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Mathematical modelling of concrete carbonation with moving boundary

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ABSTRACT

This paper presents the mathematical models describing the diffusion of carbon-dioxide in concrete with considering the effect of concrete carbonation. The effect of concrete carbonation on carbon-dioxide diffusion is modelled by using a sink term added in the diffusion equation. It is shown that, when the carbonation reaction is much faster than the diffusion process, the diffusion of carbon-dioxide in carbonated concrete can be treated as the diffusion problem with a moving boundary, representing the diffusion front or the carbonation depth. An analytical solution is also derived for the diffusion problem with moving boundary.

Keywords: Modelling; carbon-dioxide; diffusion; concrete carbonation; moving boundary.
1. Introduction

The corrosion of steel in reinforced concrete structures is the major concern of infrastructure owners and operators. Two major causes that are connected to corrosion of reinforcing steel in concrete structures are the carbonation and chloride attack. Carbonation is a set of reactions between atmospheric carbon-dioxide and alkaline components of concrete, producing a carbonated surface layer in which the pore solution pH value is depressed to near-neutral levels [1,2,3]. A secondary effect of carbonation, also significant in terms of its influence on reinforcing steel corrosion, is that it can cause the release of bound chloride ions into the pore solution phase of concrete that contains a modest level of chloride salts as a contaminant, thus exacerbating the corrosive nature of the electrolyte [4,5]. The carbon-dioxide diffusion has been investigated in capillaries and in a cavity with N₂-CO₂ mixture [6,7]. A variable–density single-phase incompressible model has been developed for numerical simulation of the DDC (dissolution–diffusion–convection) process of carbon-dioxide [8]. In addition, carbonation can also influence the diffusion of chloride ions in concrete as it can alter the pore volume and pore structure and thus the transport properties of concrete [9,10,11]. In certain cases the permeability of carbonated concrete may increase, as in the case of concrete made with blended cements such as blast furnace slag and fly ash concrete [9,10]; in others, it may decrease as in ordinary Portland cement concrete [4,11]. In urban and industrial areas,
where environmental pollution results in a significant concentration of carbon-dioxide, carbonation-initiated reinforcement corrosion prevails [12]. While in highways and marine or coastal structures, chloride ions, originating from deicing salts or seawater, are transported through the concrete pore network and micro-cracks and depassivate the oxide film covering the reinforcing steel and thus induce the corrosion of reinforcing steel [13]. The worst situation is when a concrete structure is subjected to both carbonation and chloride attack [14]. A recent study [15] reported that the probability of the corrosion initiation for the combined action of carbonation and chloride attack is almost two times higher than the case in which the two attacks are considered separately. This illustrates the difficulty that arises when the presence of more than one corrosion-inducing agent contributes to aggressiveness of the exposure conditions for a particular structure.

Extensive research work has been carried to understand how carbon-dioxide transports in concrete pore medium and how it reacts with cement products in concrete. Saetta et al. [16] presented a two-dimensional finite element model for the illustration of concrete carbonation mechanism. The model was used to analyse the effects of multi-dimensional moisture, heat and carbon-dioxide transport through concrete on the corrosion of a reinforcing bar placed at the corner of a concrete structure. Steffens et al. [17] developed a theoretical model to predict the carbonation of concrete structures. The model described the movement and retention of heat, moisture and carbon-dioxide by means of balance equations and diffusion laws. The governing equations of the model were solved numerically using finite element techniques. Liang and Lin [18] presented a mathematical model with a set of one-dimensional linear diffusion equations to simulate the transport problems of carbon-dioxide, chloride and sulphate ions in concrete.
Isgor and Razaqpur [19] proposed a nonlinear finite element approach for modelling coupled heat transfer, moisture transport and carbonation processes in concrete for tracing the spatial and temporal advancement of the carbonation front in concrete structures with and without cracks. The numerical results were compared with available experimental data. Kumazaki [20] presented a mathematical model of carbon-dioxide transport in concrete carbonation process. The model was described by using a parabolic type equation with a nonlinear perturbation such that a coefficient of the time derivative contains a non-local term depending on the unknown function itself. Zhang [21] developed a mathematical model of carbonation process in porous concrete materials. The model was solved numerically using uncoupled finite volume method. Numerical simulations under normal and accelerated carbonation conditions were presented. Zhu et al. [22] proposed a comprehensive model to simulate the transports of carbon-dioxide, chloride ions, heat and moisture in concrete. The model was validated using several sets of experimental data.

