

## **SIMULATION OF HYDRATION PROCESS AND MICROSTRUCTURE DEVELOPMENT OF UHPC PASTE CONTAINING FLY ASH AND SILICA FUME**

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### **Abstract**

Ultra-high performance concrete (UHPC) is attractive for infrastructure constructions in the future because of its superior properties. Ternary cementitious system containing fly ash and silica fume has been widely adopted for UHPC mix design. This paper presents a numerical model for the simulation of the hydration process and the microstructure development of UHPC paste containing fly ash and silica fume. In the numerical simulation, both the filler effect and pozzolanic reaction of fly ash and silica fume were considered, as well as the nucleating effect of fly ash and silica fume on the hydration process of cement in the early age. The simulated results were discussed and validated against the experimental data. The simulated microstructure and pore structure of UHPC paste were presented. It can be concluded that the UHPC paste containing fly ash and silica fume is extremely dense, which results in the excellent properties of UHPC.

### **Résumé**

Les bétons fibres ultra-performants (BFUP), grâce à leurs propriétés exceptionnelles, sont intéressants pour la construction d'infrastructures. Des systèmes cimentaires ternaires sont souvent adoptés pour leur formulation. L'article présente un modèle numérique pour la simulation du processus d'hydratation et de formation de la microstructure, pour des pâtes de BFUP à base de cendre volante et de fumée de silice. Dans les simulations, les effets de remplissage, les réactions pouzzolaniques des deux additions ainsi que l'effet de nucléation au jeune âge sont pris en compte. Les résultats des simulations ont été discutés et validés par comparaison avec des résultats expérimentaux. On conclut que la pâte de BFUP à base de cendre volante et de fumée de silice présente une forte compacité, d'où découlent les excellentes propriétés du matériau.

## 1. INTRODUCTION

Over the last twenty years, remarkable advances have taken place in the research and application of ultra-high performance concretes (UHPC), which exhibit outstanding mechanical properties and excellent durability. Compared with normal concrete, structures built with UHPC can be smaller in size and have a longer service life, thereby the raw materials and maintenance cost can be reduced. Therefore, UHPC are supposed to be promising civil engineering material in the future.

In recent years, use of supplementary cementitious materials, e.g. fly ash (FA), silica fume (SF), blast furnace slag and limestone, as replacement of Portland cement has gained big attention. This is not only because of the benefits on the reduction of environmental pollution but also the improvement of concrete properties. Because of the high pozzolanic activity of SF, it is regarded as one essential component for UHPC mixture. A high amount of cement content in UHPC has negative effects on the heat of hydration and cause shrinkage problems. Replacing cement with FA is a feasible solution to these problems. Moreover, FA also shows filler effect and pozzolanic effect in the UHPC paste, which modifies the microstructure of the UHPC paste. So the ternary cementitious system, i.e. cement, FA and SF, has been widely adopted for UHPC mix design [1-3].

It is well-known that the performance of cementitious materials is closely related to their microstructure. So for UHPC paste, the microstructure is essential for evaluating its mechanical properties and durability. But the hydration kinetics of UHPC paste is different from that of normal Portland cement paste due to the presence of pozzolanic additives and very low water to binder ratio (w/b). The pozzolanic reaction and low w/b result in a very dense and homogeneous microstructure. The aim of this study is to propose a numerical model for simulating the hydration process and microstructure development of UHPC paste containing fly ash and silica fume. The simulation results were discussed and validated against experimental measurements. The hydration and microstructure simulation of UHPC paste could also be an effective tool for mix design.

## 2. THE HYDRATION AND MICROSTRUCTURE OF UHPC PASTE CONTAINING FA AND SF

The hydration of UHPC paste containing FA and SF is more complicated than that of pure Portland cement since that three components react simultaneously and influence each other. The low w/b makes the hydration process of UHPC paste to be more particular.

