5th International PhD Symposium in Civil Engineering –
Walraven, Blaauwendraad, Scarpas & Snijder (eds),
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Microstructural aspects of cement hydration – ultrasonic waves and numerical simulation

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ABSTRACT: In this paper, an ultrasonic shear wave reflection method was adopted to mimic the microstructural evolution of hydrating Portland cement pastes with different water/cement-ratios (0.35, 0.5 and 0.6) cured under a constant temperature of 25°C. The reflection coefficient measured with this technique was correlated to microstructural parameters of the cement pastes. The application of numerical simulation has shown that the ultrasonic wave reflection technique can be used to efficiently monitor the microstructural evolution of cementitious materials.

1 INTRODUCTION

A new ultrasonic technique, called wave reflection method, was introduced by McSkimin et al [1] in 1950s. The idea is to predict material properties by analyzing the information of reflected waves at the interface of a buffer and a testing material. The method was first applied to cementitious materials by Stepiπnik et al in 1981 [2]. This one-sided nondestructive ultrasonic technique was used to monitor the stiffening process of Portland cement concrete [3]. It proved to be an efficient method to describe the setting and hardening behavior of not only plain concrete, but concrete with chemical admixture as well [3,4]. Since then, more work has been done in this area. During extended research, it was found that the development of the wave reflection factor (WRF) is in good correlation to in-situ compressive strength evolution of cement-based materials at early age [5]. A procedure for strength prediction based on measured reflection loss has been proposed.

The ultrasonic wave reflection method has been proved to be a functional NDT method, which can monitor early age properties of cement-based materials [2–5,12]. However, the mechanism of the WRF evolution and the correlation between WRF and the microstructural development of cementitious materials were not investigated in the previous studies. This paper focuses on the question whether the trend of WRF development reflects the microstructural evolution of the tested material. Since the microstructural development is the key parameter which controls material properties, such as workability, setting and hardening, strength, elastic moduli, the understanding of this mechanism becomes extremely important. Correlations between the measured WRF and the microstructural development of the material need to be established.

The development of the microstructure during cement hydration can be simulated by computer modeling. In the past decades, a few cement hydration models have been developed worldwide. One of the models, called HYMOSTRUC3D [6,7], which is a continuum model, provides us with an opportunity to study the microstructural evolution of cement-based materials. In this model, the hydration progress in cementitious materials is mimicked based on hydration stoichiometry. Hydrated and unhydrated cement particles are considered as the solid phase. The microstructural parameters including pore distribution, volume fraction and the connectivity of the solid and pore phase can be simulated by the model.

This paper aims to compare results of wave reflection measurements with the properties of the solid phase obtained from numerical simulations using HYMOSTRUC3D. The correlation of connectivity of the solid phase and the WRF development were studied in detail. It is shown that the solid phase is a major factor that influences the wave propagation properties of cementitious materials.

2 MATERIALS AND METHODS

2.1 *Materials*

Ordinary Type I Portland cement provided by Lafarge was used for all experiments. The chemical composition is listed in Table 1. The Blaine surface area is 365 m^2/kg.

Plain cement pastes with water/cement-ratios of 0.35, 0.5 and 0.6 were tested. The specification of ASTM standard C305 [8] was followed during the mixing of cement pastes. A constant temperature of 25°C of curing condition was used. All specimens were sealed in molds throughout the whole period of experiments.

2.2 *Ultrasonic wave reflection method*

The wave reflection factor was calculated by the information obtained from wave reflection tests. The apparatus is shown in Fig. 1. A steel plate with a thickness of 12 mm was used as a buffer

Table 1. Chemical compositions of Portland cement Type I – Lafarge.

Chemical data	SiO_2	CaO	Al_2O_3	Fe_2O_3	C_3S	C_3A
Percent	20.4	65.3	4.8	2.8	68	8

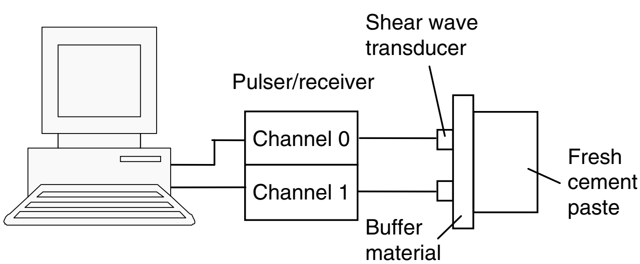

Figure 1. Experimental apparatus for wave reflection measurements.

