A STUDY OF HYDRATION OF CEMENT PASTES BY REFLECTION OF ULTRASONIC SHEAR WAVES. PART I: APPARATUS, EXPERIMENTAL METHOD AND APPLICATION EXAMPLES

ŠTUDIJ HIDRATACIJE CEMENTNIH PAST Z ODBOJEM STRIŽNEGA ULTRAZVOČNEGA VALOVANJA. PRVI DEL: NAPRAVA, MERILNA METODA, PRIMERI APLIKACIJ

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In this work an apparatus employing a novel nondestructive method based on the reflection of ultrasonic shear waves is described. Application possibilities for studies of the early hydration process of pastes in selected hydraulic, mostly cementitious materials are presented. The results obtained demonstrate, that the acoustic shear wave method presented is quite sensitive to different parameters (composition, water/cement ratio, fineness, grain size distribution, addition of additives) which influence the hydration process of these materials. Applications to curing process following, in time domain, of non-cement compounds are possible. On the basis of an evaluation of these and other ongoing experimental studies a compact 'hardness and cure meter' for industrial testing and for research will be constructed.

Key words: ultrasound, hydration, cement, shear waves, reflection, elasticity, viscosity

V prispevku sta opisani nova naprava in metoda za neporušno sledenje hidratacije hidravličnih materialov. Naprava je osnovana na merjenju odboja ultrazvočnih strižnih valov. Prikazani rezultati meritev hidratacije, zlasti cementnih past, kažejo, da je opisana metoda zelo občutljiva na različne parametre (sestava, razmerje voda/cement, finoča, porazdelitev velikosti zrn, uporabljeni aditivi), ki vplivajo na proces hidratacije teh gradiv. Metoda je uporabna tudi za časovno sledenje procesa strjevanja drugih ne-cementnih materialov. Na osnovi evaluacije prikazanih rezultatov in meritev, ki potekajo, bo zgrajen kompaktni 'merilec hidratacije in strjevanja' za uporabo pri laboratorijski ali procesni kontroli v proizvodnji ter pri raziskavah.

Ključne besede: ultrazvok, hidratacija, cement, strižni valovi, odboj, elastičnost, viskoznost

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 and stiffness. The duration of the transition periods from one type of behavior to another 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 type of waves, generally used are compressional (longitudinal) which travel in solids, liquids and gases. The parameter measured is usually the longitudinal velocity related to the modulus of elasticity. The same method can be used for the early age hydration studies of cement pastes but due to the pour transmission of the pressure waves and relative insensitivity of longitudinal sound velocity to the formation of rigid gel (CSH) structures in the slurry in the early ages (pre-induction, induction and early acceleration) of hydration, few articles have been published[1,2,3]. A method for determining the setting time of a cement slurry based on the transmission of pulsed acoustic shear waves was recently patented[4].

A novel method for early age hydration studies of cement pastes based on the reflection of pulsed acoustic shear waves was also reported[5]. In this work the reflection coefficient of a pulsed ultrasonic shear wave and the relative phase difference of the incident and reflected waves from the surface of the cement paste sample were measured. From the reflection data, the shear modulus of elasticity G and the viscosity η of some cement pastes are calculated. Since all these quantities are changing in the process of hydration, the method gives specific informations on its kinetics. Noticeable in these experiments is a very good signal/noise ratio. Of course, special and rather expensive commercial equipment (frequency synthesizer, rf gated amplifier, dual gate boxcar integrator) was used.

Recently a prototype of an apparatus, based on a modified reflection method and simplified home-built electronics, has been constructed with the aim of making a compact, portable, commercial instrument for hydration hardening studies and consistency determinations of hydraulic materials like cement, gypsum and their derivatives. The apparatus is being extensively tested in or-

der to determine its application possibilities and to improve its performances (signal/noise ratio, long term stability, influence of parameters like temperature and humidity, adherence of pastes to the measuring head). Such data are needed in order to make a final commercial version of the instrument. Its details will be described elsewhere. Herewith a brief description of the apparatus and of the method is given. A pleiad of preliminary results, demonstrating the present performance of the apparatus and some possible research and technological applications to hydraulic materials, is presented and discussed. It is also shown that the method is sensitive to cure (drying out) hardening.

2 EXPERIMENTAL PROCEDURES

2.1 Materials

All materials tested, unless specifically stated, were commercial, generally available hydraulic products:
– hemihydrate gypsum (supplier "Mavrica", Slovenia),
– fast hardening cement powder Vezur (product of Cinkarna, Celje, Slovenia),
– white cement BPC 45A and aluminous cements I 40 (AC 75) and I 50 (AC 65) were (obtained from ICI, Istra Cement International, Pula, Croatia),
– white joint filler powder (product of TKK, Srpenica, Slovenia),
– blast furnace slag Portland cement PC15z 45b (producer Salonit Anhovo, Slovenia),
– sand for mortar pastes CEN-NORMSAND DIN EN 196-1 (producer FMP, Baden Germany),
– two components UHU plus epoxy (producer UHU GmbH, Germany).

Cement chemists convention of shortened notation for various compounds is used in this paper.

The pastes were prepared by thoroughly mixing corresponding powders with an adequate amount of distilled water. Although the amount of the paste needed is small (about 2 g), about 10-times larger quantities were used in order to warrant homogeneously mixed samples.

