RELAXATION–POLARIZATION CHARACTERISTICS OF A CEMENT–WATER SYSTEM IN A MAGNETIC FIELD

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The kinetics of structure formation and the water-retention ability of a cement paste are investigated by measuring its relaxation–polarization characteristics.

Moist bodies containing small pores are relaxation–polarization systems as regards the effect of a magnetic field [1].

In studying the relaxation–polarization properties of a cement–water system it is necessary to take account of the fact that during the solidification process the physical state of the system from an elastic–plastic–viscous cement paste to a solid crystalline body. Accordingly we divide the whole hardening process into two periods [2]. The first, or structure-formation period, begins immediately after the mixing of the cement paste and proceeds with a predominance of coagulation processes. It is characterized by the gradual transformation of all water into the bound state. The second, or structure-strengthening period, proceeds with a predominance of crystallization processes in which structure strengthening occurs as a result of an increase in the number of particles of colloidal dimensions of the solid phase per unit volume.

To study the relaxation characteristics in the polarization of the system in a magnetic field it was necessary to determine the kinetics of the change and the absolute magnitude of the specific magnetic susceptibility during these two characteristic stages of hardening of the cement–water system.

The magnetic susceptibility was measured on a ballistic arrangement for determining the susceptibility of weakly magnetic materials [4] using a magnetic field of 320 Oe in the magnetizing solenoid.

The experiments were performed with cements of various chemical–mineralogical composition (Table 1) and industrial water of fixed composition and temperature. The cement–water system was

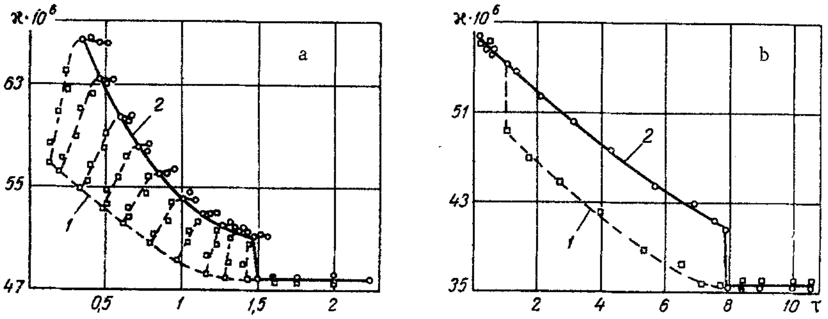

Fig. 1. Specific magnetic susceptibility of cement paste as a function of the time of hardening (h) for: a) W/C = 1.0 K_{NC}; b) W/C = 1.8 K_{NC}. 1) Initial values of susceptibility; 2) values of $\varkappa$ after relaxation; black points mark the beginning of setting according to Vicat.

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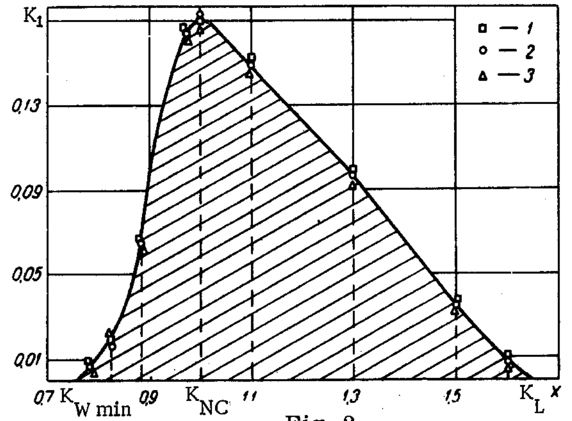

Fig. 2

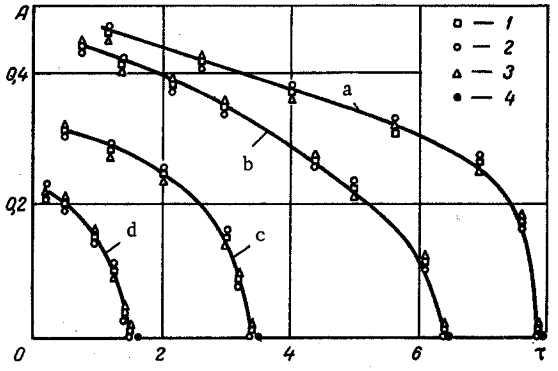

Fig. 3

Fig. 2. Magnetic lag K_1, of a cement paste as a function of X. 1) Portland cement from Krichevsk plant; 2) Portland cement from Volkovisk plant; 3) sulfate-resistant cement from Sebryakovsk plant.

Fig. 3. Coefficient A as a function of the solidification time (τ, h) of a cement paste. a) W/C = 1.8 K_{NC}; b) 1.65 K_{NC}; c) 1.3 K_{NC}; d) 1.0 K_{NC}. 1) Portland cement from Krichevsk plant; 2) Portland cement from Volkovisk plant; 3) sulfate-resistant cement from Sebryakovsk plant; 4) beginning of setting according to Vicat.

studied for values of X ($X = (W/C)/(K_{NC})$ from 0.7 to 2.0 [3]. The specimens were made and compacted in accord with GOST 310-60.

