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6 **Mathematical modelling of concrete carbonation with moving boundary**

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12

13 **ABSTRACT**

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

21 **Keywords:** Modelling; carbon-dioxide; diffusion; concrete carbonation; moving boundary.

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24 **1. Introduction**

25 The corrosion of steel in reinforced concrete structures is the major concern of
26 infrastructure owners and operators. Two major causes that are connected to corrosion of
27 reinforcing steel in concrete structures are the carbonation and chloride attack. Carbonation is
28 a set of reactions between atmospheric carbon-dioxide and alkaline components of concrete,
29 producing a carbonated surface layer in which the pore solution pH value is depressed to near-
30 neutral levels [1,2,3]. A secondary effect of carbonation, also significant in terms of its
31 influence on reinforcing steel corrosion, is that it can cause the release of bound chloride ions
32 into the pore solution phase of concrete that contains a modest level of chloride salts as a
33 contaminant, thus exacerbating the corrosive nature of the electrolyte [4,5]. The carbon-dioxide
34 diffusion has been investigated in capillaries and in a cavity with N₂-CO₂ mixture [6,7]. A
35 variable-density single-phase incompressible model has been developed for numerical
36 simulation of the DDC (dissolution-diffusion-convection) process of carbon-dioxide [8]. In
37 addition, carbonation can also influence the diffusion of chloride ions in concrete as it can alter
38 the pore volume and pore structure and thus the transport properties of concrete [9,10,11]. In
39 certain cases the permeability of carbonated concrete may increase, as in the case of concrete
40 made with blended cements such as blast furnace slag and fly ash concrete [9,10]; in others, it
41 may decrease as in ordinary Portland cement concrete [4,11]. In urban and industrial areas,

42 where environmental pollution results in a significant concentration of carbon-dioxide,
43 carbonation-initiated reinforcement corrosion prevails [12]. While in highways and marine or
44 coastal structures, chloride ions, originating from deicing salts or seawater, are transported
45 through the concrete pore network and micro-cracks and depassivate the oxide film covering
46 the reinforcing steel and thus induce the corrosion of reinforcing steel [13]. The worst situation
47 is when a concrete structure is subjected to both carbonation and chloride attack [14]. A recent
48 study [15] reported that the probability of the corrosion initiation for the combined action of
49 carbonation and chloride attack is almost two times higher than the case in which the two
50 attacks are considered separately. This illustrates the difficulty that arises when the presence of
51 more than one corrosion-inducing agent contributes to aggressiveness of the exposure
52 conditions for a particular structure.

53 Extensive research work has been carried to understand how carbon-dioxide transports in
54 concrete pore medium and how it reacts with cement products in concrete. Sietta et al. [16]
55 presented a two-dimensional finite element model for the illustration of concrete carbonation
56 mechanism. The model was used to analyse the effects of multi-dimensional moisture, heat and
57 carbon-dioxide transport through concrete on the corrosion of a reinforcing bar placed at the
58 corner of a concrete structure. Steffens et al. [17] developed a theoretical model to predict the
59 carbonation of concrete structures. The model described the movement and retention of heat,
60 moisture and carbon-dioxide by means of balance equations and diffusion laws. The governing
61 equations of the model were solved numerically using finite element techniques. Liang and Lin
62 [18] presented a mathematical model with a set of one-dimensional linear diffusion equations
63 to simulate the transport problems of carbon-dioxide, chloride and sulphate ions in concrete.

64 Isgor and Razaqpur [19] proposed a nonlinear finite element approach for modelling coupled
65 heat transfer, moisture transport and carbonation processes in concrete for tracing the spatial
66 and temporal advancement of the carbonation front in concrete structures with and without
67 cracks. The numerical results were compared with available experimental data. Kumazaki [20]
68 presented a mathematical model of carbon-dioxide transport in concrete carbonation process.
69 The model was described by using a parabolic type equation with a nonlinear perturbation such
70 that a coefficient of the time derivative contains a non-local term depending on the unknown
71 function itself. Zhang [21] developed a mathematical model of carbonation process in porous
72 concrete materials. The model was solved numerically using uncoupled finite volume method.
73 Numerical simulations under normal and accelerated carbonation conditions were presented.
74 Zhu et al. [22] proposed a comprehensive model to simulate the transports of carbon-dioxide,
75 chloride ions, heat and moisture in concrete. The model was validated using several sets of
76 experimental data.

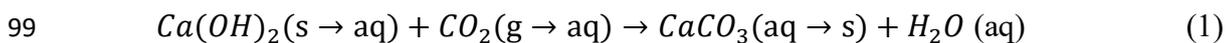
77 The above survey of literature shows that many mathematical models have been
78 developed to describe the carbonation phenomena in concrete. However, most of existing
79 models are difficult to use either because they require too many input data or because they were
80 developed for some specific application cases. In this paper a mathematical model describing
81 the diffusion of carbon-dioxide in concrete with considering the effect of concrete carbonation
82 is developed. The diffusion model is established using Fick's first law, whereas the effect of
83 concrete carbonation on carbon-dioxide diffusion is modelled by using a sink term added in
84 the diffusion equation. The present diffusion model is simplified to the diffusion problem with
85 a moving boundary representing the diffusion front or the carbonation depth when the

86 carbonation reaction is much faster than the diffusion process. An analytical solution is also
87 derived from the diffusion problem of moving boundary for calculating corresponding
88 carbonation depth.