2.2 Apparatus

A simple block scheme of the apparatus is shown in **Figure 1**. The apparatus consists of a measuring head, home-built ultrasonic transmitter/receiver electronics, an A/D converter and a PC computer with proprietary software for data collection. The measuring head consists of a fused quartz rod with diameter of 28 mm and 50 mm in length. On one end (bottom) a piezoelectric (PZE) ultrasound transducer, acting as transmitter and receiver, is mechanically fastened. The other end (top) is shaped in a form of a precut cone. The cone end measuring surface is round with a 10 mm diameter. The two end surfaces are flat, very parallel and highly polished, the cone mantel surface is rough. The sample to be tested is smeared on the round measuring surface, a few mm over the cone

mantel and (3 to 5) mm in height. The amount of the sample needed for one measurement is small (about 2 g).

All measurements presented here were made with the measuring head operating at 20 MHz and under the same ambient conditions; temperature of $(24 \pm 2)°C$ and constant humidity $(45 \pm 5)\%$. They were checked, round the clock, with a calibrated thermo-hygrograph positioned beside (and outside) a dewar. The condition of constant temperature and humidity was achieved by placing a donut shaped glass container, partially filled with water-soaked cotton, half way down the quartz rod. The whole assembly was then inserted into a dewar with the open side covered.

The ultrasonic pulsed echo method presented here is very fast (every 1 msec one echo train is triggered). Since the hydration processes in cementitious materials are very slow (e.g., early hydration in the Portland cement pastes takes place several days) and the number of influential variables is high, a multihead apparatus (one instrument serving several measuring heads) is being developed.

The sharp peaks on most diagrams shown are calibration marks, their heights corresponding to a 1 db change in the reflection coefficient, $\Delta r = 1$ db.

2.3 Method

When an ultrasonic wave hits the interface between the quartz and the cement paste, it is partially reflected back into quartz and partially refracted into the paste. The reflected wave, on reaching the quartz's transducer side surface, excites the PZE crystal giving an electric signal (echo). In the case of a normal incidence, the ratio between the amplitudes of the reflected (A_2) and of the incident (A_1) wave is the reflection coefficient r, which can be expressed as
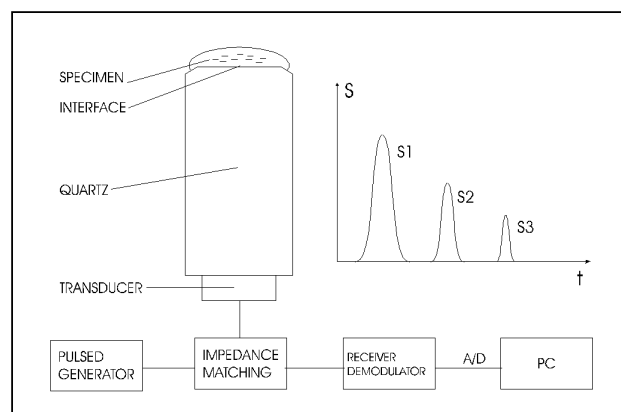

Figure 1: Block schema of the ultrasonic pulse echo apparatus for hydration studies of hydraulic materials by the shear wave reflection method
Slika 1: Shema aparature za meritve poteka hidratacije in polimerizacije materialov z metodo odmeva ultrazvočnega valovanja na meji dveh sredstev.

$$r = \frac{A_2}{A_1} = \frac{Z_2 - Z_1}{Z_2 + Z_1} \qquad (1)$$

where Z_1, Z_2 are the acoustic impedances determined by the viscoelastic properties of each of the two interface forming media[6]. In an isotropic, homogenous fluid, for the case of an incident shear wave

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

where ρ is the mass density and ω the angular sonic frequency. In general, the acoustic impedance of a medium is thus a complex quantity and it can be written in the form

$$Z = R + iX \qquad (3)$$

with its real and imaginary parts related to the viscoelastic properties of the medium by the following equations

$$\eta = \frac{RX}{\rho} \qquad (4)$$

$$G = \frac{R^2 - X^2}{\rho} \;. \qquad (5)$$

Thus, by 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 from an interface formed with the medium of known acoustic impedance. In general, the reflection coefficient is a complex quantity, which can be written in the form

$$r = r_0(\cos\phi + i\,\sin\phi) \;, \qquad (6)$$

where r_0 is the magnitude of the reflection coefficient and the ϕ is the shift of the phase angle between the incident and the reflected wave. By combining equations (4), (5) and (6) the following expressions for the shear acoustic impedance are obtained

$$R_2 = Z_1 \frac{1 - r_0^2}{1 + r_0^2 + 2r_0\,\cos\phi} \;, \qquad (7)$$

$$X_2 = Z_1 \frac{2r_0\,\sin\phi}{1 + r_0^2 + 2r_0\,\cos\phi} \qquad (8)$$

Thus, the unknown impedance (R_2, X_2) and consequently the viscoelastic properties (G_2, η_2) can be evaluated from the reflection data, by known value for the acoustic impedance of medium 1 [$Z_1 = (8.29\times10^6, 0)$ Ns/m^3 for quartz] and with the assumption that the medium 2 mass density remains constant during the hydration process ($\rho = 2.0$ kg/dm^3 for cement pastes).

It has been shown experimentally[5], for the particular case of the quartz-cement paste interface, that the relative phase change is quite small with very little influence on the magnitude of G. The error in evaluating G from equations (7) by taking $\phi = 0$ is insignificant. This observation is rather important since the measurements of ϕ

make the instrumentation more difficult. In this case the impedance of medium 2 is real, $Z_2 = (R_2, 0)$, and

$$Z_2 = Z_1 \frac{1 - r_0}{1 + r_0} \qquad (9)$$

and the equation for the modulus G reduces to

$$G_2 = \frac{Z_1^2}{\rho_2}\left(\frac{1 - r_0}{1 + r_0}\right)^2 . \qquad (10)$$

The shear strength can thus be calculated from equation (10) using the measured reflection coefficient data. Since the acoustic pressure excitations (pulses) are of very high frequency, the G values obtained are dynamic properties.

