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THE EFFECT OF $NaNO_3$ AND $Ca(HCOO)_2$ ADDITION ON THE HYDRATION OF VIBRATORY REGROUND CEMENT AT —6 °C AND +20 °C

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Vibratory regrinding of cement and that of cement with an antifreeze admixture accelerates the growth of early compressive strength of cement pastes kept at −6 °C. A major proportion of the mix water remains in the form of unfrozen solution in vibratory reground pastes. Both the hydraulic activity of the cement and the efficiency of the antifreeze admixture are increased. The X-ray phase composition, thermal analysis and habitus of the hydration products formed are indicative of a higher degree of hydration of cement in vibratory reground pastes cured at −6 °C and at +20 °C.

INTRODUCTION

Cement pastes free of antifreeze admixtures hydrate very slowly at subzero curing temperatures. A solid macrostructure in a paste free of admixture is not formed even after 28 days of hydration at —10 °C. Up to 91 % of the mix water will freeze in a concrete mix already at —3 °C [1].

An addition of 2 wt. % of $NaNO_3$ and 2 wt. % of $Ca(HCOO)_2$ to cement [2, 3, 4] will substantially speed up the conversion of clinker minerals to their hydration products, thus rendering the respective concrete applicable even at subzero temperatures.

The present study deals with the effect of vibratory regrinding of cement, and that of cement containing the admixture, on its hydration in paste at —6 °C and at +20 °C, as well as with the conversion of the clinker minerals to their hydration products, and the creation of macrostructure in hardened cement paste at various time intervals and different conditions of its curing.

EXPERIMENTAL

Materials

The cement pastes were prepared from class 400 Portland cement Rohožník having the standard strengths listed in Table I. The chemical composition and properties of the cement are given in Table II. In addition to this, chemically pure sodium nitrate and calcium formate were used as admixtures.

Experimental method

Cement paste with a water-cement ratio $v/c = 0.4$ free of antifreeze admixture, and with 4 wt. % of the admixture (2 wt. % of sodium nitrate +2 wt. % of calcium formate) were used in the tests.

Table I

Standard strengths of the PC 400 Rohožník cement

Days	Cement strength, MPa	
	tensile bending	compressive
1 day	3.0	13.1
3 days	5.0	26.0
7 days	6.8	36.9
28 days	7.2	52.4

Table II

Composition and properties of the cement employed

Component	Insoluble residue	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O	K_2O	Ignition loss
Content wt. %	1.84	19.28	6.91	3.42	60.98	1.69	2.53	0.31	0.90	1.77

Properties of the cement	Density kg m^{-3}	Specific area $m^2\ kg^{-1}$	Content of	
			C_3S	C_3A(Bogue)
	3140	336.2	43.2	12.0

Table III

Specific surface area of the cement, that of vibratory reground cement, and that of jointly reground cement and antifreeze admixture, particle size below 63 μm (sedimentation analysis in kerosene)

Property of cement paste	Original untreated cement PC 400 Rohožník		Vibratory reground cement 5 min.		Vibratory reground cement 10 min.	
	without admixture	with admixture	without admixture	with admixture	without admixture	with admixture
Specific surface area m^2/kg	336.2	331.0	443.6	456.2	503.5	516.5
Particle size below 63 μm, %	89.96	88.47	92.14	94.31	94.63	97.89

The effect of vibratory regrinding of cement and joint regrinding of cement containing 4 wt. % of the admixture was investigated on additional samples of cement pastes. The vibratory regrinding was effected in a vibratory ball mill with a useful capacity of 5 kg of dry mixture. The sedimentation analysis of the cement and its specific surface area after 5 minutes and after 10 minutes of vibratory grinding are given in Table III. The initial and final sets of the cement pastes prepared are listed in Table IV.

Table IV

Initial and final set of the cement, vibratory reground cement with an admixture of 4 wt. % of the antifreeze admixture, and that of cement reground jointly with the admixture

Type of cement	Initial set	Final set
Original, not reground	3 hr 15 min.	4 hr 25 min.
Original, with admixture	2 hr 35 min.	3 hr 30 min.
Cement reground for 5 min., with admixture	1 hr 45 min.	3 hr
Cement reground for 10 min., with admixture	2 hr 5 min.	3 hr 10 min.
Cement reground jointly with admixture, 5 min.	1 h 30 min.	2 hr 35 min.
Cement reground jointly with admixture, 10 min.	— 45 min.	2 hr 25 min.

The amount of water required for achieving the standard paste workability amounts to 81.5 ml, which corresponds to a water-cement ratio $v/c = 0.272$. The same water-cement ratio was employed in the preparation of all the other test specimens.

The cement pastes were formed into 120x20x20 mm prisms which were cured at the chosen temperatures of —6 °C and +20 °C in a medium with relative humidity exceeding 95 %. The strengths of the pastes were determined at the selected time intervals.

After stopping the hydration of other paste samples with a mixture of aceton and ether, X-ray diffraction patterns and thermal curves were made, porosity according to ČSN 72 2447 determined, and finally scanning electron micrographs taken of the fracture surfaces of the hardened cement pastes.

RESULTS AND DISCUSSION

The basic data on the hydration of pastes from the original cement and from that of vibratory reground PC 400 Rohožník cement, after curing for 24 hours at —6 °C and at +20 °C in a medium with relative humidity higher than 95 %, are given in Table V.

