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Application of a microwave impulse technique to the measurement of free water content in early hydration stages of cement paste

J. Pavlík[a], V. Tydlitát[a], R. Černý[a,*], T. Klečka[b], P. Bouška[b], P. Rovnaníková[c]

[a]*Department of Structural Mechanics, Faculty of Civil Engineering, Czech Technical University, Thákurova 7, 16629 Prague 6, Czech Republic*
[b]*Klokner Institute, Czech Technical University, Šolínova 7, 160 00 Prague 6, Czech Republic*
[c]*Institute of Chemistry, Faculty of Civil Engineering, Technical University of Brno, Žižkova 17, 662 37 Brno, Czech Republic*

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Abstract

A microwave impulse method is designed and employed to the monitoring of residual moisture content in early hydration stages of cement paste. Complementary experiments consisting in determination of the times of beginning and end of setting and of the course of bending strength, compression strength, Young's modulus and hydration heat production during the early hydration period are performed in order to find possible correlation between the measured moisture changes, development of mechanical parameters and hydration heat release. It is observed that the fastest decrease of residual moisture content roughly agrees with the early stages of the hardening process, i.e., with the time period between the end of setting and the moment when first measurable values of mechanical parameters are obtained.
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1. Introduction

During the hydration process, the cement paste is transformed from a thixotropic fluid state to a clay-like form and finally to the hardened state. During the clay-like phase, concrete is relatively stable in shape but it does not have sufficient strength. Exposing a concrete element to a mechanical load during this stage can lead to destruction of the element. Also, the transition from the clay-like phase to the hardened phase is not sharp, and it is not easy to identify the exact time when the material can be considered as really hardened. For instance, the concrete has to achieve a certain minimal strength to be unmoulded and exposed to some limited mechanical load during the construction process. Therefore, reliable information on the development of material properties during the curing process on a building site is required.

In laboratory conditions, the most reliable and recognized methods for monitoring cement hydration are X-ray diffraction, electron microscopy and thermal analysis (see, e.g., Refs. [1–3]), which are able to determine the concentration of products of chemical reactions. However, these methods are not continuous and are not suitable for investigating the hydration processes in situ.

Another method of determining the course of hydration processes is monitoring of free water (sometimes called "evaporable water," which is probably a more realistic expression) content. Water reacts with all principal compounds of Portland cement, which results in the formation of various hydrates. The amount of water necessary for these reactions is relatively high, so that the changes of free water content in the hydrating mixture are easily detectable.

A variety of methods based on measuring water content were applied to the characterization of the course of cement hydration within the last decades. Among them, electrical methods based on measuring electrical conductivity and/or dielectric properties of hydrating mixtures were the most frequent because they are continuous and in principle applicable to monitor the hydration processes not only in laboratory conditions but also in the building site. Tamas [4] measured the electrical conductivity of fresh cement pastes. McCarter and Afshar [5] measured complex impedance of fresh cement paste in the time interval of 5 min to 24 h after

* Corresponding author. Tel.: +42-2-2435-4429; fax: +42-2-2431-0775.
E-mail address: cernyr@fsv.cvut.cz (R. Černý).

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mixing in the frequency range 20 Hz to 300 kHz. McCarter [6] later extended his measurements to the 100 kHz to 10 MHz range.

Reboul [7] was probably the first to apply a microwave technique to monitoring hydration in fresh cement paste (previous applications of microwave methods were limited to hardened cement paste; see, e.g., Refs. [8,9]). He determined the complex permittivity of fresh cement paste at 3 GHz by a resonance method. Gorur et al. [10] used a reflection–absorption microwave method for determination of dielectric properties of cement paste in the time interval 5 min to 70 h after mixing at 9 GHz. Moukwa et al. [11] used a front surface reflection microwave method to monitor the hydration processes of cement during the first 24 h period at 10 GHz. Zhang et al. [12,13] measured dielectric properties of various cement pastes for the time period up to 30 h by a reflection–transmission microwave technique at 9.5 GHz. They found the microwave method to be more sensitive to the cement hydration than the calorimetric method and more suitable to study very early cement hydration. Thompson [14] investigated the quality of concrete during curing using an open-ended coaxial probe/waveguide microwave method in the frequency range 10–500 MHz up to 76 h after mixing.

Measuring the water content in building materials by microwave techniques is currently a well-recognized treatment in building science. There is a several-decades-long tradition of these measurements. The first applications appeared in the 60s [8,17], and a variety of different experimental techniques were designed in the subsequent decades (for a survey of most of the existing setups see, e.g., Ref. [18]). Within the last 10–15 years, an increasing number of commercial companies also offered moisture meters based on microwave principles (see Ref. [14] for a list of major manufacturers). However, the basic setups are well known and the microwave components became very efficient, small and relatively cheap within the last years, probably due to the progress in commercial satellite transmission and TV. Therefore, the experimental laboratories of universities and research institutes mostly build their microwave moisture meters themselves from the commercially produced components, which makes it possible to adjust the particular setup for a specific purpose.

