



Aging of air pollution control residues from municipal solid waste incinerator: Role of water content on metal carbonation

Pin-Jing He ^{a,*}, Qun-Ke Cao ^a, Li-Ming Shao ^a, Duu-Jong Lee ^b

^aState Key Laboratory of Pollution Control and Resources Reuse, Tongji University, Shanghai 200092, China

^bChemical Engineering Department, National Taiwan University, Taipei, Taiwan, 10617

Received 4 March 2005; accepted 6 June 2005

Available online 5 July 2005

Abstract

This work studies the effect of water content on the aging of APC residues, with a liquid to solid ratio (L/S) of 0.25 or 10, aged with or without exposure to ambient air. After the residue was mixed with water, CaSO_4 and $(\text{Na,K})\text{Al}_3(\text{SO}_4)_2(\text{OH})_6$ in the raw sample yielded ettringite. When CO_2 were available, this ettringite was further transformed to gypsum, calcite and possibly gibbsite. Experimental data revealed that the concentrations of Pb, Zn, Cd, Hg, and Cu fell with age, whereas that of Cr increased. Given $L/S=10$, excess Ca^{2+} ions were present in the suspension, so a precipitate of primarily calcite crystals of sizes under $5\ \mu\text{m}$ formed on the air–water surface. This layer significantly reduced the rates of decline of Pb, Zn, Cd and Hg contents, and also reduced the increasing rate of Cr content in the suspension. This result follows from the mass transfer barrier of CO_2 added at the air–water surface and the occurrence of subsequent chemical reactions in the suspension. An estimate of the mass transfer rate revealed that the rate-controlling step with $L/S=10$ was the dissolution and diffusion of CO_2 in the bulk solution. However, at $L/S=0.25$, the rate-limiting step was the dissolution of metals from ash particles. Water content is a very important process factor, whose distribution in the sample, and the resulting competition between carbonate ion flux and heavy metal flux, govern the reaction time required during the natural aging process.

© 2005 Elsevier B.V. All rights reserved.

Keywords: Municipal solid waste incinerator; Air pollution control residues; Aging; Carbonation

1. Introduction

Air pollution control (APC) residues from municipal solid waste (MSW) incinerators are typically

classified as hazardous waste because they contain large amounts of leachable heavy metals, soluble salts and trace organic pollutants, which must be disposed of with care (Reijnders, 2005). He et al. (2005) reported for the first time the characteristics and pollution potentials of APC residues generated in an incinerator in Shanghai. When the APC residues were wet and exposed to air, aging (or natural weathering) occurred. Carbonation is regarded as the main

* Corresponding author. Tel.: +86 21 65986104; fax: +86 21 65986104.

E-mail addresses: solidwaste@mail.tongji.edu.cn,
xhpjk@mail.tongji.edu.cn (P.-J. He).

mechanism of the aging-induced reduction of the solubility of metals, owing to the low solubility of heavy metal carbonates. Accordingly, aging has been proposed to be a means of immobilizing residues that are contaminated with heavy metals (Macias et al., 1997; Walton et al., 1997; Bin-Shafique et al., 1998; Valls and Vázquez, 2001; Venhuis and Reardon, 2001; Ecke et al., 2002).

Aging is a complex process of numerous interrelated chemical reactions, including carbonation, hydrolysis, hydration, dissolution/precipitation, complexation with organic and inorganic ligands, surface complexation, surface precipitation, sorption, formation of solid solutions and oxidation/reduction (Sabbas et al., 2003). Table 1 lists the literature examines the effect of APC residues aging on metal immobilization. The partial pressure of CO₂ and the reaction time were proposed more important parameters than the amount of water added or the temperature of fly ash carbonation (Ecke et al., 2003). Water is a critical ingredient in carbonation, but an excess of water suppresses CO₂ diffusion into the suspension (Fernández Bertos et al., 2004). By establishing that carbonation is much faster under dynamic conditions than under static conditions, Fernández Bertos et al. (2004) established that the diffusion of CO₂ into ash particles is the rate-controlling step. The optimal liquid to solid ratio (*L/S*) was 0.2–0.3 for APC residues, using pure CO₂ at pressure of three bars.

If the transfer rate of CO₂ were the rate-controlling step of the aging of APC residues, then the way in which water is added and distributed within samples should significantly affect the rate of carbonation. Table 1 demonstrates that the *L/S* ratios considered in the literature are under 0.6, and claims are made of the effect of CO₂ on aging without experimental support. In this work, APC residues with *L/S*=0.25 and 10 were aged with or without exposure to ambient

air. This study shows that the distribution of the added water considerably influences the aging process, via mechanisms that are discussed in certain detail.

2. Materials and Methods

The APC residues employed in this study were sampled from the Yuqiao MSW Incineration Plant (mass burn) in Shanghai, which treats approximately 1000 tons of MSW daily. The plant removes acid gas from the flue gas stream using lime slurry (10% w/w); heavy metals and dioxins using activated carbon (50 mg m⁻³), and particulates using bag filters. The APC residues were collected from the semidry reactors and the fabric filters, containing particles from the incineration chamber, reaction products and some excess reactants, primarily Ca(OH)₂. The raw residues had a low water content of 0.37% w/w.

Fernández Bertos et al. (2004) posited that the optimal *L/S* is 0.2–0.3 for APC residues. Accordingly, in this study, raw ash was mixed with distilled water to a moisture content of 20% w/w (*L/S*=0.25 w/w) to form a sample with a low to moderate moisture content. Then, some of the wet ash was sealed in a 500 ml PE bottle that contained no air; the rest of the sample was spread in enamel trays to a thickness of 20 mm and exposed to ambient air. Mineralogical analyses of both samples using a D/max 2550 X-ray diffractometer (XRD, Rigaku Corporation, Japan), were conducted before and after 30-day test. Comparing the data for the sealed and the spread samples elucidated the possible effect of exposure to CO₂ on ash characteristics.

