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# Study on the development of the microstructure in cement-based materials by means of numerical simulation and ultrasonic pulse velocity measurement

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**Abstract**

The formation of microstructure in cementitious materials was simulated with a numerical model. Simulation results have been verified by measuring the evolution of the ultrasonic pulse velocity (UPV). In this contribution, the applied computer-based cement hydration model is presented. The UPV measurements are also presented and evaluated. Experiments were performed on concrete mixtures with water/cement ratio 0.40, 0.45 and 0.55. The concrete was cured isothermally at 10, 20, 30 and 40 °C. Correlations between the development of the microstructure and the evolution of UPV were found. Two critical processes were individuated. The first is the percolation threshold of the solid phase. The second is the full connectivity of the solid phase. Both in the experiments and in the numerical simulations it was possible to distinguish these critical stages. These stages are discussed and conclusions are drawn regarding the potential of numerical simulation models in the study of early age cementitious materials for quantitative analysis of hydration processes.



*Keywords:* Fresh concrete; Microstructure; Characterization; Modeling; Ultrasound

## 1. Introduction

Understanding the development of the microstructure during cement hydration is a primary goal of concrete material science in both theoretical and experimental studies. Several recent studies [1–3] have shown that the formation of the microstructure of cementitious materials can be simulated by numerical or computer-based digitized modeling. On the other hand, characterization of changes in the ultrasonic pulse velocity permits to follow cement hydration and to monitor the development of microstructure at early age [4–7]. Comprehending the relation between the ultrasonic pulse velocity (UPV) and specific aspects of microstructure evolution during cement hydration would help to understand how critical process variables affect the hydration process and hence to develop better hydration models for cement-based systems.

Cement hydration is a complex chemical process involving the change from the suspension state to the solid state. During the suspension period, the ultrasonic velocity is not very sensitive to the growth of structure in the paste [4]. The water/air phase, especially the air bubbles present in the water, acts as the dominant factor that determines the UPV [8,9]. As cement grains gradually dissolve and nucleate, the connection of smaller particles leads to clusters that form a percolating solid network. The ultrasonic pulse propagation path switches from the liquid phase to the solid phase. The UPV reveals a significant increase after the appearance of this solid percolation threshold, as the stiffness of the cement paste largely depends on the connection of the solid phase. It is noticed that beyond this stage the influence of the solid phase becomes dominant instead of air bubbles on the UPV.

As already pointed out by Krautkraemer and Krautkraemer [10], the UPV in a material is strongly affected by its stiffness. Once the relation between UPV and the connectivity of the solid phase is determined, other properties, such as stiffness and strength, can be obtained.

The principal aim of this study was to determine the evolution of the microstructure in hardening cement-based materials, with particular emphasis on the

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percolation threshold and on the connection of the solid phases. To reach this goal, a three-dimensional cement hydration model was used and the UPV measurements were performed. The relation between the connectivity of the solid phase in the model and the evolution of the UPV in early-age concrete was investigated.

## 2. Modeling of hydration and microstructure development

For the simulation of the reaction processes and of the formation of the microstructure in cement-based systems, the numerical model HYMOSTRUC was developed [2]. In this model the degree of hydration is simulated as a function of the particle size distribution and the chemical composition of the cement, of the water/cement ratio and of the reaction temperature. In a computer digitized format of HYMOSTRUC, the cement particles are modeled as digitized spheres randomly distributed in a three-dimensional body and the hydrating cement grains are simulated as growing spheres [11]. As cement hydrates, the cement grains gradually dissolve and a porous shell of hydration products is formed around each grain. 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 promotes the outward growth of these particles (Fig. 1a). As hydration progresses, the growing particles become more and more connected. The material changes from the state of a suspension to the state of a porous elastic solid.

As shown in Fig. 1b, a cube of hydrating paste was simulated to determine the relationship between the development of microstructure and the UPV. In studies by Bentz and Garboczi [12], the connectivity and percolation properties of the solid phase were found to be related to the UPV. To assess connectivity and percolation, a "burning" algorithm was used. In this study, a serial section algorithm associated with an overlap algorithm will be employed and will briefly be explained hereafter.