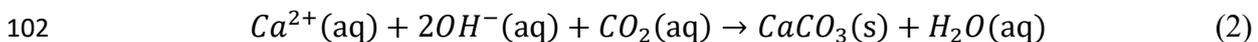
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90 **2. Modelling of carbon-dioxide diffusion in concrete with general carbonation reaction**

91 Concrete carbonation commonly takes place after the atmospheric carbon-dioxide, CO₂,
92 diffuses into concrete from the air through concrete gaseous phase. The chemical reactions
93 occurring during concrete carbonation can be broken down into two stages. One is the
94 dissolving of CO₂ in pore solution and the other is the reaction of the dissolved CO₂ with the
95 hydration products (mainly calcium ions) within the cement phase of concrete. The detailed
96 description of the reactions for concrete carbonation can be found in the work of Bary and
97 Sellier [23]. Nevertheless, the following represents the main reaction taking place during the
98 concrete carbonation [24],



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



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

104 The transport of CO₂ in concrete gaseous phase can be described by using Fick laws with
105 considering the consumption of CO₂ due to carbonation as follows [25,26,27],

$$106 \quad \frac{\partial c}{\partial t} = \nabla(D\nabla C) - Q_{CO_2} \quad (3)$$

107 where C in kg/m^3 is the content of CO_2 freely diffusing in concrete gaseous phase, t in s is the
 108 time, D in m^2/s is the diffusion coefficient of CO_2 in concrete gaseous phase, and Q_{CO_2} in $\text{kg}/(\text{s}-$
 109 $\text{m}^3)$ is the sink term representing the consumption rate of CO_2 due to carbonation, which can
 110 be approximated as follows [21,28],

$$111 \quad Q_{\text{CO}_2} = \frac{\partial S}{\partial t} = k_t(S_a - S) \quad (4)$$

112 where S in kg/m^3 is the content of CO_2 consumed due to carbonation, k_t in s^{-1} is the reaction
 113 rate constant, and S_a in kg/m^3 is the available content of CO_2 that can be consumed at a given
 114 condition.

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

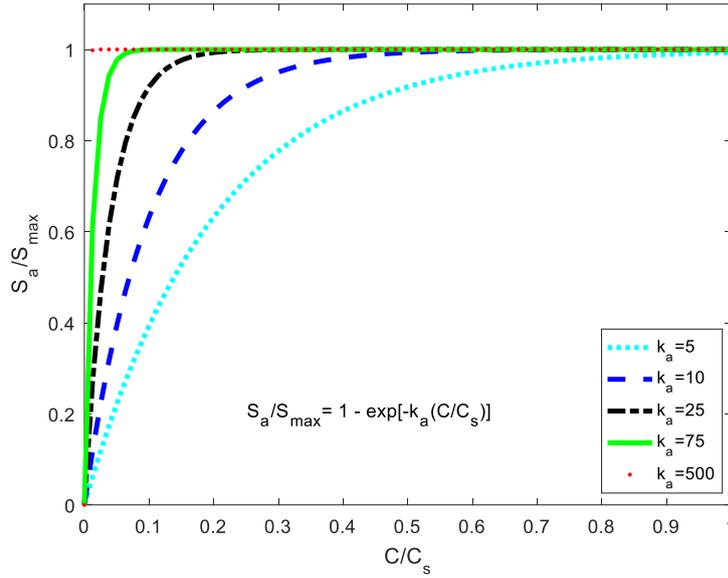
$$119 \quad S_a = S_{\text{max}} \left[1 - \exp \left(-\frac{k_a C}{C_s} \right) \right] \quad (5)$$

120 where S_{max} in kg/m^3 is the maximum content of CO_2 that can be consumed in carbonation, C_s
 121 in kg/m^3 is the content of CO_2 on the exposed surface (i.e. the content of CO_2 in environment
 122 where the concrete is exposed), and k_a is a dimensionless constant, which is used to reflect the
 123 effect of CO_2 concentration in gaseous phase on the relationship between S_a and S_{max} . The
 124 reaction rate constant k_t and dimensionless constant k_a can be determined using experimental
 125 data obtained from concrete carbonation tests. In general, they would be dependent on the
 126 temperature and relative humidity of the environment surrounding the concrete and the
 127 properties of concrete raw materials. Fig.1 graphically shows the relationship between S_a and
 128 C . It can be seen from the figure that when $k_a \rightarrow \infty$, $S_a = S_{\text{max}}$; indicating that S_a is a constant

129 except at the point of $C=0$. Substituting Eq.(5) into (3) and (4), it yields,

130
$$\frac{\partial C}{\partial t} = \nabla(D\nabla C) - k_t S_{max} \left[1 - \exp\left(-\frac{k_a C}{C_s}\right) - \frac{S}{S_{max}} \right] \quad (6)$$

131
$$\frac{\partial S}{\partial t} = k_t S_{max} \left[1 - \exp\left(-\frac{k_a C}{C_s}\right) - \frac{S}{S_{max}} \right] \quad (7)$$



132

133 **Fig. 1.** Relationship between S_a and C .

