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PREDICTION OF THE CHEMICAL SHRINKAGE OF PORTLAND CEMENT

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Abstract

Chemical shrinkage is one of the main reasons leading to the early age deformation of concrete. Hence, the prediction of chemical shrinkage is an important issue for evaluating the deformation of concrete and its influence on the durability of concrete structures. There is still room to improve the accuracy for predicting the chemical shrinkage of cement, because some empirical assumptions were involved in traditional methods such as Paulini equation. In this study a discrete algorithm was proposed to deal with the stoichiometry's conversion of tricalcium aluminate (C_3A) and (tetracalcium aluminoferrite) C_4AF with ongoing hydration of cement. Based on this discrete algorithm, the volume evolution of phases in cement paste and the chemical shrinkage of cement were calculated. The chemical shrinkage of cement in W/C 0.3 and W/C 0.4 were simulated using this method and compared with the results of experiments and Paulini equation. It was found that the calculated chemical shrinkage of cement in W/C 0.3 and 0.4 are in good agreement with experiments, respectively. In comparison with Paulini equation, the proposed method was more accurate for predicting the chemical shrinkage of Portland cement, because the nonlinear relationship between the chemical shrinkage and degree of hydration of cement can be simulated by dealing with the stoichiometry's conversion of C_3A and C_4AF with ongoing hydration.

Keywords: Chemical shrinkage, Portland cement, Tricalcium aluminate, Tetracalcium aluminoferrite

1. INTRODUCTION

The products normally occupy less volume than the reactants for the hydration of cement. This volume difference is defined as chemical shrinkage. Generally, chemical shrinkage is one of the main reasons leading to the early age deformation of concrete such as autogenous shrinkage, which increases the cracking risk of concrete structures [1]. Hence, the prediction of chemical shrinkage is an important issue for evaluating the deformation of concrete and its influence on the durability of concrete structures.

In many reports, empirical equations such as Paulini equation [2] were used to calculate the chemical shrinkage of cement. However, because some empirical assumptions were involved in these calculations, there is still room to improve the accuracy for predicting the chemical shrinkage of cement. This study focusses on pure Portland cement system. Since Portland cement mainly consists of tricalcium silicate (C_3S), dicalcium silicate (C_2S), tricalcium aluminate (C_3A), tetracalcium aluminoferrite (C_4AF), the chemical shrinkage of cement could be calculated on condition that the degree of hydration and the stoichiometry of these components in cement are obtained. The degree of hydration of individual component in cement can be predicted using cement hydration models such as CEMHYD3D, HYMOSTRUC3D, μic, and empirical equations [3]. With the development of cement chemistry, many equations were proposed to describe the stoichiometry of individual component in cement (see Figure 1). Generally, the stoichiometry of the hydration of C_3S and C_2S are considered to be constant with ongoing hydration of cement, while that of the hydration of C_3A and C_4AF depend on the actual amount of gypsum ($C\bar{S}H_2$) and ettringite ($C_6A\bar{S}_3H_{32}$) in the system [4,5]. Because not only the actual amount of gypsum and ettringite are dynamic change, but also the hydration rates of C_3A and C_4AF are normally different, it is difficult to determine the stoichiometry of the hydration of C_3A and C_4AF at different ages.

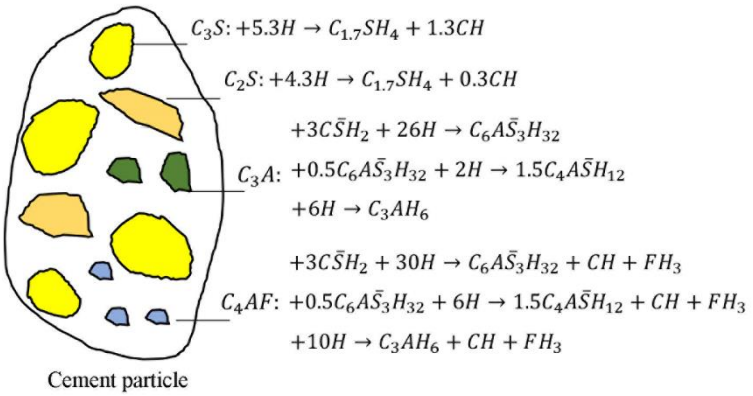


Figure 1: Stoichiometry of the hydration of individual component in cement

This study focused on determining the stoichiometry of the hydration of C_3A and C_4AF with ongoing hydration of cement by proposing a discrete algorithm. Based on this algorithm, the volume evolution of phases in cement paste and the chemical shrinkage of cement were accurately predicted.

