

EARLY AGE PROPERTIES OF PORTLAND CEMENT PASTES INVESTIGATED WITH ULTRASONIC SHEAR WAVES AND NUMERICAL SIMULATION

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Abstract

In this paper, the correlation of reflection loss measured by an ultrasonic shear wave reflection method and the microstructure in cement-based material is investigated. Three cement pastes (Portland cement type I) with different water-cement ratios (0.35, 0.50 and 0.60) cured at 25 °C were examined. The ultrasonic shear wave reflection factor (WRF) was measured by the wave reflection technique. Reflection loss was calculated based on WRF measurement. Initial and final setting time were obtained by Vicat Needle tests. Thermogravimetric tests were conducted to observe the hydration process of cement pastes. To obtain the evolution of the microstructure in cement pastes, a numerical cement hydration model, HYMOSTRUC3D, was applied. Correlations between the microstructural evolution (e.g. growing of solid phases, percolation threshold of solid phases, and capillary porosity) calculated by HYMOSTRUC3D model and the reflection loss have been established. From this study, it was found that the WRF behavior is closely related to the microstructural evolution, such as, the total solid phase volume, the connectivity of solid phase and the pore structure. The study shows that, the wave reflection technique, as a non-destructive testing method, can be used to monitor the microstructural evolution of cementitious materials at early ages.

1. Introduction

A number of failures of large concrete structures^[1,2] during construction have been reported in the last decades. One of the reasons for the failures was overestimating strength of concrete at early age, so that forms were removed unsafely and the partially matured concrete was not strong enough to support upper levels of the structure. From these failure examples, we can learn that having reliable information about early age properties of the material is essential to guarantee life-time performance of structures. A good in-situ testing method, which can monitor intrinsic early age properties of cementitious materials, is urgently needed.

Most widely used methods to test early age properties of structural materials are nondestructive testing (NDT) methods, which can provide some information about the material properties without destroying the structure. A popular method used nowadays is the maturity method^[3]. Maturity of cement hydration is defined as a function of time and curing condition. This method can be used to predict strength development by correlating strength and maturity. A disadvantage of this method is, however, that a continuous reading of temperature is

required. Ultrasonic pulse velocity method^[4-6] is another NDT method which is widely used in the field of cementitious materials. By accessing both sides of the specimen, ultrasonic waves are transmitted from one side to the other. Wave velocity can be calculated according to wave travel time. The elastic moduli and strength are related to the wave velocity. A large amount of experimental work was conducted in the research laboratories. Empirical formulae between ultrasonic wave velocity and strength were established^[6].

A new ultrasonic technique, called wave reflection method, was introduced by McSkimin et al^[7-8] 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 Stepišnik et al in 1981^[9]. This one-sided nondestructive ultrasonic technique was used to monitor the stiffening process of Portland cement concrete^[10], and it was proved to be an efficient method to describe setting and hardening behavior of not only plain concrete, but concrete with chemical admixture as well^[11, 29]. Since then, more work has been done in this area. During the extended research, it was found that development of wave reflection factor (WRF) has a good correlation to in-situ compressive strength evolution of cement-based materials at early age^[12]. Further investigations have shown that evolution of reflection loss measured by the ultrasonic wave reflection technique has a strong bi-linear relationship to strength development^[13-15]. A procedure for strength prediction based on measured reflection loss has been established.

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

The development of 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^[16-18], which is a continuum model, provides us with an opportunity to study the microstructural evolution of cement-based materials. In this model, the hydration progresses in cementitious materials are mimicked based on hydration stoichiometry in the model. Hydrated and unhydrated cement particles are considered as solid phases. The microstructural parameters including pore distribution, volume fraction and the connectivity of solid phases and pore phases can be simulated by the model.

In this paper, the experimental work on WRF was conducted. In addition, the connectivity of solid phases was applied by using HYMOSTRUC3D. Connectivity of solid phases was examined. Correlation of connectivity of solid phases and WRF development were studied in detail, since solid phases are believed to be the major part as far as wave propagation is concerned.

2. Materials and Methods

2.1 Materials

Ordinary Type I Portland cement provided by Lafarge was used for all experiments. The chemical compositions are listed in Table 1. The Blaine surface area is 365m²/kg.

