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APPLICATIONS OF PULSED USWR METHOD FOR MATERIALS STUDIES

UPORABA PULZNE USWR METODE V RAZISKAVAH MATERIALOV

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In this contribution some application possibilities for nondestructive following, in time domain, of the early hydration processes of hydraulic pastes and reaction hardening of selected materials with a new apparatus employing pulsed ultrasonic shear waves reflection (USWR) method, are shown. The home-made apparatus USWR-2 Hardening meter is described. The sensitivity of the instrument to important parameters (rheology, composition, water content, fineness, particle size distribution, addition of additives, temperature, ageing) influencing a material behavior is eminent from the results obtained so far, offering several laboratory testing applications.

Key words: ultrasound, shear wave, cement, hydration, hardening

V prispevku so prikazani rezultati študije hidratacije in strjevanja izbranih materialov s pomočjo prototipa merilca strjevanja. Merilec (Hardening meter, USWR-2) je nov, doma razvit in konstruiran instrument. Osnovan je na metodi merjenja odboja pulznega ultrazvočnega strižnega valovanja (metoda USWR). Opisani aparat je posebno primeren za neporušno časovno sledenje začetnega dela procesa hidratacije (vezanje in strjevanje) past pripravljenih iz hidravličnih materialov. Prikazani rezultati pričajo na veliko občutljivost metode na spremembe vplivnih parametrov (reologija, sestava, vsebnost vode, finoča, velikostna porazdelitve zrn, dodatek aditivov, temperatura, staranje) na proces hidratacije, s čemer se ponujajo številne možnosti laboratorijske uporabe merilca.

Ključne besede: ultrazvok, strižno valovanje, cement, hidratacija, strjevanje

1 INTRODUCTION

When an ultrasonic wave hits an interface between two media, it is partially reflected and partially refracted. The reflection coefficient r is determined by the acoustic impedances Z_1, Z_2 of each of the two interface forming media. The latter are related to the viscoelastic properties G, the dynamic shear modulus, and η, the dynamic viscosity. One way of determining the acoustic impedance of a medium is by measuring r from an interface formed with a medium of known Z. This technique is implemented in our apparatus in which the medium 1 is a very pure fused quartz rod. It has been shown experimentally for a quartz/cement paste interface, that the relative phase changes of the shear wave on reflection are quite small with little influence on the magnitude of G when evaluated from the reflection data[1]. In this cases the modulus G_2 is related to the square of the Δr change by the equation $G_2 = (1/4\rho_2)[Z_1(\Delta r)]^2$, valid for samples in which Δr is small[2]. It has also been shown that the amount of the hydration α of a paste is proportional to $-\Delta r$ (minus sign because r is decreasing on hardening)[3].

2 APPARATUS

2.1 General

A model of an apparatus using the pulsed USWR method has been briefly described already[2]. In the exploration studies of the method and of the apparatus a number of difficulties appeared with this model, the main one being long term stability and reproducibility of the results. The model has therefore been discarded and a completely new apparatus, *USWR-2 Hardening meter*, shown in **Figure 1,** was designed and constructed. Its electronics operates on quite different principles with well defined ultrasonic rf pulses and a new measuring head design. Further, the apparatus allows the use of four measuring heads simultaneously. Its basic components are[4]: main frame box with transmitter/receiver electronics, A/D converter board and power supply, the measuring heads, PC computer (with suitable software).

2.2 Measuring head

Measuring head is of rugged construction and consists of a cylindrical aluminum body (ϕ *=30, l= 40 mm*) into which a very pure fused quartz rod of rectangular cross-section (a *= 10, b = 16 mm*) and length l *= 50 mm* is rigidly fastened. The two end surfaces of the quartz rod are flat, very parallel and highly polished. On one end (bottom) a PZE ultrasound transducer, acting as transmitter and receiver, is hard bonded. On the other end (top), with a measuring surface of *2 cm*^{2}, the sample to be tested is smeared. The thickness of the sample (typically a few *mm*) can be adjusted by sliding a sample mould (teflon or plexi-glass) up or down the external surface of the quartz rod **(Figure 1)**. The amount of the