The study of the magnetic susceptibility of the cement–water system required making completely identical specimens and performing a large number of experiments. The experiments were repeated many times and the points plotted on the graphs are the averages of a number of experiments under identical conditions.

Graphs were plotted of the change in specific magnetic susceptibility during the hardening process. Figure 1 shows that during the first stage of the hardness of a cement paste a certain time is required to establish the final values of the magnetic susceptibility $\varkappa$ in the polarization in a magnetic field. This variation of $\varkappa$ can be explained by the thermodynamic theory of magnetic lag.

When a material is polarized in a magnetic field its magnetic state is not established instantaneously but requires a certain time which is sometimes very appreciable. The delay in establishing the magnetic state, called the magnetic lag, depends on the structural features of the system. Data in the literature indicates that the phenomenon of magnetic lag has been investigated mainly for magnetically soft ferromagnetics in which the new magnetic state is established in seconds or fractions of a second.

In our experiments on magnetic lag (magnetic viscosity) the time to establish a new magnetic state is measured in minutes, and the phenomenon is called superviscosity. Superviscosity is characterized by slow relaxation processes and is commonly observed in such complex multiphase systems as cement paste.

To rate the magnitude of the magnetic lag we introduce the coefficient of magnetic lag K_1:

$$K_1 = \frac{\Delta\varkappa}{\varkappa'},$$

where $\varkappa'$ is the steady reading of the specific magnetic susceptibility and $\Delta\varkappa$ is the increase in susceptibility with time.

Figure 2 shows $\Delta\varkappa/\varkappa'$ as a function of the relative water content of the system X; this enables one to judge the magnitude of the magnetic lag of the cement paste.

The data show that the phenomenon of magnetic lag appears during the formation of coagulation structure of the cement paste. The maximum of the magnetic lag which occurs for a cement paste of normal consistency (W/C = 1.0 K_{NC}), coincides with the maximum of the specific magnetic susceptibility. For W/C = 0.7 K_{NC} and W/C = 1.65 K_{NC} there is no magnetic lag.

TABLE 1. Chemical Composition of Cements

Cement	Chemical composition							K_{NC}
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	L.O.I.	
Portland cement from Volkovisk plant	25,75	5,29	4,8	58,86	2,37	2,09	2,25	0,27
Portland cement from Krichevsk plant	25,50	4,28	5,7	61,15	0,84	1,99	1,64	0,276
Sulfate-resistant cement from Sebryakovsk plant	26,79	4,56	4,99	57,22	0,82	1,52	2,52	0,25

The study of the phenomenon of magnetic lag makes it possible to determine the water-retaining ability of a cement paste. This is one of its most important characteristics, determining the formation and subsequent development of the coagulation structure of the cement paste.

From Fig. 2 it is seen that for $K_1 = 0$, the limiting water–cement ratio $K_L \approx 1.65\ K_{NC}$ which characterizes the water-retaining ability of the cement paste, agrees with the data of I. N. Akhverdov [3]. The lower value of water-retaining ability $0.76\ K_{NC}$ can be called the minimum capacity of the cement $K_{W\ min}$. For $W/C = K_{W\ min}$ solvation sheaths are formed around the cement grains, but these sheaths are so thin and elastic that there is a repulsion between individual solvated particles. When water is added the thickness of the water films is increased, and at $W/C = K_{MW} = 0.876\ K_{NC}$ the prerequisites for the formation of a strong coagulation structure are established. For $W/C < K_{W\ min}$ the water in the system is insufficient for the formation of solvation sheaths. In this case there is no magnetic lag and the specific magnetic susceptibility readings do not change with time.

It should be noted that during polarization in a magnetic field individual domains of the system are instantaneously aligned with the field. For a cement paste with $K_{W\ min} \geq W/C \geq K_L$ these are primarily free (unbounded) water and cement grains which do not have water sheaths. In this case the polarization occurs instantaneously and is equal to the magnetization $\varkappa H$. The magnetic lag is largest for cement paste of normal consistency. This can be explained by the fact that for $W/C = 1.0\ K_{NC}$ the system is most tightly packed and a long time is required to overcome the forces of interaction between solvated particles and to establish a new magnetic state in the polarization of the system in a magnetic field. When the water content of the system is increased the coefficient of magnetic lag is decreased since free water appears in the system. The phenomenon of magnetic lag is most interesting for $W/C \geq K_L$ (Fig. 1b). In this case the solvated particles of cement paste are so far apart that they do not interact with one another. Since the cement grains remain separated and the suspending medium is viscous the suspension in unstable and sedimentation (water separation) occurs, characterized by the transport of matter with a relative velocity proportional to the acceleration due to gravity. Therefore there is no magnetic lag in cement pastes of such composition immediately after mixing, and the new magnetic state of the system is established instantaneously. Only after the sedimentation processes have ceased (45 min for a mixture with $W/C = 1.65\ K_{NC}$ and 65 min for $W/C = 1.8\ K_{NC}$, Fig. 1b) and a sediment has formed in which the particles can interact with one another, does the phenomenon of magnetic lag appear.