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

Chemical Data	SiO ₂	CaO	Al ₂ O ₃	Fe ₂ O ₃	C ₃ S	C ₃ A
Percent	20.4	65.3	4.8	2.8	68	8

Plain cement pastes with water-cement ratio: 0.35, 0.5 and 0.6 were tested. The specification of ASTM standard C305 [20] 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 WRF Test

The wave reflection factor was calculated by the information obtained from ultrasonic wave reflection tests. The apparatus used for this test is shown in Figure 1. A steel plate with a thickness of 0.5 inch was used as a buffer material. Two transducers with 2.25MHz central frequency were coupled to the steel plate. The transducers were connected to pulsers, which in turn were connected to a personal computer. The data collection was controlled by a computer program.

According to the theory of wave reflection [19], when an ultrasonic wave traveling through a medium hits the boundary between two materials with different acoustic properties, it is partially reflected back and partially transmitted into the medium on the other side of the boundary. The reflection and transmission of wave energy at the interface of two media are functions of the densities of the media and the velocities of the wave that travels through the media. For normal incidence of shear wave, the reflection coefficient can be defined as:

$$WRF = \frac{A_r}{A_i} = \frac{\rho_2 v_2 - \rho_1 v_1}{\rho_2 v_2 + \rho_1 v_1} \quad (1)$$

where WRF is the wave reflection factor between material 1 and 2, it is defined as the amplitude ratio between reflected wave and incident wave, which can be obtained directly from experimental measurement. WRF is also a function of relative mechanical properties of buffer material and tested material as reflected in the second part of equation (1). Here, ρ_1 and ρ_2 are the mass densities of material 1 and 2; v_1 and v_2 are the wave velocities in material 1 and 2, respectively. Since ultrasonic amplitude ratios are usually measured in decibel, 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.

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

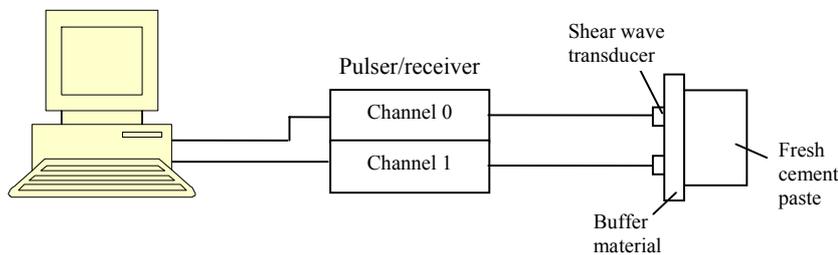


Figure 1. Experimental apparatus for wave reflection measurements

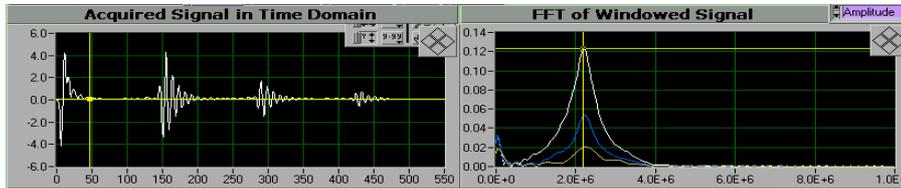


Figure 2. Reflected echoes in time domain and transformed frequency domain

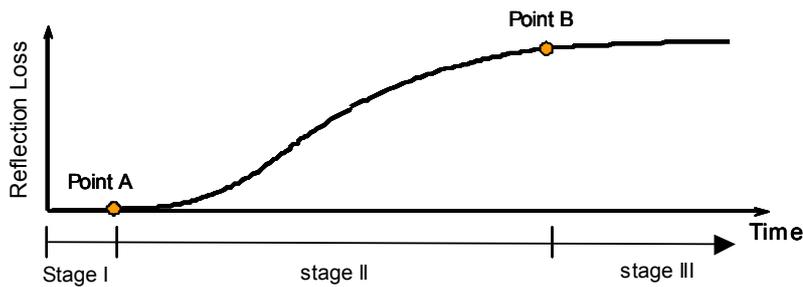


Figure 3. Development of reflection loss of cement paste

Time-signals of ultrasonic shear waves were captured by the computer setup during the tests. To calculate reflection loss, ultrasonic signals in time domain need to be translated into frequency domain by a Fast Fourier Transform (FFT) algorithm. Figure 2 shows the first, second and third wave echoes reflected from the interface of steel plate and cement pastes in time domain and transformed into frequency domain.