Measurement of r_0 in the manner suggested by Eq. (1) is not possible with a 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_1 of the incident wave can not be determined). Instead, the first and second back echoes (**Figure 1**) can be used for determining the reflection coefficient. The difference of the logarithmic values of the signal amplitudes (s_1, s_2) of these two echoes is related to r_0 by the equation

$$\Delta = \log\left|s_1\right| - \log\left|s_2\right| = -\log r_0 - \log r_0^* , \quad (11)$$

where r_0^* represents the change of the magnitude of the reflection coefficient during one passage of the quartz rod without taking into account the changes in amplitudes due to the cement paste. The main contribution to r_0^* is the reflection on the quartz/detector interface.

Thus, by plotting Δ vs. t, the time dependence of (log r_0) and of (r_0) can be obtained. It should be noted that air and liquids with low viscosity do not support shear waves (the wave is fully reflected when medium 2 is air or water, i.e., $r_0 = 1$) and therefore $\Delta(t = 0) = $ const. This is also the case when medium 2 is a rather fluid cement paste smeared on the measuring surface immediately after mixing. Once the paste begins to hydrate (harden), some of the wave refracts into the paste and the difference $\Delta(t)$, consequently r_0, becomes progressively smaller. The time dependence [$\Delta(t) - \Delta(t = 0)$], which is equal to log r_0, is solely due to the changes of r_0 because of the hydration occurring in the paste. By substituting r_0 with ($1 - \Delta r_0$) in Eq. (10), we obtain

$$G_2 = \frac{Z_1^2}{\rho_2}\left(\frac{\Delta r_0}{2 - \Delta r_0}\right)^2 , \qquad (12)$$

which directly relates the measured reflection data with the shear strength. In pastes, in which Δr_0 is small (the case at the very early age of hydration in the materials considered), Eq. (12) can be approximated with

$$G_2 = \frac{Z_1^2}{2\rho_2}\,\Delta r_0^2 \;. \qquad (13)$$

The shear stress G of the hydrating hydraulic paste is thus proportional to the square of the change in the reflection coefficient.

One of the most important quantities specifying the quality of a cement is its compressive strength σ. As discussed later, σ is proportional to $E^{1/2}$ and thus to $G^{1/2}$, since the two muduli are linearly related

$$G = E/2(1 + \mu) \qquad (14)$$

where μ is Poisson number. Eq. (14) is valid for a homogenous isotropic elastic solid. There is no evidence that a similar relationship is valid also for the fresh cement paste, 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 mudulus E, and hence the shear modulus G, will increase and thus the measurement of G gives an indication of the rate of structure build-up at early ages after mixing. Since G and Δr_0 are related via Eq. (12), Δr_0 changes of r_0 reflect the growing of the compressive strength σ of a cement paste in a proportional way (within the frame of postulated assumptions). In all diagrams presented here the changes Δr_0 and not magnitudes r_0 vs. time t are plotted. In this way these diagrams resemble to the diagrams of increasing compressive strength time development during hydration obtained with other methods. It is in this sense that changes in the reflection coefficient in further text are sometimes equated with the hardness.

3 APPLICATIONS

Hydration of gypsum:

The ultrasonic reflection coefficient measurements of gypsum pastes with three different water/gypsum (w/g) ratios; a) 0.5, b) 0.4 and c) 0.6, are shown in **Figure 2**. The early stage shapes of these curves show a short induction period followed by a fast rate of change Δr_0, both strongly dependent on the w/g ratio. In this time interval
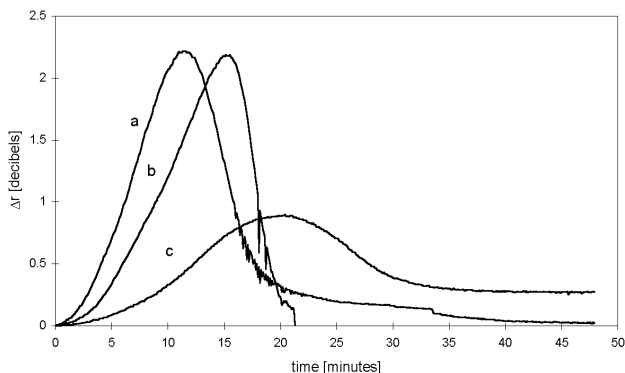

Figure 2: Hardening of gypsum pastes with three different w/g ratios; a) 0.5, b) 0.4, and c) 0.6
Slika 2: Strjevanje sadrne (gips) paste pri treh različnih razmerjih voda/sadra; a) 0.5, b) 0.4, and c) 0.6

the curves resemble a sigmoidal dependence similar to that obtained from measurements of total hydration vs. time with other methods[7].

For the practical use of gypsum, by the producer recommended mixing ratio gypsum/water is 2:1 (w/g = 0.5). The curve corresponding to the paste with this ratio is shown in **Figure 2a**. Indeed, the reflection measurements indicate that the start of the intensive hydration and the hardness maximum in samples with higher w/g ratios shifts to longer times. Further, the hardness maximum decreases with the increasing w/g ratio. In addition, all samples indicate an apparent decrease in hardness at longer times, the rate of which becomes smaller with the increasing w/g ratio. A similar behavior was observed, but not explained, in gypsum using compressional acoustic waves in transmission mode[8]. This behavior is not quite understood. We tend to think that some free water is slowly being released into the pores of the hardened gypsum, reaching also the quartz/gypsum interface, which results in an increased reflection and thus to an appreciable reduction of Δr_0. This explanation agrees with the visual observation that the sample contact surface is of moist appearance after removal from the measuring head and that the adhesion of the sample to the head surface diminishes after hydration.

