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Ultrasonic measurements during early-stage hydration of ordinary Portland cement

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The variations of ultrasonic pulse velocity, peak amplitude of transmitted pulse and heat evolution rate were measured during the hydration process of ordinary Portland cement with water/cement ratio (W/C ratio) ranging from 0.4 to 0.6 at environmental temperatures between 20 and 40° C. The change of heat evolution rate reflected the kinetics of hydration and was sensitively affected by the W/C ratio and environmental temperature. The velocity and peak amplitude were compared with the heat evolution rate to investigate the correlation of elastic properties and structural development with the kinetics of hydration. The dependence of the velocity and the peak amplitude on W/C ratio and environmental temperature are discussed in terms of the concentration of solid phase in the cement paste varying with W/C ratio and the extent of hydration.

1. Introduction

Portland cement is composed of a number of rather impure chemical constituents. The main compounds are the anhydrous compounds tricalcium silicate (C_3S), dicalcium silicate (β-C_2S), tricalcium aluminate (C_3A) and an alumino-ferrite phase (C_4AF). In the presence of water, all these compounds react in a complex manner to give certain forms of hydrated material which gradually replace the water in the spaces between the cement grains and eventually provide a matrix that effectively binds the composite mass of cement grains together.

Hydration is all the reactions of cement with water. The hydration reaction itself is of central interest in the study of cement and many methods already exist to study the hydration of Portland cement. Since each method gives a limited information and the process of hydration is complex, total knowledge on the hydration of cement is still rather incomplete due to the complex process.

Ultrasonics have been used successfully for continuous and non-destructive monitoring of the changing physical properties associated with the strength development of cement paste during hydration.

Lawrence *et al.* [1] studied the hydration of C_3S along with the effects of various admixtures by the use of longitudinal ultrasonic waves. Stepišnik *et al.* [2] calculated the shear modulus and dynamic viscosity changes during the hydration of Portland cement by measuring the reflection coefficient of ultrasonic waves in hydrating cement. The development of shear modulus was associated with the geometry of the grain growth, assuming that the elastic shear modulus is directly proportional to the volume of hydrated phase.

Munir and Taylor [3] investigated the hydration process of high-alumina cement using ultrasonic propagation techniques. A correlation between the wave velocity and amplitude and the breaking strength of the cement was demonstrated. The wave velocity and amplitude varied with the water to cement ratio [3]. The influence of inorganic and organic admixtures on the hydration of ordinary Portland cement (OPC) was investigated by Wilding and Double [4] using combined calorimetric and ultrasonic pulse velocity techniques.

In this work, calorimetric and ultrasonic measurements were simultaneously performed during the hydration of OPC with various water/cement ratios by weight (W/C ratio) at various environmental temperatures.

2. Experimental procedure

2.1. Specimen and mould

A commercial OPC (Ssangnyong, Korea), mixed with distilled water was moulded in a 10 cm × 10 cm × 4 cm acrylic jig. The evaporation of water was prevented during hydration by covering the top face of the mould.

2.2. Heat evolution rate measurement

The heat evolution rate during hydration was measured by the conduction calorimetric method. The environmental temperature was maintained constant during hydration in the oven. The heat evolution rate of hydrating cement paste is proportional to the temperature difference between the hydrating cement paste and the environment. The temperature of the hydrating cement paste was measured by an embedded chromel–alumel thermocouple.

2.3. Ultrasonic pulse velocity and peak amplitude measurements

The ultrasonic pulse velocity and peak amplitude were

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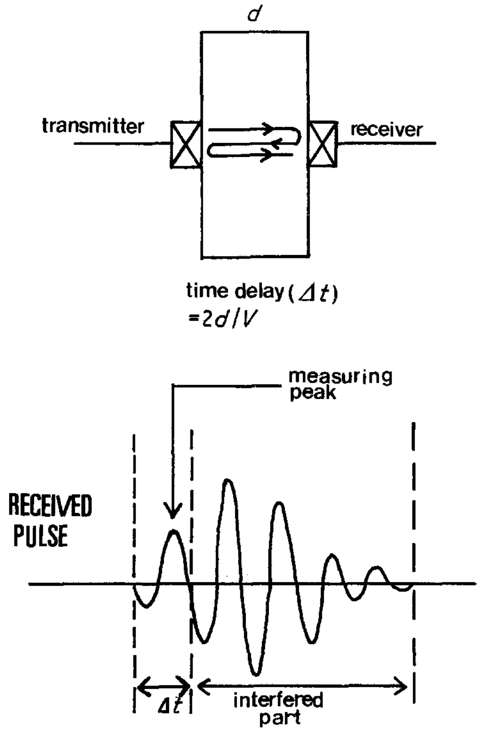