134 Eqs.(6) and (7) are the governing equations which can be used to determine the content
 135 of CO_2 diffusing in concrete gaseous phase and the content of CO_2 consumed during concrete
 136 carbonation. The corresponding initial and boundary conditions of $C(t,x)$ and $S(t,x)$ can be
 137 expressed as follows,

138 Initial conditions:

139
$$C(0, x) = 0 \quad (8)$$

140
$$S(0, x) = 0 \quad (9)$$

141 Boundary conditions:

142
$$C(t, 0) = C_s, \quad C(t, \infty) = 0 \quad (10)$$

143
$$S(t, 0) = S_{max}, \quad S(t, \infty) = 0 \tag{11}$$

144 Eqs.(6)-(11) completely describe the transport problem of carbon-dioxide in concrete with
145 taking into account the effect of concrete carbonation. Eqs.(6)-(11) can be solved using
146 numerical methods such as the finite difference method [26,27]. Fig.2 shows the distribution
147 profiles of $C(t,x)$ and $S(t,x)$ at a given time for various different values of k_a and k_t , obtained
148 from the numerical solutions. It can be seen from the figure that the distribution pattern of the
149 concentration profile of CO_2 is more sensitive to the profile constant k_a describing S_a than to
150 the reaction rate constant k_t . An important feature that can be observed is the idealized situation
151 of $k_a \rightarrow \infty$ and $k_t/D \rightarrow \infty$ (red line shown in Fig.2) in which the diffusion of CO_2 accompanied by
152 the instantaneous and irreversible consumption of a limited amount of the diffusing CO_2 ,
153 leading to a sharp front of the consumed CO_2 . In front of the advancing boundary the content
154 of the freely diffusing CO_2 is zero, while behind it the content of the consumed CO_2 is complete.
155 This problem is similar to the heat flow in a medium which undergoes a phase change at some
156 fixed temperature, accompanied by the absorption or liberation of latent heat.

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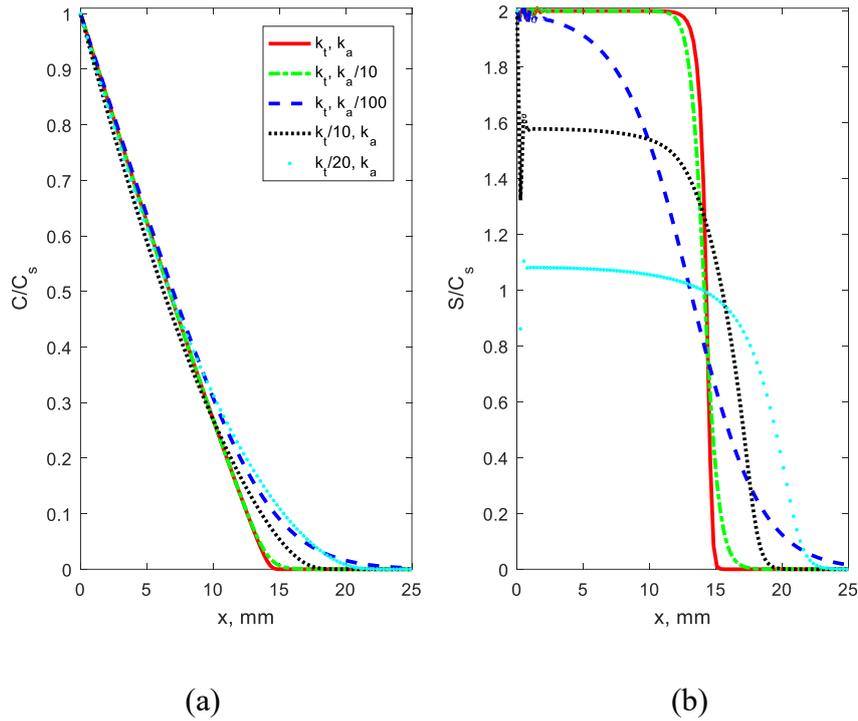
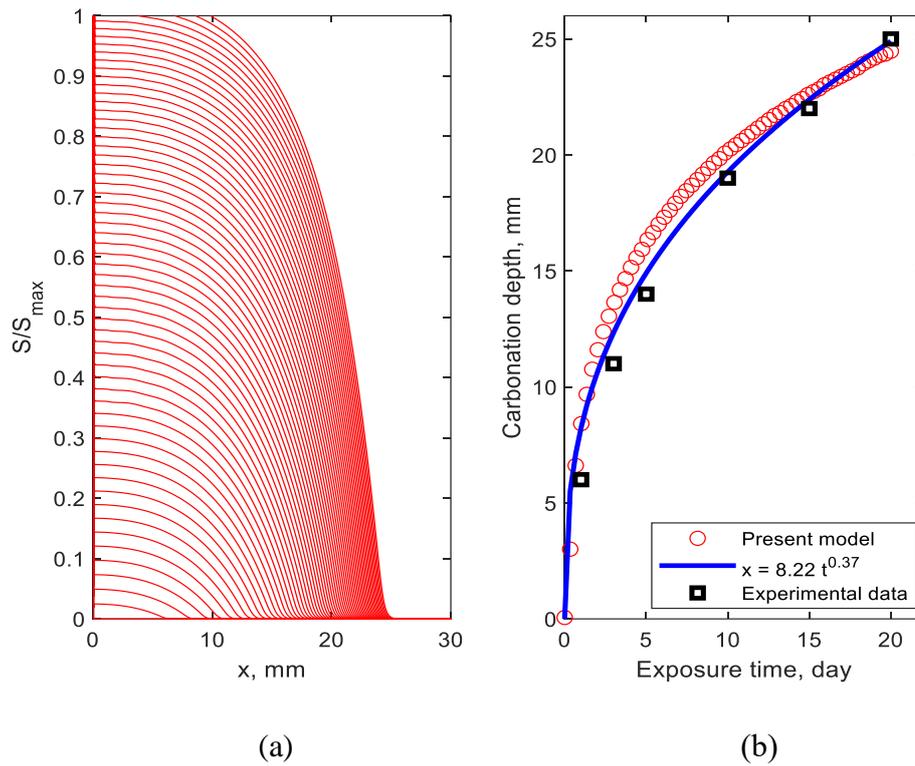