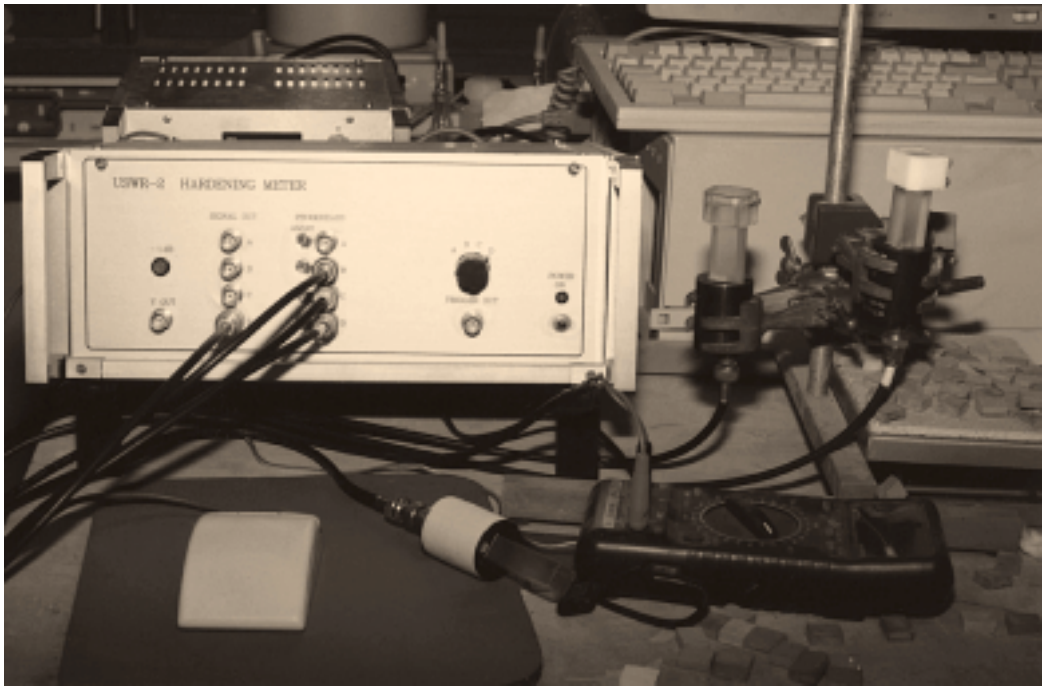

Figure 1: USWR-2 Hardening meter
Slika 1: Merilec strjevanja USWR-2

sample needed for one measurement is small (a few grams).

Hydration/hardening processes quite often last very long and the multitude/complexity from the influential parameters is high. For this reasons the apparatus shown is constructed in a multi-head version, with four measuring heads operating simultaneously. In **Figure 1** three are shown (two in use, one free) each of which is connected to the main frame with a coaxial cable. It is not necessary for the head to operate in the up-right position. For temperature dependence hydration/hardening studies the measuring head as a whole could be inserted in a variable temperature oven.

2.3 Principles of operation

A pulse generator excites the transducer with a short (*4 μs*), low power (*2 W*) rf pulse (*12 MHz*) every *1 ms*. The result is a rf ultrasonic shear wave pulse with an amplitude A_1 traveling to the top end of the quartz with shear sound velocity c_s. 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 s_1 echo reflects back into the quartz rod, 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 a smaller amplitude. The bouncing of the echo repeats again giving a third echo and so on. The result is an echo train with repetition of *1 ms*. The time interval between the echoes is $2l/c_s$. The number of echoes in a train 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 signal amplitudes with a preset amount of signal averaging prior being sent to a PC. With a software program installed one can continuously view the Δr change in real time on a PC monitor.

Incorporated in the apparatus is a calibration option. When triggered (manually) it creates a signal with the height corresponding to a *1 db* change. This calibration mark is superimposed as a sharp spike on the display.

2.4 Performance

The transmitter/receiver continuously function as soon as the apparatus is switched on. For the past *5 months* it has been left turned on except for short failures of the mains. During this period the apparatus experienced about 10^7 pulsed echo trains without failures. A very important characteristics for the rather long lasting hydration measurements is a good long term stability. At present it is estimated to be ± *0.05 db/ 24 h* and one order of magnitude better for the short term (*/1 h*) stability. The equipment is stabilized after a *15 min* warm-up.