2. MODELLING APPROACHES

As presented in Figure 2, the main inputs of this approach included the mineral compositions and particle size distribution of cement, and the water to cement ratio (W/C) of cement paste. The hydration time of cement was divided into several time steps. In each step, the HYMOSTRUC3D model was used to simulate the degree of hydration of individual component in cement. Then, a discrete algorithm was used to determine the stoichiometry of individual component in cement, particularly that of C_3A and C_4AF. Eventually, the volume evolution of phases in cement paste and the chemical shrinkage of cement were calculated.

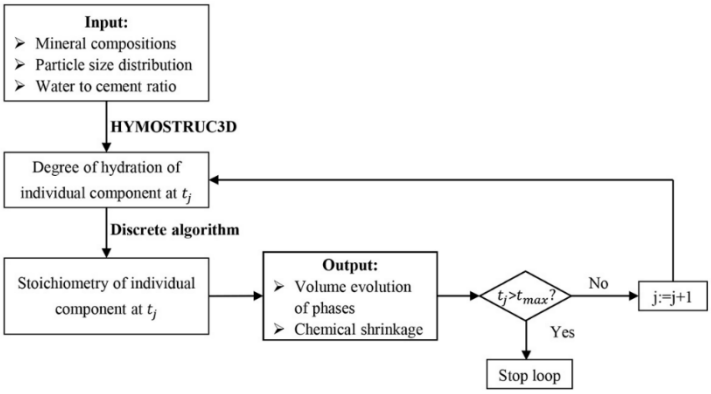


Figure 2: Flowchart of the discrete algorithm for calculating the chemical shrinkage of cement

2.1 Degree of hydration

This study used the HYMOSTRUC3D model to obtain the degree of hydration of individual component in cement at each step. In this model, the reaction rate of cement particles was calculated as a function of the chemical composition and particle size distribution of cement, and the water content and temperature of system. The process of using the HYMOSTRUC3D model to obtain the degree of hydration of individual component in cement can be found in [6].

2.2 *Stoichiometry of cement hydration*

It was assumed that the stoichiometry of the hydration of C_3S and C_2S are constant with ongoing hydration of cement. The stoichiometry of the hydration of C_3A and C_4AF depend on the actual amount of gypsum and ettringite in the system. As schematically shown in Figure 3, three stages were assigned: In stage 1, C_3A and C_4AF reacted with water and gypsum to generate ettringite. In stage 2, all gypsum was consumed, and C_3A and C_4AF reacted water and ettringite to generate AFm ($C_4A\bar{S}H_{12}$). In stage 3, all ettringite was consumed, and C_3A and C_4AF reacted water to generate C_3AH_6.

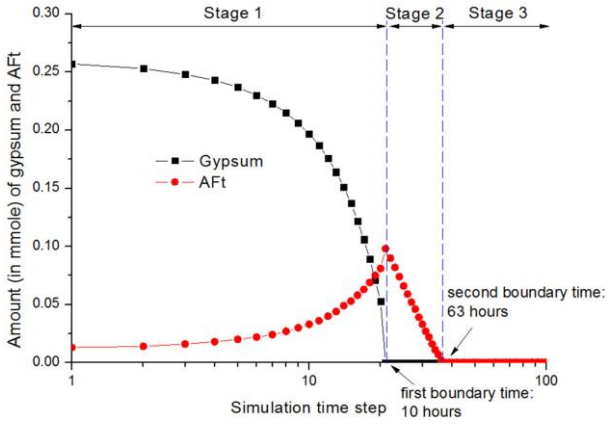


Figure 3: Schematic representation of three stages for determining the stoichiometry's conversion of C_3A and C_4AF

The key point of this discrete algorithm is to determine the degree of hydration of C_3A and C_4AF at the boundary time between different stages.

The condition of the first boundary time is:

$$3.0 \times \left(n_{con,1st,C_3A} + n_{con,1st,C_4AF}\right) = n_{gyp} \quad (1)$$

where $n_{con,1st,C_3A}$ and $n_{con,1st,C_4AF}$ are the amount of reacted C_3A and C_4AF at the first boundary time, respectively.

