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Mathematical modeling of CO_2 uptake by concrete during accelerated carbonation curing

Sormeh Kashef-Haghighi, Yixin Shao, Subhasis Ghoshal *

Department of Civil Engineering, McGill University, Montreal, QC, Canada

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ABSTRACT

Accelerated CO_2 curing is a promising carbon capture and storage technology that can provide durable, pre-cast concrete products. A mathematical framework for predicting CO_2 uptake and distribution during carbonation curing is presented, incorporating equations describing CO_2 gas transport, dissolution in concrete pore water and reaction with cement compounds. The numerical simulations show that carbonation reaction of tricalcium silicate, the most abundant and reactive compound in cement, was the rate-controlling process for CO_2 uptake. The specific surface area of compounds available for reaction determines the rate and extent of uptake. The 30-minute carbonation efficiency increased from 16.5% to 23% with a two-fold increase in the total specific surface area. The rate of CO_2 uptake by cement doubled with a two-fold increase in CO_2 gas partial pressure, but the extent of carbonation did not change significantly due to the formation of solid carbonation products on reactive surfaces and in the pore space.

1. Introduction

Carbon dioxide capture and storage (CCS) technologies are being developed for reduction of CO_2 emissions from fossil fuel-based industries [1]. Accelerated carbonation curing of concrete is considered as a carbon dioxide mineral sequestration technology in which CO_2 reacts with cement, a material rich in calcium compounds, under moderate temperatures and pressures to form thermodynamically stable calcium carbonate [2,3]. The CO_2 will remain sequestered as $CaCO_3$ unless dissolved by acid. Furthermore, the energy required for concrete curing and the associated CO_2 emissions will be significantly reduced if accelerated CO_2 curing with low pressure flue gas is used instead of conventional steam and autoclave curing. The energy required for steam and autoclave curing of 1 m^3 of concrete is 0.59 and 0.71 GJ and it can be reduced to less than 0.013 GJ using carbonation curing with flue gas compressed to 0.11 MPa [3]. Moreover, this technology forms a concrete product with significantly enhanced resistance to surface permeation, sulfate attack and freeze-thaw cycling [4]. The rapid strength development by carbonation can alone translate to economic benefits in comparison to conventional curing [5,6]. Products which can be manufactured with accelerated CO_2 curing include concrete blocks, bricks or modular building elements [2]. It is estimated that approximately 1.5 million metric tons (Mt) of CO_2 can be sequestered annually in concrete masonry units (CMU) alone [7]. With annual CO_2 emissions of 54 million metric tons from the U.S. cement industry [8], CO_2 sequestration in CMUs can lead to carbon emission reduction of nearly 3%.

To date, there have been no reports on modeling the CO_2 uptake during the accelerated curing process. Past efforts on modeling CO_2 uptake in concrete is based on natural carbonation of mature concrete structures, referred to as passive carbonation of concrete. In this latter process, the atmospheric CO_2 diffuses into concrete and reacts with calcium hydroxide, the main hydration product of cement, resulting in a decrease of pH which initiates corrosion of steel reinforcement bars and leads to deterioration of reinforced concrete structures [9–11]. Mathematical models have been employed to estimate the penetration depth of CO_2 in concrete structures during passive carbonation [12–16] but models for estimating penetration depths during accelerated CO_2 curing have not been reported.

There are significant differences between the passive carbonation in aged concrete and accelerated carbonation curing in terms of CO_2 gas transport and carbonation reactions. In accelerated CO_2 curing, the cement is hydrated only for a short time and thus CO_2 largely reacts with the unhydrated cement compounds, tricalcium silicate ($3CaO.SiO_2$ or C_3S) and dicalcium silicate ($2CaO.SiO_2$ or C_2S), rather than the hydration products. The composition of concrete in passive carbonation is, however, mainly composed of hydration products calcium hydroxide ($Ca(OH)_2(s)$ or $CH(s)$) and calcium silicate hydrate gel ($3CaO.2SiO_2.3H_2O$ or C–S–H). Furthermore, the CO_2 mass transport dynamics in the two processes are different as the accelerated carbonation curing is carried out with partial pressures of CO_2 typically higher than atmospheric CO_2 partial pressures [5,17], whereas passive carbonation involves only diffusion of atmospheric CO_2 into the concrete matrix.

