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Experimental study and numerical simulation on the formation of microstructure in cementitious materials at early age

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Abstract

The formation of microstructure in early age cement paste and concrete was examined with an ultrasonic experimental set-up. Research parameters included the influence of curing temperature (isothermal curing at 20, 30 and 40 °C), water/cement ratio (0.40, 0.45 and 0.55) and amount of aggregate. In parallel with the experiments, the cement hydration model HYMOSTRUC was utilized to simulate the formation of the microstructure. In this study, the cement paste was considered as a four-phase system consisting of water, unhydrated cement, hydration products and that part of the hydration product that causes the contact between the hydrating cement grains (so called "bridge volume"). A correlation has been found between the growth of bridge volume calculated with the model and the changes in the pulse velocity. It is believed that ultrasonic pulse velocity (UPV) measurements can represent a valuable tool to investigate the development of the microstructure at early age.

Keywords: Cement; Hydration products; Microstructure; Modeling

1. Introduction

Knowledge of the microstructural evolution of cementitious materials at early age is essential for forecasting their performance. Therefore, experimental studies and numerical simulations become increasingly important to understand the formation of the microstructure. Despite the huge amount of literature devoted to various experimental techniques to measure the early-age behavior of cementitious material, applying and modelling these techniques is still not easy. For example, the application of scanning electron microscopy image and small angle X-ray scattering is limited by the complicated preparation of the samples [1,2]. The interpretation of mercury intrusion porosimetry measurements generates confusion [3]. Recently, one of the nondestructive techniques, i.e., ultrasonic pulse velocity (UPV) measurements, has attracted increasing attention for monitoring the early-age behavior of cementitious materials [4–8]. The UPV technique is often used to establish the uniformity of concrete and to estimate its in-situ strength. The advantages of the use of this technique include its accuracy, easy test procedure and nondestructive characteristics.

However, the use of ultrasonic pulse technique has also a great potential for a quantitative description of the development of microstructure in early-age concrete. The limitation of previous studies on the ultrasonic pulse technique is due to the lack of suitable computer-based cement hydration models, which can simulate the development of the microstructure. In the cement hydration model HYMOSTRUC [9], the growth of the contact area between hydrates is interpreted as the bridge volume. The bridge volume concept is convenient for use in monitoring hydration kinetics. This has been proven by UPV measurements and will be discussed in this paper.

In this paper, the experimental and theoretical basis of the relationship between the UPV and the growth of the bridge volume during cement hydration are examined. The purpose of this research is trying to find: (1) What is the correlation between UPV and the microstructure formation? (2) How is this correlation affected by the water/cement ratio and curing temperature? (3) How do

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the answers to these questions help us improve the use of ultrasonic technique to monitor cement hydration kinetics and microstructure evolution? It will be shown that UPV measurements can represent a valuable tool to investigate the development of the microstructure at early age.

2. Materials and methods

A block diagram of the experimental set-up is shown in Fig. 1. The ultrasonic transducers and temperature probe are mounted in a $150 \times 150 \times 200$ mm^3 steel mould. The measurements of the compressional wave velocities follow essentially the procedure described in Ref. [10]. The main advantage of this set-up is that the transducers can be directly contacted with the specimen through a piece of plastic membrane to avoid the attenuation of the wall of the steel mould. The temperature of the whole system is controlled by a cooling system with an accuracy of $\Delta T = 0.1$ °C. All control units are connected to an industrial computer. The data are automatically stored in the computer for later analysis.

The compressional wave velocity is calculated from the ratio of the length of the specimen to the time taken for a wave pulse to traverse the specimen.

A series of experiments was performed. Table 1 contains the main data of the tested specimens, including the imposed curing temperature (isothermal curing at 20, 30 and 40 °C), water/cement ratio (0.40, 0.45 and 0.55) and amount of aggregate. Measurements started 15 min after mixing. No special treatment was imposed to remove the extra air bubbles from the specimens except vibration. The compressive strength tests on cubes $150 \times 150 \times 150$ mm^3 are performed at an age of 1, 3 and 7 days, respectively.

