

Study of the hygrometric condition of cement stone and concrete

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Abstract. Cement systems are thermodynamically non-equilibrium, non-linear systems. Since it is far from equilibrium, it must be characterised by structure formation processes. Here it is necessary to consider the definition of 'structure formation'. This term is used in two meanings. The first is generally accepted in concrete science - the formation of mechanical bonds between the dispersed particles of a solidifying system as a result of ongoing chemical and physicochemical processes, culminating in the formation of a solid body - the cement stone and concrete. The second meaning of the term describes the emergence of dissipative structures, i.e. the destruction of the initial homogeneity of the system due to the emergence of streams, concentration gradients, chemical waves, etc.

By measuring the parameters of the resulting dissipative structures of different formation methods, it is possible to assess the degree of disequilibrium in the solidifying system and hence the directed methods of structure formation and structure optimisation.

It should also be noted that a non-linear, non-equilibrium hydration process leading to a concentration potential difference proceeds with equal probability in all directions. Applying a gradient of a high-intensity physical field to the disperse system, one should expect a synchronisation of the fluctuations of the concentration potential of local areas of the disperse system, which will result in a sharp increase of the physical and mechanical properties of the hydration products of the binder and of the concrete in general.

1 Introduction

As shown in [8], the magnitude of the gravitational field gradient is insufficient for significant synchronization of oscillations of the concentration potential in hydration processes. It can be achieved by imposing a high intensity physical field gradient on the

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disperse system [1-4].

The influence of the external vibratory peristaltic pressure on the dissipative structure is particularly great. Moreover, the latter has a significant influence on the vibration process parameters, increasing the amplitude and frequency of oscillations [9, 10], and also becomes their initiator, intensifying the values of technological parameters.

Concrete mixtures can be represented as a rather complex elastic-plastic-viscous body with time-varying properties. The nature of the change in properties can be assessed from the kinetics of the change in the hygrometric state of concretes of different moulding methods (Fig. 1).

Due to its rheological properties, concrete mix can be deformed by various process factors. The degree of deformation is highly variable and decreases with decreasing compaction intensity or normal hydrostatic pressure. The normal or combined pressures acting on the concrete mix are absorbed by the water, increasing the hydrostatic pressure in the system. The amount of hydrostatic pressure varies greatly depending on the way the concrete mix is formed. Obviously, the change in the amount of chemically bound water between 5 and 28 days shown in Figure 1 a can only be explained by the action of this factor. As a result of the high hydrostatic pressure on the solvated cement grains, binder hydration proceeds under different conditions. Experiments have shown that at $(V/C)_{ost} = 0.27$ the amount of chemically bound water increases by a factor of two compared to vibrated concrete [11]. The same data was confirmed by comparing the amount of physically bound water in samples of different formations. Some inaccuracy in the data is due to water loss from natural evaporation of the specimens. Hyperdense modified concrete is formed from a matrix of cement stone with drastically different properties [12]. Kinetics of change in the hygrometric state of concretes various shapes [5-8].

