Pergamon

Cement and Concrete Research 30 (2000) 1633–1640

CEMENT AND CONCRETE RESEARCH

Hydration of cementitious materials by pulse echo USWR Method, apparatus and application examples

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Received 3 February 2000; accepted 20 June 2000

Abstract

In this paper, a novel nondestructive method based on a pulse echo ultrasonic shear waves reflection (USWR) technique is described. The method is implemented in a home-built field testing apparatus of which construction and operating principles are briefly explained. With the instrument, the time dependence of the reflection coefficient r due to the hydration of cementitious materials is measured automatically with the result continuously displayed and recorded. The changes of the reflection coefficient Δr with time are related to the changes of the viscoelastic properties, in particular to the dynamic shear modulus G of the material investigated. From the application examples on selected cementitious materials shown, the sensitivity of the method and of the apparatus to different parameters (composition, water/solid ratio, fineness, addition of additives, aging) is evident. Possible practical applications are nondestructive measurements of the shear rigidity of the fragile CHS structures with no external shearing applied and cement setting time determinations.

Keywords: Cement paste; Hydration; Elastic moduli; Rheology; Ultrasonic shear wave reflection

1. Introduction

The rheological properties of hydraulic materials — water slurries during the early age of hydration, i.e., during some time after mixing with water — encompass a wide range of behavior from nearly Newtonian fluid at the instant of mixing, through viscoelastic Voigt-type behavior to rock-hard Hooke's elastic solid with considerable compressive strength. The duration of the transition periods from one type of behavior to another depends on the material investigated and varies from a few minutes in the case of gypsum to several hours in Portland cement pastes.

Acoustic waves are being used successfully for the determination of mechanical properties of hardened cement pastes and concrete. The types of waves generally used are compressional which travel in solids, liquids and gases [1,2]. The parameter measured is usually the longitudinal velocity c_L related to the modulus of elasticity E. The same method can be used for the early age hydration studies of cement pastes, but due to the pour transmission of the p-waves and relative insensitivity of c_L to the formation of the rigid gel CSH structures in the pastes in the early ages (preinduction, induction and early acceleration) of hydration, limited literature is available [3–7]. A method for determining the setting times of cement slurries based on the transmission of pulsed acoustic shear waves was recently patented [8]. A pulsed acoustic transverse wave reflection method for early hydration of cement pastes was first reported two decades ago [9]. In this work, the reflection coefficient r of a pulsed ultrasonic shear wave and the relative phase difference φ of the incident and reflected waves from a quartz/cement paste interface were measured. From the reflection data, the dynamic shear modulus G and the dynamic viscosity η of some cement pastes were calculated. Since these quantities are changing in the process of hydration, the method gives specific information on its kinetics. Noticeable in these experiments is a very good S/N ratio. Of course, special and rather expensive commercial equipment was used. To the author's knowledge, no other reports have surfaced for more then a decade. Some works on the use of the shear wave reflection for setting and hardening of cement-based materials have appeared very recently [10].

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0008-8846/00/$ – see front matter
PII: S0008-8846(00)00352-5

In 1966, a project to build a laboratory prototype of an apparatus, based on a modified pulse echo ultrasonic shear waves reflection (USWR) method and simplified home-built electronics, has been started with the aim of making a compact, portable instrument for hydration (gypsum and cement-based materials) and reaction (alumina ceramics, gluing compounds) hardening kinetics studies [11,12]. The laboratory prototype was extensively tested in order to improve its performances (long-term stability, S/N ratio, accuracy, reproducibility, influence of temperature, adherence of the samples to the measuring head, transducer geometry, sample ambient conditions) and to determine its application possibilities [13]. With the data obtained, a field testing prototype — Hardening meter USWR-2 — was constructed [14]. Herewith, a description of the pulse echo USWR technique and of the apparatus with some application examples to hydraulic materials is presented. A more extensive presentation of other results, demonstrating further possible research/technological applications to hydraulic materials, will be given in a subsequent paper.