In each of the sixteen cylindrical chambers, 100 g raw ash was thoroughly mixed with 1 l distilled water (*L/S*=10 w/w) and then kept still with its upper surface exposed to air, to determine whether the dif-

Table 1
Literature works considering ash aging process

Works	<i>L/S</i> (w/w)	CO ₂	Metals studied	Remarks
Ecke et al. (2003)	0, 0.5	0.03% and 50% v/v	Pb, Zn, Cd, Cr	Flow chamber
Shimaoka et al. (2002)	0–0.6	0–30% v/v	Pb	Flow chamber
Kim et al. (2003)	0.05–0.2	10% v/v	Pb, Ca, Cd	Aged with bottom ash
Fernández Bertos et al. (2004)	0–0.6 (opt. 0.2–0.3)	Pure CO ₂ (3 bars)	Pb, Zn	Shaken or still chambers
This work	0.25, 10	0.03% v/v	Ca, Cd, Cr, Cu, Ni, Pb, Zn, As, Hg	Still chamber

fusional resistance of CO₂ limits the rate of carbonation with a large amount of water. The amount $L/S=10$ was adopted since it is also the recommended ratio in numerous leaching standard tests, including EN 12457 (EU), EPTSW (China), JLT 13 (Japan), and DIN38414 S4 (Germany). The ash quickly settled to a bottom layer with a thickness of 20 mm. CO₂ could be supplied only from the top surface of the water. Such a test involves a sample with a high moisture content. In the sixteen chambers that contained APC residues at $L/S=10$, a thin layer of precipitate would rapidly form on the top surface of the water. In eight chambers, this thin layer was not touched during the test. In the other eight chambers, this layer was carefully removed after it had formed. Ecke et al. (2002) revealed the rather high solubility (>5–10%) of fly ash at $L/S=10$ and 25 °C. Suspension samples were extracted from the supernatant layer at 0, 8, 24, 48, 96, 144, 360 and 720 h, and were filtered using a 0.45 μm membrane before their pH and metal concentrations were measured. An AA-6501F FAAS (Shimadzu Corporation, Japan) was used to analyze the levels of Ca, Cd, Cr, Cu, Ni, Pb and Zn, and a XGY1012 AFS (atomic fluorescence spectrometer, Institute of Geophysical and Geochemical Exploration of the Chinese Academy of Sciences, China) was used to measure the concentrations of As and Hg. The variability of pH measurement was within 0.08, and heavy metals concentration within 2%. The cross-sectional compositions of the heavy metals on the particle surface were scanned using a scanning electron microscope (Philips XL30) equipped with an energy dispersive X-ray spectrometer (EDAX DX4).

3. Results and discussion

3.1. APC characteristics

Table 2 lists the leaching characteristics of the APC residues through the Extraction Procedure for Toxicity of Solid Waste (EPTSW). Independent tests revealed that the surface area of this ash sample was about 5 m² g⁻¹, so the material was not very porous. Notably, the leachate pH of ash, and the concentrations of Hg and Pb in leachate all violate the current national standards of China, so the material is classified as hazardous. Additionally, the calcium concentration in the leachate is high, at approximately 3000 mg l⁻¹, indicating that the carbonic acid is easily precipitated.

3.2. Effects of carbonation on mineralogy of APC residues ($L/S=0.25$)

Comparing the XRD spectra of the raw ash sample and the carbonated ash ($L/S=0.25$), the latter contained calcite and gypsum (Fig. 1). No calcite appeared in the sealed sample without air available, and the gypsum content was not substantially increased. Rather, ettringite [Ca₆Al₂(SO₄)₃(OH)₁₂·26H₂O] had formed in the wet and sealed residues. Shimaoka et al. (2002) also observed similar compounds in their scrubber residues, and found that aging almost completely eliminated them. Accordingly, CaSO₄ and (Na,K)Al₃(SO₄)₂(OH)₆ in raw ash might react initially with water to produce ettringite, which was transformed to more stable forms of sul-

Table 2

Leaching characteristics of the APC residues samples based on Extraction Procedure for Toxicity of Solid Waste (GB5086.1-1997, 1997)

Item	pH	As/(mg l ⁻¹)	Cd/(mg l ⁻¹)	Cr/(mg l ⁻¹)	Cu/(mg l ⁻¹)	Hg/(mg l ⁻¹)	Ni/(mg l ⁻¹)	Pb/(mg l ⁻¹)	Zn/(mg l ⁻¹)
This study*	13.0	0.001	0.04	0.36	0.13	0.164	0.18	63.6	2.26
Average**	12.6 (0.3)	0.001 (0.001)	0.12 (0.07)	0.23 (0.17)	0.25 (0.17)	0.14 (0.16)	0.38 (0.20)	88 (40)	4 (2)
Limited value***	12.5	1.5	0.3	10	50	0.05	10	3	50

Item	Electric conductivity/(ms cm ⁻¹)	Cl ⁻ /(mg l ⁻¹)	SO ₄ ²⁻ /(mg l ⁻¹)	Ca/(mg l ⁻¹)
This study*	27.1	8600	1900	2950
Average**	31.6 (3.4)	10,000 (3190)	1300 (600)	3410 (670)

* Referring to the leaching characteristics of the APC residues used in this study.

** The data cover leaching tests for ten APC residues sampled from the Yuqiao MSW Incineration Plant at different seasons in 2 years (He et al., 2004). The values in the bracket mean standard deviation.

*** According to the national standard of China to be classified as hazardous materials (GB5085.1-1996, GB5085.3-1996, 1996).

