STUDY OF THE STRUCTURIZATION KINETICS IN HARDENING DISPERSION SYSTEMS BY THE INTERNAL FRICTION METHOD

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An experimental study was made concerning changes in the internal friction in a disperse material during hardening and the effect of the initial solid-to-liquid contents ratio on the structurization process.

According to our latest concepts [1-4], changes in the rheological properties of a dispersion system are the main indicator of a stronger interaction between particles of the dispersed phase and of the spatial structurization during hardening. The rheological properties of a material are determined by the nature of the relaxation processes which develop in a structure as a result of a departure from thermodynamic equilibrium during deformation.

The magnitude of internal friction, which can be calculated from measurements of the rheological parameters of a material [5, 6], does most generally characterize the total effect of the various relaxation processes.

Restoring a thermodynamic equilibrium within the boundaries of individual microstructure elements in a deformed specimen requires much less time than the transition of an entire system to an equilibrium state. For a study of the microstructurization kinetics in a disperse material during hardening, therefore, one must measure the rheological parameters during short loading periods which correspond to the high-frequency range of the relaxation spectrum.

At present, the response of a dispersion system to short-time loads is studied by ultrasonic pulse [7] or other dynamic methods [8, 9]. Indirect dynamic methods yield only a qualitative description of the structurization process, however, inasmuch as the parameters which characterize the propagation of an acoustic wave through a nonhomogeneous disperse medium are determined not only by the rheological properties of the structure but also foremost by the effects of scatter at the inhomogeneities [10].

For a more thorough study of the rheological properties of a structure during its formation, it is necessary to follow both the deformation process and the stress field in a specimen directly while a short-time quasistatic load is applied.

In this article we show the results of such studies which have been made on aqueous cement dispersions according to the procedure outlined in [11].

The gist of the test procedure was as follows. A longitudinal stress pulse was induced by a cylindrical specimen of the test material 1 (Fig. 1), which had been shaped in a special vessel, by striking one end of it. A change in the stress field of the material during relaxation within a time equal to the pulse duration was determined by the displacement mode of a ballistic pendulum 2 touching the cylindrical specimen at the other end. The strain–time relation was established on the basis of the velocity of the free specimen end when unconstrained by the pendulum [12]. Owing to the low strength of the material during the initial stages of the hardening process and, therefore, also to the necessity of measuring displacement pulses of small amplitudes, we used for this a laser with an external adjustable mirror [13]. In order to record the motion of the pendulum and of the specimen, we had mounted on them miniature mirrors 3

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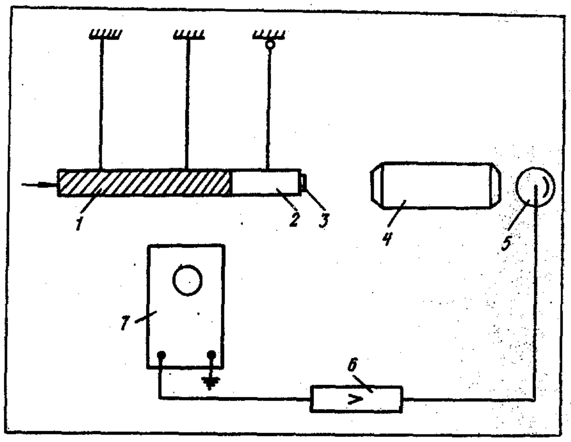

Fig. 1. Schematic diagram of the measuring apparatus: 1) specimen; 2) ballistic pendulum; 3) mirror; 4) laser; 5) photoreceiver; 6) amplifier; 7) oscillograph with memory circuit.

adjustable by means of a mechanism relative to the optical axis of the laser 4. A displacement of such a mirror caused modulation of the laser beam at a frequency

$$f = \frac{2vs}{l}.$$

The modulated beam was picked up by a photoreceiver 5 and a signal from here, after amplification, was transmitted to the input of an oscillograph 7 with a memory circuit. Using a helium–neon laser (wavelength l = 6328 Å) ensured a resolution of 0.3 μ in our measurements.

