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Volumetric strains of cement-based mortars caused by ice formation in terms of frost resistance diagnostics

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Abstract. The paper presents the volumetric strain test results of differently composed cement mortar samples during the phase transformation of water into ice, and juxtaposes the results with other relevant indicators, such as the water absorption and the degree of filling pores with water. It also presents the possibility of using these observations in terms of frost resistance diagnostics. The investigation covered non-air-entrained mortars, which were also subjected to the vacuum treatment and vibration to reduce the air content. It was found experimentally that the volumetric strain of mortar samples soaked in water under vacuum at $\Delta V/V < 2‰$ means the mortar of high frost resistance. $\Delta V/V > 4‰$ indicates that the mortar requires air-entraining regardless of the microstructure and kind of cement.

Key words: cement mortar, volumetric strains, absorption, degree of filling, frost resistance.

1. Introduction

The registered strains of the frozen concrete and mortar are used in the standard and comparative tests as a diagnostic tool in the studies of frost resistance [1–12]. These are in most cases linear deformations examined after a defined number of freeze/thaw cycles. Alternatively, the deformations are evaluated after each cycle according to the procedure defined by the ASTM C 671 standard. Such measurements reflect the combined effect of the internal microstructure damage, without the possibility of a deeper analysis of their origins and the course.

Linear strains measured during a single freeze cycle, connected with the effects of the phase transformation of water into ice, are far less used in the researches [1, 2]. In this case the problem arises due to the difficulty of separating the effects of thermal deformations from the effects of the phase transition strains. In this context an attempt to record and evaluate volumetric strains is even more difficult and problematic. After the thermal influence has been eliminated, the volumetric strain – clearly resulting from the phase change of water into ice – can be used as a diagnostic tool to assess with a certain degree of approximation not only the intensity of the destructive process, but also the freezing/non- freezing water ratio (in simple terms: less and more strongly adsorbed). Indirectly, it also permits drawing the conclusions about the influence of the initial material composition on its physical reaction during freezing. In terms of practical utility, the short duration and a relatively low cost of the test are its significant features.

Frost resistance of concrete is undoubtedly associated with the absorption. There are stipulations defining the maximum permissible water absorption for concrete exposed to cyclic freezing. However, the practical use of the absorption coefficient in the diagnosis raises some doubts. It is a known fact that the frost damage occurs mainly due to an excessive pressure generated in the pores by the freezing water, which is dependent not only on the total water content in the material, but also on the degree of its adsorption and the presence of the empty voids capable of absorbing the excess water during crystallization.

The effects of unfrozen water movement as a result of the phenomenon described as a cryo-suction [7] or mechanism of micro-ice-lens formation [12] are also discussed. Regardless of the details of the various theories important is the extent to which the material is able to resist resulting stresses and at what point begins its destruction. The total effect of water transformation and movement between the pores can be observed to some extent by measuring the volumetric strain of a material sample. The quantitative description of this phenomenon is proposed in [7]. An empirical approach to the problem through the use of a method for determining the volumetric strain of mortar samples during freezing is presented. The results are discussed in terms of frost resistance.

2. The subject and methods of research

The study focused on the cement mortar samples whose composition is presented in Table 1.

A policarboxilate-based superplasticizer was used to improve the workability of some mixes with a lower w/c ratio (Table 1). The mixtures were not air-entrained. They were subjected to the vacuum treatment to reduce the air content in three steps: 15 seconds of vibration, 15 seconds of vacuum treatment and then 30 seconds of simultaneous vacuum treatment and vibration. The air content was determined in accordance with the PN-EN-1015-7 standard, using a TESTING apparatus with the operational volume of 1 dm^3. Despite the described procedure a certain amount of air remained in

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the mortars. The difficulty in removing the air excess observed in mortars of 0.30 water/cement ratio was associated with a significant increase in internal cohesion of the mixes containing more superplasticizer. The vacuum treatment and vibration should be extended in time. Consequently the comparative analysis of parameters of mortars with different values of water/cement ratio may be distorted to some extend.