The sample with the w/g ratio (= 0.4) smaller then recommended behaves in a peculiar way (**Figure 2b**). The start of the intensive hydration is somewhat prolonged and the hardness maximum somewhat reduced compared to the recommended mix with w/g = 0.5. Further, the rate of the Δr_0 decrease after hydration is much faster, resulting eventually in the break of the contact evident as a sudden drop in the signal at t = 22 minutes.

Parallel to the reflection measurements, visual observations of the changes with time in the plasticity of pastes immediately after mixing with water were made. The sample b), fluid initially, starts to harden almost immediately. After 3 min. the mix is no longer usable and after 5 min. becomes hard. The sample a), declared by the producer as the best mix, fluid initially, begins to harden after 2 min., after 5 min. is no longer usable and becomes hard after 8 min. These observations indicate the possibility of practical application of this method for the determination of characteristic setting times (length of plastic state or serviceable time, beginning of binding, time when smoothing can begin) in production of gypsum based plaster materials. A comparison of these times obtained with ultrasonic and conventional method (DIN 1168) is planned.

Hydration of Portland cement:

Ordinary Portland cement (OPC) is a multi-component system. Its hydration is a sequence of overlapping chemical reactions between anhydrous klinker components (C_3S, C_2S, C_3A, C_3AF), gypsum (CSH_2) and water (H), leading to continuous cement slurry thickening and hardening[9]. Although hydration of C_3S, the principal

constituent, with a concentration as high as 70%, is often used as a model for the hydration of OPC cement many additional parameters are involved. From chemical point of view, OPC hydration is a complex dissolution/precipitation process in which the various hydration reactions proceed simultaneously at differing rates, their contributions to the total degree of hydration at a given time being proportional, of course, to their concentrations in the cement powder. The phases also influence each other. None of the clinker material is pure.

In discussing hydration of C₃S and OPC or PC cements five hydration stages are arbitrarily defined: preinduction, induction, acceleration, deceleration and diffusion. The duration of preinduction period is only a few minutes, during and immediately following mixing. In this period the wetting of the powder and a rapid initial hydration, a layer of CSH gel is formed over the anhydrous surfaces of cement particles. Due to this layer very little hydration activity is going on in the following induction (known also as dormant) period, lasting a few hours at room temperature. The termination mechanism of the induction period is still a debate among cement chemists. At the end of the induction period only a small % of cement particles has hydrated.

The acceleration and deceleration periods (collectively known as setting period), represent the interval of most rapid hydration. During the acceleration period, solid CH crystallizes from solution and CSH gel deposits into the available water-filled spaces. The hydrates intergrow, a cohesive network is formed and the system begins to developed strength. The porosity of the system decreases as consequence of the deposition of hydrates. Eventually, the transportation of ionic species and water through the network of CSH gel is hindered, and the hydration rate decelerates. At ambient conditions, these events occur within several days, the total degree of hydration reaching a value of about 30%.

Hydration continues at a slow pace owing to the ever-decreasing system porosity, the network of hydrated products becomes more and more dense, and strength increases. The duration of the diffusion period is indefinite at ambient temperatures. The total degree of hydration after 7, 28 and 90 days is about 40, 60 and 80%, respectively.

Cement is also a polysize system. In ball milling process the size of the grains varies from (1 to 100) μm. The rate of reaction in most particulate systems depends on the surface area of the reactants. OPC and PC cements have typical Blaine surface in the interval (3000 to 3800) cm²/g, whereas rapid hardening cements have surfaces up to 6000 cm²/g. The Blaine surface is, however, not sufficient to characterize the fineness of a cement when it comes to a more detailed description of relationship between the fineness and the strength development. It has been pointed[10] and experimentally demonstrated[11] that the shape of the rate of total hydration vs. time curves is clearly related to the shape of the particle size distribution (PSD) of a given cement. In **Figure 3** reflec-
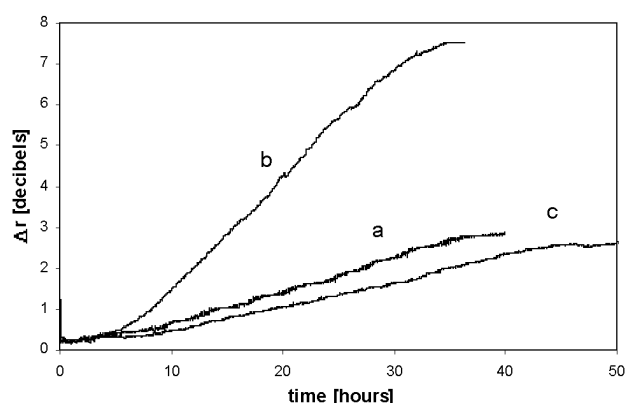
Figure 3: Reflection coefficient changes during early hydration of three PC15z 45b cement pastes with the same w/c ratio (= 0.50) but with different grain sizes: a) normal cement, b) fraction ≤ 20 μm, c) fraction (50 ÷ 80) μm
Slika 3: Sprememba odbojnega količnika v zgodnji fazi hidratacije cementa PC15z 45b z istim v/c razmerjem (=0.5) toda različno velikostjo zrn a) normalni cement, b) frakcija ≤ 20 μm, c) frakcija (50 ÷ 80) μm

tion coefficient changes during early hydration of three cement pastes, made with the same w/c ratio (= 0.50) and with different grain sizes: normal cement PC15z 45b (3a) and fractions sieved from the same cement to sizes ≤ 20 μm (3b) and (50 ÷ 80) μm (3c), are shown. These results demonstrate the sensitivity of the shear wave ultrasonic method to PSD indicating the possibility of its use as a complementary method in cement production.