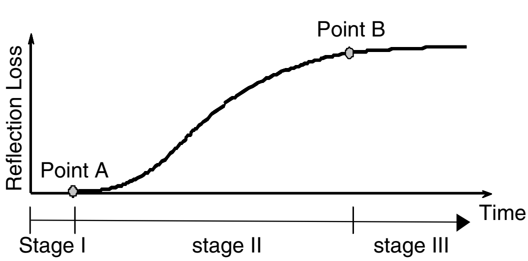

Figure 2. Development of reflection loss of cement paste.

material. Two transducers, with 2.25 MHz central frequency were coupled to the steel plate. The transducers were connected to pulsers, which in turn were connected to a computer.

According to the theory of wave reflection [9], for normal incidence of shear wave at a plane interface, the reflection coefficient can be defined as:

$$\mathrm{WRF} = \mathrm{A_r} / \mathrm{A_i} \tag{1}$$

where WRF is the wave reflection factor, which is defined as the amplitude ratio between reflected wave A_r and incident wave A_i. Since ultrasonic amplitude ratios are usually measured in decibel, the reflection loss, R_L as shown in equation (2), which is another form of reflection coefficient, is often used. The reflection loss will be used in the later part of this paper for the convenience of data analyzing.

$$R_L = -20 \bullet Log(WRF) \tag{2}$$

Time-signals of ultrasonic shear waves were captured by the computer setup during the tests. To calculate the reflection loss, ultrasonic signals in time domain need to be translated into frequency domain by a Fast Fourier Transform (FFT) algorithm.

A typical curve of reflection loss can be divided into three stages (Fig. 2). During stage I, the paste can be considered as cement particles suspended in water. Since water is very weak in supporting shear wave, there is almost no reflection loss during this period. As hydration goes on, the amount of the solid phase, which can support shear waves increases rapidly. So reflection loss increases greatly during stage II. When the solid phase reaches a certain value, its rate of increase slows down. This is reflected by a small increase of reflection loss in stage III.

2.3 *Particle Size Distribution (PSD) analysis*

The analysis of the particle size distribution provides direct information of the fineness of the cement powder, which is an important factor of the rate of hydration. A Low Angle Laser Light Scattering (LALLS) method was applied. Four tests have been done and average values were used in the later numerical simulation work. Fifty percent of cement particles are smaller than 14.3 μm. The volume weighted mean value of particle diameter is 18.5 μm.

2.4 *Thermogravimetric analysis of cement paste*

Thermogravimetric Analysis (TGA) is considered as an efficient approach, which can provide information about the degree of hydration of cement pastes [10]. The Powers-Brownyard model was applied to evaluate the TGA results. In this model, hydrated cement paste is assumed in the general case to comprise three components: unhydrated cement, hydration product (gel) and capillary pores. The water present in the paste was categorized as evaporable and non-evaporable water [10]. By relating the content of non-evaporable water at a certain age to that for complete hydration, the degree of hydration (α) at this age can be obtained as shown in equation (3). The content of non-evaporable water for complete hydration ($w_n/c_{complete}$) can be obtained from the potential Bogue composition [10] of the cement. Typical values for $w_n/c_{complete}$ range from 0.23 to 0.25.

$$\alpha(t) = \left[\frac{w_n}{c}(t)\right] \Big/ \left[\frac{w_n}{c_{complete}}\right] \tag{3}$$

3 NUMERICAL SIMULATION

3.1 *General principle of HYMOSTRUC3D*

In this study, the HYMOSTRUC3D [6,7] model was used to simulate the development of the microstructure in cement pastes. With this model, the rate of cement hydration was modeled as a

