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Numerical modeling of supercritical carbonation process in cement-based materials

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ABSTRACT

In this paper, a mathematical model is developed to simulate the physical–chemical coupling process of supercritical carbonation in cement-based materials. This model takes into account the rate of chemical reaction, mass conservation for gas–liquid two phase flow, diffusion and dispersion of CO_2 in water, energy conservation for porous medium and the solubility of CO_2 in water. Numerical results are obtained and compared with experimental results. The degree of carbonation, temperature, gaseous pressure, moisture content and saturation of water within the material are predicted and presented. The influence of material saturation, temperature and pressure of supercritical CO_2 on carbonation depth is investigated through parametric studies. The comparisons with test results suggest that the coupled model can be used to predict carbonation process of cement-based materials under supercritical conditions.

1. Introduction

Concrete carbonation can have both positive and negative effects on concrete properties. A carbonation process decreases the porosity of a cement based material, which can enhance its strength and reduce its permeability [1]. However, the process decreases the pH value of pore solution and thus has negative effect on the durability of reinforced concrete structures [2]. A better understanding of concrete carbonation process will help, e.g., the construction industry, to assess long term performance of the material and also how a controlled carbonation process can be utilized to improve the physical properties of concrete. Other issues associated with carbonation of cement-based materials include safety and long term performance of borehole systems used in underground CO_2 storage, where the presence of supercritical CO_2 is constant and over a very long time scale.

It is well known that when the temperature and pressure exceed their critical values, i.e. 304.12 K and 7.38 MPa, respectively, CO_2 will form a supercritical fluid ($SCCO_2$) phase that has excellent properties such as low viscosity, high diffusion ability and high density. $SCCO_2$ can easily penetrate into the pores of porous media [3]. Carbonation taking place under the above conditions is called supercritical carbonation, in contrast to nature carbonation where the pressure and temperature are both below the above mentioned critical values. There were some experimental studies on supercritical carbonation of cement-based materials. For example, Hartmann et al. [4] investigated the effect of $SCCO_2$ treatment on cemented radioactive waste-forms under various CO_2 pressure and temperature conditions. Short et al. [5,6] carried out supercritical carbonation experiments on glass-fiber reinforced cement materials. They found that supercritical carbonation treatment could significantly increase the strength and toughness of glass-fiber reinforced cement in a few hours. García-González et al. [7] examined the effect of $SCCO_2$ on the carbonation of Portland cement pastes. Recently, Li [8] and Feng [9] carried out some experiments on cement mortar, concrete blocks and tiles under supercritical conditions.

Apart from the above experimental work, there were also some numerical investigations on natural carbonation. Saetta et al. [10–12] proposed a mathematical model for natural carbonation that considered moisture and heat transfer, diffusion of carbon dioxide and rate of carbonation. Papadakis [13] developed a mathematical model for natural carbonation subject to a range of ambient relative humidity. A comprehensive review of the theoretical models of natural carbonation was published recently by Han et al. [14]. The review has shown that most of the existing theoretical models were based on Fick's first law. However, under supercritical conditions, pressure difference rather than concentration is the main driving force of diffusion and the properties of the supercritical fluid are significantly different to those under natural carbonation conditions. Hence, the commonly-used theoretical models of natural carbonation are no longer suitable for modeling supercritical carbonation. On the basis of Darcy's law, Henderson et al. [15] proposed

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a mathematical model for modeling and simulating supercritical fluid through porous media. Saski et al. [16] developed a two phase flow mathematical model to analyze the flow of supercritical CO_2 injected into subsurface of rock masses, where Darcy's law and the equation of state for supercritical CO_2 were used. However, in the above work, the process of carbonation was not considered.

To address the above mentioned issues, this paper attempts to establish a new mathematical model that can include the effect of chemical reactions, gas–liquid two phase flow, heat transfer, diffusion and dispersion of CO_2 dissolved in water. One of the main contributions of this model is that the concentrations of CO_2 in the pore and in the water are considered separately by introducing the solubility of CO_2 under supercritical conditions. The proposed mathematical model is solved numerically by the finite element method. The obtained numerical results are compared with those from supercritical carbonation tests on cement mortar and concrete. Parametric studies are then conducted to study the degree of carbonation, temperature, gaseous pressure, moisture content, saturation of water, etc. during the carbonation process. The influences of intrinsic permeability, saturation, temperature and pressure of $SSCO_2$ on carbonation depth are also studied. It can be concluded that the present mathematical model can be used to predict the carbonation process of cement-based materials under $SCCO_2$.

