Measurement of Cement Hydration by Ultrasonics

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Measurements of the reflection coefficient for ultrasonic waves were used to follow the hydration kinetics of cement pastes under various conditions. The development of the shear modulus of elasticity and the dynamic viscosity were calculated from the data, which also were used to determine the geometry of the grain growth.

Many methods already exist to study the hydration of portland and other cements; each method renders specific information on the process, its kinetics, and its products, thus complementing the knowledge obtained by other methods. Since total knowledge on the hydration of cements is still rather incomplete, more and different methods are necessary to close the gap.

Ultrasonics have been used successfully for determinations of mechanical properties of hardened cement paste and concrete. For the study of hydration, they were used by Lawrence et al.[1] who studied the hydration of calcium silicates influenced by admixtures by measuring the propagating velocity of sound pulses in paste cylinders. Recently, Van Wallendael[2] presented information on measurements of cement hydration by measuring the energy of ultrasonic waves transmitted through cement paste.

The present measurements are based on the ultrasonic waves reflected from a hardening paste. The amplitudes of incident and reflected waves are determined, together with their relative phase difference, and the data used to calculate the reflection coefficients, the shear moduli of elasticity, and the viscosities of pastes. Since all these quantities change in the course of the hydration process, the process itself will be discussed.

Experimental Procedure

Acoustic impedance was measured by the ultrasonic experimental setup shown in Fig. 1. The ultrasonic transducer, fixed on the surface of one end of the quartz bar, transforms the radio frequency pulse of 15 MHz into a shear acoustic wave propagating along the bar. When the shear wave hits the interface between quartz and the cement paste, it is partially reflected and partially refracted into the paste. The reflected shear wave is transformed back to an electric signal by the piezoelectric transducer. The signal is sent through the receiver into the box-car integrator to detect its amplitude, and into the phase comparator to measure the phase difference between the incident and the reflected wave.

In the case of normal incidence, the ratio between the amplitude of the reflected (A_2) and incident (A_1) wave is the reflection coefficient (r_0), which can be expressed[3] as

$$r_0=\frac{A_2}{A_1}=\frac{Z_2-Z_1}{Z_2+Z_1} \tag{1}$$

where the acoustic impedences (Z_1 and Z_2) are determined by the viscoelastic properties of the media. For the case of incident shear waves it is

$$Z=(\rho K)^{1/2} \tag{2}$$

where ρ is the mass density, the real part of K (the elastic coefficient) represents the shear elastic modulus (G) and the imaginary part is the product of the viscosity (η) and the angular sonic frequency (ω):

$$K=G+i\eta\omega \tag{3}$$

where i is the imaginary part of the complex number.

Thus, the acoustic impedance is the complex quantity

$$Z=R+iX \tag{4}$$

(where R is the real part of the acoustic impedence and X is the imaginary part) with the relation to the viscoelastic properties of the medium

$$\eta=RX/\rho\omega \tag{5}$$

and

$$G=(R^2-X^2)/\rho \tag{6}$$

By knowing Z, the properties of a medium can be evaluated.

Shear impedance was determined from measurements of r_0 for a shear wave at the interface between a fused quartz bar and the sample measured (Fig. 1). The complex reflection coefficient

$$r=r_0(\cos\phi+i\sin\phi) \tag{7}$$

consists of r_0 and the shift of the phase angle (ϕ) between the incident and reflected wave. They are related to the shear acoustic impedance by the following formulae

$$R_2=Z_1\frac{1-r_0^2}{1+r_0^2+2r_0\cos\phi} \tag{8}$$

and

$$X_2=Z_1\frac{2r_0\sin\phi}{1+r_0^2+2r_0\cos\phi} \tag{9}$$

The shear elastic modulus (G) and η can be evaluated from the reflection data using Eqs. (5) and (6). They were calculated with respect to the acoustic properties of quartz ($Z_1=8.29\times10^6$ Ns/m^{-3}), with the assumption that the cement paste density was 2.0 ± 0.1 kg/dm^3, and that it remained constant during the hydration process. The absolute error in determining r_0 was ±0.01, and for $\phi\pm0.05$ rd. Thus, the calculations of G are correct to ±300 MPa, and the calculations of η are correct to ±1 Pa/s.

