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SETTING TIMES MEASUREMENTS OF PORTLAND CEMENTS WITH PULSED USWR METHOD

MERJENJE ČASOV VEZANJA PORTLAND CEMENTOV S PULZNO USWR METODO

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In this paper we present the results of parallel measurements on PC cements; the setting times with a standard Vicat apparatus and the reflection coefficient changes Δr during early hydration with a pulsed ultrasonic shear wave reflection (USWR) hardening meter. The measurements were carried out on the same samples and under the same ambient conditions. In contrast to the Vicat needle test, the USWR method gives continuous information on the stiffening and hardening process over time via Δr changes, as the rigidity of the pastes grow on hydration. The magnitudes of the Δr change in selected cement pastes (CEM I 52.5R and PC 30dz 45s) at Vicat setting times are used to determine the correlation between the two methods. Through such calibration the setting times of production samples can be satisfactorily measured with the USWR method.

Key words: ultrasound, shear wave, cement, setting times, Vicat apparatus

V prispevku so prikazani rezultati vzporednih meritev časov vezanja PC cementov z Vicatovim aparatom in meritve časovnih potekov začetne hidratacije s prototipom merilca (USWR-2 Hardening meter) strjevanja osnovanem na odboju pulznega ultrazvočnega strižnega valovanja. Meritve so opravljene na identično pripravljenih vzorcih pri enakih pogojih. V nasprotju z Vicatovim aparatom, USWR metoda daje zvezno časovno informacijo o procesu vezanja in strjevanja via spremembe refleksijskega koeficienta Δr zaradi porasta trdnosti paste v procesu hidratacije. Iz velikosti spremembe Δr v izbranih (CEM I 52.5R in PC 30dz 45s) cementnih pastah pri Vicatovih časih vezanja je vzpostavljena korelacija med obema metodoma. S tako kalibracijo se lahko časi vezanja cementnih vzorcev v proizvodnji zadovoljivo merijo s predlagano USWR metodo.

Ključne besede: ultrazvok, strižno valovanje, cement, časi vezanja, Vicat-ov aparat

1 INTRODUCTION

When cement is mixed with water of around (25 to 35)% by weight, the result is a paste which displays considerable plasticity and maintains it for a period of time (dormant period). After a while the paste begins to stiffen, less and less plasticity is observed. Finally the plasticity is gone and the paste becomes brittle, although it is still without any sizable strength. This stiffening process is setting and is the result of the reaction between cement and water. The gain in strength, the hardening, takes place subsequent to the setting. It is customary to talk about initial setting, which is basically the beginning of the stiffening, and final setting which is marked by the disappearance of the plasticity. A standard technique for measuring the setting times (initial t_i and final t_f) in PC cement production is the Vicat method[1]. With the Vicat apparatus (t_i, t_f) are obtained by measuring the passage of time required from the initial contact of cement with water to when two needles of different cross-sections penetrate, to specified depths, cement paste samples of normal consistency prepared by a standardized procedure[1]. The values of the setting times obtained in this manner are not related to a fundamental rheological property in a simple manner.

A novel method of measuring (t_i , t_f) of cements using the pulsed USWR method has recently been proposed[2]. The pulsed USWR method is based on the measuring of the changes Δr of the reflection coefficient from an interface formed by two media[3]. When an ultrasonic shear wave pulse hits an interface between two media, it is partially reflected and partially refracted. The reflection coefficient r can be determined by the acoustic impedances Z_1, Z_2 of each of the two interface forming media, which are in turn related to the viscoelastic properties G, the dynamic shear modulus, and η, the dynamic viscosity[4]. This method is realized in the USWR-2 Hardening meter[3] used in these measurments in which the medium 1 is very pure fused quartz with $Z_1 = 8.29 \times 10^6$ Ns/m^3. It has been shown experimentally for the quartz/cement paste interface[5], that the relative phase changes of the incident and reflected wave are quite small with little influence on the magnitude of G evaluated from reflection measurements. In this case the shear modulus G_2 of a cement paste is related to the changes of the reflection coefficient Δr by the equation

$$G_2 = \frac{Z_1^2}{4\rho_2} \Delta r^2 ,$$

valid for small Δ r changes (a few db)[3]. The shear modulus is thus proportional the square of the Δr change. It has also been shown that the compressive strength σ and the hydration rate α are proportional to -Δr (minus sign because r is decreasing on hardening)[2,4].

