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Measurement of setting process of cement pastes using non-destructive ultrasonic shear wave reflection technique

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Abstract

In the paper a new setup for measuring setting and hardening process of cementitious materials, using a non-destructive ultrasonic shear wave reflection technique and designed with the objective to be easily used in-situ, is described. Using the developed setup, the measurements can be performed by slight deepening of a measuring head into a paste in a mold or by placing the paste into a mold fixed on a measuring head. To test the proposed methodology, cement pastes with different compositions were prepared and exposed to different curing temperatures. Significant differences in the evolution of a change of a shear wave reflection coefficient Δr in time were observed, indicating ability of the method to monitor setting process of cement pastes. Moreover, some interesting phenomena in the solidification process of the materials can be identified. A linear relationship between development of the Δr and penetration resistance d_p values in time was found, allowing development of a simplified procedure to determine both initial and final setting times of the material.

Keywords: Cement paste, Ultrasonics, Shear wave, Setting, Wave reflection method.

1. INTRODUCTION

On a large construction site, it is often difficult to estimate properties of cement based materials accurately due to differences in curing conditions between a lab and construction site. Among these, setting times are usually considered as the most important properties of early age cement based materials. Development of a suitable, reliable, and easy manageable non-destructive testing (NDT) method which enables continuous monitoring of the early age hydration and formation of structure process, including initial and final setting times, is therefore of considerable importance.

Advances in measurement and computer technology during recent years have allowed the development of many advanced methods to monitor the setting and hardening process of cement based materials. Among others, different ultrasonic (US) methods turned out to be very effective and reliable in evaluating microstructural changes during the early age hydration process of various cementitious materials, including ultra-high performance materials [1]. Due to unambiguous importance of both the initial (t_I) and final (t_F) setting times, a comprehensive research has been performed to estimate these essential characteristics with the use of the US methods. Using US wave transmission (USWT) technique, some procedures have been developed to identify the initial setting time based on various P-wave velocity threshold values [2–6]. Alternatively, certain features on the US P-wave velocity curves can be used to estimate the initial setting time, namely the first inflection point [5-8], the time when the P-wave velocity reaches velocity in water [5,6], the time when P-wave velocity starts to increase [9], or the intersection of three straight lines tangent to the P-wave velocity curve [10].

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Usually, USWT method can only be performed by accessing two sides of the specimen which often limits its practical application. To overcome this inconvenience, US wave reflection (USWR) method has been developed which requires one contacting surface. The technique was first applied to cementitious materials by Stepišnik et al. [11] and was extended further by Valič [12]. During the last decade, many studies have been performed to analyze the possibility of using this NDT US technique to describe setting and hardening behavior of different cementitious materials. Relationships between a shear wave reflection coefficient r (-) or a reflection loss RL (-) and the parameters which control properties of cementitious materials have been established. Correlation between a change of the reflection coefficient Δr and compressive and bending strength was reported by Valič and Vuk [13] and strong linear relation between RL and degree of hydration was found [14,15]. However, this relationship is not unique and is influenced by water/cement ratio. On the contrary, unique linear relationship was found between RL and decrease of capillary porosity [14] and RL and compressive strength [16]. Moreover, numerical simulations have shown that the development of RL is closely related to the development of some parameters that describe microstructural evolution of cementitious materials. Using HYMOSTRUC3D model [17,18], unambiguous relation between RL and specific contact area of solid phase was established [16].

Due to the practical usefulness of the USWR method, studies have been performed to determine the initial and final setting times using this NDT US technique. According to the original research performed by Valič et al. [19], both t_I and t_F times were found to appear at the same level of Δr , independently of w/c ratio changing from 0.25–0.30. Sun et al. [14,16] performed a similar study on three cement pastes with w/c ratios equal to 0.35, 0.50, and 0.60 and suggested to define a specific value of RL within a certain interval of probability to indicate the occurrence of the initial setting regardless of w/c ratio. On the contrary, they indicated that final setting can not be defined by using a specific value of RL . According to Voigt et al. [20] a consistent relationship between t_I and the point at which the $RL - t$ curve starts to increase could be identified. Using L-wave pulse reflection technique, Ozturk et al. [21] indicated that t_I and t_F setting times coincide with the time of the first inflection point on the curve representing the development of the shear wave reflection coefficient WRF in time and the time when the $WRF - t$ curve starts to increase after having reached its minimum, respectively. Chung [22] found out that the initial set occurs later than the onset of stiffening of the material, indicated by a rapid change in the slope of the $\Delta r - t$ curves [23].

These results indicate the ability of USWR method to monitor the setting behavior of cement-based materials. However, since a very limited number of parameters which influence hydration kinetics have been used in previous studies [14, 16, 19-21], additional experiments are necessary to analyze the possibility of using USWR method to estimate both t_I and t_F times in more detail. Consequently, relationship between the setting times and USWR method is worthy of further investigation [16].

For this purpose, a comprehensive experimental work was performed with the results presented in this article. A new USWR apparatus was developed aimed to develop an instrument which can be easily and effectively used in-situ. Evolution of the change of the shear wave reflection coefficient Δr and penetration resistance d_P with time were measured simultaneously on twenty cement pastes with various compositions and exposed to different curing temperatures to get a relevant and appropriate relationship between these two characteristic parameters. The influence of water/cement ratio (w/c), ambient temperature (T_A), cement type, cement fineness (BS), and amount of C_3A on the $\Delta r - d_P$ relationship was studied. On the basis of these results, a simplified procedure to determine both initial and final setting times is presented.

2. EXPERIMENTAL MATERIALS AND METHODS

2.1 Experimental methods

2.1.1 Ultrasonic Wave Reflection Method

A basic model of an apparatus using pulse USWR method has been already described by Valič [12]. However, during the recent years, several ideas for improvements came out with the objective to develop an instrument which can be easily and effectively used in-situ. As a result, a new apparatus USWR-4

Hardening meter was constructed in a multi-head version with four measuring heads operating simultaneously, allowing the measurements to be performed at four different locations.

A detailed description of the principles of operation and performance of the apparatus is beyond the scope of this paper and can be found in [12]. However, some basic description is necessary to properly track the focus of the article. The USWR-4 Hardening meter is shown in Fig. 1 and consists of a main frame box with transmitter/receiver electronics, A/D converter board and power supply, measuring heads, and PC computer with suitable software. Measuring heads are of rugged construction and consist of a cylindrical aluminum body ($\Phi = 30$ mm, $l = 40$ mm) in which a very pure fused quartz rod of rectangular cross-section ($a = 10$ mm, $b = 16$ mm) and length $l = 50$ mm is rigidly fastened. On the bottom end a PZE ultrasound transducer, acting as a transmitter and receiver, is hard bonded. A typical measuring sensor is shown in Fig. 1a. On the top end, with a measuring surface of 2 cm², the sample to be tested is smeared (Fig. 1b) which can be easily performed at laboratory conditions. Alternatively, the quartz rods can be simply pushed into the sample (Fig. 1c) or installed on the surface of the concrete element, allowing the measurements to be performed in-situ.