When water is added into the UHPC paste containing FA and SF, cement begins to dissolve and hydrate immediately. Meanwhile, the hydration kinetics of cement is influenced by the presence of FA and SF. In the early age, i.e. the dissolution and nucleation period and phase boundary controlled stage, the hydration of cement is accelerated by three mechanisms: (1) Dilute effect: under the same w/b ratio the replacement of cement by fly ash and silica fume augments the water to cement ratio (w/c) thus promotes the hydration extent of cement by more water availability. (2) The FA and SF particles would act as nucleation sites for hydration products, e.g. CSH,  $\text{Ca}(\text{OH})_2$  (CH), thus help to accelerate the hydration process of cement; (3) Due to the high pozzolanic reactivity of SF, CH can be consumed by the pozzolanic reaction of SF, which also speeds up the cement hydration process to some extent. In the late age, i.e. the diffusion controlled stage, the hydration rate of cement is considered to be controlled by the diffusion of water, calcium ions, silica, and et al. in the hydration

products. So it will not be remarkably influenced by the presence of FA and SF in the late reaction stage.

SF is a very reactive pozzolanic material because of its extreme fineness and very high amorphous SiO<sub>2</sub> content. The pozzolanic reaction of SF consumes CH crystals and generates pozzolanic CSH [4], modifying the microstructure of the UHPC paste. Even if SF does not react with CH, the micro-filler effect of SF would also increase the packing density of UHPC paste and refines its pore structure. However, many researchers pointed out that there is high degree of agglomeration of SF in concrete for its small particle size [5-7]. The size of the agglomerated SF particles depends on the dispersion state during mix. The largest particles agglomerated SF could be around 20 μm if SF is not dispersed well [7]. The agglomeration size of SF after mixing is important for pozzolanic reaction rather than the individual size, as this reaction would start from the surface of the agglomerated SF particles, and then the reaction front penetrates into the inner of the SF agglomeration [7, 8]. This agglomeration of SF reduces its effectiveness on improving the properties of concrete because of its large diameter and relatively low pozzolanic activity.

FA is believed to be inert in the early age due to its low pozzolanic activity. Research showed that significant pozzolanic reaction of FA would not occur until after at least 7 days [4]. It actually depends on the pozzolanic activity of FA, curing condition, and some other factors. In UHPC paste, besides the pozzolanic effect, FA also acts as micro-aggregates to strengthen the paste because of its intrinsic high mechanical properties.

For UHPC paste, because of the low w/b, water is not sufficient for the hydration of cement and the pozzolanic reaction of FA and SF. Large amount of cement clinkers, FA and SF particles will remain unreacted in the UHPC paste. And due to the low water content, remarkable changes of phase content of UHPC paste was only detected between the first and second hydration day and up to the seventh day [3]. After seventh day, little phase changes were measured because the free water is mostly consumed by the cement hydration and pozzolanic reaction. So the hydration of cement in UHPC paste always stops earlier than that in cement paste with high w/c.

During the hydration process an extremely dense and compact UHPC microstructure is formed. Fig 1 shows a BSE (Back-scattered electrons) image of UHPC paste containing FA and SF after 28 hydration. Details on the proportion and the test method are described in Section 4. Large amount of non-reacted cement and FA particles still existed in paste, and large capillary pores were hardly seen.