Samples of cement paste were prepared by mixing a commercial

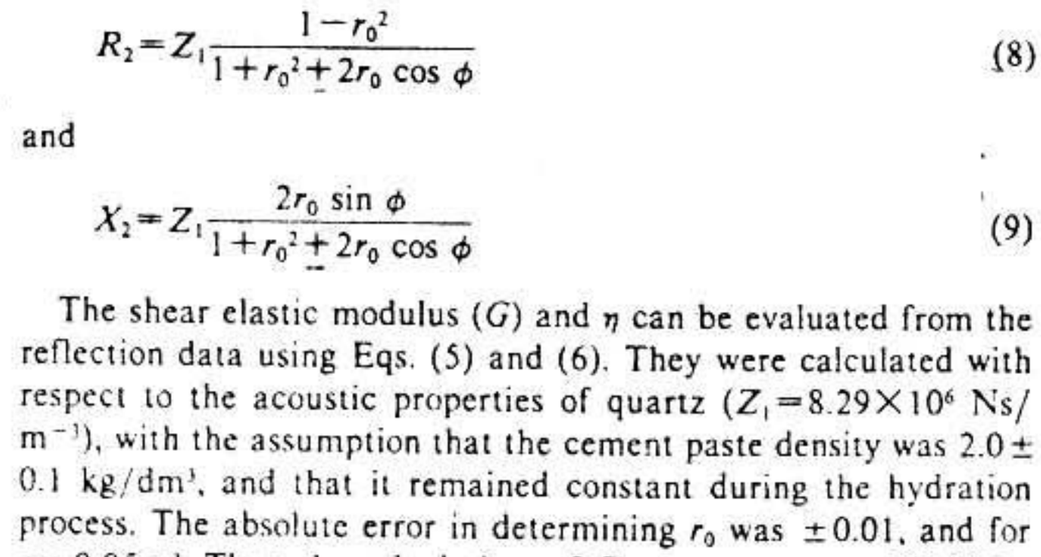

Fig. 1. Setup for ultrasonic measurements.

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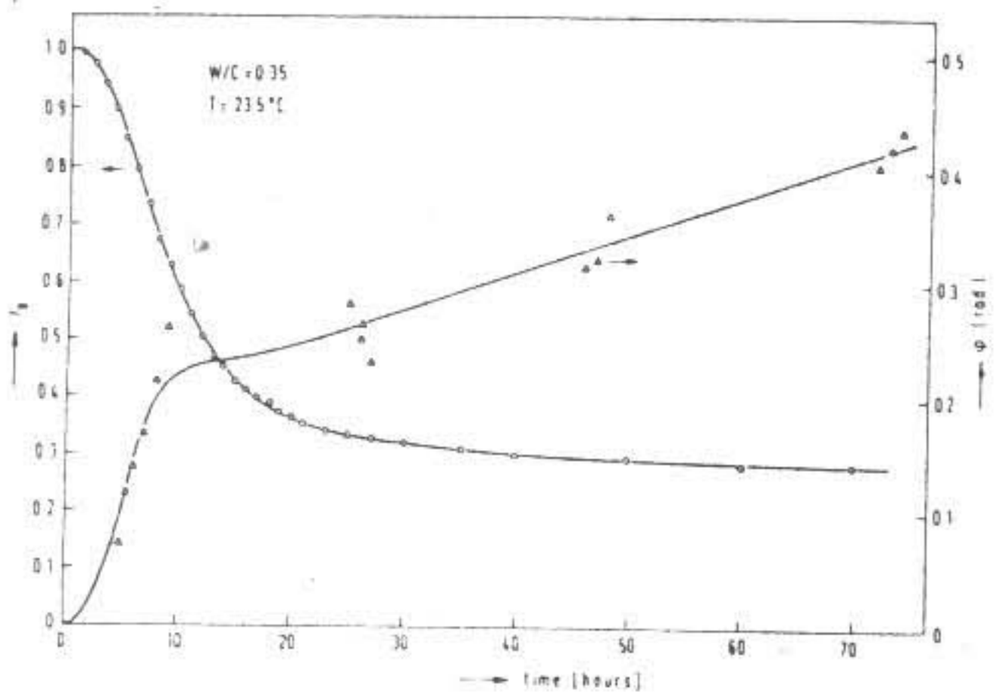

Fig. 2. Variation of reflection coefficient and phase shift during hydration of pure portland cement.

