MODELLING OF MICROSTRUCTURE OF ASR INFLUENCED CEMENT-BASED MATERIALS

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Abstract

ASR (alkali-silica reaction) is one of the toughest durability problems in engineering. However, the damage induced by ASR is still fairly unpredictable due to the lack of microstructural information of cement-based materials affected by ASR, while the microstructure determines the global performance. In order to fill this gap, a multiscale simulation model of ASR is under development. The basic theory and assumptions about this multiscale model can be found in [8]. This paper illustrates how the microstructure evolution of cement-based materials induced by ASR is achieved by this model. In the model, the entire chemical process including dissolution of reactive aggregate, nucleation and growth of ASR products (alkali silicate complex, calcium alkali silicate complex), is quantitatively simulated based on the kinetic and thermodynamic parameters. Furthermore, the 3D heterogeneous aggregate is numerically simulated using stereology based on the data from 2D thin-section. As a result, the dissolution degree of aggregate, the amount and location of ASR products and the porosity change can be traced. These micro parameters can be used for the simulation of crack formation in mesoscale. Similarly, the macroscale damage can be predicted based on the simulation results from mesoscale.

Keywords: ASR; microstructure; multi-scale modelling; heterogeneous aggregate; kinetics and thermodynamics;

1. INTRODUCTION

The famous deleterious chemical reaction between pore solution and reactive aggregate in existing concrete structures was firstly named alkali-silica reaction (ASR) by Stanton in 1940s [1]. One of the reaction products, ASR gel, is a kind of hydrophilic expansive product, which causes extensive cracking in concrete. Numerous concrete structures, such as dams and bridges, have been suffering from durability and safety issues due to ASR. Modelling is needed to analyse the behaviour of ASR-affected structures, thus evaluating the safety level, providing

suggestions about the reinforcement of the degraded structures, and also in view of preventative measures for to-be-built structures.

The global mechanical performance of a structure is determined by the structure of its constituents on micro-scale. Therefore, there are two basic aspects involved when simulating the ASR process in concrete: 1) the modelling of the chemical reaction and diffusion process at micro-scale, and 2) the modelling of mechanical response including expansion and cracking of concrete at macro-scale. The first aspect determines the microstructure change of concrete induced by ASR and the resulting expansion. The second aspect illustrates how the material and the structure degrade. A comprehensive ASR model should combine these two aspects. Unfortunately, due to the complexity of the influencing factors of ASR (reactivity of silica in aggregate, humidity, alkali amount etc.), such a model is missing now. Instead, theoretical [2, 3], semi-empirical [4, 5] and numerical models [6, 7] have been mainly developed depending on the observed response of ASR-affected concrete or laboratory experiments at a mesoscopic or a macroscopic scale. Most of these models either introduce too many parameters or the chemical reaction mechanism is simplified as a single parameter, which is far from reality.

In order to construct such a comprehensive model, a multiscale simulation model of ASR is under development in Ghent University in cooperation with Delft University of Technology. The basic theory and method of this comprehensive model are introduced in the conference paper [8]. In this paper, the simulation of the first aspect - the chemical reaction and diffusion process at micro-scale is described. The output of this model is the evolution of the microstructure of concrete induced by ASR including the porosity change, the amount and location of ASR products, and the change of the pore solution properties. These results will be used as input parameters in the future mesoscale model to simulate the cracking progress and to further obtain the whole crack pattern induced by ASR at macroscale. However, due to the lack of accurate input parameters (under experiments) as discussed in section 2.3, no comparable simulation results are stated. The paper mainly focuses on how to implement such a numerical model based on the proposed theory and method.

2. METHODOLOGY

As we know, ASR is a chemical reaction happening between pore solution in concrete and reactive silica in aggregates. Thus, at microscale, the initial simulation domain is composed of three parts as shown in Fig.1: 1) cement paste, 2) ITZ between cement paste and aggregate, and 3) heterogeneous aggregate at microscale. The microstructure of cement paste including ITZ is simulated using a new numerical cement hydration model developed by TU Delft [9]. The microstructure of heterogeneous aggregate is simulated based on the 3D crystal size distribution of reactive silica.

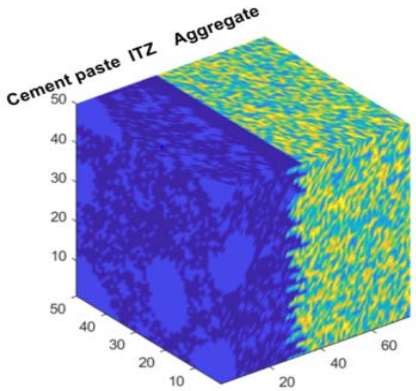


Figure 1: Illustration of the simulation domain at the initial state(unit:).