3. Results and discussions

3.1. Effect of curing temperature and water/cement ratio on UPV

The effect of the water/cement ratio on the ultrasonic properties was examined for mixtures with water/cement ratio of 0.4, 0.45 and 0.55. Results are shown in Fig. 2. It is evident that for the same curing temperature, mixtures with a higher water/cement ratio show lower values of the pulse velocity. This effect can be explained by the difference in the amount of solid phases in pastes with different water/cement ratio.

The influence of curing temperature on the UPVs determined for the cement paste is plotted in Fig. 3a for the first 24 h and Fig. 3b for the first 3 days. Fig. 4a shows the effect of curing temperature on the UPV of concrete in the first 24 h and Fig. 4b for 7 days.

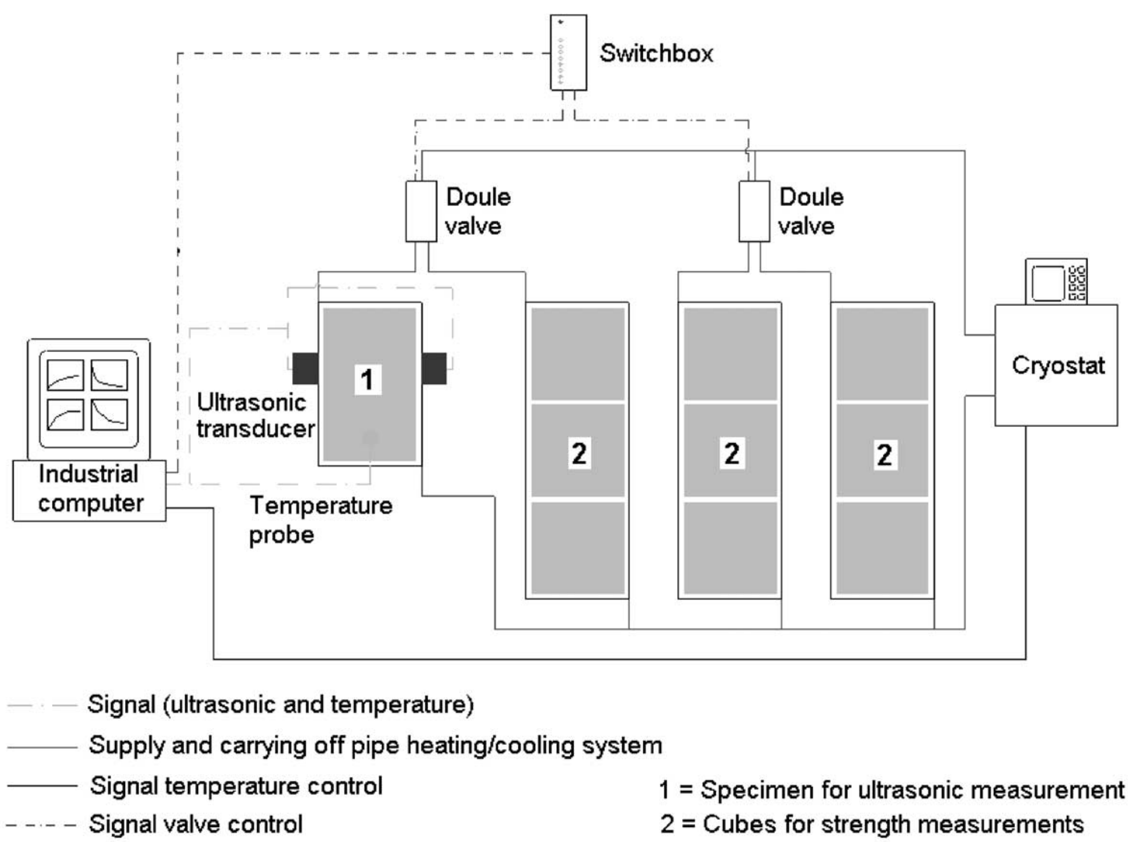

Fig. 1. Experimental set-up for monitoring UPV in young concrete.

Table 1
Mix proportions

Specimen no.		Cement type	Cement content (kg/m^3)	Aggregate content (kg/m^3)	w/c [-]	Temperature (°C)	Curing age (days)
Concrete	PCA16350-40	CEM I/32.5	350	1942	0.40	20, 30,40	7
	PCA16350-45	CEM I/32.5	350	1884	0.45	20, 30,40	7
	PCA16350-55	CEM I/32.5	350	1792	0.55	20, 30,40	7
Cement paste	PCP-40	CEM I/32.5			0.40	20, 30,40	3
	PCP-45	CEM I/32.5			0.45	20, 30,40	3
	PCP-55	CEM I/32.5			0.55	20, 30,40	3

Based on the analysis of the experimental results, three characteristic stages in the evolution of the UPV can be distinguished (Fig. 5).