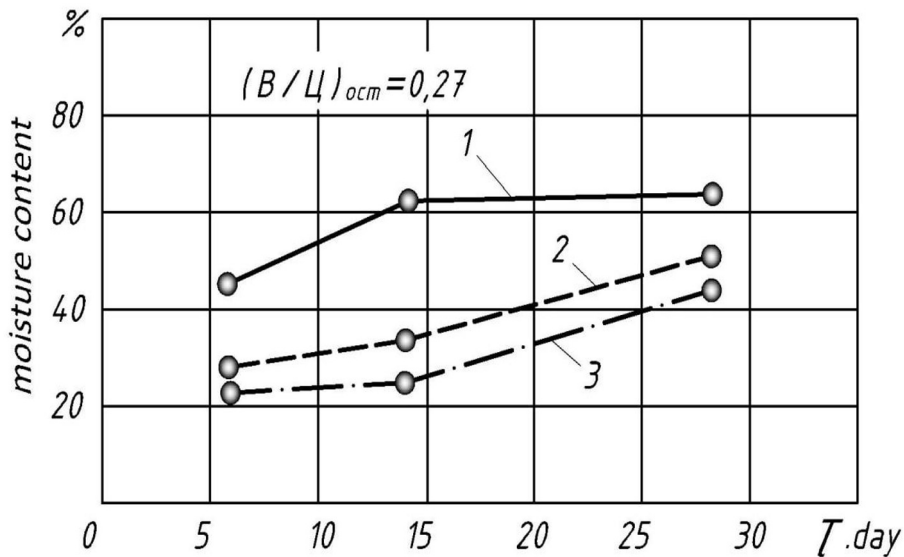


Fig. 1. (a) chemically bound water: 1 - hyper compacted modified concrete (GUMB), $(V/C)_{st} = 0.37$; 2 - Vacuum-assisted modified concrete (VCMV), $(V/C)_{st} = 0.50$; 3 - Vibrated compacted concrete (VC), $(V/C)_{st} = 0.27$.

Kinetics of the change in the hygrometric state of concretes made from different types of forms

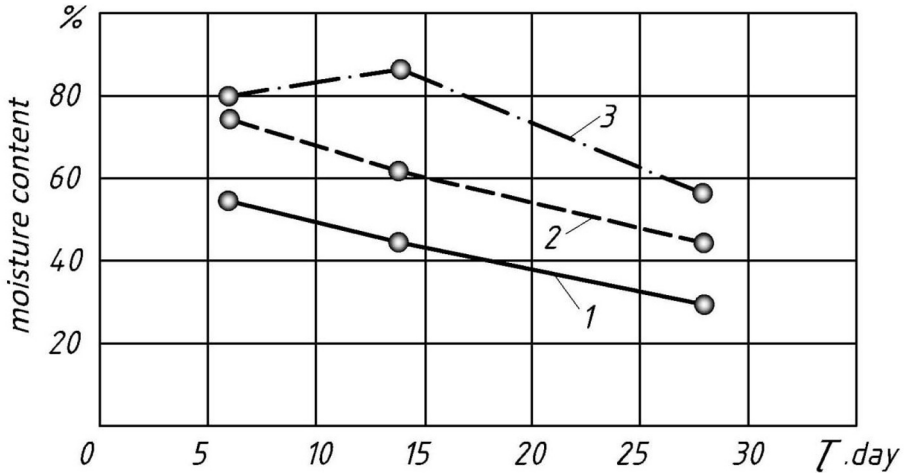


Fig. 1. (b) physically bound water: 1- GUMB, $(V/Z)_{st} = 0.37$; 2- VCMV, $(V/Z)_{st} = 0.50$; 3- VB, $(V/Z)_{st} = 0.27$

The maximum convergence of the cement grains and the intensification of the hydration regime correspond to the development of a special regime of structure formation. Such a regime is characterised by the formation of a water film of minimum thickness, maximum convergence of binder particles, fine and coarse aggregates. It is particularly important that the complex hypercompaction and modification of the hardening mixture creates special conditions for the formation of the contact zone of the cement stone and aggregate particles. High-intensity compaction creates the conditions for the formation of a pseudohard body whose deformation is manifested as elastic aftereffects. It creates the conditions for maximum packing of particles of different sizes and optimises the thickness of the contact layers with the lowest possible material porosity. High compaction of the concrete mix, combined with extreme squeezing of the mixing water, results in a uniform water-cement ratio in all layers of the concrete mix. This is due to the high and constant level of hydrostatic water pressure. This results in the formation of a contact layer between the cement paste and the aggregate under high compressive pressures, which is confirmed by the test data.

Microhardness of contact layers of concrete cubes from 20x20x20 to 50x50x50mm with ground surface was investigated. The microhardness value was characterised by the size of the diamond cone impression. A summary of the experimental data for the cementitious material is shown in Table 1.

The micro-hardness parameters of the cement stone given in the table show that the strength of the intergranular zone is considerably inferior to that of the contact zone. The difference in microhardness parameters is particularly noticeable for vibro-compacted concrete. *A slightly greater convergence of the indentation diameters is observed in vacuum-modified concrete [13, 14]. However, even in this case the diameters of imprints in the intergranular zone are 15... 17% larger than similar values in the contact zone of the aggregate. It has been shown for the first time that in hypercompact modified concrete, unlike conventional concrete, the strength of contact and intergranular zone of cement stone is practically the same if $(V/C)_{ost}$ is close to the value of LH of cement used [15].

The established experimental fact not only explains the increased tensile strength of concrete but also determines the value of the optimum $(V/C)_{ost}$. At its value close to the

LH value, the contact zones of the cement stone practically overlap, which determines the high tensile strength of such concretes.