From the point of view of physical mechanisms, the microwave measurement systems can be divided into three groups, reflection, transmission and resonance systems. Among the reflection systems, the open-ended coaxial probe/waveguide method belongs to the most frequently used within the last decade (see, e.g., Refs. [14,16,19]). Also, an ''infinite sample'' method based on the analysis of the interference pattern produced by the incident and reflected waves from a sample put into a waveguide was successfully employed [11]. Examples of transmission-based methods can be found in Refs. [8,9,17,20]; resonance systems are only rarely used with building materials (e.g., Ref. [7]). Some of the basic methods can be conveniently combined in one experimental setup, a logical combination presents the reflection–transmission method as it was demonstrated, for instance, in Ref. [10].

The aforementioned methods work with continuous microwaves. Another possibility way of determining the moisture content using microwaves is to measure the travel time and absorption of a short (about 100 ps) microwave impulse through a material specimen of a known thickness [15]. The advantage of such a method is that the measurements are completely nondestructive and that large surfaces can be scanned rapidly.

Microwave techniques can certainly be considered as very powerful and recognized tools for monitoring hydration processes at present. They are continuous and their precision in the determination of water content is very good. However, the classical reflection or reflection–transmission methods are mostly suitable to laboratory measurements only because they require a specimen to be put into a waveguide or resonance cavity (e.g., Refs. [7,10–12]). Some of the reflection-based techniques might be applicable in situ, as for instance the open-ended coaxial probe method [14], but it can be envisaged that problems could arise in very early hydration stages when the material is still in a thixotropic fluid state and the surface does not yet have a stable shape. On the other hand, transmission methods are suitable for the measurements also in the very early stages, but for higher thickness of structural elements the detected power might be low, which can significantly decrease the precision of determination of water content.

A solution to these problems might be the use of pulsed radar techniques. Maierhofer and Wöstmann [15] successfully employed a microwave impulse technique for measurement of water content in bricks, limestone and porous concrete, and the sensitivity of the method was found to be satisfactory even at very high moisture content. Therefore, the application of the method looks reasonable also for measurements with fresh concrete.

In this paper, a microwave impulse technique is designed and employed for monitoring moisture content in early hydration stages of cement paste. The course of decrease of free water content in the cement paste specimens is discussed, using a comparison with measurements of beginning and end of setting, bending strength, compression strength, Young's modulus and hydration heat production during the early hydration period.

2. Theoretical principles

From the physical point of view, propagation of microwaves in a moist building material can be considered as propagation of electromagnetic waves in an absorbing medium.

The simplest solution of Maxwell equations for the electric field intensity E is that of a plane, time harmonic

wave, which for a wave propagating in the z direction can be expressed (see, e.g., Refs. [21,22]) as follows

$$E = E_0 e^{-i(\omega t - \tilde{k} z)}, \tag{1}$$

where ω is the angular frequency and $\tilde{k}$ is the complex wave number,

$$\tilde{k} = \frac{\omega}{\tilde{c}} = \omega\sqrt{\mu\tilde{\varepsilon}}, \tag{2}$$

where $\tilde{c}$ is the complex velocity of the wave propagation in the given medium, μ is the permeability and $\tilde{\varepsilon}$ the complex permittivity. Assuming a nonferromagnetic medium, i.e., $\mu \sim \mu_0$, μ_0 is the permeability of vacuum, we can write

$$\tilde{c} = \frac{1}{\sqrt{\mu_0\tilde{\varepsilon}}} = \frac{1}{\sqrt{\mu_0\varepsilon_0\tilde{\varepsilon}_r}} = \frac{c_0}{\sqrt{\tilde{\varepsilon}_r}}, \tag{3}$$

where $\tilde{\varepsilon}_r$ is the complex relative permittivity, ε_0 is the permittivity of vacuum, c_0 is the wave propagation velocity in vacuum.

Combining Eqs. (2) and (3) we obtain

$$\tilde{k} = \frac{\omega}{c_0}\sqrt{\tilde{\varepsilon}_r}, \tag{4}$$

and using the notation $\tilde{k} = k' + ik''$, $\tilde{\varepsilon}_r = \varepsilon_r' + i\varepsilon_r''$, then

$$k' = \frac{\omega}{c_0}\sqrt{\varepsilon_{r1}} \tag{5}$$

$$k'' = \frac{\omega}{c_0}\sqrt{\varepsilon_{r2}}, \tag{6}$$

where

$$\varepsilon_{r1} = \frac{1}{2}\left(\sqrt{(\varepsilon_r')^2 + (\varepsilon_r'')^2} + \varepsilon_r'\right) \tag{7}$$

$$\varepsilon_{r2} = \frac{1}{2}\left(\sqrt{(\varepsilon_r')^2 + (\varepsilon_r'')^2} - \varepsilon_r'\right). \tag{8}$$

Substituting Eqs. (5)–(8) into Eq. (1) we arrive at

$$E = E_0 e^{-k''z} e^{-i(\omega t - k'z)} = E_0 e^{-z\frac{\omega}{c_0}\sqrt{\varepsilon_{r2}}} e^{-i\omega\left(t - \frac{z}{c_0}\sqrt{\varepsilon_{r1}}\right)}$$
$$= A(z) e^{-i\omega\left(t - \frac{z}{c_f}\right)}, \tag{9}$$

where $A(z)$ is the amplitude of the wave,

$$A(z) = E_0 e^{-z\frac{\omega}{c_0}\sqrt{\varepsilon_{r2}}}, \tag{10}$$

and c_f is equivalent to the phase velocity of a wave propagating in a nonabsorbing medium,