Figure 1 Interference by reflection and selection of measuring peak.

measured by a transmission technique using a Pundit generator and Matec attenuation recorder (Model 2470B). Resonant-type transducers of 54 kHz frequency were attached to both sides of the mould. The Pundit provides a d.c. output voltage proportional to the transit time through hydrating cement paste of the transmitted ultrasonic wave. The pulse velocity was obtained by measuring the transit time at a given path length of the mould, 4 cm.

The d.c. output voltage of the Matec attenuation recorder is proportional to the peak amplitude of a selected part of the transmitted pulse. The transmitted pulse is subject to interference from the reflections at each side of the mould, and care was taken to avoid the effects of interferences. The first echo is the back-reflected wave in our geometry of the mould. The received pulse interferes with the back-reflected wave after a time $2d/V$, where V is the velocity and d is the distance between transducers; thus for the maximum possible velocity $V = 4000\,\mathrm{m\,sec^{-1}}$ and $d = 4\,\mathrm{cm}$, $2d/V = 20\,\mu\mathrm{sec}$. Therefore, the part of the oscillations in a period, $1/54\,\mathrm{kHz} = 18.5\,\mu\mathrm{sec}$, does not interfere with the reflected wave. Hence the amplitude of the first oscillation was selected for measurement of the attenuation caused by hydrating cement paste (see Fig. 1). The peak amplitude of the transmitted ultrasonic wave is measured after the pulse of resonant frequency is received. The experimental set-up is shown in Fig. 2. All data were recorded by an Apple II computer through an 8-bit A–D converter. The measurements were carried out over a 48 h period from 10 min after mixing, with a reading cycle of every minute for the first hour and every five minutes during the remaining 47 h. The experiments were performed for various W/C ratios ranging from 0.4 to 0.6 at an environmental temperature between 20 and 40° C.

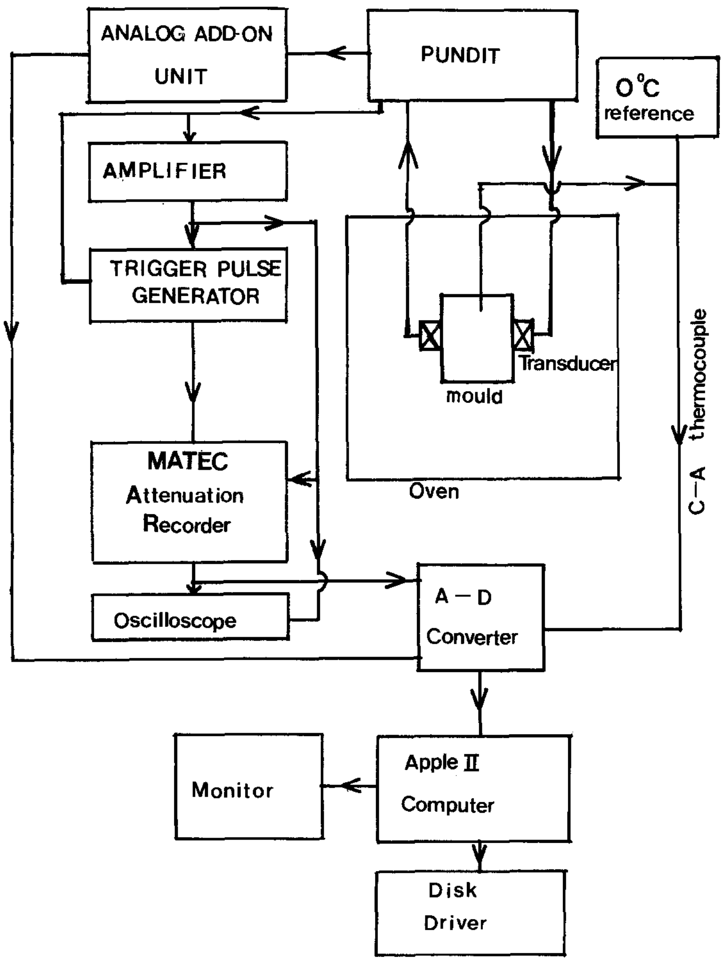

Figure 2 The experimental set-up.