Stage I goes from a suspension system to the solid phase percolation threshold. In this early age, a relatively low value of the UPV was observed for both the cement paste and the concrete mixture. These values were smaller than the UPV in water (1430 m/s) and even smaller than in air (340 m/s). According to Keating and Hannant [6] and Sayer and Dahlin [7], this phenomenon is caused by air entrapped in the paste. In general, there are two reasons, which cause the existence of air bubbles in fresh mixture. First, there is a certain amount of air bubbles in the mixing water. Secondly, a huge number of tiny air bubbles is entrapped into the paste during mixing. During this first period, hydrates are formed in a very low amount. It is believed that in this period the entrapped air bubbles play a dominant role for the evolution of the UPV. Although removal of entrapped air bubbles can be done in laboratory, we will always face this problem in concrete construction practice. According to Povey's experimental results [12], the influence of entrapped air bubble in a fresh mixture can be taken into account in a model. In Fig. 6, it is clear that a very small amount of undissolved air causes a strong reflection and attenuates the sound wave velocity in a water/air system. Once the volume fraction of entrapped air bubbles is determined in fresh mixtures, the influence of the entrapped air bubbles on the UPV can be deduced from Fig. 6.

At a certain time, a solid percolation path is formed in the hydrating paste. The UPV then propagates through the solid

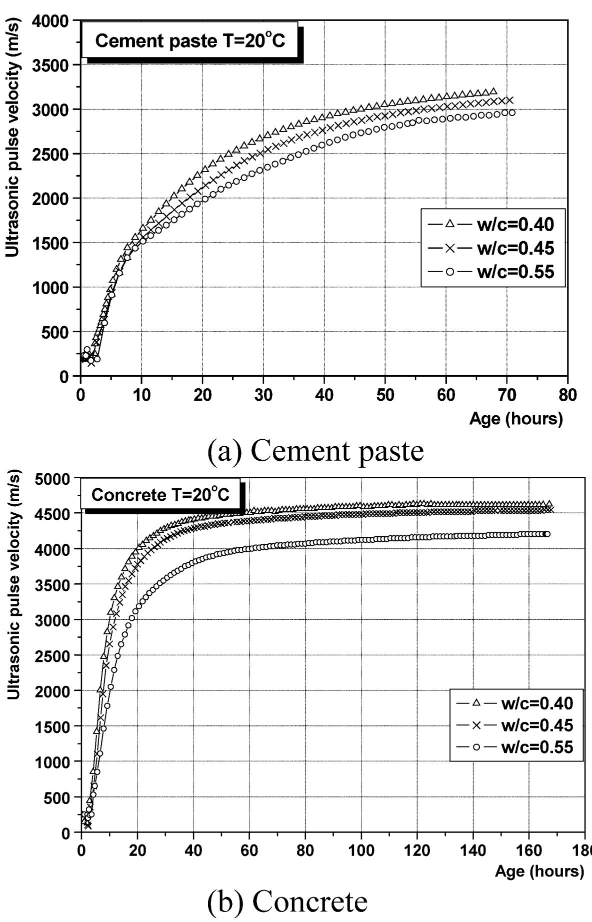

Fig. 2. Influence of the water/cement ratio on the UPV.