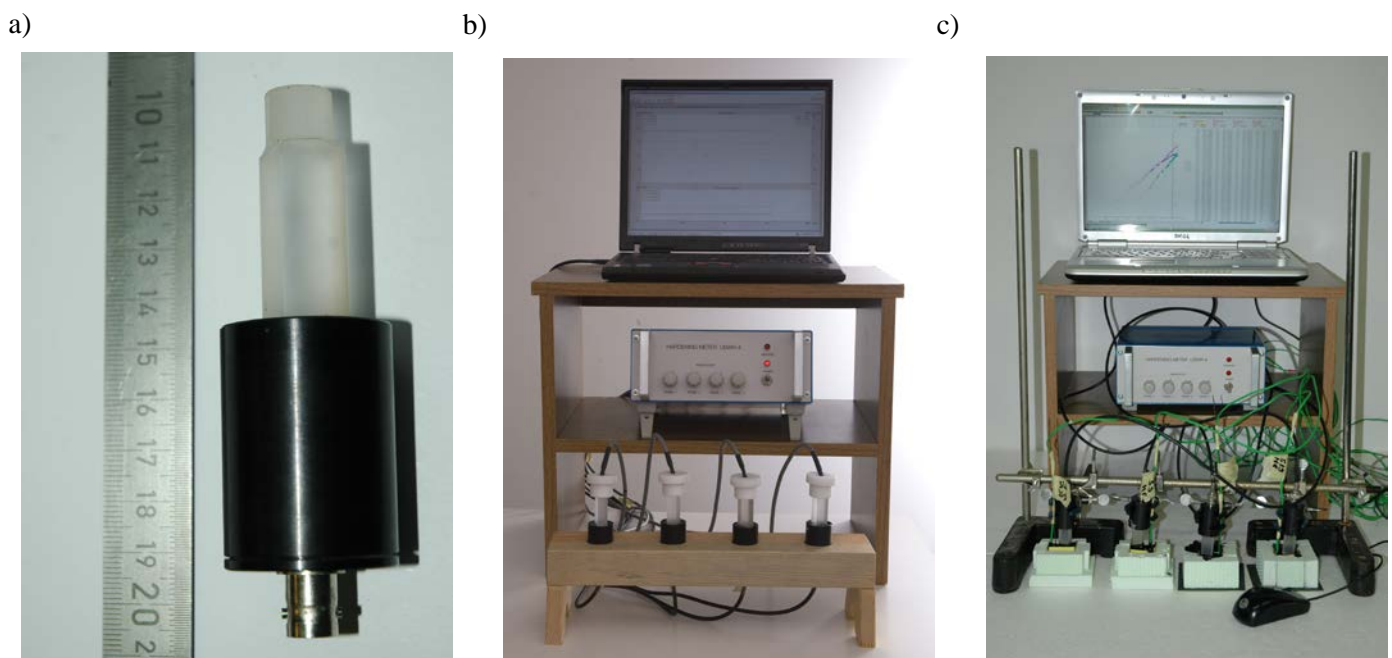


Fig. 1. USWR 4-Hardening meter with four measuring heads operating simultaneously; a) typical measuring sensor, b) possibility of laboratory application, c) possibility of in-situ application.

The principle of the USWR method consists of monitoring a dimensionless shear wave reflection coefficient r at the interface formed by a quartz buffer material and the cement paste. Quartz has smaller acoustic impedance than steel resulting in a wider range in that the r changes [24]. The measuring head is brought in contact with the cement paste immediately after mixing. As a result of the hydration process, hydration products develop, resulting in a larger amount of a solid phase in the structure of the material. Consequently, US wave propagation characteristics of the material are changing continuously, resulting in a variation of r obtained from the amplitudes of successive reflections received from the buffer/cement paste interface in real time. As the time progresses, the amplitude of the first echo remains constant while the amplitudes of higher order echoes are changing constantly, resulting into echoes with smaller amplitudes and consequently lower values of the shear wave reflection coefficient r . The shear wave reflection coefficient r is obtained by measuring s_1 and s_2 back echo amplitudes with a preset amount of signal averaging prior being digitalized and sent to PC computer, resulting into relatively smooth $r - t$ curves. The signals are obtained with a repetition rate of 1 ms. A detailed theoretical description of the r determination can be found in [12]. In this study, the change of the reflection coefficient Δr (i.e. $\Delta r = 1 - r$) will be used in presenting the reflection coefficient data, which is increasing with the continuing hydration process [12].

2.1.2 Vicat method

As a supplementary method standard Vicat Needle tests according to European EN 196-3 standard were performed on all cement paste mixtures simultaneously to the USWR measurements. The method is based on measuring depth of penetration d_p' of a steel cylinder needle into the cement paste. The penetration tests were performed at regular time intervals until the cement paste was completely set, resulting into a $d_p - t$ diagram for each cement paste mixture, where d_p represents the distance between the needle and the base plate (i.e. $d_p = 40 - d_p'$). According to the relevant standard, the time when the d_p reaches value of 6 ± 3 mm, measured to the nearest minute, was determined from the obtained $d_p - t$ curve and defined as the initial setting time t_I of the material. The time of the last measurable d_p value, representing the final value of the $d_p - t$ curves (i.e. the value of d_p close to 40 mm) was chosen as the final setting time t_F in this study. After that (at the next consecutive test time), the penetration into the material was not possible any more.

2.1.3 Statistical methods

Basic descriptive statistics were used to quantitatively describe main features of a collection of experimental data, namely maximum, minimum, and median values. To measure dispersion that accompanies the median, an interquartile range (IQR) was used, being the range of values within which reside the middle 50% of the scores (i.e. the distance between the upper Q_3 and lower Q_1 quartiles).

2.2 Experimental materials

2.2.1 Cements

The cements used in the investigation were Type I and Type II Portland cements with the characteristics presented in Table 1. AC and BS in the table stand for the clinker content and Blaine surface of the cement, respectively. The calculated Bogue compositions of the cements (mass fractions) were deduced from a chemical characterization.

Table 1. Basic characteristics of the cements used in the study.

cement type	AC [%]	BS [cm ² /g]	C ₃ S [%]	C ₂ S [%]	C ₃ A [%]	C ₄ AF [%]
CEM II/A-S 42,5R	> 80	4260	32.85	46.32	10.36	10.47
CEM I 52,5 R	> 95	4310	57.70	13.00	6.90	8.90
CEM I 42,5 N	> 95	2640	60.20	13.60	7.20	9.30
CEM I 42,5 N SR	> 95	3130	55.90	21.90	2.30	15.00

2.2.2 Cement pastes

Twenty different cement pastes were prepared to reach a wide range of hydration kinetics on which to test the proposed methodology. The pastes are summarized in Table 2 and can be divided into five groups, depending on the cement paste composition and curing temperature. Labeling of the pastes is according to a dominant variable of each group.

To get three different values of cement fineness, cement types CEM I 52,5R and CEM I 42,5N were used separately and one mixture (BS = 3490 cm²/g) was prepared by combining these two cements in equal amounts. This was possible due to very similar chemical composition of these cements. Similar procedure was used to obtain three values of C₃A where cement types CEM I 42,5N SR and CEM I 42,5N were used.

Table 2. Cement paste mixtures used in the study.

Mixture label	Cement type	w/c	SP [cm ² /g]	C ₃ A [%]	T _A [°C]
w/c = 0.30	CEM II/A-S 42,5R	0.30	4260	10.4	20
w/c = 0.35	CEM II/A-S 42,5R	0.35	4260	10.4	20
w/c = 0.40	CEM II/A-S 42,5R	0.40	4260	10.4	20
w/c = 0.50	CEM II/A-S 42,5R	0.50	4260	10.4	11
	CEM II/A-S 42,5R	0.50	4260	10.4	21
	CEM II/A-S 42,5R	0.50	4260	10.4	26
	CEM II/A-S 42,5R	0.50	4260	10.4	32
w/c = 0.60	CEM II/A-S 42,5R	0.60	4260	10.4	11
	CEM II/A-S 42,5R	0.60	4260	10.4	20
	CEM II/A-S 42,5R	0.60	4260	10.4	26
	CEM II/A-S 42,5R	0.60	4260	10.4	32
w/c = 0.65	CEM II/A-S 42,5R	0.60	4260	10.4	20
CEM I 42,5 N					
SP = 2640 cm ² /g C ₃ A = 7.2%	CEM I 42,5 N	0.50	2640	7.2	20
CEM I 42,5 N SR					
C ₃ A = 2.3%	CEM I 42,5 N SR	0.50	3130	2.3	20
CEM I 52,5 R					
SP = 4310 cm ² /g	CEM I 52,5 R	0.50	4310	2.6	20
CEM I 42,5 N					
	CEM I 42,5 N	0.40	2640	7.2	20
CEM I 42,5 N SR					
	CEM I 42,5 N SR	0.40	3130	2.3	20
CEM I 52,5 R					
SP = 3490 cm ² /g	CEM I 52,5 R	0.50	3490	7.1	20
	CEM I 42,5 N				
C ₃ A = 4.8%	CEM I 42,5 N	0.50	2800	4.8	20
	CEM I 42,5 N SR				

2.2.3 Sample preparation and experimental procedure

About 80 cm³ of each cement paste was mixed according to European EN 196-1 standard. For all cement pastes, the duration of mixing was 2 min from the initial contact of cement with water. Afterward, about 2 cm³ of the material was smeared into the mould and all the samples were sealed with thermoplastic laboratory film to prevent water evaporation.

Within the present study, Δr measurements started immediately after casting (i.e. 2 min after first contact of cement with water) and were carried out continuously over duration of approximately 40 hours after mixing. US measurements were conducted in a climate chamber at $T_A \pm 1^\circ\text{C}$ and 60% relative humidity.

