



Pb stabilization in fresh fly ash from municipal solid waste incinerator using accelerated carbonation technology

Jiang Jianguo*, Chen Maozhe, Zhang Yan, Xu Xin

Department of Environment Science and Engineering, Tsinghua University, Beijing 100084, PR China

ARTICLE INFO

Article history:

Received 7 November 2007

Received in revised form 14 April 2008

Accepted 14 April 2008

Available online 22 April 2008

Keywords:

Accelerated carbonation technology (ACT)

Municipal solid waste incinerator (MSWI)

Fly ash

Heavy metal

ABSTRACT

Carbonation technology with CO₂ absorption was used to enhance the stabilization of heavy metals in fresh fly ash from a municipal solid waste incinerator (MSWI). The influence of fundamental parameters affecting the stabilization of heavy metals, especially Pb and diffusivity and reactivity of CO₂, was evaluated. The results indicated that the addition of 10% or more of water could remarkably accelerate the absorption of CO₂ and could also accelerate the stabilization of MSWI fly ash. The stabilization of MSWI fly ash is not distinct within 1 d in the air atmosphere for low content of CO₂ (0.03%). The result of the XRD analysis indicated that CO₂ could combine with Ca(OH)₂ to form CaCO₃ and CO₂ could also combine with heavy metal oxide to form heavy metal carbonate in the adsorption of CO₂. The TGA analysis showed that MSWI fly ash has the sequestration capability of 3% (w/w) CO₂. The sequestration of CO₂ has a large impact on Pb, and the exchangeable Pb can be converted into carbonated form in rich CO₂ condition to be stabilized.

© 2008 Elsevier B.V. All rights reserved.

1. Introduction

Integrated waste management is to deal with society's waste in an environmentally and economically sustainable method. Under the framework of integrated waste management, thermal treatment represents an appropriate option for reducing the amount of waste to be landfilled. It also allows waste hygienization [1].

Municipal solid waste incineration (MSWI) fly ash is incinerated at high temperatures and cooled rapidly afterwards. The material is then unstable under atmospheric conditions. The incineration of municipal solid waste generates solid residues, bottom ash and fly ash, as well as atmospheric emissions containing approximately 12% (v/v, dry gas) of CO₂ [2].

For the alkalescence and heavy metal leaching, the MSWI fly ash ranks within the list of national hazardous wastes. The establishment of emission standards has led to an improvement of air pollution control (APC) systems for flue gas treatment, primarily due to more efficient separation technologies. However, this development has increased both the amount and pollution potential of APC residues. CO₂ is one of the Kyoto gases. The consequences resulting from the increasing concentration of human-induced greenhouse gases are central to the debate over global change. There is a considerable discussion at scientific and industrial levels about how to best limit the emission.

1.1. Stabilization of fly ash

Over the past three decades, the stabilization technology of MSWI has developed significantly [3]. However, regarding the conventional stabilization technologies, there are some problems that cannot be ignored, such as the long-term stabilization and the cost of stabilization pharmacy. In addition, carbonation is one of the important topics in recent research on long-term leaching of heavy metals.

1.2. Natural carbonation

Weathering will stabilize the material by changing its mineralogical characteristics. It will have some positive effects on decreasing heavy metal leaching [4,5]. Carbonation has been recognized to be an important step in the weathering process [6]. It involves the CO₂ dissolution in water at initially alkaline conditions. This causes pH to decrease and calcite to precipitate until the material is in equilibrium with CO₂. Moreover, heavy metals can be trapped in the newly formed minerals. Calcite is the predominant newly formed mineral during fly ash maturation [4,5].

1.3. Accelerated carbonation technology

On weathering areas, the CO₂ source is the atmospheric CO₂. However, it has been proved that the natural carbonation process can be accelerated, using different sources of CO₂ and a few methods [7–9]. Moreover, accelerated carbonation may represent

* Corresponding author. Tel.: +86 10 62783548, fax: +86 10 62773438.
E-mail address: jianguoj@tsinghua.edu.cn (J. Jianguo).