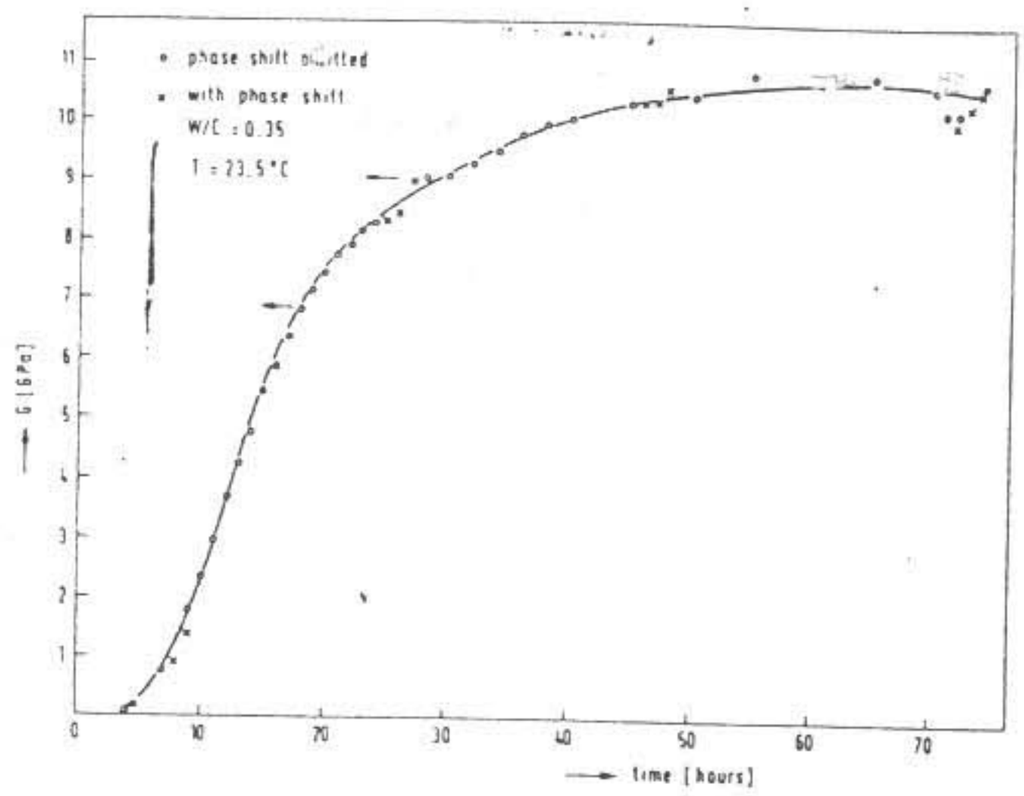

Fig. 3. Shear modulus vs time during hydration of pure portland cement.

portland cement* with the indicated amount of water and additives. Then the paste was spread on top of the quartz bar in a layer 3–4 mm thick, and covered by a small glass cup containing moist cotton to prevent evaporation.

Results and Discussion

In Fig. 2, the hydration of pure portland cement* at $w/c = 0.35$ is observed through the decrease of r_0 and the increase of ϕ. For the latter, the abrupt change in direction at $\approx$10 h is significant for transition into the solid state. Figure 3 shows G of the same system. The error of omitting ϕ is insignificant for the magnitude of G. Since the measurement of ϕ also makes the instrumentation more sophisticated, in further work only r_0 was determined. It was also convenient to express the measurements of r_0 in decibels (dB).

