Experimental study on ultrasonic pulse velocity evaluation of the microstructure of cementitious material at early age

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This paper describes an ultrasonic experimental set-up to monitor the development of the microstructure of fresh concrete at different temperatures (isothermal curing at 10, 20, 30 and 50 °C) and water/cement ratios (0.40, 0.45 and 0.55). The Ultrasonic Pulse Velocity (UPV) is used as an indication for microstructure development of concrete at early age.
The results indicate that the ultrasonic pulse velocity largely depends on the water/cement ratio and state of hydration during the first 24 hours. The numerical cement hydration simulation model HYMOSTRUC is used for investigating the relation between the change of microstructure and the evolution of ultrasonic pulse velocity. The relation between ultrasonic pulse velocity and compressive strength is almost linear at early stage. The ultrasonic pulse velocity method is proved to be applicable in the recording and monitoring the microstructure development and strength at early stage.

Key words: **ultrasonic pulse velocity, cementitious material, early age, microstructure.**

1 Introduction

The development of the microstructure of cement-based materials at early age is an important research area in which a variety of techniques are being used. These techniques include scanning electron microscopy image, small angle X-ray scattering and mercury intrusion porosimetry [1-3]. All these methods show limits in the application possibilities. From an engineering point of view, there is a need for characterizing the formation of the microstructure by an accurate, cost-effective measurement method. Ultrasonic pulse velocity measurement, a non-destructive method, could be such a method.
Ultrasonic material analysis is based on a basic principle of physics: the motion of any wave will be affected by the medium through which it travels. For many cement-based materials, the ultrasonic transition time can be correlated with the state of cement hydrates interconnect and the state of capillary water as well as some microstructural features. In young concrete, with the progress of hydration, the solid phases in the system become more and more connected. The result of this change will lead to a shorter transition time.
The measurement of the ultrasonic pulse velocity has been used for a long time to characterize the behavior of cementitious materials systems at early age. Studies [4-5] have shown that for cement

paste, the pulse velocity is governed by the fluid phase just after mixing until the time the hydrates become interconnected. The ultrasonic wave is sensitive to the time when the interconnection takes place.

Furthermore, Boumiz [6] presented a combined experimental approach measuring ultrasonic velocity, electrical conductivity, and heat flow. From measured compressional and shear velocity, a percolation approach is used to analyze the early development of the elastic modulus. The occurrence of the percolation threshold was considered when an "infinite" cluster of connected grains had formed throughout the material.

Until now, there is no systematic model in acoustic researches that describes the change in the formation of early-age microstructure caused by state of hydration and water/cement ratio changes. In this research, which is based on the numerical cement hydration model HYMOSTRUC, the correlation between ultrasonic pulse velocity and microstructure parameters is presented.

2 Modelling of microstructural development of cementitious materials

HYMOSTRUC [7,8,9] is a model that describes the hydration of cement particles in cement paste and in concrete mixtures. In this model, hydrating cement grains are considered as gradually expanding spheres. As cement hydrates, the cement grains gradually 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 cement particles that are not embedded completely in a cluster. These particles are modeled as "bridging" particles. As the hydration progresses, the growing particles become more and more connected because of the appearance of the "bridging". As a result, the material changes from the state of a suspension to a porous elastic solid. This change of microstructure during cement hydration can be characterized with ultrasound propagation.

3 Methods and materials

3.1 Experimental set-up and control system

The experimental setup designed at Delft University of Technology is shown in Figure 1. The ultrasonic transducers and temperature probe are integrated in a 150x150x200 mm steel mould. The ultrasonic measurement is conducted using a PUNDIT plus equipment with a 54 kHz transducer.

In order to avoid the influence of the wall of the steel mould in ultrasound propagation, two holes with a 54 mm diameter are made in the wall. The transducers are fixed by a PVC ring and coupled directly through a piece of plastic membrane stuck on the inner wall of the mould, four springs used to adjust the transducer's contact pressure to guarantee good contact with the specimen. The temperature of the whole system is controlled by a cooling system with an accuracy of $\Delta T=0.1°C$. Temperature is measured by one Pt 100 sensor. All control units are connected to an industrial computer. Software controls the experiments and automatically records the hydration time and ultrasonic pulse transition time.

