Research Article

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Hydration And Microstructure Of Astm Type I Cement Paste

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Abstract: In this paper, the hydration and formation of the microstructure of ASTM type I cement paste were investigated experimentally and by means of modelling. Scanning electron microscope (SEM) image analysis was carried out to quantify the hydration of Portland cement. Mercury intrusion porosimetry (MIP) was also conducted to measure the porosity and pore size distribution. The experimental data was compared with the modeling results by HYMOSTRUC3D. The experiments and modeling in this investigation are able to provide the insight into the hydration and formation of microstructure of ASTM type I cement paste.

Keywords: Hydration; Microstructure; Portland cement; ASTM type

1 Introduction

When the Portland cement is mixed with water, the hydration process is initiated. As the hydration process progresses, the hydration products are gradually formed both into the center of cement particles and water filled pores [1]. A three dimension network is gradually built up and becomes denser and denser. As this network develops, the cement paste is able to bear loading. Therefore, the mechanical properties of cement paste are closely associated with the hydration and formation of microstructure [1]. Meanwhile, with the progress of hydration, the capillary pores becomes smaller and smaller and the connectivity between them decreases apparently [1, 2]. This change in

pore structure significantly decreases the transportation and diffusion of aggressive substances, such as chloride and sulphate into the paste from outside environment [3, 4]. This can improve the durability of cement paste effectively.

In order to gain a better view into the potential of the mechanical properties and durability of ASTM type I cement paste, the hydration and formation of microstructure of this type of cement were investigation in this paper.

There are various experimental techniques which can be used to investigate the hydration and microstructure of cement paste. X-ray diffraction (XRD) and thermogravimetric analysis (TG/DTA) can be applied to roughly determine the types and approximate contents of different phases in cement paste [5–8]. In comparison, scanning electron microscope (SEM) can be used not only to quantify the contents of different phases, but also to observe the topography and distribution of solid phases in two dimensions [2, 8, 9]. In this study, SEM image analysis was carried out to quantify the hydration of Portland cement. Mercury intrusion porosimetry (MIP) was also conducted to measure the porosity and pore size distribution.

For the simulation of hydration and formation of microstructure in cement paste, there are several active models, such as CEMHYD3D, HYMOSTRUC3D and DuCom [2, 10–13]. In this paper, HYMOSTRUC3D was employed to simulate the hydration and formation of microstructure of ASTM type I cement paste. At the same time, the experimental data was compared with the modeling results.

2 Materials and experiments

2.1 Materials

In this study, the Portland cement used is ASTM type I cement. The chemical compositions of this cement are listed in Table 1. The fineness of this type of cement is 461.6 m²/kg. For the mixture, the water to cement ratio (w/c) is 0.5. All the samples were cured at 20°C under seal conditions.

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Table 1: Chemical compositions of ASTM type I cement

Compound	Weight (%)
CaO	63.82
SiO ₂	20.09
Al ₂ O ₃	3.87
SO ₃	3.50
Fe ₂ O ₃	1.69
MgO	2.22
Na ₂ O	0.30
K ₂ O	0.39
TiO ₂	0.16
MnO	0.05
Bogue compositions	
C ₃ S	68.7
C ₂ S	5.8
C ₃ A	7.4
C ₄ AF	5.1

2.2 SEM observation

Cement paste at the age of 1, 3, 7 and 28 days was used to prepare samples for SEM measurements. The preparation of samples, which includes drying, epoxy impregnation, grind and polishing, was implemented according to the literature [2]. From the previous study [2], it was reported that around 12 frame images (the magnification is 500X and the image size is 1424 × 968 pixel) are required in order to get reliable results. In this study, 40 frame images were captured for each sample.

2.3 MIP test

The samples for MIP test were prepared according to the procedures introduced in the literature [2]. The method for drying the samples was the same as that for SEM measurements.

3 Modeling

The hydration and the formation of microstructure of the ASTM type I cement paste were simulated by HY-MOSTRUC3D. The model starts from cement particles randomly distributed in a three-dimensional body according to water/cement ratio [14]. The cement particles gradually dissolve and a porous shell of hydration products is formed around the particles.