Table 1
Mortar compositions

Type of cement[1)]	w/c	water[2)] [kg]	cement [kg]	sand [kg]	superplasticizer[3)] [%]	Air [%]
CEM I	0.30	3.750	12.5	25.0	2.37	4.4
	0.37	4.625	12.5	25.0	0.50	2.2
	0.45	5.625	12.5	25.0	–	0.9
	0.53	6.625	12.5	25.0	–	0.8
CEM II/A-V	0.37	4.625	12.5	25.0	0.50	1.3
	0.45	5.625	12.5	25.0	–	1.1
	0.53	6.625	12.5	25.0	–	0.9
CEM II/B-V	0.30	3.750	12.5	25.0	0.60	2.4
	0.37	4.625	12.5	25.0	0.50	1.1
	0.45	5.625	12.5	25.0	–	1.0
	0.53	6.625	12.5	25.0	–	0.7
CEM III/A	0.30	3.750	12.5	25.0	0.40	4.0
	0.37	4.625	12.5	25.0	0.25	2.1
	0.45	5.625	12.5	25.0	–	0.9

1) in accordance with EN 197:
- CEM I: Portland cement (content of clinker min. 95%)
- CEM II/A-V: Portland-composite cement (content of siliceous fly ash 18%)
- CEM II/B-V: Portland-composite cement (content of siliceous fly ash 33%)
- CEM III/A: Blastfurnace cement (content of blast furnace slag 56%)

2) total amount of water including water contained in admixture

3) % by weight of cement

The cubes measuring 100×100×100 mm were formed in moulds, which were put into sealed plastic bags and stored at the temperature of 20±2°C. After 24 hours the samples were removed from the forms and stored for six days in water. After that time the samples measuring ∅30 mm, h = 100 mm were drilled off. The prepared samples were stored for 14, 76, 166 and 256 days, respectively, in the specified temperature and moisture conditions (temperature 20±2 °C, RH 50±5%). Seven days before the beginning of the tests the samples were saturated (after a 30-minute vacuum treatment degassed, distilled water was poured over the sample).

The samples, dried to a constant weight state at the temperature of 105°C were used to determine the volumetric density and absorption. The volumetric water absorption A_v was calculated as the ratio of the pore-filling water volume in the sample to the sample volume in dry state. The porosity was determined as a difference between specific density and bulk density. The bulk density of mortar was determined by the hydrostatic method, and the specific density of mortars was determined in Le'Chatelier's flask using ethyl alcohol. The degree of filling pores DFP was calculated as the ratio of the water volume to the total porosity of material.

The volumetric strains of the samples during freezing $\Delta V/V$ were registered by the DAVS method (Differential Analysis of Volumetric Strains) [3]. The method of the differential analysis of volumetric strains (DAVS) allows the observations of the effects of freezing on the whole of the material sample. The scale of the issue, i.e. the separation of the cooling-related thermal deformations from the volumetric strains directly related to the transformation of water into ice, has been limited by applying a comparative dilatometer (containing a sample without water) as well as an introduction of additional corrective amendments. The DAVS method (RAO abbreviation being used in Polish) has been used in a variety of versions since 1986 [9]. The idea of the test was inspired by earlier works [10, 11] focused on the concrete aggregates tests performed in a single dilatometer.

In the tests presented in the paper, the water-saturated sample was placed in a steel measuring dilatometer. In the second dilatometer, a control sample of the same dimensions and approximately the same thermal deformability coefficient was located – Fig. 1. The reference sample did not include water. The dilatometers were equipped with calibrated measuring tubes and temperature sensors placed inside the samples and outside the dilatometers. The dilatometers were filled with kerosene to the "0" level on the measuring tubes. Each sample was freezing in the thermostat which made it possible to obtain a programmed temperature change profile as a function of time. When cooling to a temperature of −25°C the level of kerosene in the tubes and the temperature inside and on the surface were recorded. The tests focussed on comparing the volumetric strains of a cylindrical mortar sample measuring ∅30 mm, h = 100 mm. The strains difference $\Delta V/V$ at temperature −20°C was analysed in the paper.