2. Method

When a pulse of an ultrasonic wave hits an interface, e.g., quartz/cement paste, it is partially reflected back into quartz and partially refracted into the paste. In the case of a normal incidence, the ratio between the amplitudes of the reflected (A_r) and of the incident (A_i) pulse is the complex reflection coefficient $\tilde{r}$, which can be expressed as:

$$\tilde{r} = \frac{A_r}{A_i} = \frac{Z_2 - Z_1}{Z_2 + Z_1}, \tag{1}$$

where Z_1, Z_2 are, in general complex, acoustic impedances determined by the viscoelastic properties of each of the two interface-forming media [15]. The acoustic impedance for a shear wave in an isotropic, homogenous medium is:

$$Z = \sqrt{\rho(G + i\omega\eta)}, \tag{2}$$

where ρ is the mass density and ω the angular sonic frequency. Eq. (2) can also be written in the form $Z=(R+iX)$ with its real and imaginary parts related to G and η of the medium by the equations:

$$\eta = \frac{2RX}{W\rho}, \tag{3}$$

$$G = \frac{R^2 - X^2}{\rho}. \tag{4}$$

Thus, knowing Z, the viscoelastic properties of a medium can be evaluated.

One way of determining the acoustic impedance of a medium is by measuring the reflection coefficient $\tilde{r}$ from an interface formed with a medium of known Z. The complex reflection coefficient defined with the Eq. (1) can be written in the form:

$$\tilde{r} = r(\cos\varphi + i\sin\varphi), \tag{5}$$

where r is its magnitude and φ the phase angle shift between the incident and the reflected waves. By combining Eqs. (3), (4) and (5), the two components of the shear acoustic impedance are [Eqs. (6) and (7)]:

$$R_2 = Z_1 \frac{1 - r^2}{1 + r^2 + 2r\cos\varphi}, \tag{6}$$

$$X_2 = Z_1 \frac{-2r\sin\varphi}{1 + r^2 + 2r\cos\varphi}. \tag{7}$$

The unknown impedance $Z_2=(R_2,X_2)$ and consequently the viscoelastic properties (G_2,η_2) can thus be evaluated from the reflection data from the known Z value of medium 1 and with the assumption that the medium 2 mass density remains constant during the hydration process. The medium 1 in the apparatus presented is fused quartz with $Z_1 = 8.29 \times 10^6$ Ns/m^3 [15]. An easy way to verify the Z value for the quartz used in the measuring head of the apparatus is described in Section 3. Regarding the assumption about the density of the medium 2, i.e., of cement pastes, it is generally accepted that it does not change much during hydration (<1% during 1-year period). The shrinkage of cement pastes of normal consistency is less then 0.1% in the first 24 h for Portland cements [16]. Also, practically no change of the density is experimentally noticed when measuring r (by observing the recess of the outer surface of the paste sample which is leveled with the topside of the sample holder after filling). The densities do vary slightly with the water/cement (w/c) ratio. For w/c values between those of normal consistency and 0.60, they fall within (2.0 ± 0.1) kg/dm^3. The densities of some of the pastes used in these experiments were actually measured with the results within the stated range. The density of fully hydrated Portland cement is 2.13 kg/dm^3 [16].

It has been shown experimentally for the fused quartz/cement paste interface that the relative phase changes during the hydration are quite small with little influence on the magnitude of G when evaluated from Eq. (6) by taking $\varphi = 0$ [9]. This observation is rather important since the measurement of φ makes the instrumentation more complex and difficult. In this case, Z_2 is real [Eq. (8)]:

$$Z_2 = Z_1 \frac{1 - r}{1 + r}, \tag{8}$$

and the equation for G reduces to:

$$G_2 = \frac{Z_1^2}{\rho_2}\left(\frac{1 - r}{1 + r}\right)^2. \tag{9}$$

By substituting r with $(1-\Delta r)$ in Eq. (9), we obtain:

$$G_2 = \frac{Z_1^2}{4\rho_2}\left(\frac{\Delta r}{1-\Delta r/2}\right)^2, \quad (10)$$

which directly relates the measured reflection coefficient changes Δr with the growing shear rigidity in the hydration process. In the pastes in which Δr is small (<0.20) — the case of cement pastes in the first few hours of hydration or pastes with higher w/c ratio — Eq. (10) can be approximated with:

$$G_2 = \frac{Z_1^2}{4\rho_2}(\Delta r)^2, \quad (11)$$

meaning, that the shear modulus G of a hydrating paste is proportional to the square of the reflection coefficient change.