A typical curve of reflection loss can be divided into three phases as shown in Figure 3. During stage I, the paste can be considered as cement particles suspend 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 solid phases, which can support shear waves increases rapidly. So reflection loss increases greatly during stage II. When solid phases reach a certain value, its rate of increase slows down. This is reflected by a small increase of reflection loss in stage III.

Although turning points (A&B) between stage I and II, stage II and III were found in previous research [10, 11, 15], these points were not well defined. In this paper, correlations between reflection loss development and microstructural evolution are established and presented.

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. Low Angle Laser Light Scattering (LALLS) method [30] 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 . Volume weighted mean value of particle diameter is 18.5 μm .

2.4 Setting Time Test

Initial and final setting time were determined through Vicat needle tests as specified by ASTM Standard C191-99[21]. Needle settlements were read every 10 minutes. The mean values of readings from three batches were used to define the initial and final setting time of each plain paste mixture.

2.5 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 [24, 25]. The Powers-Brownyard model was applied. 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 [22]. 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 [32] of the cement. Typical value for $w_n/c_{complete}$ is somewhere between 0.23 and 0.25.

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

3. Microstructure Simulation

The hydration of cementitious materials is a complex process. Although hydration is a chemical process, the changes that happens in the structure is reflected by the changing of physical status of the material. Knowing what happens inside the material during hydration can help to understand material behavior better.

In this study, the HYMOSTRUC3D [16, 17, 26] model was used to simulate the development of microstructure in cement pastes. With this simulation model, the rate of cement hydration was modeled as a 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. In this model, the hydration products are considered as solid phases. The capillary pores are considered as the space between the hydration products. The development of the microstructure of cement paste during its hydration are shown in Figure 4 for a sample with $w/c=0.6$.

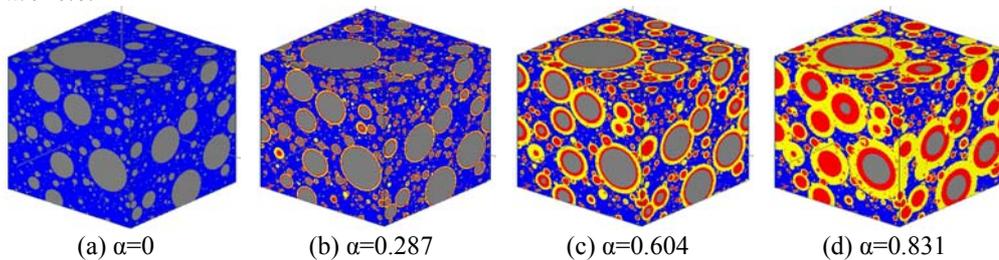
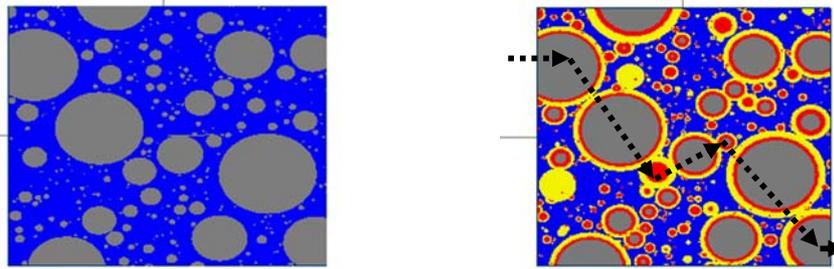


Figure 4. Growing of solid phases at different degree of hydration ($w/c=0.6$)



(a) initial status: solid particles suspended in water (b) solid phase is percolated
 Figure 5. Percolation of solid phase during hydration

In HYMOSTRUC3D [26], a serial section algorithm and an overlap criterion was used to access the phases fraction and the connectivity of the phases. The percolation phenomena of solid phases or pore phases can be obtained from this algorithm. A 3D simulated structure with 0.25 μm spacing and 400 serial sections was employed in this calculation. 2D section images are shown in Figure 5 for convenience of description. The critical degree of hydration, when the solid phases become percolated from unpercolated is considered as the percolation threshold [22, 26-28, 31].

When a specific condition was used, some experimental calibrations have been performed in order to check the simulations. The particle size distribution, the degree of hydration and the capillary porosity are three most important parameters that need to be calibrated. Values of model parameters that determine the kinetics of cement hydration [16] are modified until errors between simulated and experimental results are within acceptable region. The calibration results compared with the experimental results are shown in Figure 6, 7 and 8.