The above two parameters were related to the degree of hydration of C_3A and C_4AF at the first boundary time, respectively:

$$n_{con,1st,C_3A} = \frac{\alpha_{1st,C_3A} \times f_{C_3A}}{M_{C_3A}} \quad (2)$$

$$n_{con,1st,C_4AF} = \frac{\alpha_{1st,C_4AF} \times f_{C_4AF}}{M_{C_4AF}} \quad (3)$$

where α_{1st,C_3A}, f_{C_3A}, M_{C_3A} and α_{1st,C_4AF}, f_{C_4AF}, M_{C_4AF} are the degree of hydration, weight fraction and molar mass of C_3A and C_4AF, respectively.

In order to solve Eq. (1) to Eq. (3), it is assumed that the ratio of α_{1st,C_3A} to α_{1st,C_4AF} is close to the ratio of α_{C_3A} to α_{C_4AF} at the previous hydration step. Accordingly, it holds that:

$$\alpha_{1st,C_4AF} = \frac{n_{gyp}}{3.0 \times \left(h_{1st,C_3A/C_4AF} \times \frac{f_{C_3A}}{W_{C_3A}} + \frac{f_{C_4AF}}{W_{C_4AF}}\right)} \quad (4)$$

$$\alpha_{1st,C_3A} = h_{1st,C_3A/C_4AF} \times \alpha_{1st,C_4AF} \quad (5)$$

where $h_{1st,C_3A/C_4AF}$ is the ratio of α_{C_3A} to α_{C_4AF} at the previous hydration step for the first boundary time.

The condition of the second boundary time is:

$$n_{re,1st,AFt} - n_{con,2nd,AFt} = 0 \quad (6)$$

where $n_{re,1st,AFt}$ is the amount of ettringite produced in the first stage, and $n_{con,2nd,AFt}$ is the amount of ettringite consumed in the second stage.

Based on Eq. 6, the degree of hydration of C_3A and C_4AF at the second boundary time can be calculated from the ratio of α_{C_3A} to α_{C_4AF} at the previous hydration step for the second boundary time using the similar method in the first stage:

$$\alpha_{2nd,C_4AF} = \frac{\begin{pmatrix} 2 \times n_{re,1st,AFt} + \alpha_{1st,C_3A} \times f_{C_3A}/M_{C_3A} - \\ h_{2nd,C_3A/C_4AF} \times \alpha_{1st,C_4AF} \times f_{C_3A}/M_{C_3A} \end{pmatrix}}{h_{2nd,C_3A/C_4AF} \times \frac{f_{C_3A}}{M_{C_3A}} + \frac{f_{C_4AF}}{M_{C_4AF}}} \quad (7)$$

$$\alpha_{2nd,C_3A} = h_{2nd,C_3A/C_4AF} \times \left(\alpha_{2nd,C_4AF} + \alpha_{1st,C_4AF}\right) - \alpha_{1st,C_3A} \quad (8)$$

where α_{2nd,C_3A} and α_{2nd,C_4AF} are the degree of hydration of C_3A and C_4AF at the second boundary time, respectively. $h_{2nd,C_3A/C_4AF}$ is the ratio of α_{C_3A} to α_{C_4AF} at the previous hydration step for the second boundary time.

(3) The volume evolution *of phases in cement paste and the chemical shrinkage of cement*

Based on the stoichiometry of cement hydration in different stages, the volume evolution of phases in cement paste including reactants: C_3S, C_2S, C_3A, C_4AF, gypsum and capillary water, and hydration products: CSH gel, CH, AFt, AFm, C_3AH_6 and FH_3 were calculated from the degree of hydration of individual component in cement. The chemical shrinkage of cement was calculated as the volume difference of reactants (C_3S, C_2S, C_3A, C_4AF, gypsum and capillary water) to hydration products (CSH gel, CH, AFt, AFm, C_3AH_6 and FH_3).

To validate this model, the chemical shrinkage of cement with a composition of C_3S 56.2%, C_2S 19.61%, C_3A 6.54%, C_4AF 8.91% and gypsum 3.5% was simulated and compared with the experimental data from literature [7]. The particle size distribution of cement can be found in [7], and the W/Cs of cement pastes were 0.3 and 0.4.