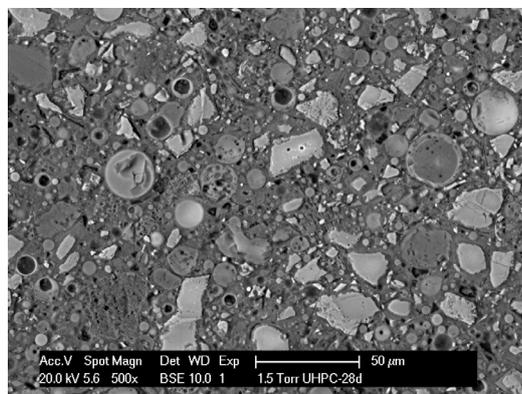


Figure 1: Microstructure of UHPC paste containing FA and SF

### 3. SIMULATION OF HYDRATION AND MICROSTRUCTURE DEVELOPMENT OF UHPC PASTE CONTAINING FA AND SF

Simulation of hydration and microstructure of UHPC paste containing FA and SF was extended from the 3D cement hydration computer model HYMOSTRUC3D [9]. Nguyen [10] extended the original HYMOSTRUC3D model to simulate the hydration and microstructure development of cement blended with rice husk ash (RHA). In his model, only binary system was considered. In order to simulate the hydration of UHPC paste containing FA and SF, which is a ternary system, the model has to be further modified, especially the reaction kinetics.

#### 3.1 Basic rate equations

A modification has been made on the reaction kinetics of cement in UHPC pastes to take the nucleating effect of FA and SF into account based on the original HYMOSTRUC3D model. Similar to the CEMHYD3D model [11], in the phase boundary stage, the increment of penetration depth of cement particles was modified to be proportional to the ratio of initial total surface area of the mixture to the initial cement surface area. For the simulation of the kinetics of pozzolanic reaction of FA and SF, a similar approach was adopted as same as for RHA in [10]. It was assumed that the reaction rate of FA and SF particles was initially determined by a boundary reaction, and when the shell of reaction product reached a certain thickness, this process changed into a diffusion controlled process. The rate of pozzolanic reaction of FA and SF also depends on the availability of CH. For simplification, the influence of superplasticizer on the reaction kinetics was not taken into account in the simulation. The basic rate equations were expressed by:

$$\frac{\Delta \delta_{in,x,j+1}^{cem}}{\Delta t_{j+1}} = K_0^{cem}(\cdot) \times \Omega_1^{cem}(\cdot) \times \Omega_2(\cdot) \times \Omega_3(\cdot) \times F_1^{cem}(\cdot) \times [F_2^{cem}(\cdot) \times (\frac{\delta_{tr}^{cem}(\cdot)}{\delta_{x,j}^{cem}})^{\beta_1}]^\lambda \times (\frac{S}{S_0})^{1-\lambda} \quad (1)$$

$$\frac{\Delta \delta_{in,x,j+1}^{FA}}{\Delta t_{j+1}} = K_0^{FA}(\cdot) \times \Omega_1^{FA}(\cdot) \times \Omega_2(\cdot) \times \Omega_3(\cdot) \times F_1^{FA}(\cdot) \times [F_2^{FA}(\cdot) \times (\frac{\delta_{tr}^{FA}(\cdot)}{\delta_{x,j}^{FA}})^{\beta_1}]^\lambda \times C_{CH} \quad (2)$$

$$\frac{\Delta \delta_{in,x,j+1}^{SF}}{\Delta t_{j+1}} = K_0^{SF}(\cdot) \times \Omega_1^{SF}(\cdot) \times \Omega_2(\cdot) \times \Omega_3(\cdot) \times F_1^{SF}(\cdot) \times [F_2^{SF}(\cdot) \times (\frac{\delta_{tr}^{SF}(\cdot)}{\delta_{x,j}^{SF}})^{\beta_1}]^\lambda \times C_{CH} \quad (3)$$

where:

$K_0^{cem}(\cdot)$ ,  $K_0^{FA}(\cdot)$ ,  $K_0^{SF}(\cdot)$  : the basic rate constant for cement, FA and SF;

$\Omega_1^{cem}(\cdot)$ ,  $\Omega_1^{FA}(\cdot)$ ,  $\Omega_1^{SF}(\cdot)$  : the reduction factor accounting for the water withdrawal effect on cement, FA and SF particles;

$\Omega_2(\cdot)$  : the reduction factor accounting for the water shortage in the pore system;

$\Omega_3(\cdot)$  : the reduction factor accounting for the amount of water in the hydrating mass;

$F_1^{cem}(\cdot)$ ,  $F_1^{FA}(\cdot)$ ,  $F_1^{SF}(\cdot)$  : the temperature function accounting for the effect of the curing temperature on the rate of the reaction process of cement, FA and SF;

$F_2^{cem}(\cdot)$ ,  $F_2^{FA}(\cdot)$ ,  $F_2^{SF}(\cdot)$  : the temperature function accounting for the effect of the curing temperature on the morphology and formation of structure;

$\lambda$ : a factor, depending on the rate controlling mechanism, when  $\lambda=0$  for phase boundary reaction and  $\lambda=1$  for diffusion controlled reaction.