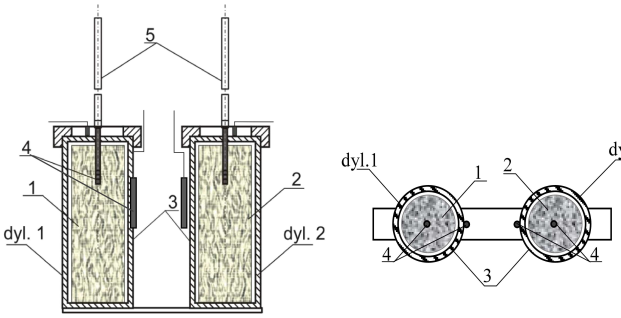

Fig. 1. Set-up of measuring dilatometers: 1 – water-saturated tested sample, 2 – control sample, 3 – measuring dilatometers, 4 – temperature sensors, 5 – measuring tubes

The analysis was conducted using the results of the work [4, 5] and the results of, which was performed separately, while maintaining the identical methodology and the sample elements composition. The more detailed information on the source of the analyzed data is shown in Table 2.

3. Results and analysis

Table 2 presents the test results, which were then used for further analysis. Figures 2, 3 and 4 show the parameters A_v, DFP and $\Delta V/V$, depending on the time, the curing conditions, the type of cement, and water/cement ratio.

Table 2
The mortar properties

Type of cement	Age of the sample, days	w/c = 0.30			w/c = 0.37			w/c = 0.45			w/c = 0.53			Source
		A_V [%]	DFP [%]	ΔV/V [‰]	A_V [%]	DFP [%]	ΔV/V [‰]	A_V [%]	DFP [%]	ΔV/V [‰]	A_V [%]	DFP [%]	ΔV/V [‰]	
CEM I: Portland cement (content of clinker min. 95%)	28 (V)	14.5	72.6	1.0	17.6	81.3	1.8	20.4	86.4	2.0				[4]
	90 (V)	14.5	70.5	1.5	17.5	79.0	3.7	20.4	87.2	5.1				[4]
	180 (V)				17.1	80.7	3.9	20.3	85.0	5.3	22.2	91.3	7.0	[5]
	270 (V)				17.1	80.4	3.7	20.1	84.4	5.1	22.3	92.9	6.9	[5]
	180 (W)				13.6	69.4	1.5	16.5	73.9	1.5	18.8	79.8	2.3	[5]
	270 (W)				13.4	70.1	1.4	16.2	75.2	1.7	18.7	81.6	2.4	[5]
CEM II/A-V: Portland-composite cement (content of siliceous fly ash 18 %)	180 (V)				17.0	84.8	5.1	20.5	88.3	8.8	22.1	92.7	10.3	[5]
	270 (V)				17.9	89.6	5.1	20.8	90.3	8.8	22.5	94.7	10.4	[5]
	180 (W)				13.9	73.8	1.3	16.8	77.8	1.9	18.9	84.9	2.7	[5]
	270 (W)				13.4	72.5	1.1	16.5	76.4	1.6	19.6	89.4	2.7	[5]
CEM II/B-V: Portland-composite cement (content of siliceous fly ash 33%)	28 (V)	14.1	88.9	1.0	17.2	92.2	1.7	20.2	90.2	7.7				[4]
	90 (V)	15,1	88.6	0.8	18.7	94.9	4.4	21.1	93.6	7.6				[4]
	180 (V)				18.7	98.9	4.7	20.7	92.3	7.4	22.4	97.0	11,3	[5]
	270 (V)				18.9	99.0	4.8	21.0	99.0	7.3	22.6	97.9	11.4	[5]
	180 (W)				14.3	83.2	1.8	16.9	80.9	2.1	19.9	92.2	2.7	[5]
	270 (W)				13.8	81.3	1.4	16.1	77.1	2.1	19.5	91.4	2.6	[5]
CEM III/A: Blastfurnace cement (content of blast furnace slag 56%)	28 (V)	16.4	80.0	1.0	20.3	91.2	2.1	22.8	95.4	2.7				[4]
	90 (V)	15.7	75.2	1.4	18.9	84.8	3.9	22.6	94.2	5.6				[4]

(V) – vacuum absorption after a period of drying (temp. +20±2°C, RH 50±5%), (W) – samples continuously stored in water,
A_V – volumetric absorption, DFP – the degree of filling pores, ΔV/V – volumetric strain recorded at −20°C.

