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Ultrasonic monitoring of the setting of cement-based materials: Frequency dependence

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HIGHLIGHTS

- The ultrasonic wave reflection measurement is applied to investigate the setting.
- The wave reflection shows frequency dependence during the setting of cement paste.
- The 2.6 MHz-wave probes faster evolution of shear impedance than the 4.6-MHz wave.
- The frequency dependence is due to the complex pore path and its contraction with hydration.

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ABSTRACT

The microstructure of cement-based materials evolves during cement hydration. The foundation of the microstructure is laid during the setting period of concrete. This study experimentally monitors the evolving microstructure network of very early-age cement paste during the setting period. The ultrasonic wave reflection method was applied to probe paste samples, which allows us to obtain the frequency dependence of mechanical impedance. The frequency dependence is due to the development of a pore network and hence inversely describes the initial setting of concrete. A total of 11 cement paste mixes were prepared a different water-to-cement ratios and with the use of various admixtures. Finally, the critical time of frequency-dependent impedance is compared with the initial setting time measured by a Vicat needle test, and the results are discussed with the length of pore path.

1. Introduction

Freshly mixed cement-based materials at rest gain resistance to external loading even before its setting and hardening. Consequently, slip-form concrete pavement obtains its shape stability [1] and the form pressure of self-consolidating concrete rapidly decreases even before the setting time of concrete [2,3,40]. This is generally explained with thixotropy in the rheology of concrete. Industrial need and recent advances on self-consolidating concrete have motivated scientists to investigate the evolving microstructure as well as the rheology of cement-based materials during this pre-setting period.

In the period before and after the setting, the network of dispersed cement paste particles develops and grows with solid percolation. Percolation theory was applied to account for the connected solid phase [4–6], and the effective connection according to the contact area between solid phases was studied to explain the evolution of the elastic modulus [7]. The connection of the growing cement particles initiates a solid-phase porous network [8], which causes the phase change of the concrete mixture. Finally, the porous network gradually fills up with hydrates. Sant et al. [43] presented various experimental techniques to investigate the setting of cement-based materials. In the paper, it is noted that the experiment related to the setting needs special care due to immature microstructure. This study proposes a new technique to experimentally monitor the evolving network during the setting period.

Ultrasonic techniques have been widely used for monitoring the evolution of the microstructural network, because the use of invasive methods can have critical effects on the premature microstructure [9]. The ultrasonic pulse velocity (usually abbreviated as UPV) is a through-transmission measurement. An increase of UPV indicates a rise in the modulus of a material. The embedded transducer is also used to monitor the P-wave (primary wave or longitudinal wave) velocity and to overcome a limitation about

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boundary condition during the measurement [35]. The shear wave can be used to probe the development of a solid phase [10,39], but before setting or hardening of concrete the shear wave can hardly propagate through material due to a disconnected solid phase (approximately less than 12 h after it is mixed). On the other hand, ultrasonic wave reflection (UWR) is a one-sided approach that measures the mismatch coefficient of the mechanical impedances between a buffer (reference) material and a sample. A single pulse excited by the transducer's own resonance is reflected at the interface between the buffer and sample. The reflection coefficient depends on the evolving properties of the sample. The shear wave in the UWR technique does not need to be propagated through the thickness, which could be a limit for field application on concrete structures. The UWR technique still needs more application study on concrete in field. Nevertheless, looking at it the other way round, no through-transmission allows us to sensitively monitor the change of immature microstructure during the setting of cement paste.

Various applications using the UWR technique have been reported in the literature. Monitoring the hardening of cement-based materials is the first task and the results are sometimes correlated with the strength gain. Stepignik et al. [11] introduced UWR measurement for tracking cement hydration. Ozturk et al. [12] and Rapoport et al. [13] advanced the technique with shear waves to probe the solidification of cement-based materials, where the sample was assumed as a Hookean solid. The studies conducted by Subramaniam et al. [14], Akkaya et al. [15], Sun et al. [16], Kim et al. [17], Chung et al. [37], and Trtnik et al. [38] tried to find a correlation between the strength gain and variables from the wave reflection measurement. Voigt et al. [18–20] also reported comparisons with other physical signatures such as non-evaporable water amount, microstructural parameters, and temperature rise. However, the assumption of a Hookean solid is too early for cement-based materials during the setting period. Subramaniam et al. [21], Sun et al. [22], and Wang et al. [23] therefore analyzed the signal measured on very early-age cement-based materials based on the theory of viscoelasticity. In addition, Subramaniam and Wang [24] adopted the Biot theory of poroelasticity for the purpose.

This paper discusses the frequency dependence on the UWR signal, which is due to the complex pore path and its contraction with hydration process. A total of 11 cement paste mixtures were examined, where the samples were proportioned with various water-to-cement ratios and various admixtures such as a high-range water-reducing admixture (HRWRA), a viscosity modifying admixture (VMA), and a mineral admixture.