3 APPLICATION EXAMPLES

Several application examples can be found in the references given. Herewith a few new ones are added. The sensitivity of the USWR method and of the

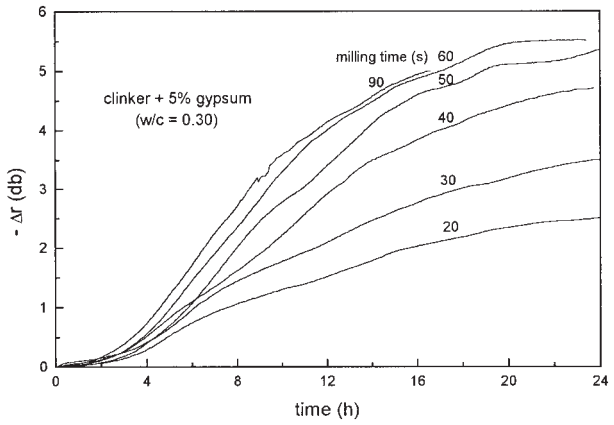

Figure 2: Hydration of a blend (clinker + 5% gypsum) milled for different time periods

Slika 2: Hidratacija mešanice (klinker + 5% gips) mletega različno dolgo

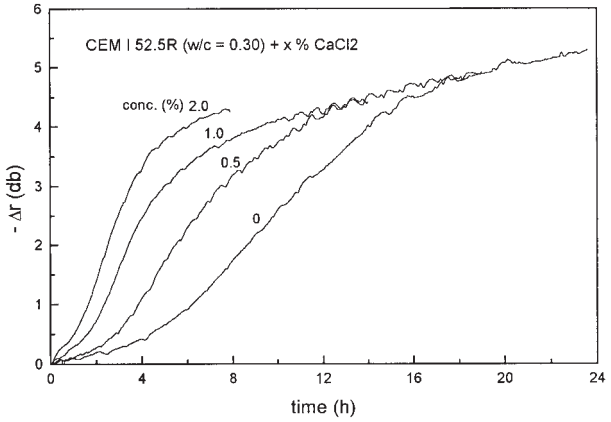

Figure 4: Hydration of CEM I 52.5R pastes with different amounts of $CaCl_2$ added

Slika 4: Hidratacija past narejenih iz CEM I 52.5R cementa z različno količino dodanega $CaCl_2$

apparatus to the fineness of a material is shown in **Figure 2**. The material used is clinker with standard *5%* anhydrous gypsum added and milled for different times with a laboratory mill (type Herzog). The samples were prepared by manually mixing *3 g* of powder with the corresponding amount of distilled water. It is apparent that the amount of hydrated material at comparable times differs by almost a factor of 3 for the two extreme milling times. The *90 s* curve is terminated after *16 h* due to the loss of contact resulting from large sample contraction on hydration. The *40 s* curve initially grows faster then the 50 s curve. This may be due to the manual mixing of small amounts of highly thixotropic behavior of the cement pastes. Further experiments are being made to correlate the USWR results with Blaine specific surface and laser obtained grain size distribution.

The sensitivity of the method to the ageing of a cement is shown in **Figure 3**. The material, PC 30dz 45s cement, used in these experiments was aged by exposing about *1/2 kg* of cement powder, spread in a layer about *5 mm* thick, to a constant humidity (*50%*) and temperature (*22°C*). Small quantities of cement powder were removed on corresponding days and stored in sealed plastic containers. The pastes *(w/c = 0.40)* were prepared similarly as above. The effect of ageing on the early hydration is quite drastic. The same results were obtained on pastes with *w/c = 0.30*. Further studies are needed for the explanation of the behavior shown.

The sensitivity to the addition of additives is presented in **Figure 4.** The pastes, hand mixed CEM I 52.5R cement powder (*3 g*) with distilled water, to which a corresponding amount of $CaCl_2$ was added, is used. The well known acceleration effects on the early hydration due to the $CaCl_2$ addition are apparent from these results. Some *Δr vs. t* curves terminate earlier due to the loss of sample/quartz contact.