$$c_f = \frac{c_0}{\sqrt{\varepsilon_{r1}}}. \tag{11}$$

If an electromagnetic impulse is propagating through an absorbing medium of a known thickness Δz, we can measure basically two quantities. The first is the travel time Δt of the impulse, i.e., the time necessary to pass the distance Δz, and the second is its attenuation a after passing Δz,

$$a = \frac{A(\Delta z)}{A(0)}.$$

Using Eqs. (10) and (11), we obtain

$$\ln a = -\frac{\omega}{c_0}\sqrt{\varepsilon_{r2}}\Delta z \tag{12}$$

$$\frac{\Delta z}{\Delta t} = \frac{c_0}{\sqrt{\varepsilon_{r1}}}. \tag{13}$$

Substituting Eqs. (7) and (8) into Eqs. (12) and (13), we finally arrive at a system of two algebraic equations for the unknown real and imaginary parts of the complex relative permittivity, ε_r', ε_r'', in the form

$$\frac{1}{2}\left(\sqrt{(\varepsilon_r')^2 + (\varepsilon_r'')^2} + \varepsilon_r'\right) = \left(\frac{c_0\Delta t}{\Delta z}\right)^2 \tag{14}$$

$$\frac{1}{2}\left(\sqrt{(\varepsilon_r')^2 + (\varepsilon_r'')^2} - \varepsilon_r'\right) = \left(\frac{c_0 \ln a}{\omega\Delta z}\right)^2, \tag{15}$$

which leads to the following relations for ε_r', ε_r''

$$\varepsilon_r' = \left(\frac{c_0}{\Delta z}\right)^2\left[(\Delta t)^2 - \left(\frac{\ln a}{\omega}\right)^2\right] \tag{16}$$

$$\varepsilon_r'' = -2\left(\frac{c_0}{\Delta z}\right)^2\frac{\Delta t}{\omega}\ln a. \tag{17}$$

For very small attenuation of the electromagnetic wave in the material, i.e., $\ln a \to 0$, the relations (16) and (17) can be simplified into the form

$$\varepsilon_r' = \left(\frac{c_0\Delta t}{\Delta z}\right)^2 \tag{18}$$

$$\varepsilon_r'' = -2\frac{c_0}{\omega\Delta z}\sqrt{\varepsilon_r'}\ln a. \tag{19}$$

In the case that we can measure only the time difference $\Delta t_{21} = \Delta t_2 - \Delta t_1$, where t_2 is the travel time of the impulse to pass the distance Δz in the measured material and t_1 the respective travel time in the air, we use, instead of Eq. (13), the modified formula

$$c_0(\Delta t_2 - \Delta t_1) = \Delta z(\sqrt{\varepsilon_{r1}} - 1). \tag{20}$$

Instead of Eq. (14) we then have

$$\varepsilon_{r1} = \frac{1}{2}\left(\sqrt{(\varepsilon_r')^2 + (\varepsilon_r'')^2} + \varepsilon_r'\right) = \left(\frac{c_0(\Delta t_2 - \Delta t_1)}{\Delta z} + 1\right)^2 \quad (21)$$

and using Eq. (15), we can write the equivalents of Eqs. (16) and (17) in the form:

$$\varepsilon_r' = \left(\frac{c_0(\Delta t_2 - \Delta t_1)}{\Delta z} + 1\right)^2 - \left(\frac{c_0 \ln a}{\omega \Delta z}\right)^2 \quad (22)$$

$$\varepsilon_r'' = -2\left(\frac{c_0(\Delta t_2 - \Delta t_1)}{\Delta z} + 1\right)\left(\frac{c_0 \ln a}{\omega \Delta z}\right). \quad (23)$$

In the practical measurements of moisture content in a building material, it is necessary to determine the dielectric properties of dry and moist specimens. As the relative permittivity of water is at least one or two orders of magnitude higher than that of the most common building materials, it is relatively easy to determine the amount of water in the particular specimen. This determination can be done either theoretically or experimentally. There is a variety of effective medium concepts making it possible to estimate the permeability of porous materials from the known permittivities of their compounds, typically water, air and the porous matrix (see, e.g., Refs. [23–25]), but the calculated values often suffer substantial differences from the experimental ones. Therefore, determination of calibration curves is mostly unavoidable.

3. Design of the microwave moisture meter

In the design of the microwave moisture meter, we defined the following basic requirements to the device: (a) it should be able to perform both laboratory and field measurements, (b) it should enable measurements both on specially adjusted specimens and on real structural elements, (c) the financial expenses should be as low as possible but a reasonable precision of the device must be retained.

As follows from the overview of the microwave techniques given in the Introduction section, the points (a) and (b) exclude automatically the methods, where measurements are performed in waveguides or resonance cavities such as in Refs. [7,11,12]. The condition of applicability in field conditions can be met for instance by the reflection–transmission methods using horn antennas (e.g., Ref. [8]) or by the open ended coaxial probe methods (e.g., Ref. [14,16]) but the financial expenses for this type of methods might be quite high; for instance, the microwave vector network analyzer itself is relatively expensive, and additional requirements to the necessary software might also be anything but cheap.

Application of a microwave impulse technique (such as described in Ref. [15]) can be considered as a reasonable compromise between the price and the necessary precision (the points (a) and (b) are easy to meet). The most expensive parts in building such an experimental setup are the oscilloscope and impulse generator but if one does not require high-class technique, the prices are much lower than for any other setup for microwave measurements and the accuracy is still reasonable. Together with the general advantages of the impulse techniques, namely the rapid surface scanning and absolutely nondestructive character, the aforementioned arguments have led us to a conclusion to build an experimental setup based on pulsed radar principles.