Table V

Strength and results of thermal analyses of PC 400 Rohožník cement pastes after hydration for 24 hours at −6 °C or at +20 °C in a medium of min. 95 % relative humidity

Vibratory regrinding for	Type of cement paste	Strength in MPa, 1-day curing, at −6 °C, tens. bend.	Strength in MPa, 1-day curing, at −6 °C, compr.	Strength in MPa, 1-day curing, at +20 °C, ten. ben.	Strength in MPa, 1-day curing, at +20 °C, compr.	Temperature, °C	Total loss %	H_2O bound in %	$Ca(OH)_2$ content of H_2O, %	$Ca(OH)_2$ content of CO_2, %	Total $Ca(OH)_2$ content %
—	standard, not reground, $v/c = 0.4$	0	0	3.0	10.2	−6 +20	7.30 9.92	2.96 4.10	4.70 7.28	4.23 5.36	8.93 12.64
—	standard, not reground + 4 % of admixture	0	0.8	1.1	6.0	−6 +20	11.17 11.63	4.10 3.82	7.52 9.64	6.95 7.25	14.47 16.86
5 min.	reground cement + 4 % of admixture	0	1.3	1.8	9.8	−6 +20	10.72 12.20	3.87 3.99	7.52 9.40	6.64 7.85	14.16 17.25
10 min.	reground cement + 4 % of admixture	0	1.9	2.5	11.0	−6 +20	12.08 13.68	4.22 3.99	8.93 11.52	7.55 9.06	16.48 20.58
5 min.	cement reground jointly with 4 % of admixture	0	1.7	2.3	9.7	−6 +20	10.60 11.74	3.76 4.10	7.05 7.99	6.80 7.70	13.85 15.69
10 min.	cement reground jointly with 4 % of admixture	0	2.1	2.0	10.2	−6 +20	11.17 12.54	3.87 3.87	7.99 9.87	7.10 8.31	15.09 18.18

Table VI

Strength of PC 400 Rohožník cement pastes after hydration for various periods time and in various curing conditions

Vibratory regrinding, minutes	Type of cement paste	Tensile bending strength, MPa				Compressive strength, MPa			
		Conditions of curing				Conditions of curing			
		+20 °C, r.h. 95 %			28 days at −6 °C + 365 days at +20 °C	+20 °C, r.h. 95 %			28 days at −6 °C + 365 days at +20°C
		time in days				time in days			
		1	7	28		1	7	28	
—	standard, not reground, $v/c = 0.4$	3.0	7.7	10.9	—	10.2	27.7	37.5	—
—	standard, not reground, +4 % of admixture	1.1	7.2	9.6	6.6	6.0	28.3	38.0	58.6
5 min.	reground cement +4 % of admixture	1.8	7.2	7.5	7.6	9.8	37.3	45.8	55.3
10 min.	reground cement +4 % of admixture	2.5	7.3	8.5	7.0	11.0	30.9	44.3	54.7
5 min.	cement reground jointly with 4 % of admixture	2.3	7.6	7.8	6.2	9.7	35.5	44.7	56.8
10 min.	cement reground jointly with 4 % of admixture	2.0	6.1	10.0	6.0	10.2	41.2	48.1	50.3

The comparative paste showed no strength after 24 hours of hydration at —6 °C. Pastes with 4 wt. % of the antifreeze admixture achieved useful compressive strengths. Vibratory regrinding of cement and that of cement with the admixture, has significantly contributed to the growth of early strengths of the pastes cured for 24 hours at —6 °C.

The increase in strengths of pastes of identical composition after hydration of 24 hours at +20 °C was slightly retarded compared to the strength of cement paste free of antifreeze admixture. This fact can be attributed to the effect of Na^+ ions on the hydration of cement pastes with an admixture of $NaNO_3$ and $Ca(HCOO)_2$ [5, 6].

The results of thermal analysis prove that in the presence of the antifreeze admixture the content of water bound in the hydration products tends to increase substantially as does the content of calcium hydroxide in cement pastes kept for 24 hours at —6 °C, compared to their content in a paste free of the admixture.

The data on hydration of cement pastes, made from the original and from the vibratory reground cement, taking place for 24 hours at +20 °C indicate that the content of bound water is mildly lower in cement pastes with the antifreeze admixture compared to those without the admixture. On the other hand, however, the antifreeze admixture raises markedly the content of $Ca(OH)_2$ in hardened cement.

The degree of hydration of cement pastes with the antifreeze admixture, made from the original and from the vibratory reground cement and kept for 24 hours at —6 °C, is approximately identical and higher than that of cement paste free of admixture and hydrating for 24 hours at +20 °C.

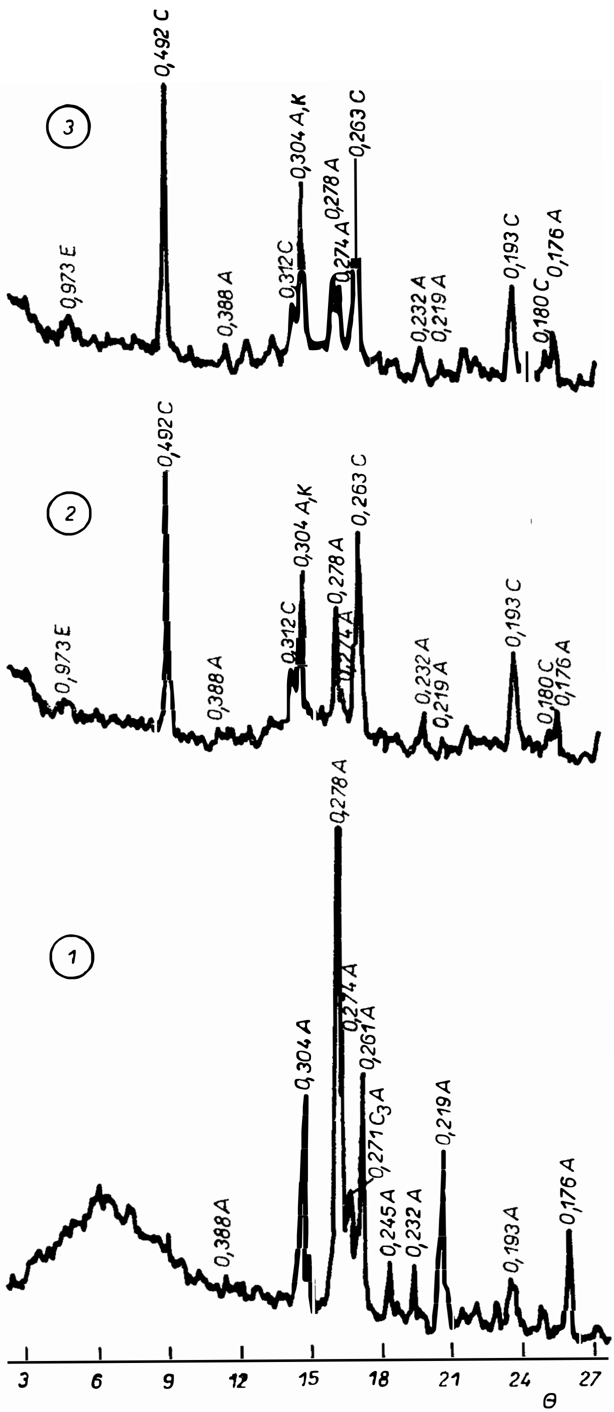
The strengths of the cement pastes at various time intervals are given in Table VI.

