AN EXAMINATION INTO THE METHODS OF HARDENING CONCRETE AS THESE RELATE TO THE POROUS STRUCTURE AND TO THE MANNER IN WHICH MOISTURE IS BOUND TO THE CEMENT STONE OF THE CONCRETE

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We examine the porous structure and the form and energy of binding moisture to the cement stone and liquid portion of concretes which are hardened by heat treatment in an electromagnetic field, in a vapor medium, and under conditions of normal humidity.

Cement concretes are currently the basic construction material and they represent typical capillary-porous bodies. The engineering characteristics of the concretes therefore depend in great measure on the interaction – in the broadest sense of that word – of the cement and the cement stone with water. The chemical interaction of the cement with water has been studied in detail, whereas the behavior of the adsorbed and capillary moisture within the cement stone, as well as the porous structure of the latter, have been the subject of considerably less investigation. At the same time, the micro- and macroporous structure of the cement stone and the state of the weakly bound moisture within the stone significantly affect both the technological properties of the concrete and the progress of the chemical reactions within the latter.

Moreover, it is primarily the capillary and adsorbed moisture that participates in the mass transfer with the ambient medium in operational concrete structures, i.e., from an energy standpoint, the moisture is weakly bound to the cement stone. The forms and energy of this moisture bond are governed primarily by the porous structure of the cement stone, and the formation of this structure can be controlled during the process of concrete hardening. The nature of the resulting porosity, its magnitude, its depth, and the rate of cement hydration are functions of the temperature–humidity conditions of the process involved in the consolidation of the cement and the hardening of the cement stone.

We know that various forms of heat–moisture treatment are employed to speed up the hardening of concrete.

The Institute of Heat and Mass Transfer of the Academy of Sciences of the Belorussian SSR has, in recent years, developed and introduced on an extensive scale an industrial method for the heat–moisture treatment of concrete in an electromagnetic field [1, 2]. Therefore, an integrated study of the properties of concrete being hardened under these conditions is of considerable interest.

TABLE 1. The Chemical and Mineralogical Composition of Portland Cement

Chemical composition, %									kN	Moduli		Theoretical mineralogical composition, %			
Number	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	CaO free	soluble deposit		silicate	alumina	C_3S	C_2S	C_3A	C_4AF
0,78	22,6	4,61	5,11	63,0	1,47	2,38	—	—	0,83	0,87	2,17	43	34	3	18

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TABLE 2. Compositions of the Investigated Concretes

Concrete form	Component flow rate, in kg/m³ of concrete					Mobility of concrete mixture, cm
	Portland cement	sand with a size modulus of 1.81	gravel ('keramzit' filler) fraction, mm		water	
			5—10	10—15 (20)		
Standard, heavy	525	605	360	720	180	2—4
Concrete with a porous clay filler	500	660	282	262	205	1—2

TABLE 3. Moisture Content at Critical Points on the Thermograms for the Drying of Cement-Stone Specimens

Specimen designation	Final drying temperature, °C	Moisture content as a percentage of the weight of the dry cement stone					
		total from 2nd point of thermogram	maximum hygroscopic, from 3rd point on thermogram	adsorbed moisture		most intensively bound moisture	
				multilayer from 4th point on thermogram	single layer, from 5th point on thermogram	from 6th point on thermogram	from 7th point on thermogram
N	105	9,7	7,5	5,6	4,0	1,9	0,8
E		8,6	6,7	4,1	3,1	2,4	1,5
S		7,3	5,7	4,0	2,7	—	—
N	120	12,0	9,8	7,5	5,45	4,35	3,65
E		10,7	7,9	6,35	4,85	2,8	2,35
S		7,9	5,65	4,8	3,75	—	—

The studies described in this paper were conducted along two lines: the cement stone was used to study the porous structure and the forms and energy of the moisture bond; specimens of concrete were used to study certain of the technological properties (resistance to corrosion, permeability, frost resistance).

The specimens of the cement stone and the concretes were made of Portland cement (570 kg/cm²) produced at the "Bolshevik" plant in Vol'sk (Tables 1 and 2).

The cement stone was produced by hardening a cement paste with a water-to-cement ratio of 0.326. Correspondingly, the liquid portion of the concretes exhibited the identical water/cement ratio (including the moisture which wets the surfaces of the coarse and fine fillers).

