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Kyoto University
Mathematical modeling of concrete carbonation process with hysteresis effect

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1 Introduction

From civil engineering point of view it is very important to investigate concrete carbonation process. On this subject Böhm and Muntean have already proposed a one-dimensional free boundary as a mathematical model for concrete carbonation and discussed the well-posedness of the problem, mathematically, in [16, 17]. Recently, the simplified model of the problem are studied in [4, 5, 6, 7, 8, 9, 10]. In particular, one of these results is concerned with large time behavior which guarantees that the $\sqrt{t}$-law for carbonation front is true. Here, we note that $\sqrt{t}$-law is well-known as an experimental result and means that the carbonation front behaves like $\sqrt{t}$ for sufficiently large $t$. In such previous results hysteresis effect are neglected, although we can find hysteresis loops in graphs of some relationships between parameters obtained by experiments. The aims of this paper are to show a mathematical modeling process for concrete carbonation process on a 3-dimensional domains with consideration of hysteresis effects and to review recent results on this model. Our modeling is due to Maekawa-Ishida-Kishi [15], Maekawa-Chaube-Kishi [14] and Muntean [16].

The outline of carbonation process can be described as follows: $\text{CO}_2(g)$ from the atmosphere enters the porous structure of concrete-based materials via the air parts of the pore where it quickly dissolves in pore water, that is

$$\text{CO}_2(g) \leftrightarrow \text{CO}_2(aq).$$

In the pore water, $\text{CO}_2(aq)$ reacts fast with available alkaline species (in particular with $\text{Ca(OH)}_2(aq)$), i.e.

$$\text{CO}_2(aq) + \text{Ca(OH)}_2(aq) \rightarrow \text{H}_2\text{O} + \text{CaCO}_3(aq).$$

From the reaction formula (1.2) we conclude that we need differential equations describing the conservation laws for moisture and carbon dioxide in order to establish a mathematical model for concrete carbonation. Then we shall discuss the conservation laws for moisture in section 2 and carbon dioxide in section 3.

Throughout this paper we use the following notations: $t$ is time, $u, v, w$ and $y$ are concentrations of $\text{CO}_2$ in water and in air, $\text{Ca(OH)}_2$ and $\text{CaCO}_3$ in water, respectively, $p$ is the pore pressure, $\rho_l$ is the density of liquid, $R$ is the gas constant, $\theta$ is the temperature
(given constant), $M_l$ is the molecular mass of liquid, and $h$ is the relative humidity. In [15, p. 121] they assume that

$$p = \frac{\rho_l R \theta}{M_l} \log h.$$ 

Then we can put $p = C_l \log h$ in this paper, where $C_l = \frac{\rho_l R \theta}{M_l}$.

2 Conservation law for moisture

In this section we formulate a moisture transport model under consideration the multi-phase dynamics of liquid and gas phases.

First, the conservation law for moisture is given as follows (see [15, p. 120] and [14, (4.2) in Chapter 4]):

$$\frac{\partial}{\partial t} (\rho \phi S_l) + \text{div} J_w = Q_{hyd},$$  

(2.1)

where $\phi$, $S_l$, $J_w$ and $Q_{hyd}$ are functions describing the porosity, the degree of saturation, the flux of moisture and water consumption due to hydration, respectively. Moreover, it is supposed that $\phi = \phi(z)$, where $z$ the ration of amount of consumed Ca(OH)$_2$ for total amount of Ca(OH)$_2$ (see [15, (23)]), and $\phi$ is a continuous function on $\mathbb{R}$ satisfying

$$\phi \geq \phi_0 > 0 \text{ and } \phi' \geq 0 \text{ on } \mathbb{R},$$

where $\phi_0$ is a positive constant. The typical example of $\phi$ is given as Figure 1.