When an acoustic pulse travels through a disperse medium, one notes a change in the pulse form and in the spectral makeup, owing to a strong attenuation of the high-frequency harmonics. It thus becomes possible to establish nearly quasistatic loading conditions at the input end of the specimen, with appropriate specimen dimensions and pulse amplitude.

The strain amplitude in our specimen did not exceed the linearity limits of the stress–strain relation, which had been determined by prior measurements. We studied the effect of the initial liquid-to-solid contents ratio in the suspension on the structurization kinetics in the disperse material. For this study we used grade 400 Portland cement of the following mineral composition: 58.8% C_3S, 13.0% C_2S, 14.20% C_4AF, and 5.84% C_3A. A study of changes in the rheological properties of the hardening cement paste has revealed the following trends. During the first 35-120 min after mixing (depending on the water-to-cement ratio and on the conditions of hardening), the stresses generated in a specimen due to strains of a magnitude $\varepsilon \sim 10^{-5}$ relax completely within a very short time $\tau \sim (3\text{-}4) \cdot 10^{-5}$ sec. Here the sensitivity of our measuring instruments was not adequate enough to yield the actual shape of the relaxation curves. During the next stage of hardening the rheological behavior of the material changes: under a constant strain the stresses relax to a certain limiting level σ_r, while the shape of the relaxation curves approaches an exponential one. In this way, the rheological behavior of the test material within loading times and load amplitudes as in our experiment ($\varepsilon \sim 10^{-5}$, $t \sim 10^{-4}$ sec) corresponds to the rheological behavior of a model standard-linear body, while the hardening of the material may be regarded as a continuous change in the model parameters.

On the basis of test data relating to well-known formulas for a standard-linear body [5], we have calculated the modulus defect Δ_E and the mechanical loss tangent $\tan\varphi$ at the frequency ν = 20 kHz. The results for a hardening paste with a 0.28 water-to-cement ratio are shown in Fig. 2a.

According to the diagram, the initial stage of structurization is characterized by a decrease in internal friction within the system. The modulus defect also diminishes fast. The regularity of the process becomes interrupted by a short interval of increasing Δ_E and $\tan\varphi$, after which both again decrease at a generally slower rate.

These observed trends in the mechanical properties of the system indicate that, while the material hardens, the relaxation processes which occur in a structure under load abate. As a result, the system response to momentary loads becomes predominantly elastic. Inasmuch as the development of elastic stresses is connected with the formation of a polycrystalline structure, the phenomenon of a temporarily increasing modulus defect and mechanical loss tangent should be regarded as a result of partial breakdown due to internal stresses.

A complete stress relaxation in a deformed specimen, which is observed during the initial stages of the hardening process, indicates that there is no single structural skeleton in the system which would ensure elasticity levels measurable by our method.

It is reasonable to characterize the structurization kinetics by the time Θ_1 (Fig. 2a) from the start of mixing to the instant T_1 when stress σ_r rises above zero, the time Θ_2 from instant T_1 to instant T_2 when $\tan\varphi$ and Δ_E both become maximum, and time Θ_3 during which Δ_E changes from $\Delta_{E\,max}$ to $\Delta_{E\,max}/10$. The amplitude of the breakdown effect may be characterized by the peak height on the $\tan\varphi$ curve. It may