Fig. 4 (A) shows the influence of temperature on the hydration process, and Fig. 4(B) shows the influence of the water:cement

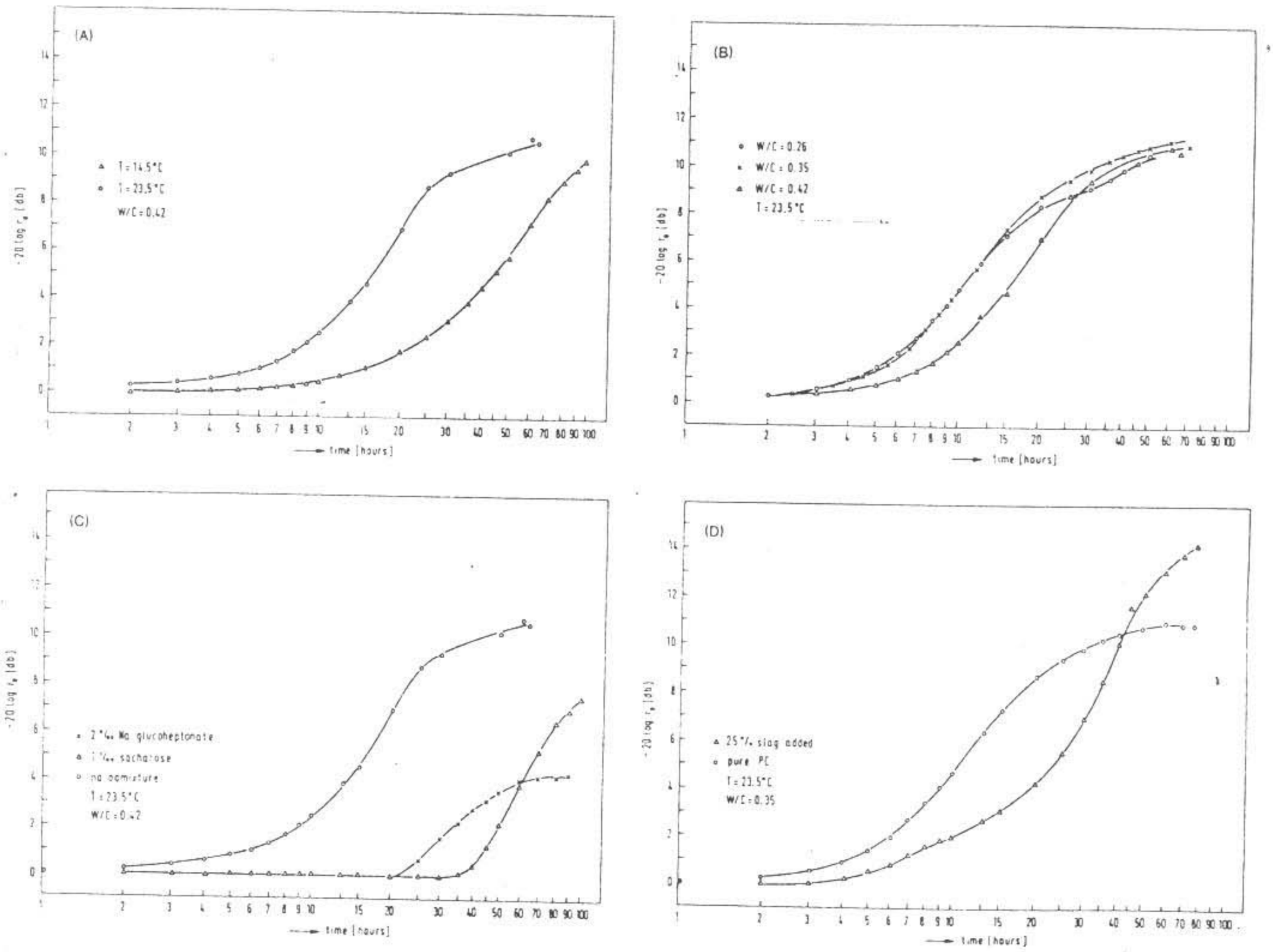

Fig. 4. Effect on cement hydration of (A) temperature, (B) *w/c* ratio, (C) retarding admixtures, and (D) addition of slag, as indicated by variation of reflection coefficient.