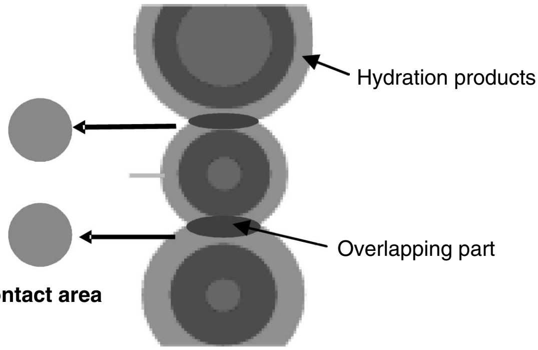

Figure 3. Concept of contact area [11].

function of the particle size distribution, the chemical composition of cement, the water/cement-ratio and the reaction temperature. In the model, the cement particles are assumed to be spherical. Particles of the same size are considered to hydrate at the same rate. At first, hydration reactions are assumed to be phase-boundary reactions. At later stages, when the shell of reaction products has reached a certain predefined thickness, the reactions become diffusion controlled. The simulation starts from a random distribution of cement particles in a cubic cell. During hydration, the cement grains gradually dissolve and a porous shell of hydration products is formed around the grain. Cement particles with smaller particles embedded in their outer shells from a "cluster". The process of embedding smaller particles in a bigger particle's outer shell is quantified with a mathematical series, in which the particle size distribution and the water/cement-ratio are the dominating parameters. As hydration progresses, the growing particles become more and more connected. Thus a porous structure is formed.

3.2 *Scales of the microstructural parameters*

The microstructure of cementitious materials can be described by parameters that belong to a range of different scales. Typical large scale characteristics are parameters describing the volumetric composition of a material. Consequently, the degree of hydration, the volume fraction of the total solid phase and the capillary porosity are chosen as three basic volumetric parameters.

Another important characteristic of cementitious microstructures is the connectivity of the constituent phases. This connectivity can again be quantified in different perspectives. One possibility is to determine the volume fraction of the individual phases that is inter-connected. Thus, the volume fraction of the connected solid or pore phase will be investigated. By following this systematic, important information about the development of the connectivity of the phases in time can be derived. An example of this kind of information is the percolation threshold of the solid phase, which is defined as the time at which solid starts to be interconnected from one side to another [7]. A second way to characterize the connectivity of the solid phase is by describing the degree of the inter-particle bonding. The contact area between the solid particles is an alternative way to characterize the connectivity of the solid phase [11]. If a cluster of connected solid particles is considered as shown in Fig. 3, the contact area for this cluster is the sum of the areas that establish the connection between the individual particles. HYMOSTRUC3D computes the specific contact area of the hydrated cement particles, which is defined as the contact area per unit volume of cement paste at a given age.

3.3 *Calibration of the model*

When a specific condition was used, some experimental calibrations have been performed in order to validate the simulations. The particle size distribution, the degree of hydration and the capillary

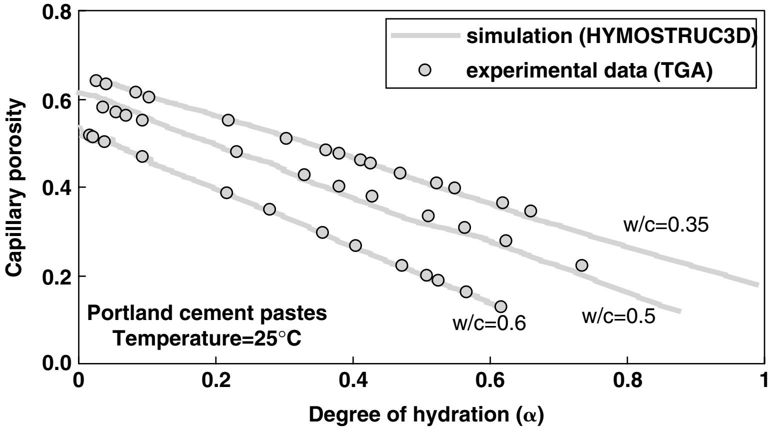

Figure 4. Calibration for degree of hydration and capillary porosity.

porosity are three of the most important parameters that need to be calibrated. The degree of hydration calculated by HYMOSTRUC3D was compared to the TGA experimental results. The parameters that determine the kinetics of the cement hydration used in the simulation were adjusted until the errors between simulated and experimental results were within an acceptable region. Similar to the degree of hydration, the capillary porosity was also determined during the simulation. The correlations between capillary porosity and degree of hydration were plotted in Fig. 4. It is shown that the HYMOSTRUC3D simulation results matches well with the experimental data.