One of the most important quantities specifying the quality of cement is its compressive strength σ. This is proportional to $E^{1/2}$ and thus to $G^{1/2}$ since the two moduli are linearly related via the Poisson relation:

$$G = E/2(1+\mu), \quad (12)$$

where μ is the Poisson number. Eq. (12) is valid for homogenous, isotropic, elastic solid. There is no evidence that a similar relationship is valid also for fresh cement pastes, but it is accepted that, as the number of physical and chemical linkages via hydration increases, they do exhibit some elements of elasticity or elastic–plastic behavior. The elastic modulus E and hence the shear modulus G increase, and thus, the measurements of G give an indication of the rate of structure build-up in the early ages after mixing. Since G and Δr are related via Eq. (10), the Δr changes also reflect the growing of the compressive strength σ of a cement paste, which is, following Eq. (11), proportional, i.e., $\sigma \propto \Delta r$, for small values of Δr.

3. Apparatus

A simple block scheme of the field testing apparatus for pulse echo shear wave reflection coefficient measurements is shown in Fig. 1. The apparatus consists of a mainframe box with transmitter/receiver electronics, an A/D converter board, a power supply, a measuring head and a PC computer (with suitable software).

The measuring head is of rugged construction and consists of a cylindrical aluminum body ($\phi=30$, $l=40$) into which a very pure fused quartz rod of rectangular cross-section ($a=13$, $b=16$) and length $L=62$ is rigidly fastened (dimensions in millimeters). The two end surfaces of the quartz rod are flat, very parallel and highly polished. On one end (bottom), a PZE ultrasound shear wave transducer, acting as transmitter and receiver, is hard-bonded. On the other end (top), with a measuring surface of about 2 cm^2, the sample to be tested is smeared. The thickness of the sample

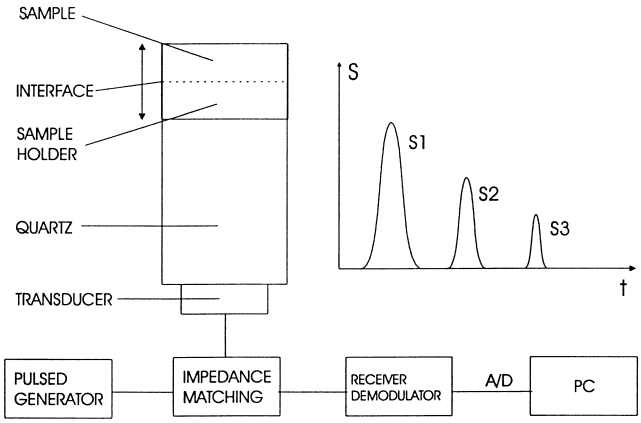

Fig. 1. Block schema of the pulse echo USWR apparatus.

(typically 10 mm) can be adjusted by sliding a sample mould (Teflon or Plexi glass) up or down the external surface of the quartz rod (Fig. 1). The amount of the sample needed for one measurement is small (10 g or less).

Measurement of r in the manner suggested by Eq. (1) is not possible with high-enough accuracy, since there is a significant interference between the full-scale excitation of the transducer and the bottom surface echo (i.e., the amplitude A_i cannot be determined). Instead, the first (s_1) and second (s_2) back echoes (Fig. 1) are used for determining the reflection coefficient as follows. A pulse generator excites the transducer with a short (4 μs) low-power (2 W) rf pulse (17 MHz) every 1 ms. The result is a rf ultrasonic shear wave pulse with an amplitude A_i traveling to the top end of the quartz with the shear sound velocity c_{s_1}. When hitting the quartz/sample interface, the pulse is partially reflected back into the quartz. The reflected wave, on reaching the quartz's transducer side surface, excites the PZE crystal giving an electric signal (first back echo s_1). Part of the returning wave reflects back into the quartz rod and travels to the interface where it is partially reflected again. On the return to the transducer, it excites another echo (second back echo s_2) with smaller amplitude. The bouncing of the pulsed wave repeats again giving a third back echo (s_3) and so on. The result is an echo train with repetition of 1 ms. The time interval between the echoes is $2L/c_{s_1}$. The number of echoes in a train (about 10) depends on the reflection coefficient r of the interface and on the internal losses due to the absorption, scattering and divergence of the ultrasound beam. The coefficient r is obtained by measuring s_1 and s_2 back echo amplitudes with a preset amount of signal averaging prior being collected by a PC computer. With a software program installed, one can then continuously view the Δr change in real time on a PC monitor.