The above survey of literature shows that many mathematical models have been developed to describe the carbonation phenomena in concrete. However, most of existing models are difficult to use either because they require too many input data or because they were developed for some specific application cases. In this paper a mathematical model describing the diffusion of carbon-dioxide in concrete with considering the effect of concrete carbonation is developed. The diffusion model is established using Fick’s first law, whereas the effect of concrete carbonation on carbon-dioxide diffusion is modelled by using a sink term added in the diffusion equation. The present diffusion model is simplified to the diffusion problem with a moving boundary representing the diffusion front or the carbonation depth when the
carbonation reaction is much faster than the diffusion process. An analytical solution is also derived from the diffusion problem of moving boundary for calculating corresponding carbonation depth.

2. Modelling of carbon-dioxide diffusion in concrete with general carbonation reaction

Concrete carbonation commonly takes place after the atmospheric carbon-dioxide, CO\textsubscript{2}, diffuses into concrete from the air through concrete gaseous phase. The chemical reactions occurring during concrete carbonation can be broken down into two stages. One is the dissolving of CO\textsubscript{2} in pore solution and the other is the reaction of the dissolved CO\textsubscript{2} with the hydration products (mainly calcium ions) within the cement phase of concrete. The detailed description of the reactions for concrete carbonation can be found in the work of Bary and Sellier [23]. Nevertheless, the following represents the main reaction taking place during the concrete carbonation [24],

\begin{equation}
Ca(OH)\textsubscript{2}(s \rightarrow \text{aq}) + CO\textsubscript{2}(g \rightarrow \text{aq}) \rightarrow CaCO\textsubscript{3}(\text{aq} \rightarrow s) + H\textsubscript{2}O (\text{aq})
\end{equation}

where the dissolved Ca(OH)\textsubscript{2} in pore solution will quickly decompose into calcium and hydroxide ions. Thus, Eq.(1) can be also expressed as follows,

\begin{equation}
Ca^{2+}(\text{aq}) + 2OH^- (\text{aq}) + CO\textsubscript{2}(\text{aq}) \rightarrow CaCO\textsubscript{3}(s) + H\textsubscript{2}O(\text{aq})
\end{equation}

where “g”, “aq” and “s” are the abbreviation of gaseous, aqueous and solid phase, respectively.

The transport of CO\textsubscript{2} in concrete gaseous phase can be described by using Fick laws with considering the consumption of CO\textsubscript{2} due to carbonation as follows [25,26,27],

\begin{equation}
\frac{\partial C}{\partial t} = \nabla(D\nabla C) - Q_{CO2}
\end{equation}
where $C$ in kg/m$^3$ is the content of CO$_2$ freely diffusing in concrete gaseous phase, $t$ in s is the time, $D$ in m$^2$/s is the diffusion coefficient of CO$_2$ in concrete gaseous phase, and $Q_{CO2}$ in kg/(s-m$^3$) is the sink term representing the consumption rate of CO$_2$ due to carbonation, which can be approximated as follows [21,28],

$$Q_{CO2} = \frac{\partial S}{\partial t} = k_t(S_a - S)$$

where $S$ in kg/m$^3$ is the content of CO$_2$ consumed due to carbonation, $k_t$ in s$^{-1}$ is the reaction rate constant, and $S_a$ in kg/m$^3$ is the available content of CO$_2$ that can be consumed at a given condition.