Thus, the new method of measuring the setting times of cements proposes to correlate the levels of the Δr change at the (t_i , t_f) times determined with the standard Vicat apparatus for different cement types. With such a calibration the setting times can be adequately measured with the USWR method.

2 EXPERIMENTAL DETAILS

Two types of cement, CEM I 52.5R and PC 30dz 45s, were studied, the first with shorter and the second with longer setting time. About 20 kg of cement powder of each type was separated from a production batch. The measurements were performed in the Department for Physical and Mechanical Testing of Hydraulic Materials, Cement d.o.o., Salonit, Anhovo. In the laboratory, in which the Vicat and USWR measurements took place, a constant temperature of (22±2)°C and a relative humidity of (55±5)% is maintained round the clock. It is very important that the storage of the ingredients (cement, water) used and the preparation of the cement pastes takes place at the same temperature. The Vicat tests were carried out on pastes made from the selected cements in parallel to the regular cement production quality control daily testing, about 20 Vicat tests per day, 6 days a week. Normal consistency pastes (600 g of powder + about 170 ml of tap water) were prepared[1] and the setting times measured by standard procedures[1] performed by different technicians. A small amount (about 3 g) of the cement paste left over as a surplus when filling the Vicat ring mould was used for the USWR measurements. The pastes in both measurements were thus the same, excluding errors which could otherwise result from differences in their preparation.

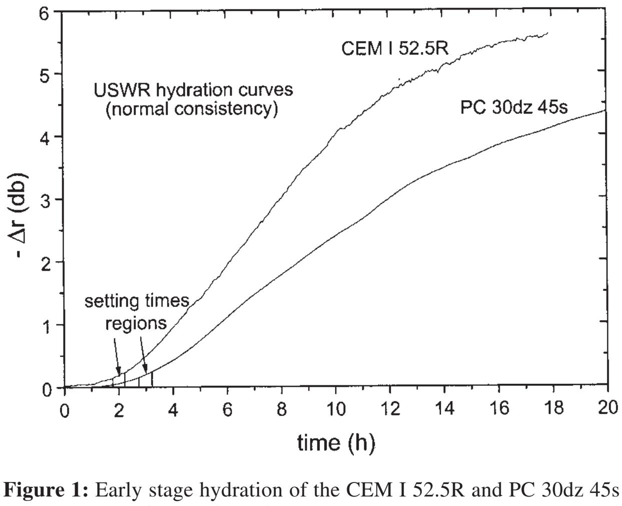

Figure 1: Early stage hydration of the CEM I 52.5R and PC 30dz 45s cement pastes of normal consistency

Slika 1: Začetna hidratacija CEM I 52.5R and PC 30dz 45s cementne paste normalne konsistence

The ultrasonic measurements were made with the prototype pulsed *USWR-2 Hardening meter*[6,7]. In contrast with Vicat, the USWR method gives a continuous information about the hydration (setting and hardening) process over time. The teflon holder was covered with a piece of flat glass in order to prevent drying out from the top. In all measurements the thickness of the samples was 6 mm.

3 RESULTS

In **Figure 1** the Δr changes in the reflection coefficient during early stage (20 h) hydration of the two, CEM I 52.5R and PC 30dz 45s, cement pastes of normal consistency (average w/c = 0.285 and 0.275, respectively) are shown. The magnitudes of the corresponding Δr changes in the regions of the two (t_i , t_f) setting times; (110, 140) min and (160, 200) min for CEM I 52.5R and PC 30dz 45s, respectively are shown.

In **Figure 2a** the USWR hydration curves in the very early period (4 h) are shown for 13 different pastes of normal consistency made with the samples of CEM I 52.5R from the same production batch. Similar results are shown in **Figure 2b** for 8 pastes made with PC 30dz 45s cement. The time t = 0 corresponds to the time of the first contact with water. It takes 3 min to mix the sample according to a pre-programmed sequence. An additional 2 min are required for controlling the normal consistency of each sample with the Vicat apparatus and to fill the USWR teflon sample holder. The w/c ratios of these samples in order to obtain normal consistency varied slightly from 0.285 to 0.286 and 0.270 to 0.275 for CEM I 52.5R and PC 30dz 45s, respectively. The dashed vertical lines indicate the average Vicat setting times (t_i , t_f). The horizontal solid bars are the maximal absolute uncertainties of the Vicat mean (t_i , t_f) setting times.