The simulation flow chart is given in Fig 2. Firstly, the aggregate microstructure domain is simulated as detailed in section 2.2. Secondly, the reactive silica will be dissolved once the alkalis are present on the site through transportation, which results in the ion concentration change in the pore solution. Once the supersaturated condition is reached, nucleation will start. Finally, mass ASR products will be formed by the growth of the formed nucleus.

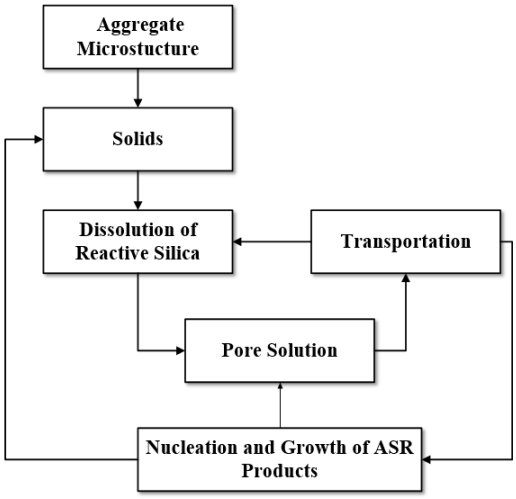


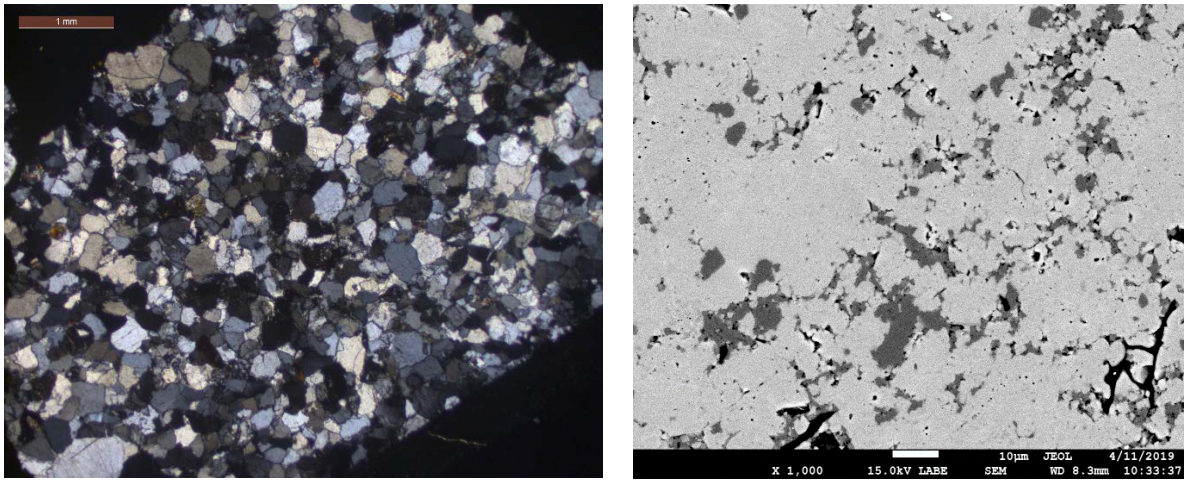
Figure 2: The simulation flow chart

2.1 Initialization

In the microscale model, the microstructure of aggregate, especially the distribution of reactive silica phases, is a fundamental input parameter to the model. In this model, The microstructure of aggregate at microscale will be simulated and introduced into the model as the initial step of the simulation. A brief introduction of this method is given in the following paragraph.

When considering 3D microstructure, CT scans are often a good choice. However, it is not applicable in the case of ASR based on mainly two reasons: 1) The resolution of CT scan is not always high enough to capture all the microstructural information of the reactive silica such as the cryptocrystalline silica (crystal size is less than 4 μm). 2) It is difficult to obtain a representative sample for a specific kind of aggregate. A big amount of aggregates need to be scanned, which causes a big time and economic burden.

