higher than the limit for non-hazardous wastes.

The carbonation process did not have an effect on the level of Cl$^-$, sulphate and F$^-$ released, which is contrary to the results of a study conducted by Fernandez Bertos, who found that the chloride and sulphate content of carbonated Air Pollution Control (APC) residues decreased significantly following carbonation [14].

The results of the present study revealed that the leaching of Cl$^-$ did not decrease in response to carbonation. From the viewpoint of reusing the fly ash, the most efficient method of removing the chloride and sulphate from the fly ash appears to be water washing. However, washing MSWI fly ashes to remove salts has already been investigated and found to lead to a high concentration of heavy metals in the washed water, especially Pb and Zn [20]. Based on the results of the present study, carbonation prior to the water washing process has the advantage of having the same efficiency of removing chloride and sulphate as water washing process, while not lead to the critical heavy metal (Pb, Zn, and Cu) released on large degree which was a problem during the water washing process. Fig. 8 shows the amount of Cl$^-$, sulphate and F$^-$ released from samples with different w/s ratios during the water washing of carbonated fly ash. The results of the above experiments revealed that the optimum carbonation of fly ash occurred when an L/S ratio of 0.25 was used. Furthermore, to keep the pH of the washed water approximately neutral, the water washing experiment was performed using fly ash that has been subjected to carbonation at an L/S ratio of 0.25 with a carbonation time of
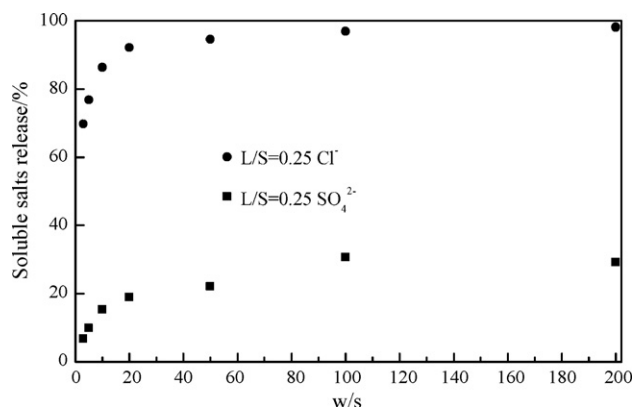
240 h. As shown in Fig. 8, when the w/s ratio increased, the level of soluble salts released increased. However, when the w/s ratio was greater than 10, the level of Cl$^-$ released increased slowly. When the w/s ratio was increased from 3 to 200, the removed ratio of Cl$^-$ and sulphate were 69.67–98.13% and 6.63–30.65%, respectively. In addition, the level of F$^-$ released from the carbonated fly ash during the water washing process at w/s > 10 was below the detection limit; therefore, this data is not presented in Fig. 8.

3.3. Thermal analysis

The thermal characteristics of the fly ash before and after carbonation were examined by the thermogravimetry (TG) and differential thermal analysis (DTA) (NETZSCH STA 409C). To accomplish this, approximately 20 mg aliquots of the fly ash samples were placed inside an aluminum crucible. The samples were then heated linearly at a rate of 30 °C/min to 1350 °C under an inert atmosphere of nitrogen.

Samples were analyzed by simultaneous TG/DTA prior to and after carbonation (Fig. 9). The TG/DTG analyses of the original fly ash revealed the presence of three weight losses.

The first weight loss between 400 °C and 530 °C was probably related to the decomposition of CaCO$_3$. The second weight loss between 530 °C and 750 °C, which was probably related to

Fig. 8. Cl and sulphate released in the leachate during the water washing of carbonated fly ash (L/S = 0.25, t = 240 h).
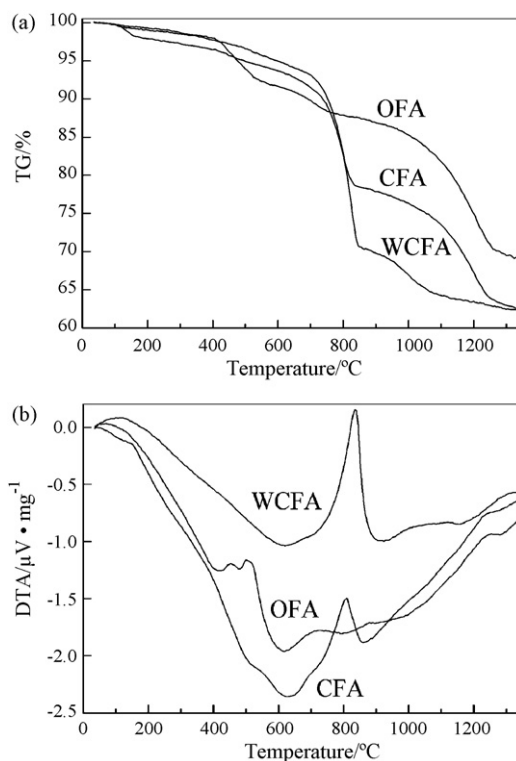