The most important part of any pulsed radar method is an impulse generator. It should be able to generate very short impulses of an approximately triangular shape, with an amplitude of minimally several volts. A lower amplitude would require an extremely high sensitivity of the input circuits of the oscilloscope and in addition, it would decrease the allowable value of microwave losses between the transmitting and receiving antennas; in other words the maximum thickness of the specimen would be lowered. The lower signal/noise ratio resulting from a lower amplitude would also decrease significantly the accuracy of results because the evaluation would be more difficult.

The width of the impulse also has certain limitations. The transmitting and receiving antennas are formed in principle by a coaxial/waveguide reducer and a horn for the transfer of microwave energy into and from the free space. The waveguide is, from the point of view of microwave energy transfer, a high-pass frequency filter; the whole reducer is usually adapted for a certain band. Therefore, the antenna itself can be considered as certain filter. For our measuring device, we have chosen the frequency range 7–8 GHz, mainly in order to follow the previous successful realization of a similar device by Maierhofer and Wöstmann [15], and employed the R84 waveguide. Taking into account the rules of harmonic analysis, the necessary width of the impulse should be about 150–250 ps. The impulse repetition rate is not a critical factor of the design. Considering the necessary real-time display, it should be in the range of approx. 200–5000 Hz. This type of impulse generator is not commonly commercially available, therefore it was developed for this specific purpose by the Czech company Radan.

Another unavoidable compound of the experimental setup is the sampling oscilloscope with a sufficient sensitivity (about 1 mV), bandwidth of input circuits (at least 9–10 GHz) and sweep unit resolution (at least 50–100 ps). Classical display of the oscilloscope might be sufficient provided that the signal is recorded by a digital camera or camcorder. This simple solution brings very substantial money savings compared to using a digital sampling oscilloscope while retaining reasonable accuracy. The stability of the display (and consequently the time resolution) is affec-

ted by the trigger circuits of the oscilloscope and by the jitter of the synchronization signal. Therefore, the synchronization is derived directly from the main signal using a proper coupler (power divider). Admissible level of the signal for the input synchronization circuits is achieved by the magnitude of coupling or by putting standard coaxial decays in the branch circuit. The necessary access time of synchronization circuits (approximately 50 ns) is ensured by putting the delay line into the path of the main signal.

The connection of horn antennas to the generator and oscilloscope is done by coaxial cables. The length of the cables has to be chosen under consideration of two contradictory factors, namely the mechanical attainability of the specimen and the cable losses. A reasonable compromise retaining a sufficient sensitivity of the system is about 2–3 m.

4. Experimental setup

The measuring system is relatively compact and consists of three basic components (see Fig. 1), namely the impulse generator, the applicator and the sampling oscilloscope.

The generator GPSI-1a (Radan) produces triangular impulses of a width of 250 ps and amplitude 2 V. It consists of the impulse generator itself, its feed circuits, controlling, auxiliary and protecting circuits. The energy output is realized by three SMA coaxial connectors. These signals make it possible to determine the reference and measured position of the impulse and to synchronize the sampling oscilloscope.

The applicator connected to the generator output ensures the necessary exposure of both measured and reference specimens. It consists of two pairs of transmitting and receiving antennas formed by coaxial/waveguide reducers and horns. The pairs of antennas are fixed parallel in separate holders ensuring a defined position, and therefore also stability and reproducibility of measurements. The specimens of the tested materials are put into the applicator between the measuring antennas. The sample thickness is limited mechanically to about 100 mm; from the electrical point of view, it is limited by the attenuation in the measured material and sensitivity of the oscilloscope. The dynamics of the signal is over 20 dB.

The sampling oscilloscope Tektronix 7603 analyses the impulse signals. He has a 7T11A sampling sweep unit and two 7S11 sampling units with an S-4 sampling head. The time resolution of the oscilloscope is about 10 ps and the sensitivity 2 mV. The frequency range is up to 14 GHz. The signal from the oscilloscope display is recorded by a digital camera and analyzed by a PC.

5. Material samples

The cement paste was prepared using Portland cement CEM I 42.5 R (ENV 197-1) (Králův Dvůr, CZ) and water. The water to cement ratio $w = 0.3$ was chosen in our experiments. The specimens had a board shape with a thickness of 23 mm. Five specimens were always used for the particular measurement.