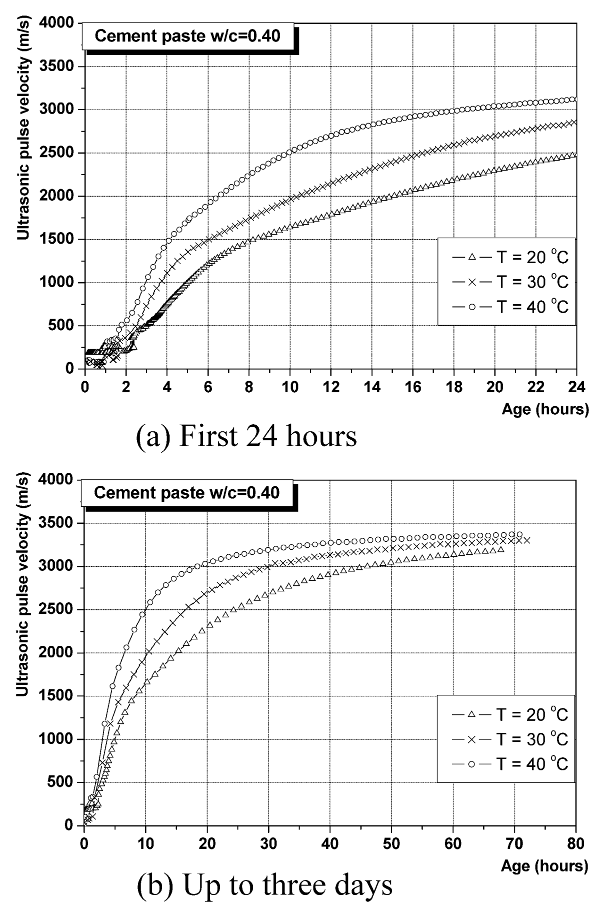

Fig. 3. Influence of curing temperature on UPV of cement paste.

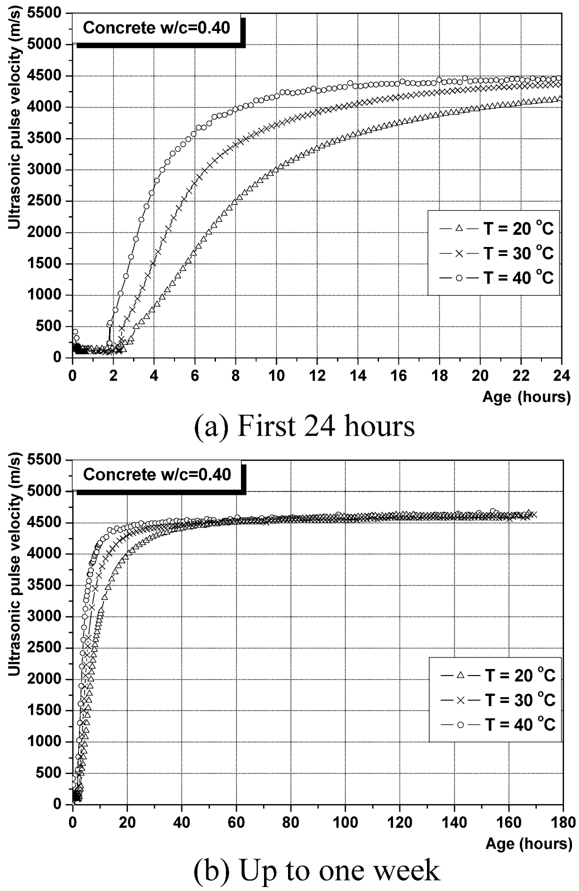

Fig. 4. Influence of curing temperature on UPV of concrete.

phase instead of through the liquid phase. A notable acceleration of UPV was found in the Stage II. This acceleration is caused by a number of phenomena. Firstly, in the water/air system, the relative amount of entrapped air bubbles and their position change with the hydration process. The entrapped air bubbles migrate to the surface of the concrete due to bleeding. As a result, the amount of entrapped air is reduced. Secondly, after the first few hours in the dormant period, as the cement dissolves and nucleation take place, the solid phases become more and more connected and the material changes from a suspension system to the state of a porous elastic solid. During this stage, it is believed that the UPV is controlled by the reduction of the amount of entrapped air bubbles and the amount of the connected solid phase. According to Ref. [12], the connectivity of solid phases can be indicated by the concept of "bridge volume" of hydration production. Hence, the development of microstructure during cement hydration can be quantitatively described with the correlation between the evolution of UPV and the increase of the bridge volume, which will be discussed later.