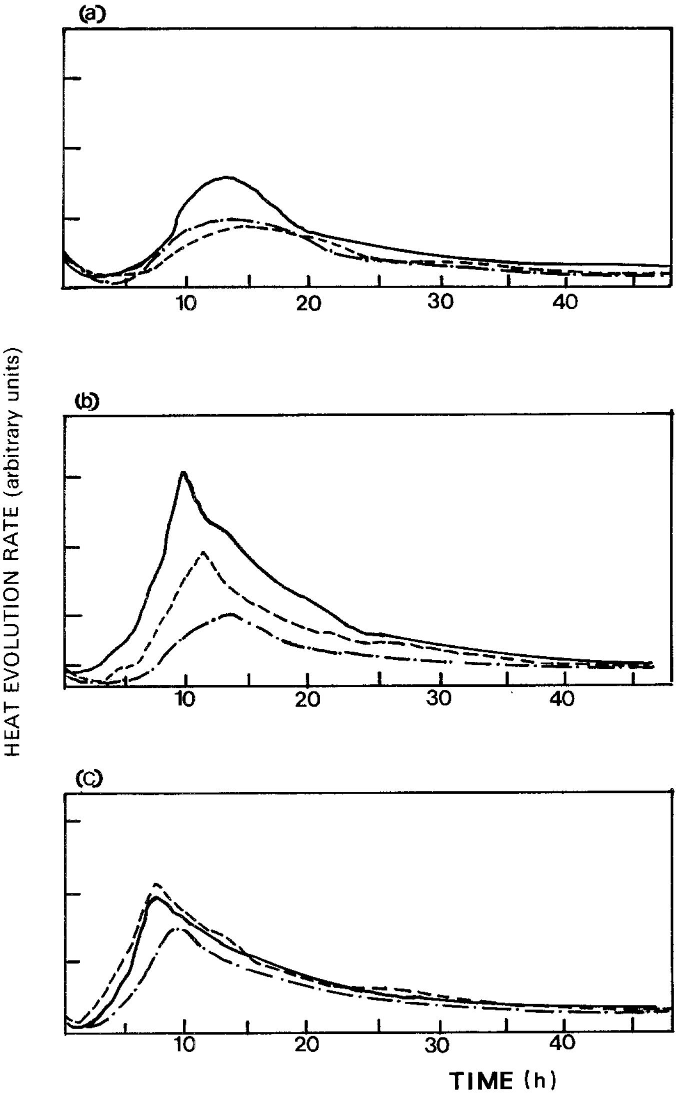

Figure 3 The heat evolution rate against time. Environmental temperature, T = (a) 20° C, (b) 30° C, (c) 40° C. W/C = (——) 0.4, (– – –) 0.5, (–·–·–) 0.6.

3. Results and discussion

3.1. The heat evolution rate

The heat evolution rate is proportional to the hydration rate due to the exothermic nature of the reaction.

The results of heat evolution rate measurements against time at environmental temperatures of 20, 30, and 40° C for W/C = 0.4, 0.5, and 0.6 are shown in Figs 3a, b and c, respectively. The profile exhibits three stages of variation; the induction stage, where the heat evolution rate is low for the first few hours, the acceleratory stage in which the rate increases, and the deceleratory stage in which the rate decreases. The general form of the profile is much the same as those reported previously by other workers [5–7].

3.2. Ultrasonic pulse velocity

The hydrating cement paste changes from the fluid to solid state through setting and hardening. Therefore, the elastic properties of the paste, and consequently the pulse velocity, change as the hydration proceeds.