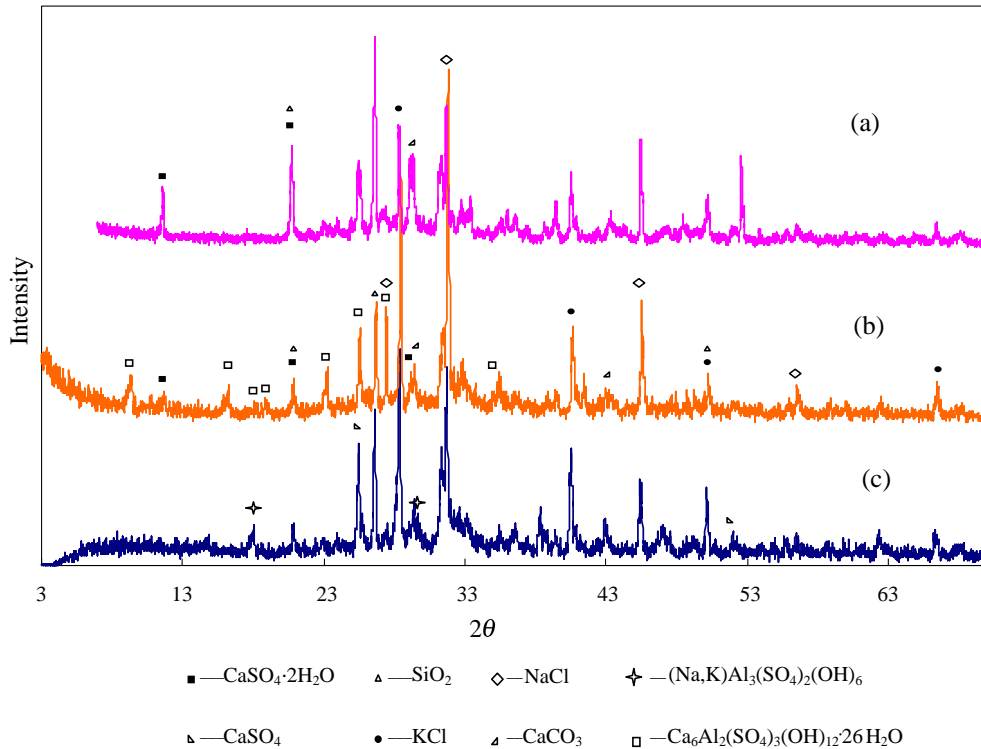


Fig. 1. The XRD spectra of the APC residues. (a) aged sample, (b) wet and sealed sample, (c) raw sample.

fate, carbonate and hydroxide, gypsum, calcite and possibly gibbsite, when CO_2 was present.

Fig. 2 displays typical SEM/EDS images of the raw and aged samples. The elemental compositions of the sample surfaces were estimated by averaging more than 40 images taken of the samples at random. The contents of the main elements in the raw residues followed the sequence $\text{O} > \text{C}$, Ca , Si , $\text{Cl} > \text{K}$, Na , Al , S (Fig. 3). In the aged residues, the abundance of C and O increased significantly from 12.4% to 24.9%, and from 33.1% to 47.0%, respectively, supporting to the conclusion that carbonation occurred in the ash samples by natural aging.

3.3. Aging of APC residues ($L/S=10$)

The SEM micrographs reveal that the layer of precipitate noted in the $L/S=10$ tests contains much calcite (Fig. 4(a)) with scattered spots of gypsum (Fig. 4(b)). Most of the precipitate was fine crystals of calcite that were smaller than $5 \mu\text{m}$, packed

closely into a compact skin layer on the surface of the water. This occurrence was unsurprising because the concentration of calcium ions was approximately 3000 mg l^{-1} and the top water surface represented the only route along which CO_2 could enter. Fig. 5 presents the pH evolutions of the suspension of APC residues ($L/S=10$) with and without the surface precipitate layer. Initially, the fly ash suspension was at pH 12.4. During the 720 h test, the pH of the suspension with the precipitate layer remained almost unchanged. In extended tests, the pH of the suspension remained above 12 for a month (data not shown). In the test with precipitate layer removed, the pH fell slowly from 12.4 to about 10.6 over 50 to 360 h. Some earlier studies also established that the pH of the fly ash suspension declined to around 10 (Hjelmar and Birch, 1997; Shimaoka et al., 2002; Bone et al., 2003; Ecke et al., 2003). After about 8 h, three distinct behaviors were observed. The concentrations of Pb , Zn , Cd , Hg and Cu began to fall

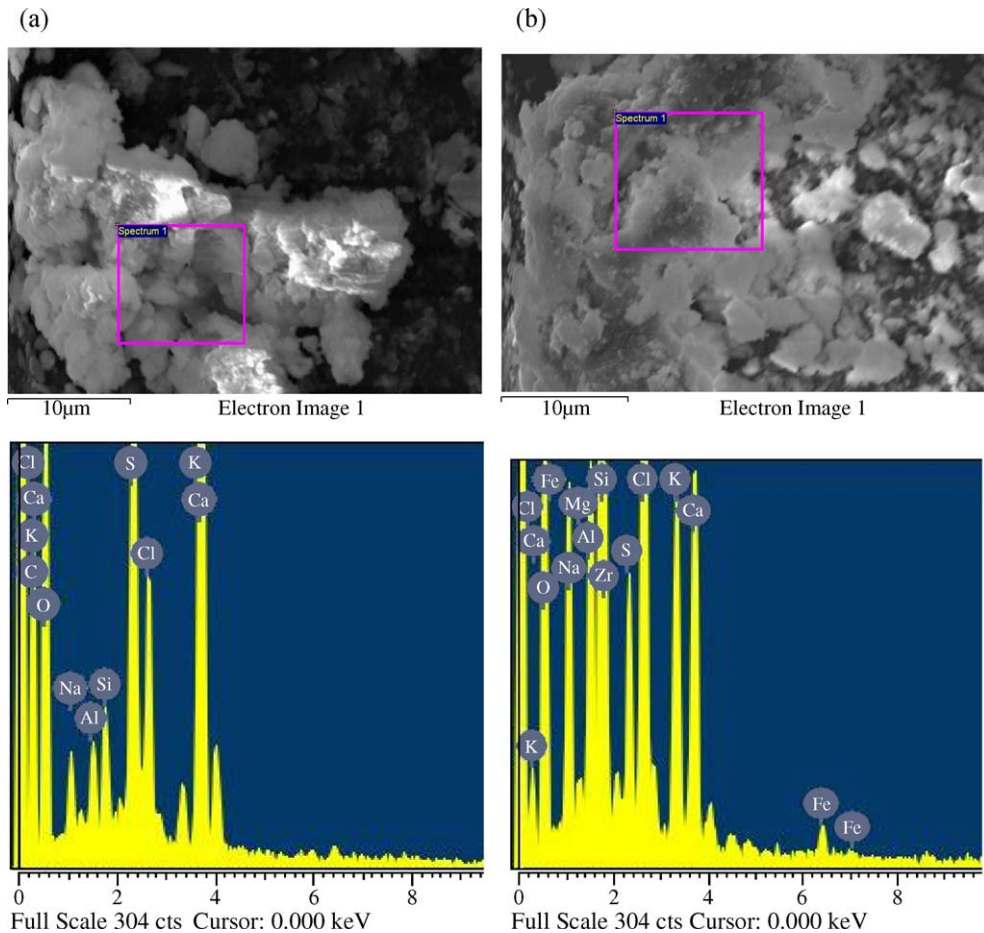
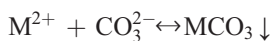