Consequently, it can be concluded that in a hypercompacted concrete, a cementitious matrix is formed which is isotropic from the surface of the aggregate to the central intergranular layers. Such a matrix is characterised by high adhesion to the aggregate surface, which is approximately equal to its cohesive properties.

Table 1. Parameters of micro-hardness of cement stone in concretes different curing methods

№	Type of concrete	(V/D) to begin	(V/C) ost	Average diameter of diamond taper impression, μm	
				Contact area	Inter-Air area
1	Hyper-density modific GUMB concrete	0.35	0.27	27.2	27.0
		0.40	0.29	32.3	34.4
		0.45	0.32	36.5	39.6
2	Vacuumiro-modified VKMB Concrete	0.35	0.28	28.7	32.7
		0.40	0.30	33.6	40.9
		0.45	0.34	40.2	46.6
3	Vibroplot-WB" unfinished concrete	0.35	-	42.3	57.2
		0.40	-	44.8	58.7
		0.45	-	48.8	59.9

**Note.* The averaged diameter of the diamond cone impression (μm) is the result of least-squares data processing (results from 70 to 200 experiments).

The established rules are well supported by the petrographic analysis of the concrete structure observed in the transparent thin sections (Fig. 2).



Fig. 2. Microstructure of hyper-compacted modified concrete (excerpt)

2 Methods

The kinetics of binder-aggregate interaction in a hardening dispersion system can be estimated by microcalorimetric methods. The heat release of hardening cement paste at different hydrostatic pressures can be estimated. The heat release of hardening cement characterises the average rate and intensity of the hydration processes, determined by the amount of heat released per unit time.

Most modern calorimeters operate according to the principle described by E. Calvet and A. Prat [16-20]. The study of the differential switching scheme of microcalorimeters makes it possible to eliminate systematic and random errors due to small fluctuations in the thermostat temperature.

Measurements with the MID-200 were made continuously during the first day after preparation of the mixture. The differential and integral heat release characteristics of the solidifying mixture were recorded. The experiments were carried out in the laboratory of the Institute of Physical Chemistry of the Academy of Sciences of the Republic of Uzbekistan.

3 Results and discussion

A constant temperature of $E = 291$ K was maintained in the microcalorimeter during the measurements. The heat release kinetics of cement pastes with different compaction methods are shown in Fig. 3. The heat release of cement pastes ($V/C = 0.31 \dots 0.40$) differs significantly from each other.

The differential heat release of cement pastes modified by squeezing out excess water during hypercompaction is particularly good. In these, high heat release is observed for up to one day of setting. On the other hand, in the vibrated samples, the change in heat release rate essentially ceases after 7 days (Table 1).

After eight hours of hardening of the hyper-compacted concrete, the heat release rate intensifies, indicating recrystallisation processes as well as stabilisation of the cement stone structure. Practically, the general heat release pattern can be observed in Figure 3. The above experimental data indicate the profound effect of hydrodynamic pressure on the hydration processes of the binders.

A comparison of the micro-hardness data of the cement stone with the micro-calorimetric data shows that between aggregate and