The presence of the antifreeze admixture in cement pastes reduces slightly the growth of bending strength after 1, 7 and 28 days of their curing at +20 °C compared with the paste free of admixture. Already after 7 days of hydration at +20 °C, the strengths of paste with antifreeze admixture are identical with or higher than those of the standard paste, and significantly higher after 28 days. This difference is particularly marked in the case of paste made from vibratory reground cement, where the increase in compressive strength amounts up to 8—11 MPa compared to the strength of paste free of the antifreeze admixture. The bending and compressive strengths of cement pastes with the antifreeze admixture are approximately the same after curing for 28 days at —6 °C and for 365 days at +20 °C. This indicates a favourable effect of vibratory regrinding of cement, particularly on the early compressive strength at —6 °C and at +20 °C.

The relative contents of hydration products and the main clinker minerals in the cement pastes were determined by comparing the characteristic diffraction intensities on X-ray diffraction patterns (Figs. 1, 2, 3).

The content of $Ca(OH)_2$ was determined according to the intensity of diffraction at 0.492 nm. The degree of conversion of unreacted alite or belite is characterized by the doublet in the region of 0.274 and 0.278 nm, which generally corresponds to the two clinker minerals.

Fig. 1. X-ray diffraction patterns of the PC 400 Rohožník cement, cement paste prepared from unground cement with the antifreeze admixture hydrating in high-humidity atmosphere for 365 days at +20 °C, and for 28 days at —6 °C and additional 365 days at +20 °C; C — $Ca(OH)_2$, A — alite, E — ettringite, K — calcite; 1 — original cement PC 400 Rohožník, 2 — 365 days, +20 °C, 3 — 28 days at —6 °C + 365 days at +20 °C.


3
0,973 E
0,492 C
0,388 A
0,312C
0,304 A,K
0,278 A
0,274 A
0,263 C
0,232 A
0,219 A
0,193 C
0,180 C
0,176 A
2
0,973 E
0,492C
0,388 A
0,312C
0,304 A,K
0,278 A
0,274 A
0,263 C
0,232 A
0,219 A
0,193 C
0,180C
0,176A
1
0,388A
0,304 A
0,278 A
0,274A
0,261A
0,271 C3A
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0,219 A
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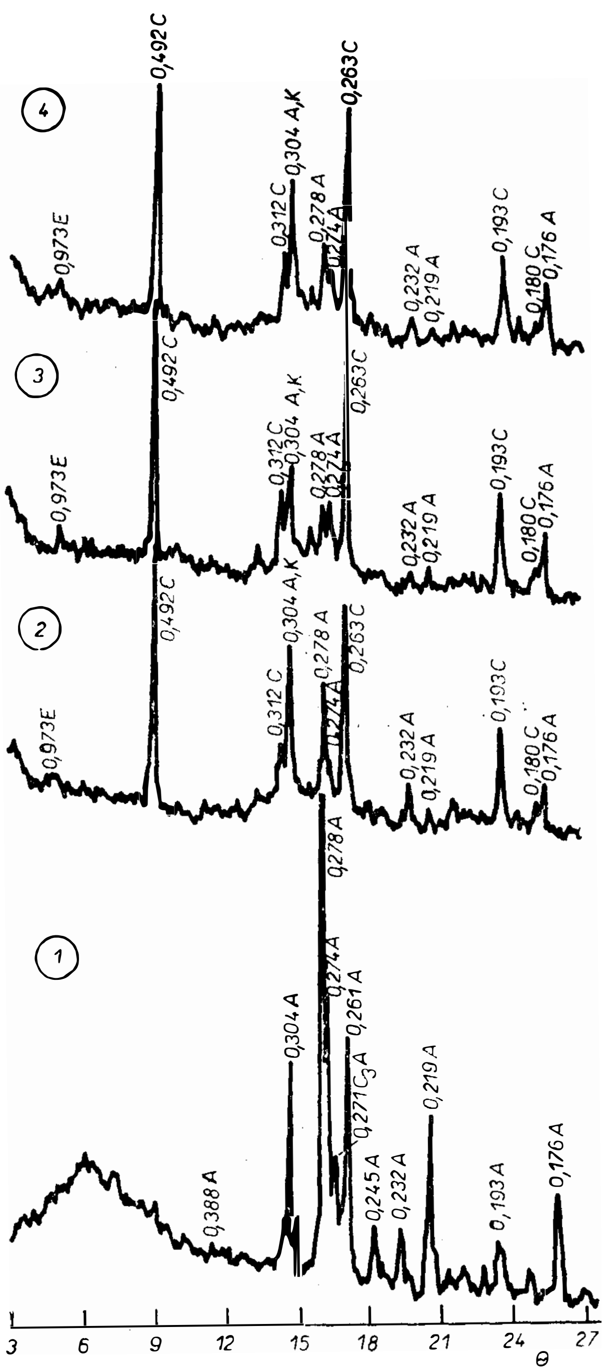
4
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Fig. 1 shows an X-ray diffraction pattern of the cement not subjected to vibratory regrinding and containing 4 wt. % of the antifreeze admixture, following hydration for 365 days in a medium of high humidity, and for 28 days at —6 °C, and then at +20 °C respectively. The two samples contain an approximately equal amount of $Ca(OH)_2$. The conversion of alite and belite to the hydration products is more extensive in the case of paste which had first been cured for 28 days at —6 °C.