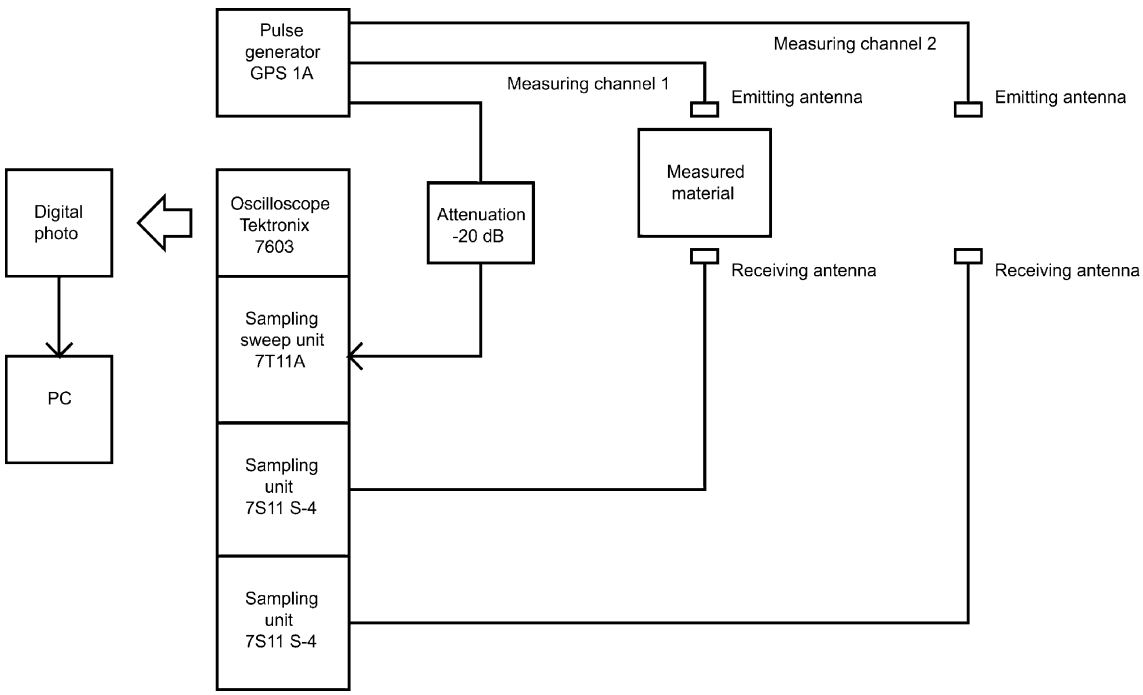

Fig. 1. Experimental setup of the microwave impulse technique for moisture measurements.

6. Calibration

The microwave impulse technique introduced in this paper belongs to the relative methods (indirect methods), which determine the amount of water in the specimen on the basis of measuring another physical quantity (permittivity in this particular case), which has a clear relation to the amount of water in the material. Therefore, it has to be calibrated in an appropriate way.

Generally, there is only one quite objective method that can be employed for the calibration of moisture meters based on indirect methods for water determination, namely the gravimetric method. However, a straightforward application of the gravimetric method to the calibration during the early hydration stage of cement paste is a very difficult procedure. The classical gravimetric treatment consisting in hot air drying at 105 °C cannot be employed because the reaction rates in hydration processes strongly depend on temperature. Vacuum drying at 20 °C is excluded automatically because moisture determination takes at least several days. Practically the only reasonable treatment in this case consists in water removal from the sample by washing out by a fluid that is soluble in water and nonreactive with cement, such as ethanol with ethyl ether or isopropyl alcohol with ethyl ether, and subsequent gravimetric analysis. However, this method is far from ideal because it is questionable whether all of the free (in fact physically and physically–chemically bound) water can be removed from the sample in this way, particularly for a material with a fine pore structure where the van der Waals forces on the pore walls can play a very important role.

Therefore, we used a mixed gravimetric–theoretical treatment for the calibration. We employed two gravimetric values, namely the initial moisture content just after mixing the cement with water and the saturated moisture content in hardened cement paste and the value of permittivity of dry hardened cement paste as the basic quantities for assigning the measured values of permittivity of hydrating cement paste to the respective moisture content. The shape of the permittivity vs. moisture content curve between the dry and saturated state was approximated using a theoretical mixing rule. We used the symmetric relation for the relative permittivity of a solid–water–air mixture determined by Polder and van Santen [26] in the form:

$$\frac{\varepsilon_m - 1}{\varepsilon_m + 2\varepsilon_m} = v_a \frac{\varepsilon_a - 1}{\varepsilon_a + 2\varepsilon_m} + v_w \frac{\varepsilon_w - 1}{\varepsilon_w + 2\varepsilon_m} + v_b \frac{\varepsilon_b - 1}{\varepsilon_b + 2\varepsilon_m}, \quad (24)$$

where ε_m is the permittivity of the mixture (in our case the cement paste); ε_b and v_b the permittivity and the volumetric ratio of the solid phase (in our case the cement stone), respectively; ε_a and v_a the permittivity and the volumetric ratio of the air ($\varepsilon_a = 1$); ε_w and v_w the permittivity and the volumetric ratio of water (for 7 GHz at room temperature $\varepsilon_w = 69.362$; see Ref. [27]).

For determination of the dependence of the permittivity of the mixture on the volumetric water content in cement paste we have measured first the basic values of density, saturated moisture content and permittivity of fresh and hardened cement paste. The data is given in Table 1.

We can see that the saturated moisture content of the hardened cement paste decreased by approximately 4% (kg/kg) compared to the fresh cement paste. This fact has to be considered in the further course of the calibration procedure.

For the density of the cement paste with the water to cement ratio $m_w/m_c = 0.3$ we can write

$$\frac{m_w}{(m_w + m_c)\rho_w} + \frac{m_c}{(m_w + m_c)\rho_b} = \frac{1}{\rho_m}. \quad (25)$$

where ρ_m is the density of the mixture, ρ_b the density of the solid phase and ρ_w the density of water. Therefore,

$$v_w = \frac{m_w \rho_m}{(m_w + m_c)\rho_w} = 0.45877 \quad (26)$$

$$v_b = 1 - v_m = 0.54123 = \frac{m_c \rho_m}{(m_w + m_c)\rho_b} \quad (27)$$

and $\rho_b = 2825.4$ kg/m^3.