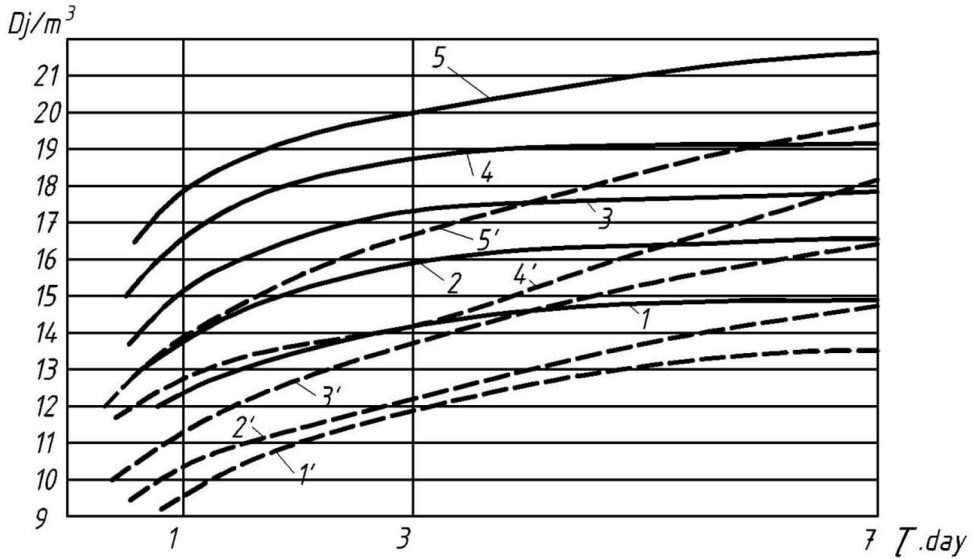


Fig. 3. Heat release kinetics of cement pastes at different sealing methods: 1,2,3,4,5 - hyper-compacted concrete with $(V/C)_{st} = 0.31; 0.33; 0.37; 0.40$; 1', 2', 3', 4', 5', - vibro-compacted concrete, same.

Table 2. Comparison of experimental data on heat release of cement pastes in real time

№	Parameters concrete composition		Heat release in J/m ³ per term (in days)		
	V/C	C, kg/m ³	1	3	7
a) Hyper-compacted concrete					
1	0.31	530	12.5	14.3	15.0
2	0.33	490	13.9	15.9	16.7
3	0.35	460	15.3	17.4	17.9
4	0.37	430	16.8	19.0	19.3
5	0.40	397	18.1	20.1	21.8
b) Vibrated concrete					
1	0.31	530	9.6	11.9	13.7
2	0.33	490	10.4	12.1	14.8
3	0.35	460	11.3	13.8	16.5
4	0.37	430	12.8	14.2	18.1
5	0.40	397	13.9	16.8	19.8

The cement matrix undergoes a physico-chemical interaction which results in the formation of a contact zone consisting of boundary layers in the cement stone and aggregate and the interface between them. The bond between the cement paste and the aggregate surface is tens of times greater than that between the aggregate and the vibrated concrete. This explains the significant increase in tensile strength of the concrete compared to conventional concrete. As shown above, when concrete prisms split, the interface between aggregate and cement stone disappears and becomes a diffuse intermediate layer.

The mechanics of the formation of a diffusion layer during the interaction of hydrating cement can be illustrated as follows. On the surface of the aggregate, especially freshly crushed aggregate, there are always unsubstituted valences of the boundary ions of the crystal lattice facing the adjacent phase. Due to the presence of free bonds, the solution ions

are in close contact with the surface of the solid under hydrostatic pressure and are oriented in a certain way on it. This is due to the presence of polymineral constituents, in particular carbonate particles (CaCO_3), which are isomorphic with cement clinker minerals. In this case, the surface of the carbonate aggregate is the best adsorbent for the hydrated cement, in which Ca^{++} ions appear within minutes of mixing. The quantity of these ions increases continuously during the setting process. The surface of the limestone binds the Ca^{++} from the mortar, promoting the formation of dense crystalline aggregates and accelerating the hydration process. Hydration of the most hydrophilic aluminate components of Portland cement clinker during crystallisation on the limestone surface initially involves CaCO_3 molecules in its lattice, forming calcium hydrocarboaluminate $3\text{CO-Al}_2\text{O}_3 - \text{CaCO}_3 - 11\text{H}_2\text{O}$ [17, 18]. Calcium hydrocarboaluminates bind almost twice as much water as hydroaluminates ($3\text{CaO-Al}_2\text{O}_3 - 6\text{H}_2\text{O}$). Silicate constituents of Portland cement clinker during hydration in the presence of carbonates also increase the amount of bound water [19]. In the hardening products of tri-calcium silicate in the presence of carbonates a reduction of up to 25% of free calcium hydroxide content is observed. In the contact layers of cement stone bordering the surface of the limestone aggregate an increased content of CO_2 , and in the surface layer of the aggregate the presence of silica is detected, indicating the possibility of exchange reactions between calcium hydrosilicates and carbonates [20]. Thus, the intermediate layer between the carbonate aggregate and the cement stone is a zone of physico-chemical interaction between cement hydration products and carbonates.

4 Conclusions

Analysis of the hygrometric state of the concrete and DTA confirmed that the amount of chemically bound water in the GUMB binder was 23-39% higher than in concrete subjected to vacuum or vibro-compaction.

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