Assume that the calcium ions in the pore solution are initially uniformly distributed and the process of their transport in the pore solution is much slower than that of their reaction taking place during carbonation. In this case the carbonation rate will be mainly controlled by calcium ions and $S_a$ can be assumed to have the following expression,

$$S_a = S_{\text{max}} \left[ 1 - \exp \left( -k_a C_s \right) \right]$$

where $S_{\text{max}}$ in kg/m$^3$ is the maximum content of CO$_2$ that can be consumed in carbonation, $C_s$ in kg/m$^3$ is the content of CO$_2$ on the exposed surface (i.e. the content of CO$_2$ in environment where the concrete is exposed), and $k_a$ is a dimensionless constant, which is used to reflect the effect of CO$_2$ concentration in gaseous phase on the relationship between $S_a$ and $S_{\text{max}}$. The reaction rate constant $k_t$ and dimensionless constant $k_a$ can be determined using experimental data obtained from concrete carbonation tests. In general, they would be dependent on the temperature and relative humidity of the environment surrounding the concrete and the properties of concrete raw materials. Fig. 1 graphically shows the relationship between $S_a$ and $C$. It can be seen from the figure that when $k_a \to \infty$, $S_a=S_{\text{max}}$; indicating that $S_a$ is a constant.
except at the point of $C=0$. Substituting Eq.(5) into (3) and (4), it yields,

\[
\frac{\partial C}{\partial t} = \nabla (D \nabla C) - k_t S_{\text{max}} \left( 1 - \exp \left( -\frac{k_a C}{C_s} \right) - \frac{S}{S_{\text{max}}} \right) \quad (6)
\]

\[
\frac{\partial S}{\partial t} = k_t S_{\text{max}} \left( 1 - \exp \left( -\frac{k_a C}{C_s} \right) - \frac{S}{S_{\text{max}}} \right) \quad (7)
\]

![Fig. 1. Relationship between $S_a$ and $C$.](image)

Eqs.(6) and (7) are the governing equations which can be used to determine the content of CO$_2$ diffusing in concrete gaseous phase and the content of CO$_2$ consumed during concrete carbonation. The corresponding initial and boundary conditions of $C(t,x)$ and $S(t,x)$ can be expressed as follows,

**Initial conditions:**

\[
C(0, x) = 0 \quad (8)
\]

\[
S(0, x) = 0 \quad (9)
\]

**Boundary conditions:**

\[
C(t, 0) = C_s, \quad C(t, \infty) = 0 \quad (10)
\]
\begin{align}
S(t, 0) &= S_{\text{max}}, \quad S(t, \infty) = 0 \quad (11)
\end{align}

Eqs. (6)-(11) completely describe the transport problem of carbon-dioxide in concrete with taking into account the effect of concrete carbonation. Eqs. (6)-(11) can be solved using numerical methods such as the finite difference method \cite{26,27}. Fig. 2 shows the distribution profiles of \( C(t,x) \) and \( S(t,x) \) at a given time for various different values of \( k_a \) and \( k_i \), obtained from the numerical solutions. It can be seen from the figure that the distribution pattern of the concentration profile of \( \text{CO}_2 \) is more sensitive to the profile constant \( k_a \) describing \( S_a \) than to the reaction rate constant \( k_i \). An important feature that can be observed is the idealized situation of \( k_a \to \infty \) and \( k_i / D \to \infty \) (red line shown in Fig. 2) in which the diffusion of \( \text{CO}_2 \) accompanied by the instantaneous and irreversible consumption of a limited amount of the diffusing \( \text{CO}_2 \), leading to a sharp front of the consumed \( \text{CO}_2 \). In front of the advancing boundary the content of the freely diffusing \( \text{CO}_2 \) is zero, while behind it the content of the consumed \( \text{CO}_2 \) is complete. This problem is similar to the heat flow in a medium which undergoes a phase change at some fixed temperature, accompanied by the absorption or liberation of latent heat.
Fig. 2. Effects of $k_t$ and $k_a$ on the distribution profiles of (a) CO$_2$ in gaseous phase and (b) consumed CO$_2$ due to carbonation ($k_c=10^{-6}$ s$^{-1}$, $k_a=500$, $D=1.5 \times 10^{-11}$ m$^2$/s, $S_{max}/C_s=2$, $\sqrt{Dt}=15.3$ mm).

It is also observed from Fig.2 that when $k_t$ or $k_a$ is small the front of the consumed CO$_2$ profile is not steeply straight but slowly decreases with increased distance, indicating that the carbonation reactions still take place in part of the carbonated zone. The transport of CO$_2$ in the carbonated zone thus can be divided into two sub-zones. One is the fully carbonated zone in which the transport of CO$_2$ is governed by diffusion only; the other is the partially carbonated zone in which the transport of CO$_2$ is governed not only by diffusion but also by carbonation.