![Figure 1](image)

Since we consider the dynamics of liquid and gas phases, the flux of moisture is described with the sum of he fluxes of moisture due to and liquid $q_l$ and vapour $q_v$ phases, that is,

$$J_w = q_l + q_v.$$

On account of the statement in [15, p.120] and [14, (4.53)] we assume that

$$q_l = -K_l \nabla p, \quad K_l = \frac{\rho_l \phi^2}{50 \eta} (\int_0^{r_c} r dV)^2,$$

where $K_l$ is the liquid conductivity, $\eta$ is the viscosity of fluid under non-ideal conditions, $r$ is the pore radius, $r_c$ is the pore radius in which the equilibrated interface of liquid and
vapor is created and $V$ is the normalized pore volume. Here, $\eta$ is given by $\eta = a(1 + H_d^2)$, where $a$ is a positive constant and $H_d$ is determined by a hysteresis operator $\mathcal{H}_0$ with the input function $h$, that is, $H_d = \mathcal{H}_0(h)$. Then we may assume that for some hysteresis operator $\mathcal{H}$

$$\eta = \mathcal{H}(h), \quad 0 < a \leq \mathcal{H}(h) \leq a(1 + b),$$

where $b$ is a positive constant.

Next, from [15, p.121] and [14, p.46] we have $r_c = -\frac{2\gamma}{p}$ and $V = 1 - \exp(-Br)$, where $\gamma$ and $B$ are given positive constants. Accordingly, we obtain

$$\int_0^{r_c} r dV = \int_0^{r_c} rV'(r)dr = \int_0^{r_c} (Br) \exp(-Br)dr = \frac{1}{B} \left( \frac{2B\gamma}{p} \exp\left(\frac{2B\gamma}{p}\right) - \exp\left(\frac{2B\gamma}{p} + 1\right) \right).$$

By using $p = C_l \log h$, we see that

$$\int_0^{r_c} r dV = \frac{1}{B} \left( \frac{2B\gamma}{C_l \log h} \exp\left(\frac{2B\gamma}{C_l \log h}\right) - \exp\left(\frac{2B\gamma}{C_l \log h} + 1\right) \right)$$

so that

$$K_l = \frac{\rho_i \phi^2}{50B^2 \mathcal{H}(h)} \left( \frac{2B\gamma}{C_l \log h} \exp\left(\frac{2B\gamma}{C_l \log h}\right) - \exp\left(\frac{2B\gamma}{C_l \log h} + 1\right) \right)^2.$$

On the flux of moisture due to vapor phase movement it holds that

$$q_v = -K_v \nabla p,$$

where $K_v$ is the vapor conductivity. In [15] they suppose that

$$K_v = \hat{K}_v \phi(1 - S)h,$$

where $\hat{K}_v$ is a positive constant. From the above argument we observe that

$$J_w = -(K_l + K_v)C_l \frac{\nabla h}{h}. \tag{2.2}$$

From now on in order to be able to deal with (2.2) by the system of partial differential equations we give some estimates for $\frac{K_l}{h}$ and $\frac{K_v}{h}$. We may assume that $0 \leq h \leq 1$, physically. By putting

$$\bar{K}_l(h) = \left( \frac{C_B}{\log h} \exp\left(\frac{C_B}{\log h}\right) - \exp\left(\frac{C_B}{\log h} + 1\right) \right)^2,$$

where $C_B = \frac{2B\gamma}{C_l}$, and elementary calculations we can show

$$\lim_{h \downarrow 0} \frac{\bar{K}_l(h)}{h} = +\infty, \quad \lim_{h \uparrow 0} \frac{\bar{K}_l(h)}{h} = 1.$$
and there exists a positive constant $\bar{\kappa}$ such that

$$\frac{\hat{K}_l(h)}{h} \geq \bar{\kappa} \quad \text{for } 0 < h \leq 1.$$

Due to [16, (2.61)] the right hand side of (2.1) is supposed that

$$Q_{\text{hyd}} = \phi S([u]^+)^{q_1}([w]^+)^{q_2},$$

where $q_1$ and $q_2$ are positive constants with $q_1, q_2 \geq 1$. We note that $S$ is determined by the hysteresis operator $S$ with input function $h$ (see [14, Figure 4.10, p.79]). Also, we may assume that $0 \leq S(h) \leq 1$.