Table 1
Main chemical composition of fly ashes (%)

CaO	38.7926
Cl	13.9484
SiO ₂	12.5811
SO ₃	8.6277
Na ₂ O	6.865
K ₂ O	4.9198
Al ₂ O ₃	4.0613
Fe ₂ O ₃	3.8176
MgO	2.3411
P ₂ O ₅	1.1413
TiO ₂	1.0524
ZnO	0.7064
PbO	0.2833
Br	0.1693
CuO	0.169
Cr ₂ O ₃	0.1388
MnO	0.1164
BaO	0.0904
SnO ₂	0.0819
SrO	0.0774
NiO	0.0188

a proper pre-treatment stage prior to either recycling or landfilling fly ash [1]. The carbon dioxide source can be either pure CO₂ or any other CO₂-rich gas such as incinerator emissions. Consequently, CO₂ sequestration capacity could be another interesting possibility of ash utilization. This process could help to reduce the greenhouse effect and also reduce fly ash storage duration by accelerating weathering reactions [9–11].

2. Materials and methods

2.1. Samples

2.1.1. Fly ash description

The fly ash used in this investigation was sampled from a MSWI facility in Shenzhen of China. The rate of water content of the fresh fly ash was 3%. It was sealed and remained in shadow in order to be fresh when it was collected. The particle size distribution of ash was below 212 μm, which was optimum for this experiment.

2.1.2. X-ray fluorescence (XRF)-analysis

Their chemical composition in major elements was measured and analyzed (Table 1).

Table 1 reports that fly ash contained much CaO and Ca(OH)₂ because of the injection of a vast scale of lime mortar. The alkaline environment was good for stabilization of the heavy metal. Besides, fly ash contained a great deal of chlorine, perhaps because of the richness of NaCl and KCl in the municipal solid waste.

2.1.3. Leaching tests

Roll over leaching procedure (the method standard for leaching of solid wastes in China, GB 5086.1-1997) was used in this experiment. The leaching tests were performed at an initial liquid to solid ratio (L/S) of 10:1 with distilled water (pH 7). Samples were rotated at 30(±2) rpm during 18 h. After this leaching time, samples were filtered at 45 μm and the pH was measured. Metal concentrations

in the leachates were analyzed by inductively coupled plasma and atomic emission spectrometry (ICP-AES). The results are in Table 2.

Table 2 indicates that concentration of Pb²⁺ was greater than the identification standard for hazardous wastes and the standard for pollution control on the security landfill site (Chinese standard). And in the next study, the focal point was the stabilization of Pb²⁺.

From Tables 1 and 2 we can learn that Zn and Cr exist as a stable state for the large content while there is few leaching.

2.2. Methods

2.2.1. Carbonation experiment with different water–solid ratios

For the optimum water content, samples of fly ash of the selected size fraction ($x < 212 \mu\text{m}$) were carbonated with CO₂ for 5 min in the same polythene bottles (1 L), at different water–solid ratios ranging between 0 and 0.7. Then the samples were rotated at 30(±2) rpm during 2 h for several times to fully react. From this segment, samples W₀–W₇ were made and collected.

2.2.2. Carbonation experiment with CO₂ pressure experiment

For the optimum CO₂ pressure, samples of dry ash and ash with 20% water were gassy with nitrogen, air, mixed gas A (10% CO₂ and 90% N₂), mixed gas B (50% CO₂ and 50% N₂) and pure carbon dioxide, respectively, for 5 min in the polythene bottles (1 L). Then the samples were rotated at 30(±2) rpm during 2 h for several times to fully react. From this part, samples P₁–P₅ and Q₁–Q₅ were made and collected.

2.2.3. Leaching tests

The above W₀–W₇, P₁–P₅ and Q₁–Q₅ went through leaching tests. The method of leaching tests is given in Section 2.1.3.

2.2.4. Mineralogy and microstructure analysis

The mineralogy and microstructure of carbonated and non-carbonated ash were analyzed by X-ray diffractometer (XRD) and scanning electron microscopy (SEM), respectively. Accepted equipments in this experiment were D/max-rB X-ray diffractometer (XRD) and S-4500 field emission scanning electron microscopy (SEM).

