Effect of supercritical carbonation on the strength and heavy metal retention of cement-solidified fly ash

Xiaoxiong Zha\textsuperscript{a,*}, Jiaqian Ning\textsuperscript{a}, Mohamed Saafi\textsuperscript{b}, Lijun Dong\textsuperscript{a}, Jean-Baptiste
Mawulé Dassekpo\textsuperscript{a}, Jianqiao Ye\textsuperscript{b,*}

\textsuperscript{a} Department of Civil and Environmental Engineering, Shenzhen Graduate School, Harbin Institute of Technology, 518055 China
\textsuperscript{b} Department of Engineering, Lancaster University, Lancaster LA1 4YR, UK

* Corresponding author.

E-mail address j.ye2@lancaster.ac.uk (J. Ye) and zhaxx@hit.edu.cn (X.X. Zha)

Abstract

This paper presents both experimental and multi-physics studies on the carbonation and heavy metal retention properties of cement-solidified fly ashes. Cement-solidified fly ash samples with 40\% and 60\% fly ash ratios were tested for carbonation depth after being supercritically carbonated. Tests were also carried out for compressive strength and retention capacity of heavy metals of the samples before and after supercritical carbonation. Using CO\textsubscript{2} absorption instead of calcium carbonate to measure carbonation degree, a multi-physics model was developed and combined with a leaching model to study the impact of carbonation on Cu and Pb leaching from the cement-solidified fly ash. The results show that supercritical carbonation has both positive and negative impacts on the strength and retention capability of heavy metals of the cement-solidified fly ashes, which suggests that both the carbonation conditions and the amount of fly ash recycled in cementitious materials should be properly controlled to maximize potential positive effect.

Keywords: Cement-solidified; supercritical carbonation; fly ash; compressive strength; leaching rate.
1. Introduction

Protection of the public from hazardous pollutants in the environment has always been an important priority for most industrialized countries, where a significant portion of the pollutants is related to the increasing demands for energy. The data published by the International Energy Agency stated that the energy consumption had increased by 50.52% from 1990 to 2014. Consequently, the appearance of environmental problems poses a serious threat to the living environment of human beings, such as heavy metal pollution caused by municipal solid waste incineration (MSWI) fly ash [1, 2], global warming due to carbon dioxide (CO₂) emissions [3], and so forth.

Municipal solid waste (MSW) has been always one of the most challenging problems in the management of modern cities. There are about 254 million tons of garbage produced annually in China, namely approximately one kilogram per person per day, the total amount of which is about one third of the world’s annual trash output [4]. The rapid growth of waste causes serious limitations in the development of a city, if it is not handled properly [5]. In recent years, MSWI has been widely used owing to its advantage on capacity reduction and energy recovery efficiency [6, 7]. However, the by-product of MSWI, such as fly ash [8], contains heavy metals that still have serious negative impact on the surrounding environment [9], or can even cause irreparable damage to human health. Therefore, the environmental threat from fly ash cannot be ignored and the development of an economic, efficient and eco-friendly application of fly ash is one of the most important measures to address the current situation.

From the perspective of the construction industry, fly ash can be used as a cement replacement material [10] to develop high performance concrete. Besides the superiority in the value of recycling [11] and CO₂ emissions [12], fly ash can also reduce hydration heat and improve workability [13], as well as durability of concrete [14]. A concrete component with a high fly ash replacement ratio has little impact on the bond strength with conventional concrete [15],
which may also have higher shear strength [16]. Hence, using MSWI fly ash as partial replacement for cement in concrete mixes is potentially feasible [17].

To further develop the potential material, the mechanical properties, durability and leaching performance of the cement-solidified fly ash were studied [18, 19]. Cement solidification technology is an effective waste solidification method, which obviously reduces the leaching toxicity of harmful substances, especially heavy metals, in cement-solidified fly ash [17]. Leaching tests were also conducted to verify the feasibility of the technology [14]. Leaching in a solidified body varies with water-cement ratios and also types of leachants, e.g. deionized or mineralized water. Pure water appeared more aggressive than mineralized water [20]. Moreover, a multi-physics leaching model of a solidified body was also developed and the simulation results were compared with those from leaching experiment of Sr and Cs [21].

Cement-based materials are porous, in which the pores form the channels that leak heavy metals, resulting in a reduced capacity of retaining them in the solidified body [22]. Carbonation of cement-based materials can improve the pore structure of the material, and therefore reduces its porosity [23]. The technique has been used to treat waste to reduce leaching toxicity of certain metals [24]. Recently, research on accelerated and supercritical carbonation, i.e., carbonation under elevated temperature and pressure were carried out [21]. When the temperature and pressure of CO\(_2\) exceed their respective critical states (\(T_c=31.26^\circ\text{C}, P_c=7.39\text{MPa}\)), the CO\(_2\) is said under its supercritical state (SCC) [25]. Other supercritical carbonation models of cement mortar and cement include Refs. [13, 26, 27]. To study the effect of carbonation on the leaching resistance of hazardous waste cement solidification, Zha et al. [21] develop a model using the finite element software COMSOL Multiphysics. The parametric studies from the numerical simulations revealed that carbonation could significantly improve the retention capability of cementitious solids containing hazardous wastes.