As an example, Fig.3a shows the profiles of the consumed CO$_2$ at various different times obtained from the present model. It is obvious from the figure that the carbonation reactions still take place in the zone behind the carbonation front. The carbonation depth for a given time
can be obtained from the carbonation front. By identifying the carbonation fronts from the profiles of consumed CO$_2$ obtained at various different times we can find the relationship between the carbonation depth and exposure time, which is plotted in Fig.3b. To demonstrate the present model, experimental data [1] obtained from accelerated carbonation tests are also superimposed in the figure. The experimental work was carried out inside a test chamber with CO$_2$ concentration about 50 percent. The specimens tested were mortars with high water-to-cement ratio 0.8. The parametric values used in the simulation are chosen to match the experimental data. The results shown herein illustrate that the relationship between the carbonation depth and exposure time may not necessarily follow the time square root relation when the carbonation reactions are not faster than the diffusion speed of CO$_2$ in the gaseous phase. Note that, in many carbonation tests of concrete the carbonation depth is determined by using the phenolphthalein indicator solution [25,28], which is a colourless acid/base indicator and can turn purple when its pH value exceeds 9. However, this test does not give the depth of maximum ingress of CO$_2$ (i.e., the front point of partially carbonated zone) since the CO$_2$ in the partially carbonated zone may cause a decrease in the pH-value beyond the carbonation depth indicated by the phenolphptalein spray test, but their pH value may still be over 9.
Fig. 3. (a) Profiles of consumed CO$_2$ at various different times. (b) Variation of carbonation depth with exposure time ($k_t=4.25 \times 10^{-7}$ s$^{-1}$, $k_a=5000$, $D=6.0 \times 10^{-11}$ m$^2$/s).

In most cases, however, the chemical reaction between the carbonate ions and the calcium ions in pore solution is much quicker than the diffusion of the CO$_2$ in the gaseous phase. Hence, the reaction can be assumed to take place only at the diffusion front, whereas the transport of CO$_2$ can be assumed to take place only in the gaseous phase of the carbonated concrete. The consumption of CO$_2$ in the diffusion front can be assumed to be controlled by the availability of the Ca(OH)$_2$ or calcium ions in the pore solution. Under these assumptions, both $k_a$ and $k_t/D$ can be assumed to be infinitely large and the corresponding diffusion model described above requires only three constants $D$, $C_s$ and $S_{\text{max}}$; each has a clearly physical meaning. Physically, this may represent the natural carbonation case where CO$_2$ ingress is relatively slow, whereas
the carbonation reaction is relatively fast.

Note that there is some numerical difficulty for solving Eqs.(6)-(11) when \( k_a \to \infty \) and \( k_t/D \to \infty \). Nevertheless, numerically, one can employ any large numbers for \( k_a \) and \( k_t/D \) to achieve the approximate solutions of the idealised case of \( k_a \to \infty \) and \( k_t/D \to \infty \). As a numerical example, Fig. 4 shows the distribution profiles of \( C(t,x) \) and \( S(t,x) \) obtained at three different times that correspond to the parametric values \( \sqrt{Dt} = 8.82 \) mm, 12.5 mm and 15.3 mm, respectively, when \( k_a = 500 \) and \( k_t = 1.0 \times 10^{-6} \) s\(^{-1}\) (\( \sqrt{k_t/D} = 211 \) m\(^{-1}\)) are employed. It is clear from the figure that the distribution profiles of \( S(t,x) \) terminate nearly abruptly in all of the three times. The infinite gradient at the diffusion front leads to some oscillations in the start point of the profiles. This implies that if care was not taken in the selection of spatial and time intervals, the numerical solution may become inaccurate.

![Fig. 4](image_url)

**Fig. 4.** Concentration profiles of (a) CO\(_2\) in gaseous phase and (b) consumed CO\(_2\) at different
times ($k_t=10^{-6}$ s$^{-1}$, $k_a=500$, $D=1.5 \times 10^{-11}$ m$^2$/s, $S_{\text{max}}/C_s=2$).