Fig. 2. Effects of k_t and k_a on the distribution profiles of (a) CO₂ in gaseous phase and (b) consumed CO₂ due to carbonation ($k_t=10^{-6} \text{ s}^{-1}$, $k_a=500$, $D=1.5 \times 10^{-11} \text{ m}^2/\text{s}$, $S_{max}/C_s=2$, $\sqrt{(Dt)}=15.3 \text{ mm}$).

It is also observed from Fig.2 that when k_t or k_a is small the front of the consumed CO₂ 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 CO₂ in the carbonated zone thus can be divided into two sub-zones. One is the fully carbonated zone in which the transport of CO₂ is governed by diffusion only; the other is the partially carbonated zone in which the transport of CO₂ is governed not only by diffusion but also by carbonation. As an example, Fig.3a shows the profiles of the consumed CO₂ 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

173 can be obtained from the carbonation front. By identifying the carbonation fronts from the
174 profiles of consumed CO₂ obtained at various different times we can find the relationship
175 between the carbonation depth and exposure time, which is plotted in Fig.3b. To demonstrate
176 the present model, experimental data [1] obtained from accelerated carbonation tests are also
177 superimposed in the figure. The experimental work was carried out inside a test chamber with
178 CO₂ concentration about 50 percent. The specimens tested were mortars with high water-to-
179 cement ratio 0.8. The parametric values used in the simulation are chosen to match the
180 experimental data. The results shown herein illustrate that the relationship between the
181 carbonation depth and exposure time may not necessarily follow the time square root relation
182 when the carbonation reactions are not faster than the diffusion speed of CO₂ in the gaseous
183 phase. Note that, in many carbonation tests of concrete the carbonation depth is determined by
184 using the phenolphthalein indicator solution [25,28], which is a colourless acid/base indicator
185 and can turn purple when its pH value exceeds 9. However, this test does not give the depth of
186 maximum ingress of CO₂ (i.e., the front point of partially carbonated zone) since the CO₂ in
187 the partially carbonated zone may cause a decrease in the pH-value beyond the carbonation
188 depth indicated by the phenolphthalein spray test, but their pH value may still be over 9.

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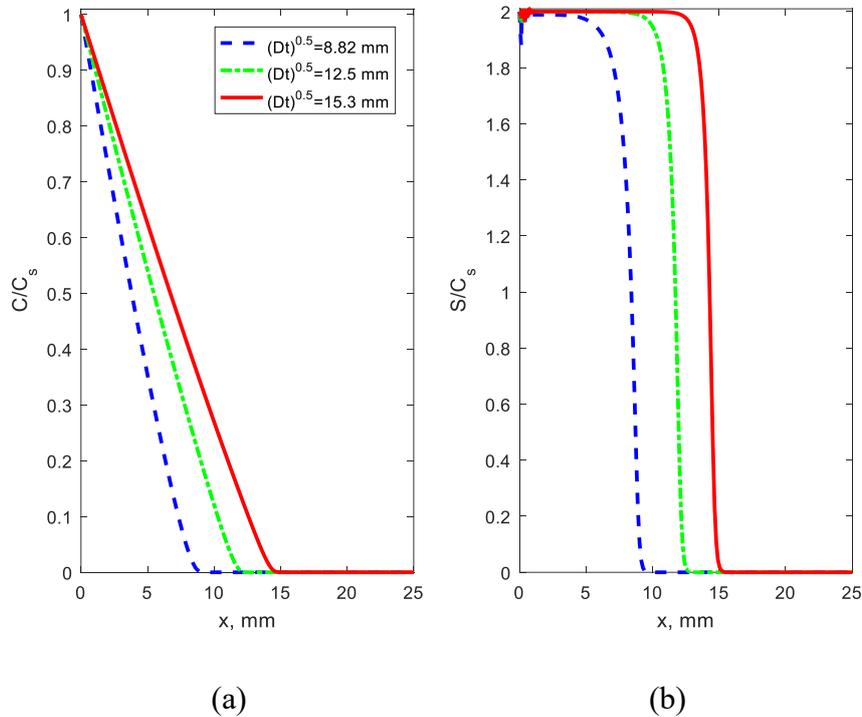
Fig. 3. (a) Profiles of consumed CO₂ at various different times. (b) Variation of carbonation depth with exposure time ($k_r=4.25 \times 10^{-7} \text{ s}^{-1}$, $k_a=5000$, $D=6.0 \times 10^{-11} \text{ m}^2/\text{s}$).