4 RESULTS AND DISCUSSION

4.1 *Reflection loss (R_L), degree of hydration (α) and capillary porosity (P_c)*

The relationship between the reflection loss of the three tested cement pastes and the degree of hydration is given in Fig. 5. The degree of hydration was determined from the amount of the non-evaporable water measured by TGA described in the previous section of this paper. It can be seen from the figure that for each paste mixture, the relationship between the reflection loss and the degree of hydration shows a strong linear trend over the plotted time period. By comparing the relationships for the different water/cement-ratios, it is obvious that the slope of the regression line changes. The difference in the slopes of the regression lines indicates that the reflection loss is not only a function of the progress in hydration but also a measure of microstructural properties that are influenced by the water/cement-ratio.

In the previous research [12], the correlation of reflection loss and the capillary porosity of the Portland cement pastes was established. There is a linear relationship between the reflection loss and the simulated capillary porosity. A decrease of the capillary porosity due to hydration is followed by a steep increase of the reflection loss. To the three tested pastes, the changing rate of reflection loss with respect to the decrease of capillary porosity is independent of the water/cement-ratio. The relationship between the reflection loss and the relative decrease of the capillary porosity of the cement pastes with different water/cement-ratios is shown in Fig. 6, where P_{c0} is defined as volume fraction of the total pore phase at original state.

4.2 *Reflection loss (R_L) and volume fractions of the solid phase*

Based on the microstructural simulation of each mixture, the fraction of total solid phase (Ts) and the fraction of connected solid phase (Cs) were calculated. The percolation thresholds (t_p) and the reflection loss at this point are listed in Table 2.

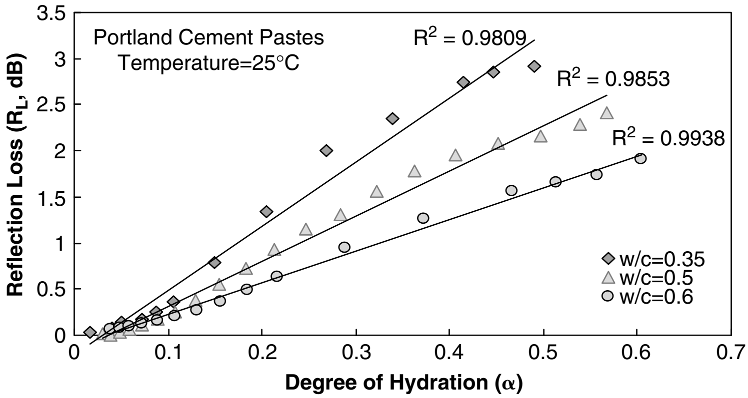

Figure 5. Correlation of reflection loss and degree of hydration.

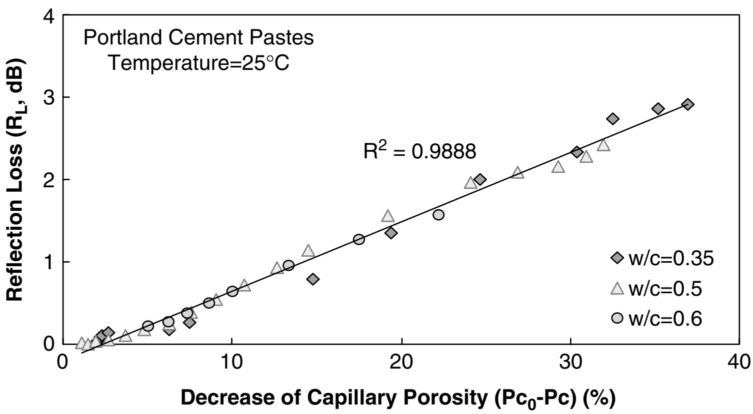

Figure 6. Correlation of reflection loss and decrease of capillary porosity.