The specific dimensions of the parts of the measuring head are not decisive for the results. An exception is maybe the length of the quartz rod, which should not be too short in order for the echoes in the echo train to be sufficiently separated. For practical reasons, an excessive length is not

desired either. Its length does not influence the resolution of the reflection coefficient. A good contact between the quartz and the paste is required. This is not a problem with Portland cement pastes. Such a contact with the mold is not necessary, nor is the mold itself. The measuring head can be simply deepened upside down or horizontally into the paste. The reason for using a mold is primarily for ease of the removal of the hardened paste from the head, material savings and defining identical environ conditions for comparative measurements. The angle of the incidence must be very normal in order to avoid secondary echoes from the sidewalls to interfere with the principal echoes. This requires a parallelism for the two end surfaces of about 10 min angular. By measuring the time between any two echoes with a CRT, the value of Z_1 can be easily determined with the USWR apparatus. With this value and with the known length L, the speed of sound c_{s_1} can be obtained and Z_1 ($=\sqrt{\rho_1 c_{s_1}}$) calculated using the known value $\rho_1 = 2.2$ kg/dm^3 for the fused quartz density. Within the experimental accuracy ($<\pm 1\%$), the value so obtained is equal to the value reported in Section 2.

The amplitudes (s_1,s_2) of the first two echoes are proportional to ($A_i r$) and ($A_i r^2 r_o$), respectively, where r_o is a constant representing the reflection coefficient during one passage of the quartz rod with no sample (with quartz/air interface). The main contribution to r_o is the reflection on the quartz/transducer interface. The ratio of the two echo amplitudes is:

$$s_2/s_1 = r r_o. \tag{13}$$

The constant r_o in Eq. (13) can be obtained (eliminated) by measuring the two echoes with no sample (medium 2 being air or water). The air or liquid with low viscosity (like water) does not support shear waves. A shear wave is fully reflected on such interfaces (i.e., r_{air} and $r_{H_2O} = 1$). Therefore, $(s_2/s_1)_{air} = r_{air} r_o = r_o$ and the reflection coefficient can be obtained from the ratio:

$$r = (s_2/s_1)_{sample}/(s_2/s_1)_{air}. \tag{14}$$

The value $(s_2/s_1)_{air}$ is essentially a normalization factor characteristic for each measuring head. Eq. (14) infers two echo signals to be collected by a PC, requiring two A/D channels. It turns out that the data collection can be simplified. The echo amplitude s_1 can be internally (electronically) amplified $u_1 = k s_1$ to a preset level, e.g., u_0. Therefore, $(u_1)_{sample} = (u_1)_{air} = u_0$. The second echo s_2 is amplified with the same amplification factor k, giving a signal $u_2 = k s_2$ and therefore:

$$r = (u_2)_{sample}/(u_2)_{air}. \tag{15}$$

This technical improvement, incorporated in the apparatus, allows measuring r by collecting only one signal, reducing the A/D channel requirements to one per measuring head. In a typical measurement, one starts the measurement to collect data with no sample for a few minutes and then, with the apparatus running, the sample is smeared. The short initial part of the signal trace gives the constant values $(u_2)_{air}$ needed to normalize the sample signal curve according to Eq. (15). The signal is stored at the end of the experiment automatically and saved in the form of a .txt data file, which can then be processed with any data analyses software (e.g., Origin).

During the hydration, $r(t)$ decreases with time (from the value of 1), the changes being due to the hydration products build-up. In presenting the reflection coefficient data, it is better to plot the change of the reflection coefficient [Eq. (16)]:

$$\Delta r(t) = 1 - r(t), \tag{16}$$

which is increasing with the continuing hydration process. In this way, the $\Delta r(t)$ diagrams resemble the diagrams of the increasing degree of hydration $\alpha(t)$ and of the compressive strength $\sigma(t)$ time development during hydration obtained with other methods. It is in this sense that the $\Delta r(t)$ changes in further text are sometimes equated with the hardness.