2.2.5. Thermogravimetry analysis–differential thermal analysis (TGA–DTA)

At 1 atm of CO₂ and 40 °C, TGA–DTA was done with the non-carbonated ash. The figures of TGA and DTA of fresh fly ash and the carbonated ash were gained.

3. Results and discussion

3.1. Influence of water–solid ratio

The samples with different water contents were carbonated. Pb²⁺ concentration and pH of leachate of fly ash are as follows (see Fig. 1). These experiments indicate that the optimum w/s ratio should be 0.1 or more.

It is known that water is necessary for the carbonation reaction to proceed, and water content is an important parameter

Table 2
Heavy metals content of fly ash (mg L⁻¹)

Heavy metals	Pb	Cu	Cr	Zn	Ni	Cd
Measured data	42.38	0.366	0.063	3.856	0	0.006
Identification standard for hazardous wastes	3	50	10	50	10	0.3
Standard for pollution control on the security landfill site	5	75	12	75	15	0.5

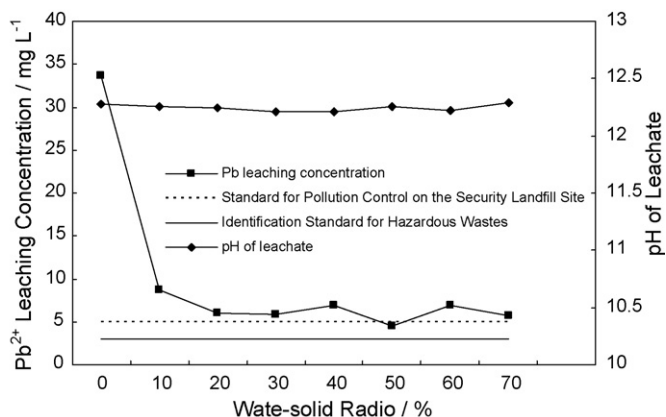


Fig. 1. Influence of water–solid ratio.

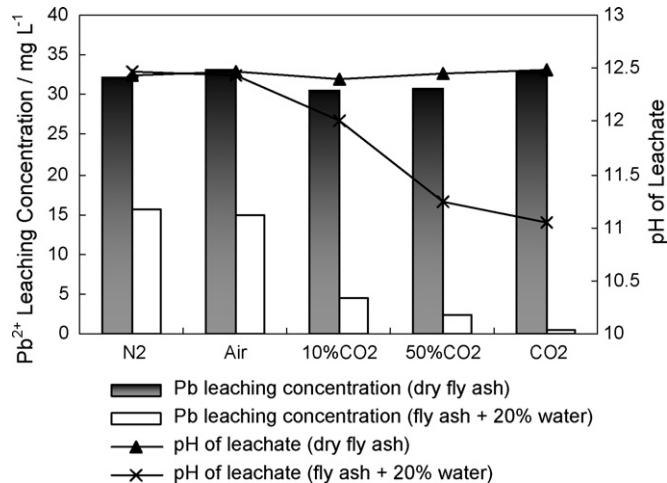


Fig. 2. Influence of CO₂ pressure.

of the reaction. We can see that the reaction does not occur for totally dried samples and the leaching concentration of heavy metals Pb²⁺ are decreased with the increase of water–solid ratio. This result is expected, since the carbonation reaction occurs in the aqueous phase. The optimum w/s ratio seems to be 0.1 or more. The leaching concentration of heavy metals Pb²⁺ is below 10 mg/L when the water–solid ratio is 10–70%. And among them when the water–solid ratio is 50%, the leaching concentration of heavy metals Pb²⁺ reaches the minimum 4.52 mg/L, which is below the Identification Standard for Hazardous Wastes and the Standard for Pollution Control on the Security Landfill Site.

The reaction mainly occurs in the pores of the solid matrix. Too little water decreases the reaction activity of solid and gas, but too much water hinders the diffusion of CO₂ into the pores of a solid. Pore water hydrates and solvates the CO₂ and dissolves the Ca²⁺ ions from the solid phase to react and form calcium carbonate. At low w/s ratios, the material's gas permeability is increased, and the CO₂ effectively diffuses into the solid.

