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Relating ultrasonic measurements on fresh concrete with mineral additions to the microstructure development simulated by CEMHYD3D

Nicolas Robeyst [a], Christian U. Grosse [b], Nele De Belie [a,*]

[a] Magnel Laboratory for Concrete Research, Ghent University, Department of Structural Engineering, Technologiepark Zwijnaarde 904, B-9052 Ghent, Belgium
[b] Non-destructive Testing Lab, Center for Building Materials, Technische Universität München, Baumbachstr. 7, D-81245 Munich, Germany

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ABSTRACT

Ultrasonic measurements can be used to monitor concrete setting. To relate these measurements to fundamental changes in the cement paste, the results have been compared to the microstructure development as simulated with an adjusted version of the pixel model CEMHYD3D. The adjustments were validated by comparison with results of isothermal calorimetry, electron microscopy and thermal analysis. Mixtures in which the Portland cement was replaced by different dosages of blast-furnace slag and fly ash were tested. A multi-variate and multi-way regression was then performed between the ultrasonic results and the microstructure quantities.

For most microstructure parameters, the smallest difference between the simulated and predicted values is achieved with the models starting from the ultrasound frequency spectra. However, the difference with the ones based on the velocity and energy ratio remains often restricted. The degree of cement hydration, solid percolation and formation of hydration products is clearly related to the ultrasonic measurements. Only the pore space percolation does not relate to the measurements at all.

1. Introduction

The potential and advantages of ultrasonic measurements to monitor the setting process of mortar or concrete have been elaborated by the author in previous publications [1–3] and by other researchers such as Reinhardt and Grosse [4], Voigt et al. [5] and Lee et al. [6]. The change in velocity, amplitude and frequency content of compression waves (p-waves) sent through a hardening specimen indicate the change in stiffness of the sample. The corresponding microstructure development in the cement paste fraction fundamentally causes this change from fluid to solid, but is however still difficult to be monitored experimentally. While the hydrated microstructure at a certain age can be investigated in two dimensions using scanning electron microscopy (SEM), the three-dimensional microstructure change from viscous suspension to solid is difficult to observe with traditional laboratory equipment. The microstructure development of the cement paste includes the formation of hydration products (solid phase) and pore structure (pore phase). The fraction of solid particles, connected from one side to the other (solid percolation) is the parameter which is most directly related to the setting [7] and can best be measured in three dimensions. Rapoport et al. [8] suggested that also the pore space depercolation might influence the ultrasonic measurements during setting. Pore space depercolation occurs when no complete pathway of water from one side of the specimen to the other exists anymore. Even after solid percolation, the ultrasonic measurements are still affected by the microstructure as the hydration products fill up the pore space and thereby increase the elastic moduli.

Computer simulation models offer an alternative for laboratory experiments to study the microstructure changes in fresh cement paste during setting and also enable three-dimensional observations. The relation between early-age microstructure development and ultrasonic velocity change has been investigated by Ye [7] with computer simulations for ordinary Portland cement (OPC). The largest velocity increase occurred during setting when the cement hydrates start to percolate and form complete pathways of connected particles for the ultrasonic pulse wave. The study was however restricted to the ultrasonic wave velocity and blended cement types were not investigated.

1.1. Objectives

In this research, the relation between ultrasonic measurements and fundamental changes in the cement paste is investigated for several mixtures with ordinary Portland cement (OPC) and

* Corresponding author. Tel.: +32 9 264 55 22; fax: +32 9 264 58 45.
E-mail address: Nele.DeBelie@UGent.be (N.D. Belie).

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additions such as fly ash (FA) and blast-furnace slag (BFS). To simulate the microstructure changes, CEMHYD3D was selected as computer model. The objectives of this study can be divided into two parts. First, the CEMHYD3D model was extended to include considerations of pH of the pore solution, and to be applicable to cement blended with BFS and FA. The original version will be indicated as CEMHYD3D v.3, the adjusted version as v.3n. The adjustments were validated by comparison with results of isothermal calorimetry, electron microscopy and thermal analysis. Secondly, the measured ultrasonic velocity, energy and frequency spectrum were related to volume fraction (connected) solid phase and other microstructure parameters with the support of the extended CEMHYD3D model. For this purpose, a multi-variate and multi-way regression was performed between the ultrasonic results and the microstructure parameters.

1.2. Simulating microstructure development

Several cement microstructure models have already been developed, which can mainly be divided into vector (e.g. HYMOSTRUC [9]) and discrete models (e.g. CEMHYD3D [10]). Details about these models can be found in the work of van Breugel [11] and Bentz [10].

CEMHYD3D offers the possibility to simulate the hydration of blended cement, which is necessary for this study. Moreover, the open-source code allows the user to adjust the model if necessary. In CEMHYD3D, cement particles are represented by a spherical collection of voxels (1 μm^3) to which mineralogical phases are assigned according to the clinker distribution on a SEM image. The autocorrelation function is calculated which expresses the probability that the neighbouring pixels will be of the same phase. This spatial correlation is then applied in three dimensions. The chemical reactions between these pixels are simulated by cellular automaton (CA) rules, applied to the pixels of the microstructure forming potential reaction sites for a given iteration [12].