The hydrating paste is thought to consist of a solid phase and a porous phase which is classified into gel and capillary porosity. The concentrations of these phases in the total volume are related to the initial W/C ratio and the extent of hydration, h (= volume of hydrated cement/volume of initial cement), by the following relations for 100 g cement with 3.15 g cm^{-3} specific gravity [8]:

$$\begin{aligned}\text{Solid part} &= \text{unhydrated cement} + \text{inner products}\\ &\quad + \text{outer products}\\ &= \frac{31.8(1-h)}{31.8+100R} + \frac{31.8h}{31.8+100R} + \frac{17.158h}{31.8+100R}\\ &= \frac{31.8+17.158h}{31.8+100R}\end{aligned}$$

$$\begin{aligned}\text{Water} &= \text{gel water} + \text{capillary water}\\ &= \frac{19.04h}{31.8+100R} + \frac{100R-42.04h}{31.8+100R}\\ &= \frac{100R-23h}{31.8+100R}\end{aligned}$$

$$\text{Empty capillary} = \frac{5.842h}{31.8+100R}$$

where R = W/C ratio. Fig. 4 shows the dependence of these concentrations on the extent of hydration for various W/C ratios. The concentration of empty capillary is negligible for the concentrations of water phase and solid phase for the W/C ratios used in the present work. Therefore, the hydrating cement paste can be regarded as a two-phase medium which consists of a water phase saturated in porosity and a solid phase.

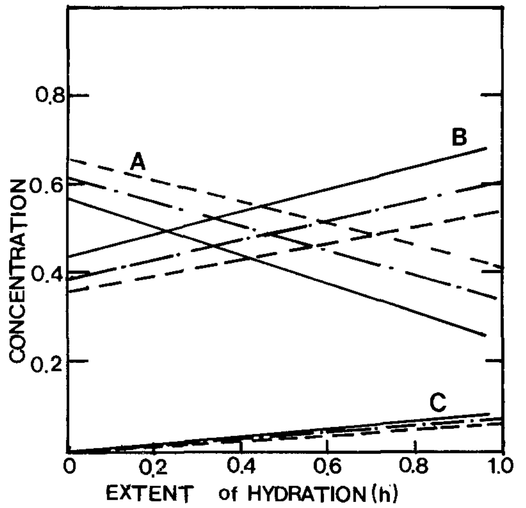

Figure 4 The concentrations of various phase against the extent of hydration, *h*. A = water phase, B = solid phase, C = empty capillary. W/C = (——) 0.4, (–·–·–) 0.5, (– – –) 0.6.

The ultrasonic pulse velocity of the hydrating paste varies with the concentrations of solid and water phase. A simple model for the pulse velocity in the hydrating paste is that the transit time through the paste is equal to the sum of the transit times through each phase; the pulse velocity, V, can then be expressed as

$$V = \frac{V_s V_w}{V_s - (V_s - V_w)C_s}$$

where C_s is the concentration of solid phase, V_s the pulse velocity in the solid phase and V_w the pulse velocity in the water phase.

Though an exact solution for the pulse velocity in the hydrating paste is not obtainable, however the pulse velocity is higher for higher concentrations of the solid phase. The concentration of the solid phase increases during hydration; consequently an increase of the pulse velocity with hydration is expected.

3.2.1. The stages of hydration

The change of pulse velocity during hydration is generally divided into nearly three stages for all W/C ratios and environmental temperatures as shown in Figs 5a, b and c:

Stage I: The ultrasonic pulse velocity remains nearly constant.

Stage II: The velocity increases almost linearly.

Stage III: The rate of the velocity change decreases, followed by near-saturation.

The changes of the velocity and heat evolution rate during hydration for W/C = 0.4 at environmental temperature 30° C are shown in Fig. 6. Stages I, II and III correspond well to the induction, acceleratory and deceleratory stages of the heat evolution rate, respectively.

The microstructural development of hydrating paste in these stages have been studied extensively by the electron microscope and the results are summarized as follows [9–12].