The pulse echo USWR method presented here is very fast (one echo train every 1 ms). Since the hydration processes in cementitious materials are rather slow (e.g., early hydration in the PC cement pastes takes place several days) and the number of influential parameters is high, a multi-head apparatus (one instrument serving several measuring heads) has been constructed and successfully tested. The information on constructional/operational details with the results demonstrating technical performances (reproducibility, accuracy, long-term stability and temperature stability, etc.) of the apparatus will be presented in a separate paper. Therefore, only some general figures are included here. The transmitter/receiver continuously functions as soon as the apparatus is switched on. For the past 14 months, it has been left turned on except for short periods (failures of the mains, longer holidays). During this period, the apparatus experienced about 10^8 pulsed echo trains without failures. The instrument is stabilized after about 15 min warm-up time. The accuracy of measuring r is $<\pm 0.5\%$ and better when echoes are high (for smaller Δr). The long-term stability of the apparatus is $<\pm 0.2\%/24$ h (obtained by running one of the measuring heads without the sample). The temperature stability of the measuring head is less then —0.2%/°C — when measuring r (obtained by putting the whole measuring head without the sample in an oven and measuring the signal level by varying T from room temperature to 60°C). The inaccuracies due to temperature fluctuations and drifts can be corrected by simultaneously measuring the probe's temperature with the built-in temperature sensor. Repeated measurements of the same sample and with the same measuring head give identical $r(t)$ curves providing identical conditions in all respect. For this ultimate reproducibility, it is required that the ingredients, with which the sample pastes are prepared, have the same temperature for all samples. This is quite often not observed in praxis. Another factor influencing the reproducibility is

the preparation of the pastes, especially when handmixing small amounts of low-water-content samples. In all cases, the reproducibility is better in the early part of the hydration when the reflected echoes are high.

The operating frequency is chosen such that the wavelength λ of the sound wave in quartz ($\lambda = 0.220$ mm) is small compared to the size of the media (rod or sample) through which it travels. In this way, there is no need to consider interferences due to the shape or dimensions of the media. On the other hand, λ is larger than the inhomogeneities in the pastes and the wave sees it as homogenous matter (the RRSB position parameter for cement grains $x' \leq 20$ μm) in the small measuring volume, a thin layer at the interface encompassed by the measuring surface and a penetration depth of approximately one wavelength λ or a fraction of it. Other inhomogeneities like air bubbles, which are a problem in the transmission experiments [5], do not seem to matter in the case of pure pastes. The measured reflection coefficient r is an average over the small volume. The contact surfaces of the hardened pastes, after removing them from the measuring head, are smooth under the microscope with magnification of $\times 100$. This is no longer so in the case of mortar samples, where large proportions of standard sand are mixed. On the contact surface, individual scattered and visible little holes of various sizes appear. The corresponding USWR curves show small undulating behavior likely associated with the air bubbles [12]. Nevertheless, information on the early hydration of mortars can be obtained with the USWR method. Experimental work, including sample de-airing, is in progress.

4. Application examples

All materials used were commercial, generally available products. PC cements are produced by Cementarna, Salonit-Anhovo, Slovenia. The additives, two retarders (Retard M, Retard R2) and two accelerators (Alfa accelerator, Tiksokret), are standard products of TKK, Srpenica, Slovenia. The first three additives named come in liquid form, Tiksokret, as a powder. The pastes were prepared by thoroughly mixing corresponding powders with an adequate amount of distilled water for 3 min and then smeared into the mould. Although the amount of the paste needed is small, about 15 g of cement was used in order to warrant more homogeneously mixed samples. All samples were sealed with thermoplastic laboratory film to prevent evaporation from the top.

In Fig. 2, the $\Delta r(t)$ dependence for three different types of cements (CEM I 52.5R, CEM II/A-S 42,5R, CEM II/B-M 42,5) with the same w/c ratio of 0.30 and for time periods of up to 35 h is presented ($T = 21$°C, RH = 50%).