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 CO₂ in the gaseous phase. Hence, the reaction can be assumed to take place only at the diffusion front, whereas the transport of CO₂ can be assumed to take place only in the gaseous phase of the carbonated concrete. The consumption of CO₂ 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_{max} ; each has a clearly physical meaning. Physically, this may represent the natural carbonation case where CO₂ ingress is relatively slow, whereas

204 the carbonation reaction is relatively fast.

205 Note that there is some numerical difficulty for solving Eqs.(6)-(11) when $k_a \rightarrow \infty$ and
206 $k_t/D \rightarrow \infty$. Nevertheless, numerically, one can employ any large numbers for k_a and k_t/D to
207 achieve the approximate solutions of the idealised case of $k_a \rightarrow \infty$ and $k_t/D \rightarrow \infty$. As a numerical
208 example, Fig.4 shows the distribution profiles of $C(t,x)$ and $S(t,x)$ obtained at three different
209 times that correspond to the parametric values $\sqrt{Dt} = 8.82$ mm, 12.5 mm and 15.3 mm,
210 respectively, when $k_a=500$ and $k_t=1.0 \times 10^{-6} \text{ s}^{-1}$ ($\sqrt{k_t/D}=211 \text{ m}^{-1}$) are employed. It is clear from
211 the figure that the distribution profiles of $S(t,x)$ terminate nearly abruptly in all of the three
212 times. The infinite gradient at the diffusion front leads to some oscillations in the start point of
213 the profiles. This implies that if care was not taken in the selection of spatial and time intervals,
214 the numerical solution may become inaccurate.

215



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217

218 **Fig. 4.** Concentration profiles of (a) CO_2 in gaseous phase and (b) consumed CO_2 at different

219 times ($k_t=10^{-6} \text{ s}^{-1}$, $k_a=500$, $D=1.5 \times 10^{-11} \text{ m}^2/\text{s}$, $S_{max}/C_s=2$).

220

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

222 For the case where the carbonation reactions are fast while the carbon-dioxide diffusion
223 is slow the transport model described in Section 2 can be simplified by assuming $k_a \rightarrow \infty$ and
224 $k_t/D \rightarrow \infty$. To avoid the numerical difficulty when solving the idealised case of $k_a \rightarrow \infty$ and
225 $k_t/D \rightarrow \infty$, the transport problem of carbon-dioxide in concrete with taking into account the
226 effect of concrete carbonation described in Section 2 is now treated as the diffusion problem of
227 particles in which part of particles are trapped in stationary holes. By considering the mass
228 change of the total CO₂ in a unit volume of concrete in a time interval dt , the following mass
229 conservation equation can be established,

$$230 \quad \frac{\partial C_T}{\partial t} = \nabla(D\nabla C) \quad (12)$$

231 where $C_T=C+S$ in kg/m³ is the total content of CO₂ in concrete. The right-hand-side of Eq.(12)
232 is the flux gradient based on the Fick's first law, in which C in kg/m³ is the content of CO₂
233 freely diffusing in the gaseous phase of carbonated concrete. The initial and boundary
234 conditions of $C_T(t,x)$ can be expressed as follows,