This study presents the development of a mathematical model for CO_2 transport and uptake during accelerated CO_2 curing of concrete. The model incorporates the dynamics of CO_2 gas advection, dispersion,

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* Corresponding author. Tel.: +1 514 398 6867; fax: +1 514 398 7361.
E-mail address: subhasis.ghoshal@mcgill.ca (S. Ghoshal).

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gas–liquid mass transfer and carbonation reactions of all reactive cement compounds which undergo carbonation. The model results were compared to measurements of CO_2 uptake during accelerated carbonation curing of a compacted cement mortar specimen in a 1-D flow-through reactor, reported previously [3]. The system of equations was also transformed to dimensionless form in order to compare the rate-controlling effects of concurrent physiochemical processes such as the CO_2 gas advection, CO_2 gas–liquid mass transfer and carbonation reaction rate on CO_2 uptake in cement. The model, thus, may be used to calculate the CO_2 uptake for different cements and carbonation process parameters.

2. Carbonation experiment and model framework

2.1. Experimental materials and methods

Compacted cement mortar specimens were prepared with General Use (GU) Portland cement (St. Lawrence Cement), river sand with fineness modulus of 2.3 (Bomix) and tap water as described elsewhere [3]. Briefly, the fresh mixture of cement, water and sand was compacted in a steel mold, and sealed in a PVC shell 1 h after casting. The compacted cement mortar specimens were carbonated in a 1-D flow-through reactor with a gas mixture of 20% or 40% high purity CO_2 in nitrogen balance (Praxair Inc). A CO_2 gas sensor (Quantek model 906 NDIR) was used to monitor the concentration of CO_2 in the effluent gas of the reactor and CO_2 uptake in the specimen during the carbonation process. The carbonation efficiency was also calculated based on measurements of the total carbon content of carbonated specimens carried out with an Eltra CS-800 carbon combustion infrared analyzer. Our experimental set-up ensures constant temperature and inlet CO_2 pressure during carbonation curing and thus allows the chemical and CO_2 transport modeling without accounting for temperature and pressure changes. Details on carbonation curing experiments in the 1-D flow-through reactor can be found in an earlier publication [3].

The porosity and surface area of compacted cement mortar specimens were measured using Mercury Intrusion Porosimetry (MIP) and Brunauer–Emmett–Teller (BET) nitrogen sorption. A Micrometrics 9320 Mercury porosimeter, with a pressure range of sub-ambient to 207 MPa was used for pore size range of 0.006-237 μm [3]. The BET nitrogen sorption method was used for measuring the exposed surface area of compacted cement mortar in pore size range of 1.7-300 nm using a Micromeritics TriStar 3000 instrument at 77.3 K. The total specific surface area of pores used in the carbonation model was defined from the surface area in pore size range of 1.7-300 nm from BET and the surface area in pore size range of 0.3-237 μm from MIP.

2.2. The model framework

Accelerated carbonation of the compacted cement mortar specimen in a 1-D flow-through reactor (Fig. 1) was modeled. The partial differential equation used for calculation of CO_2 concentration in gas phase ($[CO_2(g)]$) includes three terms for advection, dispersion and gas–liquid mass transfer to pore aqueous phase:

$$\frac{\partial(\varepsilon\varphi^a[CO_2(g)])}{\partial t} = D_{CO_2(g)}\frac{\partial^2(\varepsilon\varphi^a[CO_2(g)])}{\partial x^2} - v\frac{\partial(\varepsilon\varphi^a[CO_2(g)])}{\partial x} - r_{CO_2(aq)}. \quad (1)$$

The pore space was unsaturated, therefore, the total porosity, ε, is divided into two parts: φ^a for the pore fraction filled with air and φ^w for the pore fraction filled with liquid water which were calculated based on the water produced or consumed during hydration and carbonation reactions. In the above equation, $D_{CO_2(g)}$ is the dispersion coefficient of CO_2 gas, v is the seepage velocity of CO_2 gas and $r_{CO_2(aq)}$ is the rate of CO_2 dissolution to pore water. The dispersion coefficient, $D_{CO_2(g)}$, was calculated by fitting the experimentally obtained breakthrough curve of an unreactive tracer gas (N_2) at the same flow-rate as the CO_2 gas mixture.