The hydration kinetics of a single particle, x , is described by a formula which gives the rate of penetration of the reaction in an individual cement particle at time t_j [1]:

$$\frac{\Delta\delta_{in,x,j+1}}{\Delta t_{j+1}} = K_0(.) \cdot \Omega_1(.) \cdot \Omega_2(.) \cdot \Omega_3(.) \cdot F_1(.) \quad (1)$$

$$\cdot \left[F_2(.) \cdot \left(\frac{\delta_{tr}(.)}{\delta_{x,j}} \right)^{\beta_1} \right]^\lambda$$

where $\Delta\delta_{in,x,j+1}$ is the increase of the penetration depth in time step Δt_{j+1} ; Δt_{j+1} is the basic rate factor of the boundary reaction; δ_{tr} is the transition thickness (μm), being the thickness of the product layer $\delta_{x,j}$ at time t at which the reaction of particle in view changes from the phase-boundary reaction into a diffusion controlled reaction. The parameters Ω_i describe the various effects of water on the cement hydration mechanisms and the parameters F_i take into account the influence of temperature of the hydration process.

As the hydration progresses, the growing particles become more and more connected. In this way, the material changes from the state of a suspension to the state of a porous elastic solid - microstructure.

4 Results and discussion

4.1 SEM observation

Based on the BSE image analysis, the fractions of different phases as a function of hydration time are shown in Figure 1.

The fraction of cement, as it is known, decreases as the hydration progresses and thus the amount of hydration products increases. The porosity correspondingly reduces. It is interesting to note that after one day hydration, around 48% of total space has been occupied by calcium silicate hydrates (CSH) and only 18% for the unhydrated cement particles. Compared to the cement of CEM I 32.5, after one day hydration the fraction of CSH is about 26%, while about 23% for unhydrated cement when the w/c is the same [2]. After the age of 7 days, the hydration of ASTM type I cement becomes much slower. During the age of 7 days and 28 days, the fraction of unhydrated cement decreases by about 2.5%. Correspondingly, the fraction of CSH increases by about 23%. It shows that the reaction of this type of cement is fast at the early age. This can be contributed to the relative high fraction of C₃S and low fraction of C₂S. And it can be also caused by the high fineness of this cement. It is also interesting to note that the

Figure 1: Area fractions of different phases from SEM measurements. CH is calcium hydroxides. UHC is unhydrated cement and CSH is calcium silicate hydrates.

Figure 2: BSE images of the microstructure of the cement paste at different age.

calcium hydroxides (CH) increases very slightly during the period from 1 day to 28 days. It can be explained that with the high w/c ratio, the ferrite can react with ettringite and CH to produce garnets [2]. It also can be caused by the uniform distribution of CH, and thus the total observed area of the samples is not sufficient to achieve the correct fraction of CH [2]. The porosity decreases significantly during the hydration of the first 7 days. At the age of 28 days, the porosity is only 9%. What should be mentioned is that gel pores cannot be observed by a BSE detector with 500X magnification. The fraction of pores shown in Figure 1 only includes the capillary pores of which the size is larger than hundreds of nanometers depending on the magnification.

Figure 2 shows the microstructure of the cement paste at different age. From the images, it can be observed that the CSH gel is formed around unhydrated cement particles. CH shows hexagonal plate morphology and forms in large voids. As the hydration processes, the microstructure becomes denser and denser. Moreover, from the segmented BSE images of pore structure (Figure 3), the connectivity of the pore gets worse as cement paste gets matured.

By coupling the curves of different phases and the microstructure in Figure 2 and 3, it can be found that the microstructure of ASTM type I cement is very dense at the age 28 days.

Figure 3: BSE images of the pore structure (black colour) of the cement paste at different age.

Figure 4: Porosity and pore size distribution of ASTM type I cement paste by MIP test.