2. Experiment

2.1. Sample preparation

Cement paste samples mixed with Portland Type I cement were investigated. Their mix proportion is listed in Table 1. The first group was prepared with different water-to-cement ratios (*w*/*cm*). These values for Mixes C1, C2, C3, and C4 are respectively 35%, 40%, 50%, and 60% by weight. The second group with Mixes C5 and C6 incorporated a HRWRA. A polycarboxylate-based admixture with a solid content of 30% by weight and 1.04 specific gravity (ADVA 360, W. R. Grace & Co.) was evaluated. The HRWRA dosage for Mixes C5 and C6 were respectively 0.1% and 0.6% of cement mass while both mixes had a *w*/*cm* of 35%. The third group with Mixes C7, C8, and C9 was designed to show the effect of the VMA used in the study, which was synthetic with a solid content of 3% and a specific gravity of 1.002 (V-MAR 3, W. R. Grace & Co.). The VMA dosages for Mixes C7, C8, and C9 were respectively 0.2%, 0.4%, and 0.6% of cement mass and their mix proportion was a *w*/*cm* of 35% and they had a HRWRA dosage of 0.6%. In the fourth group a mineral admixture was used. It was wet-processed attapulgite clay composed of magnesium aluminosilicate (Acti-gel 280, Active Minerals International, LLC). Due to its small size at nanoscale, it is usually called nanoclay. The nanoclay addition for Mixes C10 and C11 was respectively 0.2% and 0.6% of cement mass. Their mix proportion was a *w*/*cm* of 35% and they had a HRWRA dosage of 0.6%.

Table 1
Mix proportions of prepared samples.

Label	Description	Water (g)	Cement (g)	HRWRA (g)	VMA (g)	Clay (g)
C1	*w*/*cm* = 35%	524	1498	–	–	–
C2	*w*/*cm* = 40%	558	1394	–	–	–
C3	*w*/*cm* = 50%	612	1226	–	–	–
C4	*w*/*cm* = 60%	654	1090	–	–	–
C5	HRWRA = 0.1%	524	1498	1.5	–	–
C6	HRWRA = 0.6%	524	1498	9	–	–
C7	VMA = 0.2%	524	1498	9	3	–
C8	VMA = 0.4%	524	1498	9	6	–
C9	VMA = 0.6%	524	1498	9	9	–
C10	Clay = 0.2%	524	1498	9	–	3
C11	Clay = 0.6%	524	1498	9	–	9

Each one-liter volume sample was mixed. The mixing protocol was fixed for all samples: (1) water soaking for 2 min; (2) low-speed planetary mixing for 5 min; (3) scraping the mixing bowl within 1 min; and finally (4) medium-speed planetary mixing for 5 min. The duration for casting the samples in the UWR mould took approximately 3 min. The UWR measurement was then performed in a chamber maintaining a relative humidity of 60% and a temperature of 18 °C, where the sample was covered with polymer film to prevent water evaporation.

Aside from the UWR experiment, a conventional Vicat needle test [25] was applied to replicated samples of Mixes C1 to C4. The measured initial and final setting times are reported in Table 2 where their bulk densities are also listed. The setting time of cement paste is affected by *w*/*cm* as expected: a high water content delays the setting time. The ultrasonic pulse velocity (UPV) of Mix C2 (*w*/*cm* of 40%) was also measured using P-wave through-transmission method. The thickness of unset cement paste was 3 cm. Three samples of freshly mixed cement paste were prepared and averaged result is plotted in Fig. 1. Measurement was performed every 30 min during 24 h. Increase of UPV was investigated as expected. The monitoring of UPV can reflect a hardening and solidification of fresh mixture but hardly indicates a setting process or setting time. In addition, the yield stress and plastic viscosity of Mixes C1 to C6 were measured with a rheometer (RS150, HAAKE GmbH). The shear stress was measured with an increasing shear rate up to 100 s^{-1}, and the Bingham parameters were extracted by a nonlinear regression. Details of the rheological test can be found in the literature [26]. Fig. 2 shows the rheograph of the samples. As expected, a higher *w*/*cm* decreases both the yield stress and plastic viscosity and the use of HRWRA reduces the yield stress dominantly.

2.2. UWR measurement

The UWR experiment measures the mechanical impedance of a sample compared to that of a buffer material with known properties. A shear wave was used to sensitively monitor the solid-phase evolution in this study. Fig. 3 shows the experimental setup of the UWR measurement. The setup is principally the same with that used in the previous study except the use of two different transducers. A single sample was prepared by following the process described in the previous section and distributed into two containers. The inner diameter of the container was 100 mm and the sample is filled up to 100 mm in height. The bottom of the containers was specially designed to mount a transducer. One container had 2.25 MHz transducer and the other had 5 MHz transducer. A pulser-receiver (500PR; Panametrics Inc.) was used to generate a single 400 V-peak square pulse and receive the reflected signals. A contact-type transducer, of which the center frequency is 2.6 MHz (V154; Panameterics Inc.) or 4.6 MHz (V156; Panameterics Inc.), was located beneath the buffer. A pulse applied on one side of the buffer material is reflected on the other side where the cement paste is placed. Received signals were

Table 2
Comparison of the setting time of the cement paste samples.

w/*cm* (%)	Density (kg/m^3)	Initial setting (h)	Final setting (h)	1st Critical time (h)	2nd Critical time (h)	The impedance at the 2nd critical time (MRayls)
35	2038	3.40	5.60	2.2	2.6	0.02
40	1920	4.00	6.20	2	4.3	0.37
50	1809	4.75	7.05	1.5	5.6	0.41
60	1733	6.25	9.00	2	5.9	0.39