From Fig. 1, we can see that CO₂ absorption and moisture added have no obvious effect on the pH of fly ash leachate, and the pH is in equilibrium as 12.3. And this also shows that little CO₂ has not enough power to change the pH of the whole chemical equilibration system of strong alkaline fly ash.

3.2. Influence of CO₂ pressure

The results can be seen in Fig. 2. It shows the pH of leachate and the Pb leaching concentration of two kinds of samples which are carbonated in such gases as N₂, air, mixed gas A, mixed gas B, and CO₂.

It is difficult to carbonate the ash without water, and the Pb releases are almost the same among these five kinds of gas.

However, with 20% water they are different. Using pure CO₂ has a good result and brings a low Pb release. The Pb releases are below the Identification Standard for Hazardous Wastes and the Standard for Pollution Control on the Security Landfill Site. Too low content of CO₂ in the air makes the result not obvious. After treatment with the CO₂ in mixed gases, there are low leaching concentrations of Pb, and maybe because of the limitation of bottle's size, the results show a little worse than that when the gas is pure carbon dioxide. And after we collect the carbonated fly ash and repeat the process for thrice, the similar results are obtained as the pure CO₂.

When water exists, CO₂ (aq) hydrates to form H₂CO₃ and H₂CO₃ ionizes to H⁺, HCO₃⁻ and CO₃²⁻. This occurs almost instantaneously, making the pH fall by approximately 2 units. Then CO₃²⁻ could combine with Pb²⁺ to form a stable carbonate mineral such as PbCO₃.

3.3. Mineralogy changes

Table 3 shows the major mineral compounds identified by XRD in fly ash, before and after carbonation, in order of decreasing relative concentration. The main alterations in the mineralogy of fly ash resulting from carbonation at the optimal conditions identified can be examined by X-ray diffraction.

The intensity of the peaks corresponding to calcite and silica are higher in the carbonated samples. They have very noisy signals due to their heterogeneity and complex mineralogy. The presence of calcite in the initial samples is due to partial, earlier weathering of the

Table 3 Major compounds found in fly ash before and after carbonation

Fresh fly ash		Carbonated fly ash	
Quartz	SiO ₂	Quartz	SiO ₂
Portlandite	Ca(OH) ₂	–	–
Calcium oxide	CaO	–	–
Halite	NaCl	Halite	NaCl
Gehlenite	Ca ₂ Al ₂ SiO ₇	Gehlenite	Ca ₂ Al ₂ SiO ₇
Zinc oxide	ZnO	–	–
Calcite	CaCO ₃	Calcite	CaCO ₃
Sylvite	KCl	Sylvite	KCl
Anhydrite	CaSO ₄	Anhydrite	CaSO ₄
Lead oxide	Pb ₃ O ₄	–	–
Calcium chloride hydroxide hydrate	CaCl ₂ ·Ca(OH) ₂ ·(H ₂ O) ₂	–	–
–	–	Gypsum	CaSO ₄ ·(H ₂ O) ₂
–	–	Calcium silicate hydrate	Ca _{1.5} SiO _{3.5} ·xH ₂ O

ash. There is an increase in the degree of crystallinity in the diffractograms resulting from carbonation. In the non-carbonated sample, there is some evidence of hydration by the existence of minor peaks for portlandite $\text{Ca}(\text{OH})_2$, which are absent in the carbonated sample.

Heavy metal Pb and Zn mainly exist as oxide in the fly ash— Pb_3O_4 or ZnO . With carbonation, CO_2 could react with Pb_3O_4 and ZnO to form other compounds, which could stabilize the heavy metal in the ash. So after carbonation, Pb_3O_4 is missing; for the trace amount, there is no detectable existence of Pb after the carbonation.

The richness of NaCl and KCl in the ash may correlate with the flavor of salt in China.

In hydrated systems, carbonation will produce some calcium silicate hydrate, and this binding material could also stabilize heavy metal to a certain extent.

3.4. Microstructure changes

Fig. 3 reveals distinct differences in the morphology between carbonated and non-carbonated samples.