3. RESULTS AND DISCUSSIONS

3.1 Degree of hydration

As shown in Figure 4, the simulated degree of hydration of cement in W/C 0.3 is close to that in W/C 0.4 at very early age, while is smaller than that in W/C 0.4 at later age. This is because the influence of W/C on the hydration rate of cement is insignificant at early age. With ongoing hydration, the volume of consumed water is increased, and the hydration rate of cement in the paste with smaller W/C becomes smaller than that in the paste with higher W/C. The above trend is consistent with the experimental data.

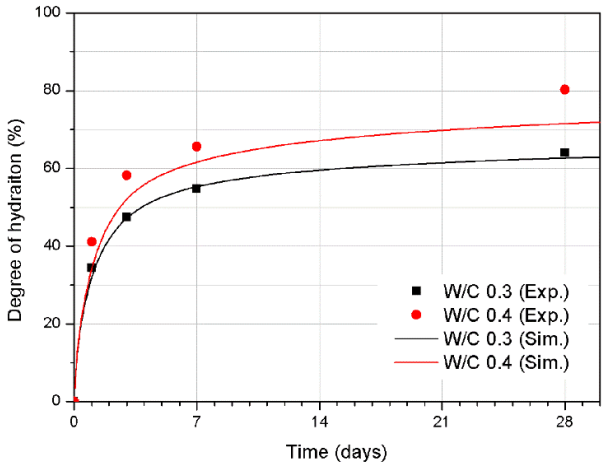
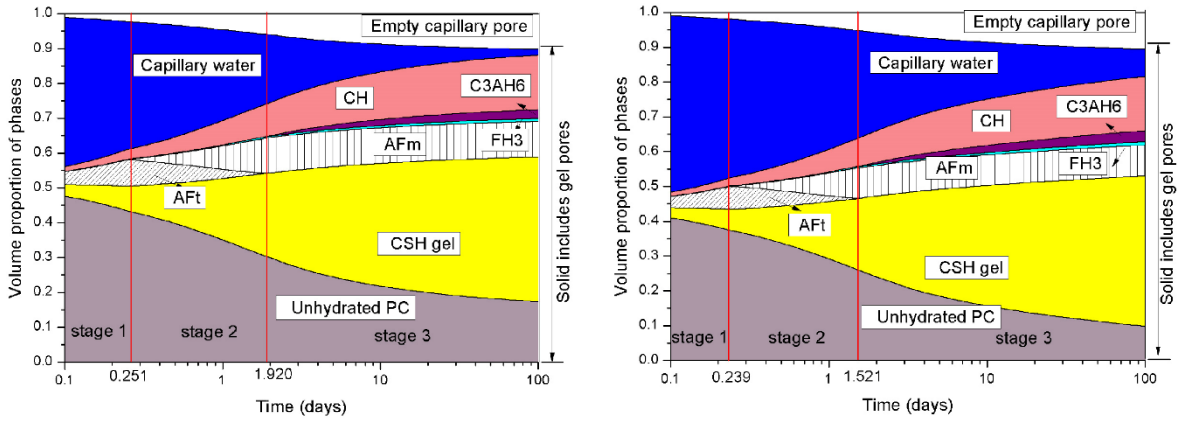


Figure 4: Degrees of hydration of cement in W/C 0.3 and 0.4: simulation (Sim.) *versus* experiment (Exp.)

3.2 Volume evolution of phases

Figure 5a and b show the simulated volume evolution of phases in W/C 0.3 and 0.4, respectively. Table 1 lists the degrees of hydration of C_3A and C_4A at different boundary times. According to Figure 5, the first and second boundary times for W/C 0.4 are earlier than that in W/C 0.3, respectively. As presented in Table 1, however, W/C 0.3 and 0.4 exhibit similar degrees of hydration of C_3A and C_4AF at each boundary time. This is because the boundary times depend on the hydration rates of C_3A and C_4AF, which are earlier in the paste with higher W/C, while the degrees of hydration of C_3A and C_4AF at boundary times depend on the compositions of cement, particularly the amount of gypsum, C_3A and C_4AF (see Eq. (4), (5), (7) and (8)).