An alternative way to obtain the 3D reactive silica distribution is by numerical simulation. Firstly, 2D particle distribution (with clear particle outline, sometimes the outline of the cluster of crystal particles when the particle size is too small) images should be acquired through thin sections or SEM-BSE images as shown in Fig.3. Based on these images, we are able to not only identify the reactive silica phases but also obtain the quantitative particle size distribution including the maximum ellipse length and the number of reactive silica particles using image software. Inputting these 2D data into a 3D stereology model CSD [10], the 3D crystal size distribution per unit volume of the reactive silica or other minerals can be calculated and corrected based on the 2D particle size distribution. The microstructure of aggregate can then be simulated. The shape of the crystal is assumed as an irregular one, which is more realistic. The roadmap of this method is shown in Fig.4. Using this method, lots of aggregates can be sampled and tested at the same time. With the help of image software, it is easy to obtain sufficient microstructure information. However, the localization of the reactive silica cannot be obtained through this method. In this model, particles are randomly parked in the aggregate domain.



(a) (b)

Figure 3: (a) A thin section of sandstone; (b) A SEM-BSE image of siliceous limestone (grey: cluster of silica particles, white: calcium carbonate).

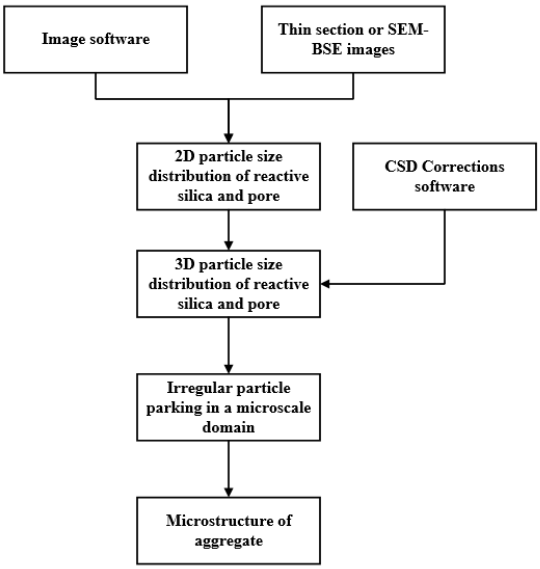


Figure 4:Roadmap about how to simulation an aggregate

2.3 Input Parameters

As stated before, this model is to mimic the entire chemical process of ASR including the dissolution of reactive silica, nucleation and growth of the products. The input parameters include the kinetic rates of the above processes respectively. More details can be found in [8].

2.3.1 Dissolution of reactive silica

ASR starts from the dissolution of reactive silica, which is influenced by the silica surface area, the temperature, pH, ionic strength and under saturation degree. The dissolution rate of silica is calculated according to the comprehensive equation proposed in [11] as shown below.

$$R_{diss} = \left(A_s \mathrm{A} e^{-E_A/RT_K}\right)(a_{OH})^{0.5}(I)^{0.2}\left(1-\frac{Q}{\mathrm{K}}\right) \quad (1)$$

Where A_s is the mineral area of the reactive silica (mm^2); A is the Arrhenius pre-exponential factor ($mole/mm^2/s$); E_A is activation energy (kJ / mole); R is gas constant (8.314J /K / mole); T_K is absolute temperature (K); a_{OH} is the activity of hydroxide ions; I is the ionic strength; Q is the reaction activity quotient; K is the dissolution equilibrium constant of reactive silica.

According to equation (1), the kinetic parameters need to be determined for dissolution are E_A, A and K respectively. Based on the microstructure disorder, there are mainly seven silica phases namely well-crystallized quartz, crypto to microcrystalline quartz, chalcedony, cristobalite, tridymite, opal, amorphous silica in order of increasing reactivity. The activation energies of these silica phases can be found in the literature [12], which is in the range from 46 kJ / mole to 96 kJ/mole. The Arrhenius pre-exponential factor of silica dissolution in base solution is around 0.01 $mole/mm^2/s$ [11]. For the dissolution equilibrium constant, lots of data can be used from a thermodynamic database, such as the LLNL database [13]. The value of $\log K$ of these silica phases lies between -2.71 and -4. The thin section results reveal which reactive silica phases are contained in the aggregate. The microstructure of the aggregate is simulated based on the crystal size distribution results of each reactive silica phase. The

dissolution rate calculated according to the above equation can be assigned to each node in the domain.

2.3.2 Nucleation and growth of ASR products

As stated in [8], the nucleus is assumed to be formed independently, the probability of forming a nucleus in the solution can be calculated via Poisson distribution. According to this assumption, the probability $P_{\geq 1}$ that at least 1 nucleus has formed in a time interval t can be calculated with equation (2)-(4).

$$J = AS\exp\left(-\frac{B}{ln^2 S}\right) \quad (2)$$

$$N = JVt \quad (3)$$

$$P_{\geq 1} = 1 - exp(-N) \quad (4)$$

Where J is the nucleation rate; S is the saturation degree; A and B are kinetic and thermodynamic parameters for nucleation, respectively; N is the average number of nucleus formed in a time interval t. V is the volume of the solution.