4.2 MIP test

The results from MIP tests are shown in Figure 4. It can be learned that the total porosity decreases from 0.33 at the age of 3 days to 0.25 at the age of 28 days. At the same time, as shown in Figure 3(b), there are two peaks from the pore size distribution differential curve. These peaks represent the pore diameters corresponding to the higher rate of mercury intrusion per change in pressure [2]. These peaks are called “threshold”, “critical” or “percolation” pore diameters [15]. In cement paste, the first peak is general considered as corresponding to the capillary porosity, while the second peak is corresponding to the gel pore [2]. For

the case of this study, the pore diameters corresponding to the first peak decreases from 0.47 μm at the age of 3 days to 0.16 μm at the age of 28 days. In comparison, this value decreases from 0.034 μm to 0.019 μm . Moreover, the porosity corresponding to the first peaks decreases as the paste get matured. On the contrary, it increases for the second peaks as the hydration processes. It means that the capillary pores are gradually occupied by CSH and the microstructure becomes denser and denser.

It is worthy of noting that the porosity from MIP test is much higher than that from SEM measurement. As mentioned before, the porosity from SEM measurement only includes the capillary pores of which the size is hundreds of

Figure 5: Degree of hydration of cement paste as a function of hydration time.

nanometers. In comparison, from the MIP test, the pores with the size of several nanometers can be taken into account. That is reason why the porosity from MIP test is larger than that from SEM measurement.

5 Modeling results

The hydration of ASTM type I cement was simulated by HYMOSTRUC3D. The degree of hydration from simulation is shown in Figure 5. The simulated results were compared with the experimental data from ESEM measurements. From the comparison, it can be found that the degree of hydration from simulation is in a good consistency with the data from SEM measurements, which was calculated by the fraction of unhydrated cement:

$$\alpha(t) = [f_c(t_0) - f_c(t)] / f_c(t_0) \quad (2)$$

where $\alpha(t)$ is the degree of hydration as the function of hydration time t ; $f_c(t_0)$ is the volume fraction of cement at time $t = 0$ and $f_c(t)$ is the fraction of cement at time t , which can be represented by the area fraction of unhydrated cement from SEM measurement [16].

As known, the degree of hydration is one of the most important properties of cement pastes. Through the simulation, the degree of hydration in the long term can be predicted, which is difficult to achieve by experiments in laboratory.

As shown in Figure 6, the porosity from the simulation is lower than the MIP results and higher than that from the SEM measurement. As mentioned before, the porosity from MIP test includes the pores with the size of sev-

Figure 6: Porosity of cement paste as a function of hydration time.

eral nanometers, while for the SEM measurement only the pores with the size of several hundreds nanometers can be tested. In the simulation, the volume of gel pores is included in the hydration products. This is the reason why the porosity from simulation is lower than the MIP results. In comparison, to some degree, minimum size of the pores from simulation is smaller than that in the SEM measurement. Therefore, the porosity from simulation is slightly higher than that from SEM measurement.

From Figure 7, it can be learned that the amount of hydration products from the simulation is slightly higher than that from the SEM measurement. It is reasonable while the porosity from the simulation is higher than the SEM measurement results and the degree of hydration between the simulation and SEM measurement is almost the same.

Based on the comparison of the modeling results to the experimental results, it can be learned that HYMOSTRUC3D is able to simulate the hydration of ASTM type I cement very well. With the simulation, the basis properties of the cement paste in the long term can be predicted. And these properties can be used to evaluate the durability and mechanical properties of the cement paste.

6 Conclusions

In this paper, the hydration and formation of the microstructure of ASTM type I cement paste were investigated by experiments and modeling. Scanning electron microscope (SEM) image analysis was carried out to quantify the hydration of Portland cement. Mercury intrusion

Figure 7: Fraction of hydration products of cement paste as a function of hydration time.

porosimetry (MIP) was also conducted to measure the porosity and pore size distribution. HYMOSTRUC3D was employed to simulate the hydration and formation of microstructure of this cement paste. From the experimental and simulation results, the conclusions can be drawn as follow:

- Because of chemical compositions and the fineness, the hydration of ASTM type I cement processes fast at the early age. After 7 days, the hydration becomes much slower.
- The microstructure of ASTM type I cement is dense at the age of 28 days, which is good for the mechanical properties and durability of the materials.
- The simulation of hydration of ASTM type I cement by HYMOSTRUC3D shows a good agreement with the experimental data. Through this model, the hydration of ASTM type I cement in the long term can be predicted.

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