Fig. 9. TG–DTA curve of original fly ash (OFA), carbonated fly ash (CFA) produced by carbonation for 240 h and carbonated fly ash after the GB leaching test (WCFA).

Table 6
Heavy metals obtained following each of the steps in the BCR three-step sequential extraction scheme (%).

Item	Step	Cu		Zn		Pb		Cd		As		Sb	
		Mean	RSD	Mean	RSD	Mean	RSD	Mean	RSD	Mean	RSD	Mean	RSD
Original fly ash	Step 1	0.65	0.61	0.72	2.80	16.86	0.47	0.17	4.94	28.55	3.17	0.06	10.06
	Step 2	35.48	1.20	21.10	0.11	24.68	0.71	63.75	0.81	20.72	4.18	11.85	0.79
	Step 3	5.39	1.14	8.63	0.19	8.64	0.43	1.71	6.73	65.33	1.44	11.42	0.83
	Residue	54.24	0.89	65.35	3.34	65.56	1.41	37.43	1.14	15.67	2.99	72.15	1.13
	$\sum$ 3 steps + residual	95.76		95.80		115.75		103.06		130.26		95.48	
Accelerated carbonated fly ash	Step 1	7.94	0.80	11.27	0.18	4.36	0.94	42.90	2.02	22.31	0.29	1.35	1.71
	Step 2	26.76	0.87	11.59	1.11	36.02	0.93	28.02	0.79	21.33	4.37	14.15	0.46
	Step 3	5.43	1.55	5.99	0.48	7.14	1.62	1.24	6.41	48.63	0.92	7.28	2.10
	Residue	60.15	1.67	68.54	0.57	57.35	1.50	40.45	2.11	15.96	0.76	82.23	3.21
	$\sum$ 3 steps + residual	100.27		97.38		104.87		112.61		108.22		105.01	
Natural carbonated fly ash	Step 1	2.66	0.59	4.18	0.81	0.53	0.68	14.38	2.04	16.33	3.32	4.53	1.23
	Step 2	30.53	0.72	15.81	0.25	37.03	0.87	47.59	1.88	18.88	4.31	10.80	1.42
	Step 3	5.77	0.82	7.19	0.49	7.42	1.43	1.54	11.72	57.60	0.41	12.19	0.46
	Residue	57.54	0.56	61.45	2.32	61.24	0.45	30.43	1.87	24.15	2.15	86.43	0.89
	$\sum$ 3 steps + residual	96.49		88.63		106.22		93.95		116.96		113.95	

RSD: relative standard deviation.

the decomposition of calcium hydroxychloride obtained when exposing $Ca(OH)_2$ to HCl [31], corresponded to a weight loss of 7.1%, while the third weight loss between 750 °C and 1300 °C, which was likely associated with decomposition of sulphate and the evaporation of NaCl and KCl, corresponded to a weight loss of 27.8%.

Similarly, the TG/DTG analyses of the carbonated fly ash revealed the presence of three weight losses. The first weight loss between 100 °C and 200 °C was associated with the loss of hydration water from the carbonated ash and corresponded to a weight loss of 1.6%. The second weight loss was associated with the decomposition of $CaCO_3$ to CaO and the consequent loss of CO_2 and corresponded to a weight loss of 17.8%. The decomposition of calcium carbonate occurred between 415 °C and 845 °C; therefore, the weight loss between 415 °C and 850 °C was considered to correspond to the carbonate content of the sample [2]. The third weight loss between 850 °C and 1300 °C was associated with the decomposition of sulphate and the evaporation of NaCl and KCl and corresponded to a weight loss of 15.3%.

The TG/DTG analyses of carbonated fly ash following the GB leaching test revealed that, after water washing, the majority of the soluble salts were removed. The TG curve gave a weight percentage loss of the initial mass, so the total weight loss observed for the WCFA was relatively higher. As a result, the weight loss that occurred between 850 °C and 1300 °C was smaller for the carbonated fly ash after leaching than for the original fly ash or the carbonated fly ash.

