A STUDY OF CONCRETE HARDENING AT TEMPERATURES BELOW ZERO

V. M. Kazanskii, É. D. Breitman,
T. I. Rozenberg, and M. F. Kazanskii

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The porosity, strength, permeability, and frost-resistance kinetics in concrete hardening at a below-zero temperature have been studied by the methods of heat and mass transfer.

During concrete laying in the North or in winter elsewhere, the concrete hardens under conditions which are very different from normal conditions mainly because of the low temperature and also because of the soluble salts usually added to the sealant water (to avoid ice formation). For this reason, the kinetics

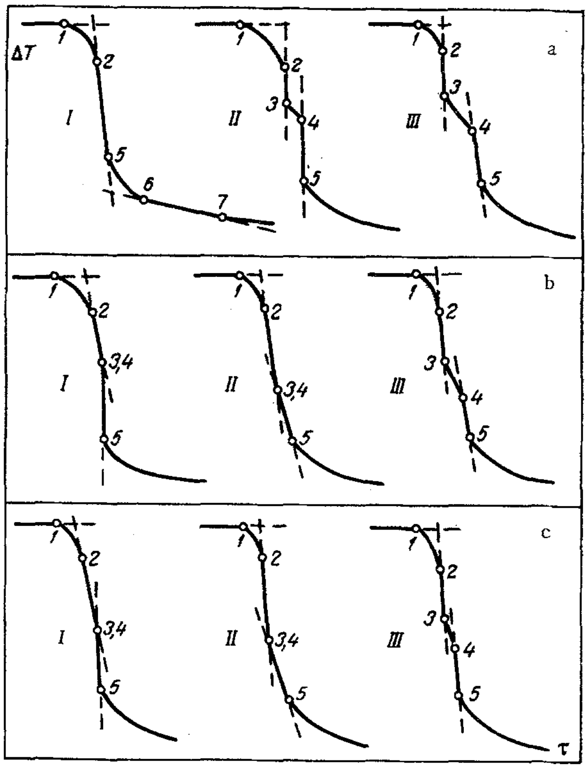

Fig. 1. General shape of drying-process thermograms for cement stone at various times of the hardening cycle. Specimen without additives (a): I) 3 h; II) 24-170 h; III) 7-28 days. Specimen with calcium nitrate and urea added (b): I) 5-13 h; II) 49-130 h; III) 7-28 days. Specimen with calcium nitrate added (c): I) 4-24 h; II) 29-70 h; III) 5-28 days. Difference between specimen temperature and air temperature ΔT (°C), time τ.

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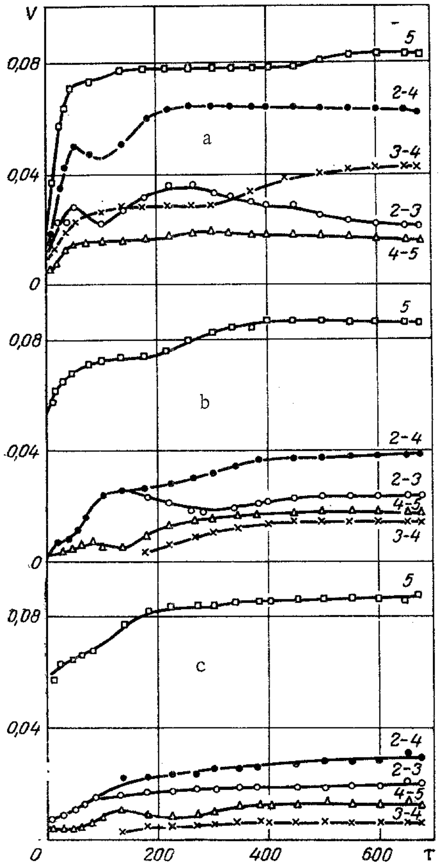

Fig. 2. Differential porosity ($V \cdot 10^3$ m^3/kg) as a function of hardening time (τ,h), for cement stone: (a) without additives; (b) with calcium nitrate and urea; (c) with calcium nitrate.

of concrete formation and the properties of already formed "cold" concrete are peculiar in some aspects; they can be properly studied only by a combination of several independent methods. Interesting results have been obtained, for instance, the application of mass and heat transfer methods [1] in conjunction with other conventional methods.

In this article the authors show the results of such a combined analysis applied to the kinetics of porosity development, to the various forms of water bonds, and to certain physicomechanical properties of "cold" concrete with an addition of calcium nitrate and urea prepared by the Special Materials Laboratory at the All-Union Scientific-Research Institute of Pipeline Construction [2].