2. Mechanism of supercritical carbonation

2.1. General description of the main process of carbonation

Concrete and cement carbonation is a complex multi-physics and multi-phase coupling process that encompasses mass transport, momentum transport, heat transfer, as well as chemical reactions. Fig. 1 shows a square concrete block (Fig. 1a) subject to the pressure and temperature of gaseous CO_2 on all external surfaces. Fig. 1b shows the composition of difference phases of the concrete at a representative location, where mass transport (processes 1 and 2) and heat transfer (process 3) occur due to the temperature and pressure differences. Fig. 1c illustrates the process of dissolution (process 4), diffusion and dispersion of CO_2 in water (process 5), and the chemical reactions resulting in carbonation (process 6).

Concrete can be considered as a porous media consisting of solid, liquid and gaseous phases. Under supercritical conditions, mass transport of CO_2 takes place due to pressure gradient that also causes mass transport of the liquid. The temperature difference within the material during the process of supercritical carbonation results in heat transfer in the porous media. Since the CO_2 concentration in the pore is high, only part of the gas will dissolve in the water. The process of diffusion and dispersion of the dissolved CO_2 occurs as a consequence of the concentration difference and liquid flow. Carbonation of cement-based materials is traditionally defined as the chemical reaction between CO_2 and the products of cement hydration, though chemical reactions also take place between CO_2 and other hydration products and the residual unhydrated cement compounds. Normally, the carbonation process can be simply described by the following chemical reaction [10]:

$$CO_2 + Ca(OH)_2 \xrightarrow{H_2O} CaCO_3 + H_2O. \quad (1)$$

According to the above analysis, supercritical carbonation includes the following four main processes:

1) Carbonation reaction
2) Diffusion and dispersion of the CO_2 dissolved in water
3) Mass transport of liquid and gas
4) Energy balance of porous media

2.2. The differences between natural and supercritical carbonation

In principle, the chemical reaction process under supercritical conditions is similar to that under natural carbonation conditions. However, the reactions of carbonation are accelerated under supercritical conditions. The accelerated reaction is due to easy penetration of the supercritical fluid into the micro-pores of the cement, providing continuous availability of hyper-stoichiometric, fresh reactant, as well as the ability of the dense CO_2 to solubilize the reaction product [17].

There are some other differences between nature and supercritical carbonation processes, as shown in Table 1, which are all considered in the following mathematical modeling.

Under natural carbonation conditions, the source of CO_2 is from the air where the concentration of CO_2 is low and can be measured properly by concentration percentage. Under supercritical conditions, however, the gas composition is mainly of CO_2. Thus, CO_2 concentration under different temperatures and pressures cannot be defined effectively by using the concept of concentration percentage. A different measurement of CO_2 concentration under supercritical conditions must be used. Additionally, supercritical CO_2 cannot be treated as an ideal gas, and the equation of state for a real gas should be used.

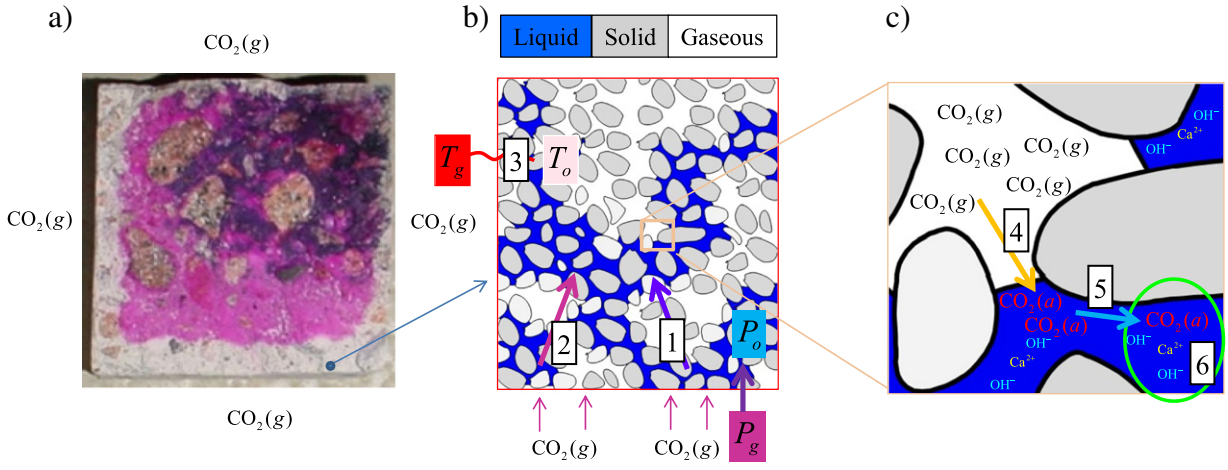

Fig. 1. Simple illustration of supercritical carbonation. (a). Concrete block in CO_2; (b). Representative material composition showing mass transport of gas (1), mass transport of liquid (2) and heat transfer in porous media (3); (c). Dissolution of CO_2 (4), diffusion and dispersion of the dissolved CO_2 (5) and carbonation (6)).