Fig. 3 illustrates this by showing fracture surfaces of fly ash before and after carbonation. The appearance of the non-carbonated ash is granular and rough, and individual grains are clearly visible. The carbonated sample reveals a less porous solid where crystalline reaction products are clearly evident, and some fibrous material fills in the pore space.

During carbonation, CO_2 is sequestered and the three polymorphs of calcium carbonate may be produced. The morphology of calcite is characterized by small, tightly packed crystals of acicular shape. Some microcracking is also noticeable caused by the volume expansion during the reaction, or the thermal stresses during accelerated carbonation [12].

After carbonation, a calcite-rich matrix filling the pores of the system can be observed when analyzing wastes containing heavy metals. The residual non-carbonated grains are enveloped by a silica-rich decalcified rim which also encapsulates heavy metals such as Pb.

3.5. Sequestration capability of CO_2

The figure of TGA and DTA of fly ash is in Fig. 4.

The TG analysis shows that the fly ash has the sequestration capability of 3% (w/w) CO_2 . Initially there is a steep rise in the consumption of the gas, which then slows down until the sample is saturated. When carbonating the ash for 2 h, 90% of the reaction takes place in the first 20 min at the speed of 0.88 L/kg min.

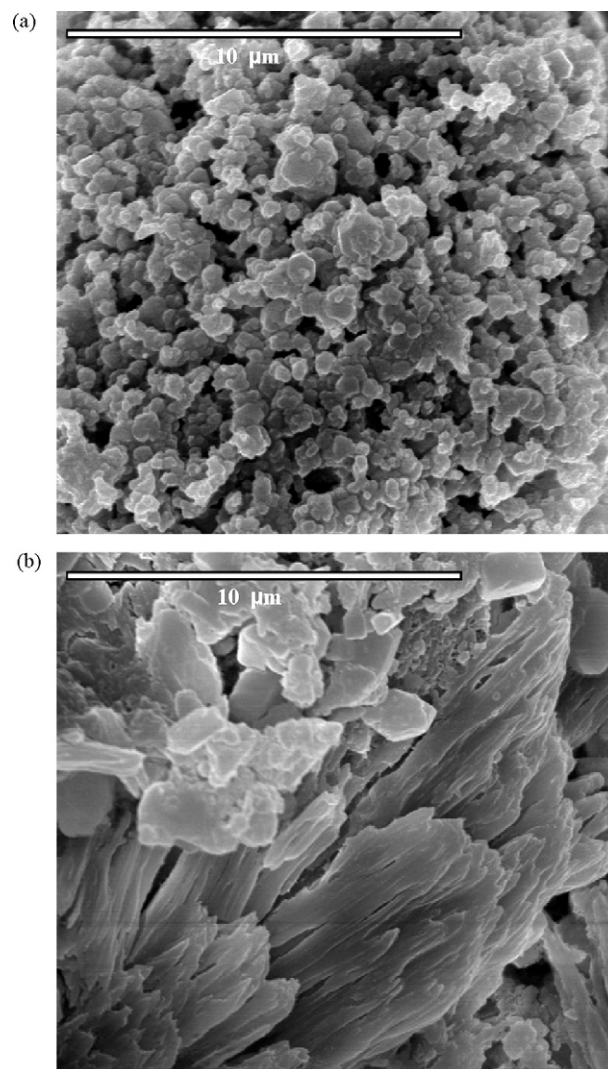


Fig. 3. SEM pictures of non-carbonated (a) and carbonated (b) fly ash.

For fly ash, the velocity of consumption of CO_2 after 2 h is rather slow.