Fig. 2. The SEM/EDS spectra of APC residues samples. (a) raw residues, (b) aged residues.

(Fig. 6(a)–(e)). Those of Ca and Ni remained unchanged (Fig. 6(f)–(g)), and that of Cr increased (Fig. 6(h)).

When many metal ions are present in a solution, the one that must bond with the least CO_3^{2-} to form the carbonate precipitate settles first. The reaction equilibrium between the divalent metal ion and the carbonate ion is:



The minimum concentration of CO_3^{2-} required to form MCO_3 precipitate at a given metal ion concentration is $[\text{CO}_3^{2-}]_0 = \frac{K_{sp}}{M^{2+}}$. Table 3 presents the calculated $[\text{CO}_3^{2-}]_0$ with the metal ion concentrations in the initial ash suspension ($L/S=10$).

The data in Table 3 demonstrate that when CO_2 was dissolved and transferred from the top water surface, the order of precipitation was Pb^{2+} , Ca^{2+} , Zn^{2+} , (Cu^{2+} , Hg^+), Cd^{2+} . With the exception of Ca^{2+} , which was abundant in the fly ash and was supplied by continuous dissolution with aging (shown later), the concentrations of the other five metal ions decreased with aging (Fig. 6(a)–(e)). The very high concentration of Ca^{2+} easily precipitated when CO_3^{2-} was available, promoting the formation of the noted surface precipitate layer in the test.

The CO_3^{2-} concentration was as high as around 0.03 mol l^{-1} to precipitate Ni^{2+} , which was not achievable in the test herein. This observation reveals why the Ni^{2+} concentration remained unchanged throughout the test.

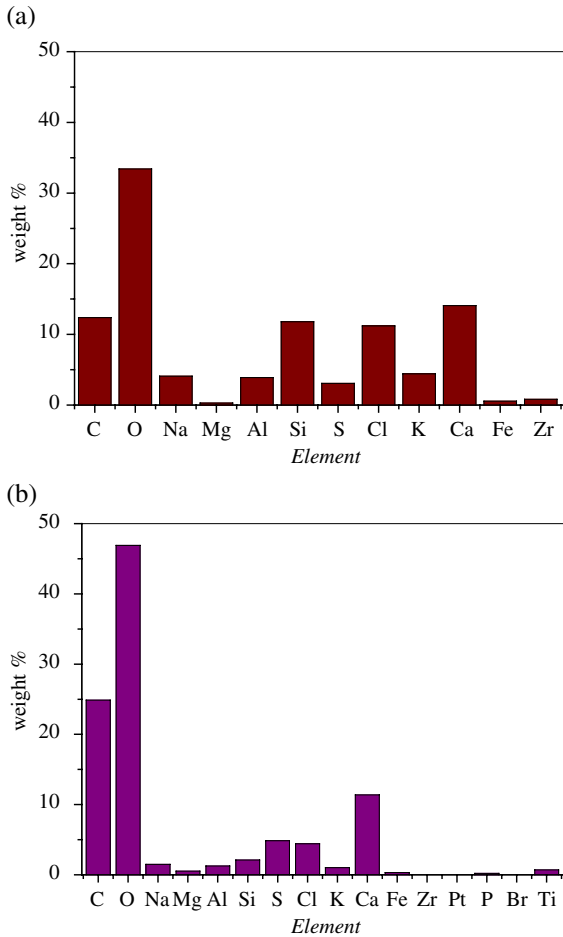


Fig. 3. Mean weight percents of main elements of APC residues samples. (a) raw residues, (b) aged residues.

Unlike for the other metals examined, the concentration of Cr increased with aging, probably because Cr³⁺ was oxidized by dissolved oxygen to the more soluble form, Cr⁶⁺ (Ecke et al., 2003).

The decline in the concentrations of Pb, Zn, Cd and Hg, but not Cu, was faster in the test without a surface precipitate layer than in the test with a surface layer. This observation is attributable to the provision of a mass transfer barrier by the compact surface layer, through which CO₂ had to pass. For example, the drop in the concentration of Pb from 105 to 25 mg l⁻¹ took 150 h in the test without a surface precipitate layer. When the surface layer was present, the time required exceeded 720 h. The corresponding times required for the drop in the concentration of Zn from 15–20 mg

l⁻¹ to around 3 mg l⁻¹ were 100 and 400 h, respectively. Accordingly, when APC residues were mixed with water, the rate of carbonation varied greatly with the manner in which the precipitate was formed and where it was precipitated. When a compact precipitate was formed on the pathway of the CO₂, although the chemical equilibrium calculation revealed the same results, the corresponding carbonation reaction was substantially slower.

Fig. 6(h) unsurprisingly reveals that more Cr was present in soluble form in the test without a precipitate surface layer than in the test with a surface layer, because the compact surface layer also slowed the dissolution of oxygen into water. However, the increase in the dissolution of Cr became marked only after 100–150 h of testing. An optimal period of aging should be used to immobilize heavy metal. In this particular test, the optimal time was 100 h, without the release of Cr, which detrimentally affects the management of residues.