In Fig. 3, the $\Delta r(t)$ time dependence in the early, first 8 h hydration period for CEM II/B-M 42,5 pastes with three different w/c ratios is displayed. The w/c ratio of 0.26

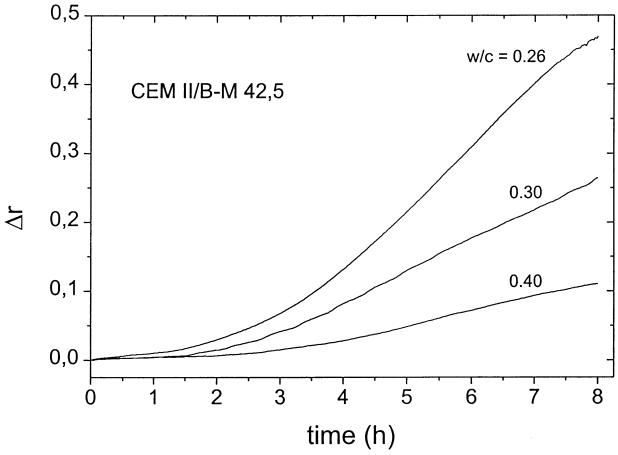

Fig. 3. The Δr change during the early hydration of CEM II/B-M 42,5 pastes with different w/c ratios.

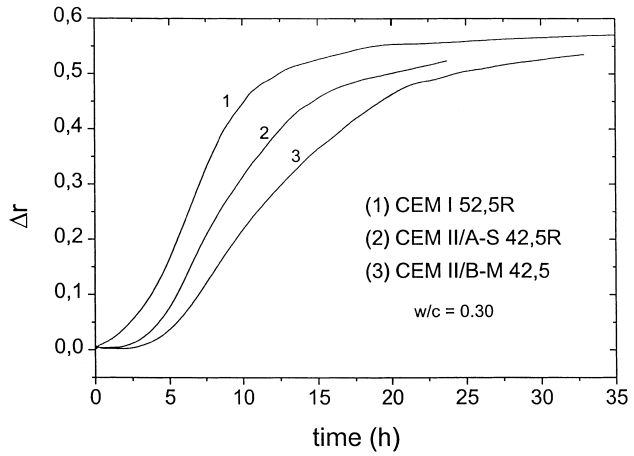

Fig. 2. The Δr change during the early hydration of three pastes made with different cements but with the same w/c ratio.

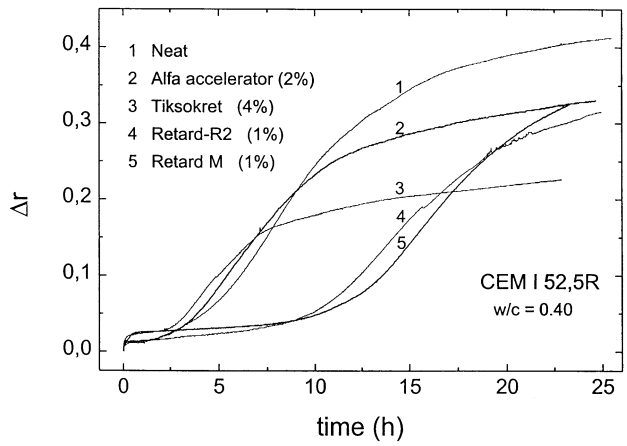

Fig. 4. USWR behavior of cement CEM I 52.5R in the presence of different additives.

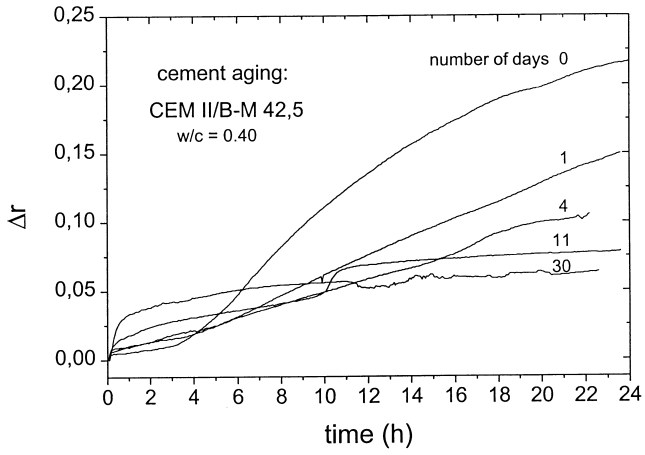

Fig. 5. Hydration of cement pastes prepared with aged CEM II/B-M 42,5.

corresponds to the normal consistency sample. The measurements were made at $T = 22°C$, RH = 60%.

In Fig. 4, the USWR $\Delta r(t)$ hydration curve for CEM I 52.5R paste with w/c = 0.40 is compared with the four USWR curves for the same CEM I 52.5R paste (w/c = 0.40) mixed with small amounts of commercial additives (two accelerators and two retarders). The pastes were handmixed powders with distilled water to which the corresponding amounts, herein expressed in standard terms as concentration by weight of cement (BWOC), of additives were added. The concentrations used are all within the producer's recommended range.