In these equations, the input parameters are the equilibrium constants of ASR products to calculate the saturation degree, A and B for ASR products respectively. In this model, the ASR products are divided into two types: alkali-silica gel and calcium-alkali silica gel. The equilibrium constants are obtained from [11]. For A and B, unfortunately, there is no such nucleation data in the literature. Experiments are needed to be done. In conformity with equation (2), $\ln(J/S)$ should be a linear function of $1/ln^2 S$. The thermodynamic parameter B can be estimated from the slope of the best-fit straight line, while the kinetic parameter A can be derived from the intercept to that line. Lots of methods can be used to get the nucleation rate such as by detecting the turbidity change or electricity change of the solution. In this research, the yellow molybdate method is used to determine the nucleation rate J based on the silica polymerization theory. More details can be found in [14].

According to the silica polymerization theory, the nucleation rate of silica is mainly influenced by the temperature, saturation degree, pH and ionic strength. In our model, the temperature is set as 298.15K. And A and B should be different at different pH or ionic strength. Experiments are designed considering the saturation degree, pH and ionic strength. A compiled table about A and B at different pH and ionic strength corresponding to the pore solution properties in concrete will be acquired in the end.

For the growth of silica, except the four influential factors stated above, the formed nanoparticle size also affects the growth rate, which makes it hard to do the experiments. However, lots of research proved that the rate-limiting step of ASR is the dissolution of silica. Therefore, the growth rate of ASR products can be obtained assigning directly as the dissolution rate of silica or via experiments. On the other way, all of these parameters can also be determined by parameter studying.

2.3.3 Ions transport and boundary conditions

The transport of ions will be simulated via the Lattice Boltzmann method [15]. In this model, the ions include $K^+, Na^+, OH^-, H_2SiO4^{2-}, H_4SiO_4,$ and Ca^{2+}. The input parameters are the diffusion coefficients. The cement paste domain is simulated with the simplification that the domain is saturated with water during the simulation. Hereinafter, the diffusion coefficients are the effective coefficients in the liquid phase and porous phase. The fluid flow is ignored. The

diffusion coefficients of these ions in different phases are used from [16] as shown in Table 1 . The diffusion coefficients in the high density phases such as aggregate and low density such as alkali-silica gel are reduced by a factor of 80 and 720, respectively.

Table 1: Diffusion coefficients of ASR related ions in different phases, $\times\ ^{-9}$

m^2/s Ions	K^+	Na^+	OH^-	H_2SiO4^{2-}	H_4SiO_4	Ca^{2+}
Water	1.8	1.33	5.3	0.7	0.53	0.71
[a]HD CSH; Calcium-alkali gel; Unhydrated cement; Aggregate; [c]Other hydration products	1.8/80	1.33/80	5.3/80	0.7/80	0.53/80	0.71/80
[b]LD CSH; Alkali-silica gel	1.8/720	1.33/720	5.3/720	0.7/720	0.53/720	0.71/720

a: high density CSH
b: low density CSH
c: CH, $Ca_4Al_2(SO_4)(OH)_{12}6H_2O$, $Ca_3Al_2(OH)_2$

A periodic boundary condition is applied for the ion transport in the simulation.

3. MICROSTRUCTURE OUTPUT

The entire microstructure data file can be printed in a full or as a system summary sheet. Specific characteristics, such as the percentage of silica reacted, pore volume, amount of the ASR products, and ions concentration change can all be calculated and plotted vs time. The microstructure can also be represented graphically. A 2D or 3D distribution map of different phases can be represented by different colors.

An important point is that the data file contains information about the system which can be retrieved and refined in many ways. In future, the simulated cement-based microstructure induced by ASR can be compared to a real microstructure.

4. CONCLUSION

ASR is one of the toughest durability problems in concrete engineering. The model discussed in this paper describes the chemical reaction process including the dissolution of the reactive silica, nucleation and growth of the products of ASR in three-dimensional space. It has the potential for predicting the microstructure change induced by ASR from a wide variety of reaction conditions. The output is the basic parameters for the multiscale model towards the goal of simulating the entire cracking process resulting from ASR in concrete.

The model provides a means for studying the implications of various assumptions about the alkali silica reactions by comparing the results of model calculations with the results of laboratory experiments. The model can be continuously updated to accommodate new experimental and theoretical developments and thus it will be a concise representation of the current state of knowledge.

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