3.4. Rate-controlling step

Insights into carbonation can be gained by comparing the incorporated mass transfer rate with the chemical reaction rate. For the system adopted for L/S=10, CO₂ dissolves at the top water surface, according to Henry's Law:

$$\begin{aligned}
 \text{CO}_2 \text{ mol fraction } (x_0) &= \frac{p_e}{E} = \frac{30}{1.66 \times 10^8} \\
 &= 1.8 \times 10^{-7} \quad (\text{mol mol}^{-1})
 \end{aligned}
 \tag{1}$$

where,

p_e CO₂ partial pressure, 30 Pa in air;
E Henry coefficient, Pa, for CO₂ in water, which is 1.66 × 10⁸ Pa at 25 °C.

If, as posited by Fernández Bertos et al. (2004), the diffusion of CO₂ into ash particles is the rate-controlling step in ash carbonation, then an order-of-magnitude estimate of the rate at which dissolved CO₂ is transferred from the top surface to the bottom layer of residues is as follows:

$$N_{A,\text{CO}_2} = D \cdot \frac{x_0}{L}
 \tag{2}$$

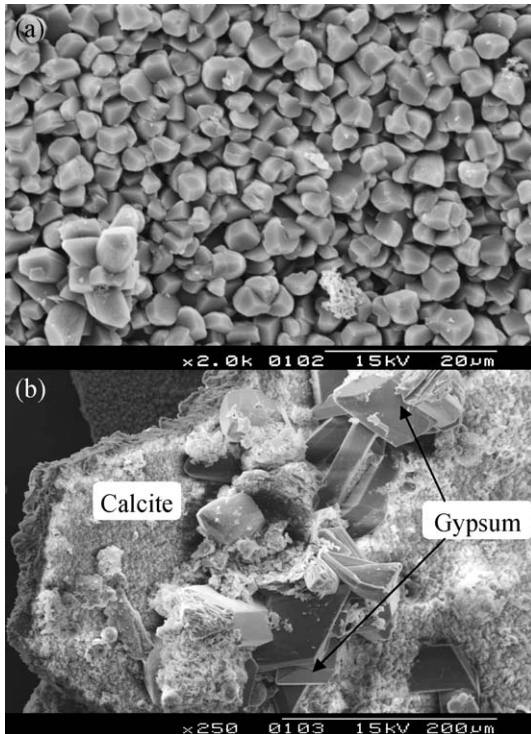


Fig. 4. The SEM micrographs of the surface precipitate layer with the magnification of (a) 2000 \times and (b) 250 \times .

where,

- N_{A,CO_2} Rate of diffusion of dissolved CO_2 from the top surface to the bottom layer of residues;
 L thickness of water above the ash layer, 0.08 m herein;
 D diffusion coefficient of CO_2 in water at 25 $^{\circ}C$, $1.96 \times 10^{-9} m^2 s^{-1}$.

The CO_2 concentration on top surface of the water (x_0) = $1.8 \times 10^{-7} \times 5.56 \times 10^4 = 1 \times 10^{-2} mol m^{-3}$. Accordingly, the rate of CO_2 diffusion is approximated as $N_{A,CO_2} = 1.96 \times 10^{-9} \frac{m^2}{s} \times \frac{0.01 mol m^{-3}}{0.08 m} = 2.45 \times 10^{-10} mol (m^2 s)^{-1}$. The cross-sectional area of the top water surface is $(\pi/4) \times (0.12 m)^2 = 0.0113 m^2$, yielding a diffusional flow of $9.97 \times 10^{-9} mol h^{-1}$. If, however, all CO_2 is assumed to convert to CO_3^{2-} after it is dissolved in water, given that the diffusion coefficient of the latter in water is only $0.92 \times 10^{-9} m^2 s^{-1}$, the corresponding diffusional flow would be even lower. Hence, the above estimate is an upper limit on the diffusional flow of carbonate ions.

Consider the consumption of Pb^{2+} as an example of the calculation. The lead concentration fell from $104 mg l^{-1}$ to almost zero over 100–700 h (Fig. 6(a)). The minimum quantity of Pb^{2+} consumed in the chamber was estimated as $(1 l \times 104 mg l^{-1} / (207 g mol^{-1})) = 5 \times 10^{-4} mol$. Therefore, the time taken for CO_2 to transfer from top surface to bottom residues layer to precipitate all lead is around $(5 \times 10^{-4} mol / 9.97 \times 10^{-9} mol h^{-1}) = 50,000 h$, two to three orders of magnitudes above the experimental values (order of $10^2 h$). Accounting for this huge time span difference could be difficult, even when the effects of enhanced gas adsorption on the alkaline solution or those of transient mass transfer caused by local depletion of carbonate ions are considered. Accordingly, the chemical reaction could proceed effectively in the ash particles that settled in the bottom layer. Rather, the chemical reaction preferentially proceeds in the bulk solution, beginning after the CO_2 has dissolved and hydrolyzed at the top surface of the water. The dissolution and diffusion of CO_2 in the bulk solution is the rate-

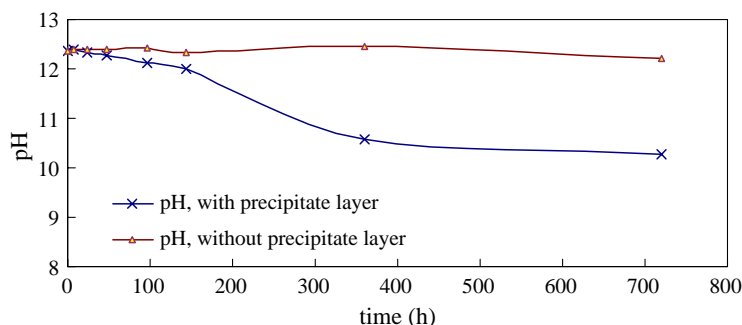


Fig. 5. pH evolutions of suspensions of fly ashes with or without surface precipitate layer.

limiting step of the carbonation of ash suspension ($L/S=10$).