The effect of vibratory regrinding of cement taking 5 minutes and 10 minutes respectively on the formation of hydration products is illustrated by Fig. 2. All the cement pastes are formed with a distinct content of $Ca(OH)_2$ of approximately identical diffraction intensities. The amounts of unhydrated clinker minerals is markedly higher in the cement pastes made from cement (not subjected to regrinding) after hydration for 365 days at +20 °C. The cement jointly reground with the antifreeze admixture has a similar effect on the hydration of cement pastes (Fig. 3) as revealed by a roughly equal or mildly increased content of $Ca(OH)_2$ and a decrease of the intensity of unreacted alite and belite in the samples of vibratory reground pastes compared to those prepared from unground cement.

The diffraction patterns of cement pastes containing 4 wt. % of the antifreeze admixture indicate that their structure contains approximately the same high amount of $Ca(OH)_2$ after hydration for 365 days in a humid medium as after 28 days at —6 °C and then at +20 °C. Vibratory regrinding of cement and that of cement jointly with the admixture result in a slight increase in the $Ca(OH)_2$ content in the cement pastes. The different course of hydration of the cement pastes is distinctly revealed by the kinetics of conversion of unreacted alite and belite into their hydration products. In all the pastes which had been initially cured at —6 °C, the content of unhydrated clinker minerals is always lower than that in pastes kept permanently in the humid medium. Vibratory regrinding of cement and that of cement ground jointly with the admixture will raise the degree at which alite and belite are converted to the hydration products (Figs. 2 and 3) in comparison with their conversion in pastes prepared from the cement not subjected to regrinding, and using the same conditions of long-term curing (Fig. 1).

It may therefore be concluded that the degree of hydration achieved in cement pastes containing the antifreeze admixture and initially exposed to the temperature of —6 °C is higher than that in the same paste kept permanently in the humid atmosphere. This effect is promoted by vibratory regrinding of the cement, or joint regrinding of the cement with the admixture.

The data on hydration of cement pastes containing 4 wt. % of the antifreeze admixture and cured in a humid atmosphere after previous exposure for 28 days to the temperature of —6 °C, are listed in Table VII. The results of thermal analysis show that the content of bound water in cement pastes kept at first for 28 days at —6 °C is mildly higher compared to that in the paste exposed to the humid atmosphere only. A similar dependence is also characteristic of the loss in the total

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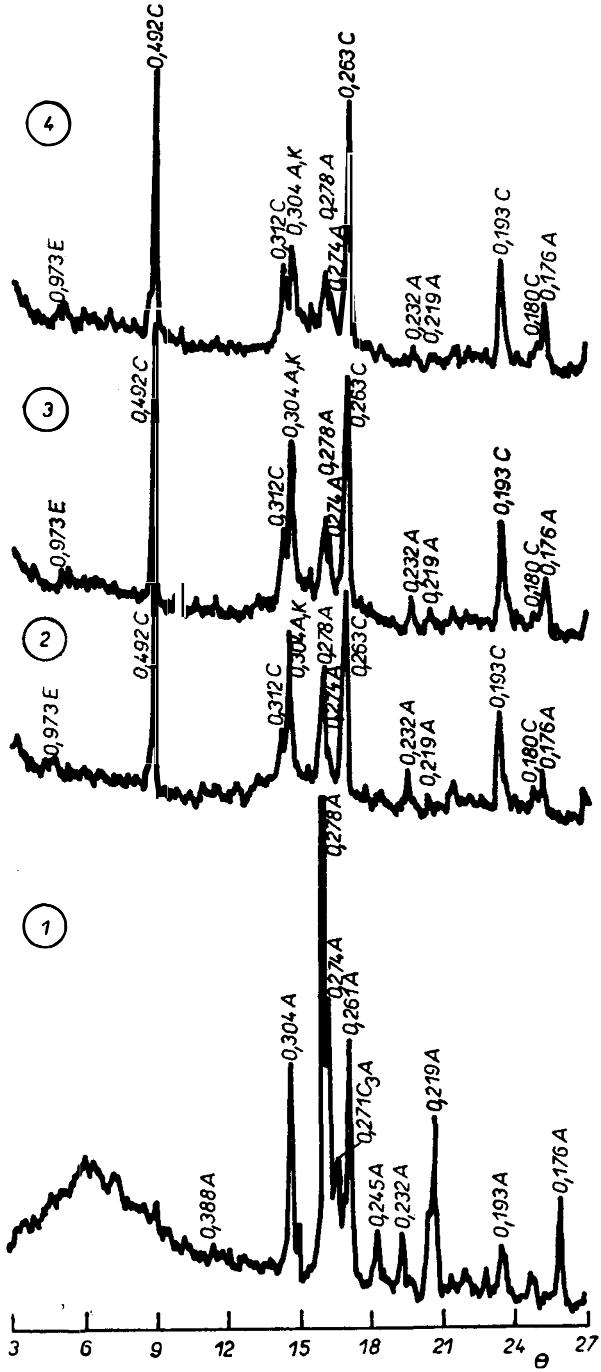
Fig. 2. X-ray diffraction patterns of cement PC 400 Rohožník, cement paste prepared from unground cement with antifreeze admixture (kept in high-humidity atmosphere for 365 days at +20 °C), cement paste made from vibratory reground cement (5 min and 10 min) and unground admixture, after hydration taking 28 days at −6 °C and then 365 days at +20 °C; C—$Ca(OH)_2$, A—alite, E—ettringite, K—calcite, 1 — original cement PC 400 Rohožník, 2 — 365 days at +20 °C, cement not reground, 3 — 28 days at −6 °C + 365 days at +20 °C, vibratory reground cement, 5 min. 4 — 28 days at −6 °C + 365 days at +20 C, vibratory reground cement, 10 min.