$\delta_{tr}^{cem}(\cdot)$ ,  $\delta_{tr}^{FA}(\cdot)$ ,  $\delta_{tr}^{SF}(\cdot)$  : the transition thickness of cement, FA and SF particles, at which the reaction for the particle in view changes from a boundary reaction into a diffusion controlled reaction;

$\delta_{x,j}^{cem}$ ,  $\delta_{x,j}^{FA}$ ,  $\delta_{x,j}^{SF}$  : the total thickness of the product layer of cement, FA and SF particles with diameter  $x$  at the end of time step  $\Delta t_j$ .

$\beta_1$ : an empirical constant;

$C_{CH}$ : the factor accounting for the reaction of CH phase with FA and SF. If CH content at time  $t_j$  is enough for the pozzolanic reaction of FA and SF at time step  $\Delta t_j$ ,  $C_{CH}$  equals to 1, otherwise, it is reduced with a value of available CH content relative to the required CH content for the pozzolanic reaction of FA and SF at time  $t_j$ .

Details on determination of the parameters listed in Eq. (1), (2) and (3) were described in [9, 10]. Reduction factors and temperature functions can be calculated with the composition of the paste and the degree of reaction of each component at each time step. New parameters, e.g. the basic rate factors  $K_0^{FA}(\cdot)$ ,  $K_0^{SF}(\cdot)$  for FA and SF, were deduced by fitting the experiment results, i.e. CH content at different ages, in papers [4, 12-14].

### 3.2 Degree of reaction

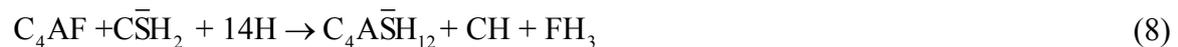
The degree of reaction of cement, FA and SF particles in UHPC paste can be calculated with the same method described in [9, 10]. The overall reaction degree of cement, FA and SF at time  $t_j$  ( $\alpha_j^{cem}$ ,  $\alpha_j^{FA}$ ,  $\alpha_j^{SF}$ ) can be computed as:

$$\alpha_j^i = \frac{1}{G_i(x_{\max}^i - 1)} \sum_{z=x_{\min}^i}^{x_{\max}^i-1} \alpha_{z,j}^i \cdot W_z^i \quad (4)$$

Where  $i$  stands for the type of the particle, i.e. cement, FA and SF;  $x_{\min}^i$  and  $x_{\max}^i$  mean the minimum and maximum size of  $i$  particles;  $G_i(x)$  is the Rosin-Rammler function, which was used to simulate the size distribution of  $i$  particles.  $W_z^i$  is the mass of  $i$  particles in fraction  $F_x$ . The value of the  $G_i(x)$  and  $W_z^i$  can be obtained with the information on the particle size distribution of  $i$  particles.  $\alpha_{z,j}^i$  means the reaction degree of  $i$  particles with size  $z$  at time  $t_j$ , and can be calculated with the penetration depth of the  $i$  particles with size  $z$ , which can be determined with the basic rate equations.