In this paper, further modifications on, e.g, the carbonation rate equation, specific heat of CO\(_2\) and change of porosity caused by carbonation, are made based on the simulation model
proposed by Zha et al. [27] for cement-solidified fly ash. The simplified form of the leaching
model [21] is adopted to estimate the leaching of Cu and Pb. The carbonation and leaching
models are used together to build a combined model for the multi-physics carbonation-leaching
problem. Then, carbonation, strength and leaching experiments are carried out for 40% and 60%
cement-solidified fly ash to validate the modified models and study the effect of carbonation
and fly ash ratio on the performance of the cement-solidified fly ash.

2. Mathematical modeling

2.1 Equations of supercritical carbonation process

Based on the natural carbonation model by Saetta et al. [23], Zha et al. [27] proposed a model
for supercritical carbonation, where (1) Darcy’s law was used in place of Fick’s law; and (2)
the change of CO_2 concentration in pore solution was assumed to be equal to that of its solubility,
i.e., assuming that there was always sufficient dissolved CO_2 to participate in the carbonation
reaction under supercritical carbonation conditions.

The equations to be solved include the carbonation rate equation, the mass conservation
equation of CO_2, the gas-liquid two-phase flow equations and the energy conservation equation,
as shown in equation (1).

\[
\begin{align*}
\frac{\partial R_c}{\partial t} &= \alpha_1 f_1(h) f_2(g) f_3(R_c) f_4(T) \\
\frac{\partial g}{\partial t} &= \frac{\partial m_g}{\partial t} \\
\frac{\partial (n S_a \rho_a)}{\partial t} + \nabla \cdot (\rho_a \mu_a) &= q_a \\
\mu_a &= -\frac{k \cdot k_{uw}}{\mu_a} (\Delta P_a) \\
(\rho C_v)^{\text{eff}} \frac{\partial T}{\partial t} &= \nabla \cdot (k_{uw} \nabla T) - (C_s \rho_s \mu_s \mu_{uw} + C_w \rho_w \mu_w) \cdot \nabla T
\end{align*}
\]

where \( R_c \) is the degree of carbonation; \( \alpha_1 \) is the carbonation rate coefficient, indicating the
variation rate of carbonation degree under ideal conditions; \( f_1(h), f_2(g), f_3(R_c) \) and \( f_4(T) \) denote,
respectively, the effect of humidity, CO_2 concentration, carbonation degree and temperature on
the carbonation rate; \( g \) is the mass concentration of CO_2; \( m_c \) is the solubility; \( n \) is the porosity
of the cement-based materials; $S_{\alpha}, \rho_{\alpha}, \mu_{\alpha}, q_{\alpha}, k_{\alpha}, \mu_{\alpha}, P_{\alpha}$ and $C_{\alpha}$ are the saturation, density, Darcy velocity, source item accounting for chemical reaction or precipitation, relative permeability coefficient, dynamic viscosity, pressure and specific heat of component $\alpha$, respectively. The subscript, $\alpha$, can be either $g$ or $w$ denoting gas or liquid phases, respectively; $k$ is the inherent permeability; $(\rho C_q)_{eff}$ is the equivalent heat capacity; $k_{eff}$ is the equivalent thermal conductivity.

2.2 Modification of carbonation equations

Numerous studies on supercritical carbonation of cement-based materials have been conducted [27-29]. However, the adopted theory, e.g., equation (1), is not generally applicable to all the cement-based materials, especially to the materials with admixtures. In this paper, some modifications are introduced to extend its applicability to include cement-solidified fly ash.

2.2.1 Modified carbonation reaction rate equation

The main chemical reactions during the carbonation process of cement-based materials are shown in equation (2), in which C-S-H stands for calcium silicate hydrate.

$$\begin{align*}
\text{Ca(OH)}_2 + \text{CO}_2 & \rightarrow \text{CaCO}_3 + \text{H}_2\text{O} \\
\text{C-S-H} + \text{CO}_2 & \rightarrow \text{CaCO}_3 + \text{SiO}_2 \cdot n\text{H}_2\text{O}
\end{align*}$$

(2)

The carbonation rate was estimated in the previous model [27] on the basis of the measurement of the calcium carbonates generated during the process, i.e., the carbonation degree is calculated by the following equation:

$$R_c = \frac{cc}{cc_{max}}$$

(3)

where $cc$ is the amount of calcium carbonate produced in the carbonation process and $cc_{max}$ is the $cc$ when the material is fully carbonated.