For the determination of the dependence of permittivity ε_m of the cement paste with a constant porosity on the moisture content using Eq. (24), we first calculated the permittivity of the solid phase ε_b. Assuming that the permittivity of the dry hardened cement paste is known (see Table 1), and adding to the volumetric ratio of the solid the difference in saturated moisture content (3.95%, see Table 1), we arrived at $\varepsilon_b = 12.75$ (in Eq. (24) only the term on the left-hand side and the last term on the right-hand side are not equal to zero).

In the calculation of the dependence of ε_m on the volumetric moisture content, the volumetric ratio of the solid, $v_b = 0.54123$, was assumed to be constant, and the volumetric moisture content was changed from the saturated moisture content to zero. The volumetric moisture content and the mass moisture content were converted using Eq. (26). In this way, we obtained the calibration curve shown in Fig. 2, where dependence of the ratio of permittivity of the moist paste to the permittivity of the water saturated cement

Table 1
Basic data for calibration

Material	Density (kg/m^3)	Moisture (% kg/kg)	Saturated moisture content (% kg/kg)	ε_m
Fresh cement paste	1988 ± 1	23.08	23.08	31.2
Hardened cement paste	1700 ± 8	0	19.13	5.5

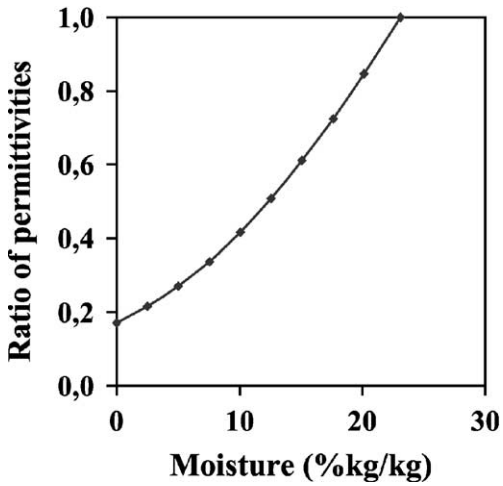

Fig. 2. Calibration curve of the microwave impulse method for cement paste with the water to cement ratio 0.3.

paste at constant porosity on the mass moisture content is presented.

7. Experimental results and discussion

Fig. 3 shows free moisture content in the hydrating cement paste, which is defined as the mass of free water in the mixture during the hydration process divided by the sum of the initial masses of cement and water, in dependence on the duration of the hydration reaction for the first day, measured in a climatic chamber at the surrounding temperature of 23 °C. We can see that in the initial part of the curve, approximately 3 h from the beginning of the hydration process, the moisture content slightly increases. The main decrease of free water content occurs in the time period from 3 to 6.5 h, then the free water content remains approximately constant to about 28 h.

Fig. 4 shows the free moisture content as a function of time, measured at the surrounding temperature of 40 °C. Apparently, the curve exhibits a similar character as in the case of that for 23 °C in Fig. 3. The initial increase of measured moisture content is finished sooner, at about 1.3 h, and it not so remarkable as in Fig. 3. The main decrease of moisture content is concentrated to the time interval from 5 to 7 h after the beginning of the hydration process. Therefore, we can conclude that the effect of temperature on our measured results was not clearly evidenced in the temperature range from 23 to 40 °C.

It should be noted that the slight increase of free water content in the initial phase, which was observed in all our experiments, is apparently not realistic. This is probably due to the effect of inaccuracy in the interpretation of the measured values of permittivity that may be caused by the changes of dielectric properties of hydration products in this hydration phase. Very similar results were obtained lately by Kuráž et al. [28] who attributed the irregularities in the free moisture vs. time functions to the temperature changes in the cement paste due to the release of hydration heat.

In order to find the possible correlation of the measured moisture vs. time curve to the other significant parameters characterizing the early hydration stages of cement paste, we have done complementary experiments. We measured the times of beginning and end of setting, and the course of bending strength, compression strength, Young's modulus and hydration heat production during the early hydration period.

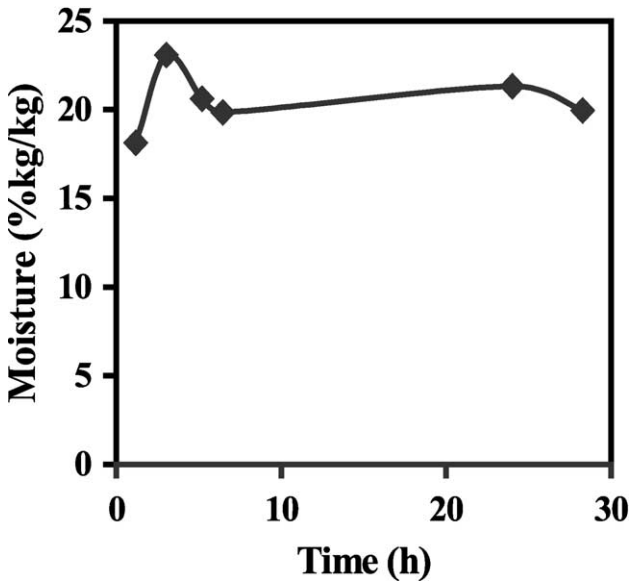

Fig. 3. Dependence of free moisture content in hydrating cement paste on the time duration of hydration reaction determined by the microwave method for the time period up to 1 day from the beginning of the hydration process at 23 °C.