Consider a cubic sample that occupies a set $P \subset R^d$ of the physical space ($d = 2$ in two-dimensions and $d = 3$ in three-dimensions). The serial section algorithm was used to determine whether an arbitrary point $r$ belonged either to the subset of the solid phase $S$ or to the subset of the capillary pore phase $L$ in each layer. Thus, the sample $P$ contained two disjoined subsets: $P = S \cup L$ with $S \cap L = 0$, where 0 is the empty set. Furthermore, the overlap algorithm checked each one of the six faces of this spatial point on its up-layer and down-layer and examined whether this point was connected with its neighbors of the same phase. This procedure was repeated until the final layer of the body. Therefore, two new subsets of the connected solid phase $S'(S' \subset S)$ and the connected capillary pore phase $L'(L' \subset L)$ were found. The ratios $T_{(S)} = V_{(S)} V_{(P)}$ and $T_{(L)} = V_{(L)}/V_{(P)}$ gave the volume fractions of the total solid phase and the total capillary pore phase, where $V_{(S)}$, $V_{(L)}$ and $V_{(P)}$ denote the volume of solid phase, capillary pore phase and total sample, respectively. The ratios $C_{(S)} = V_{(S')}/V_{(P)}$ and $C_{(L)} = V_{(L')}/V_{(P)}$ represent the connectivity of the solid phase and of the capillary pore phase, where $V_{(S')}$ and $V_{(L')}$ denote the connected solid phase volume and the connected capillary pore volume.

## 3. Materials and methods

The experimental setup for the UPV measurements is shown in Fig. 2. The ultrasonic transducers and temperature probe are integrated in a $150 \times 150 \times 200$ mm$^3$ steel mould. The ultrasonic measurement is conducted using a portable ultrasonic non-destructive digital indicating tester (Pundit Plus) with a 54 kHz transducer.

In order to avoid the influence of the wall of the steel mould on the ultrasound propagation, two holes with a 54 mm diameter are made in the wall of the mould. The transducers are fixed by a PVC ring and coupled with the sample directly through a piece of plastic membrane

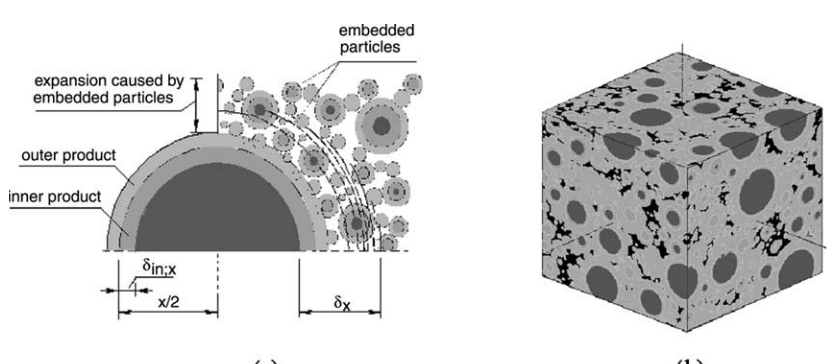


Fig. 1. Formation of microstructure in hardening cement paste (after [2]). (a) Cement particles interaction mechanism. (b) Simulated cement paste ($100 \times 100 \times 100$ μm$^3$). Black color denotes capillary pore.

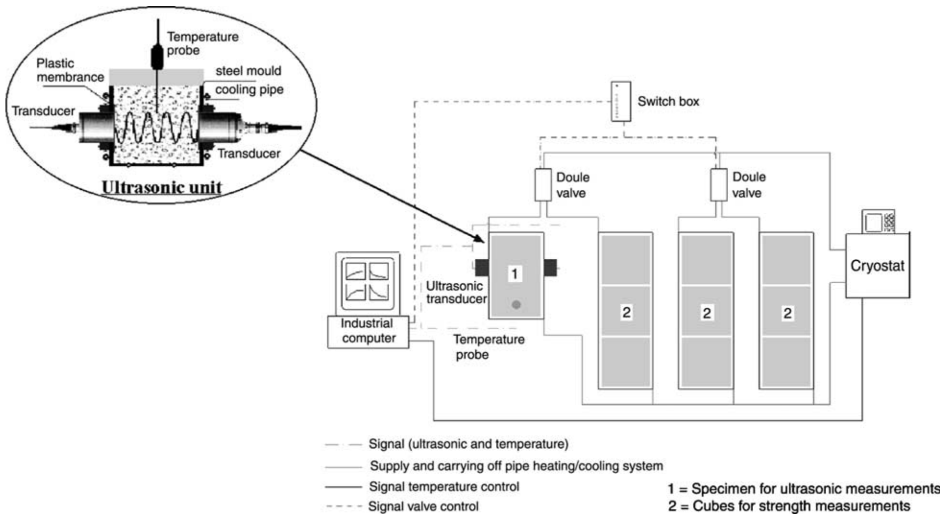


Fig. 2. Experimental setup for monitoring UPV in young concrete.