However, the using of calcium carbonate production to measure carbonation degree has its limitations and can be inaccurate in assessing carbonation degree. Calcium carbonate generated by carbonation is an insoluble substance which can be trace dissolved in the pore solution, and reacts with $\text{CO}_2$ and water to form dissolvable calcium bicarbonate under high levels of dissolved $\text{CO}_2$ [30]. Also, calcium carbonate exists not only with the form of the single-
compound in carbonated cement-based materials, but also binds to other remaining products, e.g. to SiO\textsubscript{2} and H\textsubscript{2}O to form xCaCO\textsubscript{3}·ySiO\textsubscript{2}·zH\textsubscript{2}O [31]. This paper proposed an alternative estimation of carbonation degree based on measuring the CO\textsubscript{2} absorbed in the carbonation process, which takes a full account of all reactions with CO\textsubscript{2}. Hence the following carbonation degree equation is proposed:

$$R_c = \frac{c}{c_{max}}$$

(4)

where \(c\) is the CO\textsubscript{2} absorbed by cement-based materials, \(c_{max}\) is the CO\textsubscript{2} absorbed after being fully carbonated, which can be assessed by phenolphthalein indicator [32] that changes the color of any non-carbonated cement to pink. The indicator is a 1% phenolphthalein ethanol solution with 1g phenolphthalein and 95% ethanol diluted to 100 ml. The calculation method of \(c_{max}\) will be discussed in the next section.

Introducing equation (4) into the first equation of equation (1) yields,

$$\frac{\partial c}{\partial t} = \alpha_1 f_1(h) f_2(g) f_3(c) f_4(T)$$

(5)

where \(f_3(c)\) denotes the effect of the absorbed CO\textsubscript{2} on the carbonation rate, which is calculated by.

$$f_3(c) = c_{max} - c$$

(6)

2.2.2 Determination of \(c_{max}\)

The calculation of the maximum CO\textsubscript{2} absorbed per unit volume by cement-based materials in the ideal state is proposed below, which is related to the amount of calcium, iron, and aluminum oxides in the material [33].

$$c_{max} = m_0 \left[ \frac{[CaO]}{M_{CaO}} - 4 \frac{[Fe_2O_3]}{M_{Fe_2O_3}} - 4 \frac{[Al_2O_3]}{M_{Al_2O_3}} \right]$$

(7)

where, \(m_0\), in kg/m\textsuperscript{3}, is the amount of cement per cubic meter cement-based materials; \(M\) and \([\ast]\), in which \(*\) can be CaO, Fe\textsubscript{2}O\textsubscript{3} or Al\textsubscript{2}O\textsubscript{3}, represent the molar mass and the mole fraction of metallic oxide in cement, respectively. In equation (7), \(M_{CaO} = 0.056\) kg/mol, \(M_{Fe_2O_3} = 0.16\)
kg/mol and $M_{\text{Al}_2\text{O}_3} = 0.102$ kg/mol.

Because the dimension of $c_{\text{max}}$ is mol·m$^{-3}$ in equation (7) and kg·m$^{-3}$ in equation (6), Equation (7) is modified as follows:

$$c_{\text{max}} = M_c m_h \left( \frac{[\text{CaO}]}{M_{\text{CaO}}} - 4 \frac{[\text{Fe}_2\text{O}_3]}{M_{\text{Fe}_2\text{O}_3}} - 4 \frac{[\text{Al}_2\text{O}_3]}{M_{\text{Al}_2\text{O}_3}} \right)$$

where $M_c$ is the molar mass of CO$_2$ ($M_c = 0.044$ kg/mol).

When cement is partially replaced with admixtures that have similar chemical components, (e.g., fly ash with major chemical constituents CaO, SiO$_2$, Al$_2$O$_3$ and Fe$_2$O$_3$), the hydration and carbonation of the resulting admixtures should be considered. However, the chemical composition of fly ashes depends on the characteristics and composition of the coal burned in e.g., a power station. Berry [22] demonstrated that there was a wide range of fly ash compositions. Fly ash is generally classified as Low-calcium Fly Ash (LFA, <10% CaO) and High-calcium Fly Ash (HFA, ≥10% CaO). For LFA, the $c_{\text{max}}$ calculated by equation (8a) using the fly ash compositions in Refs. [34, 35] is negative, and for HFA, the $c_{\text{max}}$ calculated using the fly ash compositions in Ref. [36] is ignorable when compared to that calculated for Ordinary Portland Cement (OPC) [37]. Thus, in this paper, the contribution of fly ash to CO$_2$ absorption of the cement-solidified is ignored.

Additionally, the amount of CO$_2$ absorbed during the carbonation process can be significantly reduced due to the following two reasons: (1) cement-based materials are porous material having large quantity of small and closed pores, which makes it difficult for the internal materials to contact with CO$_2$; and (2) the precipitations generated in the carbonation process accumulate on the inner surface of pores and clog the transport channels of CO$_2$, and then prevent the reaction from proceeding. Thus, equation (8a) can be modified by introducing a reduction factor, $\alpha$, as shown in equation (8b) below:

$$c_{\text{max}} = \alpha M_c m_h \left( \frac{[\text{CaO}]}{M_{\text{CaO}}} - 4 \frac{[\text{Fe}_2\text{O}_3]}{M_{\text{Fe}_2\text{O}_3}} - 4 \frac{[\text{Al}_2\text{O}_3]}{M_{\text{Al}_2\text{O}_3}} \right)$$
This paper combines numerical and experimental methods to estimate the reduction factor $\alpha$, as follows.