Hydraulic calcium silicates become rapidly activated by CO_2 , resulting in a high consumption of the gas. During accelerated

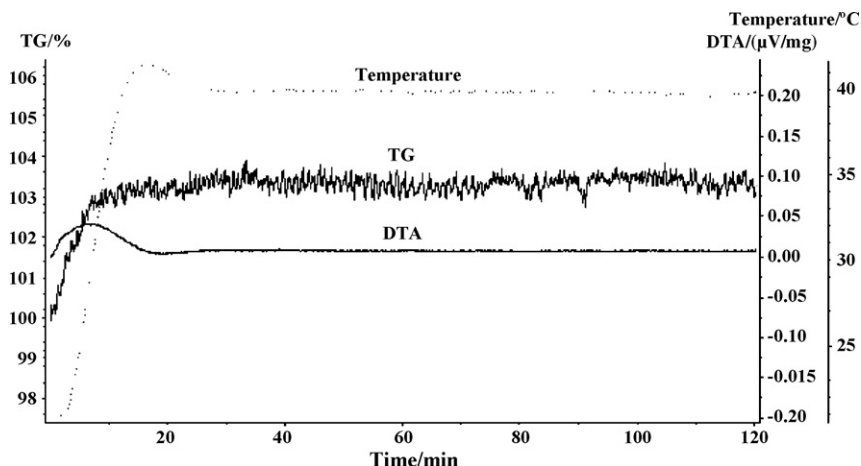


Fig. 4. TGA and DTA of fresh fly ash.

Table 4
Experiment conditions for sequential extraction procedure

Speciation	Method
Exchangeable	5 g (dry weight) of sample from batch test was shaken for 1 h at room temperature with 100 mL of sodium acetate solution (1 M NaAc, pH 8.2)
Bound to carbonates	The residual from exchangeable fraction was shaken for 5 h at room temperature with 100 mL of 1 M NaAc adjusted to pH 5.0 with acetic acid
Bound to metal oxides	The residual from bound to carbonate fraction was added with 100 mL of 0.04 M NH ₂ OH·HCl (hydroxylamine hydrochloride) in 25% (v/v) HAc. The mixture was heated to 96 ± 3 °C for 5 h with occasional agitation
Bound to organic matters	The residual from bound to metal oxide fraction was added with 15 mL of 0.02 M HNO ₃ and 25 mL of 30% H ₂ O ₂ adjusted to pH 2 with HNO ₃ , and the mixture was heated to 85 ± 2 °C for 2 h with occasional agitation. A second 15 mL aliquot of 30% H ₂ O ₂ (pH 2 with HNO ₃) was then added. The sample was heated again to 85 ± 2 °C for 3 h with intermittent agitation. After cooling, 25 mL of 3.2 M MH ₄ Ac in 20% (v/v) HNO ₃ was added and the sample was diluted to 100 mL and agitated continuously for 30 min
Residual	0.2 g (dry weight) of sample from bound to organic matter fraction was digested with 1 mL of HNO ₃ (70%), 3 mL of HCl (37%), 1 mL of H ₂ O ₂ (30%) and 3 mL HF (48%) in Teflon FA vessel using microwave heating. The digested sample was diluted to 100 mL with deionized distilled water

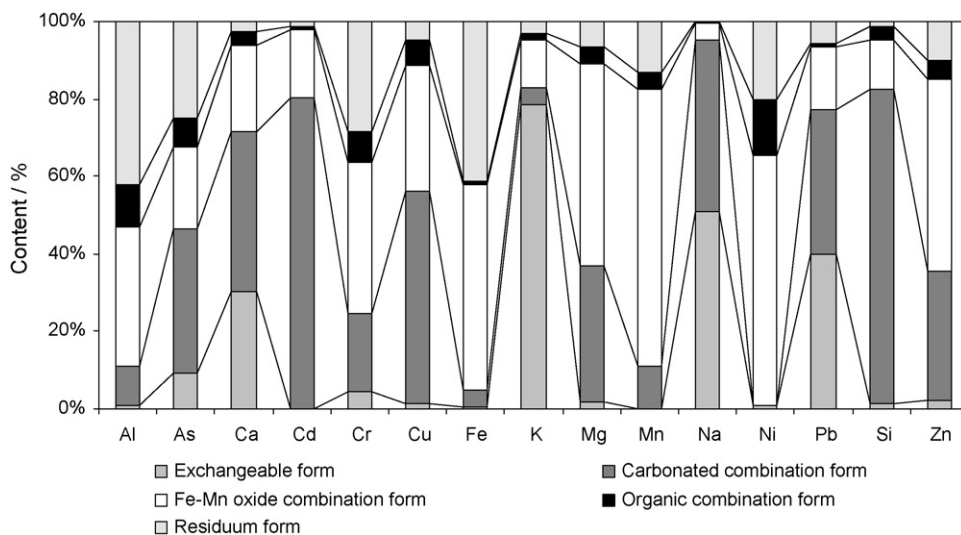


Fig. 5. Speciation of metals in fresh fly ash.