The most frequently PSD curve applied to cements is the RRSB cumulative distribution

$$R(x) = \exp[-(x/x')^n] \qquad (14)$$

where R(x) is the fraction of the particles with diameters larger then x', the so-called position parameter, defined as the size for which the residue R(x') = 1/e (or 36.8%). For Portland cements x' ≈ 20 μm or smaller[12], meaning that 63.2% of cement grains have diameters ≤ 20 μm. The exponent n (usually ≈ 1) is a measure for the dispersion of the PSD curve.

Further complexity of cement systems originate from the fact that commercial PC cements contain different kinds of filler materials in various, quite large proportions (10 ÷ 70)%. The cement used in this measurement contains, for example, up to 15% of blast furnace slag. Slags are amorphous materials in glassy state and the hydration of slags is generally slow[13]. The early hydration of PC cement/slag mixtures depends on many parameters; water/solid, slag/cement ratio, type of slag and temperature[14,15].

The situation becomes quite cumbersome in the case of mortar pastes in which, apart from cement, a large amount of sand (additional component) is added. The sand contains fine and course fractions with sizes up to 3 mm.

From the above brief overview of the complexity of PC cement systems it is obvious that any attempt to elucidate the time dependence of the reflection coefficient changes during the early hydration of PC cement-, cement/slag- and cement/mortar- pastes, requires a large amount of systematic measurements, which will be reported in Part II of this paper. Herewith the measurements of only two PC cement pastes, showing the variations in time of Δr_0 changes during the first 80 h, are presented (**Figure 4**). The purpose of slag cement- and mortar-pastes measurements was to evaluate the response of the ultrasonic apparatus when applied to longer hydration time scans (long term stability, sensitivity, adherence) and to important technical materials like mortars containing grains of sizes comparable or larger to the wavelength λ of the shear wave. In the latter case the samples can no longer be considered as homogenous and additional sound scattering on the grain boundaries takes place greatly influencing the absorption, transmission and reflection. In the cement pastes most grains are smaller then 20 μm, whereas the mortar pastes contain sand with fine- and course- grain fractions of sizes up to 3 mm. This result in a large amount of scattering of P and S ultrasonic waves and well known difficulties in transmission experiments like absence of the signal for a certain time immediately after mixing.

In reflection experiments the measured reflection coefficient is an average over a small volume, a thin layer of the paste at the interface encompassed by the measuring surface and a depth of a few wavelengths (except for samples with large w/c ratio at the very early age when the penetration depth of the acoustic waves is extremely small). The speed of the longitudinal waves c_L in the cement pastes varies between 1500 m/s, when freshly mixed (like in pure water), to about 2500 m/s after setting period and 4500 m/s for hardened pastes. Since the shear wave speed $c_S \approx c_L/2$, the wavelength λ at the operating frequency of 20 MHz varies between 0.04 mm and 0.12 mm. Since most grains in the pure cement paste are small, they can be considered as homogenous and the
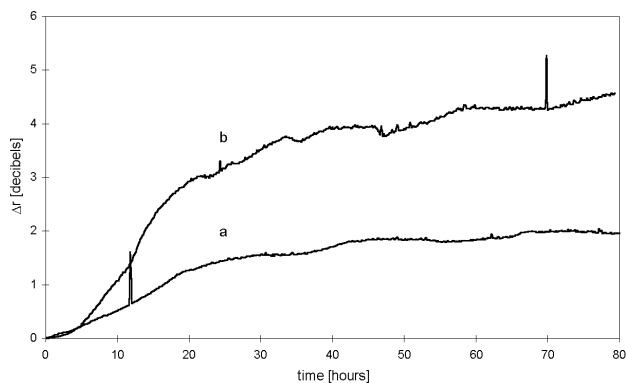
measured values of r_0 are the average values of cement pastes and are not expected to be sample dependent providing that the pastes are prepared in the same way. In the case of mortars with some larger grains present this is no longer the case. From a time of a certain degree of hydration, the contribution from solid sand to the measured average values of r_0 is expected to be high and some sample dependence can also be present. Additional measurements with mortar pastes containing sand particles of different sizes and using several lower operating frequencies must be made for the proper interpretations of the measuring results.

The curve 4a) corresponds to cement paste made of blast furnace slag cement PC15z 45b with w/c = 0.4. The curve 4b) corresponds to the mortar paste, made by adding normsand (s/c = 2) to the paste 4a). The w/c ratio of the mortar paste is slightly higher (0.45) then that of the cement paste because the mortar paste obtained with w/c = 0.40 appeared to be somewhat less fluid.

The general shape of the Δr_0 change vs. t curve for slag cement paste is an increasing function of time (**Figure 4a**), but somewhat different to sigmoidal form characteristic for gypsum. This difference can be explained with the inclusion of both, kinetic equation and complete PSD in modeling the PC cement hydration, of course, accounting for the presence of slags in this case. The change Δr_0 for this paste is steadily increasing up to a time of about 20 h indicating the end of acceleration period. From this time on the rate slowly decelerates and levels off at a time of 35 h (deceleration period). From a comparison of this curve with a corresponding curve made with OPC paste[5] it can be deduced, that the effect of slag addition to OPC is a considerable retardation of the early hydration hardening. Small Δr_0 changes centered at about 45 h and 70 h are observed. In calorimetric studies of OPC and blast furnace slag PC cements two peaks in the heat production rate vs. time curves, centered at about 20 h (larger peak assigned to the hydration of PC) and at 45 h (smaller peak assigned to slag hydration), are detected in the case of slag cements[15]. The small increase of Δr_0 at t = 45 h in **Figure 4a** could well be due to slag hydration. Additional measurements with varying amounts of slag must be made for definitive confirmation of this assignment and to understand the origin of the small increase at t = 70 h.