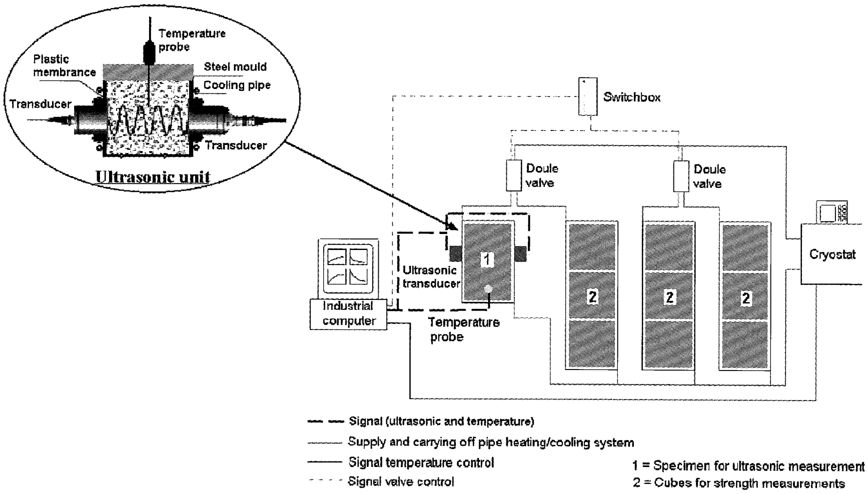


Figure 1. Experimental set-up for monitoring UPV in young concrete

3.2 Mix compositions

Table 1 contains the main data of the tested specimen. The main variables considered are water/cement ratio (w/c) and isothermal curing temperature. Maximum aggregate size is 16 mm. Though it is known [1] that air bubbles entrapped in concrete influence the initial pulse velocity readings, no treatment has been imposed to remove the air bubbles from the specimens. Measurements start 15 minutes after mixing. Under the same curing condition, the compressive strength tests on cubes, 150x150x150 mm are performed at an age of 1, 3 and 7 days, respectively.

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]
PCA16350-40	CEM I/32.5R	350	1942	0.40	10, 20, 30, 50	7
PCA16350-45	CEM I/32.5R	350	1884	0.45	10, 20, 30, 50	7
PCA16350-55	CEM I/32.5R	350	1792	0.55	10, 20, 30, 50	7

4 Results and discussion

Influence of curing age

For mixture PCA16350-55, the ultrasonic pulse velocity as a function of curing age during the first 24 hours after casting is shown in Figure 2. Figure 3 contains the data during the first 7 days and also presents the compressive strength.

During the first 5 hours, relatively low values of the pulse velocity were found for all specimens. These values are smaller than those for water (1430 m/s) and even smaller than that of air (340 m/s). Similar values were found by Reinhardt [10] for concrete made of blast furnace slag cement. Sayers [1] and Keating [2] also found similar results in the oil and gas well cement paste. They

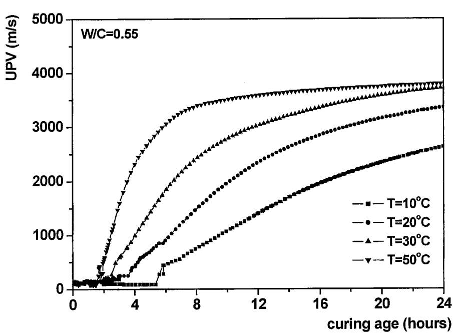


Figure 2. UPV as function of curing age (First 24 hours)

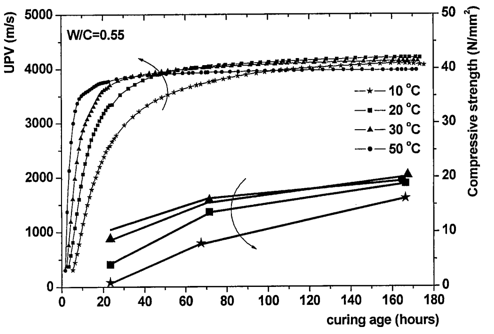


Figure 3. UPV and compressive strength as function of curing age (7 days)

explained this phenomenon as the result of entrapped air. Povey's experimental curve [11] demonstrates the influence of entrapped air in fresh concrete.

The time from the start of the test to the point when the velocity increases, depends on the temperature and the water/cement ratio. This time is generally referred to as the "dormant stage".

An acceleration of ultrasonic pulse velocity was found after the dormant stage. This acceleration is caused by a number of phenomena:

First, 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 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's take place, the solid phases become more and more connected and the material changes from suspension of cement particles in water to the state of a porous elastic solid. The characteristics of ultrasound propagation in a solid medium significantly differ from that in a suspension.

The time that the ultrasonic pulse velocity takes to reach an almost constant value varies from 30 to 100 hours, depending on the water/cement ratio and the degree of hydration.

Influence of water/cement ratio

The effect of the amount of water in a concrete mixture on the ultrasonic properties was examined for mixtures with a water/cement ratio of 0.4, 0.45 and 0.55. The effect of the water/cement ratio is shown in Figure 4. It was found that mixtures with a higher water/cement ratio have lower values of the pulse velocity. The pulse velocity is almost 8~10% higher at w/c ratio of 0.45 than that at w/c ratio of 0.55. The values for the ultrasonic pulse velocity of mixtures with a lower water/cement ratio are higher because of the higher amount of solid materials in the system. Moreover, mixtures with lower water/cement ratio contain a higher amount of aggregate, which also leads to a higher pulse velocity. Further quantitative analysis of the influence of the relative composition of concrete mixtures will be studied.