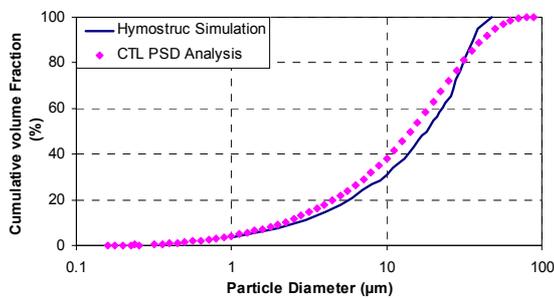


Figure 6. Particle Size Distribution (simulation and experiments)

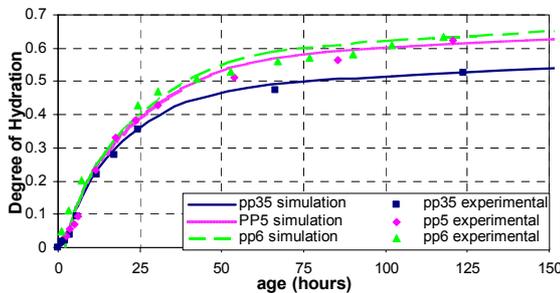


Figure 7. Development of degree of hydration (simulation and experiments)

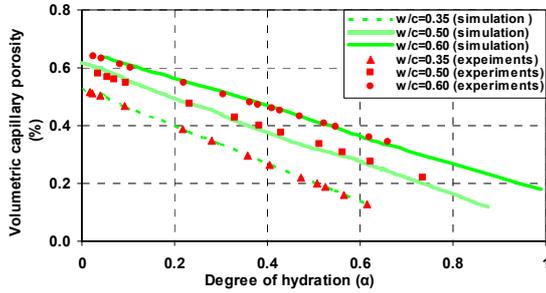


Figure 8. Capillary porosity (simulation and experiments)

4. Results and Discussion

4.1 Repeatability and Sensitivity of Reflection Loss Measurement

To be used as an efficient testing method, the repeatability requirement must be satisfied. To test the repeatability of wave reflection method, three batches of cement pastes with $w/c=0.6$ were tested. Curing conditions were strictly controlled to be the same during the wave reflection measurements. Reflection loss development curves are shown in Figure 9. Repeatability was found to be related to homogeneity of the material^[15]. Since cement paste is a relatively homogeneous material, the repeatability of wave reflection measurement is satisfactory.

Sensitivity of wave reflection measurements is shown in Figure 10. The reflection loss of the three pastes were measured up to 96 hours after sampling. It is obvious that each curve in the figure can be divided into three phases according to section 2.2. Only a part of the wave energy was reflected back at the interface of the steel plate and the cement pastes during the hardening process. The rest of the energy was dissipated in the cement pastes. At any given hydration age t , the reflection loss increases with the decrease of the water-cement ratio ($R_{L0.35}(t) > R_{L0.5}(t) > R_{L0.6}(t)$).

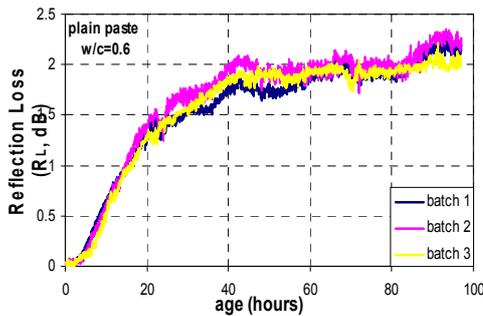


Figure 9. Repeatability of reflection loss measurement

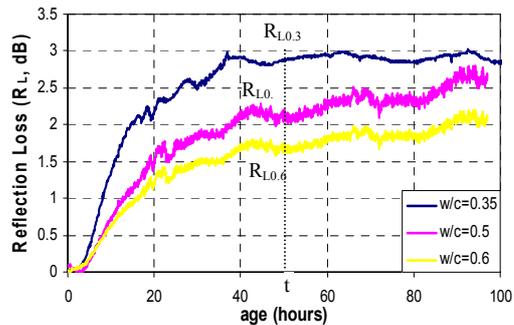


Figure 10. Sensitivity of reflection loss measurement

Table 2. Setting time and Reflection loss at the setting time

w/c ratio	t_i (hr)	t_f (hr)	$R_L(t_i)$ (dB)	$R_L(t_f)$ (dB)
0.35	3.40	5.60	0.131	0.595
0.5	4.75	7.05	0.140	0.490
0.6	6.25	9.0	0.115	0.312