The CO$_2$ absorbed by a micro-volume of cement sample can be expressed as:

$$dm = R_c c_{max} dv$$  \hspace{1cm} (9)$$

where $dm$ is the weight increment of $dv$ after carbonation. Hence, $m$ can be obtained by integrating equation (9) over the whole cement sample.

$$m = \iiint_V R_c c_{max} dv = c_{max} \iiint_V R_c dv$$  \hspace{1cm} (10)$$

where $m$ is the weight increase of cement sample after carbonation. The cylindrical Ordinary Portland Cement (OPC) paste samples having the same diameter and height of 50mm were used for carbonation. The chemical components of the OPC are CaO, Fe$_2$O$_3$ and Al$_2$O$_3$ with weights of 61.87%, 5.26% and 5.14%, respectively [37]. The average weight increase measured after carbonation was about 4.21g. A numerical model was developed and calibrated against the experimental $c_{max}$, and $\iiint_V R_c dv$ was calculated by volume integration using COMSOL.

By combining the experiment and simulation results, the reduction factor calculated by equations (10) and (8b) was $\alpha=0.178$, which, in principal, is affected by multi-factors, such as composition, mixing rule, pore characteristics, etc. Because of the limitation of the experiments, 0.178 was used in the simulations (section 3) as the reduction factor for all the CCFC composites and verified against the experimental results (section 4). Clearly, further studies on the relationship between the reduction factor and the influential factors are needed, which requires additional extensive experimental work.

### 2.2.3 Modification on the CO$_2$ specific heat

The specific heat of CO$_2$ at constant pressure was adopted previously in the equation (1). However, the pressure may change in a carbonation process, due to, e.g. a gradual reduction of available CO$_2$ as carbonation is progressing. Naturally, the effect of pressure on the specific heat of CO$_2$ should be considered. Researches on specific heat of CO$_2$ for different temperature
and pressure have been conducted by Li et al. [38] and Shi et al. [39]. The specific heat for 35°C and a pressure of 7.0 to 8.0 MPa, which was proposed by Shi et al. [39], is used here for the supercritical condition, as follows:

\[
C_v = \frac{40 + 11.5 \times (P_c - 7)}{M_c}
\]  

(11)

where \(P_c, M_c\) are the pressure and molar mass of CO\(_2\), respectively.

### 2.2.4 Modification on the change of porosity

The change in porosity is the key factor for its close link to the leaching behavior of the solidified cement. The following equation [40] was adopted previously in Zha et al. [27]:

\[
n = \begin{cases} 
    n_0(1 - 0.5R_c) & 0 \leq R_c \leq 0.4 \\
    0.8 \cdot n_0 & 0.4 \leq R_c \leq 1 
\end{cases}
\]  

(12)

where \(n_0\) is the porosity of the cement-based materials before carbonation.

Equation (12) only considers the effect of Ca(OH)\(_2\) on porosity and ignores the effect of other materials in the cement-based materials, such as C-S-H, unhydrated 2CaO·SiO\(_2\) and 3CaO·SiO\(_2\). Shen et al. [26] reported that the porosity of cement-based materials after carbonation could be reduced by more than 50%, which was larger than the value calculated by equation (12). Other literatures [21, 26, 41] also mentioned that porosity reduction could reach up to above 70%. Hence, a mathematical model based on the experiment results of Zha et al. [21], which is more accurate to reflect the variation of porosity during carbonation, is proposed below:

\[
n = \begin{cases} 
    0.4n_0 & 0.9 < R_c \leq 1 \\
    0.85 - 0.5R_c & 0.5 \leq R_c \leq 0.9 \\
    1 - 0.8R_c & 0 \leq R_c < 0.5 
\end{cases}
\]  

(13)

### 2.3 Equation of leaching process

Zha et al. [21] established the partial differential equations of leaching process on the base of Song et al. [42], which was according to the theory of non-equilibrium thermodynamic. However, from GB/T 7023-2011 [43] for leaching tests, temperature is required to be constant during the leaching process. The effect of temperature on the leaching is, therefore, neglected.
in this paper, resulting in the following equation:

\[ \nabla \cdot [\rho D \nabla C] - \lambda' \rho C + F = \rho \frac{\partial C}{\partial t} \]  \hspace{1cm} (14)

where \( \rho \) is the density of the cement-based materials; \( D \) is the effective coefficient of diffusion; \( \lambda' \) is the decay constant; \( F \) denotes the constant of absorption rate; \( C \) is the mass concentration of the leaching elements, which varies with position and time, i.e., \( C = f(x,y,z,t) \).

**2.4 Calculation of chemical activity factor**

The chemical activity factor was introduced to consider the effect of chemical fixation on the diffusion coefficient in Zha et al. [21], and it was expressed by the ratio of free element concentration to the total element. The respective values adopted for Sr and Cs was 0.7 and 0.06 [21]. Obviously, there is great difference in chemical activity factor for different elements, which might depend on the pH and the chemical compositions in a cement-solidified material.

However, to the authors’ best knowledge, there is no published researches on the calculation of chemical activity factor during a carbonation process. In this paper, the chemical activity factors of Pb and Cu were evaluated backwardly from the leaching experiment results against carbonation degree. The obtained chemical activity factors of Pb and Cu are, respectively,

\[ r_1 = (1 - 0.8R_1^3) \cdot r_{01} \]  \hspace{1cm} (15)

\[ r_2 = (1 + 33R_2) \cdot r_{02} \]  \hspace{1cm} (16)

where \( r_1, r_2 \) are the chemical activity factors of Pb and Cu respectively during carbonation, while \( r_{01} \) and \( r_{02} \) are their initial values.