In Fig. 5, the $\Delta r(t)$ time dependence in the first 24 h hydration period for paste (w/c = 0.40) made with non-exposed CEM II/B-M 42,5 cement is displayed and compared with the USWR curves for pastes made with aged CEM II/B-M 42,5 cement with the same w/c ratio. The cement used was forced aged by exposing about 1/2 kg of powder, spread in a layer about 5 mm thick, to $T = 22°C$ and RH = 50%. Small quantities of the powder were removed after being exposed for a certain number (1, 4, 11, 30) of days and stored in sealed plastic containers.

5. Discussion

The results in Fig. 2 clearly show that the $\Delta r(t)$ changes during the early hydration strongly depend on the type of cement. These cements are prepared from the same clinker with 5% of anhydrous gypsum and different amounts of filler materials (blast furnace slag) added and milled to different Blaine-specific surfaces. Noticeably, the duration of dormant period in these cements, the hydration rates in the acceleration/deceleration periods and the times at which the diffusion-limited hydration takes over are quite different for the three cement types. These results are consistent with the known observations that the initial hydration of higher Blaine cements is faster and that the addition of slag acts in the opposite way.

The results on Fig. 3 show that the $\Delta r(t)$ changes during the early hydration of the CEM II/B-M 42,5 pastes depend strongly on the amount of added water. They are consistent with other direct and indirect hydration rates measurements of cement pastes. With the reflection data of Fig. 3, the shear modulus G for the three CEM II/B-M 42,5 pastes were calculated using Eq. (10) and given value for Z_1 and ρ_2. The result is plotted against time in Fig. 6 in order to illustrate the potential of the presented pulse echo USWR technique in detecting the development of physical strength of the early structure. It is seen that in the dormant period, a very slow build-up of a structure develops. At the end of the dormant period, the structure remains quite fragile, reaching G values of < 100 MPa. Thereafter, the structure increases its stiffness very rapidly and reaches a value of 3.5 And 0.8 GPa after 8 h for the w/c = 0.26 and 0.3 samples, respectively. During the same period, the w/c = 0.40 sample remains quite fragile, reaching a G value of only 120 MPa.

In cementing, PC cement systems are routinely designed for temperatures ranging from below freezing to several hundred degrees. In other applications, cement formations are exposed to high pressures or must contend to other special requirements. Most additives are strongly influenced by the chemical and physical properties of the cement and the number of influential cement parameters is large [17]. Fig. 4 is just an illustration of the variability of additive response to the hydration behavior of one type of cement in order to demonstrate the sensitivity of the pulse echo USWR apparatus to such applications. The effectiveness of the two retarders is about the same. They retard the paste stiffening for about 5 h. Retard R2 seems to somewhat thicken the paste soon after adding water. On the contrary, the effectiveness of the two accelerators seems to be different. Tiksokret accelerates the hydration by somewhat less then 1 h, whereas Alfa accelerator does not seem to be very effective. The results also indicate that none of the additive pastes reaches the 1-day strength of the neat paste, that with

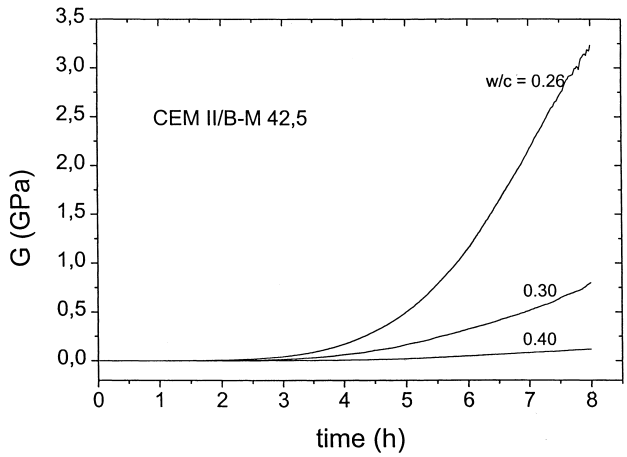

Fig. 6. The time growth of the shear modulus G during the early hydration of CEM II/B-M 42,5 cement pastes with different w/c ratios.