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] |
|---|---|---|---|---|---|---|
| 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 |

glued on the inner wall of the mould. Four springs are used to adjust the transducer's contact pressure in order to guarantee good contact with the specimen. The springs are not released until 6–8 h after casting, when the material is sufficiently hard to withstand their pressure. The temperature of the whole system is controlled by a cooling system with an accuracy of $\pm 0.1$ K. All control units are connected to an industrial computer. A software controls the experiments and automatically records the hydration time and the ultrasonic pulse transition time.

A series of experiments was performed on concrete. Table 1 contains the main data of the tested specimens. The main variables considered were water/cement ($w/c$) ratio and different isothermal curing temperatures. The maximum aggregate size was 16 mm. No special treatment was imposed to remove air bubbles from the concrete, except for 3–5 min vibration. The measurements started about 15 min after mixing.

## 4. Results and discussion

The influence of curing temperature during the first 24 h is shown in Fig. 3 in the case of water/cement ratio 0.4. In the period of the first 5 h, relatively low values of the UPV were found for all specimens. These values were smaller than the velocity in water (1430 m/s) and even smaller than the velocity in air (340 m/s). Similar results were found by [13] for concrete made of blast furnace slag cement. The reasons why very low UPV were found in the first 5 h will be discussed in Section 5.

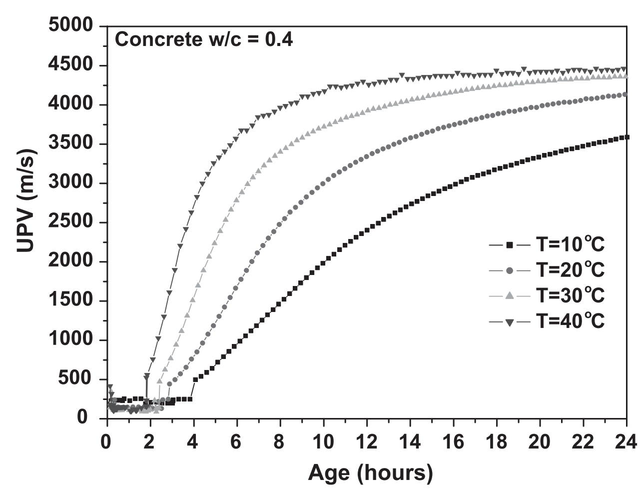


Fig. 3. Influence of curing temperature and curing age on UPV (24 h).

The time from casting to the point when the velocity increased depended on the temperature and the water/cement ratio. This time is generally referred to as the "dormant stage".

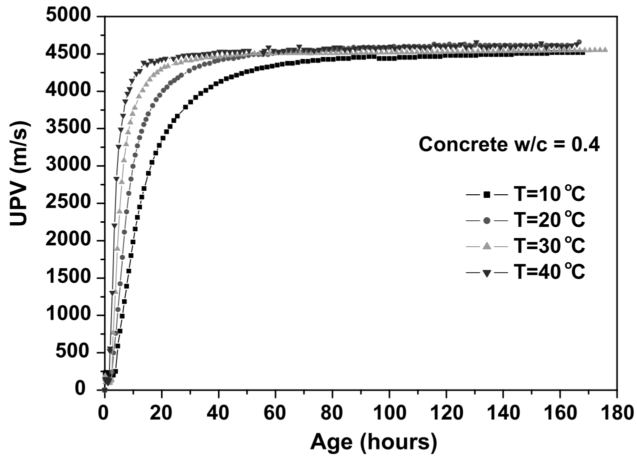


Fig. 4. Influence of curing temperature and curing age on UPV (one week).

The influence of the curing temperature and the curing age on the UPV is shown in Fig. 4. Three principal features result from the curves. Firstly, during the first 40 h, a rapid increasing UPV was registered for all specimens. Secondly, after about 60 h curing, the UPV reached a certain value and thereafter increased only slightly. Thirdly, the higher the isothermal curing temperature, the faster the increase in UPV during the first 24 h. In other words, the UPV took a shorter time to reach a plateau value for higher temperatures. After the plateau was reached, the curing temperature showed almost no influence on the UPV.