3. Modelling of carbon-dioxide diffusion in concrete with fast carbonation reaction

For the case where the carbonation reactions are fast while the carbon-dioxide diffusion is slow the transport model described in Section 2 can be simplified by assuming $k_a \to \infty$ and $k_b/D \to \infty$. To avoid the numerical difficulty when solving the idealised case of $k_a \to \infty$ and $k_b/D \to \infty$, the transport problem of carbon-dioxide in concrete with taking into account the effect of concrete carbonation described in Section 2 is now treated as the diffusion problem of particles in which part of particles are trapped in stationary holes. By considering the mass change of the total CO$_2$ in a unit volume of concrete in a time interval $dt$, the following mass conservation equation can be established,

$$\frac{\partial C_T}{\partial t} = \nabla (D \nabla C)$$  \hspace{1cm} (12)

where $C_T=C+S$ in kg/m$^3$ is the total content of CO$_2$ in concrete. The right-hand-side of Eq.(12) is the flux gradient based on the Fick’s first law, in which $C$ in kg/m$^3$ is the content of CO$_2$ freely diffusing in the gaseous phase of carbonated concrete. The initial and boundary conditions of $C_T(t,x)$ can be expressed as follows,

$$C_T(0,x) = 0 \hspace{1cm} (13)$$

$$C_T(t,0) = C_s + S_{\text{max}}, \hspace{0.5cm} C_T(t,\infty) = 0 \hspace{1cm} (14)$$

When solving Eqs.(12)-(14) for $C_T$ one has to know the content of CO$_2$ in concrete gaseous phase, which is the function of $C_T$ and $S_{\text{max}}$ and can be expressed as follows,

$$C(t, x) = \begin{cases} 
C_T(t, x) - S_{\text{max}} & C_T(t, x) > S_{\text{max}} \\
0 & C_T(t, x) \leq S_{\text{max}}
\end{cases} \hspace{1cm} (15)$$
Note that, in the region of $C_T(t,x) > S_{max}$ all holes are completely filled, whereas in the region of $C_T(t,x) < S_{max}$ the holes are not completely filled and therefore $C(t,x) = 0$. Eqs.(12)-(15) can be used for solving for $C_T(t,x)$ and thus $C(t,x)$ can be obtained.

Compared to the model described in Section 2, the model presented herein by Eqs.(12)-(15) is much simple, clear, concise and easy to solve. As a numerical example, Fig.5 shows the distribution profiles of $C(t,x)$ and $S(t,x)$ at three different times obtained from the present model. For the purpose of comparison, the results obtained from the model described in Section 2 are also superimposed in the figure. It can be observed from the figure that there is almost no difference in the results of $C(t,x)$ obtained from the two models. There is only a small difference in the results of $S(t,x)$ at the diffusion front obtained from the two models. To examine the spatial-time relationship, Fig.6 replots the three profiles of $C_T(t,x)$ shown in Fig.5 but using a combined spatial and time coordinate, $x/\sqrt(Dt)$. It can be seen from the plot that when the combined coordinate is used the profiles at three different times are merged together, indicating that the diffusion depth of CO$_2$ is proportional to the square root of the diffusing time.
Fig. 5. Comparisons of (a) CO$_2$ profiles and (b) consumed CO$_2$ profiles between general and fast carbonation reaction models (thin and thick lines represent the results of general and fast reaction models, respectively, $D=1.5 \times 10^{-11}$ m$^2$/s).

Fig. 6. Concentration profiles of total CO$_2$ at three different times plotted against combined
spatial and time coordinate \((D=1.5\times10^{-11} \text{ m}^2/\text{s})\).

4. Modelling of carbon-dioxide diffusion in concrete with moving boundary

The mass conservation equation (12) can be applied to any point in the domain \((0<x<\infty)\). However, if it is applied only to the domain \((0<x<\xi)\) where \(\xi\) is the diffusion front, then \(\frac{\partial C}{\partial t} = \frac{\partial c}{\partial t}\) since \(S=S_{\text{max}}\) is a constant in the domain \((0<x<\xi)\). Thus, Eq.(12) can be further simplified to Eq.(16),

\[
\frac{\partial c}{\partial t} = \nabla(D\nabla C) \quad 0 < x < \xi
\]

The initial and boundary conditions of \(C(t,x)\) can be expressed as follows,

\[C(0, x) = 0\quad (17)\]
\[C(t, 0) = C_s, \quad C(t, \xi) = 0\quad (18)\]

Note that \(\xi\) is the function of time, which moves forward when time increases. Thus Eqs.(16)-(18) represents the diffusion problem with moving boundary. As it is demonstrated in Section 3, the depth of the diffusion front is proportional to square root of the diffusing time.