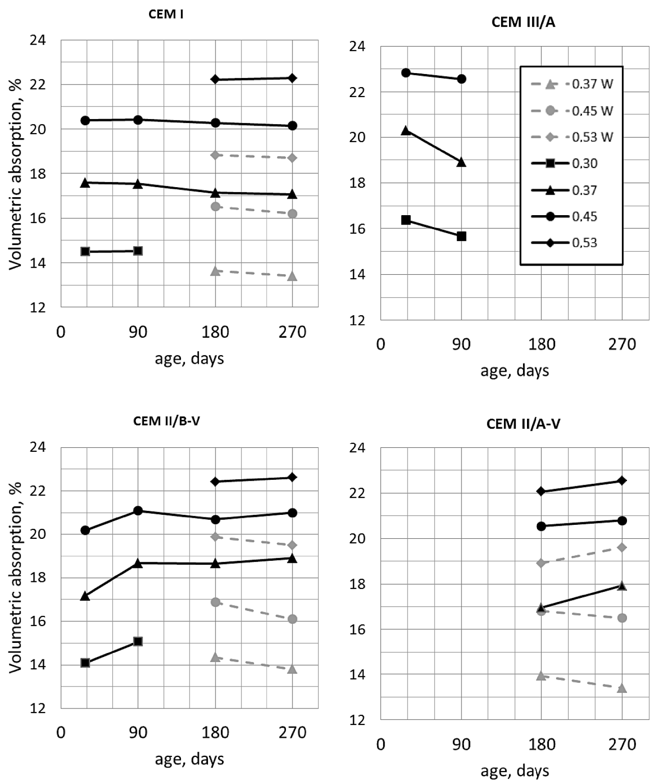

Fig. 2. Relationship between volumetric absorption A_V, age of samples and water/cement ratio (W – samples continuously stored in water, other results mean samples absorbed under vacuum)

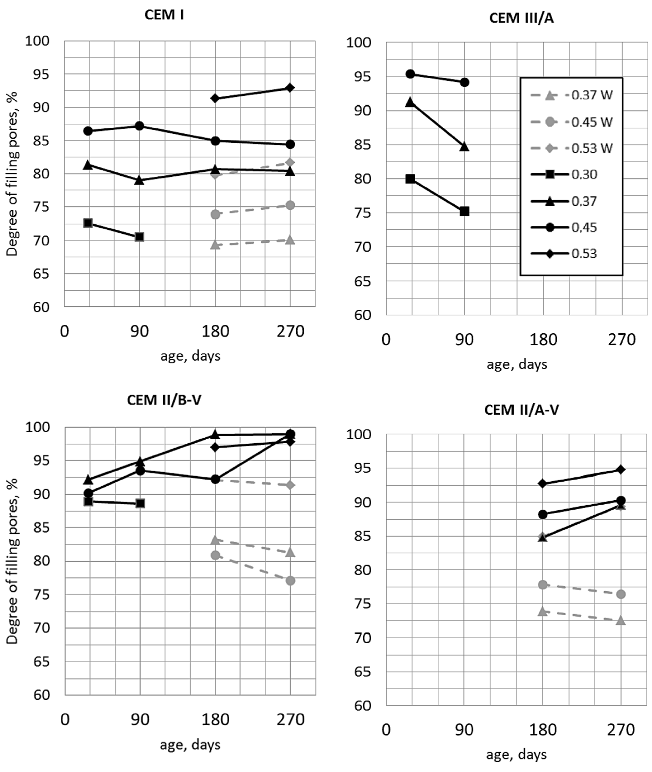

Fig. 3. Relationship between the degree of filling the pores DFP, age of samples and water/cement ratio (W – samples continuously stored in water, other results mean samples absorbed under vacuum)