The results were recorded at 1 min time intervals, resulting in a $\Delta r - t$ diagram for each cement paste mixture.

3. RESULTS AND DISCUSSION

3.1 Typical development of the Δr coefficient in time

Fig. 2 shows typical evolution of the change of the shear wave reflection coefficient Δr and the rate (numerical time derivative $d\Delta r/dt$) of Δr , labeled as $\Delta r'$, for a typical cement paste mixture during the first 24 hours. As an example, a typical shape of the waveform in time domain showing multiple reflections in the case of cement paste is presented in Fig. 3. The presented waveform belongs to the cement paste presented in Fig. 2 and was obtained at the time $t = 5.2$ h.

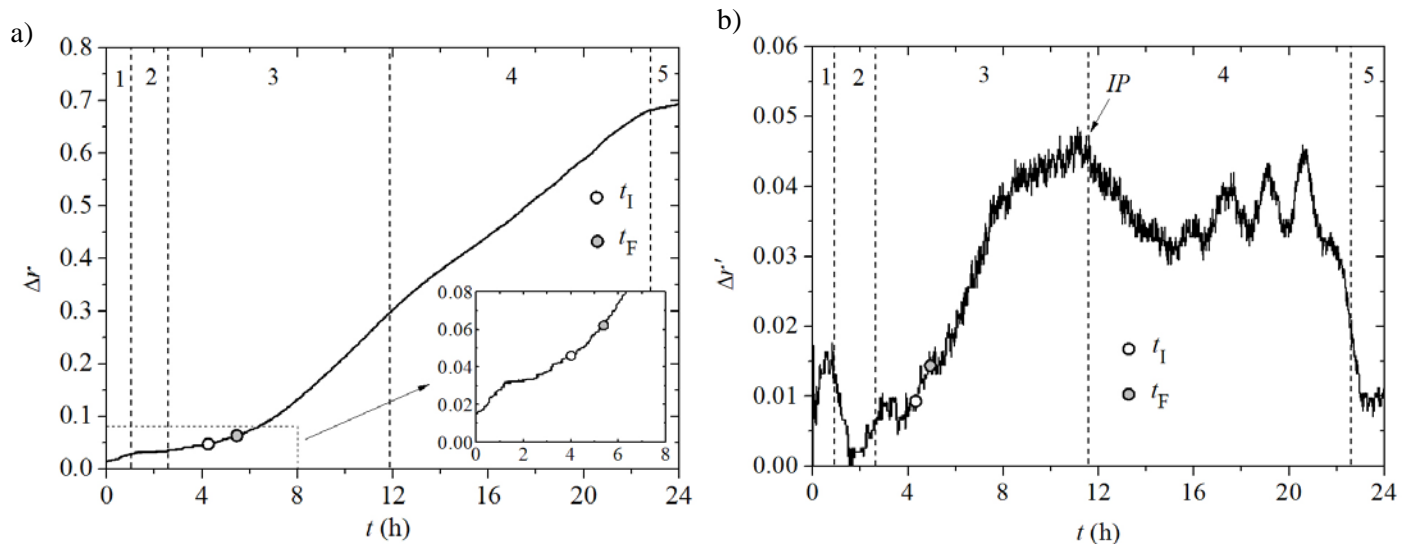


Fig. 2. Typical evolution of the Δr and rate of Δr coefficient in time; a) $\Delta r - t$ curve, b) $\Delta r' - t$ curve.

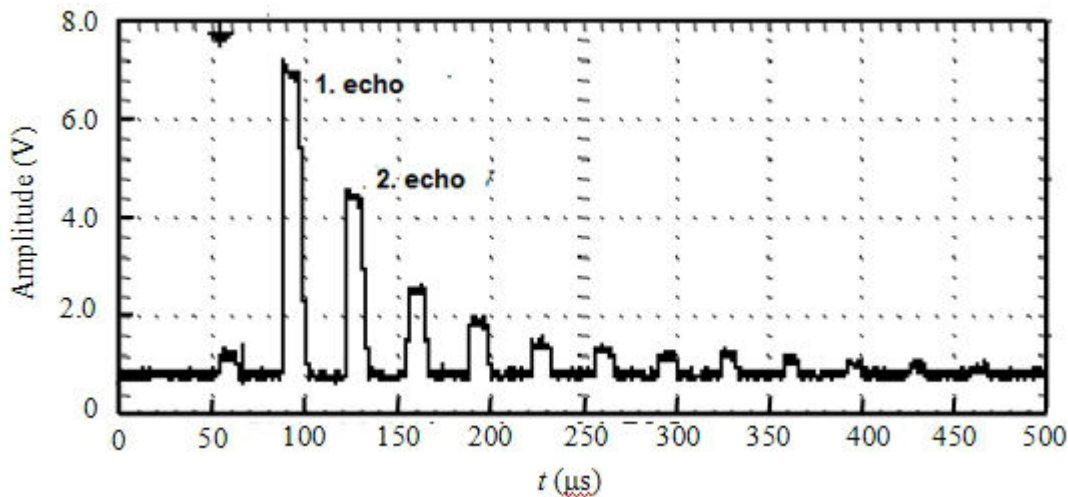


Fig. 3. Typical waveform of multiple reflections in time domain.

According to Sun et al. [14,16] a typical curve of the development of reflection loss in time can be divided into three stages. Using the presented USWR method, five stages can be defined on the basis of the Δr and $\Delta r'$ evolution in time (see Fig. 2). The partition of the hydration process into five stages corresponds well with the observations presented by some other researchers (e.g. [25]) who based their

research on the heat release during the hydration process. Stage 1 occurs immediately after water is first added to the cement. During this stage a short period of a small increase of Δr value is observed which, depending of the cement paste composition, usually lasts for about 15–30 minutes. During the 2nd stage (dormant stage), the rate of the initial reaction is slowed down and a short plateau is reached on the $\Delta r - t$ diagram, indicating a considerable plasticity of the material. During stage 3 (acceleration stage), Δr values start to increase slowly at first and faster later up to the inflection point IP , presented on the $\Delta r' - t$ curve (Fig. 2b). This characteristic point represents maximum rate of Δr evolution in time and separates stages 3 and 4. The intensive increase in Δr during the 3rd stage could be attributed to an intensive growth of different hydration products [21] and consequently increasing amount of the total and the connected solid phase in the microstructure of the material [26]. During the 4th stage (deceleration stage) the rate of Δr increase slows down (see Fig. 2b) until a final period on the $\Delta r - t$ curve is reached. At this moment stage 5 begins, representing a continuing slow increase of the Δr values.

In Fig. 2, hollow and solid circles represent initial and final setting times, respectively, and were obtained by marking points on the $\Delta r - t$ and $\Delta r' - t$ curves, corresponding to the initial (t_i) and final (t_f) setting times, determined using standard Vicat method. As can be seen from inset graph in Fig. 2a, these characteristic points appear during the period of unambiguous increase in Δr values and therefore indicate possibility of using Δr values to estimate initial and final setting times. Relationship between setting times and Δr values will be discussed in detail for all analyzed mixtures later in the article.

Unaffected steep increase in Δr values far beyond the final setting time when penetration into the material is not possible any more is also evident from Fig. 2, indicating ability of the proposed US method to detect microstructural changes that occur after the setting period of the material. As will be demonstrated later in the article, this is an important advantage over penetration resistance methods which enables observation of some interesting phenomena that occur after the setting period.

3.2 Influence of cement paste composition on the development of Δr coefficient in time

A possibility and repeatability of using the USWR method to study the influence of the cement paste composition and curing temperatures on the hydration process and formation of the material microstructure has been already briefly indicated by the authors in [27]. However, to reach the focus of this research, many additional cement paste mixtures were analyzed. As a result, development of $\Delta r - t$ curves for all analyzed cement paste mixtures is presented in Fig. 4.

First, a wide range of w/c ratio was analyzed with the results presented in Fig. 4a. As expected, mixtures with higher w/c ratio show lower Δr values which can be related to the microstructure of the cement paste. The evolution of the US pulse velocity was found to be correlated to the amount of a total and connected solid phase [26] and it is well known that these two quantities are higher in the case of lower w/c ratio.

In Fig. 4b, the influence of the cement type on the development of the Δr values in time is presented. This analysis was performed on cement paste mixtures with two different w/c ratios. Light and dark curves represent mixtures with w/c ratio of 0.50 and 0.40, respectively. It is evident that cement type has a significant influence on the evolution of the Δr values. Interestingly, higher differences between different cement types were observed in the case of lower w/c ratio.

