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The dynamic elastic modulus of hardened cement paste. Part I: A new statistical model – water and ice filled pores

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The dynamic elastic modulus and damping coefficient of hardened cement paste is measured by exciting the natural mode of oscillation of a hardened cement paste beam in a temperature range between +20 and −160°C. The damping from the system and water vapour exchange with the specimen are negligible. A new statistical model is proposed for combining the elastic moduli of the constituents: solid matrix, water, ice and air. Water-saturated specimens were measured, delivering results for the elastic moduli of solid, ice and water by applying the model.

1. INTRODUCTION

Hardened cement paste can be regarded as a highly dispersed multicomponent system consisting of solid particles, water, air and at sub-zero temperatures of ice, too. The structure ranges in size from nanometres to micrometres. There is a strong interaction between the constituents leading to a behaviour deviating from macroscopic laws: for example water is structured by surface forces [1] and the freezing point is depressed [1–6], which can be explained by thermodynamics [7,8]. The interaction is affected by dissolved ions, e.g. chlorides [9,10]. The physical behaviour of the microscopic structure influences the macroscopic mechanical properties.

The dynamic elastic modulus is therefore a powerful tool to study the structure and interaction of the components of hardened cement paste, especially when ice is formed. There have been several attempts to calculate the dynamic elastic modulus from the moduli of the constituents. For porous glass Hasselmann and Fulrath [11] used a simple linear relationship between the total elastic modulus, the modulus of the matrix and the volume fraction. For hardened cement paste Feldman [12] and Soroka and Sereda [13] proposed an exponential law. Manns [14] compared different models with respect to their applicability and proposed essentially empirical models for mortars. Hansen [15] adapted to hardened cement paste, mortar and concrete a description by Hashin [16] from the theory of elasticity. Powers [17] finally proposed a cubic law which was shown by Helmuth and Turk [18] to fit the experimental data excellently. Helmuth [19] also started from a statistical point of view to explain the multicomponent system especially after ice formation. These findings have subsequently been improved [20]. The following considerations are based on this work.

All these methods have in common that one mathematical equation is deduced to correlate the elastic modulus of the system with the moduli and volume fractions of the constituents. Recently Roelfstra and Wittmann [21,22] proposed a procedure adapting a modified finite-element method, wherein geometrical modelling is also possible.

2. THEORY

The dry hardened cement paste can be considered as a two-component system consisting of the matrix (elastic modulus E_2, volume fraction ν_2) and the air voids (elastic modulus $E_1 \simeq 0$, volume fraction ν_1). Following Powers [17] the total elastic modulus E_s of this system can be calculated from

$$E_s = E_2(1-\nu_1)^3 \qquad (1)$$

Water-saturated hardened cement paste can be regarded as a two-component system consisting of water and cement paste matrix. However, in this case the elastic modulus E_1 of water is not negligible.

There are two simple approximations (see Fig. 1) which may be used to calculate the elastic modulus of the system. The experimental results and calculations using more sophisticated models lie within the bounds of these simple approximations.

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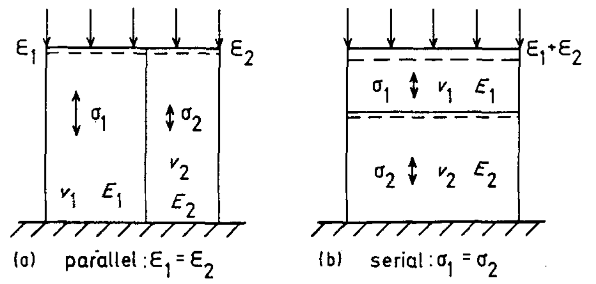

Fig. 1 Simple combinations of multicomponent systems: (a) parallel arrangement (isostrain), (b) serial arrangement (isostress).

2.1 Parallel combination

If the strain is equal in all parts then the elastic modulus of the system E_{sp} is the sum of the moduli of the constituents E_i times their volume fraction ν_i:

$$E_{sp} = \sum_i E_i \nu_i \qquad \sum \nu_i = 1 \tag{2}$$

For a two-component system Equation 2 reduces to

$$E_{sp} = E_1 \nu_1 + E_2(1-\nu_1) \tag{3}$$

This case can be visualized by a row of parallel columns, the volume fractions being ν_1 and ν_2, respectively (Fig. 1a).

2.2 Serial combination

In the second case it is assumed that stress is the same in all parts, leading to the equation for the system modulus E_{ss}

$$E_{ss}^{-1} = \sum_i \nu_i E_i^{-1} \tag{4}$$

This corresponds to a model of components arranged in series (Fig. 1b).