(a) W/C 0.3 (b) W/C 0.4

Figure 5: Simulated volume evolution of phases in W/C 0.3 and 0.4

Table 1 Degree of hydration of C_3A and C_4A at the boundary times

W/C	Boundary times	Time (days)	Degree of hydration (%)	
			C_3A	C_4AF
0.3	first	0.251	24.28	4.87
	second	1.920	69.49	19.00
0.4	first	0.239	24.31	4.83
	second	1.521	69.38	19.15

3.3 Chemical shrinkage of cement

As shown in Figure 6, the simulated chemical shrinkage of cement in W/C 0.3 and 0.4 are in good agreement with the experimental results, respectively. The relationship between the simulated degree of hydration and chemical shrinkage of cement is plotted in Figure 7. As can be seen, the line for the simulated degree of hydration and chemical shrinkage is nonlinear. This is due to the conversion of the stoichiometry of C_3A and C_4AF at different stages. The above trend is close to the experimental data. However, the blue line obtained using Paulini equation [2,7] is linear and different from the experimental data. This is probably because the conversion of the stoichiometry of C_3A and C_4AF at different stages is not considered in Paulini equation.

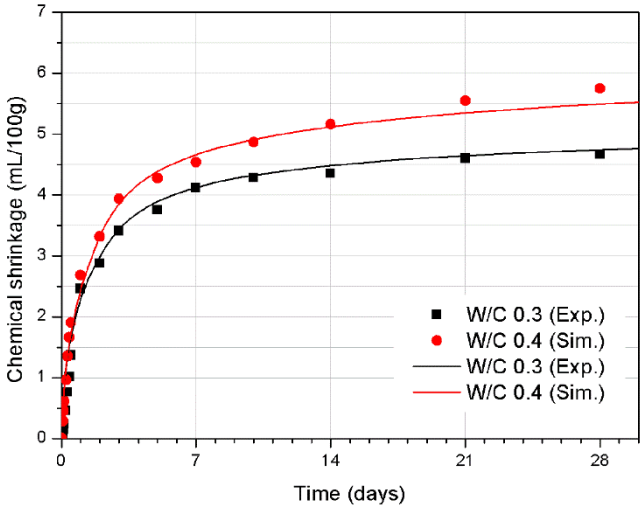


Figure 6: Chemical shrinkage of cement for W/C 0.3 and 0.4: simulation *versus* experiment

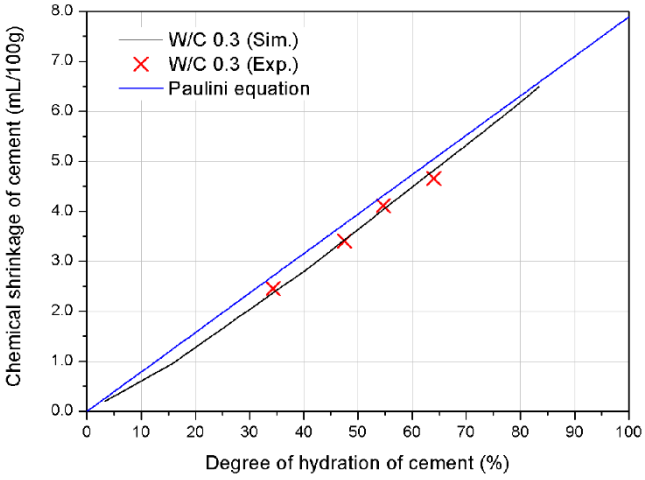


Figure 7: Degree of hydration *versus* chemical shrinkage of cement in W/C 0.3

4. CONCLUSIONS

- A discrete algorithm was proposed to deal with the stoichiometry's conversion of C_3A and C_4AF with progress of the hydration process of cement. Based on this discrete algorithm, the volume evolution of phases in cement paste and the chemical shrinkage of cement were calculated.
- The chemical shrinkage of cement in W/C 0.3 and W/C 0.4 were simulated using this method and compared with the results of experiments and Paulini equation. In comparison with the traditional method for predicting the chemical shrinkage of cement

the proposed method was more accurate, because the nonlinear relationship between the chemical shrinkage and degree of hydration of cement was simulated by dealing with the stoichiometry's conversion of C_3A and C_4AF with ongoing hydration.

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