The influence of cement fineness is shown in Fig 4c. It can be seen that cement fineness has an important influence on the evolution of Δr values and as expected, higher fineness results in a more rapid hydration process and consecutively to a more rapid evolution of the Δr .

Fig. 4d demonstrates the influence of the amount of tri-calcium aluminate (C_3A) on the evolution of the $\Delta r - t$ curves. Lower amount of C_3A results in slower evolution of the Δr values.

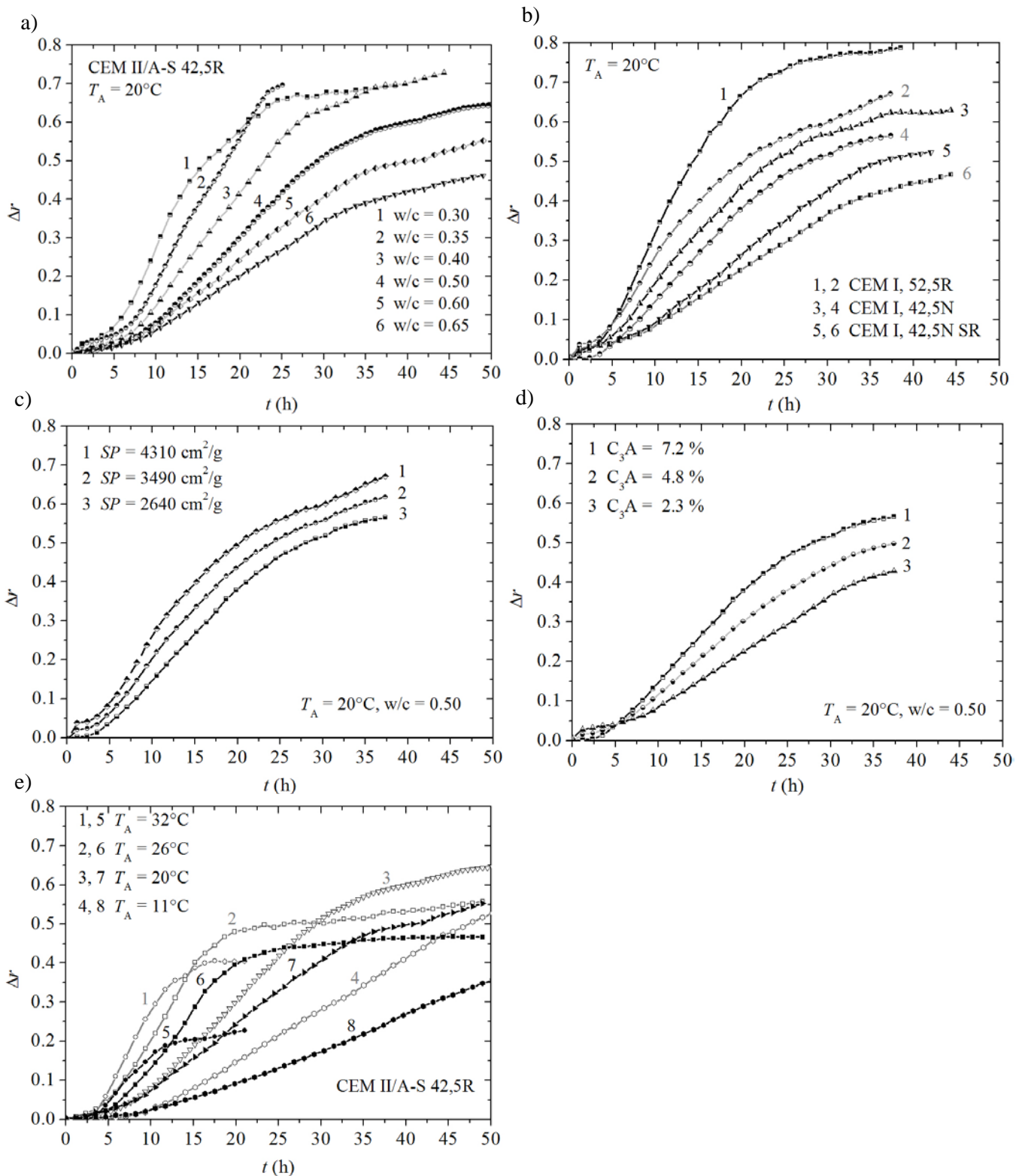


Fig. 4. The development of the Δr coefficient in time influenced by; a) w/c ratio, b) cement type, c) cement fineness, d) C_3A amount, e) curing temperature.

In Fig. 4e, the influence of curing temperature on the development of the $\Delta r - t$ curves is presented. Again, this analysis was performed on cement paste mixtures with two different w/c ratios. Light and dark curves represent the mixtures with the w/c ratio of 0.50 and 0.60, respectively. It is seen that higher curing temperatures result in a more rapid increase of the Δr values at the very beginning of the hydration process. However, as the hydration progresses, the $\Delta r - t$ curves intersect at a certain hydration time, resulting into higher long-term Δr values in the case of lower curing temperature. As can be seen from

Fig. 4e, the time of the intersection decreases with increasing curing temperature and decreasing w/c ratio. This interesting phenomenon can be attributed to a well known cross-over effect [28] which has been already observed by many researchers in the case when the influence of the curing temperature on the development of concrete compressive strength [29-31] and the influence of an initial concrete temperature on the development of adiabatic hydration curves [32] was analyzed. The cross-over effect can be explained by the fact that the increased rate of the hydration caused by higher curing temperatures does not allow sufficient time for proper distribution of various hydration products and a barrier forms around cement particles and hydration products, resulting into a weaker bond between the hydration products which hinders further hydration and formation of structure of cement based materials [17, 31, 33]. Although similar cross-over effect has been briefly presented by Sun [16], it was less evident in this case.

It is also seen that in some diagrams of Fig. 4 a very small increase in Δr values occurs at time $t = 0$, i.e. immediately after contact of the probe with the test sample. It is believed that this is due to viscoelastic nature of cement pastes at the very early hydration period in which shear modulus is a complex quantity with a very small real component [12], value of which depends on the cement paste composition. This interesting phenomenon is even more observed in Figs. 5, which show the development of the $\Delta r - t$ curves during the early hydration process (up to 12 h). The initial increase is more pronounced in the case of lower w/c ratio (see Fig. 5a and 5b) and higher cement fineness (Fig. 5g) and is attributed to a denser material in these cases. Since the effect depends on the cement paste composition, the initial increase in Δr is not influenced by different curing temperature which can be clearly seen from Figs. 5c and 5d. Interestingly, higher initial increase in Δr values was observed in the case of lower C_3A content (see Fig. 5h). Using similar USWR technique, such, but much larger changes were measured and documented in the case of visco-elastic (non-cementitious) materials, like bitumen, epoxy, and motor oils [34].

Significant differences in the evolution of the $\Delta r - t$ curves indicate that USWR method could represent an advanced NDT technique to monitor the setting and hardening process of cement based materials from the very beginning of the hydration process.

3.3 Comparison between Δr and d_p development in time

In Fig. 5, comparisons between Δr (solid curves, right y axis) and d_p (dashed curves, left y axis) development in time are presented for all analyzed cement paste mixtures. For clarity, time axes are reduced to the period from 0 – 12 hour. In the figure, initial and final setting times are presented on each $\Delta r - t$ curve as hollow and solid dots, respectively, which were obtained by marking points on $\Delta r - t$ curves corresponding to the setting times, determined from dashed $d_p - t$ curves using standard Vicat method. Dotted horizontal lines in the figures represent value of $d_p = 6$ mm, which is used as a criterion to define initial setting time (refer to section 2.1.2). In the case of the lowest curing temperature (i.e. $T_A = 11^\circ\text{C}$ in this study), the final setting times are not indicated in the figures since they appear after the first 12 hours (refer to Table 3). As expected, initial and final setting times are influenced by cement type significantly and decrease with decreasing w/c ratio and increasing curing temperature, cement fineness, and C_3A amount.