Specimens made of the cement paste and of concrete were subjected to heat and moisture treatment in electromagnetic and vaporizing chambers for periods of 4 + 4 + 3 + 3 h (holding time prior to heat treatment + elevation of temperature to 80°C + isothermal treatment at 80°C + reduction in temperature 40°C) with the relative humidity of the medium in the chambers given by φ = 85-90%. For purposes of comparison, a third batch of specimens was prepared at the same time and this batch was permitted to harden under conditions of normal humidity (T = 18 ± 2°C, φ = 85-90%). The specimens which were subjected to the heat and moisture treatment were kept under identical conditions prior to the test. Each of the cement-stone specimen batches was one month old.

The differential analysis of the water-absorption properties of the cement stone was carried out in accordance with the Kazanskii [3] method of drying thermograms.

The thermograms for all of the specimens were taken under absolutely identical conditions, with an air pressure of 150 mm Hg and an air temperature of 90°C in the thermal pressure chamber.

The specimens ranged in temperature from 60 to 90°C during the course of the recording. The final drying stage for the specimens was accomplished at 105 and 120°C. In the latter case, this final drying temperature ensured the more stable destruction of the calcium hydrosulfatoaluminate which facilitates comparison of the experimental results for each of the specimens.

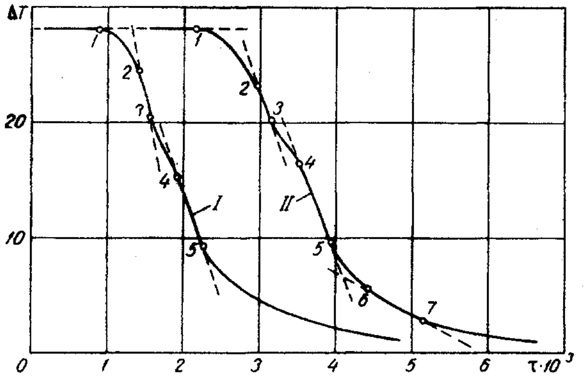

Fig. 1

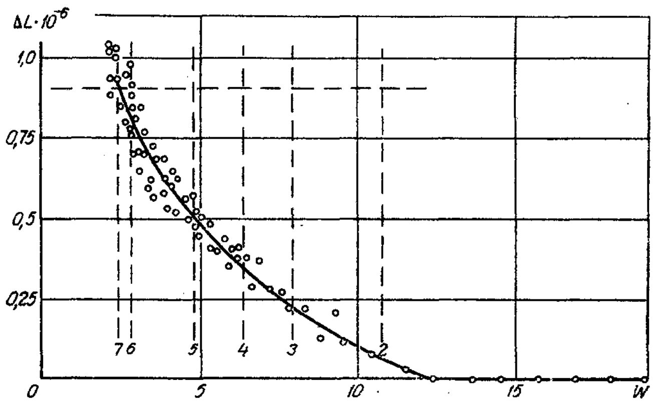

Fig. 2

Fig. 1. Thermograms from the drying of cement stones at a temperature of 120°C (ΔT is the temperature difference between sample and air, °C; τ is the time of experiment, sec): I) cement stone being steamed; II) cement stone under electromagnetic heat treatment (E) and normally humid solidification (N).

Fig. 2. Increment of specific heat of moisture evaporation from cement stone (L, J/kg) in comparison with free water at the same temperature versus their moisture content (W, %) (vertical dashed lines, maximum moisture contents).

The thermograms of the cement stones are shown in Fig. 1. The moisture contents at each critical point of the thermograms, which determine the differential water-retaining properties of the specimens being investigated, are shown in Table 3.

The specimens subjected to steaming yield a thermogram (curve I, Fig. 1) that is typical of brittle polycapillary-porous bodies (of the silica gel type) with five critical points.

Curve II shows the thermogram for the cement-stone specimens which are hardened in the process of electromagnetic heat treatment. The thermogram for the cement stone subjected to hardening under conditions of normal humidity is similar to that of the cement stone which is hardened in the process of electromagnetic heat treatment; they are therefore conditionally reflected in the single curve II.

Having analyzed Fig. 1 and Table 3, we should point out that the moisture contents at each of the thermogram critical points diminish with transition from the N (normal) specimens to the S (steaming) specimens. After electromagnetic heat treatment (E) the cement stone occupies an intermediate position with regard to moisture content.

Of significance on the thermogram is the isolation of an additional rectilinear segment (curve II) between points 6 and 7, which indicates the presence in E as well as in N specimens of the moisture (in weak chemical bond) removed at the indicated temperatures. It is significant that for specimens subjected to steaming no such segment is noted on the thermogram.