carbonation, the mixture is carbonated under a gaseous, CO₂-rich environment, which promotes rapid stiffening (in min) of the non-hydrated product into an engineering medium. The theoretical maximum CO₂ uptake capacity upon carbonation can be calculated

as a function of the chemical composition of the original material using the Stenoir formula [2]:

$$\text{CO}_2 (\%) = 0.785(\text{CaO} - 0.7\text{SO}_3) + 1.09\text{Na}_2\text{O} + 0.93\text{K}_2\text{O}$$

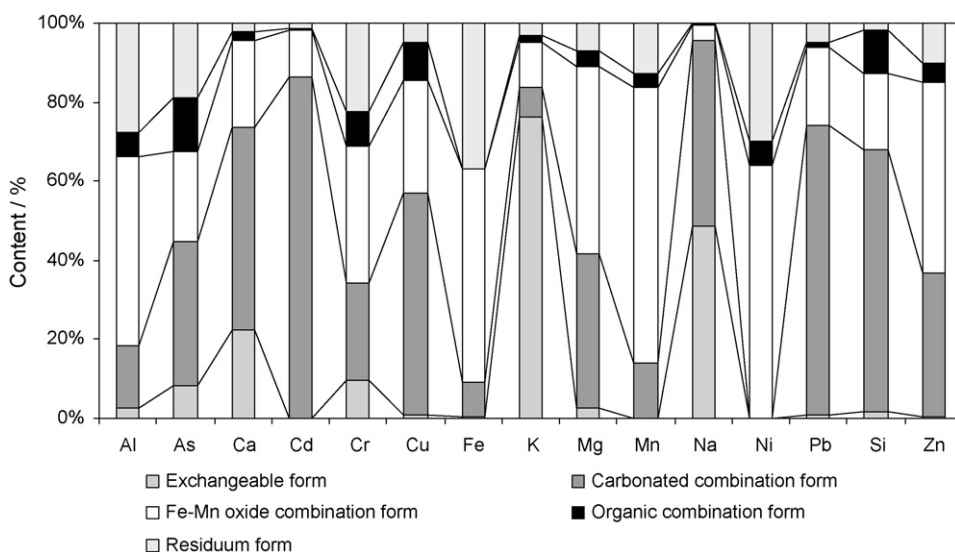


Fig. 6. Speciation of metals in carbonated fly ash.

Not all the Ca in Table 1 is CaO, therefore, according to the formula, the theoretical maximum CO₂ uptake capacity of the sample used in this investigation is less than 37.8%, and the result of the experiment is only 3% compared to the 6% mentioned regarding Europe [2]. The degree of carbonation is strongly dependent upon calcium content, though the presence of certain components might influence the effective diffusivity and reactivity of the CO₂. Pertaining to characteristics of solid waste and incinerator between China and Europe, the calcium content is different, leading to the diversity of sequestration capability of CO₂.

3.6. Results of experiment of sequentially extraction procedure

Fresh fly ash and carbonated fly ash were treated in the experiment condition for sequentially extraction procedure [13,14], seen in Table 4, and the results are in Figs. 5 and 6.

Comparing Fig. 5 with Fig. 6, we can find so many differences about the speciation of metal between fresh fly ash and carbonated fly ash. The result indicates that there is 40% exchangeable form Pb (Ex Pb) in fresh ash, which is easy to leach under natural conditions. While there is less than 1% Ex Pb and 70% carbonated form Pb in carbonated ash, which indicates that Pb is stabilized for the decrease of harmful effect.