Fig. 5 indicates that the two characteristic points appear after the dormant stage on the corresponding $\Delta r - t$ curve. Next, it can be seen from this figure and Table 3 that Δr_1 values, corresponding to the initial setting time t_i , do not appear at the same Δr level. This is an important observation and is in contrast to the results presented by Sun et al. [14], who performed a similar study on three cement pastes with different w/c ratios (0.35–0.60) and indicated that all three pastes had a very similar value of the reflection loss. The largest differences between Δr_1 values were observed for different curing temperatures (Figs. 5c and 5d) and decrease with the decreasing curing temperatures.

According to the results presented in Table 3, average Δr_1 value is 0.052 (0.050, 0.055) with a standard deviation of 0.017 where values in brackets stand for 95 % confidence interval. Differences between Δr_1 values can be attributed to different mechanisms of the USWR and penetration resistance methods and initial increase in Δr values in the case of some cement pastes (refer to section 3.2).

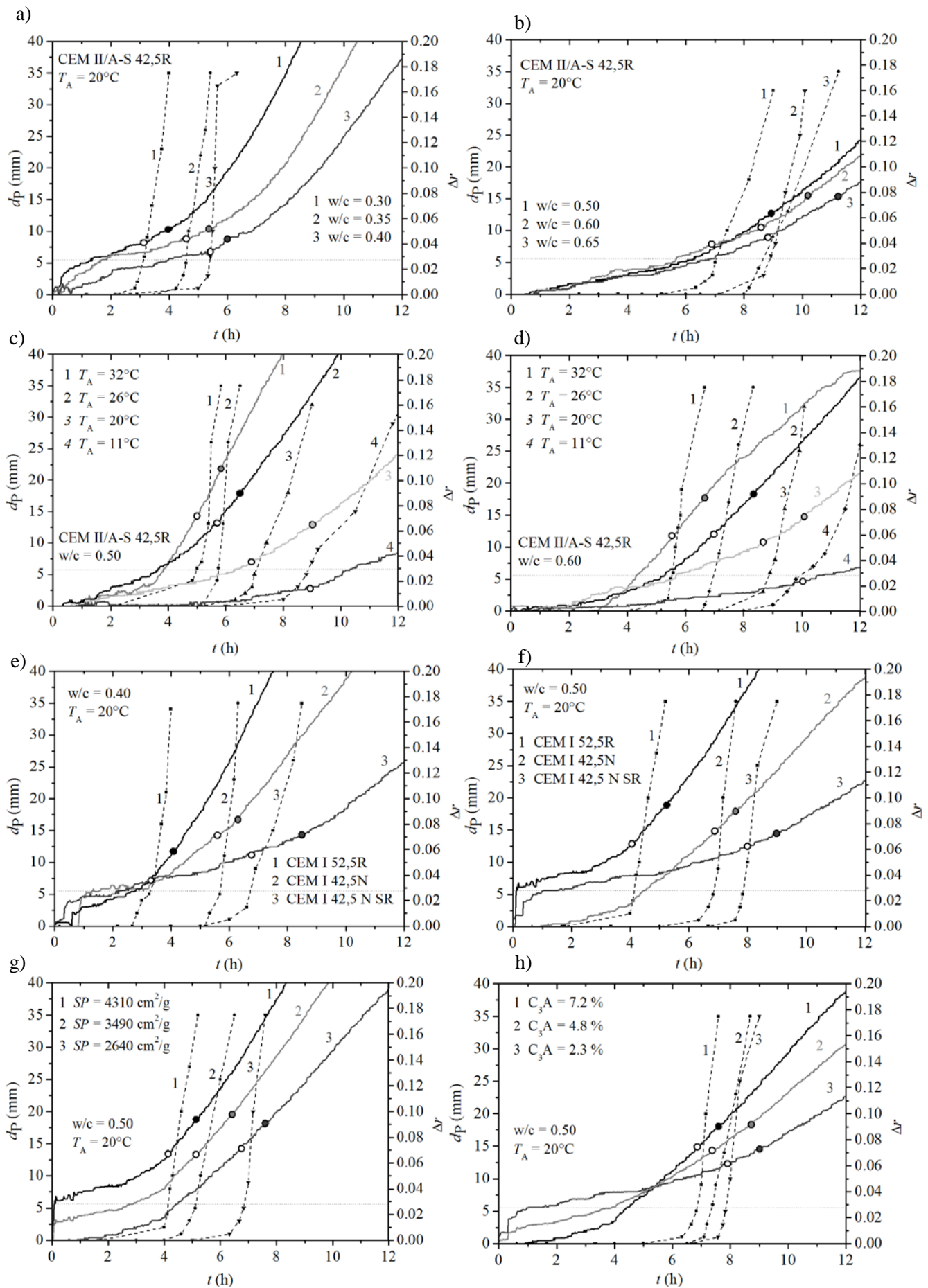


Fig. 5. Relationship between Δr and d_p development in time, influenced by; a,b) w/c ratio; c,d) curing temperature; e,f) cement type; g) cement fineness; h) C_3A amount.

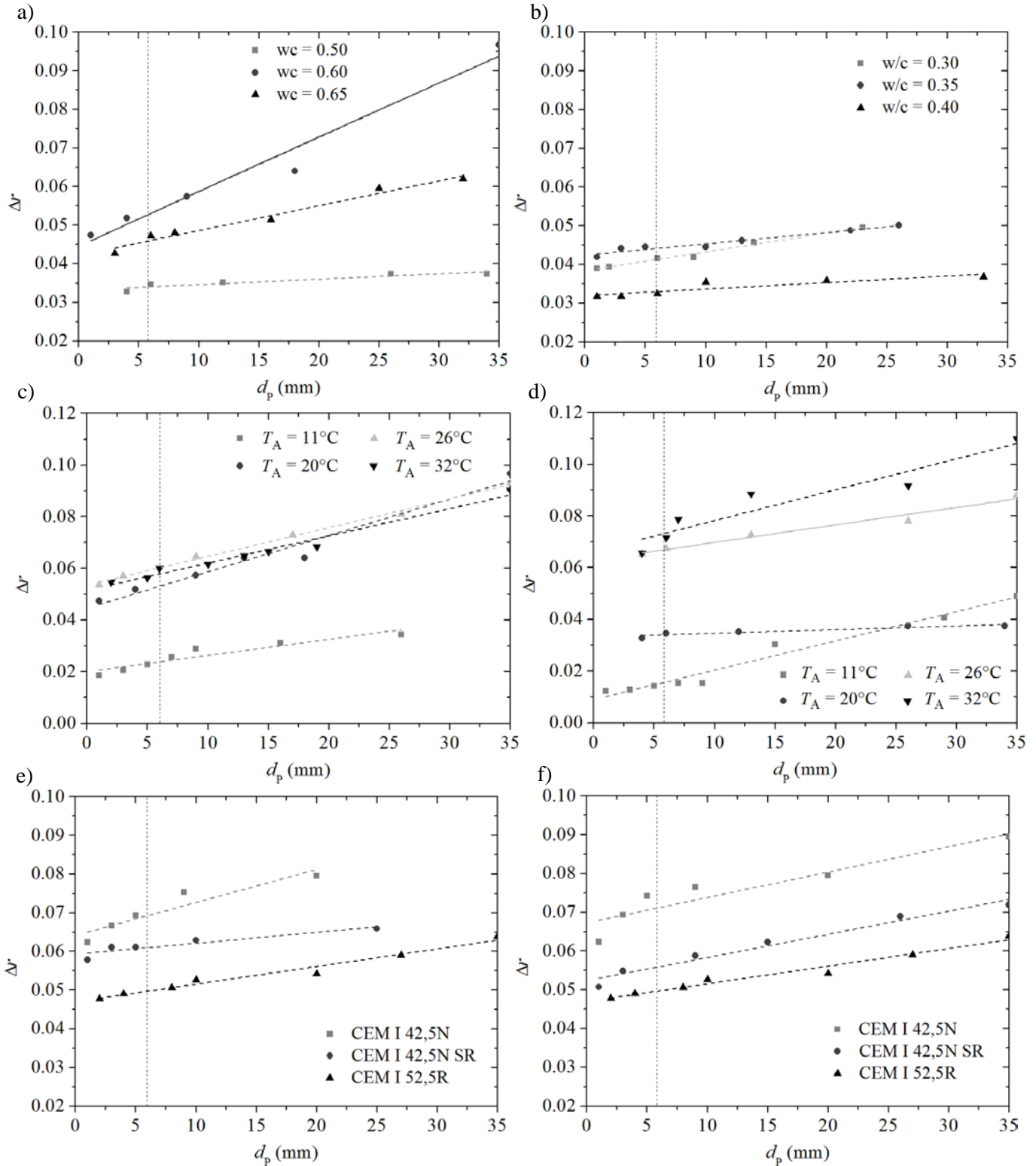
Table 3. Setting times and correlation coefficients of $\Delta r - d_p$ relationship for all cement paste mixtures analyzed in the study.