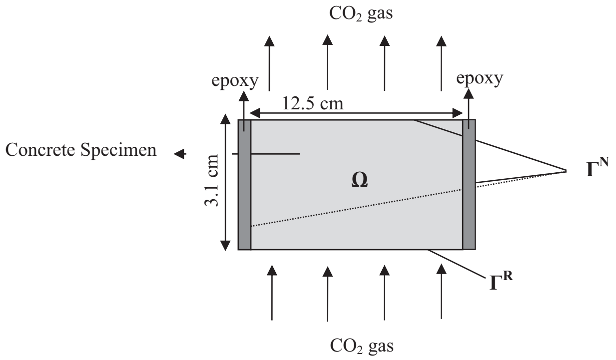

Fig. 1. Schematic view of compacted cement mortar carbonation in the 1-D flow-through reactor.

The CO_2 concentration in the aqueous phase ($[CO_2(aq)]$) is determined by the rate of CO_2 mass transfer from gas phase ($r_{CO_2(aq)}$), diffusion of dissolved CO_2 in aqueous phase in a porous matrix ($D^*_{CO_2(aq)}$) and the rate of CO_2 consumption during carbonation reactions (r_C), and is given by:

$$\frac{\partial(\varepsilon\varphi^w[CO_2(aq)])}{\partial t} = D^*_{CO_2(aq)}\frac{\partial^2(\varepsilon\varphi^w[CO_2(aq)])}{\partial x^2} + r_{CO_2(aq)} - r_C. \quad (2)$$

The diffusion coefficient, $D^*_{CO_2(aq)}$, was obtained from literature [13]. The rate of CO_2 uptake (r_C) is determined by the reaction rates of all cement compounds which participate in carbonation. These cement compounds also include the hydration products which are formed during the 4 h of hydration prior to the commencement of carbonation. The amounts of hydration products formed during this period were obtained from a mathematical model of cement hydration. The hydration and carbonation chemical reactions and reaction rate equations are described in Section 2.3.

These partial differential equations were solved numerically using a finite difference method with the initial and boundary conditions as explained in the Supplementary Material (Section S.1). Since the majority of CO_2 uptake, with gas flow-rate of 1.17 Lpm and 20% CO_2, happened within 30 min [3] and in order to reduce the long computation times, a 30-minute carbonation period was selected for mathematical analysis.

2.3. Production and consumption of reactive cement compounds during hydration and carbonation curing

The changes in cement composition during the hydration and subsequent carbonation are summarized in Fig. 2.

2.3.1. Chemical reactions during hydration period preceding accelerated CO_2 curing

Tricalcium silicate dissolves in the first seconds after water is added; however, the dissolution rate decreases rapidly, by approximately 17 orders of magnitude, before saturation [18]. The overall hydration of C_3S as shown in Table 1 (Eq. (1.1)) results in formation of calcium hydroxide and calcium silicate hydrate gel [19]. Dicalcium silicate follows the same hydration mechanism as C_3S but at a slower rate (Eq. (1.2)).

In the presence of gypsum (calcium sulfate), which is a component of cement, tricalcium aluminate ($3CaO.Al_2O_3$ or C_3A) undergoes hydration and forms ettringite ($3CaO.Al_2O_3.3CaSO_4.32H_2O$, AFt or tri-sulfate), as shown in Eq. (1.3). Calcium hydroxide produced from hydration of C_3S and C_2S is consumed in reaction with tetracalcium aluminoferrite ($4CaO.Al_2O_3.Fe_2O_3$ or C_4AF) and gypsum (Eq. (1.4)) [14]. For short hydration periods as in accelerated concrete curing, gypsum is however