Most heavy metal ions in water have a diffusion coefficient of the order of $10^{-9} \text{ m}^2 \text{ s}^{-1}$. For example,

Ca^{2+} has a diffusion coefficient of $0.79 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ in water at 25°C . If calcium ions were released from the bottom ash layer to form a highly saturated solution with an ion concentration of 10 mol m^{-3} , then the

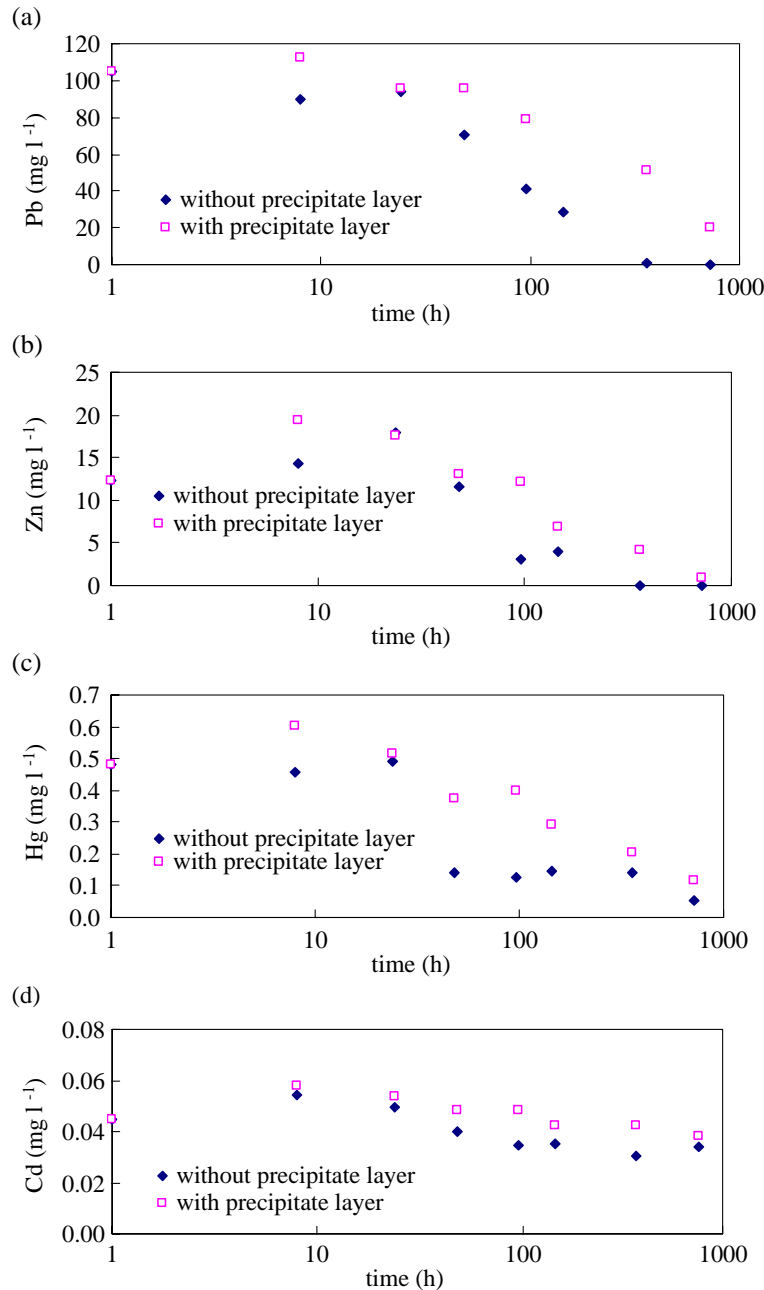


Fig. 6. Concentrations of heavy metals in supernatant with or without surface precipitate layers. (a) Pb, (b) Zn, (c) Hg, (d) Cd, (e) Cu, (f) Ca, (g) Ni, (h) Cr.

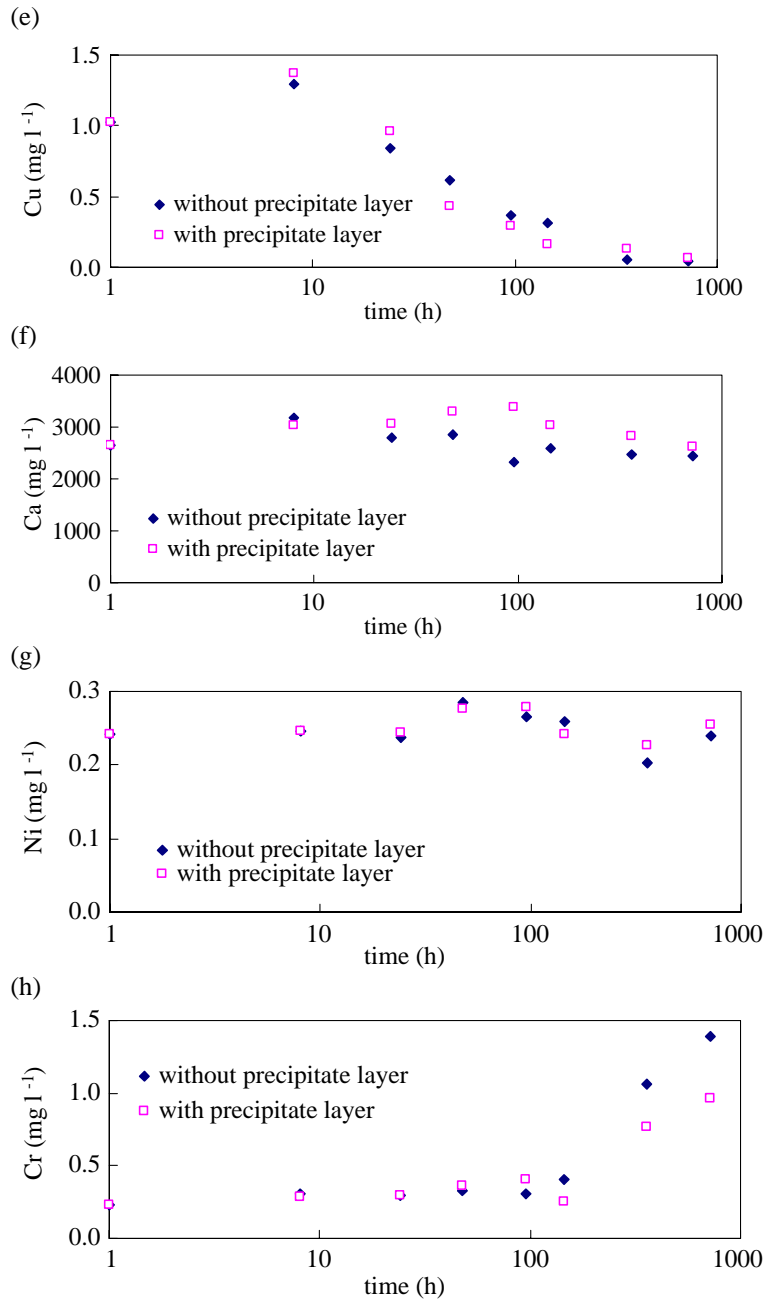


Fig. 6 (continued).