3.4. BCR sequential extraction

The results of the leaching tests only reflect the leachability of the MSWI fly ash before and after carbonation under acidic or alkaline conditions as defined by the leachate pH. Therefore, to assess the effects of various subsurface environmental conditions on leaching, the heavy metal speciation data were obtained through sequential chemical extraction.

Table 6 shows the percentages of the elements evaluated in this study that were extracted from the original fly ash, fly ash that was carbonated at an L/S ratio of 0.25 with a carbonation time of 240 h and naturally carbonated fly ash produced using a carbonation time of 41 d during each step of the extraction procedure. The recovery of metals in the four fractions were evaluated by comparing the concentrations in each of the extracts to the total concentration prior to the BCR procedure, which was taken to be 100%.

Arsenic: Following carbonation, the As in step 1 decreased. However, carbonation had no significant effect on the mineral phase of arsenic.
Cadmium: In the original fly ash, most of the cadmium was extracted during step 2. Conversely, fractions 1 and 3 were found to contain relatively little Cd. When the carbonated samples were evaluated, the amount of Cd bound to the fractions of step 1 increased. These findings indicate that the carbonation process affected the distribution of Cd between steps 1 and 2, but that it had little effect on the distribution of Cd in step 3 and in the residual fraction.
Copper: Following carbonation, the level of Cu eluted in step 1 increased, while the concentration eluted in step 2 decreased. However, carbonation had no significant effect on the oxidizing phase or the residue phase.
Lead: The concentration of Pb in the original fly ash in step 1 was 16.86%. However, following carbonation, the concentration of Pb in step 2 increased, while the concentration in step 1 decreased.
Sb: When the un-carbonated fly ash was evaluated, most of the Sb was extracted in the residue fraction. However, carbonation led to a slight increase in the level of Sb extracted in step 1 and in the residue fraction.
Zinc: Following carbonation, the concentration of Zn in step 2 decreased, while the levels in step 1 increased.

In general, the concentrations of metals extracted in step 1 were insignificant, with the exception of Pb and As. Indeed, these fractions generally contained less than 1% of the total concentration of metals in the samples. Finally, the residual fraction was most important when the Zn-bearing, Sb-bearing, Pb-bearing and Cu-bearing compounds were considered; however, this fraction was not very important when Cd-bearing and As-bearing compounds were considered.

3.5. Discussion and potential application

The results of the present study indicate that the mobilization of critical heavy metals in MSWI fly ash in response to carbonation is significant. Carbonation of the MSWI fly ash causes the pH to decrease, calcite to precipitate. For these reasons mentioned above, carbonation may be a conveniently performed as a pre-treatment method before the deposition of the fly ash when landfilling is considered [10]. In another way, because of the high CaO content in the fly ash and the high volumes of fly ash generated in China every year, the fly ash presented for carbonation has great potential for

the sequestration of CO_2 [14]. Also, the carbonated fly ash can be re-used as construction aggregates. Specially, carbonation can be a conveniently pre-treatment way for production of clinkers with MSWI fly ash. The major problem during the production of clinkers is the presence of high amounts of chloride bearing compounds like NaCl and KCl, which will make the concrete porous and decrease its strength [32]. Furthermore, chloride can cause corrosion and clogging problems of dusts and fans. Moreover, chloride causes the evaporation of heavy metals (Pb, Cd and Zn) during the clinkerization process. Washing pre-treatment of MSWI fly ash has been proved to be an effective method to remove chloride compound in raw fly ash [19,28]. But at the same time heavy metals especially Pb, Zn are extracted out with a high concentration. Alternatively, accelerated carbonation followed by a water washing process can effectively prevent the leaching of heavy metals while concurrently removing soluble salts. When utilizing this technique, the cement kiln emissions can provide CO_2 to enhance the carbonation of fly ash, thereby reducing the operation cost. Overall, this form of integrated waste management has the advantage of disposing of fly ash in an environmentally and economically sustainable way.