This fact can be explained by the higher degree of cement hydration in the process of electromagnetic heat treatment and in the hardening of the cement stone under conditions of normal humidity, as opposed to ordinary steaming.

The fact that this moisture is chemically bound and that it has entered the lattice of the crystal hydrates is borne out by the experimental data on the recording of the thermograms for the drying of specimens containing approximately 5-8% calcium hydrosulfatoaluminate of the high-hydrate form ($C_3A \cdot 3CaSO_4 \cdot 31H_2O$), and these thermograms also exhibit a rectilinear segment between points 6 and 7.

The intrinsic energy for the binding of the moisture to the cement stone was determined by the method of the specific heats of evaporation (energograms of drying) developed by Kazanskii [4]. The energograms were recorded at a constant specimen temperature of 80°C, which made it possible to compare the thermographic and energographic studies, since the specimen temperature varied within the same limits in the recording of the thermograms. The air temperature ranged from atmospheric to 40 mm Hg, and the final drying operation was carried out at 120°C.

TABLE 4. The Structural and Mechanical Properties of Concretes

Concrete form	Concrete hardening method	Resistance to frost after 200 freeze-thaw cycles: strength of concrete after 200 freeze-thaw cycles, kg/cm²	Resistance to frost: loss, %: of strength	Resistance to frost: loss, %: of weight	Impermeability to water: strength of concrete at instant of test, kg/cm²	At a pressure of 2.5 kg/cm²: penetration of water into the body of the concrete, mm	At a pressure of 2.5 kg/cm²: darkening of the concrete in lateral cross section (capillary suction), mm	At a pressure of 8.0 kg/cm²: penetration of water into the body of concrete, mm	At a pressure of 8.0 kg/cm²: darkening of the concrete in lateral cross section (capillary suction), mm	Corrosion resistance in chlorine medium: strength of concrete, kg/cm²: prior to test	Strength of concrete, kg/cm²: after 1 year	Corroded area in reinforcement after 1 year, %	Content of chloride ions which have penetrated into the concrete after one year, in mg/g of the cement stone: thickness of concrete layer, mm	total	free	chemically bound
Standard, heavy	N	522	14,0	0,12	402	13	25	5	32	434	415	2,1	5	22	13	9
													15	18	11	7
													25	13	7	6
													50	6	5	1
	E	622	8,4	1,46	475	8	17	9	30	497	482	1,6	5	18	16	2
													15	13	12	2
													25	12	10,5	1,5
													50	11	10	1
	S	590	23,4	0,7	413	18	33	21	38	396	365	4,0	5	22	17	5
													15	17	13	4
													25	16	12	4
													50	5	3	2
Concrete with 'keramzit' porous clay filler	N	376	13,0	0,1	401	10	23	12	27	213	251	6,5	Not found			
	E	363	15,4	0,15	453	3	9	7	15	253	285	3,4	Not found			
	S	303	20,3	0,4	397	14	25	17	36	209	234	6,8	Not found			

TABLE 5. Moisture Contents at the Critical Point of the Thermograms for the Drying of Cement-Solution Specimens

Specimen designation	Final drying temperature, °C	Moisture content as a percentage of the weight of the cement solution			
		total, from the 2nd point of the thermogram	maximum hydroscopic, from the 3rd point on the thermogram	layering	
				multilayer from the 4th point on the thermogram	single layer from the 5th point on the thermogram
HN	105	5,0	4,2	3,3	2,8
HE		5,2	4,3	3,4	2,7
HS		5,1	3,8	2,9	2,4
FN	105	5,4	4,5	3,8	3,1
FE		5,7	4,4	3,4	2,7
FS		5,5	4,5	3,9	3,2

Figure 2 shows the energy for the binding of the moisture to the cement stone which hardens during the course of the electromagnetic heat treatment as a function of the moisture content of the cement stone. The vertical dashed lines show the moisture content at the critical points on the thermograms for that specimen. For the cement-stone specimen hardening in the process of steaming and under conditions of normal humidity, the energograms are similar in form and differ only in the magnitude of the moisture binding energy for the various forms.

If we examine the energogram in Fig. 2 we see that the rise in the specific heat of evaporation begins near the second critical point of the thermogram. The curve is smooth in form, without break. It is very interesting that the increment in the specific heat of evaporation near the critical points 6 and 7 attains a magnitude equal to the intrinsic binding energy of the chemically bound moisture (crystal hydrate water) of the pure calcium hydrosulfatoaluminate ($0.88 \cdot 10^{-6}$ J/kg) which is shown in Fig. 2 by the horizontal dashed line.