The structure of a porous mass and the forms of water bonds involved in the hardening kinetics of cement stone with an addition of calcium nitrate and urea, as well as its specific surface, were examined by the method of drying-process thermograms [3, 4] supplemented by low-pressure and high-pressure mercury porosimetry during low-temperature nitrogen adsorption. Simultaneously with the structural analysis, measurements were also made of the compressive strength, the water and gas permeability, the frost resistance, and the hydration kinetics of concrete by the method of differential thermal analysis.

In order to study the structural porosity of cement stone in concrete by the method of drying-process thermograms, we prepared specimens of cement paste with sealant containing a 16% calcium nitrate and urea solution or a 10% calcium nitrate solution. Portland cement from the Novo Zdolbunovsk Works, grade M 500 with a 0.32 water content was used. The levels of the respective additive contents were optimal for hardening concrete at −10°C. For comparison, control specimens were prepared without additives and hardened under normal humidity conditions.

The general shape of the drying-process thermograms for the control specimens, for the specimens with calcium nitrate and urea, and for the specimens with calcium nitrate are shown in Fig. 1, where several ranges corresponding to evaporation (in accordance with the classification in [1]) can be identified: excess free water (to point 1), moisture from macropores and interstices between sand grains in the cement stone (from point 1 to point 2), meniscal moisture from interstices between sand grains and moisture from macropores with a radius $10^{-5} > r > 10^{-7}$ m (from point 2 to point 3), moisture from micropores with a radius $r < 10^{-7}$ m (from point 3 to point 4), moisture adsorbed by polymolecular layers from micropores with a radius $10^{-9} < r < 5 \cdot 10^{-9}$ m (from point 4 to point 5), moisture adsorbed by monomolecules in micropores with a radius $4 \cdot 10^{-10} < r < 10^{-9}$ m (from point 5 to point 6), and moisture retained in the cement stone by weak chemical forces (below point 6).

The drying-process thermogram for the control specimen, recorded over a period of 3 h after the beginning of the test (Fig. 1a) does not have points 3 and 4, which indicates an absence of micropores in the cement stone. On the thermogram recorded beginning at 24 h after sealant water had been added to the cement, one notes five critical points and a sufficiently distinct 3-4 segment, the latter corresponding to water evaporation from micropores. As the hardening period is extended, the shape of the thermogram changes further, namely the 3-4 segment becomes longer. The straight 6-7 segment, which corresponds to evaporation of water with a weak chemical bond, is noted only on the thermogram of the first 3 h.

The trend of the drying-process thermograms for both cement stone with calcium nitrate and urea (Fig. 1b) and cement stone with calcium nitrate alone (Fig. 1c) changes much slower. For instance, micropores (segment 3-4) appear only after 7 days in cement stone with calcium nitrate and urea, and only after 5 days in cement stone with calcium nitrate.

TABLE 1. Differences in Moisture Content (%) at the Critical Points on Thermograms

Kind of additive	Difference in moisture content (W, %) at the critical points on the thermograms			
	2-3, quantity of moisture in macro-pores	3-4, quantity of moisture in micro-pores	4-5, quantity of moisture due to poly-molecular adsorption	5, quantity of moisture due to mono-molecular adsorption and due to weak chemical bonds
Calcium nitrate	0,8	1,2	1,6	9,1
Calcium nitrate and urea	0,5	2,7	2,1	8,8

In order to evaluate the structural porosity of cement stone, it is most meaningful to establish the differences in moisture content at the critical points on a thermogram. The respective differences in moisture content, as functions of the hardening time, are shown in Fig. 2 for a control specimen as well as for specimens with calcium nitrate and urea or with calcium nitrate alone.

The kinetics of structural porosity in the reference specimen (Fig. 2a) is typical for cement stone. An increasing volume of macropores is noted after 250 h (maximum point on the 2-3 curve). During further hardening the volume of macropores decreases again while the volume of micropores (curve 3-4) increases, but the total volume of pores remains constant (curve 2-4). This trend is caused by the blockage of large pores by the products of hydration.

The rate of porosity buildup in the cement stone structure is lower in specimens with calcium nitrate and urea than in the reference specimen. According to Fig. 2b, the volume of macropores increases greatly (curve 2-3) within the first 100 h of hardening. During further hardening this increase becomes somewhat slower. Micropores in cement stone with calcium nitrate and urea begin to form 150 h after sealing has occurred. During the 150-370 h period one notes a sharp increase in the volume of micropores and its subsequent stabilization. During the same period one also notes a sharp increase in the amount of gel pores (curves 4-5 and 5). The kinetics of hydration and porosity buildup in cement stone with calcium nitrate plus urea and in cement stone with calcium nitrate alone (Fig. 2c) are analogous. In the latter case micropores appear approximately 100 h after sealing has occurred.