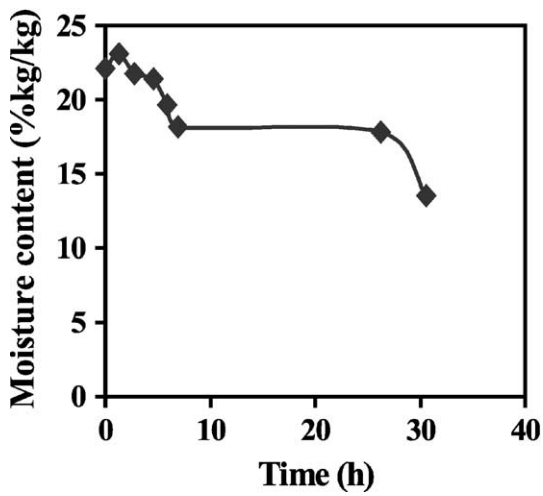

Fig. 4. Dependence of free moisture content in hydrating cement paste on the time duration of hydration reaction determined by the microwave method for the time period up to 1 day from the beginning of the hydration process at 40 °C.

The setting experiments were done using the standard Vicat device. According to the Vicat test, the setting process began after 170 min and ended after 300 min.

The bending strength was determined by the standard three-point bending test in the MTS 500-kN testing device. The specimens were of prismatic shape with the dimensions $40 \times 40 \times 160$ mm. The results are presented in Fig. 5. The first measurable value of bending strength was observed about 7 h after the beginning of the hydration process, and after 25 h it already achieved the value of 12 MPa.

Similar qualitative results as for the bending strength were also observed for the compressive strength and Young's modulus as demonstrated in Figs. 6 and 7. The compressive strength was determined by a compression test using the MTS 500-kN testing device. It was done on the parts of the specimens broken at the bending test; the specimens were compressed on the area of 2500 mm^2. Fig. 6 shows that the first measurable value of compressive strength was observed after 7 h, and after 25 h the compressive strength was about 35 MPa.

In measuring the Young's modulus, the specimens were provided by a preparative for recording the relative length changes with the measuring length of 50 mm. The preparative was provided by two LVDT sensors (PEEKEL Instruments) with the working range of ±1 mm. The sensors with the preparative were fixed to the testing prism in its middle part. The sensors registered longitudinal deformations in the whole range of loading until an apparent damage of the specimen. The compression tests were again done with the MTS 500-kN testing device; the rate of loading was chosen as 0.02 mm/s. Values of Young's modulus were derived from the measured deformations and the corresponding applied stresses. They were always related to the value of 5% of the damage stress. The results are summarized in Fig. 7. The first measurable values were obtained about 7 h after the beginning of the hydration process, and after 16 h, the Young's modulus achieved an almost constant value of about 18 GPa.

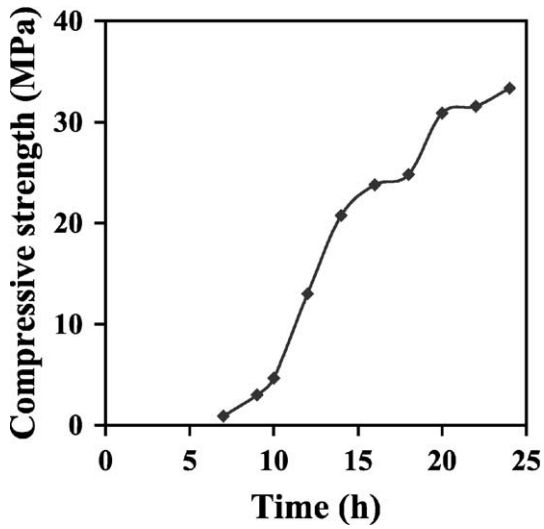

Fig. 6. Dependence of compressive strength of hydrating cement paste on the time duration of hydration reaction for the time period up to 25 h from the beginning of the hydration process.

Time development of hydration heat was measured using an adiabatic calorimeter. In this way, we can observe temperature development during the hydration process in cement paste. The measuring unit is formed by a hard polystyrene reaction vessel placed into a metallic mantel with an electrical heating spiral on the surface. The vessel and mantel are covered by a foamed polystyrene box. Temperature changes in the reacting specimen in the vessel are detected by a Pt sensor located in the cement paste; the temperature outside the reaction vessel is detected by a sensor placed on a metallic mantel. A regulating unit keeps zero temperature gradient between the measured specimen and the air outside the

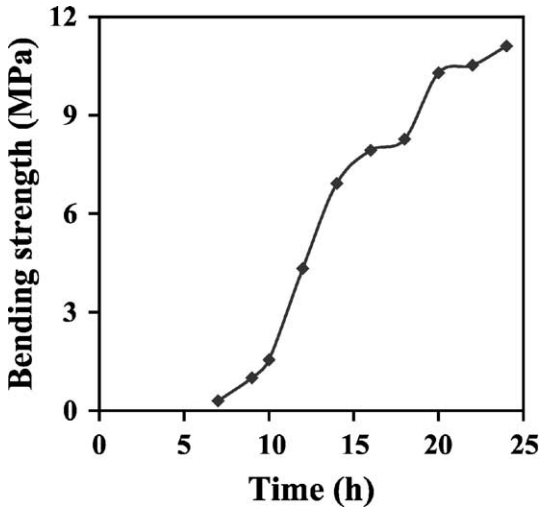

Fig. 5. Dependence of bending strength of hydrating cement paste on the time duration of hydration reaction for the time period up to 25 h from the beginning of the hydration process.