4. Conclusion

Overall, the results of this study show the potential for the use of accelerated carbonation for the treatment of fly ashes. Additionally, in this study, two fundamental parameters controlling the carbonation reaction were evaluated, the reaction time and the L/S ratio. The results of the analyses conducted in this study were as follows:

- Following carbonation, the release of Pb, Zn, and Cu was decreased significantly, while the release of As was decreased slightly and the release of Cd and Sb increased. Based on the demobilization of heavy metals, the optimum final pH of the fly ash after carbonation was 9.5–10.5.
- The optimum L/S ratio of the fly ash was found to be 0.25 for accelerated carbonation. Under this L/S ratio, the reaction time required to decrease the pH of the fly ash to 9.5–10.5 was about 7 h.
- The amount of $CaCO_3$ in the fly ashes increased following accelerated carbonation. However, the peak of $Ca(OH)_2$ and CaClOH in the diffractogram of the original fly ash disappeared following the carbonation process.
- SEM analysis revealed that the fly ash particles became coarser following carbonation. In addition, the fly ash had a lower porosity, lower tortuosity and lower pore area following carbonation as a result of agglomeration.
- The BCR procedure provided useful information for risk assessment. Specifically, BCR enabled estimation of the amount of metals that would be mobilized under different environmental conditions. The results of the BCR analysis revealed that carbonation had a significant effect on the heavy metal fractions in steps 1 and 2, but that it had very little effect on the distribution of heavy metals in step 3 and the residue fraction.
- Carbonation does not decrease the leaching of chlorides, sulphate or fluoride. Conversely, carbonation is very useful for reducing the leaching of heavy metals while concurrently removing chloride and sulphate. Carbonation may be a conveniently performed as a pre-treatment method before the deposition of the fly ash when landfilling is considered. The fly ash presented for carbonation has great potential for the sequestration of CO_2, re-used as construction aggregates. Furthermore, accelerated carbonation can be used as a pre-treatment process for the retention of heavy metals while washing the fly ash to remove the soluble salts, for example, a pre-treatment process before co-processing of MSWI fly ash in a cement kiln.

References

[1] Hjelmar, Disposal strategies for municipal solid waste incineration residues, J. Hazard. Mater. 47 (1–3) (1996) 345–368.
[2] X.M. Li, M. Fernandez Bertos, C.D. Hills, P.J. Carey, S. Simon, Accelerated carbonation of municipal solid waste incineration fly ashes, Waste Manage. 27 (9) (2007) 1200–1206.
[3] J.A. Meima, R.D. van der Weijden, T.T. Eighmy, R.N.J. Comans, Carbonation processes in municipal solid waste incinerator bottom ash and their effect on the leaching of copper and molybdenum, Appl. Geochem. 17 (12) (2002) 1503–1513.
[4] A. Polettini, R. Pomi, The leaching behavior of incinerator bottom ash as affected by accelerated ageing, J. Hazard. Mater. 113 (1–3) (2004) 209– 215.
[5] T. Van Gerven, K. Imbrechts, E. Van Keer, M. Jaspers, G. Wauters, C. Vandecasteele, Investigation of washing, heating and carbonation as treatment techniques for the improvement of environmental characteristics of MSWI-bottom ash, in view of recycling, Waste Manage. Environ. II (2004) 3–12.
[6] J. Todorovic, H. Ecke, Demobilisation of critical contaminants in four typical waste-to-energy ashes by carbonation, Waste Manage. 26 (2006) 430–441.
[7] G. Costa, R. Baciocchi, A. Polettini, R. Pomi, C.D. Hills, P.J. Carey, Current status and perspectives of accelerated carbonation processes on municipal waste combustion residues, Environ. Monit. Assess. 135 (1–3) (2007) 55–75.
[8] J.A. Meima, R.N.J. Comans, The leaching of trace elements from municipal solid waste incinerator bottom ash at different stages of weathering, Appl. Geochem. 14 (2) (1999) 159–171.
[9] J.M. Chimenos, A.I. Fernandez, L. Miralles, M. Segarra, F. Espiell, Short-term natural weathering of MSWI bottom ash as a function of particle size, Waste Manage. 23 (10) (2003) 887–895.
[10] H. Ecke, N. Menad, A. Lagerkvist, Carbonation of municipal solid waste incineration fly ash and the impact on metal mobility, J. Environ. Eng. ASCE 129 (5) (2003) 435–440.
[11] E. Rendek, G. Ducom, P. Germain, Carbon dioxide sequestration in municipal solid waste incinerator (MSWI) bottom ash, J. Hazard. Mater. 128 (1) (2006) 73–79.
[12] T. Van Gerven, E. Van Keer, S. Arickx, M. Jaspers, G. Wauters, C. Vandecasteele, Carbonation of MSWI-bottom ash to decrease heavy metal leaching, in view of recycling, Waste Manage. 25 (3) (2005) 291–300.
[13] S. Asavapisit, G. Fowler, C.R. Cheeseman, Solution chemistry during cement hydration in the presence of metal hydroxide wastes, Cem. Concr. Res. 27 (8) (1997) 1249–1260.
[14] M. Fernandez Bertos, X. Li, S.J.R. Simons, C.D. Hills, P.J. Carey, Investigation of accelerated carbonation for the stabilisation of MSW incinerator ashes and the sequestration of CO_2, Green Chem. 6 (8) (2004) 428–436.
[15] J. Zhang, J. Liu, C. Li, Y. Nie, Y. Jin, Comparison of the fixation of heavy metals in raw material, clinker and mortar using a BCR sequential extraction procedure and NEN7341 test, Cem. Concr. Res. 38 (5) (2008) 675–680.
[16] J.A. Meima, R.N.J. Comans, Application of surface complexation precipitation modeling to contaminant leaching from weathered municipal solid waste incinerator bottom ash, Environ. Sci. Technol. 32 (5) (1998) 688–693.
[17] K.M. Allal, J.-C. Dolignier, G. Martin, Reaction mechanism of calcium hydroxide with gaseous hydrogen chloride, Revue de l'Institut Français du Petrole 53 (1998) 871–880.
[18] H. Ecke, N. Menad, A. Lagerkvist, Treatment-oriented characterization of dry scrubber residue from municipal solid waste incineration (MSWI), J. Mater. Cycles Waste Manage. 4 (2) (2002) 117–126.
[19] J.M. Chimenos, A.I. Fernandez, R. Nadal, F. Espiell, Short-term natural weathering of MSWI bottom ash, J. Hazard. Mater. 79 (3) (2000) 287–299.
[20] A.J. Chandler, T.T. Eighmy, J. Hartlén, Municipal Solid Waste Incinerator Residues, Elsevier Science B.V., The Netherlands, 1997.
[21] H.A.v.d. Sloot, L. Heasman, P. Quevauviller, Harmonization of Leaching/Extraction Tests, vol. 70, Elsevier Science B.V., Amsterdam, The Netherlands, 1997.
[22] K.J. Reddy, S.P. Gloss, L. Wang, Reaction of CO_2 with alkaline solid wastes to reduce contaminant mobility, Water Res. 28 (6) (1994) 1377–1382.
[23] J.W. Morse, M.L. Bender, Partition coefficients in calcite: examination of factors influencing the validity of experimental results and their application to natural systems, Chem. Geol. 82 (1990) 265–277.
[24] A. Gutjahr, H. Dabringhaus, R. Lacmann, Studies of the growth and dissolution kinetics of the $CaCO_3$ polymorphs calcite and aragonite. II. The influence of divalent cation additives on the growth and dissolution rates, J. Cryst. Growth 158 (3) (1996) 310–315.
[25] J.D. Rimstidt, A. Balog, J. Webb, Distribution of trace elements between carbonate minerals and aqueous solutions, Geochim. Cosmochim. Acta 62 (16) (1998) 1851–1863.