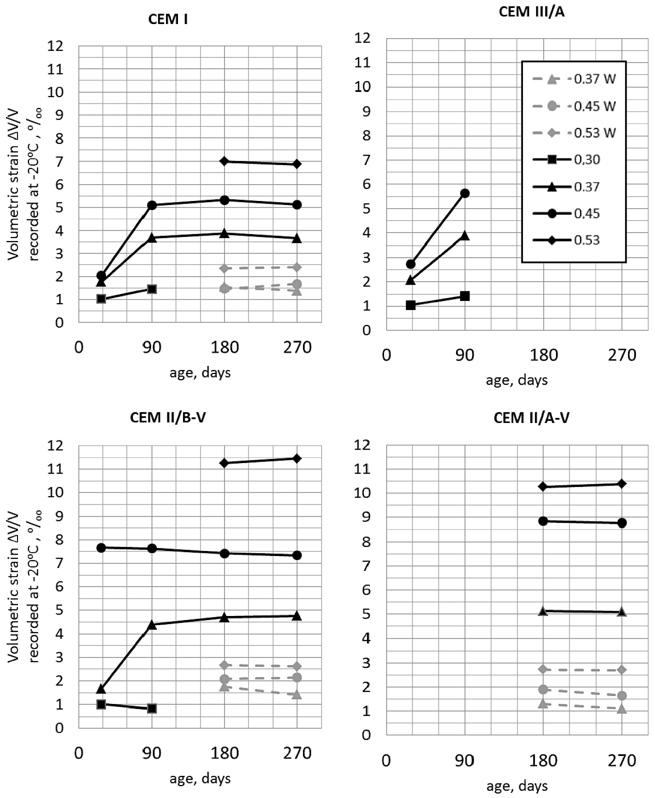

Fig. 4. Relationship between volumetric strain $\Delta V/V$ recorded at -20°C, age of samples and water/cement ratio (W – samples continuously stored in water, other results mean samples absorbed under vacuum)

In general it can be stated that microstructural properties controlling A_v, DFP and $\Delta V/V$ stabilize in up to 90 days of curing. In particular, this refers to the deformation $\Delta V/V$, due to the phase change of water when freezing mortar samples to -20°C. Clearly visible is the differentiating influence of the water/cement ratio and the type of cement. Both technological factors have a significant impact on the characteristics of the microstructure of the tested mortars which determine the amount of water in the pores, the degree of the pore filling with water and the degree of the phase transformation of water and its cumulative effect on the volumetric strain.

The comparison of mortars cured in water and mortars curing in the air confirms the effect of the cement matrix transformation as a result of a partial loss of water through evaporation. After re-soaking in water, all kinds of mortars absorbed more water and showed a much higher level of volumetric deformations. Most likely, according to the Jennings' model [6] additional capillary micropores were formed measuring from a few to several nanometers, as the effect of the compaction of the solid phase elements, mainly the CSH crystals. It is interesting that particular parameters of all mortars curing in water vary only to a small extend.

The volumetric deformations of re-soaked samples were significantly higher in comparison with the samples curing in water throughout the study period (Fig. 4), which can be explained by the decrease of water dispersion and by the limited amount of strongly adsorbed water, resulting from the physical reconstruction of the microstructure.

The type of cement significantly affects the properties of the mortars, in terms of the phenomena under consideration. Mineral additives change the internal structure of the cement matrix. Compared to the blast furnace slag, a hydraulic binder similar to Portland cement, siliceous fly ashes with their puzzolana characteristics differentiate the cement matrix in a particularly strong manner. Especially significant is the impact of ash on the growth of the DFP (Fig. 3) and volumetric strain (Fig. 4). The slag, in turn, increases overall absorption.