Thus, the following expression can be assumed for \(\xi(t)\),

\[\xi(t) = k_\xi \sqrt{D_t}\quad (19)\]

where \(k_\xi\) is a constant to be determined. The solution of Eq.(16) with the initial and boundary conditions defined by Eqs.(17) and (18) can be expressed as follows,

\[C(t, x) = C_s \left( 1 - \frac{\text{erf}\left(\frac{x}{k_\xi \sqrt{D_t}}\right)}{\text{erf}\left(\frac{k_\xi}{2}\right)} \right) \quad 0 \leq x \leq \xi\quad (20)\]

where \(\text{erf}(\cdot)\) is the error function. It is obvious from Eq.(20) that if \(k_\xi\) is known then the solution (20) for \(C(t,x)\) is completely defined. In order to determine \(k_\xi\) an additional mass conservation
equation need to be established at the point of the diffusion front, which can be expressed as
follows,
\[-D \frac{\partial C}{\partial x} = S_{\text{max}} \frac{d\zeta}{dt}\] for \(x = \zeta\) (21)

Physically, the left-hand-side of Eq.(21) represents the diffusion flux from the diffusion
zone into the zone ahead of the diffusion front; whereas the right-hand-side of Eq.(21)
represents the flux required in order that the diffusion front can advance by a distance of \(d\zeta\) in
the time interval of \(dt\). Substituting Eqs.(19) and (20) into (21), it yields,
\[\frac{k_{\zeta}}{2} \text{erf} \left( \frac{k_{\zeta}}{2} \right) \exp \left( \frac{k_{\zeta}^2}{4} \right) = \frac{c_s}{\sqrt{\pi S_{\text{max}}}}\] (22)

Eq.(22) is a nonlinear algebraic equation about \(k_{\zeta}\), which can be used to determine \(k_{\zeta}\) for
a given ratio of \(C_s/S_{\text{max}}\). After \(k_{\zeta}\) is determined it can be substituted into Eq.(19) for calculating
the depth of diffusion front \(\zeta(t)\) and Eq.(20) for calculating the profile \(C(t,x)\) of CO\(_2\). Fig.7
graphically shows the relationship between \(k_{\zeta}\) and \(C_s/S_{\text{max}}\). It can be seen from the figure that
\(k_{\zeta}\) increases with \(C_s/S_{\text{max}}\); initially very quick but it becomes slow afterwards. It is clear from
Eq.(19) that the influence of \(C_s/S_{\text{max}}\) on \(\zeta(t)\) is the same as that it does on \(k_{\zeta}\). To demonstrate
the analytical solutions presented by Eqs.(19) and (20), Fig.8 provides a comparison between
the analytical solution given by Eqs.(19)-(20) and the numerical solutions given by Eqs.(12)-(15)
for the concentration distribution profile of freely diffusing CO\(_2\). As it is to be expected,
there is no difference between the analytical and numerical solutions.

Of a particular interest is the case where \(C_s/S_{\text{max}}<<1\) and/or \(k_{\zeta}<<1\), for which case the
following approximation can be taken mathematically,
\[\frac{k_{\zeta}}{2} \text{erf} \left( \frac{k_{\zeta}}{2} \right) \exp \left( \frac{k_{\zeta}^2}{4} \right) \approx \frac{k_{\zeta}^2}{2\sqrt{\pi}}\] (23)

Hence, Eq.(22) can be simplified as follows,
Fig. 7. Variation of $k_\xi$ with $C_s/S_{\text{max}}$.