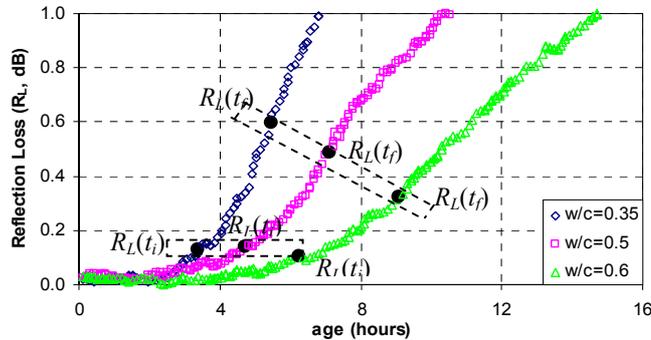


Figure 11. Correlation of reflection loss and setting time

4.2 Reflection Loss (R_L) and Setting Time (t_i , t_f)

Initial and final setting time can be considered as two critical points during cement hydration. The setting time describes the change of the physical condition of the material during the hardening procedure. It relates to not only the rate of chemical reaction inside the material, but to the load carrying capacity as well. In the previous research, the development of the reflection loss was related to temperature development or rate of heat evolution inside the material [10-11, 13-15]. It was found that turning point A on the reflection loss development curve is close to the ending point of the dormant period on heat evolution curve. Here, reflection loss is directly correlated to initial and final setting time measured by Vicat needle tests. Valič et al [29] did a similar study before. They measured cement pastes with a water-cement ratio changing from 0.25-0.35, which is a relatively small range. Both the initial and the final setting time for the pastes were found to appear at the same level of reflection loss with different water-cement ratio.

In this study, the initial and final setting time (t_i , t_f) and the appropriate values of reflection loss $R_L(t_i)$, $R_L(t_f)$ of three plain pastes with water-cement ratios equal to 0.35, 0.5 and 0.6 are listed in Table 2. Cement paste with $w/c=0.35$ has the earliest initial and final setting time.

Reflection loss development for the first 16 hours of these three pastes under same curing condition is plotted in Figure 11. The reflection loss curve has a flat part followed by a steeply increasing part. The cement paste with $w/c=0.35$ has the biggest slope at the increasing part, while reflection loss of paste with $w/c=0.6$ increases slower than the other two pastes. Initial and final setting time are plotted as solid dots on the reflection loss curves. It is obvious that at the time of initial setting, all three pastes have a very similar value of reflection loss. The mean value of reflection loss at initial setting time of these three pastes is 0.129 dB with a standard deviation value of 0.01 dB. Depending on this result, a specific value within a certain region of reflection loss can be used to define initial setting time.

Values of reflection loss at final setting time of the three pastes do not appear at the same level. The paste with $w/c=0.6$ has the smallest reflection loss at its final setting time. This result is different from what Valič [29] found as mentioned before. From Figure 11, it is obvious that the slopes of the steeply increasing part of reflection loss show a big difference. Reflection loss increases much faster for the paste with $w/c=0.35$ than the paste with $w/c=0.6$. The difference between initial and final setting time is around 2~3 hours, which is similar for the three pastes. The similar time difference between setting time and the big difference of increasing rate of reflection loss makes that the reflection loss at final setting time for these three pastes falls on

different levels. The reflection loss at final setting time decreases with increase of water-cement ratio.

4.3 Reflection Loss (R_L) and Evolution of Solid Phase in Microstructure

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. Percolation thresholds (t_p) and the reflection loss at this point are listed in Table 3. Because there are more solid particles in the cement paste with lower water-cement ratio, the percolation threshold of solid phase appears much earlier for the paste with $w/c=0.35$ than the paste with $w/c=0.6$.