Magnetic lag is characterized by the time to establish a new magnetic state in the polarization of the system in a magnetic field, i.e., by the relaxation time τ_{rel}. Relaxation processes in a magnetic field are observed during the first period of solidification (the structure-formation period) of the cement paste. During the structure-strengthening stage the system is no longer a relaxation–polarization system and we have to deal with ordinary polarization (magnetization) in a field. Studies performed in the later stages of solidification (1-28 days) also showed no relaxation phenomena. During the structure-formation stage the relaxation time for cement pastes of various compositions varies from 0 to 30 min. Figure 1 shows that τ_{rel} decreases as the system hardens, and vanishes at the instant of transition from the structure-formation stage to the structure-strengthening stage. The angle between the axis of abscissas and the straight line connecting the initial and steady readings of the specific magnetic susceptibility increases and becomes 90°C at the instant of transition. After this there is a jump in the values of the magnetic susceptibility characterizing the instant of transition to the structure-strengthening stage.

We introduce a coefficient A characterizing the kinetics of the relaxation processes in the system and equal to the ratio of the relaxation time to the specific magnetic susceptibility ($\tau_{rel}/\varkappa$) at the same time instant.

The dependence of the coefficient $A = \tau_{rel}/\varkappa$ on the time of solidification of a cement paste is shown in Fig. 3 for W/C = (1.0-1.8) K_{NC}. It can be seen that A increases with W/C. For a fixed W/C the value of $\tau_{rel}/\varkappa$ decreases in the solidification process and vanishes at the instant of transition to the second stage of hardening.

Thus from the relaxation–polarization characteristics it is possible to study the kinetics of structure formation of the cement–water system and in particular to determine the duration of the structure-formation period and the instant of transition to the structure-strengthening stage. Knowledge of the latter is necessary in concrete technology to set a time limit on the use of various external actions such as forming, vibrating, centrifuging, compressing, impressing magnetic and electric fields etc. which can lower the strength characteristics if performed at inopportune times.

Our experiments corroborate the views of N. V. Mikhailov [2] on the question of dividing structure formation in a cement–water system into a formation stage and a strengthening stage.

During the first period the cement paste is a relaxation–polarization system exhibiting a magnetic lag. The smooth variation (Fig. 1) of the stabilized readings of the magnetic susceptibility during this period (curve 2) can apparently be explained by the gradual transformation of water into the bound state during the structure-formation stage. The binding of water ceases at the beginning of the second stage of hardening (the structure-strengthening stage) which is marked by the predominance of crystallization processes. In this period, in contrast with the first stage, the system does not exhibit relaxation properties during polarization in a magnetic field. At the instant that the system makes the transition between forms of binding moisture to the material, there is a jump in the steady values of the magnetic susceptibility (Fig. 1). The transition of the system from the structure-formation stage to the structure-strengthening stage is also fixed by the point of intersection of the curve for $\tau_{rel}/\varkappa = f(\tau)$ with the axis of abscissas (Fig. 3). The latter is in good agreement with the data of P. Selwood [5] which show that the magnetic susceptibility of diamagnetic and paramagnetic materials can vary rapidly during phase transitions in the system.

The results for all cements and compositions of cement paste studied show that the instant of transition of the system from the structure-formation stage to the structure-strengthening stage can be fixed with sufficient accuracy by the jump in the specific magnetic susceptibility. It should be noted that our determination of this instant does not agree with the beginning of setting as determined by the Vicat test.

NOTATION

τ	time;
τ_{rel}	relaxation time;
H	magnetic field intensity;
$\varkappa$	specific magnetic susceptibility;
K_{NC}	coefficient of normal consistency of a cement paste (W/C for a paste of standard mobility);
$X = (W/C)/K_{NC}$	relative water content of the system;
K_{MW}	maximum water content of the cement;
W/C	ratio of the weight of water to that of cement;
$K_{W\,min}$	minimum water content of the cement;
K_L	limiting water-retaining ability of a cement paste;
K_l	coefficient of magnetic lag.

LITERATURE CITED

1. A. V. Lykov, The Theory of Drying [in Russian], Énergiya, Moscow (1968).
2. N. V. Mikhailov, Fundamental Principles of a New Technology of Concrete and Ferroconcrete [in Russian], Gosstroiizdat, Moscow (1966).
3. I. N. Akhverdov, High-Strength Concrete [in Russian], Gosstroiizdat, Moscow (1961).
4. S. G. Romanovskii, G. S. Beinard, I. M. Lyashkevich, and V. G. Kladkevich, Vestsi AN BSSR, Ser. Fiz.-Énerg. Nauk, No. 1 (1969).
5. P. Selwood, Magnetochemistry, Interscience, New York (1943).