Table 2. Critical points in the evolution of solid phase and reflection loss.

w/c ratio	t_p (hr)	t_e (hr)	$R_L(t_p)$ (dB)	$R_L(t_e)$ (dB)
0.35	1.90	37.15	0.040	2.930
0.5	3.58	41.80	0.038	2.200
0.6	5.16	52.00	0.042	1.703

The development of the reflection loss and the evolution of the solid phase for cement paste with water/cement-ratio equals to 0.6 is plotted in Fig. 7 as an example. The reflection losses at the percolation threshold of the solid phase (t_p) and the time when the solid particles are almost connected with each other (t_e) are plotted as solid dots in the figure. The solid dot on the reflection loss curve at the percolation threshold of the solid phase can be considered as Point A in Fig. 2. It indicates not only the change of physical status of the cement paste, but the connectivity of the solid phase as well. The other solid dot which is marked at the time when the time derivative of the ratio between the volume fractions of the connected and the total solid equals to 0.05% can be considered as Point B in Fig. 2, which indicates the stage changes of the reflection loss development.

From Table 2, it can be seen that values of the reflection loss at the percolation thresholds of the solid phase for the three pastes are quite similar. The mean value of the reflection losses at this

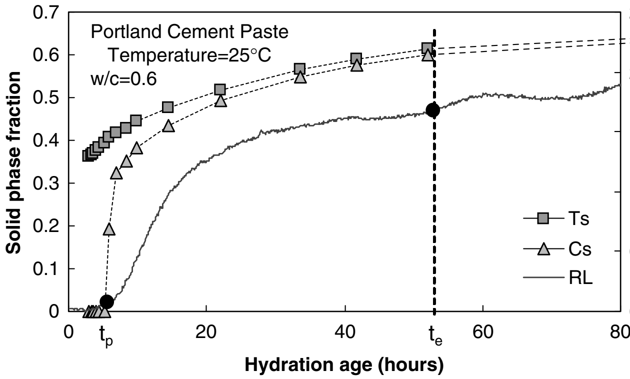

Figure 7. Correlation of reflection loss and solid volume fractions.

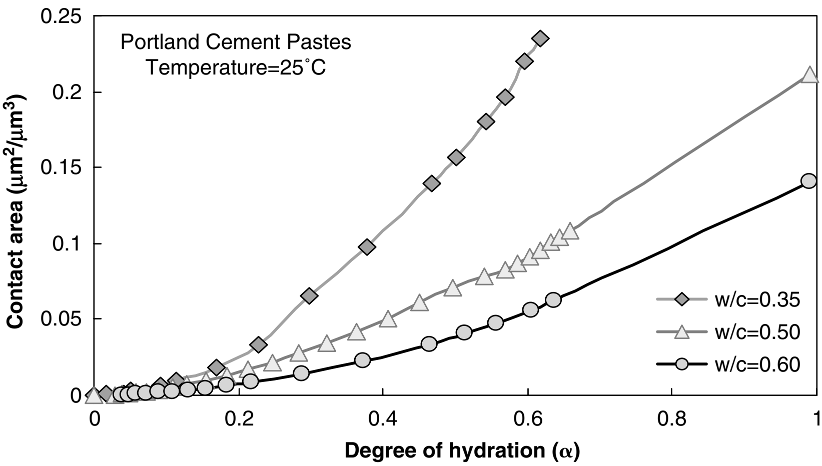

Figure 8. Correlation of specific contact area and degree of hydration.

critical point is 0.040 dB with a standard deviation of 0.0016 dB. It is reasonable to define a specific reflection loss value within a certain probability to indicate the occurrence of the percolation of the solid phase in the microstructure of the cement pastes, where the water/cement-ratio can be ignored.

4.3 *Reflection loss and contact area of solid phase*

Besides the volumetric parameters, the reflection loss can also be explained based on the percolation of the solid phase in the microstructure of the cement paste.