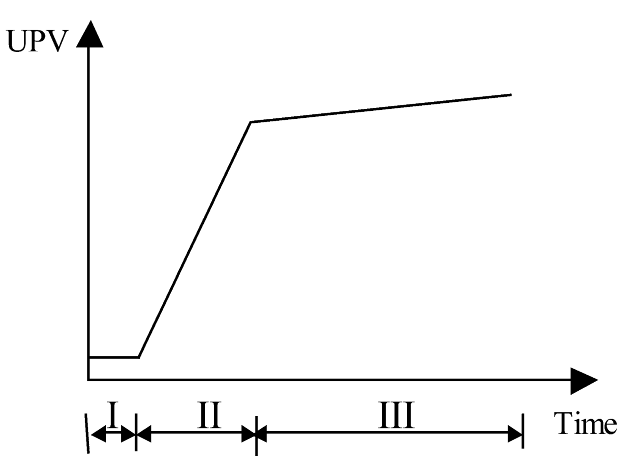

Fig. 5. Three characteristic stages of the evolution of the UPV.

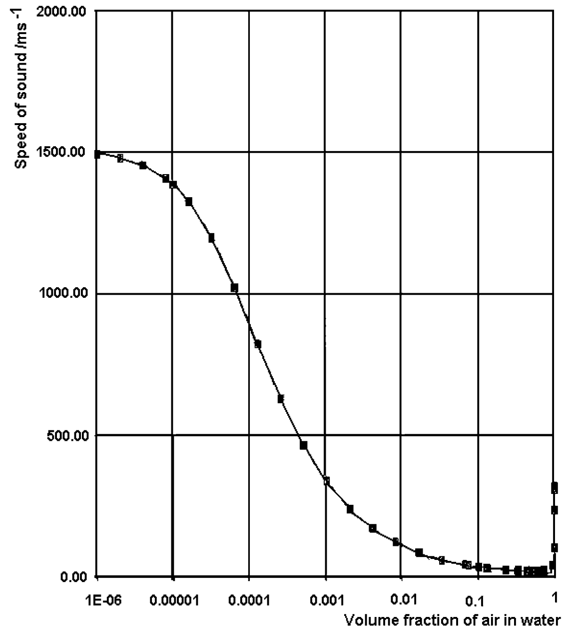

Fig. 6. The velocity of sound in air/water system at 20 °C (after Ref. [11]).

A slight increase in the pulse velocity was found in all specimens after it had reached a plateau in Stage III. In this stage, the influence of air bubbles drops and the UPV follows the total solid volume fraction.

3.2. Analysis of the connectivity in hydrating cement paste

With the HYMOSTRUC model [9,12], the increase of the bridge volume V_{br} during cement hydration can be quantified. Different subsequent stages in the hydration process are shown in Fig. 6. According to the model, the hydrating cement grains are considered as gradually "growing" spheres. As cement hydration takes place, the cement grains dissolve and a porous shell of hydration products is formed around the grain in the porous space. This results in an outward growth or "expansion" of the particles. The hydrates around the cement grains first cause the formation of small isolated clusters. Big clusters are formed when small cement particles become embedded in the outer shell of other particles, which results in a growth of these particles. The contacts between clusters are formed by