### 3.3 CH content

In the model, the CH content in the paste was calculated by the chemical equilibrium of cement hydration and pozzolanic reaction. The chemical reactions used in the model are given in Eqs.(5)-(11) [15,16]:





The pozzolanic reaction (Eq.(11)) of FA and SF will cause a reduction of CH content in the paste, so CH content ( $m_{CH}$ ) in the whole system can be determined as follows:

$$m_{CH} = m_{CH}(\text{OPC}) - m_{CH}(\text{FA}) - m_{CH}(\text{SF}) \quad (12)$$

where  $m_{CH}(\text{OPC})$ ,  $m_{CH}(\text{FA})$  and  $m_{CH}(\text{SF})$  are mass of CH produced by cement hydration and CH consumed by the pozzolanic reaction of FA and SF respectively. So the CH content is related to the mineral composition of cement, hydration degree of each phase in cement and the reaction degree of FA and SF. The determination of hydration degree of each phase in cement can be found in [10].

### 3.4 Microstructure development

In order to simulate the microstructure of UHPC paste containing FA and SF, the size distribution of each type of particle, the paste characteristics, the particle growth process were also extended for the ternary system. The effect of embedded particles on the growth of the out layer of the centre particle was also considered in the model. But due to the page limitation, details were not presented here.

## 4. EXPERIMENTAL DATA

UHPC paste, containing Portland cement (CEM I 52.5R), FA and SF, with w/b 0.18, was prepared in this study to assess the reaction degree of cement and FA and the CH content. The reaction degree of cement and FA was determined by BSE image analysis and CH content was measured by thermogravimetric analysis (TGA).

The properties of cement, FA and SF are shown in table 1.

Table 1: Properties of cement, FA and SF used in this study

Components	Cement	FA	SF
<i>Chemical properties, % by weight</i>			
CaO	65.07	5.07	0.39
SiO <sub>2</sub>	19.06	54.98	97.20
Al <sub>2</sub> O <sub>3</sub>	4.71	24.61	0.51
Fe <sub>2</sub> O <sub>3</sub>	3.49	6.33	0.18
SO <sub>3</sub>	2.40	1.03	0.26
Na <sub>2</sub> O	-	0.69	-
K <sub>2</sub> O	0.46	1.85	1.04
Loss in ignition(LOI)	1.10	-	-
<i>Physical properties</i>			
Specific mass, g/m <sup>3</sup>	3.15	2.24	2.20
Specific area, g/m <sup>3</sup>	-	-	19.5

The binder of UHPC paste consists of 50% cement, 40% FA and 10% SF by weight. A superplasticizer with 30% solid content was added during mixing. The dosage is 3.5% of the binder by weight. Freshly casted UHPC paste was cured under sealed condition at 20°C.

The point-counting method described in [17] was used to determine the reaction degree of cement and FA. At ages of 1, 3, 7 and 28 days, the specimens were split to small pieces (around 1 cm<sup>3</sup>) and freeze dried for one month. Afterwards, the samples were vacuum impregnated by epoxy resin. But due to the dense structure of the UHPC paste, the pores in the samples can't be fully filled with epoxy. So these samples were cut firstly, and then second epoxy impregnation was performed on the cutting face. After that, the samples were ground and polished carefully before BSE examination. 40 BSE images with a magnification of 500X were taken for each sample. A 7×11 grid was selected for point-counting analysis. So the overall number of the points counted for each sample is 3080. The volume fractions of cement and FA at different ages were determined with the point-counting procedures.

Due to the agglomeration, the effective density of SF in the UHPC paste is unknown. So, same procedures were performed on the samples that were prepared immediately after the final setting of the UHPC paste to determine the initial volume fraction of FA in the paste. It was assumed that the reaction degree of FA was 0 at final setting of UHPC paste. With the initial volume fraction of FA, the proportion of the paste and specific mass of FA and cement, the initial volume fraction of cement, SF and pores in the paste can be computed.

The reaction degree of cement and FA can be calculated as:

$$\alpha(t) = 1 - \frac{V_t}{V_0} \quad (13)$$

Where,  $V_t$  means the volume fraction of cement or FA in the paste at time  $t$ ;  $V_0$  means the initial volume fraction of cement or FA in the paste.

