

THERMODYNAMIC MODELING OF CARBONATION OF CEMENTITIOUS MATERIALS IN CONTACT WITH SUPERCRITICAL CO₂

Gonera Piotr Stanislaw

Master student, Dept. of Civil Engineering, The University of TOKYO, Japan

Tetsuya ISHIDA

Assoc. Prof., Dept. of Civil Engineering, The University of TOKYO, Japan

1. INTRODUCTION

Carbon dioxide Capture and Storage (CCS) is a process of capturing the carbon dioxide emitted in industrial processes such as power generation, transporting it to sequestration site and depositing underground in geological formations. Such operation can significantly reduce the amount of CO₂ emitted to the atmosphere with reduction rate of up to 90% in case of fossil fuel power plants.

In order to prevent reemission of the gas to the atmosphere, the bore holes with injection pipes inside them are protected by cement wells designed especially for this purpose.

Although CO₂ has been injected into geological formations for nearly half a century, a long-term storage is a relatively new concept. Therefore, leakage due to degradation of the cementitious materials of the well has become an essential factor in risk assessment of the CCS projects.

The storage sites are located at depths of over 1000m characterized by temperatures of 40 to 200°C and pressure of 10 to 20 MPa. Under such conditions the injected carbon dioxide is compressed significantly which enables effective storage of large amounts. However, this also involves a phase transition to the so called supercritical phase after the injection.

DuCOM is a thermodynamic analytical system developed by the authors' research group to simulate the long-term behavior of cementitious materials under arbitrary environmental conditions. The carbonation model included in the DuCOM platform can predict the equilibrium of carbonation ions, transport of the dissolved and gaseous carbon dioxide and the carbonation reaction itself under ambient and accelerated CO₂ conditions.

To address the difference between the accelerated and supercritical CO₂ conditions, the carbonation model of DuCOM needs to be modified twofold. Firstly, the properties of the supercritical CO₂ need to be included in the analytical model. This part has already been fixed by implementing a proper relationship between the pressure, solubility and diffusivity of CO₂ in the supercritical phase.

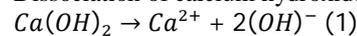
As a second step, the change in properties of the cementitious materials after the exposure was selected. The present paper focuses on the change of microstructure and chemical composition of concrete induced by exposition to the supercritical CO₂. A deep understanding of degradation of the cementitious materials subjected to supercritical CO₂ environment, coupled with the already implemented

properties of supercritical carbon dioxide, is a key to improving the model, so that it can successfully predict the carbonation under the supercritical range.

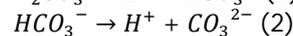
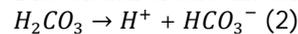
2. CARBONATION IN THE EXISTING MODEL

The carbonation process in the existing model is described by the following chemical reactions:

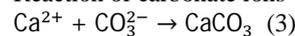
Dissociation of calcium hydroxide:



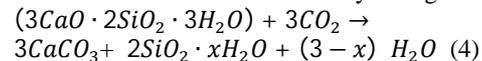
Dissociation of carbonic acid:



Reaction of carbonate ions with calcium ions:



Reaction of the Calcium-Silica-Hydrate gel with CO₂



The process begins with dissociation of the Calcium Hydroxide, one of the main hydration products, in the presence of pore water. Similarly, carbonic acid created from dissolution of the gaseous carbon dioxide is dissociated into carbonic ions. The carbonate ions are combined with calcium ones and form Calcite, main product of the carbonation process assumed in the model. Additionally, Calcium-Silica-Hydrate gel (CSH) reacts with CO₂ forming Calcite and Silica-Hydrate (or low calcium content CSH gel). It is assumed that the clinkers do not take part in the process.

As the main product of the reaction, Calcite, has a greater density than the products (Portlandite and C-S-H) we observe a volumetric expansion and decrease of porosity (void contents) in the carbonated parts. The change in phase composition is presented in Fig. 1

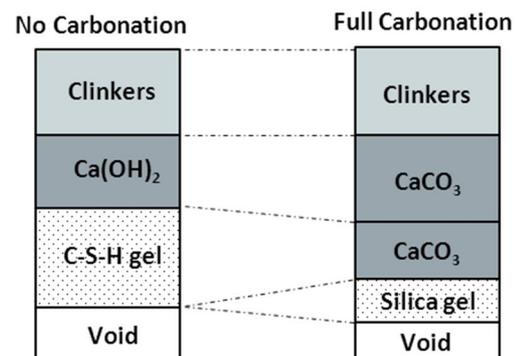


Fig. 1. Model change in composition

3. APPLICABILITY VERIFICATION

3.1 POROSITY

As a first step in verification of the applicability of the existing model to reasonable modeling of the carbonation under supercritical conditions, porosity has been adopted.