4 DISCUSSION

It is seen from **Figure 1** that the reflection coefficient in the first 20 h period changes by 5.6 db and 4.4 db for CEM I 52.5R and PC 30dz 45s cement pastes, respectively. Although the signal levels and the signal/noise (S/N) ratios in the initial setting time periods of hydration are rather low and the sensitivities (Δr/Δt) considerably reduced (by a factor of 3) with respect to its maximum occurring at t > 3.5 h and 4.5 h, respectively for the two cement types, all are high enough to give good USWR hydration curves. (The S/N ratio can be increased an appreciable amount by performing additional signal averaging. In these measurements the software allowed only every 30th measuring point to be recorded.) It is apparent from the diagrams that the hydration of the CEM I 52.5R is much faster than that of the PC 30dz 435s at comparable times.

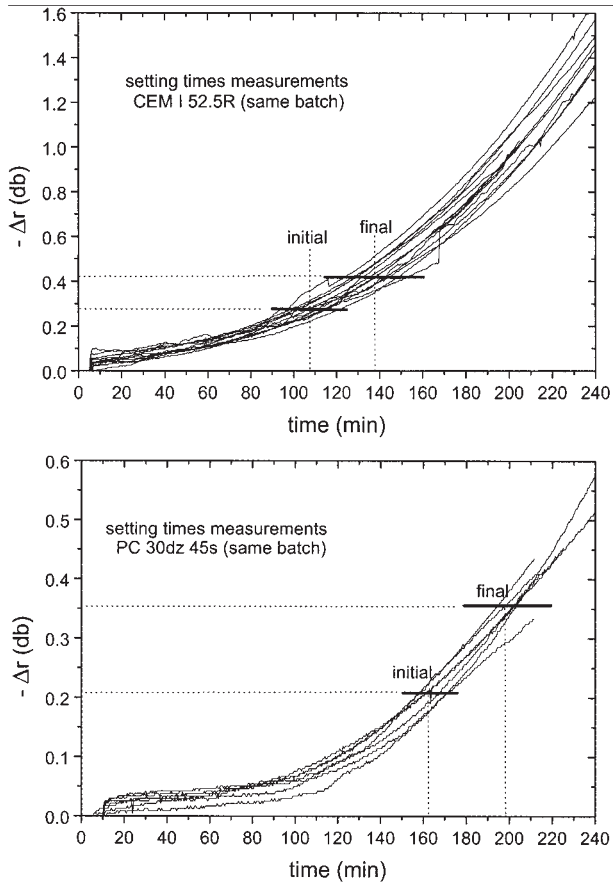

Figure 2: USWR hydration curves for pastes of normal consistency made with the cement of the same batch; **a)** CEM I 52.5R (13 curves), **b)** PC 30dz 45s (8 curves). The dashed vertical lines indicate the average setting times obtained with the Vicat apparatus and the horizontal solid bars their maximum absolute uncertainties

Slika 2: USWR hidratacijske krivulje za paste normalne konsistence narejene s cementom iste šarže; **a)** CEM I 52.5R (13 krivulj), **b)** PC 30dz 45s (8 krivulj). Vertikalni prekinjeni črti označujeta povprečne čase vezanja dobljenih z Vicato-vim aparatom, vodoravni polni črti pa njihovo maksimalno absolutno napako

In both hydration curve families of **Figure 2** an appreciable scattering is apparent although the pastes were made with the cement from one production batch. The causes of this are many. One of them is certainly the fact that the measurements were made in a production laboratory as part of regular control. The emphasis of this control is primarily to check the product for compliance with the standard[1] according to which t_i should be > 45 min for CEM 52.5R and > 60 min for PC 30dz 45s and t_f < 10 h for both cements. The presence of the large scatter, however, does not prevent us from making an evaluation of the proposed USWR setting times measuring method. After all, the idea behind these measurements is to use the method under production conditions in an industrial environment. Certainly, the above scattering has nothing (little) to do with the stability or reproducibility of the USWR apparatus.