The thermogravimetric analysis tests were conducted with 30-50 mg of powdered freeze-dried paste samples. Replicate samples were studied for each specimen at each age. The TGA was carried out between 20 °C and 1100 °C in argon with the rate of heating at 10 °C per minute. The mass fraction of CH in the hardened paste was determined with tangential approach described in [18].

## 5. RESULTS AND DISCUSSION

In order to compare the simulation and experimental results, the simulation of UHPC paste was made with the same proportion used in the experiments.

Simulation of the microstructure of UHPC pastes containing FA and SF starts by placing cement, FA and SF particles into 100 μm<sup>3</sup> cube. The particle size of cement was determined to be 3 ~ 50 μm because cement grains smaller than 2 μm often completely dissolved [19]. The interval of the particles size was 1μm. The size of FA particles was assumed to be 1 ~ 50 μm. The size of agglomerated SF particles depends on its dispersion state during mixing. In this study, according to agglomerated SF particle size in the BSE images of the UHPC paste, the size of SF particles was set to be 1~10 μm. Figure 2 shows the comparison of simulated particle size distribution of cement and FA and the experiments results measured with laser diffraction [10], as well as the simulated particle size distribution of SF.

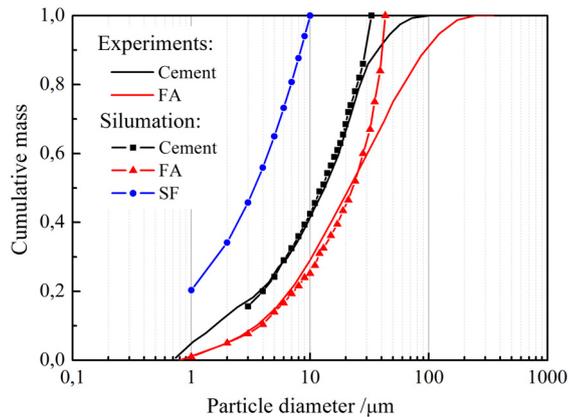


Figure 2: Simulated particle size of cement and FA compared with experiments

Figure 3 shows the reaction degree of cement and FA in UHPC paste both from simulation and experiment results. The simulated results of the reaction degree of SF were also shown in Figure 3. The mass fraction of CH in the paste from the experiments and simulation can be seen in Figure 4.

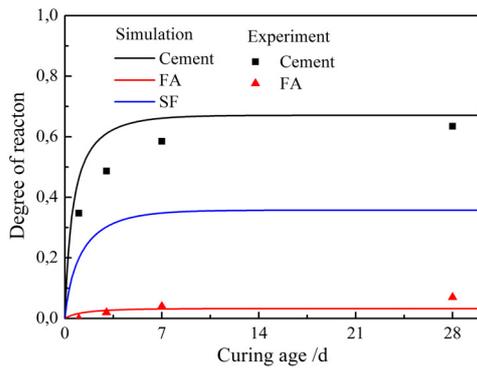


Figure 3: Comparison of degree of reaction by simulation and experiments

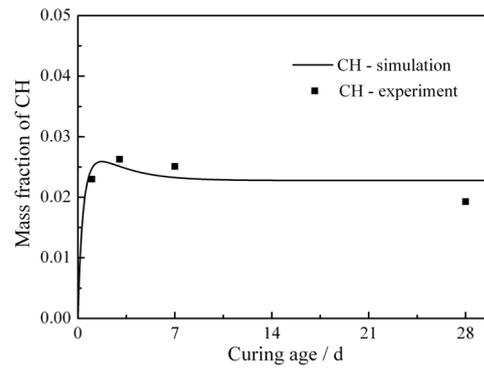


Figure 4: Comparison of mass fraction of CH by simulation and experiments

In general, the results in Figure 3 and Figure 4 indicate that the modified HYMOSTRUC3D model provides a good prediction of the hydration process of UHPC paste containing FA and SF. In the early age (~3d), the simulation results and the experimental results of the reaction degree showed the same trends, but the real reaction rate of cement was a little slower than the simulation results. It was resulted from the high dosage of superplasticizer, which was added into the UHPC paste during mixing and showed remarkable retarding effect on the hydration process of cement. In the later age (7d~28d), the simulation results matched the experimental results quite well. After about 7 days curing, the simulated reaction degree of cement, FA and SF began to keep at constant values, for that the water was totally consumed by the cement hydration and the pozzolanic reaction. Without free water, all the reactions ceased, and the reaction degree of cement, FA and SF did not change any more, as well as the simulation results for the mass fraction of CH in the paste (See Figure 4). However, the experiments results showed that reaction degree of cement and FA increased even after 7 days