**3. Numerical simulation**

**3.1 Geometric model**

In this section, carbonation and leaching of cement-solidified fly ash are simulated using the finite element software COMSOL. The solidified cement block is cylindrical having the same diameter and height of 50mm, which is placed within a cylindrical container of 120mm in diameter and 115mm in height, as shown in Fig. 1.
3.2 Carbonation model

The carbonation process using the modified model in Section 2.2 is simulated by COMSOL with specified initial values of $R_c=0$, $P_g=1 \text{ atm}$, $P_w=P_{w0}$, $T=T_0$ and $g=0$. Furthermore, the boundary conditions are modeled to represent, as close as possible, the actual reaction conditions in the laboratory experiments. As to the carbonation degree $R_c$ and the CO$_2$ concentration $g$, both mathematically satisfied the Neumann boundary conditions, i.e.,

$$\nabla \cdot \n = 0 \quad \text{and} \quad \nabla \cdot g = 0,$$

respectively. The pressure and temperature used in the carbonation model were obtained from those measured in the experiments.

The carbonation process is closely related to the chemical compositions in the cement-based materials. $c_{\text{max}}$ was introduced previously in the paper to distinguish the content of CO$_2$ absorbed by different cement-based materials after full carbonation, and the cement-solidified samples with 40% and 60% fly ash were chosen to validate the modified model. The respective $c_{\text{max}}$ calculated from equation (8b) are 46.6 kg/m$^3$ and 34.1 kg/m$^3$. After carbonated for 3 hours, the carbonation degree ($R_c$) obtained by Zha et al. [27] and the current model on the vertical sections across the center are shown in Fig. 2 and Fig. 3, respectively.
By using the model proposed in Zha et al. [27], it is not possible to consider the variation of fly ash ratio in the calculation of carbonation degree, as shown in Fig. 2, while it can be taken into account now by the modified model, as shown in Fig. 3. This is due to the introduction of $c_{\text{max}}$ that is different for different fly ash ratios (equation (8b)). In the simulation, a region is judged
as fully carbonated when its $R_c$ is larger than 0.99. The carbonation depth from Fig. 2 is about 12mm, and those obtained from Fig. 3 are about 2.3mm and 3.5mm, respectively, for cement-solidified units with 40% and 60% fly ash. The experiment studies of these will be shown in Section 4.2.

### 3.3 Leaching model

In the leaching process, the initial ion concentration $C$ in the leachant and the cement-solidified samples are set as $C=0$, $C=C_0$, respectively. The leaching from the samples to the leachant are assumed to be diffusion and due to concentration difference. The boundary of the leaching container is set as an insulation boundary, which is expressed by the Neumann boundary condition, $n \cdot \nabla C = 0$.

### 3.4 Combined model

The independent carbonation and leaching models developed from the above sections are combined to form a continuous modeling process by introducing the carbonation results, e.g. the reduced porosity caused by carbonation, directly into the leaching model. It is worth noting that the diffusion coefficient of the leaching process should be set to zero at the carbonation process to prevent any leaching, while the carbonation rate coefficient is set to zero during the leaching process.

### 4. Experiments

#### 4.1 Sample preparation

The main materials used in this study are Ordinary Portland Cement (OPC) and Fly Ash (FA). The fly ash was supplied from Nanshan waste incineration power plant in Shenzhen. To avoid the extreme situations, i.e. the strength of the sample is too low [44, 45] or the leaching concentration of heavy metals is too small to measure, 40% and 60% fly ash ratios in cement-solidified were investigated in this study. The mixture design of the samples is presented in Table 1. Each of the samples was cast into a cylinder having the same diameter and height of 50mm.
Table 1 The mixture of the cement-solidified fly ash samples

<table>
<thead>
<tr>
<th>Mass ratio of fly ash</th>
<th>Components</th>
<th>Mass (g)</th>
<th>Mixing time(min)</th>
<th>Sample No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>40%</td>
<td>Cement</td>
<td>1500</td>
<td>15</td>
<td>2/3-1~2/3-19</td>
</tr>
<tr>
<td></td>
<td>Fly ash</td>
<td>1000</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Water</td>
<td>1400</td>
<td></td>
<td></td>
</tr>
<tr>
<td>60%</td>
<td>Cement</td>
<td>1000</td>
<td>15</td>
<td>3/2-1~3/2-19</td>
</tr>
<tr>
<td></td>
<td>Fly ash</td>
<td>1500</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Water</td>
<td>1400</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The average initial Cu and Pb contents of the cement-solidified fly ash samples are shown in Table 2, which were used also in the simulations (Section 3.3) to calculate the leaching rate.