The shape of the Δr_0 vs. t curve for the mortar paste (**Figure 4b**) is quite different to the curve for slag cement paste (**Figure 4a**). Up to a time of 4 h the Δr_0 change increase with time is slower then in the slag cement paste. From this time on, $\Delta r_0/\Delta t$ rate accelerates and the absolute values of Δr_0 change become appreciably larger then in the slag cement paste indicating faster hardening and higher initial hardness at comparable times. The fast Δr_0 increase continues up to about the same time (20 h) as in the case of slag cement paste indicating the same hydration mechanism in the acceleration period. From this time on the rate slowly decelerates

Figure 4: Early stage hydration of blust furnace slag Portland cement PC15z 45b pastes: a) cement, w/c = 0.40, b) mortar, c/s/w = 1: 2: 0.45
Slika 4: Zgodnja faza hidratacije Portland cementa PC15z45b z dodatkom žlindre a) cement, v/c = 0.40, b) mešanica, c/ž/v = 1: 2: 0.45

but it does not quite level off during first 80 h. This behavior can be interpreted in the following way. The sand for standard mortar paste contains grains with fine-, medium- and course- fractions of sizes up to 3 mm. Initially solid sand grains are embedded in the rather fluid cement paste. The thickness of the cement paste between different hard sand grains and the measuring surface varies from almost close touch to a value limited by the thickness of the spacimen. The fluid paste initially prevents the shear wave to enter the paste and solid grains. Then, cement particles begin to hydrate, CHS gel and solid CH deposit and intergrow and the paste develops a weak strength. As a consequence, more of the wave refracts into the paste and the value of Δr_0 increases gradually. However, in the mortar paste the finer sand grain (aggregate which hydrates on the surface at much longer times) essentially dilute the binding cement fraction. The result is a slower initial hydration compared to pure slag cement paste and the Δr_0 vs. t curve for mortar paste is lower then the corresponding slag cement curve (**Figure 4**). Once the deposited hydrated solid component forms a percolated, connected network with a larger hard sand grain in the plastic mortar paste at the points of shortest distance from the measuring surface, a local and sudden grain-size increase of the solid material in the measuring volume occurs and more of the wave refracts into the paste, resulting in a sudden increase of Δr_0. In fact this events occur at several points at the same or slightly different times giving a continuos rather then stepwise Δr_0 vs. t curve. This process continuing, it results in an overall much faster ($\Delta r_0/\Delta t$) rates and larger Δr_0 changes then in the case of slag cement paste at comparable times and the mortar Δr_0 vs. t curve should be well above the corresponding slag cement curve. In **Figure 4** the rate of increase in the acceleration period for mortar paste is about 3-times that of the cement paste and the Δr_0 changes are 4.0 db and 1.5 db at t = 30 h, for mortar and slag cement paste respectively. A deflection in the slope in the early part (at t = 11h) and some time variations in the later part of Δr_0 vs. t curve are observed (**Figure 4b**). Whether these have something to do with the mechanism just described or with hydration of slag or sand, it is not possible to resolve with only this data. The time variations, concomitant with increased noise at longer times, may well be associated with the formation of small holes (of various diameters ranging from about 0.5 mm to very small ones and about 0.5 mm deep) on the contact surface with quartz found after removal of the hardened mortar sample from the measuring head. Such holes, probably due to air-bubbles or contraction upon hardening, have never occurred in pure cement pastes spacimen. Sample preparation in applying the pulsed acoustic shear wave technique to the case of mortars seems to play a role.

Hydration of aluminous cement:

It is well known that aluminous cements present an anomalous behavior of the setting time at lower temperatures[16]. In the temperature range (18 ÷ 30)°C the setting time becomes progressively slower as the temperature rises, and only above 30°C does the rate of set accelerate again. The longer setting times seem to be due to difficult nucleation of CAH_{10} which is the main hydrate at temperatures below 15°C. At temperatures between 18°C and 30°C, CAH_{10} is precipitated together with C_2AH_8 and AH_3 gel. At temperatures above 30°C, C_2AH_8 and AH_3 gel are together formed and convert rapidly above 45°C to C_3AH_6 and gibbsite. The w/c ratio has no influence on the phase formation behavior of CA cements.

Characteristic for aluminous cements is also the development of a high amount of heat during early hydration and a high initial hardness. Their most important hydraulic constituent is CA which reacts rapidly with water. The reactivity of aluminous cements with water increases with increasing C/A ratio. Its increased concentrations are associated with the short thickening times.

In **Figure 5** the changes in the reflection coefficient during the early hydration of three aluminous cement pastes are shown. The curves 5a) and 5b) correspond to the same type of cement (I 40) with different w/c ratios, the curve 5c) belongs to different type of cement (I 50) but with the same w/c ratio as used for one of the I 40 samples (**Figure 5b**). The essential differences between the two cements are in the relative content of the three main constituents A, C and F (40.5, 38.5, 15.8 for I 40; 51.5, 30.9, 1.7 for I 50, respectively in % for A, C and F) and in their Blaine surfaces (3200 and 3500 cm^2/g, for I 40 and I 50 respectively).