4
0,492C
0,263C
0,973E
0,312C
0,304 A,K
0,278 A
0,274 A
0,232 A
0,219 A
0,193 C
0,180 C
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0,388 A
0,304 A
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$Ca(OH)_2$ content. This indicates that from the standpoint of the long-term effect of the antifreeze admixture in cement pastes, more favourable results are obtained when the hydration starts at subzero temperatures and then proceeds at positive temperatures.

The porosity of cement pastes subjected to curing for 28 days at —6 °C and then at +20 °C is higher than that of the paste cured in moist atmosphere at normal temperature. This increase in porosity can be explained so that with the use of the antifreeze admixture, some of the water will freeze at —6 °C, whereas another part of the water will form a solution with a lower freezing point. The ice crystals are responsible for damaging the porous structure, and air bubbles arise in their place after the paste has thawn. The water produced by thawing contributes to the development of the hydration process. The smaller the proportion of frozen water, the lower the paste porosity. The antifreeze efficiency of the admixture can therefore be assesed according to the data on porosity of the cement pastes; the efficiency of the admixture is significantly raised after 10 minutes of vibratory regrinding of the cement.

In the case of joint vibratory regrinding of cement with the antifreeze admixture, the resulting increase in the specific surface area of the admixture influences directly the reduced porosity of cement pastes. From this it follows that the efficiency of the admixture is promoted by the increase in the specific area of the cement as well as that of the admixture proper.

The scanning electron micrographs of cement pastes with 4 wt. % of the antifreeze admixture also show that a compact microstructure in the paste is formed during long-term curing in humid atmosphere (Fig. 4a). The ice formed in the initial stage of hydration can be observed on the fracture surface of the paste kept at first at —6 °C (Fig. 4b). The considerable variability and non-uniformity of the surface are due to the damage done to the structure by the ice crystals and subsequently by the increased porosity. The unfavourable effect of ice is suppressed by vibratory regrinding of the cement (Figs. 4c and 4d). The fracture surfaces of pastes made from cement reground jointly with the admixture show a more uniform and compact structure (Fig. 4e), particularly when the vibratory regrinding took 10 minutes (Fig. 4d, Fig. 4f).

The figures show that the smallest amount of ice is formed in cement pastes made from cement reground jointly with the antifreeze admixture. A proportionally larger amount of water remains in the form of an unfrozen solution. The subsequent hydration at +20 °C can no longer affect the primary porous structure that had originally contained the ice crystals.

Fig. 3. X-ray diffraction patterns of cement PC 400 Rohožník, cement paste with antifreeze admixture (kept in high-humidity atmosphere for 365 days at +20 °C), cement paste prepared by joint vibratory regrinding of cement with the admixture (5 min. and 10 min.), after hydration for 28 days at —6 °C and 365 days at +20 °C, C — $Ca(OH)_2$, A — alite, E — ettringite, K — calcite 1 — original cement PC 400 Rohožník, 2 — 365 days at +20 °C, cement not reground, 3 — 28 days at —6 °C + 365 days at +20 °C, cement reground jointly with admixture 5 min, 4 — 28 days at —6 °C + 365 days at +20 °C, cement reground jointly with admixture, 10 min.

Table VII

Data on hydration of cement paste after long-term curing in humid atmosphere for 365 days after previous hydration for 28 days at −6 °C

Type of cement paste	Curing	Density kg/m³	Appar. density kg/m³	Porosity vol. %	Loss of bound H_2O in hydr. cement, %	Total loss %	Loss of $Ca(OH)_2$ from H_2O %	Loss of $Ca(OH)_2$ from CO_2 %	Total loss of $Ca(OH)_2$ in hydr. paste, %
cement +4 % of admixture	365 days humid atmosphere	2373.7	1639	30.94	9.35	19.38	11.28	9.66	20.94
cement +4 % of admixture	28 days at −6 °C + 365 days at +20 °C, relative humidity 95 %	2464.3	1616	34.42	9.58	19.84	9.40	10.57	19.97
cement reground for 5 min. +4 % of admixture		2471.1	1667	34.04	9.69	20.06	11.05	10.57	21.62
cement reground for 10 min. +4 % of admixture		2386.1	1720	27.90	10.66	21.55	11.28	10.79	22.07
cement reground for 5 min. jointly with 4 % of admixture		2442.3	1651	32.35	10.66	20.63	11.75	9.44	21.19
cement reground for 10 min. jointly with 4 % of admixture		2375.2	1771	25.44	11.51	22.34	10.34	11.02	21.36

CONCLUSION

The effect of 4 wt. % of an antifreeze admixture on the hydration of cement, that of vibratory regrinding of cement, and that of cement regrinding jointly with the admixture and curing at —6 °C and at +20 °C for various time intervals was studied.

Thermal analysis showed that after 24 hours of hydration at —6 °C, the content of water bound in the hydration product increases in cement pastes containing the admixture, and the content of $Ca(OH)_2$ is also higher than in pastes free of the admixture. At +20 °C, the admixture mildly reduces the amount of bound water and distinctly raises the content of $Ca(OH)_2$ in the hardened paste. The decrease of the content of water bound at +20 °C in the cement paste results in a slight retarding of compressive strength growth after 1, 7 and 28 days of hydration compared to an admixture-free paste. The degree of hydration of cement pastes containing the antifreeze admixture and prepared from the original cement, from vibratory reground cement and the admixture, and kept for 24 hours at —6 °C, is approximately the same as, and higher than, that of a cement paste without the admixture and following hydration for 24 hours at +20 °C.