mixture label	setting times				$\Delta r - d_p$ relationship		
	t_I (h)	Δr_I (-)	t_F (h)	Δr_F (-)	R^2_{\log}	R^2_{lin}	
CEM II/A-S, 42,5R	w/c = 0.30	3.1	0.041	4.0	0.051	0.98	0.98
	w/c = 0.35	4.3	0.043	5.4	0.051	0.93	0.94
	w/c = 0.40	5.3	0.033	6.1	0.043	0.81	0.75
	w/c = 0.50, $T_A = 20^\circ\text{C}$	6.8	0.040	9.0	0.061	0.93	0.84
	w/c = 0.60, $T_A = 20^\circ\text{C}$	8.7	0.051	10.1	0.078	0.90	0.95
	w/c = 0.65	8.9	0.042	11.2	0.078	0.96	0.98
w/c = 0.40	CEM I 52,5R	3.2	0.038	4.0	0.058	0.95	0.98
	CEM I 42,5N	5.5	0.072	6.2	0.082	0.97	0.85
	CEM I 42,5N SR	6.8	0.057	8.3	0.071	0.93	0.85
w/c = 0.50	CEM I 52,5R $SP = 4310 \text{ cm}^2/\text{g}$	4.1	0.062	5.2	0.093	0.95	0.97
	CEM I 42,5N $SP = 2640 \text{ cm}^2/\text{g}$ $C_3A = 7.2 \%$	6.8	0.074	7.7	0.091	0.92	0.83
	CEM I 42,5N SR $C_3A = 2.3 \%$	7.9	0.061	9.1	0.071	0.98	0.97
w/c = 0.50	$T_A = 32^\circ\text{C}$	5.0	0.071	5.9	0.110	0.87	0.89
	$T_A = 26^\circ\text{C}$	5.8	0.066	6.4	0.090	0.94	0.97
	$T_A = 11^\circ\text{C}$	9.0	0.013	13.1	0.048	0.96	0.97
w/c = 0.60	$T_A = 32^\circ\text{C}$	5.6	0.060	6.7	0.090	0.96	0.98
	$T_A = 26^\circ\text{C}$	7.0	0.059	8.3	0.092	0.99	0.99
	$T_A = 11^\circ\text{C}$	10.2	0.024	13.3	0.047	0.96	0.87
-	$SP = 3490 \text{ cm}^2/\text{g}$	5.1	0.068	6.5	0.098	0.98	0.98
-	$C_3A = 4.8 \%$	7.3	0.071	8.9	0.092	1.00	1.00

Similarly, Δr_F values, corresponding to the final setting times t_F , do not appear at the same Δr level, which is in agreement with the results presented by Sun et al. [14,16] and further substantiates the assumption that shear wave reflection coefficient and penetration resistance should be related to the presence of some different phenomena that appear during the stiffening process of cement pastes. Average Δr_F value was determined to be 0.074 (0.071, 0.077) in this study. Again, the largest differences were observed in the case of different curing temperatures (Figs. 5c and 5d).

In Fig. 6, relationships between Δr and d_p values are presented for the whole setting period until the cement pastes were completely set. The $\Delta r - d_p$ diagrams were obtained from Fig. 5 by plotting Δr vs. d_p values at equal times t . A dashed line indicates the initial setting (i.e. $d_p = 6 \text{ mm}$). Concerning the results presented in Fig. 6, both linear and logarithmic relationships between the change of the shear wave reflection coefficient and penetration resistance were studied. In Table 3, correlation coefficients R^2_{lin} and

R^2_{\log} , representing correlation coefficients in the case of linear and logarithmic $\Delta r - d_p$ relationships, respectively, are summarized for all analyzed cement paste mixtures. Average correlation coefficients in the case of linear and logarithmic relationships were determined to be 0.93 (0.92, 0.94) and 0.94 (0.94, 0.95), respectively, where values in brackets stand for the 95 % confidence intervals. High R^2_{lin} and R^2_{\log} values indicate that the shear wave reflection coefficient clearly reflects evolution of the (connected) solid phase in cement paste during the whole setting period. However, the $\Delta r - d_p$ relationship is not unique, proving different sensitivity of both methods to the presence of various parameters which influence the hydration kinetics.



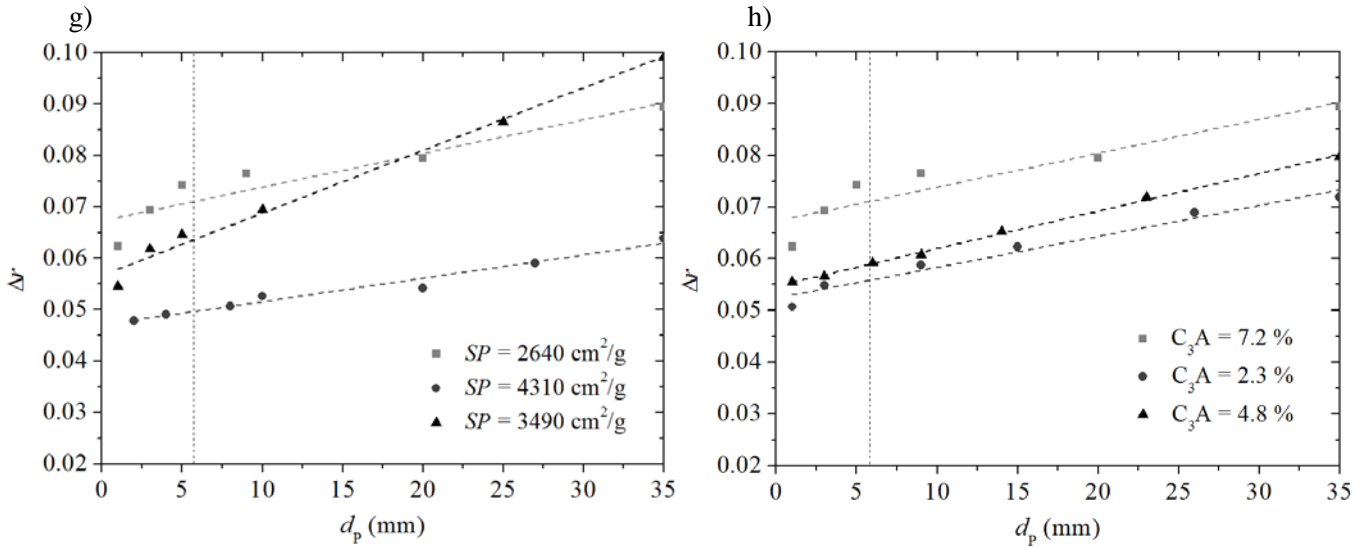


Fig. 6. Relationships between Δr and d_p values influenced by; a,b) w/c ratio, c,d) curing temperature, e,f) cement type, g) cement fineness, h) C_3A amount.

3.4 Simplified procedure to determine the initial and final setting time using USWR method

On the basis of the results presented in Fig. 6, a simplified procedure for the determination of the complete $d_p - t$ curve, including both initial and final setting time of a specific cement paste mixture is presented in Fig. 7. Since very similar R^2 values were observed in the case of both linear and logarithmic relationships (refer to Table 3), the procedure is based on the linear $\Delta r - d_p$ relationship due to its simplicity.

Consequently, two d_p (d_{pA} , d_{pB}) values (step 1) and corresponding Δr (Δr_A , Δr_B) values (step 2) have to be determined at two different times t_A and t_B (see Fig. 7a) to establish a unique $\Delta r - d_p$ relationship (step 3, Fig. 7b) over the entire setting period. These points can be chosen arbitrary during the whole setting period of the cement paste (see Figs. 7a and 7b) which significantly fastens and simplifies the procedure.

Next, a value of a corresponding shear wave reflection coefficient (step 5) at a specific d_p point (step 4, for example initial (I) or/and final (F) setting time, the value Δr_0 when the penetration resistance starts to develop etc.) can be read from the $\Delta r - d_p$ linear relationship (Fig. 7c). Finally, a time (step 7, initial setting time, final setting time, etc.) corresponding to the specific Δr value (step 6) can be determined from the $\Delta r - t$ diagram (Fig. 7d). Using this simple procedure, different characteristic points, representing important milestones during the formation of structure process, can be easily indicated on the $\Delta r - t$ diagrams.