It should be mentioned that the three pastes were not prepared in the same way. The differences are in the duration of mixing immediately after contact with water. The paste with w/c = 0.22 was smeared to the measuring head after a very short mixing time of about 30 s from contact with water. The paste was plasticine like and it seems to harden while smearing. Indeed, a small increase in the change of the reflection coefficient at the very beginning, seen on the curve (**Figure 5a**), indicates a limited hydration taking place from the very start and end-
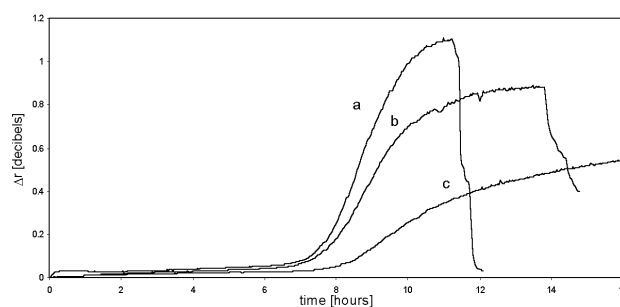

Figure 5: Early hydration of aluminous cement pastes: a) I 40, w/c = 0.22, b) I 40, w/c = 0.40, c) I 50, w/c = 0.40
Slika 5: Zgodnja faza hidratacije aluminantnega cementa: a) I 40, v/c = 0.22, b) I 40, v/c = 0.40, c) I 50, v/c = 0.40

ing after about 15 min. The other two pastes were smeared after continuous mixing for 2 min. Initially they were quite thick too, but continuos mixing for a certain time made them rather fluid (thixotropy!). Thus, when using the shear wave method described one should bear in mind the importance of paste preparations, especially in the case of fast hardening materials.

Apart from some differences in hydration at the very start, the time development of the hydration for the three pastes considered follows the same general behavior. In the case of I 40 cement (**Figures 5a** and **5b)**, the rate of Δr_0 change in the first 7 h (dormant period) is very slow and steady. Thereafter (acceleration and deceleration period) the changes are very fast and large compared to PC cements, larger being in the paste with smaller amount of water (1.1 db at 11 h for w/c = 0.22 and 0.9 db at 14 h for w/c = 0.4). The setting times (taken to be the projection on the time axis of the intersection of the two 'best' straight lines: through the early flat part and through the fast rising slope (acceleration period) of the curve for initial set t_i; through the fast rising slope and through the following slower rising slope (deceleration period) of the curve for final set t_ℓ) are: t_i more or less the same (7.5 h), t_ℓ somewhat different (9.3 h and 9.8 h) for the two pastes respectively. The amount of extra water in the two cases has a much greater effect on the hydration process in the deceleration period. The end of the deceleration period, taken at the point where Δr vs. t curve levels off, is 11.3 h and 13.6 h. Further, the higher water content seems to reduce the hardness reached in this early period as evident from the heights of the two curves. The following abrupt drops of Δr vs. t curves (at t = 11,5 h and 14 h) are due to contact loss of the sample with the surface of the measuring head.

The early hydration of I 50 cement exhibits a behavior similar to I 40 cement but in a less pronounced manner; the dormant period lasts somewhat longer (8.2 h compared to 7.5 h) with the fast Δr changes thereafter and their values (heights of the curves related to the hardness reached) considerably reduced at comparable times. This is in agreement with the fact that the reactivity of CA with water increases and thickening times shorten with increasing C/A ratio, which is 0.95 and 0.60 for I 40 and I 50 cements, respectively. The setting times for I 50, obtained from **Figure 5c**, are 8.2 and 11.1 h which are longer then those for I 40 (7.5 h and 9.8 h). It is also known that increasing CAF concentrations act in a opposing way, i.e., lengthen the thickening times and slower the hardening process. The F concentration in the two cements are quite different, 15.8% and 1.7% for I 40 and I 50, respectively. The results can be reasoned by a dominant effect of C/A concentration over the influence of F concentration on the early hardness development in aluminous cements. The same observation is valid also for the effect of the cement fineness on the time development of hydration. One would expect a shorter dormant period for the I 50 cement with higher specific surface

area which is not the case. More experiments with pastes of variable concentrations of main constituents and different grain sizes should be made to elucidate this behavior.

Hydration of fast hardening Vezur cement:

The exact composition of the Vezur powder is not given. Its basic component is aluminous cement with additives and filler material. In the instructions for use the producer recommends 3:1 mix (w/c = 0.33). Vezur powder, once mixed with water, must be used-up in (2 ÷ 5) minutes. In **Figure 6** the changes in the reflection coefficient of four Vezur based pastes during the first 80 minutes after adding water are shown. **Figures 6a** and **6b** correspond to Vezur pastes with different w/c ratios, 0.33 and 0.44, respectively. The reflection coefficient data indicate that the 3:1 paste (**Figure 6a)** hardens fast in the first 10 minutes after which time the hardening process slows down by an order of magnitude. The following parallel visual observation of the plasticity of the 3:1 paste, continuously mixed, was made. The paste can easily be mixed for 5 min after adding water, after which time it begins to thicken, becoming plasticine-like at about 10 min, hard and brittle after 30 min. At time 5 min (useable time) the change in the reflection coefficient is quite noticeable. These results indicate the possibility of application of the apparatus for determination of useable times for these materials.

A comparison of **Figures 6a** and **6b** indicate that the effect of adding extra water is an appreciable slowing down of the hardening process and a considerable reduction of the hardness reached at comparable times. An additional hardening mechanism, visible from the change in the slope of the two curves in the first 6 minutes, seems to be present. This change is more pronounced in the paste with larger amount of water.