Table 2 Cu and Pb contents in a sample

<table>
<thead>
<tr>
<th>Element</th>
<th>40% fly ash sample (g)</th>
<th>60% fly ash sample (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>0.0309</td>
<td>0.0452</td>
</tr>
<tr>
<td>Pb</td>
<td>0.1006</td>
<td>0.1462</td>
</tr>
</tbody>
</table>

4.2 Carbonation

After being cured for 28 days, the cement-solidified fly ash samples were carbonated using the CO₂ closed-cycle test system including the high-temperature and high-pressure reaction vessel, as shown in Fig. 4 [21]. The closed-cycle system was designed to recycle the CO₂ and minimize the amount of CO₂ entering the atmosphere. In the process of carbonation, the temperature was primarily controlled by the chiller, and the pressure was controlled by the pump. The controlled pressure and temperature curves are shown in Fig. 5. It is worth noting that the carbonation simulations were run only for the duration when the pressure is stabilized.
In order to determine whether the cement-solidified samples were carbonated, the mass of the cement-solidified fly ash before and after carbonation were measured and is shown in Table 3. The results show that the average percentages of mass increases of the samples are 5.416 (40% fly ash) and 4.288 (60% fly ash), respectively. The mass increases of the samples with 40% fly ash are generally larger than those of 60% fly ash, which is attributed to the larger amount of mineral components (alkaline components) in the 40% than the 60% fly ash samples. The 40% fly ash samples absorbed more CO$_2$, i.e. gained more weight than those of the 60% fly ash to
reach the same carbonation degree, which is also demonstrated by the calculation of $c_{\text{max}}$ that are 46.6 kg/m$^3$ and 34.1 kg/m$^3$, respectively for the 40% and 60% cement-solidified fly ash.

Table 3 Mass increase percentages of the cement-solidified samples after carbonation

<table>
<thead>
<tr>
<th>Mass ratio of fly ash</th>
<th>Sample No</th>
<th>Mass before carbonation (g)</th>
<th>Mass after carbonation (g)</th>
<th>Mass increase percentage (%)</th>
<th>Average mass increase percentage (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>40%</td>
<td>2/3-1</td>
<td>167.9</td>
<td>177.7</td>
<td>5.837</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2/3-4</td>
<td>170.6</td>
<td>179.7</td>
<td>5.334</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2/3-6</td>
<td>172.5</td>
<td>180.5</td>
<td>4.638</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2/3-10</td>
<td>173.3</td>
<td>181.8</td>
<td>4.905</td>
<td>5.146</td>
</tr>
<tr>
<td></td>
<td>2/3-11</td>
<td>164.5</td>
<td>171.7</td>
<td>4.377</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2/3-14</td>
<td>164.5</td>
<td>174.0</td>
<td>5.775</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2/3-16</td>
<td>169.5</td>
<td>176.4</td>
<td>4.071</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2/3-19</td>
<td>168.5</td>
<td>176.4</td>
<td>4.071</td>
<td></td>
</tr>
<tr>
<td>60%</td>
<td>3/2-6</td>
<td>164.0</td>
<td>170.8</td>
<td>4.146</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3/2-7</td>
<td>163.9</td>
<td>172.0</td>
<td>4.942</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3/2-8</td>
<td>167.3</td>
<td>174.3</td>
<td>4.184</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3/2-11</td>
<td>171.5</td>
<td>176.0</td>
<td>2.624</td>
<td>4.288</td>
</tr>
<tr>
<td></td>
<td>3/2-14</td>
<td>163.4</td>
<td>172.4</td>
<td>5.508</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3/2-15</td>
<td>165.4</td>
<td>171.4</td>
<td>3.628</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3/2-18</td>
<td>164.2</td>
<td>170.8</td>
<td>4.019</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3/2-19</td>
<td>163.6</td>
<td>172.2</td>
<td>5.257</td>
<td></td>
</tr>
</tbody>
</table>

In order to measure carbonation depth, the cross sections of the 40% and 60% fly ash samples were, respectively, inspected. Phenolphthalein indicator was sprayed on the cut and the un-carbonated zones changed color, as shown in Fig. 6. It is evident from the color change that cement-solidified fly ash samples were carbonated as the CO$_2$ penetration from the outside surfaces.
Carbonation depths were measured at 88 points randomly selected along the carbonation front of each samples. The average depths of the 40% and 60% fly ash sample are, respectively, 2.1mm and 3.0mm. The test results agree well with the simulation carbonation depths based on the modified model (respectively, 2.3mm and 3.5mm), but are significantly different with those based on Zha et al. [27] (about 12mm). The results show that the capability of absorbing CO₂ varies with chemical compositions, which further influences carbonation depth. The above comparisons confirm that using CO₂ absorption, c, rather than calcium carbonate production to measure carbonation degree in simulations is more accurate.

4.3 Strength test

Strength tests were also carried out on the samples before and after carbonation. The cement-solidified fly ash samples were divided into 4 groups in the test, i.e. the 40% cement-solidified fly ash before and after carbonation; the 60% cement-solidified fly ash before and after carbonation. Each un-carbonated group had 5 samples, while each carbonated group had 3 samples that had been carbonated for 3 hours under the supercritical condition. The test results are listed in Table 4.