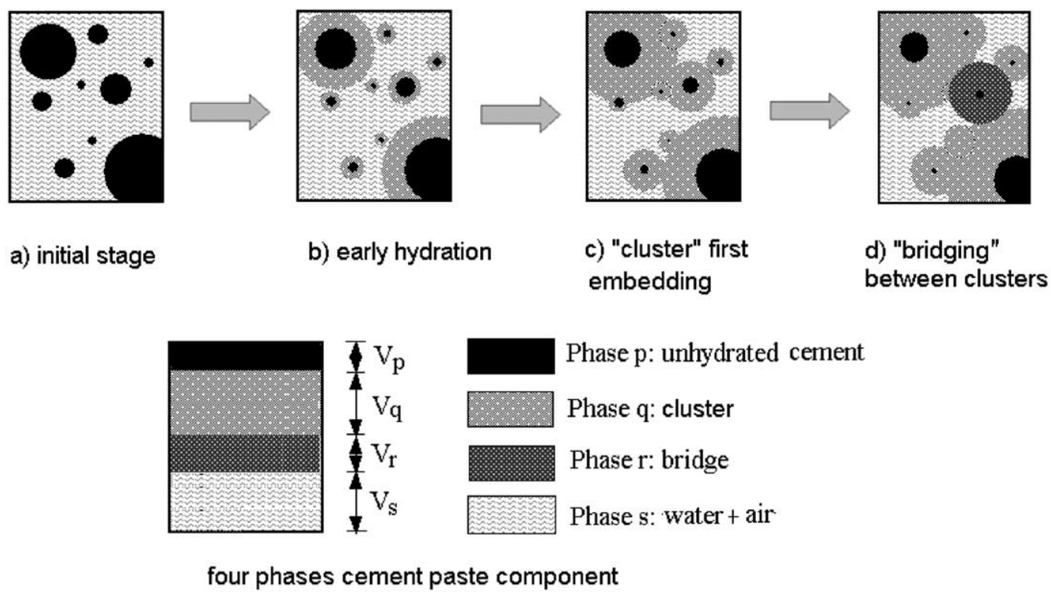

Fig. 7. Formation of the microstructure in hardening cement paste (after Ref. [12]).

cement particles that are not embedded completely in a cluster. These particles are modeled as "bridging" particles. As the hydration process progresses, the growing particles become more and more connected. Thus, at a certain degree of hydration α, the hydrating cement paste consists of an anhydrous cement phase ($p_{(\alpha)}$), a cluster volume ($q_{(\alpha)}$), a bridge volume ($r_{(\alpha)}$) and free capillary pore water and air ($s_{(\alpha)}$). These volume phases are illustrated in Fig. 7 and are calculated with Eqs. (1)–(5) as follows:

$$V_{0,\text{paste}} = V_{0,\text{cem}} + V_{0,\text{wat}} + V_{0,\text{air}} \tag{1}$$

$$p_{(a)} = \frac{(1-a)V_{0,\text{cem}}}{V_{0,\text{paste}}} \tag{2}$$

$$q_{(\alpha)} = \frac{V_{\text{clus}(\alpha)}}{V_{0,\text{paste}}} \tag{3}$$

$$r_{(\alpha)} = \frac{V_{\text{br}(\alpha)}}{V_{0,\text{paste}}} \tag{4}$$

$$s_{(\alpha)} = \frac{(1-a)V_{0,(\text{wat+air})}}{V_{0,\text{paste}}} \tag{5}$$

where $V_{0,\text{paste}}$, $V_{0,\text{cem}}$, $V_{0,\text{wat}}$ and $V_{0,\text{air}}$ are the initial volume fractions of the cement paste, the initial volume of the anhydrous cement, of the capillary pore water and air, respectively. The total cluster volume $V_{\text{clus}(\alpha)}$ must be equal

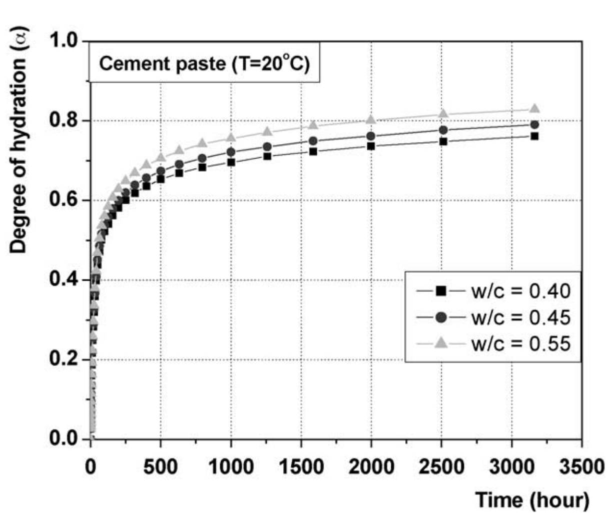

Fig. 8. Degree of hydration as function of age ($T = 20$ °C).

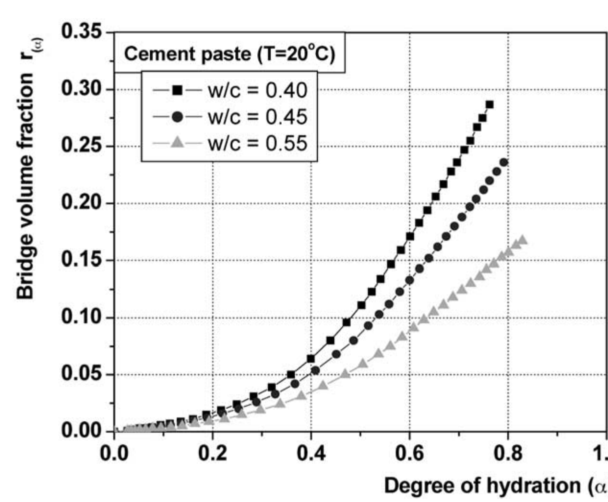

Fig. 9. The evolution of bridge volume as a function of degree of hydration ($T = 20$ °C).