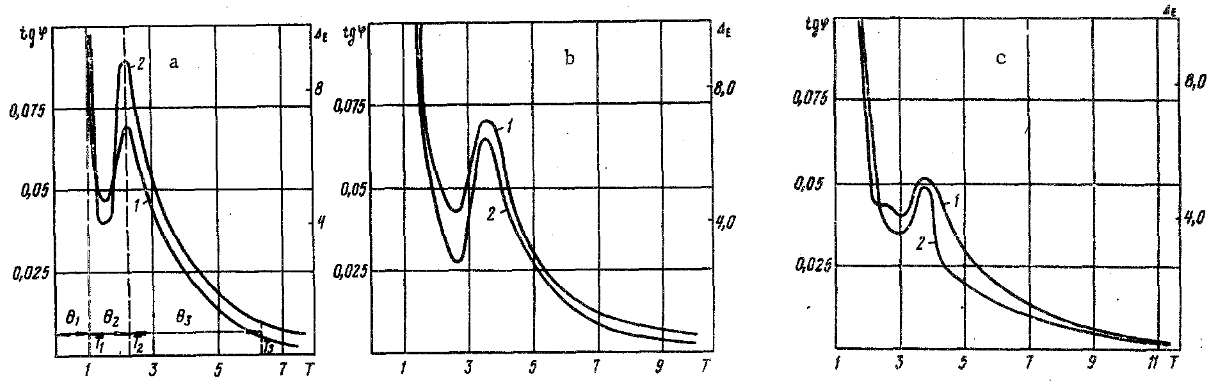

Fig. 2. Variation in $\tan\varphi$ (1) and in ΔE (2) during the hardening of cement paste with a water-to-cement ratio 0.28 (a), 0.35 (b), and 0.5 (c).

be assumed that the time Θ_1 corresponds to the induction period of the structurization process, i.e., includes the induction period of hydration plus the time necessary for forming the primary crystalline structure. Further evolution of the crystalline structure is accompanied by a partial breakdown, and Θ_2 represents the time interval from the formation of the primary skeleton to its farthest breakdown. Time Θ_3 is approximately the period, after breakdown, during which the internal friction and the modulus defect change at a slower rate and their levels stabilize.

In order to study the effect of the initial concentration of the solid phase in a dispersion system on the structurization kinetics, we prepared specimens with different water-to-cement ratios: 0.35 and 0.50. The results are shown in Fig. 2b, c.

A compilation of the data shows that, as the concentration of the solid phase in the original suspension decreases, the structurization process slows down: time Θ_3, i.e., the induction period becomes longer. The observed changes in the structurization kinetics are related to the effect which the concentration of the original solid phase has on the manner of moisture distribution in the system and on the conditions of hydrate formation.

During the initial stages of hydration there forms a gel-like porous shell around still unhydrated clinker grains [14]. At the same time, although the density of hydrate particles at the grain surfaces does not depend on the initial water-to-cement ratio [15], the volume density and the porosity of the gel structure is apparently related to this ratio. In a highly moisture-saturated medium there forms a friable gel mass which requires a longer time for hydration and for developing a spatial structure, so that time Θ_3 becomes longer. Reducing the density of the hardening structure should result in a reduction of its porosity, since the crystallization contacts per unit overall volume become fewer. On the other hand, however, a low supersaturation level prevents a fast formation of a spatial and a superficial phase, thus increasing the fraction of the contactive phase in the total volume of new structures [16]. An increase in the fraction of the contactive phase facilitates the formation of a stronger structure, since in this case more new structures participate in building up the strength characteristics of the system. It must be assumed that the effect of this last factor was predominant in our case, inasmuch as the breakdown phenomena were appreciably scaled down at a higher water-to-cement ratio. A substantial role is played also by the decrease in internal stresses within the crystalline structure where the supersaturation level becomes reduced.

NOTATION

f	is the modulation frequency of the laser beam;
l	is the radiation wavelength;
v	is the mirror velocity;
s	is a geometrical parameter of the system;
$\tan\varphi$	is the mechanical loss tangent;
Δ_E	is the modulus defect;
ε	is the strain;
t	is the load duration;
Θ_1, Θ_2, and Θ_3	are the periods of the respective structurization stages;
τ	is the relaxation period;
T	is the duration of the hardening process, h;
σ_r	is the relaxation stress.

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