The standard recommendations or construction specifications often connect the durability forecast with water absorption. Figures 5 and 6 show the dependence of DFP and $\Delta V/V$ on the volumetric water absorption.

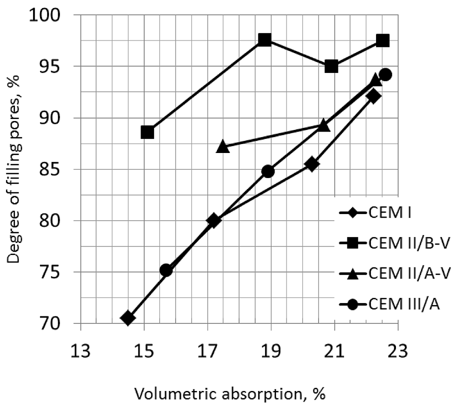

Fig. 5. Relationship between the degree of filling pores DFP, volumetric absorption A_v and the type of cement

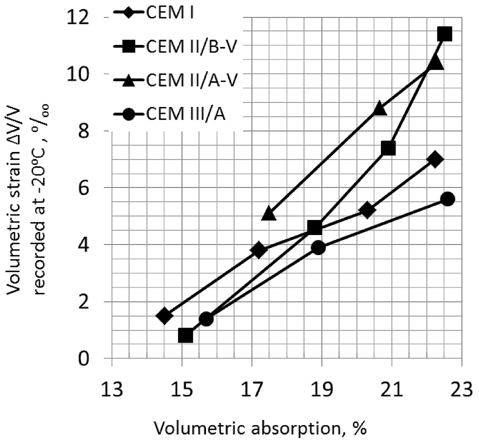

Fig. 6. Relationship between volumetric absorption A_v, volumetric strain $\Delta V/V$ recorded at -20°C, and the type of cement

The degree of filling the pores DFP was calculated by relating the volume of water evaporated in $+105^\circ$C to total porosity. The highest diversity of DFP was found at the lowest water absorption values of A_v (Fig. 5). With the increase of mortar absorption the differences between DFP decreased. Higher levels of DFP make the hydraulic system of pores in the cement matrix more "stiffened" which should result in higher values of $\Delta V/V$. However the observation of volumetric strain does not confirm a direct relationship between DFP and $\Delta V/V$ in case of mortars with the lowest values of absorption (w/c = 0.30) – Fig. 6. Despite significant differences in DFP, the volumetric strains remain at a similar low level of less than 2‰. This refers particularly to mortars constantly kept in water. It may indicate the “buffering effect” of the air left in the mortars or a high content of strongly adsorbed water (not undergoing the phase transformation to the temperature of -20°C.) This factor requires further studies using other methods: low-temperature calorimetry DSC or magnetic resonance NMR.

There is a group of pores, whose importance in the process of absorption and then freezing water redistribution is unclear. If 20 to 30% of the pores (in special cases) is not filled with water after the vacuum absorption, it may mean that the pressure difference caused by vacuum is too low to allow water to flow into some isolated voids (eg. certain ink-bottle pores). In contrast, the pressures caused by the freezing process are so large that some of the water from freezing zone can penetrate into these voids reducing the recorded value of $\Delta V/V$. The question remains concerning the morphology of pores that do not become filled with water after the vacuum infiltration or are empty despite the constant keeping of the samples in water. With the increase of absorption (w/c higher than 0.30) the value of the strain generally increases in all the tested mortars. However the increase of $\Delta V/V$ in the samples with the higher values of the DFP is the highest. The greatest variations in the $\Delta V/V$ were observed in the group of mortar presenting the highest absorptivity (w/c = 0.53).

For diagnostics as well as for design purposes it may be useful to juxtapose the test results in Figs. 7, 8 and 9. The degree of filling water DFP, absorption A_v and volumetric strain $\Delta V/V$ are shown, depending on the composition of the mortar, i.e. w/c and the type of cement. The results of tests made on samples aged 28 days were not included due to their unstabilized microstructure and neither were those of the samples stored in water. It was assumed that the typical conditions of concrete structures curing prior to the frost action are combined with the possibility of partial drying (especially in the surface layer). The mean values of test results are related to the 90, 180 and 270 days.

