Microwave study of hydrating cement paste at early age

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MICROWAVE STUDY OF HYDRATING CEMENT PASTE AT EARLY AGE

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ABSTRACT

A new method is proposed for monitoring the hydration kinetics and estimating the degree of hydration of cement paste using a small sample. The method is continuous and non-destructive. It relies upon the fact that the dielectric properties of hydrating cement are closely related to its free-water content. Advanced microwave equipment is used to observe the change in the dielectric properties.

In dit artikel wordt een nieuwe methode voorgesteld voor het volgen van de hydratatiekinetiek en het schatten van de hydratatiegraad van cement met behulp van een klein monster. De methode is continue en niet-destructief. Ze berust op het feit dat de diëlectrische eigenschappen van het hydraterende cement nauw gecorreleerd zijn met de hoeveelheid niet-gebonden water die het bevat. Voor het meten van de verandering in diëlectrische eigenschappen wordt gebruik gemaakt van een geavanceerd microgolfmeeetsysteem.

Introduction

The development of mechanical properties of concrete is strongly related to the rate of hydration of the cement used. In concrete technology, a knowledge of the strength gain at early age is of particular importance. At this moment, no easy and non-destructive method is available for the determination of the degree of hydration. The perfection of such a method would provide an impetus to the further development of concrete technology.

In modern concrete technology, accelerating, retarding, or water-reducing admixtures are often used. Almost all such admixtures bear an influence upon the early hydration reactions. It is common experience to encounter different cements reacting in an unforeseen manner.

The significance of cement hydration in premix polymer concrete has not been clarified convincingly until now. Another argument for the urgent need for a non-destructive method to study the time-dependence of hydration at an early age is the optimization of the use of industrial waste products such as fly-ash in concrete technology /1/.

It has been shown that Mössbauer spectroscopy can be used to determine the degree of hydration in a non-destructive way /2, 3/. Results obtained with this method have, however, a severe limitation in that the chemical reaction of iron containing compounds is measured selectively. By means of microwave absorption tests, the total free-water content can be determined /4, 5/. In a sealed specimen, the apparent change in water content is only caused by an internal consumption due to chemical reactions that bind water molecules. Thus, in principle, it must be possible to determine the rate of hydration by measuring microwave absorption /6,7/. Lower frequencies have been used to study the characteristic properties of adsorbed water /8,9/.

Measurement Method

A disadvantage of measuring the absorption is that it does not only depend on the physical properties of the sample, but also on its geometry. The dielectric constant determination does not have this disadvantage. Given a test-fixture in which the incident field as well as the sample geometry can be precisely controlled, the dielectric constant can be computed from the measured transmission and reflection of the sample. Such a test-fixture is shown in figure 1.

The reflection and transmission of a two-port, such as the (fresh cement paste) filled wave-guide section used in these tests, are usually characterized by the scattering parameters of the two-port. The reflection parameter S_{11} is defined as the ratio between the two complex numbers representing the instantaneous amplitudes of the reflected and the incident wave, respectively, at the reference plane*. The transmission of the sample is characterized by the parameter S_{21} which is the ratio between the instantaneous amplitude of the transmitted wave at the output reference plane* and the amplitude of the incident wave at the input reference plane*. Using the theory of guided waves, the following can be inferred**:

$$S_{11} = \frac{\rho(1 - \tau^2)}{1 - \rho^2\tau^2} \quad (1)$$

$$S_{21} = \frac{\tau(1 - \rho^2)}{1 - \rho^2\tau^2} \quad (2)$$

in which,

$$\rho = \frac{\gamma_0 - \gamma}{\gamma_0 + \gamma} \quad (3)$$

$$\tau = e^{-\gamma l} \quad (4)$$

$$\gamma = \left\{ \left(\frac{\pi}{a} \right)^2 - \epsilon_r \left(\frac{2\pi f}{c} \right)^2 \right\}^{\frac{1}{2}} \quad (5)$$

$$\text{and} \quad \gamma_0 = \left\{ \left(\frac{\pi}{a} \right)^2 - \left(\frac{2\pi f}{c} \right)^2 \right\}^{\frac{1}{2}} \quad (6)$$

* $z=0$ and $z=l$ are chosen as the input and the output reference planes (Fig. 1)

** a derivation for TEM-modes is given in /10/. An adaptation to the (rectangular wave-guide) TE_{01} -mode is easily made.