The effect of the $w/c$ ratio in concrete mixtures on the ultrasonic properties was examined for mixtures with a $w/c$ ratio of 0.4, 0.45 and 0.55 (Fig. 5). It was found that mixtures with a higher $w/c$ ratio had lower values of the UPV. After 50 h, the UPV was almost 8–10% higher for the specimen with $w/c$ ratio of 0.45 than for $w/c$ ratio of 0.55. This can be explained by the higher solid volume fraction and lower porosity of the mixtures with lower $w/c$ ratio.

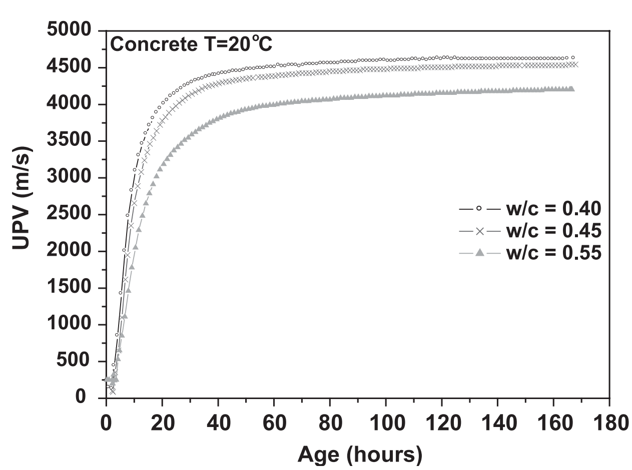


Fig. 5. Influence of water/cement ratio and curing age on UPV.

The influence of the amount of aggregates in concrete was investigated in [16], in which the concrete was considered as two phases model consisting of aggregate and cement paste. The evolution of UPV was calculated as a function of the volume fraction of each phase.

## 5. Modeling the development of microstructure and the evolution of ultrasonic pulse velocity

The hydration process and the microstructural development for a $100 \times 100 \times 100$ μm$^3$ cubic sample of cement paste were modeled. The $w/c$ ratio was 0.45 and temperature 20 °C. The serial section algorithm and the overlap algorithm were employed to determine the connectivity of each phase. A 3D simulated structure with 1 μm spacing of the sections and 100 serial sections was specified in the calculations. However, a 2D section image is shown in the figures for convenience of description.

Based on analysis of experimental data, the evolution of UPV can be simplified to three characteristic stages (Fig. 6). The physical meaning of these stages and the corresponding simulated development of the microstructure are discussed in the following.

### 5.1. Stage I: from a suspension system to the solid phase percolation threshold

In this first stage, the UPV remains constant at a very low value. This period can be related to the dormant stage of cement hydration, of which the duration largely depends on the curing temperature.

In the beginning of this period, the cement particles in the HYMOSTRUC model are randomly distributed in a volume; the cement has not yet hydrated and therefore the degree of hydration α is 0% (Fig. 7). The volume fractions of solid phase and capillary water phase are 41% and 59%. Cement particles are isolated from each other, while the capillary pore water is connected. Sayers

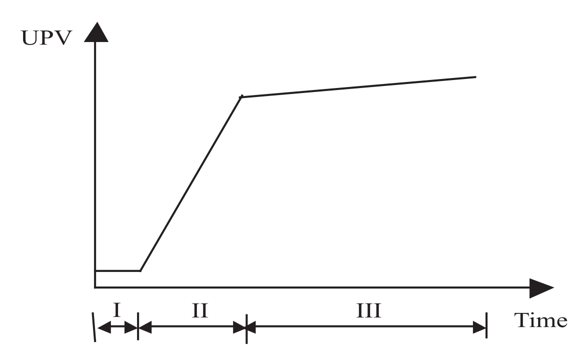


Fig. 6. Simplification of UPV in three characteristic stages.