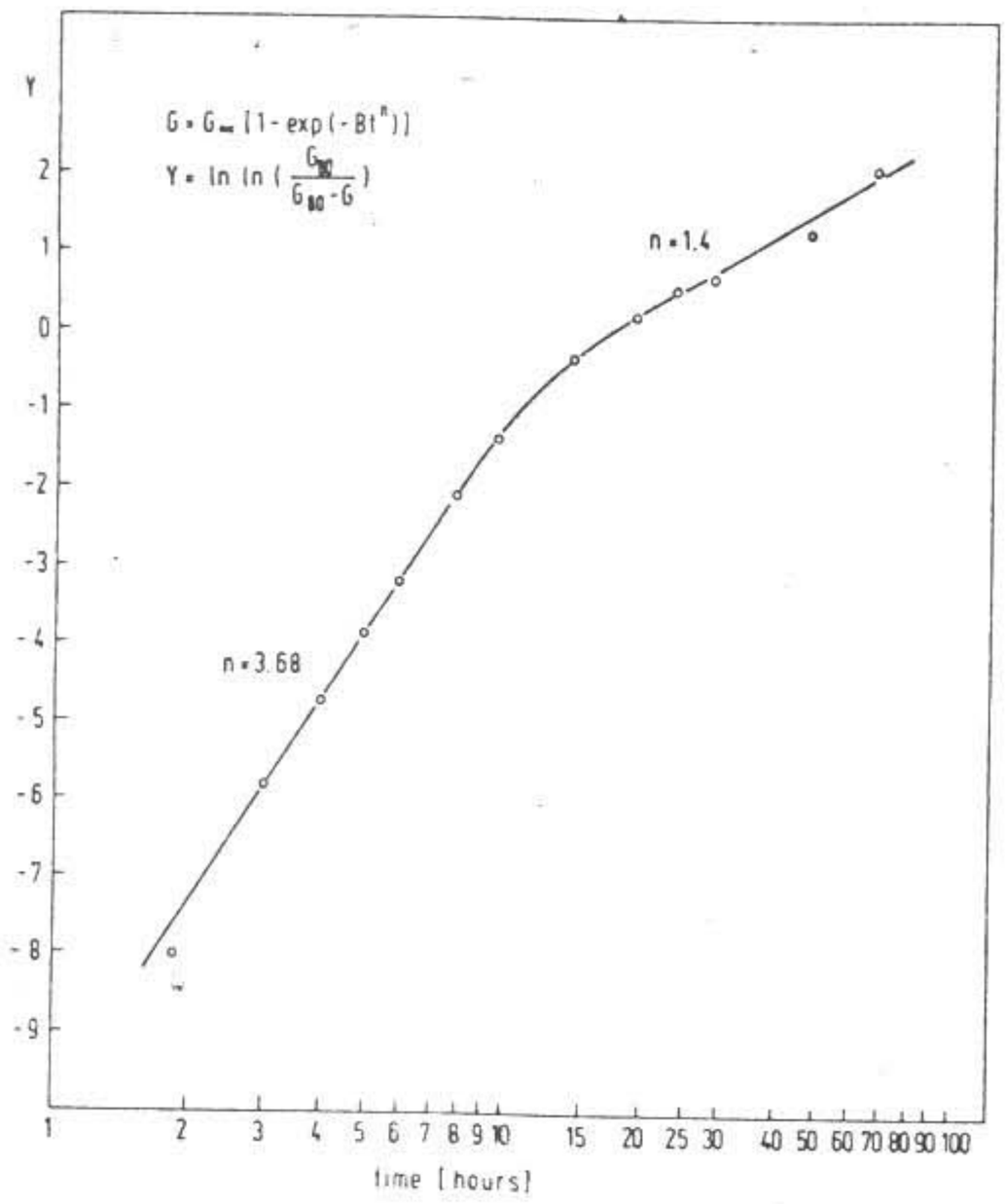

Fig. 5. Change of growth geometry during hydration (after Ref. 5).

ratio. The development at $w/c=0.26$ is interesting, where it seems that a water/cement ratio which is too low hinders further hydration of this finely ground cement.