$$235 \quad C_T(0, x) = 0 \quad (13)$$

$$236 \quad C_T(t, 0) = C_s + S_{max}, \quad C_T(t, \infty) = 0 \quad (14)$$

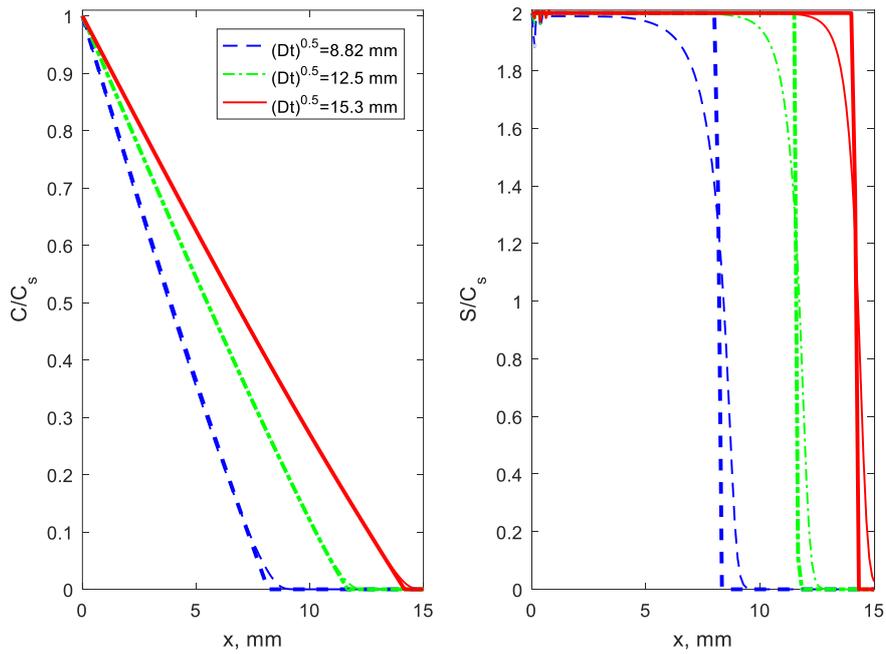
237 When solving Eqs.(12)-(14) for C_T one has to know the content of CO₂ in concrete gaseous
238 phase, which is the function of C_T and S_{max} and can be expressed as follows,

$$239 \quad C(t, x) = \begin{cases} C_T(t, x) - S_{max} & C_T(t, x) > S_{max} \\ 0 & C_T(t, x) \leq S_{max} \end{cases} \quad (15)$$

240 Note that, in the region of $C_T(t,x) > S_{max}$ all holes are completely filled, whereas in the
241 region of $C_T(t,x) < S_{max}$ the holes are not completely filled and therefore $C(t,x) = 0$.

242 Eqs.(12)-(15) can be used for solving for $C_T(t,x)$ and thus $C(t,x)$ can be obtained.
243 Compared to the model described in Section 2, the model presented herein by Eqs.(12)-(15) is
244 much simple, clear, concise and easy to solve. As a numerical example, Fig.5 shows the
245 distribution profiles of $C(t,x)$ and $S(t,x)$ at three different times obtained from the present model.
246 For the purpose of comparison, the results obtained from the model described in Section 2 are
247 also superimposed in the figure. It can be observed from the figure that there is almost no
248 difference in the results of $C(t,x)$ obtained from the two models. There is only a small difference
249 in the results of $S(t,x)$ at the diffusion front obtained from the two models. To examine the
250 spatial-time relationship, Fig.6 replots the three profiles of $C_T(t,x)$ shown in Fig.5 but using a
251 combined spatial and time coordinate, x/\sqrt{Dt} . It can be seen from the plot that when the
252 combined coordinate is used the profiles at three different times are merged together, indicating
253 that the diffusion depth of CO₂ is proportional to the square root of the diffusing time.

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(a)

(b)

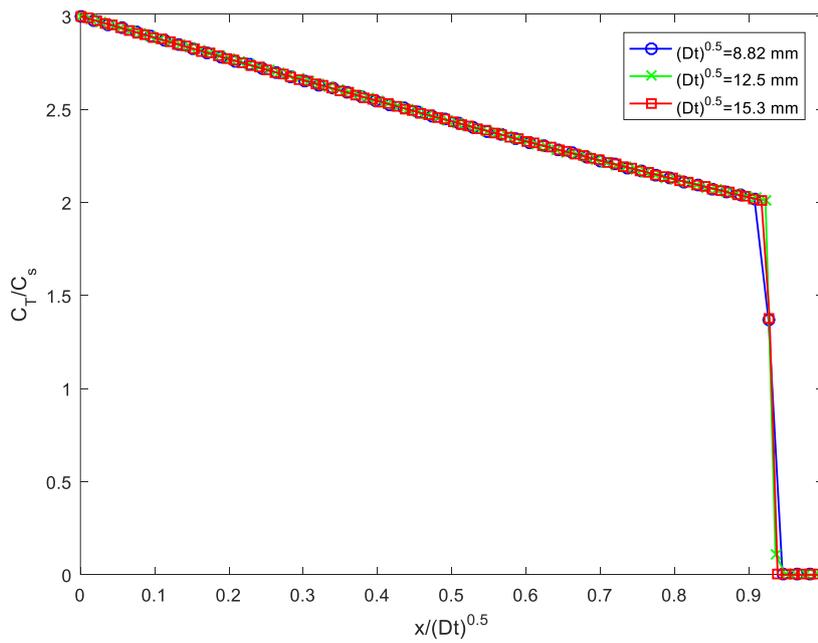
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257 **Fig. 5.** Comparisons of (a) CO₂ profiles and (b) consumed CO₂ profiles between general and
 258 fast carbonation reaction models (thin and thick lines represent the results of general and fast

259

reaction models, respectively, $D=1.5 \times 10^{-11} \text{ m}^2/\text{s}$).



260

261 **Fig. 6.** Concentration profiles of total CO₂ at three different times plotted against combined

262 spatial and time coordinate ($D=1.5 \times 10^{-11}$ m²/s).