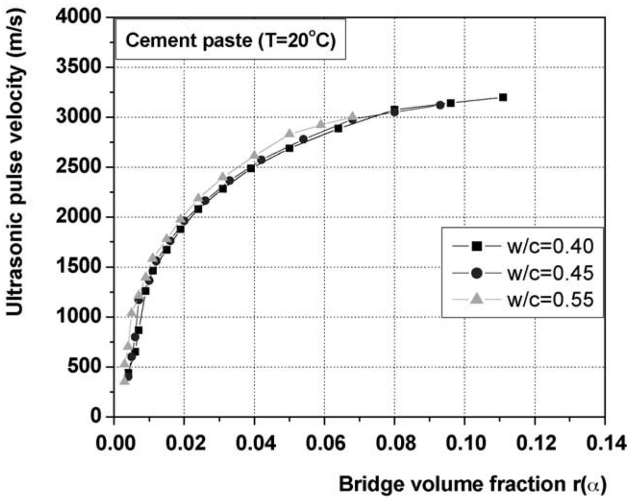

Fig. 10. Correlation between UPV and bridge volume ($T=20$ °C).

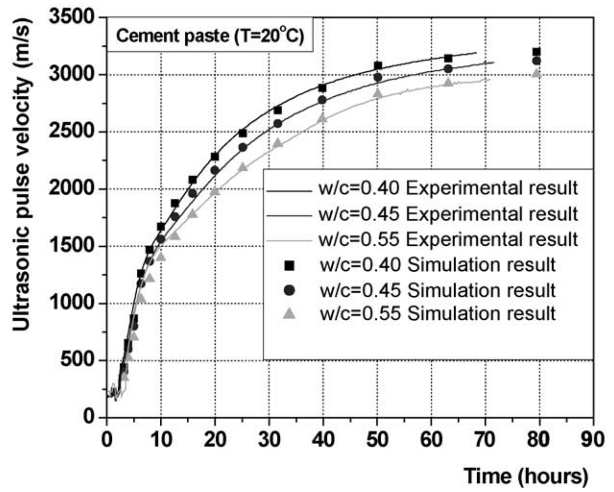

Fig. 12. Simulation of the evolution of the UPV in cement paste ($T=20$ °C).

to the total volume of the remaining cores of anhydrous cement grains plus the volume of the cement gel:

$$V_{\mathrm{clus}(\alpha)} = (1-\alpha)V_{0,\mathrm{cem}} + \alpha v V_{0,\mathrm{cem}} \tag{6}$$

where α = degree of hydration, v = ratio of the volume of the cement gel and the anhydrous cement from which the hydration products are formed.

The bridge volume V_{br} is the volume of the particles that are able to act as a bridge to neighboring clusters.

The numerical simulation results for the degree of hydration as function of time by HYMOSTRUC model is shown in Fig. 8. The evolution of the bridge volume as function of degree of hydration is presented in Fig. 9. It is noticed that the simulation model makes allowance for the fact that the lower water/cement ratio, the higher the bridge volume. The sample with higher bridge volume leads to a dense hydrated system.

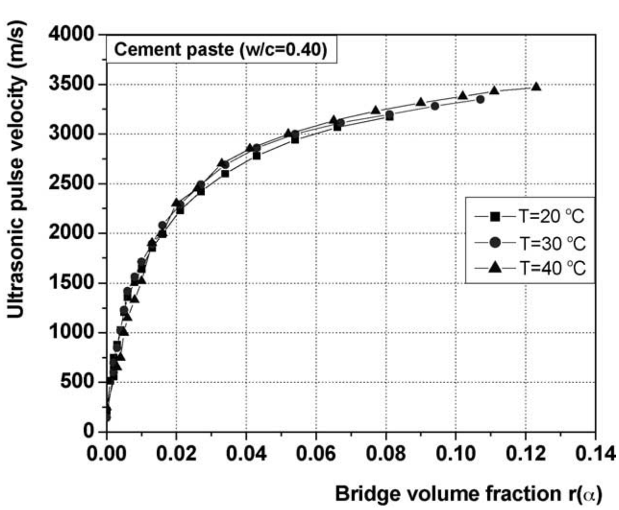

Fig. 11. Influence of temperature on the correlation between UPV and bridge volume (w/c = 0.40).