Tiksokret being the lowest. Further experiments combined with differential thermal gravimetric measurements are in progress to address these problems.

The performance of PC cement can be affected significantly by exposure to the atmosphere during storage in sacks. The principal effects of this phenomenon, known as prehydration or aeration, include increased thickening time, decreased compressive strength and heat of hydration and increased slurry viscosity [18,19]. The effects are mainly due to hydration and carbonation reactions with the air's components. The rate at which these processes occur is related to the relative humidity of the storage environment and on the type of cement. In Fig. 5, the effect of forced aging on the early cement hydration is showing up quite drastically in the USWR $\Delta r(t)$ curves. In particular, the results indicate a retardation of setting and a decrease of the early strength concomitant with an increase of stiffening in the first few hours due to the formation of ettringite and aluminate hydrate [19]. The rate of the decrease in the strength seems to take place faster during the first day of exposure. The stiffening in the first few hours is taking place gradually and in the longer exposed samples actually leads to false set. In the curve for the sample exposed for 11 days, there is an abrupt change of Δr at $t = 10$ h. The experiment was repeated with w/c = 0.30 pastes giving similar results. Further studies are needed to explain this behavior.

Albeit basing on the reflection of the waves in a small volume near the probe's end, there are good indications that the USWR method can provide useful information of the inner material. First of all, the method was originally developed as an indirect, objective method for testing cement-based materials, primarily in the early hydration period. It is demonstrated further in this paper and in previous works [12–14] that the method is very sensitive to essentially all parameters influencing the properties of the cement pastes. All of these results are compatible with those obtained by measuring other bulk properties of the cement pastes with conventional methods. Further, several experiments have been designed or planned to find a correlation between the measured reflection coefficient changes Δr with other bulk properties measured with conventional methods. Recent, parallel measurements of the 1-day changes $\Delta r_{1\ day}$ and of the compressive $\sigma_{1\ day}$ and bending $\sigma_{b,1\ day}$ strengths of mortars made with the same cements [20] give a good fit with a model based on Eq. (10). In addition, the USWR Δr curves are of sigmoid form [14], like the amount of hydrated material $\alpha(t)$ measured classically. An intuitively expected linear dependence between $\Delta r_{1\ day}$ and $CH_{1\ day}$, the amount of the $Ca(OH)_2$ after 1 day, a measure of the amount of the hydrated cement, is found using thermogravimetry [20]. Finally, with a multi-probe apparatus mentioned, one can do measurements at several spots of a larger sample. In conclusion, a possible practical example of the use of the USWR method is the measurement of the initial and final setting times. These two times, determined with the Vicat needle test, are rather arbitrary though useful for comparison of cements. They are not related to a fundamental physical property in a simple manner. It has been proposed and demonstrated [21,22] that the Portland cement setting times can be adequately measured with an USWR hardening meter. At the same time, the length of the dormant period could also be determined [14].

6. Conclusions

The suitability of the pulse echo USWR method and the sensitivity of the apparatus for early cement hydration following and testing are apparent from the results presented. The measurements are continuous, nondestructive and with no external shearing applied (no moving parts). The response time of the apparatus is less then 1 s. The earliest usable time is limited by the time needed to prepare a sample and there are practically no limitations on the duration of the measurements, extending well into the hardened state. However, the most sensitive application range is the very early hydration stage (e.g., first day) in which the rigidity rate growth is fastest.

With the apparatus, the reflection coefficient r of the ultrasonic shear waves can be very accurately measured. The changes Δr of the reflection coefficient are very sensitive to many parameters (composition, water/solid ratio, fineness, addition of additives, aging) determining the physical properties of cements. This implies some application possibilities of the instrument in research and in field testing or production control of cements, one of them being the setting times measurement [22] as a complimentary method to standard Vicat test.

A great deal of research has been carried out into the chemistry of early hydration reactions between cement and water, improving our understanding of how cement grains hydrate. However, little work has been done to relate formation of the various chemical structures quantitatively to the physical strength or elastic stiffness of the hydration of cement gel. It is shown that the changes $\Delta r(t)$ are related in a simple manner to the dynamic shear rigidity module $G(t)$. Thus, the pulse echo USWR apparatus described offers a possibility of real time following of the physical strength growth in a domain of fragile CSH structures in which few other methods exists.

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