The analysis was based on the results of frost resistance tests of identical mortars containing cement, sand and water with identical proportions and quality [4, 5]. Freeze resistance test was performed by cyclic freezing and thawing of the samples, which were not vacuum soaked but soaked in an ordinary manner. In Figs. 7, 8 and 9 the individual mortars were marked as frost resistant, not frost resistant and of uncertain resistance. Mortars which were not examined are marked in a special manner.

It is generally acknowledged that the frost resistance of concrete and mortar made of pure Portland cement and with the w/c < 0.37 is high enough and it is not required to be air-entrained with use of chemical agents. Regarding the composite cements, particularly containing puzzolana additives or mineral dust, the ratio w/c is no longer a sufficient tool to predict the durability (c is understood as the mass of all the cement components including additives).

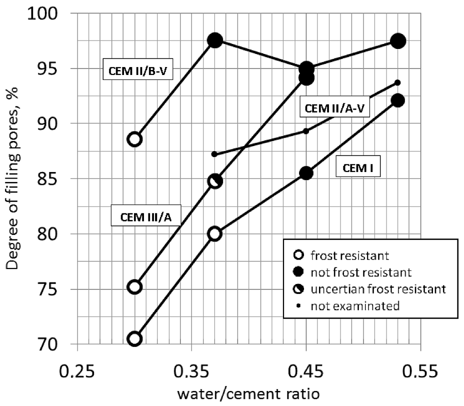

Fig. 7. Relationship between average values: the degree of filling the pores DFP, the type of cement, and the water/cement ratio

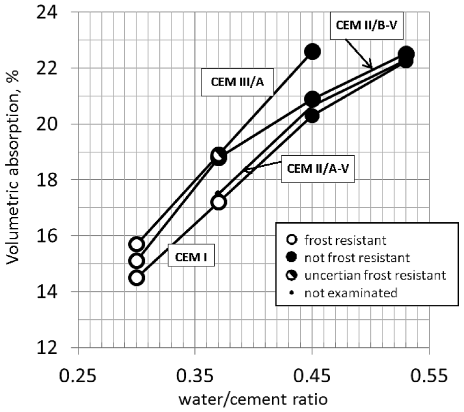

Fig. 8. Relationship between average values of volumetric absorption A_V, the type of cement, and the water/cement ratio

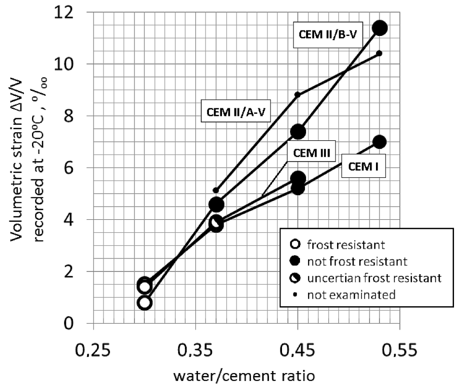

Fig. 9. Relationship between average values of volumetric strain $\Delta V/V$ recorded at -20°C, type of cement, and water/cement ratio

The analysis of the previous drawings shows that the w/c ratio is influenced strongly by the absorption of the mortar, the value of which in each case also depends on the type of cement. In Fig. 8, this relationship is clearly visible. The lowest water absorption at comparable w/c level is characteristic of mortars with CEM I, the highest of those with CEM III/A. The absorption of mortars made with cements containing fly ash is higher than in the case of the mortars with CEM I, and the more ash the cement contains the higher it is. The degree of filling pores DFP increases together with the amount of mineral additives in cement, in particular ash (Fig. 7). A similar trend is visible in the case of volumetric strain $\Delta V/V$ (Fig. 9).