2.3 New statistical model

In Fig. 2 the elastic modulus of the system is plotted as a function of volume fraction for the two cases together with experimental values. It can be concluded that a function which gives the best fit to the data should be an appropriate mixture of both arrangements. Helmuth [19] was the first to use a statistical mixture of the components for this procedure. An improved version has been proposed [20] which is outlined here. Initially, columns containing n parts are formed out of the constituents. All kinds of possible combination are taken into account. Combinations with the same number of components of each constituent but with different arrangements are equivalent. The elastic modulus E_k of such a column with k parts of E_2 and (n-k) parts of E_1 is

$$E_k = \frac{nE_1E_2}{kE_1+(n-k)E_2} \qquad 0 \le k \le n \tag{5}$$

The total number of parts n is open at this point of consideration. For a system containing two components $(n+1)$ different configurations are possible.

The probability w of finding a possible column composition out of a collective mixture of $\nu_1/\nu_2 = \nu_1/(1-\nu_1)$ is given by a binomial distribution [23]:

$$w(n,k,\nu_1) = \frac{n!}{k!(n-k)!}\nu_1^{n-k}(1-\nu_1)^k \tag{6}$$

which is equivalent to the volume fraction of this kind of column.

The elastic modulus E_s of all these parallel standing columns is then

$$E_s = \sum_{k=0}^{n} E_k w(n,k,\nu_1) \tag{7}$$

The result is still dependent on n, the number of parts of one column, which is equivalent to the number of parts which can interact in isostress without a 'horizontal' interaction. A good approximation for n can be found for evaluating dry hardened cement paste ($E_1 = 0$). In this case Equation 7 reduces to

$$E_s = E_2(1-\nu_1)^n \tag{7a}$$

A comparison with Equation 1 leads to $n = 3$. On fixing this value Equation 7 leads to

$$E = E_1\nu_1^3 + 9\nu_1^2(1-\nu_1)\frac{E_1E_2}{E_1+2E_2} + 9\nu_1(1-\nu_1)^2\frac{E_1E_2}{2E_1+E_2} + E_2(1-\nu_1)^3 \tag{7b}$$

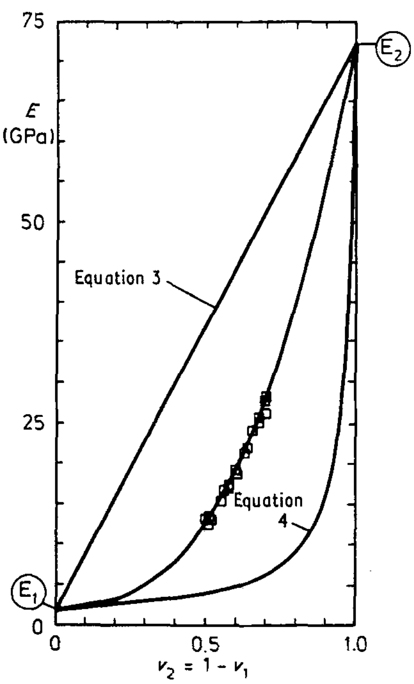

Fig. 2 The elastic modulus of a two-component system as a function of volume fraction $\nu_2 = 1-\nu_1$, calculated by Equations 3 and 4; also measured points for water-saturated hardened cement paste at 20°C. Fitted curve calculated by the statistical model using adopted values $E_1 = 1.98$ GPa (water) and $E_2 = 71.8$ GPa (solid matrix).

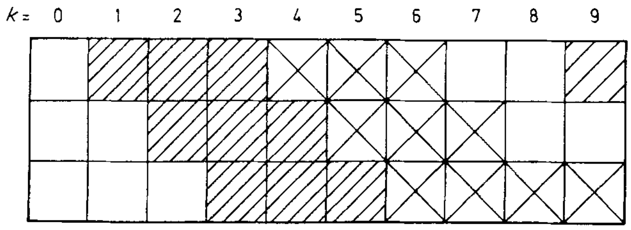

Fig. 3 Different kinds of combination of three components in columns of three constituents.