When the porous structure of cement stone without additives is compared with that of cement stone containing calcium nitrate and urea or calcium nitrate alone, on the basis of the hardening-process kinetics, one finds that at −10°C there are more micropores and gel pores in the cement stone when calcium nitrate and urea are added than when calcium nitrate alone is added. It is noteworthy that the method of drying-process thermograms is not suitable for determining the amount of pores with an effective radius $r > 10^{-5}$ m. For this reason, the apparent lower level of total porosity in cement stone with calcium nitrate than in cement stone with calcium nitrate and urea can be interpreted as a smaller amount of $r > 10^{-5}$ m pores in the latter case.

In the control specimens hardened under normal humidity conditions the total porosity after 28 days is higher than in the specimens containing additives and hardened at −10°C. The quantity of gel pores,

TABLE 2. Specific Surface of Cement Stone

Kind of additive	Specific surface (m^2/g) of cement stone, as determined by							
	method of drying-process thermograms			method of low-temperature nitrogen adsorption				
	aging time, days (24 h periods)			aging time, days (24 h periods)				
	7	28	28–28 (comb.)	7	28	28–28 (comb.)	90	180
Calcium nitrate	30,7	44,3	54,5	13,3	14,6	15,8	17,2	19,2
Urea	—	—	—	14,3	15,2	17,4	18,4	20,0
Calcium nitrate and urea	34,2	58,0	71,6	16,2	18,2	19,5	20,3	21,4
No additive	61,3	63,2	—	23,4	25,0	—	25,7	26,8

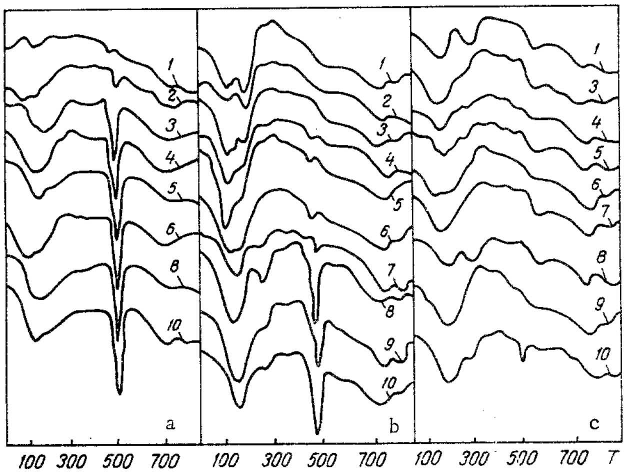

Fig. 3. Thermograms for cement stone without additives (a), with calcium nitrate and urea (b), with calcium nitrate (c), after aging for: 1) 3 h; 2) 7 h; 3) 24 h; 4) 48 h; 5) 78 h; 6) 6 days; 7) 10 days; 8) 16 days; 9) 22 days; 10) 28 days. Temperature T (°C).

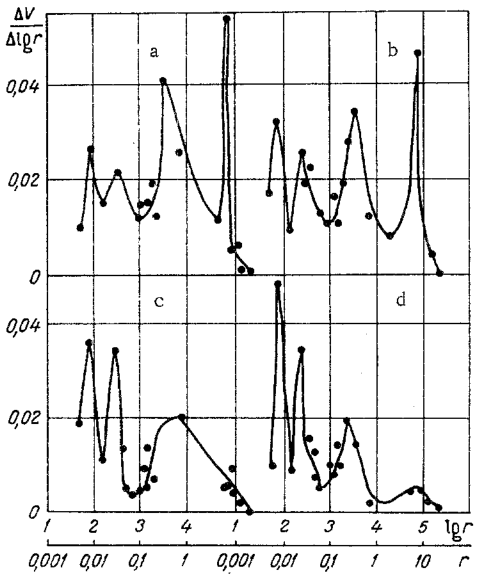

Fig. 4. Differential porosity $\Delta V/\Delta \ln r$ as a function of the pore radius r (μ), for cement stone in concrete with calcium nitrate and urea, aged for 7 days (a), 28 days (b), 90 days (c), 180 days (d).

however, is the same in the control specimens and in those with calcium nitrate and urea.

The quantity of moisture retained due to polymolecular adsorption and due to weak chemical bonds (curve 5 in Fig. 2) is the same in the specimens with calcium nitrate or with calcium nitrate and urea. The control specimen contains somewhat less moisture with a weak chemical bond, because it contains less of high-hydrate compounds.