Thus we have the following partial differential equation as the description of the mass conservation law for moisture:

$$\rho \frac{\partial}{\partial t}(\phi S) - \text{div}\left( \frac{\hat{K}_l(h)\phi(z)^2}{\mathcal{H}(h)} + \hat{K}_V C_l \phi(z)(1-S) \nabla h \right) = \phi(z)S([u]^+)^{q_1}([w]^+)^{q_2}, \quad (2.3)$$

where $\hat{K}_l(\cdot)$ is a continuous function on the interval $(0,1]$ satisfying $\lim_{h \downarrow 0} \hat{K}_l(h) = +\infty$ and $\hat{K}_l \geq \hat{\kappa} > 0$ on $(0,1]$ for a positive constant $\hat{\kappa}$.

### 3 Conservation law for carbon dioxide

The aim of this section is to provide a partial differential equation for a mathematical description of the mass conservation law for carbon dioxide. A part of the following discussion was already shown in [13].

First, the conservation law and Fick's first law lead to

$$\frac{\partial}{\partial t}(\phi((1-S)v+Su)) + \text{div}J_c = Q_g, \quad J_c = -(D_{gc}\nabla v + D_{dc}\nabla u),$$

where $J_c$ is the flux of gaseous and dissolved carbon dioxide, $D_{gc}$ and $D_{dc}$ are diffusion coefficients of gaseous and dissolved CO$_2$ in the porous media and $Q_g$ is representing the consumption rate of carbon dioxide. In [16, 17] for the reaction (1.1) it is supposed that Henry's law holds only in stable state. Now, we assume that Henry's law is always valid. This assumption implies that $p_c = H_c u$, where $p_c$ is the pressure of carbon dioxide in air and $H_c$ is Henry's constant for carbon dioxide. Also, by using ideal gas law we can obtain

$$v = \frac{H_c M_c}{RT} u,$$

where $M_c$ is the molecular mass of carbon dioxide. Thus we can rewrite the flux of gaseous and dissolved carbon dioxide as follows:

$$J_c = -(D_{gc} \frac{H_c M_c}{RT} + D_{dc})\nabla u.$$

Due to [15, p. 120] $D_{gc}$ and $D_{dc}$ have the following forms:

$$D_{gc} = K_g \phi(1-S), \quad D_{dc} = K_d \phi S,$$
where $K_g$ and $K_d$ are given positive constants. Also, from the chemical reaction theory the consumption rate of carbon dioxide $Q_g$ satisfies

$$Q_g = \frac{\partial [\text{CaCO}_3]}{\partial t} = \kappa [\text{Ca}^{2+}][\text{CO}_3^{2-}],$$

where $\kappa$ is the reaction rate coefficient of carbonation and $[a]$ indicates the concentration of the element $a$. Here, by observing (1.2) we obtain that the sum of mol concentrations of CaCO$_3$ and Ca(OH)$_2$ is conserved so that

$$\frac{1}{M_1} [\text{Ca(OH)}_2] + \frac{1}{M_2} [\text{CaCO}_3] = \text{constant},$$

where $M_1$ and $M_2$ are the molecular masses of Ca(OH)$_2$ and CaCO$_3$. By regarding that

$$w = \frac{[\text{Ca}^{2+}]}{M_3} \quad \text{and} \quad u = \frac{[\text{CO}_3^{2-}]}{M_5}$$

where $M_3, M_4$ and $M_5$ are the molecular masses of Ca$^{2+}$, CO$_2$ and CO$_3^{2-}$, we see that

$$-\mu_1 \frac{\partial y}{\partial t} = \frac{\partial w}{\partial t} = -\kappa_1 uw,$$

where $\mu$ and $\kappa_1$ are positive constants. By solving this ordinary differential equation we obtain

$$w(t) = w(0) \exp(-\kappa_* \int_0^t u(\tau) d\tau).$$

where $\kappa_*$ is a positive constant.