In order to investigate the relationship between the reflection loss and the inter-particle bonding in the microstructure, correlation of the reflection loss and contact area of solid phase is observed. As mentioned before, contact area is a microstructural parameter which can be calculated by HYMOSTRUC3D. Although the contact area is a not a measurable quantity, it provides us with an approach to quantify the intensity of the connection among the solid particles in the microstructure. The relationship between the specific contact area and the degree of hydration for different cement pastes can be described as shown in Fig. 8. For any given degree of hydration, the specific contact area is larger for the paste with smaller water/cement-ratio. This can be attributed to the volume difference of the cement contained in the pastes. For a given level of hydration, the changing

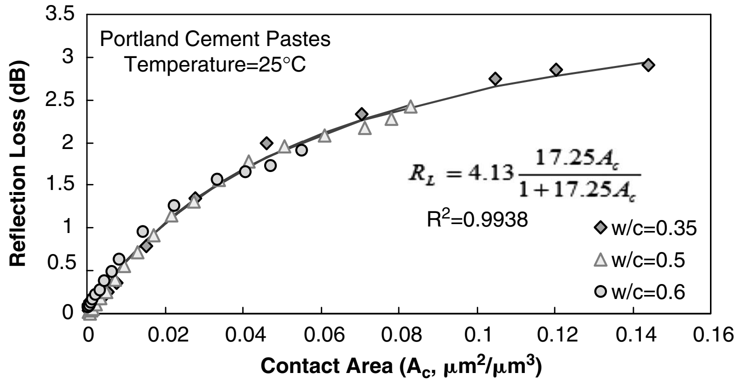

Figure 9. Correlation of reflection loss and specific contact area.

rate of the specific contact area with respect to the degree of hydration is higher for the paste with lower water/cement-ratio. For a given water/cement-ratio, the changing rate of the specific contact area with respect to the degree of hydration increases with the higher level of hydration.

Fig. 9 shows the correlation of the reflection loss and the specific contact area. It is obvious that there is a unique relationship between the reflection loss and the contact area of all the three tested cement pastes. The trend line can be described by a hyperbolic function with the values of reflection loss converging to an asymptotic value. This unique relationship compromises very well with the relationship between the reflection loss and the degree of hydration (Fig. 5) and the relationship between the contact area and the degree of hydration (Fig. 8). Based on these observations, it can be concluded that the ultrasonic wave reflection method is not only sensitive to the volume of the connected solid particles as concluded in the previous sections, it can also be directly related to the intensity of inter-particle bonding (connectivity) of the solid phase in the microstructure of cementitious materials.

5 CONCLUSIONS

From the investigations described in this paper, the following conclusions can be drawn:

(1) The reflection loss measured on Portland cement pastes with different water/cement-ratios is linearly related to the degree of hydration of the tested pastes. This relationship is valid for the pastes at early ages up to 96 hours.

(2) The changing rate of reflection loss with respect to the decrease of capillary porosity is independent of water/cement ratio.

(3) The reflection loss of the cement paste was found to be related to the development of the volume fraction of the total and connected solid phase of the cement paste obtained from the numerical simulation. It is reasonable to define a specific value of reflection loss within a certain interval of probability to indicate the occurrence of the percolation threshold of the solid phase regardless of water/cement-ratio.

(4) The specific contact area as a parameter describing the degree of the inter-particle bonding of the cement particles was found to be uniquely related to the reflection loss measurements of the cement pastes regardless of the water/cement-ratio. A hyperbolic relationship between the reflection loss and the contact area can be established.

(5) The ultrasonic wave reflection technique can be used to monitor the evolution of the microstructures of the cementitious materials during hydration. The correlations of the reflection loss and volumetric and specific microstructural parameters shows that the ultrasonic wave reflection technique measures intrinsic properties of the materials based on the microstructural evolution.

ACKNOWLEDGEMENTS

The research presented in this paper was funded by the Institute of Technology and Infrastructure of Northwestern University and the Center for Advanced Cement-Based Materials. Their financial support is gratefully acknowledged.

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