263

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

265 The mass conservation equation (12) can be applied to any point in the domain ($0 < x < \infty$).

266 However, if it is applied only to the domain ($0 < x < \xi$) where ξ is the diffusion front, then $\frac{\partial C_T}{\partial t} =$

267 $\frac{\partial C}{\partial t}$ since $S=S_{\max}$ is a constant in the domain ($0 < x < \xi$). Thus, Eq.(12) can be further simplified

268 to Eq.(16),

$$269 \quad \frac{\partial C}{\partial t} = \nabla(D\nabla C) \quad 0 < x < \xi \quad (16)$$

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

$$271 \quad C(0, x) = 0 \quad (17)$$

$$272 \quad C(t, 0) = C_s, \quad C(t, \xi) = 0 \quad (18)$$

273 Note that ξ is the function of time, which moves forward when time increases. Thus

274 Eqs.(16)-(18) represents the diffusion problem with moving boundary. As it is demonstrated in

275 Section 3, the depth of the diffusion front is proportional to square root of the diffusing time.

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

$$277 \quad \xi(t) = k_\xi \sqrt{Dt} \quad (19)$$

278 where k_ξ is a constant to be determined. The solution of Eq.(16) with the initial and boundary

279 conditions defined by Eqs.(17) and (18) can be expressed as follows,

$$280 \quad C(t, x) = C_s \left(1 - \frac{\operatorname{erf}\left(\frac{x}{2\sqrt{Dt}}\right)}{\operatorname{erf}\left(\frac{k_\xi}{2}\right)} \right) \quad 0 \leq x \leq \xi \quad (20)$$

281 where $\operatorname{erf}(\cdot)$ is the error function. It is obvious from Eq.(20) that if k_ξ is known then the solution

282 (20) for $C(t,x)$ is completely defined. In order to determine k_ξ an additional mass conservation

283 equation need to be established at the point of the diffusion front, which can be expressed as
 284 follows,

$$285 \quad -D \frac{\partial C}{\partial x} = S_{max} \frac{d\xi}{dt} \quad \text{for } x = \xi \quad (21)$$

286 Physically, the left-hand-side of Eq.(21) represents the diffusion flux from the diffusion
 287 zone into the zone ahead of the diffusion front; whereas the right-hand-side of Eq.(21)
 288 represents the flux required in order that the diffusion front can advance by a distance of $d\xi$ in
 289 the time interval of dt . Substituting Eqs.(19) and (20) into (21), it yields,

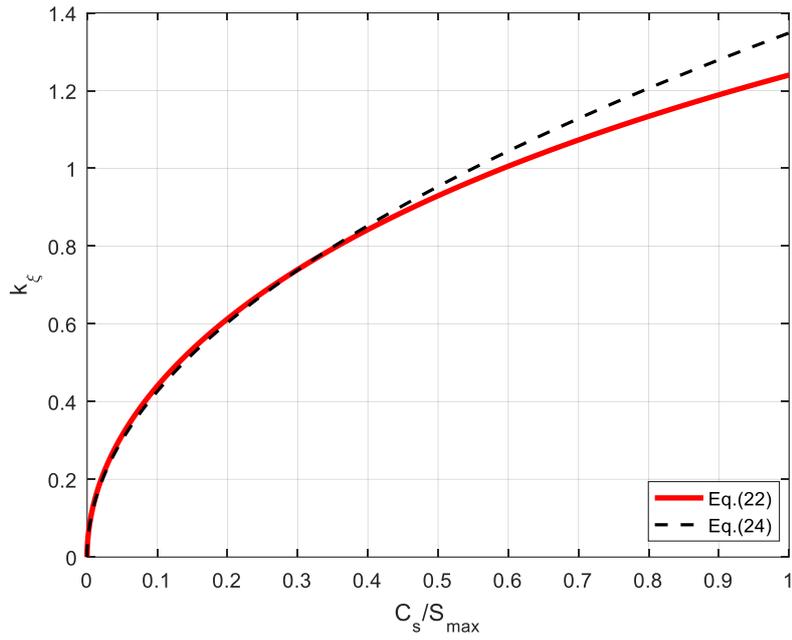
$$290 \quad \frac{k_\xi}{2} \operatorname{erf}\left(\frac{k_\xi}{2}\right) \exp\left(\frac{k_\xi^2}{4}\right) = \frac{C_s}{\sqrt{\pi S_{max}}} \quad (22)$$

291 Eq.(22) is a nonlinear algebraic equation about k_ξ , which can be used to determine k_ξ for
 292 a given ratio of C_s/S_{max} . After k_ξ is determined it can be substituted into Eq.(19) for calculating
 293 the depth of diffusion front $\xi(t)$ and Eq.(20) for calculating the profile $C(t,x)$ of CO₂. **Fig.7**
 294 graphically shows the relationship between k_ξ and C_s/S_{max} . It can be seen from the figure that
 295 k_ξ increases with C_s/S_{max} ; initially very quick but it becomes slow afterwards. It is clear from
 296 Eq.(19) that the influence of C_s/S_{max} on $\xi(t)$ is the same as that it does on k_ξ . To demonstrate
 297 the analytical solutions presented by Eqs.(19) and (20), **Fig.8** provides a comparison between
 298 the analytical solution given by Eqs.(19)-(20) and the numerical solutions given by Eqs.(12)-
 299 (15) for the concentration distribution profile of freely diffusing CO₂. As it is to be expected,
 300 there is no difference between the analytical and numerical solutions.