As mentioned before, $z$ is defined by

$$z(t) = \frac{w(0) - w(t)}{w(0)} \quad \text{so that} \quad z(t) = 1 - \exp(-\kappa_* \int_0^t u(\tau) d\tau).$$

Hence, we have the following partial differential equation:

$$\frac{\partial}{\partial t} (\phi(\rho_0(1-S) + S)u) - \text{div}(\phi(\rho_1 K_g (1-S) + K_d S)(\nabla u)) = -\kappa_1 uw, \quad (3.1)$$

with

$$w(t) = w(0) \exp(-\kappa_* \int_0^t u(\tau) d\tau), \phi = \phi(1 - \exp(-\kappa_* \int_0^t u(\tau) d\tau)).$$

4 Review of mathematical results

As we discussed in sections 2 and 3, we obtain the system \{(2.3), (3.1)\} as a mathematical model for concrete carbonation. Since both equations include hysteresis operators, it is not easy to deal with the system, directly, so that we studied the simplified equations of (2.3) and (3.1) as a first step of this research. In this section we show our previous results concerned with these equations.

First, we consider the equation corresponding to the conservation law of moisture. In [1] we treated the simplified equation of (2.3) as follows:
\[
\rho \frac{\partial h}{\partial t} - \text{div}(g(h) \nabla h) = wf, \quad w = S(h) \quad \text{in } Q(T) := (0,T) \times \Omega,
\]

where \( \Omega \) is a bounded domain in \( \mathbb{R}^N \) with \( N \geq 1 \) and \( f \) is a given function on \( Q(T) \). To obtain (4.1) from (2.3) we assume that \( \phi \) and \( \mathcal{H} \) are given positive constants, \( S \) in the left hand side is proportional to \( h \) and put \( g(h) = \frac{\hat{K}_l(h) \phi^2}{\nabla} + \hat{K}_V C_l \phi(1 - S) \). In [15, 14] the graph of \( S \) is illustrated like Figure 2.

From this graph we can observe that the trend of the hysteresis loop is anticlockwise. It is well-known that the hysteresis operator with anticlockwise can be represented by a play operator (see [11, 18], Figure 3). As mentioned in [18, 12, 3], the play operator \( w = S(h) \) is characterized by the ordinary differential equation including a subdifferential of the indicator function. In this paper in order to get the compactness we use the following approximation as the characterization for \( S \).

\[
w_t - \nu \Delta w + \partial I(h;w) \ni O \quad \text{in } Q(T),
\]

where \( w_t = (\partial/\partial t)w, \nu \) is a non-negative constant and \( I(h; \cdot) \) is the indicator function of the interval \([f_*(h), f^*(h)]\), \( f_* \) and \( f^* \) are lower and upper curves indicated in Figure 3, respectively. Moreover, \( \partial I(h; \cdot) \) is its subdifferential, that is, it is a multivalued operator given by

\[
\partial I(h; r) = \begin{cases} 
[0, \infty) & \text{for } r = f^*(h), \\
\{0\} & \text{for } f_*(h) < r < f^*(h), \\
(-\infty, 0] & \text{for } r = f_*(h).
\end{cases}
\]

Hence, under consideration of the initial and the boundary conditions we have the following initial boundary value problem PM:

\[
\begin{align*}
\rho \phi_t - \text{div} \left( \nabla G(h) \right) &= wf \quad \text{in } Q(T), \\
w_t - \nu \Delta w + \partial I(h;w) &\ni O \quad \text{in } Q(T), \\
h = h_b, w = w_b \quad &\text{on } \Sigma(T) := (0,T) \times \partial \Omega, \\
h(0) = h_0, w(0) = w_0 \quad &\text{on } \Omega,
\end{align*}
\]
where \( G(r) = \int_{0}^{r} g(s)ds \) for \( r > 0 \), \( h_{b} \) and \( w_{b} \) are given functions on \( \Sigma(T) \) and \( h_{0} \) and \( w_{0} \) are initial functions.

On this problem PM we have proved the following theorems:

**Theorem 4.1.** (cf. [1, 2]) Assume:

(A2) \( \Omega \subset \mathbb{R}^{N} \) is a bounded domain with the smooth boundary \( \partial \Omega \) for any positive integer \( N \).

(A3) \( \rho \) and \( \nu \) are positive constants and \( T > 0 \).