Table 4 Strength of the samples
<table>
<thead>
<tr>
<th>Group</th>
<th>Sample No</th>
<th>Strength (MPa)</th>
<th>Average strength (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Non-carbonated 40% fly ash</td>
<td>2/3-12</td>
<td>23.4</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2/3-13</td>
<td>17.1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2/3-15</td>
<td>20.2</td>
<td>20.9</td>
</tr>
<tr>
<td></td>
<td>2/3-17</td>
<td>20.6</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2/3-18</td>
<td>23.5</td>
<td></td>
</tr>
<tr>
<td>Carbonated 40% fly ash</td>
<td>2/3-4</td>
<td>17.9</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2/3-6</td>
<td>16.7</td>
<td>17.1</td>
</tr>
<tr>
<td></td>
<td>2/3-14</td>
<td>16.7</td>
<td></td>
</tr>
<tr>
<td>Non-carbonated 60% fly ash</td>
<td>3/2-3</td>
<td>9.1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3/2-7</td>
<td>7.1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3/2-9</td>
<td>10.4</td>
<td>9.1</td>
</tr>
<tr>
<td></td>
<td>3/2-10</td>
<td>9.2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3/2-16</td>
<td>9.6</td>
<td></td>
</tr>
<tr>
<td>Carbonated 60% fly ash</td>
<td>3/2-6</td>
<td>7.2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3/2-11</td>
<td>7.8</td>
<td>7.6</td>
</tr>
<tr>
<td></td>
<td>3/2-19</td>
<td>7.8</td>
<td></td>
</tr>
</tbody>
</table>

It is apparent from the test results that the overall strength of the carbonated samples is lower than that of the samples before carbonation. This is different from Li [28] on cement blocks without added fly ash, where the strength of cement block increased by more than 60% after carbonation. For the cement blocks tested here, the replacement of cement by fly ash reduced the size of pores [46], which made the block more sensitive to micro cracks due to the expansion of pores caused by the calcium carbonate produced during carbonation process. The earlier formation of the micro-cracks contributed to the reduction in strength of the cement-solidified fly ash.

However, the results agree with Junior et al. [47], where the compressive strength of cement paste decreased after being carbonated for 4 hours, though increase in strength occurred during the first 1-2 hours carbonation. Junior et al. [47] also showed that the longer the carbonation duration was (more than 4 hours), the greater the strength reduction would be. These might attribute to the fact that the generated calcium carbonate had exceeded the limit of the pores,
which caused additional internal pressure and micro-crack [30]. In this paper, the cement-solidified fly ash was subject to supercritical carbonation, resulting in a quick accumulation of calcium carbonate in the pores and an earlier reduction in strength.

Table 4 also shows that the average strength of the 40% samples is more than twice that of the 60% samples for before and after carbonation, i.e., the strength of the cement-solidified samples is greatly reduced as the content of fly ash increases. The results agree with those of Lombardi et al. [48], which showed that the amount of strength reduction with fly ash/cement ratio varying from 0.75 to 1.5 was about 50% which is in line with the reduction (56.5% for un-carbonated samples, 55.6% for carbonated samples) observed from this study. In summary, the duration of carbonation and the proportion of fly ash added in cement-solidified fly ash should be properly administrated to optimize their recycling value.

4.4 Leaching experiment

4.4.1 Experiment equipment and process

The cement-solidified fly ash samples required simple surface treatment to remove stains before the leaching experiment. They were placed in pre-cleaned leaching containers. 1.2 L deionized water was injected into each of the containers to submerge the samples. The containers were then sealed and placed in a leaching chamber of constant temperature ready for the leaching experiment.

Twenty cement-solidified fly ash samples were tested in the leaching experiment, which were divided into 4 groups as shown in Table 5. Each of the groups have 5 samples with the same fly ash ratio and carbonation time. The total leaching time is 42 days. Leaching rates at days 1, 3, 7, 10, 14, 21, 28, 35 and 42 were measured and group averages were calculated.

Table 5 Details of leaching experiment

<table>
<thead>
<tr>
<th>Group</th>
<th>Sample No</th>
<th>Leaching temperature(°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Non-carbonated 40% fly ash</td>
<td>2/3-2,2/3-3,2/3-7,2/3-8,2/3-9</td>
<td>25</td>
</tr>
<tr>
<td>Group</td>
<td>Sample No</td>
<td>Leaching temperature(°C)</td>
</tr>
<tr>
<td>------------------------------</td>
<td>-----------------</td>
<td>--------------------------</td>
</tr>
<tr>
<td>Carbonated 40% fly ash</td>
<td>2/3-1, 2/3-10, 2/3-11, 2/3-16, 2/3-19</td>
<td></td>
</tr>
<tr>
<td>Non-carbonated 60% fly ash</td>
<td>3/2-1, 3/2-2, 3/2-4, 3/2-5, 3/2-12</td>
<td></td>
</tr>
<tr>
<td>Carbonated 40% fly ash</td>
<td>3/2-7, 3/2-8, 3/2-14, 3/2-15, 3/2-18</td>
<td></td>
</tr>
</tbody>
</table>

The method recommended by GB/T 7023-2011 [43] was used to calculate the leaching rate of the cement-solidified fly ash.

\[ R_n = \frac{a_n / A_0}{(S / V)(\Delta t)_n} \]  

where \( R_n \) is the leaching rate of heavy metals in the \( n \)th leaching period (cm/d), \( a_n \) is the leaching mass in the \( n \)th leaching period (g), \( A_0 \) is the initial mass of heavy metals in the cement-solidified fly ash (g), \( S \) is the contact area of the sample and leachant (cm\(^2\)), \( V \) is the volume of sample, and \((\Delta t)_n \) is the days of the \( n \)th leaching period (d).