To practically demonstrate this procedure, examples of the determination of the initial t_I and final t_F setting times and corresponding Δr_I and Δr_F values are presented in Fig. 7.

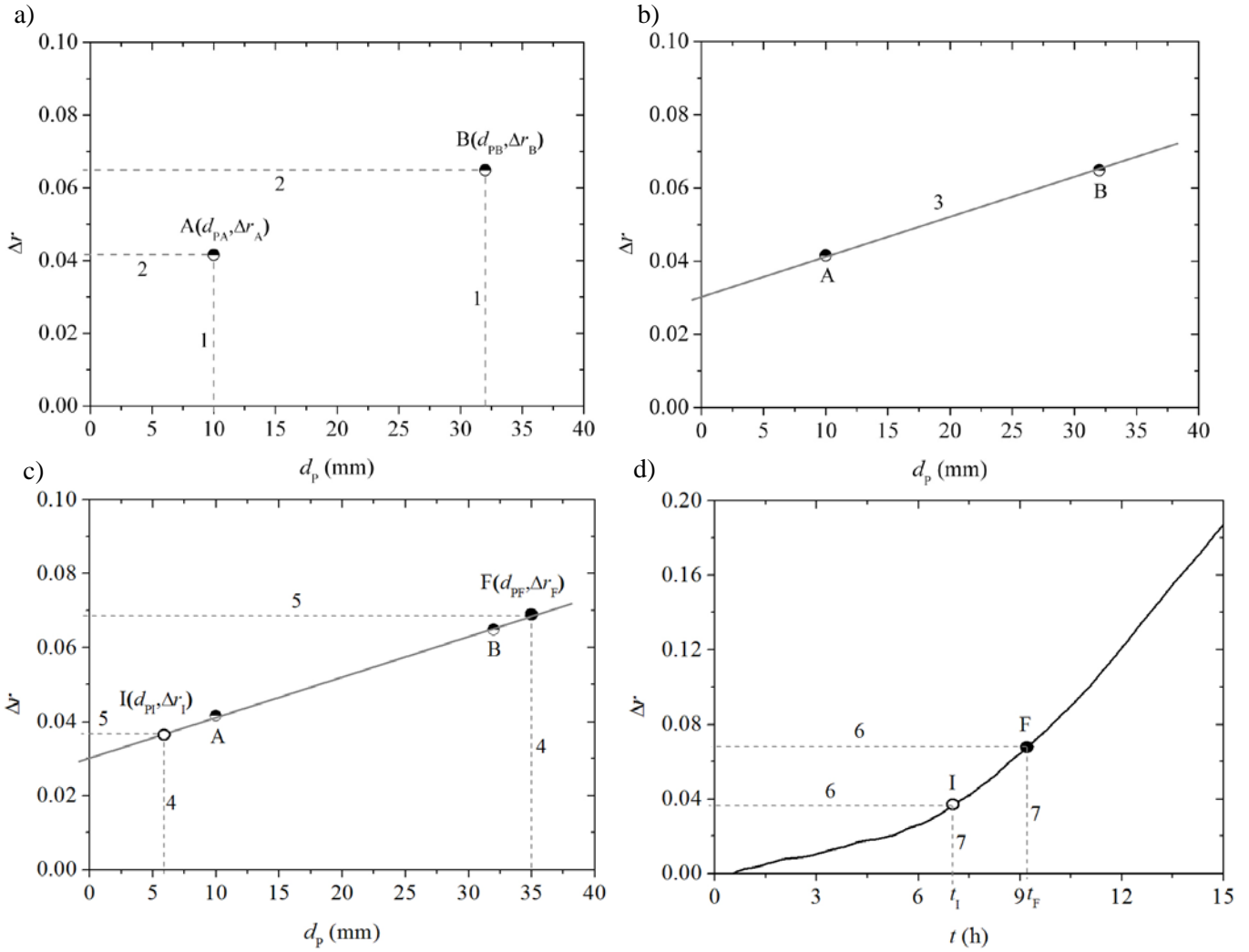


Fig. 7. Schematic representation of a simplified procedure for the determination of both initial and final setting time of a specific cement paste mixture.

3.5 Accuracy of the initial and final setting time determination

To analyze the accuracy of the proposed procedure, a technique was used which is schematically presented in Fig. 8. Since the method is based on two arbitrary Vicat points d_p , different combinations between two points, presented in Fig. 6, were analyzed to determine the influence of the selection of the basic d_p points on the t_I and t_F results. Linear relationships between all pairs of d_p and corresponding Δr points were established, resulting into several different $\Delta r - d_p$ linear relationships for each cement paste mixture (see Fig. 8).

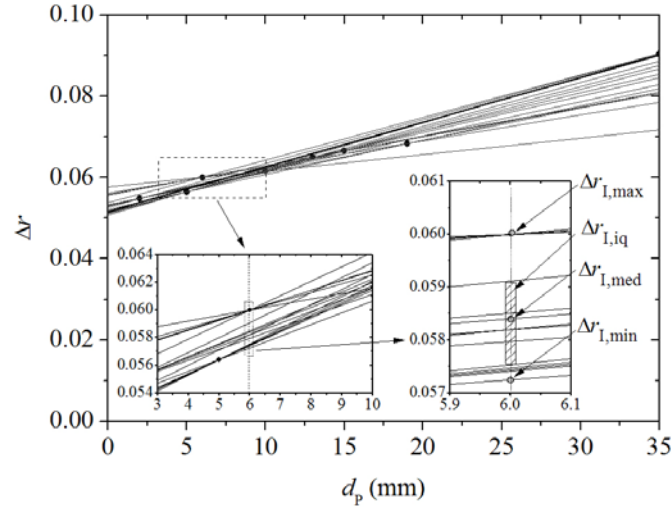


Fig. 8. Determination of the accuracy of the proposed procedure to estimate the initial and final setting times – schematic representation (initial setting time).

The values of Δr_I and Δr_F were determined for each linear relationship and descriptive statistics were used to analyze the data, which are summarized in Table 4. In the table, n , $\Delta r_{I,max}$, $\Delta r_{I,min}$, $\Delta r_{I,med}$, and $\Delta r_{I,iq}$ stand for the number of different relationships, maximum, minimum, median, and interquartile range of Δr_I values as indicated in Fig. 8. Similarly, $\Delta r_{F,max}$, $\Delta r_{F,min}$, $\Delta r_{F,med}$, and $\Delta r_{F,iq}$ stand for maximum, minimum, median, and interquartile range of Δr_F values. It can be seen that all interquartile ranges are relatively small, indicating small dispersion that accompanies the median data.

Next, t_I and t_F setting times corresponding to all Δr_I and Δr_F values were determined and similar statistical analysis was performed to analyze the accuracy of the proposed procedure in estimating t_I and t_F setting times. It can be seen from Table 5 that in the case of t_I values, the $t_{I,iq}$ values, representing interquartile ranges are relatively small for all cement paste mixtures, indicating small influence of choosing different pairs of d_p values on the t_I results and thus high accuracy of the proposed method to determine initial setting times of cement pastes. A slightly higher $t_{F,iq}$ values are observed in the case of t_F values, indicating slightly lower accuracy of the proposed method in estimating final setting times. In this case, maximum $t_{F,iq}$ was 58 min. This variability can be reduced considerably if the second point is chosen at the time closer to the predicted final setting time.