Cylindrical 10cm-high cement-paste specimens have been prepared for 3 different water-to-cement ratios. After one week of sealed curing, the sides of the cylinder have been covered with epoxide in order to assure a one-dimensional ingress of the carbonate ions. The ions could ingress the cement-paste cylinder from both top and bottom surface. Once placed in the carbonation chamber, the samples have been exposed to supercritical CO₂ under the pressure of 10MPa and temperature of 100°C for 1,4,7 and 11 days, varying on the specimen. After being cut to 2mm-thick slices at 5mm intervals along the carbonation ingress direction, their total mass porosity was measured by weighting them, once after vacuum saturation and again, after drying in 105°C for 24h.

All the obtained porosity profiles demonstrated a similar tendency and agreement with the analysis. A typical comparison of the experimental and analytical data is shown in Fig. 2. It has to be noted that despite the differences in carbonation profile measured from the top and bottom surfaces, the analytical model assumes ingress from one surface only.

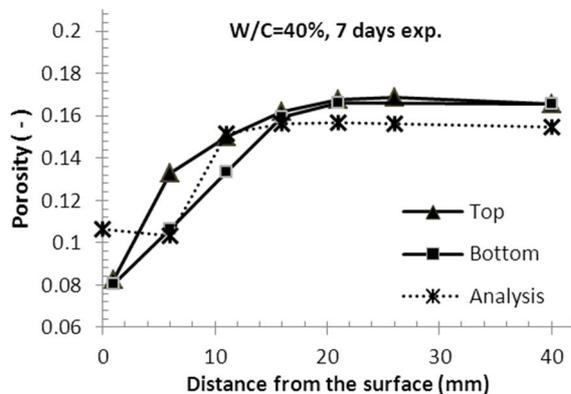


Fig. 2. Porosity profile of the representative series

The model has well predicted the change of the total porosity due to carbonation for all the examined samples. To get a wider picture of the microstructure, not only the total porosity, but also the corresponding Capillary, Gel and Interlayer porosity should be measured. This remains a task for the future study.

3.2 CHEMICAL COMPOSITION

As shown in Fig. 1. the phase composition of concrete changes significantly as the carbonation progresses. It was, therefore, of great importance to verify whether the model assumption about the change of composition hold true for supercritical CO₂-exposed samples. For this purpose, specimens used previously for obtaining porosity profiles, had their composition determined by means of XRD scanning. As all the samples

demonstrated a similar tendency, only the representative series is shown in Fig. 3.

Although most of the model assumptions hold true, the drastic depletion of clinkers in the layer closest to the surface and a very high content of CaCO₃ suggest that after time long enough, clinker phases also become consumed by the carbonation reaction. This tendency is a nuisance not observable in gaseous CO₂-induced carbonation. The current model, therefore, needs to be adjusted in order to reflect the phenomena of clinker contribution to the reaction.

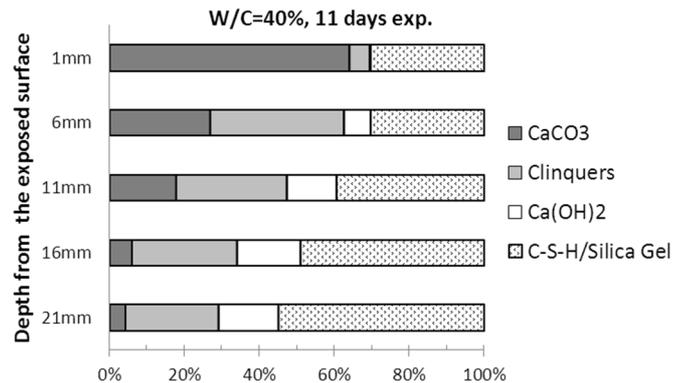


Fig. 3. Experimental change of composition

4. CONCLUSIONS

- (1) The existing model can successfully simulate the total porosity after supercritical CO₂-induced carbonation. However, further study on the porosity distribution is necessary to verify whether the whole microstructure formation process assumed by the model is accurate or not.
- (2) Clinker phases seem to play a role in the carbonation process in supercritical exposition conditions, which never occurs in case of samples subjected to the gaseous conditions. This phenomena should prioritize the future research.

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