[26] M.O. Schwartz, D. Ploethner, Removal of heavy metals from mine water by carbonate precipitation in the Grootfontein-Omatako canal, Namibia, Environ. Geol. 39 (10) (2000) 1117–1126.

[27] F. Pellegrini, C.D. Hills, P.J. Carey, K.H. Gardner, A. Maries, Sorption and desorption of Cd, Co, Cu, Ni and Zn from carbonated Portland cement, Adv. Appl. Ceram. 105 (4) (2006) 185–190.

[28] P. Freyssinet, P. Piantone, M. Azaroual, Y. Itard, B. Clozel-Leloup, D. Guyonnet, J.C. Baubron, Chemical changes and leachate mass balance of municipal solid waste bottom ash submitted to weathering, Waste Manage. 22 (2) (2002) 159–172.

[29] H. Ecke, Sequestration of metals in carbonated municipal solid waste incineration (MSWI) fly ash, Waste Manage. 23 (2003) 631–640.

[30] EC, Council decision establishing criteria and procedures for the acceptance of waste at landfills pursuant o Article 16 and Annex II of Directive 1999/31/EC, 14473/02 ENV 682, Council of the European Union, Brussels, 2002.

[31] W. Jozewics, B.K. Gulett, Reaction mechanism of dry Ca-sorbents with gaseous HCl, Ind. Eng. Chem. Res. 34 (1995) 607–612.

[32] K. Ryunosuke, Recycling of municipal solid waste for cement production: pilot-scale test for transforming incineration ash of solid waste into cement clinker, Resour. Conserv. Recycl. 31 (2001) 137–147.