1.3. Relating ultrasonic measurements to the microstructure development

During ultrasonic measurements, a large amount of data can be collected. For different mortar and concrete samples, the velocity, energy and frequency content of ultrasonic waves sent through this hardening sample are recorded in function of time. The analysis of such data sets with more than one statistical variable can be performed with multi-variate data-analysis techniques. In a previous publication, Robeyst et al. [1] related the change of the frequency spectra to the setting behaviour by multi-way data-analysis, a specialised branch of multi-variate statistics extending the standard methods for two-way data to multi-way data.

In this study, the relation between the ultrasonic results and microstructure parameters is investigated by multi-way regression. Comparable to normal linear regression, a relation between predictor (ultrasonic results) and response data (microstructure parameter) is determined. The method of multi-variate and multi-way regression analysis was chosen in order to predict the microstructure parameters based on as much ultrasonic measurement data as possible in their original two-dimensional (velocity/energy in function of sample and concrete age) or three-dimensional structure (frequency content in function of concrete sample, frequency and concrete age). Moreover, multi-way analysis allows comparing the results of all samples simultaneously and detects differences and similarities based on the variation of the entire dataset.

2. Materials and methods

2.1. Mixtures

The chemical and physical details of the OPC (CEM I 52.5 N), BFS and FA are given in Table 1. Cement paste mixtures were used to study the heat release during hydration, both by experiments and simulations. A slag-to-binder (s/b) ratio of successively 0, 0.30, 0.50, 0.70 and 0.85 and a water-to-binder (w/b) ratio of 0.5 was used for the BFS mixtures. The compositions with FA had a w/b ratio of 0.4 and a fly-ash-to-binder (f/b) ratio of successively 0, 0.35, 0.50 and 0.67.

For the ultrasonic measurements, concrete mixtures were made with a w/b ratio of 0.5 and 0.4 for BFS and FA mixtures, respectively (Table 2). However, since only cement paste can be modelled with CEMHYD3D, the corresponding simulations were performed on the cement paste fraction of these mixtures. According to Eq. (1), which is based on the principles of the MBE method (Mortier de béton équivalent) [13], the w/b ratio of this cement paste fraction was calculated to be 0.45 and 0.35 for the BFS and FA mixtures respectively.

$$\Delta f_{water} = f_{sand} \cdot A_{sand} - f_{gravel,1} \cdot A_{gravel,1} - f_{gravel,2} \cdot A_{gravel,2} \quad (1)$$

f and Δf are respectively the mass fraction and the change in mass fraction of the indicated component. The absorption coefficients were 0.009 for 0/4 sand (A_{sand}), 0.015 for 2/8 gravel ($A_{gravel,\ 1}$) and 0.014 for 8/16 gravel ($A_{gravel,\ 2}$) as determined according to EN 1097-6. Jones' multi-phase theory [14] states that the transit time of an ultrasonic wave in multi-phase media equals the sum of the transit times in each phase. The velocity in concrete and in the corresponding cement paste fraction would thus be directly related. However, the presence of sand and gravel in concrete already causes a different hydration and setting behaviour compared to cement paste due to the thermal capacity, surface area and interfacial transition zone of the aggregates. Moreover, although the increase in wave velocity and energy is mainly caused by the monitored setting, also other factors such as air bubble migration, internal settling and thixotropy affect the velocity change in time [3]. This can also cause differences between ultrasonic velocity measurements on cement paste, mortar and concrete. Finally, for the measurements of ultrasonic energy and frequency content changes,

Table 1
Chemical composition (%), mineralogical composition according to the Bogue calculations (%), specific gravity (–) and Blaine specific surface area (m^2/kg) of the cement, blast-furnace slag and fly ash.

Binder		CEM I 52.5 N[a,b]	BFS	FA[b]
Chemical composition				
CaO	C	62.21	41.70	3.21
SiO_2	S	18.84	34.09	53.58
Al_2O_3	A	5.39	10.19	26.49
Fe_2O_3	F	3.79	0.48	7.01
MgO	M	0.86	7.62	2.08
SO_3		3.06	1.71	–
CO_2		0.72	0.25	–
Na_2O		0.41	0.29	0.52
K_2O		0.77	0.37	3.58
Cl^-		0.04	0.013	–
LOI		1.89	0.48	3.90
Mineralogical composition				
C_3S		66.8	–	–
C_2S		4.2	–	–
C_3A		4.9	–	–
C_4AF		14.2	–	–
Specific gravity		3.12	2.80	2.55
Blaine		390	400	275

[a] Nomenclature according to EN 197-1.
[b] Mean chemical composition of two batches.