An example of reaction hardening, wet forming of alumina ceramics from a coagulated aqueous suspension is given in **Figure 5**. The suspension of alumina ceramics powder in distilled water *(84% Al_2O_3 + 16% H_2O)* with *2.5% AlN* added was prepared at the Institute 'Jožef Stefan'. The reaction was followed at a constant

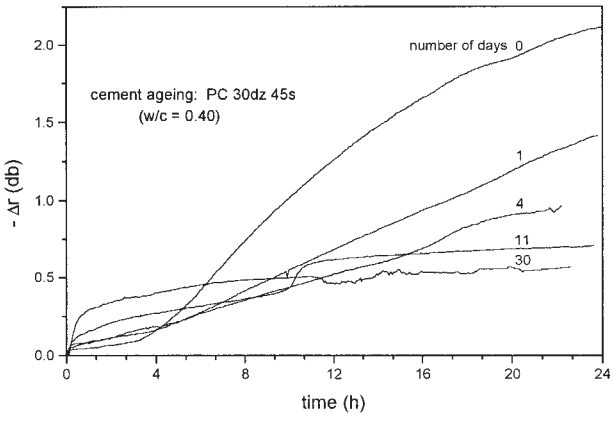

Figure 3: Hydration of pastes prepared with aged PC 30dz 45s cement

Slika 3: Hidratacija past narejenih iz staranega PC 30dz 45s cementa

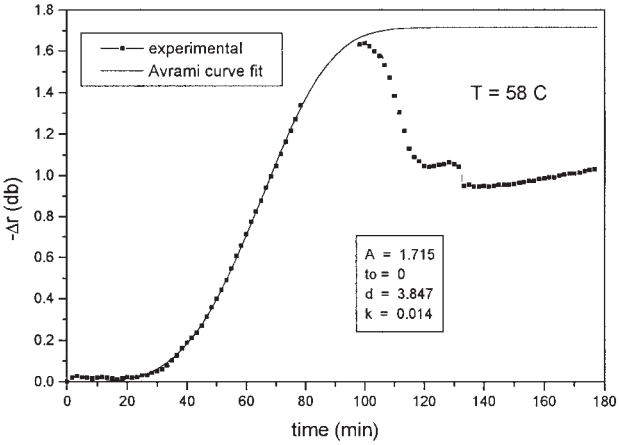

Figure 5: Reaction hardening of Al_2O_3 ceramics from aqueous suspensions

Slika 5: Strjevanje Al_2O_3 keramike z reakcijo iz vodne suspenzije

temperature of *58°C*. According to *Δr vs t* (doted) in **Figure 5**, the reaction of coagulation of the alumina ceramics, for this particular suspension and at this temperature, seems to complete in less then *100 minutes*. The same reaction at room temperature takes over *60 h*. The shape of the *Δr vs t* curve after *100 minutes* shows a fast decrease with a step change at *130 minutes*, followed by a slow increase. Similar behavoir has been found in the case of gypsum[2]. The reason for it is a gradual loss of the quartz/sample contact due to the volume contraction of the sample. This problem has recently been solved (to be published).

The forms of most USWR hydration curves seem to be sigmoidal with an induction period, the length of which depends on the amount of mixed water[3,4]. The most conventional method of describing a sigmoidal reaction is the Avrami equation:

$$\alpha = \alpha_0 + A\left\{1 - \exp\left[-(k(t - t_0))^d\right]\right\},$$

where α is the fraction of material that has been hydrated at a time *t*, t_0 the length of the induction period, α_o the amount hydrated in the induction period, *k* a parameter related to the reaction rate, *A* the total hydration due to the reaction considered and *d* an exponent depending on the time of law for new crystal formation and growth rate of an individual crystals. An Avrami fit to the experimental curve with ($t_0 = 0$, $\alpha_0 = 0$) fixed, is shown in **Figure 5**. The best fit is obtained wit $d = 3.85$, $k = 0.014$ and $A = 1.71$. The fit is very good indicating that $\Delta r(t) \propto \alpha(t)$. The fitting trials indicate the completion of the reaction after *110 min* in accordance with experiment. Further, the value of the exponent *d* is close to *4* for which the theory predicts a growth in the form of spheres. This is to be expected since the alumina ceramic powder is in the form of very fine spheres adhering together during the reaction.

A possible industrial application in the cement production quality control for measuring initial and final setting times of cements, a complimentary method to the standard Vicat apparatus, is presented in a separate paper[5].

4 CONCLUSIONS

New application possibilities for nondestructive testing and research on the hardening processes shown, e.g., early hydration of hydraulic materials, reaction hardening of some ceramics, further demonstrate the usefulness of the pulsed ultrasonic shear waves reflection (USWR) method. The new apparatus, *USWR-2 Hardening meter*, withstood extensive field testing on the basis of which commercial instruments could be available soon. The sensitivity of the apparatus to the rheology, composition, water content, fineness, grain size distribution, addition of additives, temperature, ageing, influencing a material behavior on hardening has been proved.

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