Figures 6c and **6d** correspond to two Vezur mortar pastes with different w/c and the same normsand/Vezur cement (s/c) ratios (w/c/s = 0.44:1:0.67 and 0.56:1:0.67, correspondingly). According to the producer's technical instruction No.109/97, the addition of sand in the ratio c/s = 3:1 lowers the hardness and increases the useable
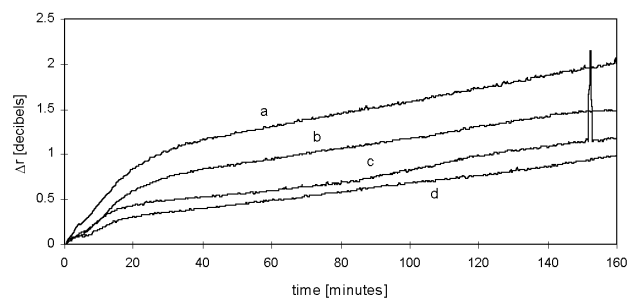

Figure 6: Hydration of the fast hardening Vezur powder pastes: a) w/c = 0.33, b) w/c = 0.44, c) w/c/s = 0.44:1:0.67, d) w/c/s = 0.56:1:0.67
Slika 6: Hidratacija hitrovezanega Vezurja: a) v/c = 0.33, b) v/c = 0.44, c) v/c/ž = 0.44:1:0.67, d) v/c/ž = 0.56:1:0.67
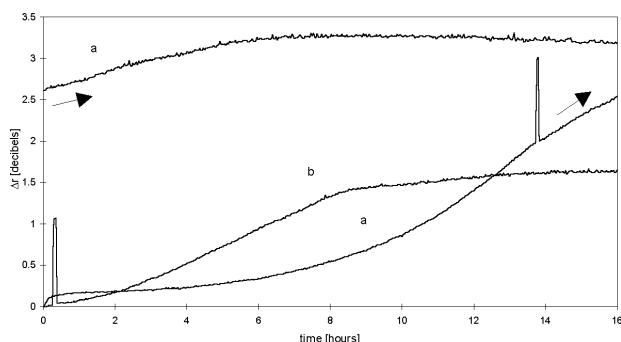
Figure 7: Hydration of two hydraulic pastes: a) white joint filler paste with w/f = 0.2, b) white cement paste with w/c = 0.5
Slika 7: Hidratacija dveh hidravličnih past: a) bela polnilna masa, v/p=0.2, in b) beli cement, v/c=0.5

time, whereas ratio 1:1 has the opposite effect. Only the measurement with s/c ratio closer with the lower sand content was made which agree with the producer's declaration in the technical note. The extra water has a somewhat different effect to that in the case of cement/water mixes. The reduction of the fast hardening in the first period is comparable in both cases. The following, slower hardening in the case of mortars, follows more or less with the same rate. Further, the reduction in hardness at comparable times is not so great and the additional mechanism in the first 6 min period is quite more pronounced. Another mechanism seems to appear at times larger then 100 min. Longer time scans with different w/c and s/c ratios are needed to elucidate these mechanisms.

Hydration of white joint filler and white cement:

The exact composition of the joint filler powder is not given but it is based on white cement, additives and filler materials (mainly calcites). In **Figure 7a** the early stage (first 32 h) hydration of white joint filler paste with w/f = 0.2, corresponding to the 4:1 ratio recommended by the producer, is shown. The figure indicates a very fast hydration process in the first few minutes after contact with water, followed by a slower one lasting (6 ÷ 7) h, after which time the hardening rate increases by a factor of 3. The hardening levels off after about 24 h. A
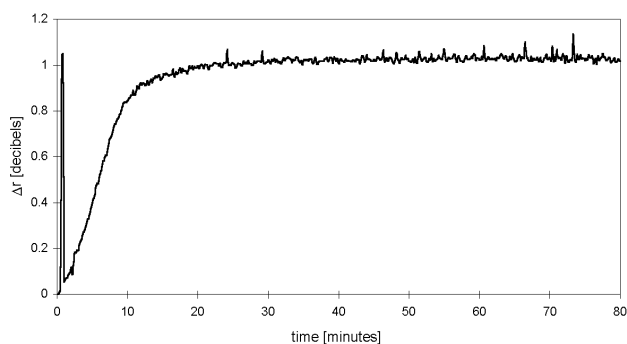
slight drop in the interval (24 ÷ 32) h is due to a small crack on the contact surface of the hardened paste observed after its removal from the measuring head.

In **Figure 7b** the early stage hydration of white cement paste with w/c = 0.5 is shown (12 h scan). It is seen, that the hardening process begins immediately after mixing with water. After 8 h the hardening rate decreases by almost an order of magnitude.

Hardening of epoxy:

The reflection coefficient changes during dry-out hardening of the two component UHU plus epoxy, mixed in 1:1 ratio, are shown in **Figure 8**. It seen from this figure, that a rather fast hardening rate in the first 10 minutes becomes much slower and almost levels off after 30 minutes. This agrees with the producer's data according to which the glue should be used-up within 5 minutes after mixing, becoming hard in 20 minutes and complete hardening achieved in 24 h. A correlation of the producer given hardness data with that obtained with ultrasonic reflection method can be made. Further, independent determination of usable times of the premixed gluing compound can be mad. A separate, more comprehensive study of different types of gluing compounds, including the dependence on different parameters (thickness, temperature, age, storage conditions), is planned.

4 CONCLUSIONS

The data presented in this paper show that the present performance of the apparatus for early hydration following of hydraulic materials, based on the pulsed echo ultrasonic shear wave method, is quite adequate. Reflection coefficient measurements are very sensitive to several important parameters characterizing these materials. Implications are a some application possibilities as complementary field testing or production control instrument and in research. It is also shown that the method is sensitive to cure (drying out) hardening, thus opening new numerous applications possibilities. In the case of mortar paste containing grains comparable or larger then the acoustic wavelength further research is needed for proper interpretation of results.

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Figure 8: Hardening of UHU plus epoxy
Slika 8: Strjevanje UHU plus epoxy lepila

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