On the basis of the resulting experimental data it is possible to evaluate the nature and magnitude of the porous cement-stone structure.

The thermogram segments between the critical points 3 and 4 corresponds to microcapillary moisture; the segment between points 4 and 5 corresponds to the moisture adsorbed at the surface of the solid cement-stone phase.

It is difficult to come to any conclusion with regard to the specific surface of the solid phase on the basis of the moisture content at point 5, since this moisture may include not only that adsorbed by the single layer, but also the hydrate water of the high-hydrate compounds.

As follows from Table 3, the heat treatment of the cement stone in an electromagnetic field improves the structure of the pore space through a substantial increase in the volume of microcapillaries ($r < 10^{-5}$ cm) in comparison to the steaming procedure, or even relative to the hardening process under conditions of normal humidity. Conversely, steaming in the manner adopted here impairs the structure of the pore space in the cement stone, increasing the microporosity; the pore volume is reduced in the microcapillaries by 50-80% relative to electromagnetic heat treatment.

It is not without interest that we note the following. We know that if the specific surface of the solid phase is increased in proportion to the increase in the volume of the microcapillary porosity, the dimensions of the crystal hydrates remain constant. However, if the specific surface of the solid phase remains constant or diminishes, which is the case for the cement stone after electromagnetic heat treatment, in this event we find an increase in the dimensions of the crystal hydrates.

These results from our study of the porous structure of cement stone have enabled us to predict the reduction in the permeability and the increase in the frost and corrosion resistance of concrete subjected to heat–moisture treatment in an electromagnetic field.

Sufficiently full confirmation of this was achieved through a series of engineering studies on the above-described concretes, hardened under various conditions.

The study into the frost resistance of concretes was carried out in accordance with the GOST 4800-59 in synthetic sea water with a salt concentration of 34 g/liter. The impermeability of the concretes to water was determined in accordance with GOST 4800-59 (at a pressure of 8.0 kg/cm^2) and on the basis of the ON-9-373-62 specification applicable to concretes for the shipbuilding industry (at a pressure of 2.5 kg/cm^2).

Our study into the corrosion resistance of conventional heavy concretes and its reinforcement (St. 3 steel, protective coating of 10 mm) was carried out outdoors at the Sivashskoe Corrosion Station of the NIIZhB, whose natural brine is distinguished by an exceptionally high concentration of chloride salts (up to 190 g/liter of Cl^-). The layer-by-layer content of chloride ions in the concrete was determined by the Fol'gart method (titration of the chloride ions with silver nitrate).

The results of this investigation are shown in Table 4, from which we see that the data from the investigation into the water impermeability and corrosion resistance of various concrete forms coincide with those of the thermographic studies and reveal a lower permeability for the E and N cement-stone specimens.

Similar data were also obtained in our study of the frost resistance of the concretes. In conclusion, the service life and protective properties of the concretes are improved relative to the reinforcement within the concretes.

The reduction in the filtration coefficients of highly corrosive media through concrete designated E is explained by the improvement in the structural properties of the cement stone as a result of the reduction in the cross sections of the capillaries and by the self-sealing of the cement stone as a result of the increase in the degree of cement hydration.

The reason for this increase in the degree of hydration in the process of electromagnetic heat treatment may possibly lie in the fact that greater amounts of water are drawn into the chemical bond than when the cement stone is hardened under different heat–moisture conditions. This probably serves also to explain the increase in the strength of such concretes with the passage of time [5].

The results of the thermographic investigations of cement stones confirm the results from the studies carried out on the liquid portion of the concrete. The structural porosity and differential water-retaining properties of the cement solution (cement + sand + water) removed from specimens of various kinds of concretes subjected to annual tests at the Sivashskoe Corrosion Station were also determined by the method of thermographic analysis (the final drying temperature was 105°C). The moisture contents for the first five critical thermogram points are shown in Table 5.

The data of Table 5 confirm the results obtained from our investigation into the permeability and resistance of the concretes, indicating the growth in the volume of the microcapillaries (given virtually equal integral porosity) in the cement solution of HE and FE concretes relative to HS, FS concretes, and even FN concrete.

Thus the results achieved by various methods show that the method of hardening the concrete depends in considerable measure on the porous structure of the cement stone, its differential water-absorption properties and, consequently, on a number of technological properties.

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