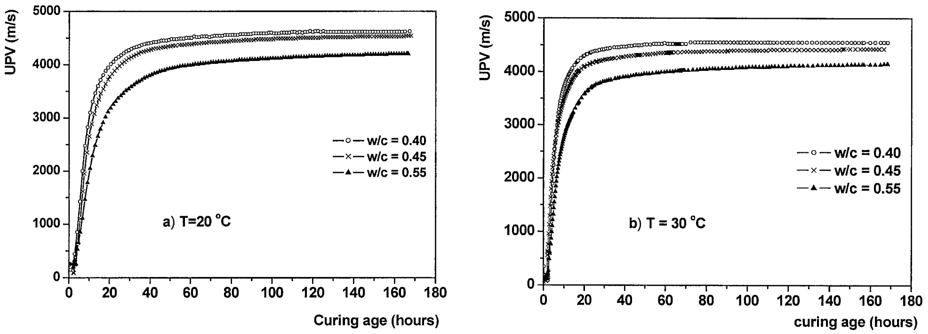


Figure 4. Influence of water/cement ratio on evolution of ultrasonic pulse velocity at different curing temperatures

Influence of temperature

The influence of temperature is illustrated in Figure 2 and Figure 3. The higher the isothermal curing temperature, the quicker the increase in pulse velocity during the first 24 hours. Moreover, the ultrasonic pulse velocity takes a shorter time to reach the constant value for higher temperatures; after the plateau is reached, the temperature shows less influence on the pulse velocity.

The Arrhenius equation may be used to model changes in reaction rate with changes in temperature. Relative changes in rate only need the activation energy term. Strictly speaking the equation only applies to a single reaction mechanism. In fact, both the activation energy and the term are likely to vary between different reactions happening during cement hydration [12]. Under this assumption, the relationship between the rate constant and the activation energy for changing in ultrasonic pulse velocity caused by temperature is:

$$K_T = K_0 e^{-E_a/RT}$$

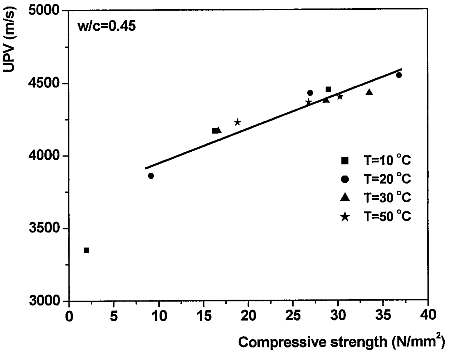
where, K_T is rate constant, K_0 is a pre-factor, E_a is the apparent activation energy, R is the universal gas constant (8.314J/(mol K)) and T is absolute temperature in Kelvin.

For mixture PCA16350-55, in the temperature range from 283 K to 323 K, the activation energy varies from 20 to 70 kJ/mol. These values are in good agreement with [7] in which the activation energy was determined by evolution of degree of hydration. The activation energy will be used in the further research.

Relation between the ultrasonic pulse velocity and the microstructure parameters

The compressive strength of concrete and the bridge volume in concrete are two parameters that, directly and indirectly, reveal the development of microstructure during cement hydration. This can be elucidated by the relationship of the ultrasonic pulse velocity with the development of compressive strength and also with the evolution of bridge volume.

As shown in Figure 5, for mixtures cured at different temperatures, the relation between ultrasonic pulse velocity and compressive strength is almost linear for strengths exceeding 10 N/mm^2 at early stage. Figure 6 presents the relation between ultrasonic pulse velocity and bridge volume in concrete calculated with HYMOSTRUC [7] at different curing temperatures. The ultrasonic pulse velocity increases with increasing bridge volume in concrete. Both correlations can be found because the increase in connectivity of the solid phase will determine the change in pulse velocity and strength of concrete at early age. Furthermore, we also note that in the same bridge volume, a lower ultrasonic pulse velocity is found at higher curing temperature. This proved that a higher curing temperature leads to a more porous structure in which the solid phase consists of hydration products with lower density.



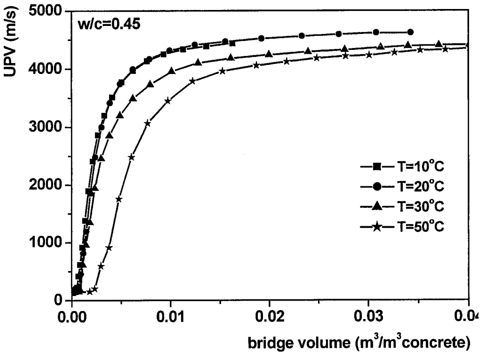


Figure 5. Relation between UPV and compressive strength of concrete.

Figure 6. Relation between UPV and bridge volume in concrete.

5 Conclusions

The ultrasonic pulse velocity measurement is a method that is suited for monitoring the development of the strength and, indirectly, of the microstructure in cement-based material at early age. This is demonstrated by an experiment in which the concrete behavior at different water/cement ratios and curing temperatures was investigated. Experimental results indicate that the evolution of ultrasonic pulse velocity during the first 24 hours depends on the water/cement ratio and on the degree of hydration. The period up to the point where pulse velocity starts to increase could be indicated as the end of the dormant stage. Lower water/cement ratio and higher temperature lead to a rapid increase of pulse velocity. Both relations between ultrasonic pulse velocity, compressive strength and bridge volume, calculated by numerical simulation in different curing temperature, indicates that the ultrasonic pulse velocity method seems applicable in the recording and monitoring of the development of microstructure and strength increase at early age.

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