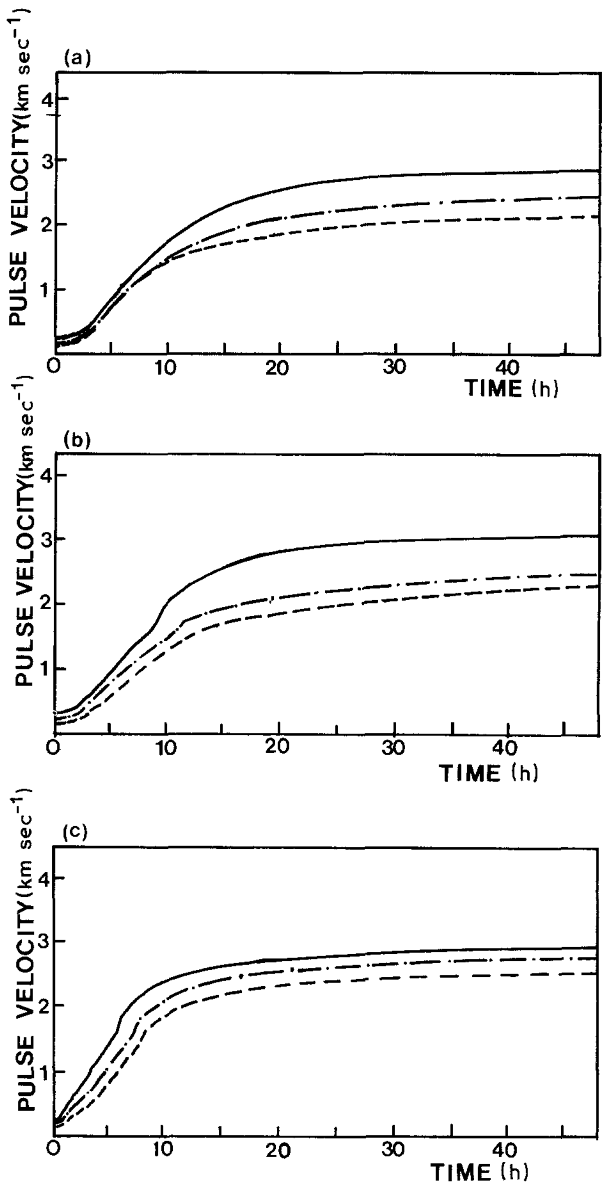

Figure 5 The ultrasonic pulse velocity against time: T = (a) 20° C, (b) 30° C, (c) 40° C. W/C = (——) 0.4, (–·–·–) 0.5, (– – –) 0.6.

(a) Induction stage: the initial reaction products, mainly the hydration product of C_3A, are formed on the surface of cement grains within the first few tens of minutes. Thereafter, microstructural developments scarcely take place.

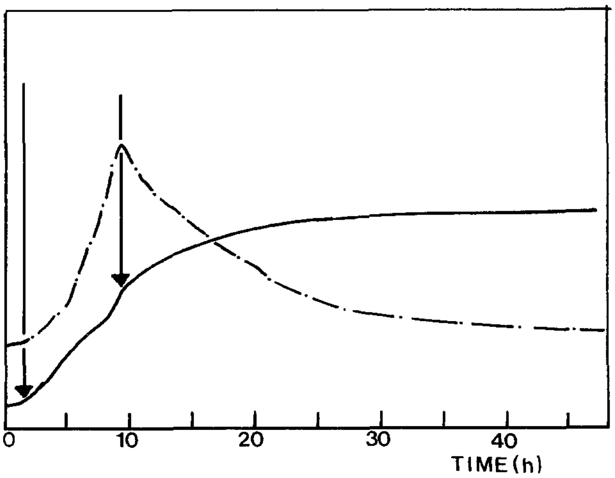

Figure 6 The correspondence of (——) pulse velocity with (–·–·–) heat evolution rate. W/C = 0.4, T = 30° C.

(b) Acceleratory stage: the rapid nucleation and growth of C–S–H and $Ca(OH)_2$ that are the hydration products of C_3S occur. Fibrillar outgrowths of C–S–H from the surfaces of cement grains fill in the space between cement grains and bond the cement grains together so that the cement sets.

(c) Deceleratory stage: the hydration products gradually fill in the space between cement grains, the space becomes more dense and the cement hardens.

The constancy of pulse velocity in Stage I reflects few reactions in the induction stage, Stage II is due to drastic changes in the elastic properties of the paste resulting from the rapid nucleation and growth of C–S–H and $Ca(OH)_2$ during the acceleratory stage, and Stage III reflects the gradual change in the elastic properties of the hardening paste during the deceleratory stage.

3.2.2. *W/C ratio dependence*

It is noticeable that higher pulse velocities are associated with lower W/C ratios in Figs 5a, b and c. The concentration of solid phase is higher for lower W/C ratios as in Fig. 4. Hence, a higher concentration means a higher velocity. On the other hand, the occurrence of nearly the same velocities for W/C ratios of 0.5 and 0.6, during initial hydration of about 10 h, can be accounted for in terms of nearly the same concentration of solid phase caused by the fact that the extent of hydration at 0.6 is higher than at 0.5 during the initial stage as shown in Fig. 3a.