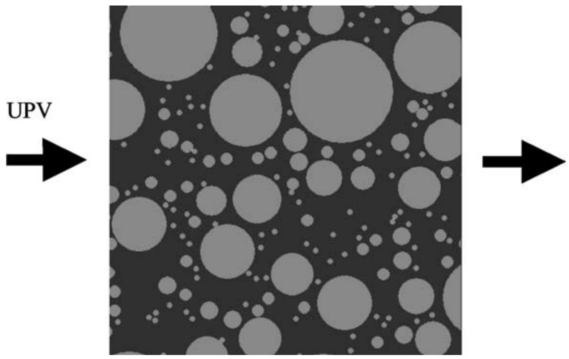


Fig. 7. Initial stage—suspension. $\alpha = 0\%$: $T_{(S)} = 41\%$, $T_{(L)} = 59\%$, $C_{(S)} = 0\%$, $C_{(L)} = 59\%$.

and Dahilin [5] considered the system in this period as a dispersion of solid particles in a liquid. The ultrasonic signal is strongly attenuated by the reflection of a huge number of tiny air bubbles in the fresh mixtures. Urick's [14] phase theory is not suitable in this case. However, if one takes into account the influence of air-bubbles according to Povey [8], a UPV value of around 200 m/s can be obtained for 1–2% air in the fresh concrete.

At the end of this period, the smaller cement particles are dissolved and embedded in the outer shell of bigger particles and small isolated clusters of solid substance are formed. These small isolated clusters are the basis of the solid network. The solid network continues to develop until it becomes connected throughout the material [15]. At this critical time a solid percolation path is formed. The UPV may now propagate through the solid phase instead of through the liquid phase; this fact leads to a steep increase in UPV (Fig. 8). This critical degree of hydration, when the system changes from a suspension of cement particles in water into an interconnected solid phase, can be considered as the percolation threshold [6].

For the paste analyzed (Fig. 9), the percolation threshold is reached at a degree of hydration of 2.7%. This is also the point where the UPV starts to increase. At this point, the total solid and the connected solid volume fractions are 52% and 30% of the paste volume, respectively. The total and the connected capillary water are both 48%, which indicates that the capillary water is still fully connected at this stage.

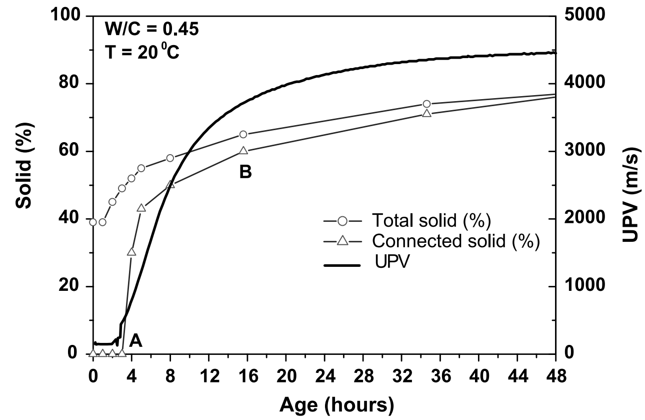


Fig. 9. Correlation between UPV and phase volume fraction.

### 5.2. Stage II: the UPV follows the connectivity of the solid phase

A period of rapid increase in the UPV appears after the dormant period. This period can last from 10 to 60 h, depending on the curing temperature and type of cement, which influences the rate of hydration. As shown in Fig. 10, where more and more hydration products become connected to each other, a rapid increase of connected solid volume fraction from 30% (Fig. 8) to 60% (Fig. 10) is found, corresponding to an increase of the degree of hydration from 2.7% to 25% in 15 h.

Due to this rapid increase of connected solid, the ultrasonic pulse can propagate through more connected solid volume. In fact, as shown in Fig. 12 from point A to point C, a sudden increase is found both in the degree of the connected solid phase and in the UPV.

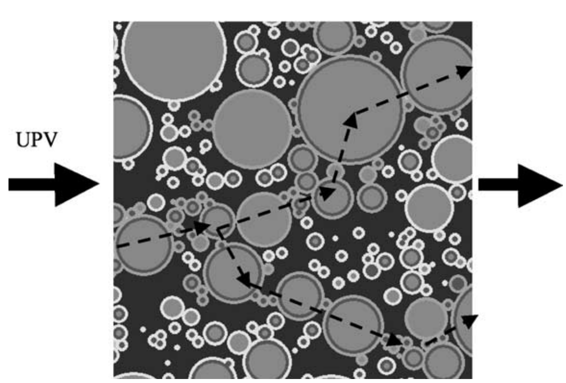


Fig. 8. Threshold of solid percolation. $\alpha = 2.7\%$: $T_{(S)} = 52\%$, $T_{(L)} = 48\%$, $C_{(S)} = 30\%$, $C_{(L)} = 48\%$.