FIG. 1

Cross section of the rectangular wave-guide showing the input and output reference planes across the device under test (DUT).

FIG. 2

Block diagram of the two-port microwave test arrangement.

In these equations, ϵ_r is the complex dielectric constant, l is the sample length, a is the width of the wave-guide, c is the velocity of light and f is the signal frequency. For a given signal frequency, these equations adequately describe the response to the incident wave as a function of the dielectric constant and the sample length. With this measurement configuration, the test procedure simplifies to the measurement of the coefficients S_{11} and S_{21} and the computation of the corresponding values of ϵ_r from their relationship to the S-parameters as expressed in equations (1) to (6).

Two port microwave S-parameters are advantageous since a variety of advanced measurement methods as well as sophisticated equipment have been developed for their measurement. The automatic network analyser system used for this investigation is capable of controlled generation of an incident signal which is coupled to the device under test (DUT) through the first port while the analyser measures the ratio of this incident signal to both the signal reflected back to the first port and that offered to the second port (see figure 2). These ratios correspond to S_{11} and S_{21} , except for a certain phase factor. This phase ambiguity results from the fact that the phase angle of the measured ratios is determined not only by the DUT, but also by the length of the connection lines. Another source of ambiguity can arise from the fact that the connection lines will not be ideal but rather behave like connection networks, causing reflections and affecting the signal passing through them, thus introducing measurement errors. Both ambiguities may, however, be practically eliminated since the connection networks are also two-ports, each of which may be characterized by a set of S-parameters. The reflection and transmission of the cascaded network, consisting of the measurement device and the connection networks can be expressed in terms of the S-parameters of the individual networks as follows :

$$M = f(S, E) \quad (7)$$

where M denotes the ratios measured by the network analyser, S denotes the S-parameters of the measurement device and E , the parameters of the connection networks.

First, M is measured for a two-port of which S is known. M and S are substituted in equation (7) to solve for E . Next, the known two-port is replaced by the measurement object and M is measured again. M and E are now substituted to solve for S . A detailed description of the procedure is given in reference /11/. The use of a computerized automatic network analyser ensures the practical elimination of the errors identified above.

The usual way to compute ϵ_r from S_{11} and S_{21} is by inferring an analytical expression for ϵ_r from equations (1) to (6). It has been shown that this approach suffers from severe error propagation /12/. To avoid this, a normalized least squares method, as described in /13/, was applied using the computer program described in /14/.

Experimental

Ordinary portland cement specified by the Dutch Standard N481 to provide high early strength at a specific surface of 4000 cm²/g (Blaine) and having an initial and final setting time of 130 and 170 minutes respectively was used in all the pastes which were carefully compacted into a 10×22.5 mm rectangular wave-guide with a length of 8 mm. The measurements were carried out at a frequency of 9 GHz using the automated network analyser system of the Microwave Laboratory of the Delft University of Technology*. The first measurement was made some 5 minutes after mixing and thereafter, an automatic recording of every measurement at intervals of 45-50 minutes. Shorter intervals can be selected; the longest continuous measurement lasted 70 hours. Common admixtures used in the tests were commercial Sugar as a set-retarder, Calcium Chloride as an accelerator and Melment as a superplasticizer. .

Results and Discussion

Figure 3 shows the computed values of the complex dielectric constants as a function of hydration time for cement pastes at three water/cement ratios: 0.3, 0.35 and 0.4. The ϵ_r curves show distinct differences for the hydrating pastes of different w/c ratios, the changes becoming more pronounced in the region 5 to 20 hours. For the sake of analysis, the curves were assumed to consist of two segments, each of which can be defined by an exponential form of equations :

$$f' = (f_0 - f_{\infty}') \cdot e^{-t/\tau_1} \quad 0 \leq t \leq t_c \quad (8)$$

$$f'' = (f_c - f_{\infty}'') \cdot e^{-t/\tau_2} + f_{\infty}'' \quad t_c \leq t \quad (9)$$

In these equations, f_0 is the starting value, f_{∞}' and f_{∞}'' are the asymptotic values for the two segments of the curve, t_c is the time at which the transition takes place and τ_1 and τ_2 are the intercepts of tangents on the asymptotes respectively as shown in figure 4. The numbers τ_1 and τ_2 can be interpreted as the time-constants of the two individual stages of hydration; a larger value indicates a lower hydration rate; and a smaller value, a higher one.