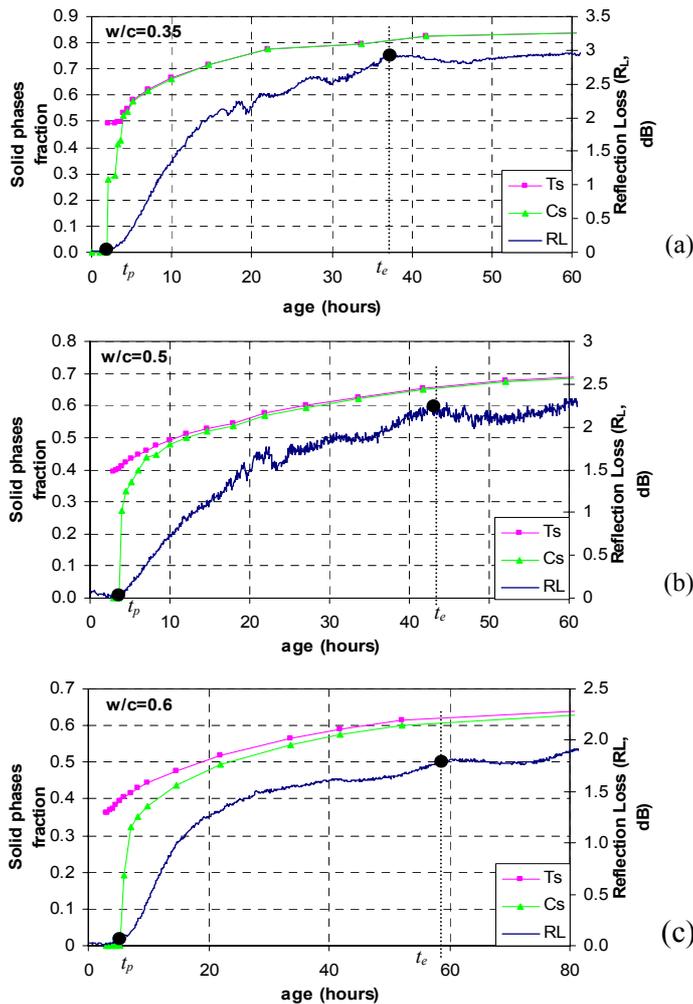


Figure 12. Correlation of reflection loss and evolution of solid phase

Table 3. 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	0.035	2.200
0.6	5.16	52.00	0.042	1.703

The development of reflection loss and evolution of the solid phase for each cement paste are plotted in Figure 12. The reflection losses at the percolation threshold of the solid phases and the time when the solid particles are almost connected with each other (t_e) are plotted as solid dots in the figure. The percolation thresholds appear earlier than initial setting time for all three cement pastes. The solid dot on the reflection loss curve at the percolation threshold of the solid phase can be considered as Point A in Figure 3. 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 most of solid phase is connected can be considered as Point B in Figure 3, which indicates the stage changes of reflection loss development. It is obvious that the development of reflection loss follows the evolution of the connectivity of solid phases. This phenomenon is quite similar to the evolution of longitudinal pulse velocity in cementitious materials^[18].

From Table 3, it can be seen that values of the reflection loss at the percolation thresholds of the solid phase are quite similar. The mean value of the reflection losses at this critical point is 0.039 dB with a standard deviation of 0.0029 dB. It is reasonable to define a specific reflection loss value within a certain probability to indicate the occurrence of percolation of solid phase in the microstructure of cement pastes, where water-cement ratio can be ignored.

4.4 Reflection Loss (R_L) and Degree of Hydration (α)

The degree of hydration is an essential parameter which controls properties of cementitious materials. Knowing the degree of hydration can help to estimate the strength and elastic moduli of the material. It directly relates to microstructural evolution, such as fraction of solid phase and capillary porosity. Since reflection loss reflects evolution of solid phase in cement paste, it should be possible to correlate the reflection loss development and the degree of hydration of the material. Figure 13 shows that there is a strong linear relation between reflection loss and degree of hydration.

The relationship between reflection loss and degree of hydration is not unique. By comparing pastes with different water-cement ratio, it can be seen that the slope of the linear regression lines changes with water-cement ratio. The paste with the lowest water-cement ratio has the biggest slope, while a high water-cement ratio corresponds to a low slope. This difference is due to the different microstructure in the cement pastes. At the same degree of hydration, the cement paste with $w/c=0.35$ has much more solid phase than the paste with higher water-cement ratio. Since solid phase is the dominant factor in wave propagation, larger amount of solid phase in microstructure corresponds to higher reflection loss.