The results of X-ray phase analysis and those of thermal analysis of hardened pastes after various periods of time of curing show that the degree of hydration of cement pastes containing the admixture and exposed to the initial temperature of —6 °C is higher than that of a paste cured permanently in a high-humidity atmosphere at room temperature. This effect is promoted by vibratory regrinding of the cement, and particularly by joint vibratory regrinding of the cement with the admixture.

The porosity of cement pastes prepared with admixture from cement not subjected to regrinding and the admixture, and first exposed to the temperature of —6 °C, exceeds that of paste permanently kept in a humid atmosphere; the porosity is due to the formation of ice in the paste structure. This negative effect of frost on the structure of the cement paste can be suppressed by introduction of the admixture in question [7]. Additional suppression of these negative effects can be achieved by vibratory regrinding of the cement, or by joint regrinding of the cement with the admixture.

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VPLYV PRÍSADY $NaNO_3$ A $Ca(HCOO)_2$ NA HYDRATÁCIU VIBRAČNE DOMIEĽANÉHO CEMENTU PRI −6 °C A +20 °C

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Vibračné domieľanie cementu a cementu spoločne s protizmrazovacou prísadou urýchľuje počiatok a dobu tuhnutia ako aj nárast počiatočných pevností v tlaku cementových kaší uložených pri teplote −6 °C.

Údaje rtg. fázovej analýzy a termickej analýzy kaší vystavených teplote −6 °C preukazujú, že v prítomnosti prísady sa podstatne zvyšuje obsah viazanej vody v hydratačných produktoch, ako aj obsah $Ca(OH)_2$ v porovnaní s ich obsahom v kaši bez prísady. Tvorba hydratačných produktov sa umocňuje ľubovoľne zvoleným spôsobom vibračného domieľania. Pre dlhodobý účinok protizmrazovacej prísady v cementovej kaši možno potvrdiť ako výhodnejší taký spôsob uloženia, kedy hydratácia cementu začína pri zápornej teplote a neskôr pokračuje pri kladnej teplote. Tento účinok sa zvyšuje vibračným domieľaním cementu spoločne s prísadou.

Pórovitosť cementových kaší vystavených účinku zápornej teploty závisí predovšetkým od tvorby ľadu v štruktúre kaše. Pri vibračnom domieľaní cementu a cementu spoločne s prísadou zostáva v stave nemrznúceho roztoku väčší podiel zámesovej vody, čo svedčí o vyššej hydraulickej aktivite cementu a protizmrazovacej účinnosti prísady.

Obr. 1. Rtg. difrakčné záznamy cementu PC 400 Rohožník, cementovej kaše z nemletého cementu s protizmrazovacou prísadou hydratujúcou jednak vo vlhkom prostredí 365 dní pri +20 °C, jednak 28 dní pri −6 °C a ďalej 365 dní pri +20 °C. C — $Ca(OH)_2$, A — alit, E — ettringit, K — kalcit; 1 — pôvodný cement PC 400 Rohožník, 2 — 365 dní, +20 °C, 3 — 28 dní, −6 °C +365 dní, +20 °C.

Obr. 2. Rtg. difrakčné záznamy cementu PC 400 Rohožník, cementovej kaše z nemletého cementu s protizmrazovacou prísadou (uloženej vo vlhkom prostredí 365 dní pri +20 °C), cementovej kaše z vibračne domletého cementu (5 min a 10 min) a nemletej prísady po hydratácii v trvaní 28 dní pri −6 °C a potom 365 dní pri +20 °C. C — $Ca(OH)_2$, A — alit, E — ettringit, K — kalcit; 1 — pôvodný cement PC 400 Rohožník, 2 — 365 dní, +20 °C nemletý cement, 3 — 28 dní, −6 °C + 365 dní, +20 °C vibračne domletý cement, 5 min. 4 — 28 dní, −6 °C + 365 dní, + 20 °C vibračne domletý cement, 10 min.

Obr. 3. Rtg. difrakčné záznamy cementu PC 400 Rohožník, cementovej kaše s protizmrazovacou prísadou (uloženej vo vlhkom prostredí 365 dní pri +20 °C), cementovej kaše pripravenej spoločným vibračným domieľaním cementu s prísadou (5 min a 10 min) pri trvaní hydratácie 28 dní pri −6 °C a 365 dní pri +20 °C. C — $Ca(OH)_2$, A — alit, E — ettringit, K — kalcit; 1 — —pôvodný cement PC 400 Rohožník, 2 — 365 dní, +20 °C nemletý cement, 3 — 28 dní, −6 °C + 365 dní, +20 °C spoločne vibračne domletý cement 5 min., 4 — 28 dní, −6 °C + 365 dní, +20 °C spoločne vibračne domletý cement s prísadou, 10 min.

Obr. 4. Snímky cementových kaší zhotovené riadkovacím elektrónovým mikroskopom; a — nemletý cement po hydratácii 365 dní pri teplote +20 °C a relatívnej vlhkosti vyššej ako 95 %, b — nemletý cement so 4 % protizmrazovacej prísady, c — 5 min vibračne domletý cement so 4 % prísady, d — 10 min vibračne domletý cement so 4 % prísady, e — 5 min spoločne vibračne domletý cement a 4 % prísady, f — 10 min spoločne vibračne domletý cement a 4 % prísady,
snímky b—f po trvaní hydratácie 28 dní pri teplote −6 °C a následne 365 dní vo vlhkom prostredí.