Hardened cement paste is usually a three-component system with the solid (E_1, v_1), the pore water (E_2, v_2) and air-filled pores ($E_3 = 0$, v_3). Now 10 different kinds of column combination are possible as shown in Fig. 3. Since $v_1 + v_2 + v_3 = 1$ and $E_3 = 0$ the system modulus is

$$E_s = E_1 v_1^3 + 9v_1^2(1 - v_1 - v_3)\frac{E_1 E_2}{E_1 + 2E_2} + 9v_1(1 - v_1 - v_3)^2\frac{E_1 E_2}{2E_1 + E_2} + E_2(1 - v_1 - v_3)^3 \quad (8)$$

3. EXPERIMENTAL PROCEDURE

For the experiments a completely sealed measuring chamber has been constructed which can be cooled to −160°C (Fig. 4). The small beam of hardened cement paste was placed on two knife-edged supports at the nodal points. Using a hammer a natural mode of oscillation was excited. The weight of the hammer, the height of fall and the hardness of the tip of the hammer were chosen so that immediately after the strike the hammer hovered over the beam and the beam over the suspension for about 300 ms. Therefore there is almost no damping due to the measuring system. The oscillation was measured by a strain gauge glued to the bottom of the beam. It was recorded via a Wheatstone bridge connected to a transient recorder and evaluated by a microcomputer. The eigenfrequency and damping coefficient were calculated. Using a correction procedure by Pickett [24] the elastic modulus was calculated from

$$E = 0.9464\frac{\rho l^4 \nu_1}{h^2}\nu_2 K$$

$$K = 1 + 6.585(1 + 0.0752\mu + 0.8109\mu^2)(h/l)^2 - 0.868(h/l)^4$$

where ρ = density, l = length of the beam, h = height of the beam, ν_1 = 1st eigenfrequency and μ = Poisson number.

To minimize heating of the beam, the resistor bridge was only switched to the strain gauge shortly before oscillation. In the measuring chamber there was also a dummy specimen with a reference strain gauge and a PT 100 resistance thermometer for temperature control. When cooling the rate was 1.6 K min^{-1}. The temperature ranged between +20 and −160°C.

4. SAMPLE PREPARATION

The beams were cut out of the middle of hardened cement paste plates. They were stored in saturated calcium hydroxide solution in desiccators until reaching the desired age of hydration. Air bubbles and voids due to self-desiccation have been carefully avoided and are negligible. The samples were measured immediately after removal from the solution to ensure complete water-saturation of the pores. The porosity was evaluated by

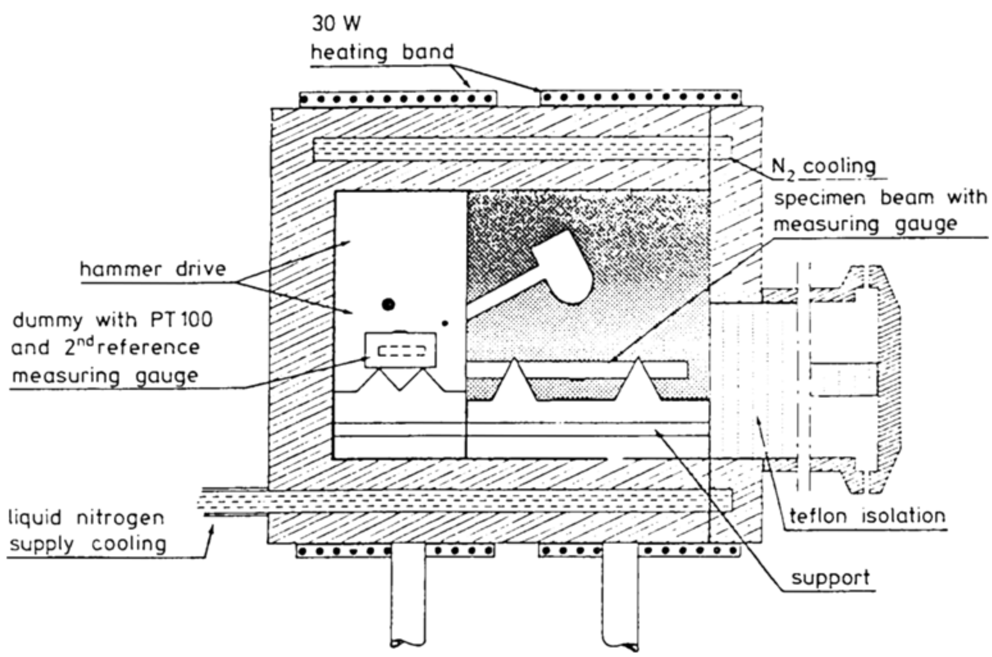

Fig. 4 Measuring chamber. The chamber is additionally thermally isolated.

drying over P_2O_5 followed by vacuum-drying to determine by weighing the loss in weight of water. The porosity was changed by varying the water/cement ratio (0.35 to 0.5) and choosing different ages of hydration (6 to 210 days). The plates were formed using special 5 mm thick moulds into which the cement paste was poured. A special technique was used to stop air bubbles forming. To prevent segregation the moulds were rotated slowly for one day after sealing. An ordinary Portland cement PZ 35F (DIN 1164) was used [20].