A computer program optimized the values of τ_1 and τ_2 and the other parameters in equations (8) and (9) to obtain the best fit to the exponential model. Such an exercise offered the possibility of evaluating the rate periods of hydration empirically from the rates of change of the dielectric constant.

The dielectric constant of water is far higher than that of hydrated cement paste which lies in the range of 10-16. The liquid phase dielectric constant

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* comparable to an improved Hewlett Packard 8542B.

FIG. 3

Complex dielectric permittivity of hydrating cement paste at w/c ratios 0.3, 0.35 and 0.4 as a function of hydration time.

changes very little during hydration, remaining very close to that of the mixing water. The decrease in dielectric constant can therefore be correlated with the decrease in "free water" or the evaporable water content with progressive hydration. In the preliminary tests, we limited ourselves to registering changes in the dielectric constant of the hydrating paste samples rather than determining its absolute values as the experiments were essentially of a qualitative nature. However, when clearly distinguishable rates of change became evident, the possibility arose of identifying the rate periods of hydration and the influence of chemical admixtures on the relative durations of these periods.

FIG. 4

Definition of parameters for the exponential decay curves

Table I lists the values of the rate constants τ_1 and τ_2 which were computed for the mixes using common chemical admixtures and for a C_3S mix at $w/C_3S = 0.35$

It can be seen from the values of τ_1 and τ_2 that the addition of a retarder to the paste reduces the rate of the reaction in the second phase while a superplasticizing admixture influences both the first and the second rate periods of hydration, as does the $CaCl_2$ accelerator as well. If the first derivative of ϵ' with respect to time t is calculated, a plot which resembles the rate of heat

First, M is measured for a two-port of which S is known. M and S are substituted in equation (7) to solve for E . Next, the known two-port is replaced by the measurement object and M is measured again. M and E are now substituted to solve for S . A detailed description of the procedure is given in reference /11/. The use of a computerized automatic network analyser ensures the practical elimination of the errors identified above.

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$$f' = (f_0 - f'_{\infty}) \cdot e^{-t/\tau_1} \quad 0 \leq t \leq t_c \quad (8)$$

$$f'' = (f_c - f''_{\infty}) \cdot e^{-t/\tau_2} + f''_{\infty} \quad t_c \leq t \quad (9)$$

In these equations, f_0 is the starting value, f'_{∞} and f''_{∞} are the asymptotic values for the two segments of the curve, t_c is the time at which the transition takes place and τ_1 and τ_2 are the intercepts of tangents on the asymptotes respectively as shown in figure 4. The numbers τ_1 and τ_2 can be interpreted as the time-constants of the two individual stages of hydration; a larger value indicates a lower hydration rate; and a smaller value, a higher one.

A computer program optimized the values of τ_1 and τ_2 and the other parameters in equations (8) and (9) to obtain the best fit to the exponential model. Such an exercise offered the possibility of evaluating the rate periods of hydration empirically from the rates of change of the dielectric constant.

The dielectric constant of water is far higher than that of hydrated cement paste which lies in the range of 10-16. The liquid phase dielectric constant

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cizer have further clarified the definitive changes that are brought about in the respective rates and periods of hydration. While it is not the intention of this paper to deduce physico-chemical mechanisms on the basis of the results obtained so far, the immense potential of such a sensitive, non-destructive and continuous test to follow the hydration of various cements and other hydraulic binders, with and without chemical admixtures must be emphasized.

Conclusions

Application of laboratory microwave equipment in conjunction with a computer to monitor the rate and degree of hydration of small-sized cement paste samples offers a new method that can potentially be used to advantage in the continuous and non-destructive study of cement hydration. The method is relatively simple and sensitive enough to detect the variations in the very early hydration reactions and their kinetics and can be relied upon for the assessment of not only common chemical admixtures prevalent in concrete technology but also the impact of other factors that bear upon the early hydration processes.

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