ВЛИЯНИЕ ДОБАВКИ $NaNO_3$ И $Ca(HCOO)_2$ НА ГИДРАТАЦИЮ ВИБРАЦИОННО ИЗМЕЛЬЧЕННОГО ЦЕМЕНТА ПРИ —6 °С И +20 °С

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Вибрационное измельчение цемента и цемента вместе с антиморозильной добавкой ускоряет начало и время застывания и рост начальных прочностей при сжатии цементных растворов, уложенных при температуре —6 °С.

Данные, полученные с помощью рентгеновского фазового анализа и термического анализа тест, подвергаемых температуре —6 °С, показывают, что в присутствии добавки существенно повышается содержание связанной воды в гидратационных продуктах и содержание $Ca(OH)_2$ в сопоставлении с их содержанием в растворе без добавки. Образование гидратационных продуктов увеличивается произвольно подобранным способом вибрационного измельчения. Для достижения длительного действия антиморозильной добавки в цементном тесте оказывается более пригодным такой способ уложения, когда гидратация цемента начинается при отрицательной температуре и далее продолжается при положительной температуре. Приводимое действие повышается вибрационным измельчением цемента вместе с добавкой.

Пористость цементных тест, подвергаемых действию отрицательных температур зависит прежде всего от образования льда в структуре раствора. При вибрационном измельчении цемента и цемента вместе с добавкой остается в состоянии незамерзающего теста большая доля смесительной воды, свидетельством чего является большая гидравлическая активносить цемента и антиморозильного действия добавки.

Рис. 1. Рентгенограммы цемента PC 400 Рогожник, цементного теста из неизмельченного цемента с антиморозильной добавкой, гидратирующей с одной стороны во влажной среде 365 дней при температуре +20 °С, а с другой стороны 28 дней при температуре —6 °С и кроме того 365 дней при температуре +20 °С; С — $Ca(OH)_2$, *A — алит, E — эттрингит, K — кальцит; 1 — исходный цемент PC 400 Рогожник, 2 — 365 дней, 20 °С, 3 — 28 дней, —6 °С, 365 дней, +20 °С.*

Рис. 2. Рентгенограммы цемента PC 400 Рогожник, цементного теста из неизмельченного цемента с антиморозильной добавкой (уложенного во влажной среде 365 дней при +20 °С), цементного теста из вибрационного измельченного цемента (5 и 10 мин.) и неизмельченной добавки при гидратации с продольжительностью 28 дней при температуре —6 °С и после того 365 дней при температуре +20 °С; С — $Ca(OH)_2$, *A — алит, E — эттрингит, K — кальцит; 1 — исходный цемент PC 400 Рогожник, 2 — 365 дней, +20 °С, неизмельченный цемент, 3 — 28 дней, —6 °С, 365 дней, +20 °С, вибрационно измельченный цемент 5 мин., 4 — 28 дней, —6 °С, 365 дней, +20 °С, вибрационно измельченный цемент, 10 мин.*

Рис. 3. Рентгенограммы цемента PC 400 Рогожник, цементного теста с антиморозильной добавкой (уложенной во влажной среде 365 дней при температуре +20 °С), цементного теста, приготовленного совместным вибрационным измельчением цемента с добавкой (5 и 10 мин.) при продолжительности гидратации 28 дней при температуре —6 °С и 365 дней при +20 °С; С — $Ca(OH)_2$, *A — алит, E — эттрингит, K — кальцит; 1 — исходный цемент PC 400 Рогожник, 2 — 365 дней, +20 °С, неизмельченный цемент, 3 — 28 дней, —6 °С, 365 дней, +20 °С, совместно вибрационно измельченный цемент с добавкой 5 мин., 4 — 28 дней, —6 °С, 365 дней, +20 °С, совместно вибрационно измельченный цемент с добавкой 10 мин.*

Рис. 4. Съемки цементных тест, полученные с помощью сканирующего электронного микроскопа; a — неизмельченный цемент после гидратации 365 дней при температуре +20 °С и относительной влажности выше 95 %, b — неизмельченный цемент с 4 % антиморозильной добавки, c — 5 мин. вибрационно измельченный цемент с 4 % добавки, d — 10 мин. ибрационно измельченный цемент с 4 % добавки, e — 5 мин. совместно вибрационно измельченный цемент и 4 % добавки, f — 10 мин. совместно вибрационно измельченный цемент и 4 % добавки; съемки b—f после 28 дней гидратирования при температуре —6 °С и последоватедьно 365 дней во влажной среде.

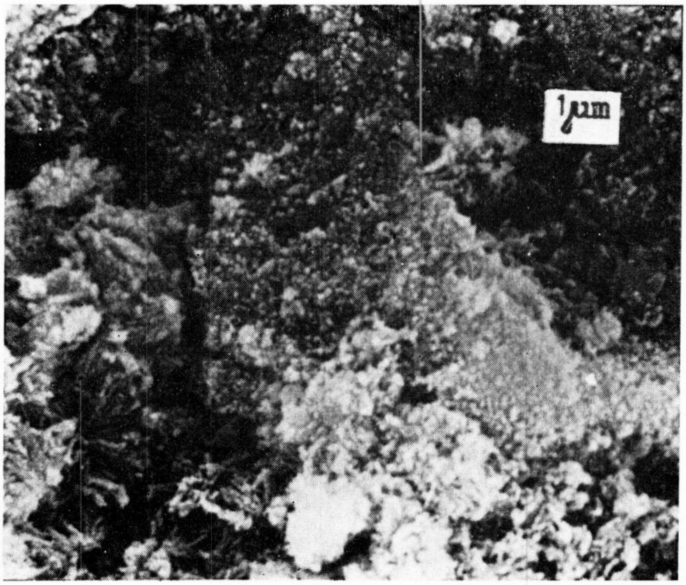


Fig. 4a.

Fig. 4b.