(A4) \( f \in L^{\infty}(Q(T)) \) with \( f \geq 0 \) a.e. on \( Q(T) \).

(A5) \( f_{*}, f^{*} \in C^{2}(\mathbb{R}) \cap W^{2,\infty}(\mathbb{R}) \) with \( 0 \leq f_{*} \leq f^{*} \leq w_{*} \) on \( \mathbb{R} \), where \( w_{*} \) is a positive constant. We put \( L_{*} = \max\{|f_{*}|_{W^{2,\infty}(\mathbb{R})}, |f^{*}|_{W^{2,\infty}(\mathbb{R})}\} \).

(A6) \( h_{b}, w_{b} \in H^{1}(\Omega) \cap L^{\infty}(\Omega) \), \( h_{0} \geq \kappa_{0} \) and \( w_{b} \geq 0 \) a.e. on \( \Omega \), and \( h_{0}, w_{0} \in H^{1}(\Omega) \cap L^{\infty}(\Omega) \), \( h_{0} \geq \kappa_{0} \) and \( w_{0} \geq 0 \) a.e. on \( \Omega \) with \( h_{0} = h_{b} \) and \( w_{0} = w_{b} \) a.e. on \( \partial \Omega \), where \( \kappa_{0} \) is a positive constant. Moreover, \( f_{*}(h_{0}) \leq w_{0} \leq f^{*}(h_{0}) \) a.e. on \( \Omega \) and \( f_{*}(h_{b}) \leq w_{b} \leq f^{*}(h_{b}) \) a.e. on \( \partial \Omega \). Then PM has at least one solution on \([0, T]\).

**Theorem 4.2.** (cf. [1, 2]) Let \( \Omega \) be the interval \((0, 1)\) and assume (A2) \sim (A6). If \( \{h_{1}, w_{1}\} \) and \( \{h_{2}, w_{2}\} \) are solutions of PM on \([0, T]\) and \( h_{1} \) and \( h_{2} \) are strictly positive on \( Q(T) \), then it holds that \( h_{1} = h_{2} \) and \( w_{1} = w_{2} \) on \( Q(T) \).

As you see Theorem 4.2, the uniqueness holds only in the one-dimensional domain. The next result deals with PM in case \( \nu = 0 \).

**Theorem 4.3.** (cf. [2]) Assume that (A2) \sim (A6) hold. Then PM has at least one solution on \([0, T]\) even if \( \nu = 0 \).

Next, we give a result concerned with (3.1), in which we assume that \( \rho_{0} = K_{g} = K_{d} = 1, \phi \) in the flux term is a constant (:= 1). Then we have the following initial-boundary value problem PC:

\[
\frac{\partial}{\partial t} \left( \phi(1 - \exp(-\kappa_{*} \int_{0}^{t} u(\tau)d\tau))u \right) - \Delta u = -\kappa_{1} w_{0} \exp(-\kappa_{*} \int_{0}^{t} u(\tau)d\tau) \quad \text{in } Q(T),
\]

\[
u = u_{b} \quad \text{on } \Sigma(T),
\]

\[
u(0) = u_{0} \quad \text{in } \Omega,
\]

where \( u_{b} \) and \( u_{0} \) are given boundary and initial functions with \( N = 3 \).

On this problem PC the following theorem guarantees the well-posedness.

**Theorem 4.4.** (cf. [13]) If \( u_{b} \in W^{1,2}(0,T;H^{1}(\Omega)) \cap L^{\infty}(0,T;H^{2}(\Omega)) \) with \( 0 \leq u_{b} \leq u_{*} \) in \( Q(T) \), where \( u_{*} \) is a positive constant, \( u_{0} \in H^{1}(\Omega) \cap H^{2}(\Omega) \) with \( u_{0} \geq 0 \) and \( u_{0} = u_{b}(0) \) on \( \partial \Omega \), and \( w_{0} \in L^{\infty}(\Omega) \) is non-negative on \( \Omega \), then PC has a unique solution on \([0, T]\).

At the end of this paper we note that a lot of open problems still remain on this topic.
References