corresponding diffusional flux from the bottom to top surface is estimated as follows; $N_{Ca^{2+}} = 0.79 \times 10^{-9} \frac{m^2}{s} \times \frac{10 \frac{mol}{m^3}}{0.08m} \times 0.0113m^2 = 4.02 \times 10^{-6} \text{ mol h}^{-1}$. This value greatly exceeds that of the

corresponding CO_2 flow ($9.97 \times 10^{-9} \text{ mol h}^{-1}$), yielding an almost constant Ca concentration throughout the aging test, as presented in Fig. 6(f). Meanwhile, the decrease in metal concentrations displayed

Table 3
Precipitation analysis of metal carbonate

Compounds	K_{sp} (25 °C) (Cai et al., 1998; Zheng and Zhu, 1999)	$[M^{2+}]/(\text{mol l}^{-1})$	$[\text{CO}_3^{2-}]_0/(\text{mol l}^{-1})$
PbCO ₃	1.46×10^{-13}	5.07×10^{-4}	2.88×10^{-10}
CaCO ₃	4.96×10^{-9}	6.64×10^{-2}	7.47×10^{-8}
ZnCO ₃	1.19×10^{-10}	1.89×10^{-4}	6.30×10^{-7}
CuCO ₃	1.4×10^{-10}	1.62×10^{-5}	8.65×10^{-6}
Hg ₂ CO ₃ *	3.67×10^{-17}	2.40×10^{-6}	6.40×10^{-6}
CdCO ₃	6.18×10^{-12}	3.99×10^{-7}	1.55×10^{-5}
NiCO ₃	1.42×10^{-7}	4.11×10^{-6}	3.46×10^{-2}

*For monovalent metal ion, $[\text{CO}_3^{2-}]_0 = \frac{K_{sp}}{[M^+]}$.

in Fig. 6(a)–(e) during aging revealed that most dissolvable Pb, Zn, Cd, Cu and Hg were released to the bulk suspension and completely consumed by carbonation in 150–700 h.

Therefore, given a water thickness of 8 cm, the rate-controlling step of aging was the dissolution of CO₂ (or CO₃²⁻) at the top water surface and its transport through and reaction in the bulk solution. The particle size or the surface area of the ash particles does not affect natural aging when the moisture content is high. Meanwhile, agitation should be able to promote the transfer rate of CO₃²⁻, whence its reaction rate in the bulk, as noted by Fernández Bertos et al. (2004).

In the tests with $L/S=0.25$, the 100 g sample was mixed with 25 g of water. Under extreme conditions in which all particle surfaces were coated uniformly with a liquid film, the mean thickness of the liquid film was 50 nm ($25 \text{ cm}^3/(100 \text{ g} \times 5 \text{ m}^2/\text{g})$). Given such a thin film, the corresponding N_{A,CO_2} was 1.6×10^6 times greater than that obtained in the $L/S=10$ tests, yielding a CO₂ flux of 700 mol h^{-1} . The ambient air cannot supply as much CO₂. Even at 1% of this value, the corresponding flux more than suffices to react with all metal ions in the ash samples within half an hour. Meanwhile, the dissolution of metals ions in the attached liquid film is far from complete. Accordingly, under this condition, the rate-limiting step is how fast the heavy metals could be transformed into ionic forms. Restated, the rate of dissolution of metals from ash particles controls the reaction rate. The particle size or surface area of the ash particles governs the rate of aging. Under this extreme condition, the water content is secondary,

and the conclusions drawn by Ecke et al. (2003) are unsurprising: the added water is not significant in relation to the reaction time and the partial pressure of CO₂.

Water content is a very important process factor, whose distribution in the sample, along with the resulting competition between the carbonate ion flux and the heavy metal flux, determines the reaction time required in this natural aging process. Accordingly, the amount of added water and the reaction time are dependent variables and should not be used as independent variables in statistical analysis to interpret experimental data.

4. Conclusions

This study examines the natural aging of APC residues from an MSW incinerator in Shanghai, considering in particular the effect of the amount of added water on the immobilization of the heavy metals. The liquid to solid ratio was fixed at 0.25 or 10 with or without CO₂ supplied from ambient air. With a L/S of 0.25, the CaSO₄ and (Na,K)Al₃(SO₄)₂(OH)₆ in the raw sample would initially react with water to yield ettringite. Then, if external CO₂ were available, the ettringite would be transformed to gypsum and calcite, along with a decline in the pH of the suspension. The C and O contents on ash particle surface also considerably increased following natural aging at ambient air exposure.

With a sufficiently high L/S (10 in this study), excess Ca²⁺ ions were present in the suspension, so a precipitate of mostly crystals of calcite that were smaller than 5 μm form on the air–water surface. With or without this surface precipitate layer, the concentrations of Pb, Zn, Cd, Hg and Cu fell with time, because of carbonation, following closely the precipitation sequence determined by chemical equilibrium calculations. The levels of Ca and Ni in suspensions were almost constant throughout the test, because the Ca²⁺ was too abundant to be completely converted and the concentration of carbonate ions required to precipitate Ni was too high to achieve. Additionally, the declining rates of Pb, Zn, Cd and Hg contents when a surface precipitate layer presented were much lower than those without a surface layer. The amount of Cr increased with

aging, whose rate was also lower when the surface precipitate layer was present. This observation follows from the fact that the added mass transfer barrier of CO₂ or O₂ at the air–water surface influences the occurrence of subsequent chemical reactions.