301 Of a particular interest is the case where $C_s/S_{max} \ll 1$ and/or $k_\xi \ll 1$, for which case the
 302 following approximation can be taken mathematically,

$$303 \quad \frac{k_\xi}{2} \operatorname{erf}\left(\frac{k_\xi}{2}\right) \exp\left(\frac{k_\xi^2}{4}\right) \approx \frac{k_\xi^2}{2\sqrt{\pi}} \quad (23)$$

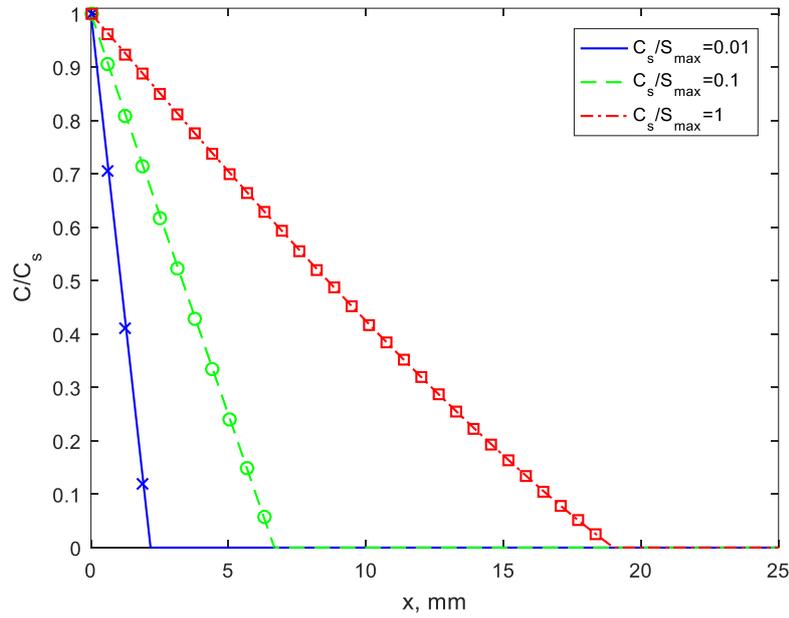
304 Hence, Eq.(22) can be simplified as follows,



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Fig. 7. Variation of k_ξ with C_s/S_{max} .



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Fig. 8. Effect of C_s/S_{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)).

310

$$k_\xi = \sqrt{\frac{2C_s}{S_{max}}} \quad (24)$$

311

The corresponding diffusion front $\xi(t)$ can be simplified as follows,

$$\xi(t) = \sqrt{\frac{2C_sDt}{S_{max}}} \quad (25)$$

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 CO₂ is much lower than the consumed content of CO₂ 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_ξ 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 CO₂ in the carbonated concrete.

CO₂ level in the atmosphere is normally expressed as parts per million or ppm. It was reported that the CO₂ 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/m³. This gives the content of CO₂ in air is about 0.479 g/m³. The maximum amount of CO₂ that can be consumed in concrete carbonation can be estimated as follows [33],

$$S_{max} = 0.75CaOCem \frac{M_{CO_2}}{M_{CaO}} = 0.377Cem \quad (26)$$

where CaO (≈ 0.64) is the amount of calcium oxide per weight of cement, Cem is the content of cement used in concrete, $M_{CO_2}=44$ g/mol and $M_{CaO}=56$ g/mol are the molar weight of CO₂ and CaO, respectively. For normal Portland cement concrete Cem is about 350 kg/m³. This gives $S_{max}=132$ kg/m³ and thus $C_s/S_{max}=0.36 \times 10^{-5}$, which indicates that Eq.(24) can be safely

334 used for most natural carbonation cases unless for specific laboratory tests where the
335 concentration of CO₂ used is much higher and the tested concrete is with supplementary
336 cementitious materials (SCMs) which may reduce the content of the cement used in concrete.

337

338 **5. Conclusions**

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

- 347 • In the diffusion model with general carbonation reaction the distribution pattern of the
348 concentration profile of CO₂ is more sensitive to the profile constant k_a describing S_a than
349 to the reaction rate constant k_r .
- 350 • It is more convenient to use the total concentration of CO₂ to model the diffusion of CO₂
351 in concrete with fast carbonation reaction, which avoids the difficulty of moving boundary.
352 The diffusion front obtained from the numerical model for the diffusion model with fast
353 carbonation reaction represents the carbonation depth.
- 354 • The analytical solution presented for the diffusion model with moving boundary can be

355 directly used to examine the effects of diffusion coefficient of CO₂ in carbonated concrete,
356 diffusing time, and the ratio of C_s -to- S_{max} on the depth of concrete carbonation.

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

361

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