The mean values of the measured Vicat (t_i , t_f) setting times and the maximum uncertainties resulting from the averaging of the results on the two types of PC cement pastes are: t_i = (107 ± 13) min, t_f = (137 ± 20) min for CEM I 52.5R and t_i = (162 ± 8) min, t_f = (199 ± 15) min for PC 30dz 45s. When measuring a given sample with the Vicat needle, one takes the needle height readings at several places on the sample surface, excluding the area around the edge of the mould, and records the average. Extreme readings on any one sample can differ by 10 min, thus a ± 5 min error has to be added to the above maximum uncertainties of the mean values (plotted in **Figure 2**). This gives a ± 13 min (± 12 %) and ± 16 min (± 10 %) standard deviation σ for the average Vicat (t_i ,t_f) values for CEM I 52.5R, respectively. The corresponding uncertainties for PC 30dz 45s are ± 8 % for t_i and ± 10 % for t_f . Thus, the Vicat scattering is quite appreciable. Notice, however, that all USWR hydration curves fall within the solid bars, i.e., within the Vicat (t_i , t_f) scatter range.

The horizontal dashed lines in **Figure 2** indicate the mean Δr levels (Δr_i , Δr_f) at the mean Vicat (t_i , t_f) setting times obtained by averaging the two Δr levels of the individual USWR hydration curves (13 in **Figure 2a**, 8 in **Figure 2b**) at their Vicat (t_i , t_f) times. The two (Δr_i , Δr_f) mean values are: Δr_i = (0.27 ± 0.07) db, Δr_f = (0.42 ± 0.08) db for CEM I 52.5R cement and Δr_i = (0.21 ± 0.04) db, Δr_f = (0.36 ± 0.05) db for PC 30dz 45s, with relatively high maximum uncertainties for the Δr_i level determining the initial setting time t_i for signal/noise reasons (which, again, could be improved). The cross points in **Figure 2** correspond to the two mean Δr levels at the average Vicat setting times.

With the two (Δr_i, Δr_f) values the USWR apparatus is in fact calibrated for the two types of cements. In **Figure 3** the calibration curves, the average of the curves in **Figure 2** for the two types of cement, are plotted on a different vertical scale. The horizontal dashed lines are the mean (Δr_i, Δr_f). If one accepts these values as those Δr

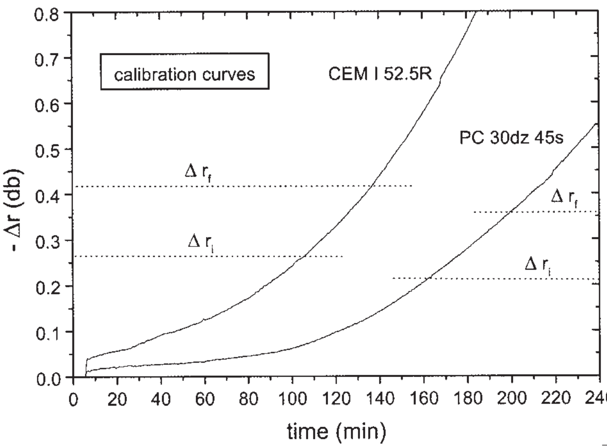

Figure 3: The calibration curve for two selected cements

Slika 3: Kalibracijske krivulje za dve izbrani vrsti cementa levels signaling the beginning and the end of setting for the two cements, the setting times (t_i , t_f) can be obtained with the USWR apparatus automatically. In particular, the following values for the USWR (t_i , t_f) are obtained from the data in **Figure 2**; (107 ± 14) min, (137 ± 14) min for CEM I 52.5R and (162 ± 6) min, (199 ± 7) min for PC 30dz 45s. The mean values for the setting times are of course the same in both cases, however the USWR values are less scattered than those obtained with the Vicat apparatus.

The measurements presented above were made on cements from the same production batch. In general, different production batches exhibit some variations in setting time, the main reason being minute differences in the raw materials. Parallel measurements of the type made in this work on cements as they come from production are being made in order to obtain production calibration curves. The initial results are quite encouraging and will be presented in a succeeding paper.

5 CONCLUSIONS

It has been demonstrated that PC cement setting times can be adequately measured with an appropriately calibrated USWR hardening meter. Calibration consists in finding the levels of the reflection coefficient change Δr at the corresponding average Vicat setting times for each cement type. The method can thus compliment the Vicat apparatus in praxis applications. Potential advantages offered by the USWR method are: objective measurements (eliminating human readings), less technician time required and the possibility of automation. Batch testing times can be reduced considerably by using a multi-probehead apparatus[7].

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