hydration and the CH content also kept decreasing in the later age. The continuously reaction of cement and FA may result from the heterogeneous water distribution. And another reason for further pozzolanic reaction may be that CH would react with FA or SF without water in UHPC paste. Meland [6] also suggested that the water involved in the pozzolanic reaction comes from CH and that no extra water is chemically combined in the formation of pozzolanic products. Further experimental investigation should be performed on the details of kinetics and thermodynamics of pozzolanic reaction happened in the UHPC paste under different conditions to verify this viewpoint. In the present simulation, the water distribution and pozzolanic reaction without consuming water were not taken into account.

Figure 5 shows the simulated microstructure of UHPC paste containing FA and SF at 28 days. Periodic boundary condition was applied for each face. The grey, light blue and pink particles represent cement, FA and SF respectively, and the dark blue areas denote the pores. The microstructure of UHPC is very dense, the porosity is 4.23% at 28days according to the simulation results. The simulated porosity is in good agreement with the value in paper [20] from experiments. Figure 6 shows a 2D pore structure of the front face of the simulated microstructure as shown in Figure 5. It can be seen that most pores in UHPC paste are isolated, which will potentially reduce the permeability of the paste. The dense microstructure is the reason why UHPC exhibit excellent mechanical properties and durability.

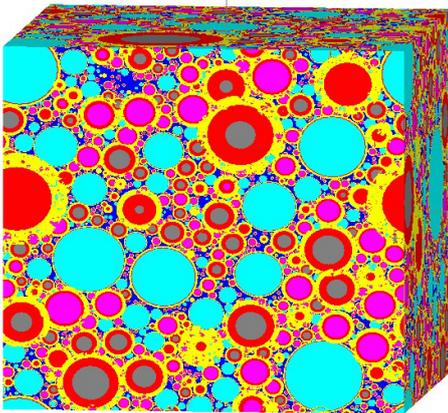


Figure 5: Simulated 3D microstructure of UHPC paste with w/b 0.18, at 28 days

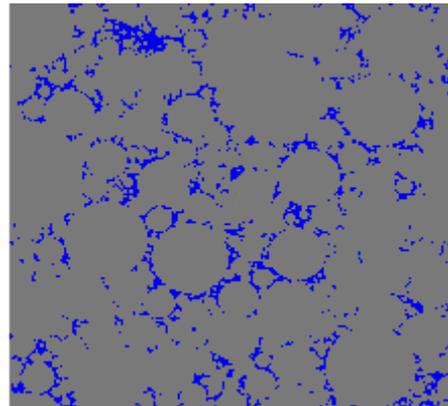


Figure 6: Simulated 2D pore structure (taken from 3D) of UHPC paste with w/b 0.18, at 28 days

## 6. CONCLUSIONS AND OUTLOOKS

- HYMOSTRUC3D cement hydration model was extended to simulate the UHPC paste containing FA and SF. Both the physical and chemical effects of the FA and SF particles were taken into account in the model.
- One type of UHPC paste with FA and SF was simulated. Generally, the simulation gave a quite good prediction on the reaction degree of cement and FA and the mass fraction of CH in the paste.
- Improvement on the model could be made by considering water distribution in UHPC paste. The kinetics and thermodynamics of the pozzolanic reaction happened in UHPC

could be revealed and integrated in the model. The effect of superplasticizer on the hydration process of UHPC paste could also be considered in the model.

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