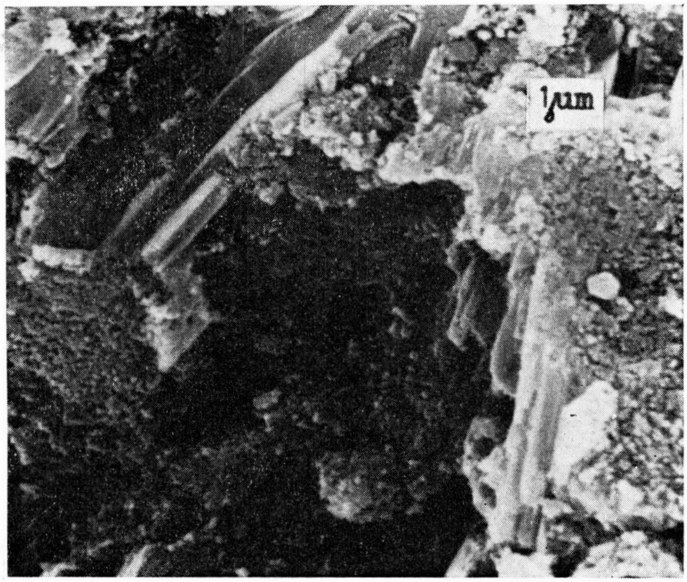


Fig. 4c.

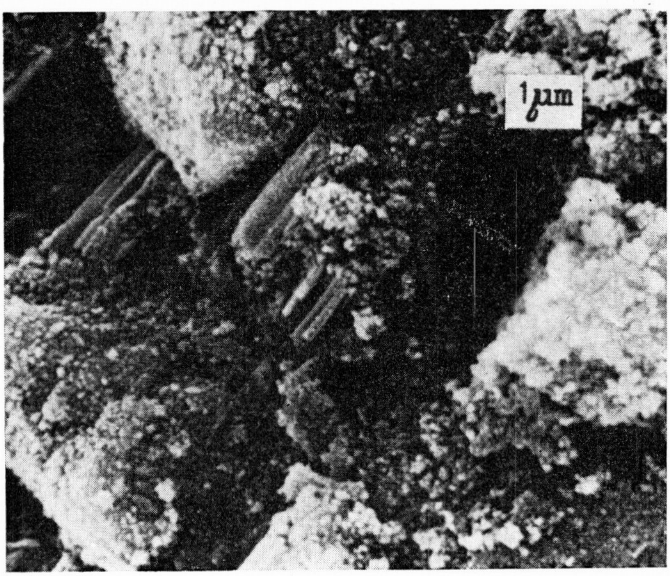
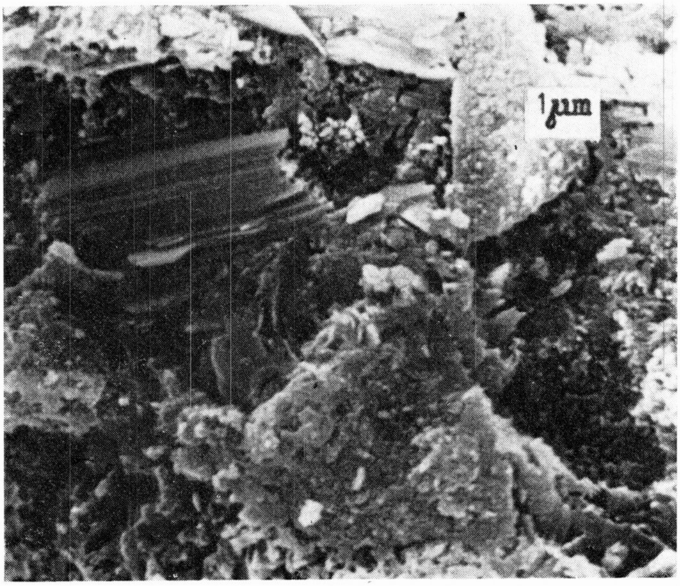
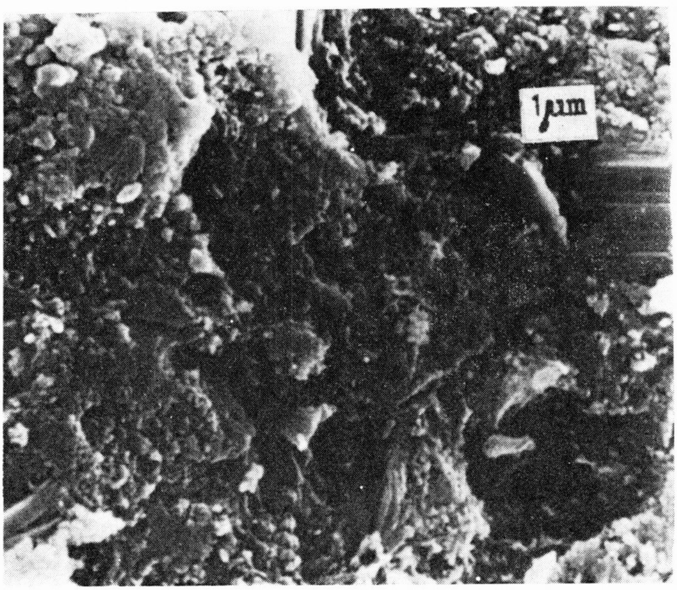


Fig. 4d.



e)



f)

Fig. 4. Scanning electron micrographs of cement pastes; a — original cement after hydration for 365 days at +20 °C and relative humidity higher than 95 %, b — original cement with 4 % of antifreeze admixture, c — cement reground for 5 minutes, with 4 % of admixture, d — cement reground for 10 minutes, with 4 % of admixture, e — cement reground for 5 minutes jointly with 4 % of admixture, f — cement reground for 10 minutes jointly with 4 % of admixture. Micrographs b—f after 28 days of hydration at —6 °C and subsequent 365 days in humid atmosphere.