3.2.3. *Dependence on environmental temperature*

The influence of the environmental temperature on the pulse velocity for a W/C ratio of 0.4 shown in Fig. 7 may be summarized as follows.

(i) The occurrence of a shorter Stage II at higher environmental temperature.

(ii) Higher pulse velocities at higher environmental temperatures during initial hydration for about 15 h, after which the pulse velocity trend is reversed, being higher at 30° C than 40° C.

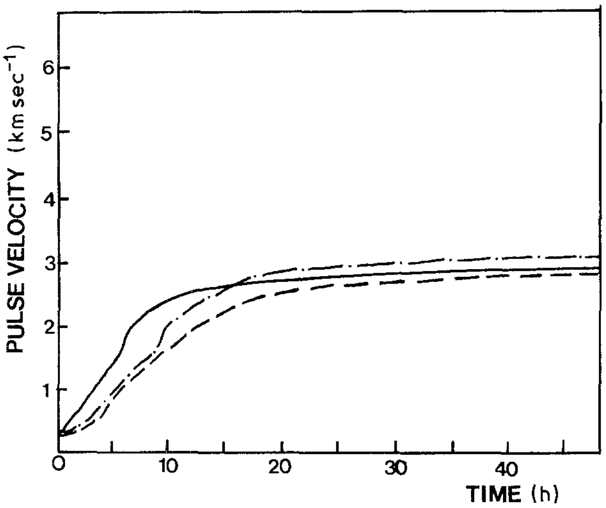

Figure 7 The influence of environmental temperature on the pulse velocity. W/C = 0.4. T = (– – –) 20° C, (–·–·–·–) 30° C, (——) 40° C.

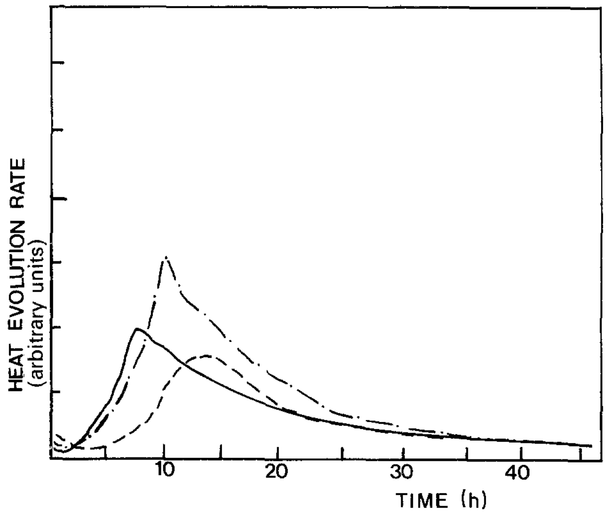

Figure 8 The influence of environmental temperature on the heat evolution rate. W/C = 0.4. T = (– – –) 20° C, (–·–·–·–) 30° C, (——) 40° C.

Fig. 8 shows the influence of the environmental temperature at 20, 30 and 40° C on the heat evolution rate for a W/C ratio of 0.4. The acceleratory stage of heat evolution rate, corresponding to Stage II, is shorter for the higher environmental temperatures. Hence, Stage II of the pulse velocity is shorter for the higher environmental temperatures.

The higher pulse velocity during initial hydration at higher environmental temperatures is attributable to the higher concentration of solid phase resulting from a greater extent of hydration, h, at higher environmental temperatures. Thereafter, the extent of hydration at 30° C becomes higher than at 40° C, and accordingly the concentration of solid phase is higher at 30° C than 40° C, as is the velocity.

3.3. The peak amplitude of the transmitted ultrasonic pulse

The attenuation caused by the hydrating paste changes with hydration, and accordingly the peak amplitude of the transmitted pulse changes. Attenuation is mainly caused by the scattering of the pulse at the boundaries of various phases such as hydrated cement, unhydrated cement and capillary pores in the paste. The cement paste, after cement grains are interconnected, is regarded as a two-phase medium with a distribution of spherical porosity saturated by water in the solid phase. The ultrasonic pulse is mainly attenuated by the Rayleigh scattering of porosity because the wavelength is much longer than the size of the porosity. The attenuation constant, α, is expressed by the Rayleigh scattering formula

$$\alpha \propto C_w f^4 = (1 - C_s) f^4$$

where f is the frequency of the ultrasonic wave, C_w the concentration of water phase and C_s the concentration of solid phase.

