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The effect of random porosity field on supercritical carbonation of cement-based materials

Min Yu [a], Hao Bao [a], Jianqiao Ye [a,b,*], Yin Chi [a,*]

[a] Department of Civil Engineering, Wuhan University, Wuhan, China
[b] Department of Engineering, Lancaster University, Lancaster LA1 4YR, UK

HIGHLIGHTS

- We studied the effect of random porosity of cement on the supercritical carbonation process of cement based materials.
- We first consider both random porosity and its spatial correlation.
- We have used maximum rather than average carbonation depth to measure carbonation.

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ABSTRACT

In this paper, the supercritical carbonation process of cement-based materials is modelled by introducing a random porosity field to simulate the heterogeneous geometry of the carbonation profile. The suitability of two different random fields of porosity, based on the probability density function (PDF) and the ellipsoidal autocorrelation function (EAF) methods, are investigated, respectively, in simulating the distribution of porosity in cement mortar. After incorporating the above random fields into an established supercritical carbonation model, it is found that with some modifications, the EAF method with consideration of spatial correlation produces better simulation of the irregularities of the carbonation zones that have been observed from experimental results. It is also found that for given average porosity and coefficient of variation, the predicted average and maximum carbonation depths have much smaller coefficients of variation. The validated EAF supercritical carbonation model is then used in parametric studies that are conducted to assess the effect of various factors on the carbonation depth of the chemical process.

1. Introduction

Carbonation is one of the main reasons affecting durability of concrete structures. Ashraf [1] and Šavija et al. [2] presented a comprehensive review on the carbonation of cement-based materials, which showed that carbonation could have both positive and negative effects on concrete properties. Carbonation has long been recognized as one of the factors causing reinforcement corrosion [3]. Carbonation causes numerous chemo-mechanical changes in the cement mortar, including changes in porosity, pore size distribution and chemistry, that can enhance its strength and reduce its permeability [4–6]. The above researches on carbonation of cement based materials were mainly on natural carbonation and its potential negative impact on the performance of existing structures. In the recent years, however, the researchers in this area have paid more attention on studying the beneficial aspects of material carbonation, due to the rapid development of the accelerated and supercritical carbonation techniques. These researches include modification of composition and microstructure of cement based materials using carbonation [7–9], use of CO_2 curing to improve material properties [10,11], CO_2 capture and storage [12] and carbonation of hazardous water materials [13]. Clearly, further research on the carbonation process of cement and concrete is required in order to maximize the benefits and reduce the negative effects caused by carbonation.

Carbonation of cement based materials is a complex multi-physics process [12,14–17], involving chemical reactions of CO_2 with CH and C-S-H; gas-liquid two phase flow; dispersion and diffusion of CO_2 in water; and temperature propagation. It is also a chemical-physical process of, e.g., calcium leaching and calcite precipitation. It is well known that carbonation will cause material property changes in porosity, coefficients of diffusion

* Corresponding authors.
E-mail addresses: ceyumin@whu.edu.cn (M. Yu), j.ye2@lancaster.ac.uk (J. Ye), yin.chi@whu.edu.cn (Y. Chi).

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and permeability, saturation and PH value, etc. At the same time, the above changes of material properties will affect the on-going chemical-physical carbonation process. Additionally, the state of CO_2 will have an impact on the chemical process. When the temperature and pressure exceed 304.12 K and 7.38 MPa, which are their respective critical values, CO_2 is in a supercritical fluid state that has a similar density of fluid and can effuse through porous materials, such as cement based materials, like a gas [18]. When the state of CO_2 are between supercritical and the natural atmospheric states, the carbonation of cement-based materials is defined as accelerated carbonation. Kinetic models of carbonation subjected to various carbonation conditions have already be developed and used often to predict depth of carbonation in cement-based materials.