Analyzing the possibility of practical use of the three indicators, it can be seen that the appropriate preparation of the mortar of w/c = 0.30 allows high frost resistance to be achieved, regardless of the type of cement. This corresponds to the conditions:

$$-A_v < 16\%,$$

$$-\Delta V/V < 2‰.$$

The role of DFP as an indicator in this case is negligible.

When w/c = 0.37 the situation changes: mortar with CEM I is frost resistant, with CEM II/B-V not frost resistant and with CEM III/A the resistance is questionable. In a close approximation it can be concluded that A_v must be less than 18% and $\Delta V/V$ below 4‰. Since both indices take values close to both frost-resistant and not frost resistant mortars, it is worth noting the role of discriminating indicator DFP. Conditions for frost-resistant mortars at w/c = 0.37 would look like this:

$$-A_v < 18\%,$$

$$-\Delta V/V < 4‰,$$

$$-\mathrm{DFP} < 80\%.$$

At values of w/c $\geq$ 0.45 sufficient frost resistance should not be expected of all the applied cements, although it is noted that during the freezing and thawing the degradation process is higher in the mortars containing composite cements. W/c ratio >0.37 in all cases indicates the need for absolute air-entrainment technology. Particularly high quality of air-entrainment is necessary when using composite cements. The issues concerning the diversity of the acceptable air-entrainment quality and the practical methods of control of the process still require additional testing.

Vacuum absorption can serve as a tool for preliminary assessment of non-air-entrained mortar microstructure in the context of its frost resistance. It can be assumed that each material aspect (cement type, w/c) corresponds to an individual boundary value A_v, below which the material does not reach the "critical level of saturation" [8], threatening its stability during freezing. At the level of the w/c = 0.30 this value was below 16%. The interpretation of this indicator requires additional comment: cyclic freezing and thawing was determined on samples soaked by an ordinary, not a vacuum method. Also the air voids remaining in the mortars, which could not be removed despite the vacuum and vibration procedure clearly distinguishes mortar of w/c = 0.30 from other mortars with higher values of w/c ratio (Table 1). For frost resistance it can act like in air-entrained cement matrix. On the other hand, volumetric strains recorded by DAVS technique (vacuum absorption) were very low: $\Delta V/V < 2‰$, indicating a relatively small expansion of the crystallizing water.

As the w/c increased, a proportional increase in the water absorption A_v was noticed in all mortars. This is an effect commonly observed in mortar and concrete technology. Interestingly, depending on the tested cement composition, an increase in the w/c caused an increasing difference in the $\Delta V/V$ deformation. At the levels of w/c = 0.45 and 0.53, all test samples were not resistant against freezing (underwent degradation) and the rate of their degradation increased together with the rates of $\Delta V/V$ and DFP. At the level of w/c = 0.37 the mortar made with pure Portland cement CEM I survived the freezing and thawing test without damage, the remaining mortar were: partially (CEM III/A) or totally destroyed (CEM II/BV). The decisive criterion for diagnostic tests, may be in this case a couple of parameters: $\Delta V/V$ and DFP. These parameters are mutually complementary. The biggest differences in the DFP caused by differences in the microstructure occur at the lowest w/c values while the value of $\Delta V/V$ are most differentiated at the highest values of w/c. In the case of tests performed it can be assumed that the mortar of w/c $>$ 0.30 are frost resistant when $\Delta V/V < 4‰$ and DFP <80%.

The advantage of the presented diagnostic tests is undoubtedly a significant shortening of the time of their performance compared to classical methods involving cyclic freezing and thawing.

4. Conclusions

The measured value of the volumetric strain of mortar samples soaked in water under vacuum may be an indicator of potential frost resistance. The value of $\Delta V/V < 2‰$ indicates the mortar of high frost resistance.

For diagnostics purposes the value $2‰ > \Delta V/V < 4‰$ needs additional supporting tool for better classification. The degree of filling pores (DFP) value below 80% indicates a potential frost resistance.

Non-air-entrained mortars with $\Delta V/V > 4‰$ are not frost resistant.

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