The hydration development of an admixture of saccharose and Na-glucoheptonate, well-known retarders, is shown in Fig. 4(C). The very low value for the final G in the latter case is surprising. Hydration mesurements of the same system by the NMR method did not show a similar anomaly.[4]

A cement made from the same clinker as the commercial cement,* but containing 25% blast furnace slag, was hydrated in parallel with the commerical cement* (Fig. 4(D)). A higher effective w/c ratio with smaller amounts of the hydration products, in the case of slag cement, is probably responsible for different initial development. After two days, the decrease of r_0 becomes considerably more noticeable in the slag cement than in the commercial cement,* which could not be explained.

A discussion of an attempt to analyze the present data on the hydration process by the kinetics model of Avrami[5] follows. In this model, the microkinetic process of granulation and growth (which does not take into account the mutual grain interaction) is described by the so-called extended volume density (V_{ex}). Thus, the extended volume is the transformed volume in the hydration process, if the overlapping of growing grains is neglected. Its growth has the following time dependence:

$$V_{ex}=Bt^n \tag{10}$$

where B is a constant and n has a value between 1 and 4, depending on the geometry of the growth. As long as there is no grain interaction, the volume density of the new hydrated phase V is identical to V_{ex}. But when two growing grains of a new phase impinge, several things may happen. The two grains may coalesce to form one larger grain, as frequently happens with gaseous bubbles and liquid drops. They may adhere to form compound grains, ceasing to grow at the common interface while continuing to grow normally elsewhere. In the third mechanism, the interacting grains may rebuff each other, pushing away and continuing to grow as though there were no impingement. Only stationary particles with adhering grain interaction alone will be discussed here. In this case, when the distribution of nuclei is uniformly random, V is given by

$$V(t)=1-\exp(-V_{ex}(t)) \tag{11}$$

In Ref. 6, a similar expression was derived on the basis of formal chemical-reaction kinetics arguments, assuming that the reaction rate is gradually slowing down.

Since the shear ultrasonic waves cannot propagate through nonviscous liquids, assume that the elastic shear modulus is directly proportional to the volume of the hydrated phase:

$$G(t)\approx V(t) \tag{12}$$

and the validity of Eqs. (10), (11), and (12) can be tested directly from the present measurements.

Using Eqs. (11) and (12), ln ln $(G_{80}/G_{80}-G)$ (G_{80} is the shear elastic modulus after 80 h) vs ln t is plotted with the supposition that

$$\ln\ln\left(\frac{G_{80}}{G_{80}-G}\right)=\ln B+n\ln t \tag{13}$$

The experimental curve for the hydration of pure commercial cement* with $w/c=0.45$ at temperature 23.5°C (Fig. 5) consists of a straight line undergoing a break at ≈12 h. The slope of the initial straight line is 3.68, which means that the power n in Eq. (10) is 3.68. The value of n defines the geometry of the grain growth; therefore one could suppose that the initial part of the grain growth is polyhedral ($n=3$–4).[5] The last part of the curve can be approximated by a line with the slope $n=1.4$ which means either that the geometry of the grain growth has changed from polyhedral to lineal or plate-like ($n=1$–2) when grains impinge, or that the shear elastic modulus is no longer proportional to V, and the elastic forces between grains ought to be considered.[5]

Conclusions

The ultrasonic measurements of the cement hydration with determination of the reflection coefficient, the shear modulus of elasticity, and the dynamic viscosity are shown to provide valuable information on the hydration kinetics and on the properties of cement plaste during the early period of hydration. The method promises to become suitable for further study of cement hydration, and may also be used in examinations of elastic properties of cement paste, although considerable work is still needed to reach complete understanding of the measurements.

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*PC 550, "Salonit," Anhovo, Yugoslavia (specific surface 4480 cm²/g, according to Blaine). For chemical composition, see Ref. 4.

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