Table 4. Statistical analysis of the accuracy of the proposed procedure to estimate initial and final setting times – Δr values.

mixture label	n	$\Delta r_I (-)$				$\Delta r_F (-)$				
		$\Delta r_{I,max}$	$\Delta r_{I,min}$	$\Delta r_{I,med}$	$\Delta r_{I,iq}$	$\Delta r_{F,max}$	$\Delta r_{F,min}$	$\Delta r_{F,med}$	$\Delta r_{F,iq}$	
CEM II/A-S, 42,5R	w/c = 0.30	8	0.0416	0.0396	0.0414	0.00044	0.0617	0.0551	0.0563	0.00146
	w/c = 0.35	12	0.0449	0.0433	0.0446	0.00110	0.0541	0.0445	0.0520	0.00178
	w/c = 0.40	9	0.0338	0.0322	0.0324	0.00038	0.0548	0.0372	0.0394	0.00892
	w/c = 0.50, $T_A=20^\circ\text{C}$	6	0.0346	0.0331	0.0340	0.00134	0.0537	0.0485	0.0470	0.0099
	w/c = 0.60, $T_A = 20^\circ\text{C}$	6	0.0552	0.0523	0.0541	0.00170	0.0967	0.0765	0.0886	0.01753
	w/c = 0.65	9	0.0473	0.0447	0.0469	0.00219	0.0673	0.0592	0.0640	0.00242
w/c = 0.40	CEM I 52,5R	12	0.0503	0.0488	0.0498	0.00037	0.0767	0.0586	0.0633	0.00297
	CEM I 42,5N	4	0.0741	0.0669	0.0695	0.00258	0.0931	0.0854	0.0904	0.00277
	CEM I 42,5N SR	6	0.0619	0.0595	0.0614	0.00087	0.0771	0.0681	0.0693	0.00271
w/c = 0.50	CEM I 52,5R $SP = 4310 \text{ cm}^2/\text{g}$	12	0.0503	0.0488	0.0498	0.00037	0.0767	0.0586	0.0633	0.00297
	CEM I 42,5N $SP = 2640 \text{ cm}^2/\text{g}$ $C_3A = 7.2 \%$	8	0.0758	0.0664	0.0729	0.00479	0.0931	0.0836	0.0895	0.00180
	CEM I 42,5N SR $C_3A = 2.3 \%$	9	0.0573	0.0538	0.0566	0.00217	0.0789	0.0719	0.0742	0.00290
w/c = 0.50	$T_A = 32^\circ\text{C}$	9	0.0781	0.0682	0.0717	0.00630	0.1443	0.0980	0.1098	0.02210
	$T_A = 26^\circ\text{C}$	6	0.0675	0.0666	0.0673	0.00059	0.0909	0.0829	0.0882	0.00462
	$T_A = 11^\circ\text{C}$	15	0.0187	0.0078	0.0155	0.00287	0.0807	0.0468	0.0491	0.01018
w/c = 0.60	$T_A = 32^\circ\text{C}$	15	0.0600	0.0573	0.0584	0.00250	0.0904	0.0716	0.0845	0.00715
	$T_A = 26^\circ\text{C}$	9	0.0617	0.0591	0.0606	0.00165	0.0948	0.0895	0.0931	0.00237
	$T_A = 11^\circ\text{C}$	10	0.0279	0.0218	0.0235	0.00236	0.0472	0.0373	0.0400	0.00625
-	$SP = 3490 \text{ cm}^2/\text{g}$	9	0.0657	0.0611	0.0652	0.00274	0.1109	0.0938	0.0992	0.00171
-	$C_3A = 4.8 \%$	12	0.0592	0.0582	0.0590	0.00048	0.0840	0.0797	0.0810	0.00147

Table 5. Statistical analysis of the accuracy of the proposed procedure to estimate initial and final setting times – t_I and t_F values.

mixture label	n	t_I (h)				t_F (h)				
		$t_{I,max}$	$t_{I,min}$	$t_{I,med}$	$t_{I,iq}$ (min)	$t_{I,max}$	$t_{I,min}$	$t_{I,med}$	$t_{I,iq}$ (min)	
CEM II/A-S, 42,5R	w/c = 0.30	8	3.23	3.02	3.15	10.0	4.67	4.23	4.38	11.0
	w/c = 0.35	12	4.73	4.41	4.70	19.0	5.63	4.68	5.45	6.6
	w/c = 0.40	9	5.45	5.05	5.45	0.0	7.10	5.75	5.83	38.0
	w/c = 0.50, $T_A=20^\circ\text{C}$	6	6.82	6.81	6.81	0.5	9.33	8.59	8.90	15.1
	w/c = 0.60, $T_A = 20^\circ\text{C}$	6	8.75	8.50	8.74	6.2	11.30	10.12	10.82	58.0
	w/c = 0.65	9	8.93	8.83	8.88	6.0	10.47	9.88	10.22	13.0
w/c = 0.40	CEM I 52,5R	12	3.75	3.73	3.75	0.0	4.63	4.08	4.23	4.7
	CEM I 42,5N	4	5.98	5.45	5.22	15.1	6.57	6.32	6.51	6.0
	CEM I 42,5N SR	6	7.38	7.17	7.28	5.2	8.88	8.10	8.20	18.0
w/c = 0.50	CEM I 52,5R $SP = 4310 \text{ cm}^2/\text{g}$	12	3.10	2.98	3.06	2.0	4.52	3.75	3.99	8.5
	CEM I 42,5N $SP = 2640 \text{ cm}^2/\text{g}$ $C_3A = 7.2 \%$	8	6.97	6.48	6.80	7.7	7.78	7.28	7.60	6.2
	CEM I 42,5N SR $C_3A = 2.3 \%$	9	7.47	7.00	7.47	28.0	9.92	9.13	9.42	24.4
w/c = 0.50	$T_A = 32^\circ\text{C}$	9	5.15	4.90	5.02	8.0	6.65	5.62	5.85	29.0
	$T_A = 26^\circ\text{C}$	6	5.77	5.72	5.74	3.0	6.57	6.25	6.47	11.3
	$T_A = 11^\circ\text{C}$	15	9.53	7.17	9.25	29.0	15.02	12.37	12.53	49.5
w/c = 0.60	$T_A = 32^\circ\text{C}$	15	5.62	5.52	5.53	5.0	6.68	5.98	6.47	16.0
	$T_A = 26^\circ\text{C}$	9	6.98	6.92	6.95	0.0	8.42	8.25	8.35	6.0
	$T_A = 11^\circ\text{C}$	10	10.53	9.70	9.95	26.0	13.80	12.38	12.75	54.2
-	$SP = 3490 \text{ cm}^2/\text{g}$	9	5.12	4.90	5.08	7.0	6.90	6.27	6.48	4.0
-	$C_3A = 4.8 \%$	12	6.57	6.47	6.52	5.2	8.98	8.32	8.50	12.0

4. CONCLUSIONS

In the context of materials and variables studied in the present work, the following main conclusions can be drawn from the obtained results:

- The change of the shear wave reflection coefficient Δr was found to be very sensitive to the formation of the internal rigid structures in cement pastes far beyond the final setting time of the material. Significant differences in the evolution of the $\Delta r - t$ curves were noticed when cement pastes with various compositions were prepared and cured at different curing temperatures, indicating a possibility of the USWR method and apparatus to study the influence of the cement paste composition on the hydration process and formation of structure of the material. This further substantiates the results presented by other authors.

- Using the presented USWR technique, a well known cross-over effect can be clearly observed and studied, proving that increased rate of the hydration caused by higher curing temperatures results into a weaker bond between the hydration products which hinders further hydration and formation of structure of cement based materials.
- Small increase in the Δr coefficient was found at the very beginning of the hydration process, the value of which depends on the cement paste composition. Since this interesting effect was not observed by other researches, it is worth of further investigation.
- The initial and final setting times can't be defined by a specific value of the Δr coefficient. The largest deviations were observed for different curing temperatures. However, a strong linear relationship between Δr and d_p values was observed for all analyzed cement pastes during the entire setting process, indicating that the development of the Δr coefficient in time clearly reflects the evolution of the (connected) solid phase in cement paste during this important hydration period. This relationship is not unique and is influenced by the cement paste composition and curing temperature.
- According to the linear $\Delta r - d_p$ relationship, complete penetration resistance curve, including initial and final setting times, can be determined on the basis of the two d_p and corresponding Δr values which can be chosen arbitrary during the entire setting period. This fastens and simplifies the procedure for determination of the initial and final setting time significantly, allows the measurements to be performed on a large number of specimens simultaneously, and eliminates the effects of technologist's inexperience and imprecision in determining the initial and final setting times of the material.

The results of this study show that presented NDT USWR method and apparatus can be effectively used to monitor the setting and hardening process of cementitious materials. Using this method, some interesting phenomena can be identified which may contribute to a better understanding of working principles of the hydration process and formation of structure of cement based materials. Four measuring heads operating simultaneously allow a large surface of the element to be tested at once, which is of great importance to withstand different kinetics of the setting process at various locations, originating from different ambient conditions and other influential parameters. The method is practical, low cost, and easily manageable and is therefore applicable in laboratory conditions as a research method as well as directly in situ.

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