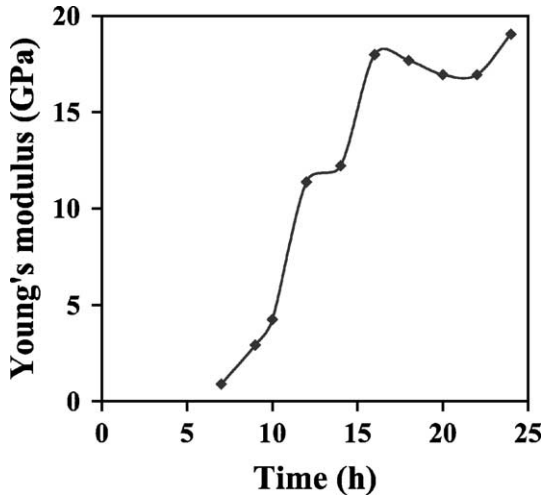

Fig. 7. Dependence of Young's modulus of hydrating cement paste on the time duration of hydration reaction for the time period up to 25 h from the beginning of the hydration process.

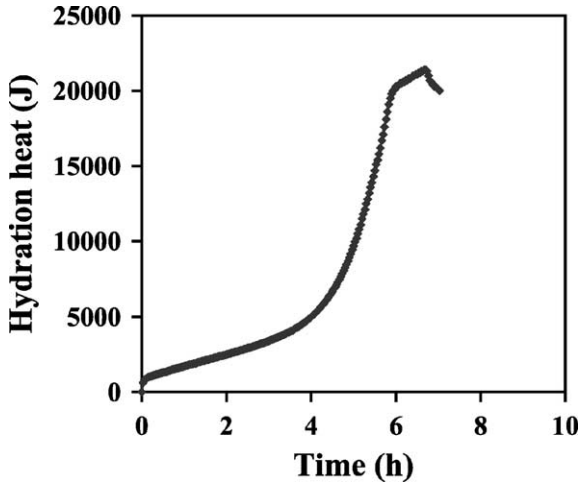

Fig. 8. Integral curve of hydration heat production for the time period up to 7 h from the beginning of the hydration process.

reaction vessel in the calorimeter. This means that thermal loss from the reaction vessel is approximately equal to zero because it is compensated by the electrical heating spiral. In the beginning of the experiment, the measuring system was set to the initial temperature of the cement. Then, water of the same temperature as cement was added quickly, and the mixture was put into the reaction vessel, covered by inert oil and closed by a thermally insulating cover.

The measured integral curve of hydration heat production in cement paste is presented in Fig. 8. Apparently, after a relatively very slow increase of the produced hydration heat during the first several hours, the main hydration process started after approximately 4 h. The second sudden change on the hydration heat vs. time curve after approximately 6 h is related to the fact that the heating system is not able to compensate for the heat loss any more because the temperature difference between the mixture and the surroundings is too high (about 70 °C).

Comparing the results of monitoring the moisture content during the hydration process in Figs. 3 and 4 with the results of mechanical tests, we can see that in the initial phase, the results of moisture measurements are in good agreement with all mechanical tests. After an initial time period with the not fully explained increase of the moisture content with time, the moisture content vs. time curves exhibited a fast decrease of moisture content between 3 and 7 h. This is roughly the time between the end of the setting process (or a little sooner in Fig. 3) and the moment when the first measurable values of bending strength, compressive strength and Young's modulus were observed.

A comparison with measurements of hydration heat production also shows a reasonable agreement. The qualitative character of changes on the curves of hydration heat production and free moisture loss due to the hydration is very similar, and the sudden changes in the hydration heat production curve begin at about 4 h after the beginning of the hydration process, which is roughly the time when the fast free moisture decrease was observed. Generally, it could be assumed that the hydration processes in the adiabatic calorimeter should be faster than in the conditions of our experimental setup for moisture measurements because they take place at elevated temperatures. While the maximum temperature of the specimen of cement paste during the moisture measurements was about 40 °C for the measurements at surrounding temperature of 23 °C, the temperatures in the adiabatic calorimeter were about 90 °C already after the first 6 h. However, the effect of temperature was not clearly evidenced in our moisture measurements as it also follows from a comparison of Figs. 3 and 4.

8. Conclusions

A microwave impulse method was designed and employed for monitoring the free water content in early hydration stages of cement paste. A comparison of the measured moisture changes with the development of basic mechanical parameters of cement paste in the early hydration stages reveals that the period of fastest moisture decrease from 3 to 7 h after the beginning of the hydration reaction roughly agrees with the time between the end of the setting process and the beginning of the hardening process characterized by obtaining first measurable values of bending strength, compressive strength and Young's modulus. The development of hydration heat exhibits both qualitatively and quantitatively similar features, but the very fast increase of hydration heat production is observed a little sooner than the beginning of the hardening process, after 4 h.

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