Fig. 8. Effect of $C_s/S_{\text{max}}$ on CO$_2$ profiles at time $\sqrt{Dt}=15.3$ mm (lines are analytical solution given by Eqs.(19)-(20) and symbol points are numerical solutions given by Eqs.(12)-(15)).

\[ k_\xi = \frac{2C_s}{\sqrt{S_{\text{max}}}} \]  \hspace{1cm} (24)

The corresponding diffusion front $\bar{\xi}(t)$ can be simplified as follows,
\[ \xi(t) = \sqrt[2]{\frac{c_s D t}{S_{max}}} \]  

Eq. (25) is identical to that proposed by Papadakis et al. [1], Houst and Wittmann [29], Hyvert et al. [30], and Klopfer [31]. Experimental validation of Eq. (25) has been reported in literature, for example, [1, 29, 30, 31, 32], and thus is not provided herein. However, it is obvious from the above derivation that Eq. (25) is only limited to the case where the surface content of CO\(_2\) is much lower than the consumed content of CO\(_2\) in carbonation; otherwise one has to use more accurate equation, Eq. (22), instead of its simplified form, Eq. (24), to calculate the carbonation depth. Fig. 7 shows the difference between \(k_\xi\) calculated from Eq. (22) and that calculated from Eq. (24), from which one can clearly see the difference between them can be ignored for \(C_s/S_{max}<0.5\). Compared with existing work, not only can the present analytical solution be used to predict the carbonation depth but also to estimate the profile of CO\(_2\) in the carbonated concrete.

CO\(_2\) level in the atmosphere is normally expressed as parts per million or ppm. It was reported that the CO\(_2\) level increases in recent years and was at 391 ppm in March of 2011, which is 0.0391% of the atmosphere. The air density can be approximately taken as 1.225 kg/m\(^3\). This gives the content of CO\(_2\) in air is about 0.479 g/m\(^3\). The maximum amount of CO\(_2\) that can be consumed in concrete carbonation can be estimated as follows [33],

\[ S_{max} = 0.75CaOCem \frac{M_{CO_2}}{M_{CaO}} = 0.377Cem \]  

Eq. (26)

where CaO (≈0.64) is the amount of calcium oxide per weight of cement, Cem is the content of cement used in concrete, \(M_{CO_2}=44 \text{ g/mol}\) and \(M_{CaO}=56 \text{ g/mol}\) are the molar weight of CO\(_2\) and CaO, respectively. For normal Portland cement concrete Cem is about 350 kg/m\(^3\). This gives \(S_{max}=132 \text{ kg/m}^3\) and thus \(C_s/S_{max}=0.36 \times 10^{-5}\), which indicates that Eq. (24) can be safely
used for most natural carbonation cases unless for specific laboratory tests where the
concentration of CO₂ used is much higher and the tested concrete is with supplementary
cementitious materials (SCMs) which may reduce the content of the cement used in concrete.

5. Conclusions

In this paper we have presented the mathematical models to describe the diffusion of
carbon-dioxide in concrete with considering the effect of concrete carbonation. Three models
have been discussed, namely the diffusion model with general carbonation reaction, the
diffusion model with fast carbonation reaction, and the diffusion model with moving boundary.
Numerical solutions have been provided for the first two models, whereas analytical solution
has been derived for the third model. Comparisons between the three models have been also
provided, which illustrates their advantages and disadvantages. From the present study the
following conclusions can be drawn:

- In the diffusion model with general carbonation reaction the distribution pattern of the
  concentration profile of CO₂ is more sensitive to the profile constant $k_a$ describing $S_a$ than
to the reaction rate constant $k_r$.

- It is more convenient to use the total concentration of CO₂ to model the diffusion of CO₂
  in concrete with fast carbonation reaction, which avoids the difficulty of moving boundary.
The diffusion front obtained from the numerical model for the diffusion model with fast
  carbonation reaction represents the carbonation depth.

- The analytical solution presented for the diffusion model with moving boundary can be
directly used to examine the effects of diffusion coefficient of CO$_2$ in carbonated concrete, diffusing time, and the ratio of $C_s$-to-$S_{max}$ on the depth of concrete carbonation.

- It is demonstrated from the present analytical solution that the square root dependence of carbonation depth on $C_s/S_{max}$ provided in many existing studies is appropriate only for the case where $C_s/S_{max}$ is very small; otherwise more accurate nonlinear equation, Eq.(22), instead of its simplified form, Eq.(24), should be used for calculating the carbonation depth.

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