The attenuation decreases as the concentration of solid phase increases. As a result, the peak amplitude of the transmitted pulse increases as hydration proceeds, and the peak amplitude is higher for the higher concentrations of solid phase.

Fig. 9 shows the time dependence of the peak

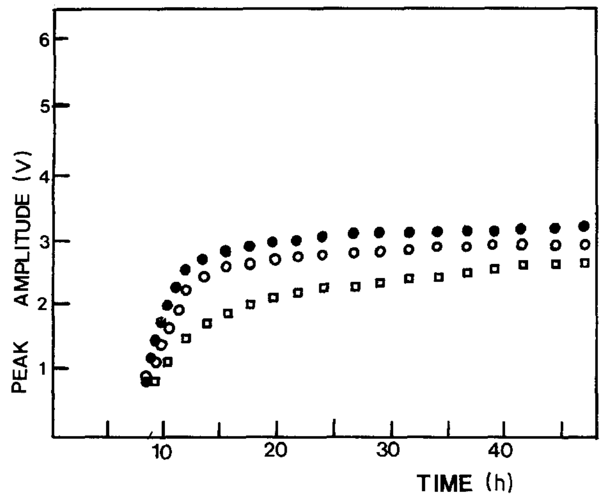

Figure 9 The peak amplitude against time for various W/C ratios: (●) 0.4, (○) 0.5, (□) 0.6.

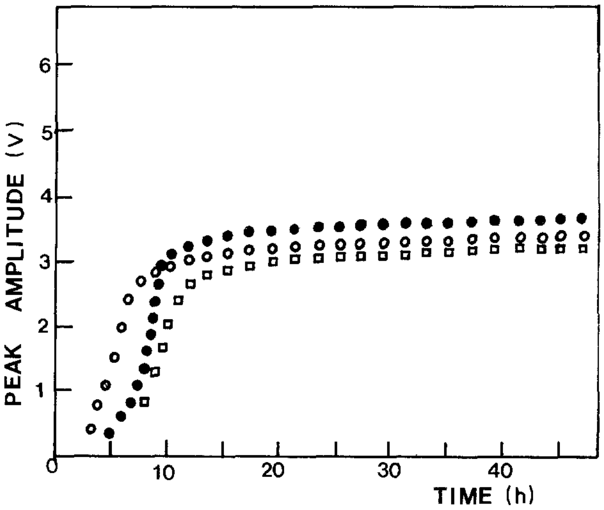

Figure 10 The environmental temperature dependence of the peak amplitude. W/C = 0.4. T = (□) 20° C, (●) 30° C, (○) 40° C.

amplitude for various W/C ratios at 20° C environmental temperature. During about 8 h from the start, the pulse of resonant frequency is not detected due to extensive attenuation, but a pulse of lower frequency (other than the resonance) is detected during this stage. After the pulse of resonant frequency is detected, the peak amplitude increases nearly linearly, then the amplitude begins to saturate. This reflects the drastic and gradual development of the paste structure during the acceleratory and deceleratory stages, respectively.

The higher amplitudes for the lower W/C ratios are attributable to the higher concentrations of the solid phase for lower W/C ratios.

Fig. 10 shows the environmental temperature dependence of the peak amplitude. The higher amplitudes for higher environmental temperatures during initial hydration for about 8 h are due to the higher concentrations of solid phase caused by the higher extents of hydration at higher environmental temperatures. Thereafter, the amplitude for 30° C is higher, since the extent of hydration at 30° C is higher than at 40° C (see Fig. 8) and so is the concentration of solid phase.

4. Conclusions

The stages of ultrasonic pulse velocity and peak amplitude changes during the hydration of ordinary Portland cement showed a good correspondence with the stages of heat evolution rate, and reflected the changes of elastic properties and structure in the hydrating paste.

The ultrasonic pulse velocity and attenuation constant were closely related to the concentration of solid phase in the cement paste. The dependence of the pulse velocity and peak amplitude on W/C ratio and environmental temperature were qualitatively analysed in terms of the concentration of solid phase varying with W/C ratio and the extent of hydration.

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