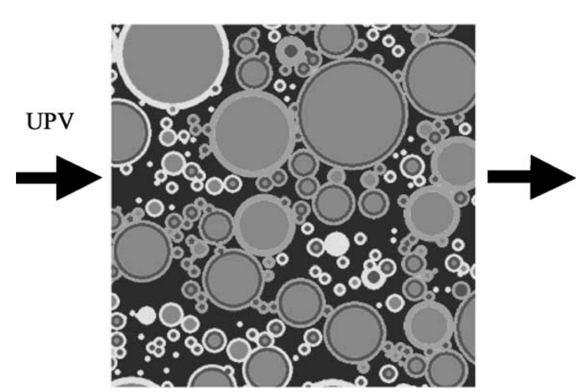


Fig. 10. Connectivity of solid phase. $\alpha = 25\%$: $T_{(S)} = 65\%$, $T_{(L)} = 35\%$, $C_{(S)} = 60\%$, $C_{(L)} = 35\%$.

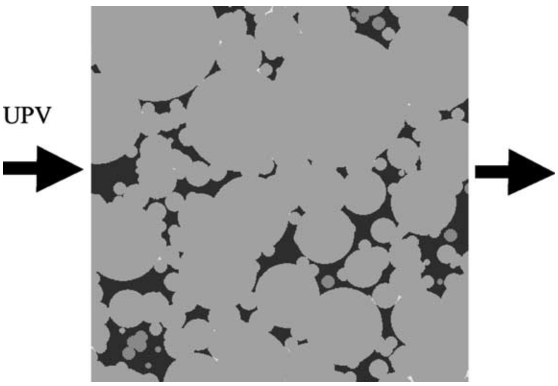


Fig. 11. Fully connected solid phase. $\alpha = 44\%$: $T_{(S)} = 78\%$, $T_{(L)} = 22\%$, $C_{(S)} = 78\%$, $C_{(L)} = 20\%$.

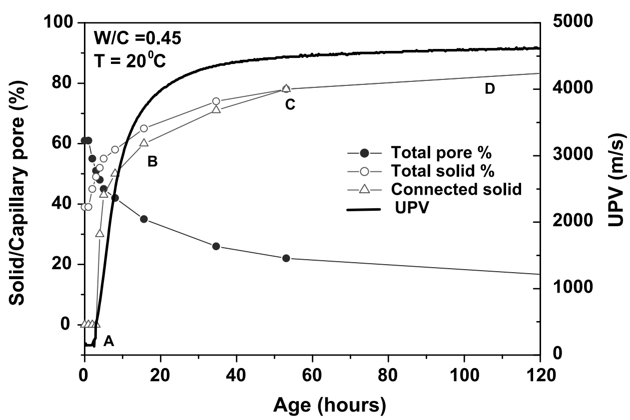


Fig. 12. Correlation between UPV and phase volume fraction.

### *5.3. Stage III: the UPV follows the total solid volume fraction*

A slight increase in the UPV is found in all specimens after the plateau is reached. When the degree of hydration is about 44%, the volume fraction of the total solid and the connected solid are both 78%, which indicates that all hydrating cement particles are connected with each other (Fig. 11). Thus, a fully connected solid frame is formed. From this point on, the increase in UPV is limited and follows the evolution of the total solid volume fraction (Fig. 12 point C to point D).

## 6. Conclusions

The computer-based simulation model HYMOSTRUC is able to simulate the development of the microstructure of cementitious materials. This has been demonstrated by comparison of the evolution of UPV and simulation results. In fact, the same tendency was found in the development of microstructure, i.e. the volume of the connected solid simulated by HYMOSTRUC, and in the evolution of UPV.

In particular, the critical processes happening during cement hydration were explained. Both experimental and simulation results showed that the period up to the point where the UPV rapidly increased could be indicated as the end of the dormant stage. This point corresponded to the threshold of solid percolation. When cement hydrates percolated through the specimen, a complete path for the UPV was formed. Ultrasonic pulse signals could then propagate from one side of the specimen to the other side, following this path. Thereafter, the quick increase of the UPV followed the rapid change of the connectivity of the solid phase. Finally, when all the solid phase was connected, the slow increase of the UPV followed the evolution of the total solid fraction.

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