Similar studies were made on cement stone specimens with calcium nitrate and urea or with calcium nitrate alone after a compounded hardening cycle: first 28 days at −10°C and next 28 days under normal humidity conditions. The differences in moisture content at the critical points on the thermograms, depending on the kind of additive, are shown in Table 1. The tabulated data indicate also that the largest amount of micropores and gel pores is formed in cement stone with calcium nitrate and urea. Moreover, the larger volume of micropores and gel pores here is offset by fewer macropores, as a result of their blockage by the products of hydration.

The physicochemical processes which occur while concrete is hardened at below-zero temperatures were studied by the method of differential thermal analysis on a Paulik derivatograph. The thermograms thus obtained are shown in Fig. 3. It is evident here that the hardening processes at below-zero temperatures are very different from conventional hardening. In the case of specimens with calcium nitrate and urea, for instance, the peak point on the thermogram, which corresponds to calcium hydroxide (at about 500°C), appears distinctly only on the 16th day, while during conventional hardening of the control specimen it appears already within the first few days.

An important indicator of the hydration rate during hardening is the specific surface of neoformations in cement stone. The specific surface of cement stone with the various additives and hardened at −10°C was determined by the method of drying-process thermograms and by low-temperature nitrogen adsorption.

The specific surface of cement stone, on the basis of drying-process thermograms, was calculated from the quantity of moisture in the second molecular layer [1] (curves 4-5 in Fig. 2). The results of

TABLE 3. Comparative Data on the Strength of Concrete with Calcium Nitrate and Urea or with Either Ingredient Alone (Water: cement ratio = 0.36)

Kind of additive	Hardening temperature	Ultimate compressive strength (10^5 N/m^2)/relative strength (% of rated strength in aging)		
		7 days (24 h	28 days (24 h	90 days (24 h
Calcium nitrate	—10 °C	65/11	190/32	333/56
Urea	—10 °C	108/18	404/68	508/85
Calcium nitrate and urea	—10 °C	186/31	497/83	590/99
No additive	Normal	398/67	595/100	625/102

these studies are shown in Table 2. It is evident here that the results obtained by both methods agree closely. The difference in the absolute values of specific surface is explained by the higher resolving power of the drying-process thermograms than of the nitrogen adsorption, because water is adsorbed not only at the outside but also at the inside surface of tobermorite-like formations. The specific surface, which characterizes the rate of hydration processes, is largest for cement stone with calcium nitrate and urea — of all the tested grades.

After longer periods of hardening, the structural porosity kinetics of cement stone in concrete with calcium nitrate and urea were studied by mercury porisotometry. The data on differential porosity in this cement stone aged for 180 days (Fig. 4) also indicate a rather high hydration rate, manifested by an increasing with time volume of micropores with an effective capillary radius smaller than 0.1 μ [5].

The presence of a microcapillary structure of cement stone in concrete with calcium nitrate and urea should ensure an appreciable increase in strength above that of concrete prepared with only the individual additive ingredients, calcium nitrate and urea respectively. The strength characteristics of concrete with calcium nitrate and urea or with either of them alone are shown in Table 3. The data here indicate that the best results, in terms of strength, at -10°C are obtained by adding the combination of calcium nitrate and urea to concrete [6]. Such a concrete attains 80% of the rated strength after aging for 28 days and 100% of the rated strength after aging for 90 days, the strength of a control specimen without additive and hardened under normal humidity conditions counting as the rated strength for reference.

The fine-capillary structure of cement stone in concrete with calcium nitrate and urea ensures a higher frost-resistance and a lower permeability. Tests have shown that concrete with calcium nitrate and urea can withstand 300 freezing–thawing cycles with a final strength 27% higher than that of control specimens after equivalent aging. Under a compound hardening cycle (first 28 days at -10°C, next 28 days under normal humidity conditions) and under pressures of 5-20 atm, the gas and the water permeability of concrete with calcium nitrate and urea is $(1\text{-}6) \cdot 10^{-14}$ and $(4\text{-}10) \cdot 10^{-17}$ $\text{m}^3 \cdot \text{sec/kg}$ respectively. Such concrete meets the V-8 specifications and is, accordingly, considered waterproof.

These results of structural and technological studies agree closely with each other, which points toward improved life characteristics of concrete with calcium nitrate and urea.

Thus, the application of heat and mass transfer methods, namely the drying-process thermograms, together with other independent methods of analysis makes it possible to study the kinetics of property changes in "cold" concrete during hardening.

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