Carbonation depth is one of the most important characteristics that are used to define the extent of the chemical process taking place during carbonation. Experimental research has shown that under either natural [19] or supercritical [19] conditions, the boundaries of carbonation zones exhibit irregular shapes characterized by distinctive maximum and minimum carbonation depths. However, current theoretical and numerical models are almost exclusively based on the assumption that the materials are isotropic and homogenous [20], resulting in an average carbonation depth [21]. In practical applications, it is the maximum, rather than the average, carbonation depth that is critical in, e,g., reinforcement corrosion analysis. Cement-based materials, especially with added aggregates, are typical examples of nonhomogeneous porous materials that consist of randomly distributed pore in the cement mortar and randomly distributed aggregates. All the above inhomogeneity will have significant impact on the distribution of carbonation depth. Pan et al. [22] considered the randomness of aggregates in their natural carbonation model and found that though the cement mortar was assumed to be uniform, the existence of aggregates led to a variable carbonation depth. Rimmelé et al. [23] studied random porosity of Portland cement by exposing it to liquid CO_2. Zha and Yu [15] investigated experimentally the carbonation depth of cement mortar subjected to supercritical conditions, which has shown a carbonation zone of irregular boundaries. Moreover, Lu et al.'s [24] experiment confirmed that saturation was also randomly distributed. Clearly, all the above randomness will play a role in the carbonation process of porous materials. Thus, in order to accurately simulate the carbonation process of cement based materials, a model that takes into account material inhomogeneity, rather than the current commonly-used model based homogenization, is essential, especially in predicting the maximum carbonation depth.

Currently, material inhomogeneity of concrete is considered by incorporating a randomly distributed aggregates or porosity model. Using a random aggregate model, Han et al. [25] studied the effect of aggregates on carbonation penetration. Huang et al. [26] and Ruan et al. [27] studied the carbonation process of concrete and obtained a non-uniform distribution of carbonation depth. There have been extensive and well developed research reported in the literature on using random aggregates models in micro-scale concrete modelling for, such as damage and failure [28,29] and ionic transport [30], etc.; For cement mortar, Diamond et al. [31] and Shi et al. [32] have shown that a log normal function could be used to model pore size distribution. To the authors' best knowledge, there is no published work on using random porosity models in supercritical carbonation research, though they have been used in some other applications. For example, Liu et al. [33] used a random porosity field of log normal distribution to simulate the heterogeneous nature of saline aquifers and study the pressure and saturation distributions of the supercritical CO_2 after injection; Li [34] studied the effect of pore size distribution on chloride diffusion in concrete. Both models did not consider spatial correlation of porosity. For detecting void content in composite materials ultrasonically, Lin et al. [34] developed a two-dimensional porosity model based on the method of ellipsoidal autocorrelation function, where spatial correlation was considered. Since the size of pores in cement mortar is small, it is difficult to simulate its pore distribution by following a random aggregate distribution model. Using a random distribution field to define the magnitude of porosity and spatial inhomogeneity of cement mortar can be a better option.

To address the issues raised above, this paper, on the basis of Liu et al.'s [33] probability density function method and Lin et al.'s [35] ellipsoidal autocorrelation function method, proposes a random distribution field for cement based materials that can take into account both random distribution of porosity and its spatial correlation. Introducing the improved random field into the supercritical carbonation model developed previously by the authors [15], new studies are carried out on the supercritical carbonation of cement based materials. Comparisons are made against the experimental tests reported also by the authors [15] to investigate the effect of random distribution of porosity in cement mortar on the carbonation depth, such that the irregular carbonation depths, particularly, the maximum and minimum depths can be statistically explained and predicted.

2. Random field model of porosity for cement-based materials

Random field models of porosity are studied in this section for modelling supercritical carbonation process in cement-based materials. The random field models of porosity based on the method of probability density function [33] and the method of ellipsoidal autocorrelation function [35] are compared.

2.1. Random field model of porosity based on probability density function

A random porosity field based on probability density function was used to simulate the heterogeneous nature of saline aquifers [33], where the function was assumed to be lognormal distribution, as shown in Eq. (1).

$$f(x) = \frac{1}{x\sigma\sqrt{2\pi}} \exp\left[-\frac{(\ln x - \mu)^2}{2\sigma^2}\right] \quad 0 < x < 1 \tag{1}$$

where x is the random porosity taking between 0 and 1; $f(x)$ is the probability density of x; μ and σ are the log mean and log standard deviation.

The relationship between μ, σ, the average porosity, ε_m, and the variance of porosity v can be represented by Eqs. (2) and (3). The coefficient of variation CV is described in Eq. (4):

$$\mu = ln\left(\frac{\varepsilon_m^2}{\sqrt{v+\varepsilon_m^2}}\right) \tag{2}$$

$$\sigma = \sqrt{ln\left(\frac{v}{\varepsilon_m^2}+1\right)} \tag{3}$$

$$CV = \frac{\sqrt{v}}{\varepsilon_m} \tag{4}$$

In order to generate a lognormal distribution of porosity defined by Eq. (1), a random generator based on the Monte Carlo method [36], which can generate any required probability density, was used. Fig. 1(a) shows the generated porosity distribution with an average porosity of 0.13 and a variance of 0.01. The probability density function of Fig. 1(a) is shown in Fig. 1(b) and compared