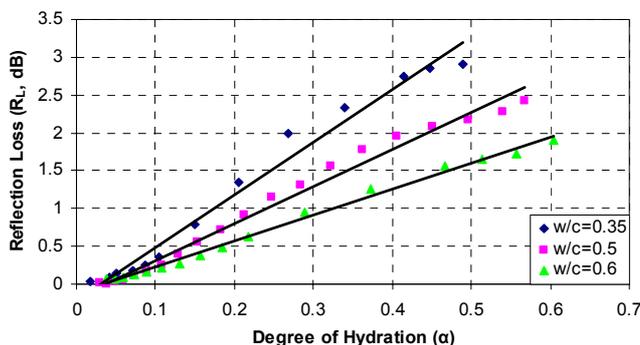


Figure 13. Correlation of reflection loss and degree of hydration

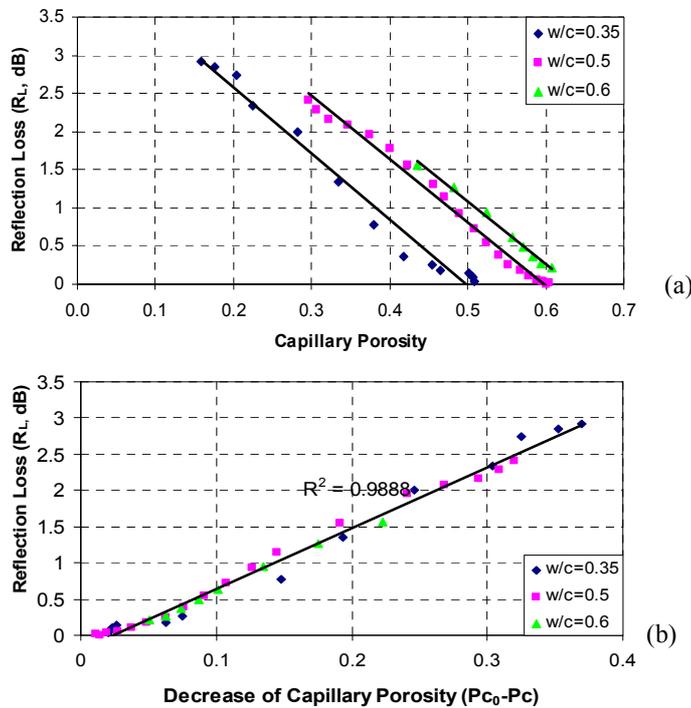


Figure 14. Correlation of reflection loss and capillary porosity

4.5 Reflection Loss (R_L) and Pore Phase

Although reflection loss and degree of hydration has a very good linear relation, there is no unique relation between reflection loss and the degree of hydration. As discussed in the previous section, the water-cement ratio should be considered as another factor, which affects reflection loss behavior. Higher water-cement ratio means lower solid content at a given level of degree of hydration. The inverse side of the solid phases is the pore phase in the structure of hydrated cementitious materials. Correlation of reflection loss and capillary porosity, which is a very important microstructural parameter, deserves exploring. Figure 14 shows the correlation of reflection loss measured by wave reflection tests and capillary porosity (P_c) calculated by HYMOSTRUC3D. A linear relation has been found. In Figure 14(a), the slopes of three regression lines are very similar. At the same time, total volume fraction of pore phase at initial stage (P_{c0}) of the cement pastes were calculated. Decrease of capillary porosity is defined as the difference between the volume fraction of pore phase at initial stage (P_{c0}) and the capillary porosity at a give degree of hydration. A unique linear relationship between reflection loss and decrease of capillary porosity was found as shown in Figure (b), which means changing rate of reflection loss with respect to decrease of capillary porosity is independent of water-cement ratio.

5. Conclusions

1. Reflection loss, calculated from wave reflection measurements can monitor the evolution of microstructural properties of cementitious materials. The reflection loss development is highly sensitive to the setting and hardening procedure of cement paste. It is reasonable to define a specific value of reflection loss within a certain interval of probability to indicate the occurrence of the initial setting regardless of water-cement ratio.

2. Final setting time of Portland cement pastes can not be defined by using a specific value of reflection loss. Water-cement ratio should be considered as another factor which affects the final setting time.
3. From the microstructural point of view, reflection loss development is governed by evolution of solid phase. Turning points on reflection loss curve can be correlated to percolation threshold of solid phase and the time when most of the solid particles are connected to each other. 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 reflection loss has a linear relationship to degree of hydration at early age. The slope of the linear trend is affected by water-cement ratio.
5. There is a linear relation between reflection loss development and evolution of capillary porosity. The relation is not unique and depends on water-cement ratio. The rate of reflection loss with respect to the decrease of capillary porosity, however, is independent of water-cement ratio.

6. Acknowledgement

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