4. Conclusion

In the future there will be increasingly large volumes of combustion wastes to be managed. Due to their composition, MSWI fly ash can be made to react with CO₂ to form materials with improved properties. Accelerated carbonation imparts chemical and mineralogical changes to the ash, which reduce their environmental impact through cementation by carbonate precipitation. This preliminary study shows the potential of using accelerated carbonation for the treatment of fly ash. Three fundamental parameters controlling the carbonation reaction have been studied, namely the ash water content, CO₂ pressure, and reaction time. The following optimum values are obtained.

The optimum water–solid ratio for the selected sample is 0.1 or more. The carbonation is better when the CO₂ pressure is 100%. The reaction time to get an optimum extent of carbonation for fly ash is 2 h, and after that time the reaction is effectively slowed down.

Accelerated carbonation imparts considerable physical and chemical changes in MSWI fly ash: the leaching of lead is markedly reduced. The amount of CaCO₃ in the ash after accelerated carbonation technology treatment is increased. The particles after carbonation become coarser due to agglomeration. The carbonated

product is a solid of lower porosity, lower tortuosity and lower pore area with calcite infilling the pore space. The formation of calcium-metal salts and metal silicate complexes has been confirmed.

The fly ash has the high sequestration capability of 3% (w/w) CO₂.

The results of experiment for sequentially extraction procedure indicate that CO₂ capture is critical for the change of modality characteristics of Pb in fly ash. There is 40% Ex Pb to become carbonated form.

Acknowledgement

The authors acknowledge the National Natural Science Foundation of China for the financial support (grant no. 50778099).

References

- [1] T. Sabbas, A. Poletini, R. Pomi, T. Astrup, O. Hjelm, P. Mostbauer, G. Cappai, G. Magel, S. Salhofer, C. Speiser, S. Heuss-Assbichler, R. Klein, P. Lechner, Management of municipal solid waste incineration residues, *Waste Manage.* 23 (2003) 61–88.
- [2] M. Fernández 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 CO₂, *Green Chem.* 6 (2004) 428–436.
- [3] D. Dermatas, X. Meng, Utilization of fly ash for stabilization/solidification of heavy metal contaminated soils, *Eng. Geol.* 70 (2003) 377–394.
- [4] 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 (2002) 159–172.
- [5] P. Piantone, F. Bodenau, L. Chatelet-Snidaro, Mineralogical study of secondary mineral phases from weathered MSWI bottom ash: implications for the modelling and trapping of heavy metals, *Appl. Geochem.* 19 (2004) 1891–1904.
- [6] 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 (2002) 1503–1513.
- [7] A. Poletini, R. Pomi, The leaching behaviour of incinerator bottom ash as affected by accelerated ageing, *J. Hazard. Mater.* B113 (2004) 209–215.
- [8] E.J. Anthony, L. Jia, J. Woods, W. Roque, S. Burwell, Pacification of high calcic residues using carbon dioxide, *Waste Manage.* 20 (2000) 1–13.
- [9] I. Majchrzak-Kuceba, W. Nowak, A thermogravimetric study of the adsorption of CO₂ on zeolites synthesized from fly ash, *Thermochim. Acta* 437 (2005) 67–74.
- [10] T.V. Gerven, E.W. 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 (2005) 291–300.
- [11] H. Ecke, Sequestration of metals in carbonated municipal solid waste incineration (MSWI) fly ash, *Waste Manage.* 23 (2003) 631–640.
- [12] M. Fernández Bertos, S.J.R. Simons, C.D. Hills, P.J. Carey, A review of accelerated carbonation technology in the treatment of cement-based materials and sequestration of CO₂, *J. Hazard. Mater.* B112 (2004) 193–205.
- [13] X. Wan, W. Wang, T.M. Ye, X.B. Gao, J.M. Yang, Y.X. Lan, Distribution and characters of heavy metals from municipal solid waste incinerator fly ash, *Environ. Sci.* 3 (2005) 172–175 (in Chinese).
- [14] L.C. Tan, V. Choa, J.H. Tay, The influence of pH on mobility of heavy metals from municipal solid waste incinerator fly ash, *Environ. Monit. Assess.* 44 (1997) 275–284.