### 4.4.2 Results and analysis

The leaching rates of Cu in the 40% and the 60% cement-solidified fly ash are shown, respectively, in Figs. 7 and 8, and those of Pb in the 40% and the 60% cement-solidified fly ash are shown, respectively, in Figs. 9 and 10.
Fig. 8 Leaching rates of Cu in 60% cement-solidified fly ash

Fig. 9 Leaching rates of Pb in 40% cement-solidified fly ash
Fig. 10 Leaching rates of Pb in 60% cement-solidified fly ash

From Figs. 7-10, the simulated leaching rates of Pb agree well those measured in the leaching tests, while the agreement between the simulated and tested leaching rates of Cu are less satisfactory. This may be owing to that the calculation method of chemical activity factor for Cu (equation (15)) was not sufficiently accurate, which should include the impacts of not only the carbonation degree, but also the pH and ionic characteristics of the cement-based materials. Further research is required in this direction. Nevertheless, the modified model has correctly predicted the decrease of the leaching rate of Cu with increase of leaching time and the increase in leaching rate after the samples were carbonated (from the Figs. 7 and 8), which is consistent with the leaching tests results.

The leaching rate of Cu in carbonated cement-solidified fly ash is generally higher than that of the un-carbonated as shown in Figs. 7 and 8. The increased leaching of Cu from the cement-solidified samples is in line with the results of Valls and Vázquez [49] and Ginneken et al. [25], but in contrast with the results of Gerven et al. [18], which may be due to the use of different types of fly ash, leachant pH, mixing ratio [19] and leaching procedures [48]. Based on the experiments of this paper, it is clear that carbonation does not help in retaining Cu in the cement-
One of the reasons is that carbonation leads to a decrease in pH of the cement-solidified fly ash (chemical retention), which deteriorates the chemical stability of Cu element in the form of hydroxide or carbonate under high-pH conditions, and is beneficial to the solubility of Cu element, thus increases the content of leachable Cu and its leaching rate [18]. The other is that though the calcium carbonate formed during the carbonation can block the leaching of the heavy metals (physical retention) [23, 50], the micro-crack induced by the over-carbonation can also promote leaching, and this may have occurred in this experiment. In addition, there is little difference in the long-term leaching rates of Cu in 40% and 60% cement-solidified fly ash, whether before or after carbonation. It can be seen from equation (17) that the leaching rate of leaching elements is proportional to the ratio of the leaching amount and the total amount of the leaching elements. In addition, for both Cu and Pb, Table 2 shows that the total amount of them is in proportional to the fly ash ratio. Thus, for a given leaching rate, the leaching amount of Cu varies linearly with fly ash ratio. A cement-solidified sample with higher fly ash ratio will leach more Cu.

The leaching rate of Pb of the carbonated cement-solidified fly ash was obviously lower than that of the un-carbonated (Figs. 9 and 10). The results agreed with those of Gerven et al. [18] and Sanchez et al. [51], but disagreed with those of Shafique et al. [52]. It is noteworthy to mention that the leaching in Shafique et al. [52] was mainly caused by micro-cracks after a significant decrease in porosity caused by carbonation. Because of the formation of lead carbonate (PbCO₃) from carbonation, Pb appears less solubility in neutral than high pH [18]. Hence, the leaching of Pb is influenced by both chemical and physical retentions. Considering the majority of the published results on leaching of Pb and the observations from this paper, it can be concluded that chemical retention has played a more important role than physical retention in reducing Pb leaching. Contrast to a rather constant long-term leaching rate of Cu for the samples with different fly ash ratios, the long-term leaching rate of Pb increases as the fly ash ratio increases. Hence, an increase of fly ash ratio will result in leaching more Pb than Cu, which can be accounted for that the amount of Pb is larger than that of Cu in fly ash (Table
Overall, it can be concluded that the effect of carbonation on the leaching of heavy metals is not always favorable.

5. Conclusions

An existing supercritical carbonation model has been modified to consider carbonation of cement-solidified fly ash of various mixture ratios. This model was further combined with a leaching model to simulate leaching of heavy metals, i.e., Cu and Pb, in cement-solidified fly ash with and without being carbonated. Carbonation and leaching tests were carried out to verify the new models. The effect of supercritical carbonation on the properties of the cement-solidified fly ash were studied both numerically and experimentally. From the study the following observations have been made:

1. Using CO$_2$ absorption instead of calcium carbonate to measure carbonation degree is more accurate in simulating carbonation process of cement-based materials with various mixtures.

2. The strength of cement-solidified fly ash after carbonation may be reduced, depending on the carbonation duration and fly ash ratio.

3. The leaching of Cu and Pb before and after carbonation have shown that carbonation is not always beneficial to the retention of heavy metals, depending on the combined effect of chemical and physical retentions.

4. Leaching of Cu and Pb increases as fly ash ratio increases, while the increase in Pb leaching is more substantial.

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**Reference**