5. RESULTS AND DISCUSSION

The specimens considered here were all water-saturated. They can therefore be treated as a two-component system, Component 1 being water and Component 2 the solid matrix. The volume fraction of water v_1 is given by the porosity. In Fig. 2 the system modulus is plotted against $(1-v_1)$ and in Fig. 5 against $(1-v_1)^3$, following the Powers potential law for results at +20°C.

Using Equation 7b the moduli E_1 and E_2 were varied to fit a continuous line to the data. For the solid matrix a modulus E_2 = 71.8 GPa was found. This is in good agreement with the results of Helmuth and Turk [18] who obtained 74.4 to 79.9 GPa and with Locher [25] who reported 70 to 80 GPa. The value E_1 = 1.98 GPa is almost identical to the modulus of compression of water, 2.0 GPa. This means that at the high frequencies used in the measurements (5 kHz) water is fully load-bearing. It does not flow out of the pores and is compressed according to its modulus of compression. It should be noted that under static loads water can flow out and

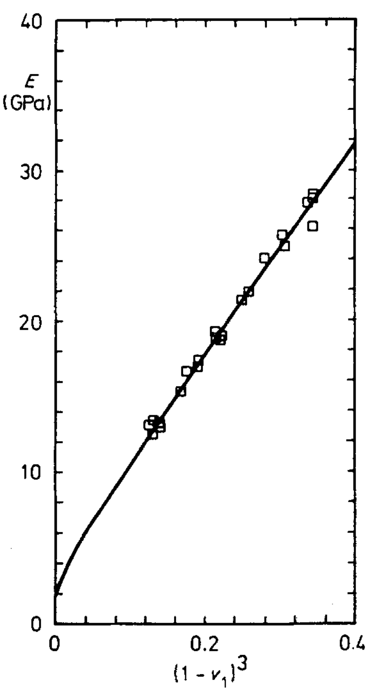

Fig. 5 Elastic modulus of the system as a function of $v_2^3 = (1-v_1)^3$ for water-saturated hardened cement paste specimen at 20°C. v_1 is the water content and the porosity.

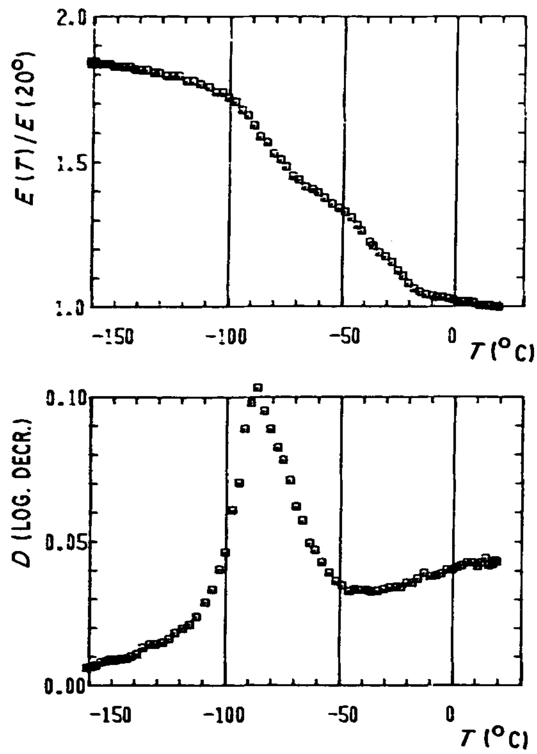

Fig. 6 Related elastic modulus and damping coefficient of water-saturated hardened cement paste as a function of temperature; porosity v_p = 40%, E_s (20°C) = 19.3 GPa.

$E_1 \rightarrow 0$. Equation 7b is then approximated by Equation 7a. At low temperatures ice is formed. However, freezing is complete only at very low temperatures [26,27].

In Fig. 6 the elastic modulus and the damping coefficient are plotted as a function of temperature. The elastic modulus increases until −160°C due to ice formation. However, in measurements by differential scanning calorimetry (DSC) first-order phase transitions could only be observed down to −50°C [21]. The remarkable increase below −50°C is therefore due to freezing of the last unfrozen thin water film on the internal surface of the cement paste. It is concluded that at −60°C all pore water apart from the water in the last layer is frozen and at −160°C there is no unfrozen water.

The damping maximum between −60 and −160°C is produced by an increased internal friction due to the solidification of the last unfrozen water layer between the ice and the solid matrix. The presence of an unfrozen liquid film can be explained theoretically [7,8].