A simple estimate of the rate of mass transfer revealed that the rate-controlling step at $L/S=10$ was not the diffusion of CO₂ into ash particles, as proposed by Fernández Bertos et al. (2004). The most important chemical reactions occur in the bulk suspension rather than on the surface of the ash particles or inside the ash particles. The dissolution and diffusion of CO₂ in the bulk solution are the rate-limiting steps in the carbonation of ash suspension ($L/S=10$). However, in $L/S=0.25$ tests, the rate-limiting step was the rate of dissolution of metals from ash particles. The water content is a very important process factor, whose distribution in the sample, along with the resulting competition between the carbonate ion flux and the heavy metal flux, determines the reaction time required during natural aging process.

Acknowledgments

We thank Shanghai Council of Science and Technology for the financial support through the project “Research on beneficial use of MSW incineration residues and its demonstration project” (032312043).

Appendix A

D	the diffusion coefficient of CO ₂ in water at 25 °C, $1.96 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$;
E	Henry coefficient, Pa, for CO ₂ in water it is $1.66 \times 10^8 \text{ Pa}$ at 25 °C;
K_{sp}	the solubility–product constant;
$N_{\text{A,CO}_2}$	the diffusion rate of dissolved CO ₂ transferred from top surface to the bottom residues layer;
$N_{\text{Ca}^{2+}}$	the diffusional flux of Ca ²⁺ from the bottom to top surface;
L	thickness of water above the ash layer, 0.08 m here;
p_e	CO ₂ partial pressure, 30 Pa in air;
x_0	CO ₂ mol fraction.

References

- Bin-Shafique S, Walton JC, Gutierrez N, Smith RW, Tarquin AJ. Influence of carbonation on leaching of cementitious waste-forms. *J Environ Eng* 1998;124(5):463–7.
- Bone BD, Knox K, Picken A, Robinson HD. The effect of carbonation on leachate quality from landfilled municipal solid waste (MSW) incinerator residues. In: Christensen TH, Cossu R, Stegmann R, editors. Proc Sardinia 2003, Ninth Waste Management and Landfill Symposium 6–10 October 2003. Italy: S. Margherita di Pula (CA); 2003.
- Cai SH, Huang SY, Zhang YR. *Elemental inorganic chemistry*. Guangzhou: Zhongshan University Press; 1998. 290–291 pp. [in Chinese].
- Ecke H, Menad N, Lagerkvist A. Treatment-oriented characterization of dry scrubber residue from municipal solid waste incineration. *Mater Cycles Waste Manage* 2002;4(2):117–26.
- Ecke H, Menad N, Lagerkvist A. Carbonation of municipal solid waste incineration fly ash and the impact on metal mobility. *J Environ Eng* 2003;129(5):435–40.
- Fernández Bertos M, Li X, Simons SJR, Hills CD, Carey PJ. Investigation of accelerated carbonation for the stabilization of MSW incinerator ashes and the sequestration of CO₂. *Green Chem* 2004;698:428–36.
- He PJ, Zhang H, Zhang CG, Lee DJ. Characteristics of air pollution control residues of MSW incineration plant of Shanghai. *J Hazard Mater* 2004;B116:229–37.
- He PJ, Cao QK, Feng JH, Xia YQ. Source characteristics of byproducts of municipal solid waste incinerator. *Environ Eng* 2005;23(4):56–9 [in Chinese, with English abstract].
- Hjelmar O, Birch H. Treatment of air pollution control residues from MSW incinerators prior to landfilling. In: Christensen TH, Cossu R, Stegmann R, editors. Proc Sardinia 97, Sixth Waste Management and Landfill Symposium, 13–17 October 1997. Italy: S. Margherita di Pula (CA); 1997. p. 535–44.
- Kim SY, Matsuto T, Tanaka N. Evaluation of pre-treatment methods for landfill disposal of residues from municipal solid waste incineration. *Waste Manage Res* (21):416–23.
- Macias A, Kindness A, Glasser FP. Impact of carbon dioxide on the immobilization potential of cemented wastes: chromium. *Cem Concr Res* 1997;27(2):215–25.
- Reijnders L. Disposal, uses and treatments of combustion ashes: a review. *Resour Conserv Recycl* 2005;43:313–36.
- Sabbas T, Polettini A, Pomi R, Astrup T, Hjelmar O, Mostbauer P, et al. Management of municipal solid waste incineration residues. *Waste Manage* 2003;23:61–88.
- Shimaoka T, Miyawaki K, Soeda M, Hanashima M, Yoshida T, Uchida T, et al. Mechanisms for the aging-induced reduction of lead solubility in scrubber residues from municipal solid waste combustion. *Waste Manage Res* 2002;20(1):90–8.
- State Environmental Protection Administration of China. Identification standard for hazardous wastes — identification for extraction causticity, GB50851-1996. [in Chinese].
- State Environmental Protection Administration of China. Identification standard for hazardous wastes — identification for extraction procedure toxicity, GB50853-1996. [in Chinese].

- State Environmental Protection Administration of China. Solid waste- extraction procedure for toxicity of solid waste — horizontal vibration method, GB50861-1997. [in Chinese].
- Valls S, Vázquez E. Accelerated carbonation of sewage sludge-cement-sand mortars and its environmental impact. *Cem Concr Res* 2001;31:1271–6.
- Venhuis MA, Reardon EJ. Vacuum method for carbonation of cementitious wasteforms. *Environ Sci Technol* 2001;35: 4120–5.
- Walton JC, Bin-Shafique S, Gutierrez N, Smith R, Tarquin A. Role of carbonation in transient leaching of cementitious wasteforms. *Environ Sci Technol* 1997;31:2345–9.
- Zheng LM, Zhu SY. Element chemistry. Beijing: Chemical Industry Press; 1999. 211–212 pp. [in Chinese].