3.3. Correlation between the bridge volume and the UPV

If a macroscopically homogeneous body consisting of different phases is subjected to a pulse wave, the UPV can be described by employing Jones's theory [13]:

$$\frac{1}{c} = \sum_{i=1}^{n} \frac{V_i}{V^* c_i} = \sum_{i=1}^{n} \frac{n_i}{c_i} \tag{7}$$

where c is the longitudinal pulse velocity of the total system, i is the phase indicator, c_i is the longitudinal pulse velocity of each phase i, $n_i = V_i/V$ is the volume percentage of each phase.

As discussed earlier, the evolution of the pulse velocity in Stage I is completely controlled by the amount of the entrapped air bubbles.

In Stage II, the cement hydration takes place and hydration products are formed. The hydrating cement paste was considered to be composed of anhydrous cement phase, cluster volume, bridge volume, capillary water and air. If the volume fractions of these four phases calculated with the HYMOSTRUC model (Eqs. (2)–(5)) are placed in the homogeneous continuous pulse model (Eq. (7)), the correlation between the growth of the bridge volume $r_{(\alpha)}$ and the evolution of the UPV in a hydrating cement paste can be derived:

$$\frac{1}{c_{\mathrm{cp}(a)}} = \beta\left[\frac{p(a)}{c_{\mathrm{cem}}} + \frac{q(a)}{c_{\mathrm{gel}}} + \frac{r(a)}{c_{\mathrm{gel}}} + \frac{s(a)}{c_{\mathrm{wat+air}}}\right] \tag{8}$$

where c_{cp} is the longitudinal velocity of the cement paste, $c_{\mathrm{cem}} = 3600$ m/s is the longitudinal ultrasonic velocity in the dense cement paste calculated according to Ref. [14]. The longitudinal ultrasonic velocity of cement gel, c_{gel}, varies from 1500 to 3300 m/s, depending on the degree of hydration. The velocity of air/water mixture, $c_{\mathrm{wat+air}}$, is taken from Povey's curve (Fig. 6). β is an empirical constant, which varies from 1.0 to 1.2.

In Stage III, the influence of the volume fraction is disregarded from Eq. (8) and the UPV only follows the total solid volume fraction.

The calculated relation between the bridge volume and the evolution of pulse velocity for different water/cement ratio at 20 °C is shown in Fig. 10. The correlation between the pulse velocity and the bridge volume appears to be independent of the water/cement ratio. In a previous study was found that the UPV is a function of the bridge volume and is independent of the curing temperature (Fig. 11) [15]. Both results indicate that the connectivity of the solid phase, in terms of the bridge volume, is a dominating parameter that determines the UPV in the cement paste. The evolution of UPV completely follows the development of the microstructure, i.e., of the increase of the bridge volume, during cement hydration.

Fig. 12 shows the simulated result obtained by applying Eq. (8) to different water/cement at 20 °C, compared with experimental results. The results of the numerical simulation are in good agreement with the experiment. This result, obtained for cement paste, can be used for describing the UPV of concrete in a satisfactory way [15].

4. Conclusions

The development of the microstructure in cementitious materials at early age can be described quantitatively either by UPV measurements or by a numerical simulation model. From the experimental results, three characteristic stages are distinguished. In Stage II, the UPV is determined by the connectivity of solid phases and the amount of entrapped air bubbles. The growth of the bridge volume simulated in the numerical model can be used as indicator for connectivity of solid phases. It turns out that the bridge volume can be considered as an unambiguous parameter, which can be used to simulate the evolution of the pulse velocity. The correlation between the growth of bridge volume and the evolution of UPV is independent of water/cement ratio and temperature. On the basis of these results, the UPV measurements can successfully be used as a nondestructive technique for monitoring the evolution of the microstructure in hardening cementitious materials.

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