At −160°C water-saturated hardened cement paste is again a two-component system consisting of the ice (E_1, v_1) and the solid (E_2, $1-v_1$). The results are plotted in Fig. 7 together with the room-temperature curves. The E_1 value for ice at −160°C is found to be 11.8 GPa. Dantl [26] measured the elastic constants of ice dynamically down to very low temperatures. Using his data the elastic modulus of ice is 10.95 GPa. This value deviates by 8% from our result, which is acceptable if one keeps in mind that in the present case the pore-ice is coupled to the matrix. The increase of the elastic modulus of the solid matrix from 71.8 GPa at +20°C to 85 GPa at −160°C is also reasonable

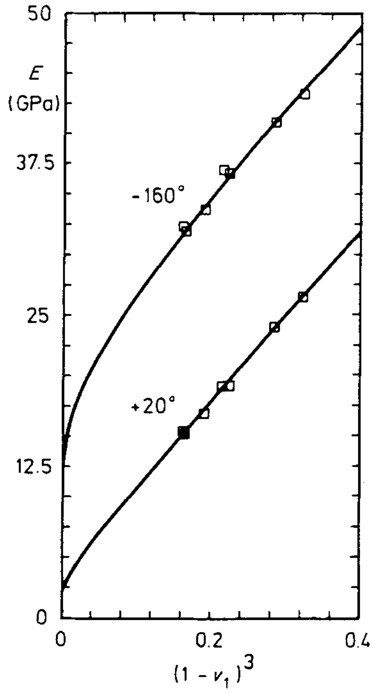

Fig. 7 Elastic modulus of the system as a function of $(1 - \nu_1)^3$ of water-saturated specimen (ν_1 is the porosity) at +20 and −160°C. Data for the fitted theoretical curves: at +20°C E_1 (water) = 1.98 GPa, E_2 (matrix) = 71.8 GPa; at −160°C E_1 (ice) = 11.80 GPa, E_2 (matrix) = 85.00 GPa.

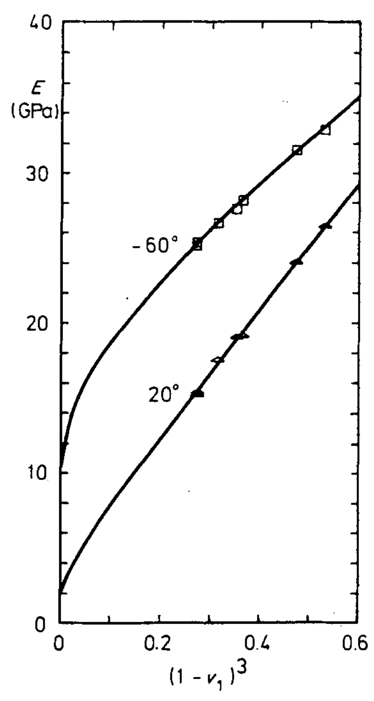

Fig. 8 Elastic modulus of the system depending on freezable water content ν_1, which is the total water content minus the unfrozen surface layers. Data for the fitted theoretical curves: at +20°C E_1 (water) = 1.95 GPa, E_2 (matrix + adsorbed films) = 45.30 GPa; at −60°C E_1 (ice) = 10.00 GPa, E_2 (matrix + adsorbed films) = 45.3 GPa.

and in agreement with the low-temperature behaviour of other materials. At −60°C there is an unfrozen layer near the surface. From dielectric measurements [20] on similar specimens it is known that as much as 6.8% of the water is unfrozen, in agreement with sorption [27] and DSC [1, 10] results. If this water is attributed to the solid matrix and ν_1 is reduced accordingly Fig. 8 is found. At +20°C the value for water is 1.95 GPa, which again corresponds to the modulus of compression. However, the modulus of the matrix with the adsorbed film reduces to 45.3 GPa. At −60°C the modulus of the matrix is unchanged at 45.3 GPa. The modulus of the ice is found to be 10.0 GPa, in excellent agreement with the findings of Dantl [26] for ice with 10.2 GPa.

6. CONCLUSIONS

1. The proposed statistical model describes the dynamic elastic modulus of a composite material like hardened cement paste at room temperature, −60°C and −160°C very well.
2. The values determined for the moduli of solid matrix, ice and water are in good agreement with published data.
3. The measurement and the evaluation provide new insights into the behaviour of the microstructure of hardened cement paste, especially at low temperatures.
4. From the data it can be concluded that at −60°C there is an unfrozen water film on the internal solid surface which is solid at −160°C.

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