THE EFFECTS OF PORE STRUCTURE ON FREEZING AND THAWING DETERIORATION

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ABSTRACT

Manufacturing of concrete resistant to freezing and thawing requires an in depth understanding of the mechanisms triggering deterioration.
Despite numerous attempts, a definitive and fully explanatory model has yet to be formulated. This paper presents part of study which analyzes influence of pore structure of cement-based matrix on the frost durability of Ordinary Portland Cement mortar is analysed. An empirical investigation was carried out on five air-entrained and one non-air-entrained mortar (with water-to-binder (W/B) ratio 0.4) subjected up to 732 freezing/thawing (F/T) cycles. Various concentrations of air-entraining admixture were used to differentiate the pore-structure of mortar. The examination of the microstructure and composition of the cement paste was performed by means of Scanning Electron Microscope (SEM) and Mercury Intrusion Porosimetry (MIP). Presented results demonstrate the magnitude of alterations to pore configuration due to pure freezing/thawing and its effect on the mechanical characteristics (compressive/flexural strength). Finally, on the grounds of apparent transformation, a generic pore size distribution of frost resistant cement-matrix is proposed.

Keywords: durability, freezing and thawing, microstructure of cement-based materials.

INTRODUCTION

Application of high strength concrete is frequently based on the assumption that it is also highly durable. Knowledge of material properties accountable for its performance, especially at microstructural level, however, is still relatively poor. Ability to withstand extremely high or low temperatures is controlled by a particular set of microstructural characteristics distinctive for environmental/service conditions. The diverse nature of the phenomena has inhibited establishment of all of the mechanisms and properties responsible for such processes. Deeper understanding of the frost resistance of concrete can only be gained through an intimate knowledge at microstructural level of frost action principles in the vicinity of the solid phase of cement-based matrix [10].

Concrete, as many porous materials, absorbs and retains moisture which makes it particularly vulnerable when exposed to repeated freezing and thawing cycles (F/T). As a consequence to water expansion, the structure suffers from internal microcracking and/or superficial scaling. Although higher strengths appear to improve the freeze-thaw resistance of concrete, they cannot always guarantee sufficient performance. Even highly valuable air entrainment does not preclude the occurrence of frost damages to the concrete-made structures. The phase transition of water into ice is a continuous process dependent upon ambient conditions such as: rate of temperature changes, relative humidity, air pressure, chemical impurities in water/vapour. The temperature of transition, however, is primarily governed by microstructural characteristics of the porous body [5, 7]. Initiated within macropores growth of ice is prohibited below -78 °C in the gel pores (with their diameters below 3 nm) [3]. The size, shape and continuity of pores control the amount and the rate of water absorption. Furthermore, they control the rate at which the excessive water is expelled from the voids under progressing ice interface [9].

Morphology of concrete and its behaviour can be analysed at different levels.
Consideration of concrete as a two-phase conglomerate (cement matrix and aggregates) is inadequate and suffers from its simplicity. More advanced models distinguish three or four levels of materials structure. A three-level classification put forward by Podvalnyi is established on the basis of two-phase conglomerates: aggregates (rigid inclusions) bonded by the matrix [18]. The first level of classification–concrete, is a cement-sand mortar (matrix) with inclusions of coarse aggregates. Second level: cement-sand mortar consists of cement paste and fine aggregates. The lowest, third level comprises hydrated mass and inclusions of clinker relicts. Any structural alterations occurring at level I or II due to continuity of transitions from level to level are apparent also at level III.
In hierarchic classification suggested by Zaitsev and Witmann four levels of structure are recognized: macro-, meso-, micro- and nanolevel [22].
At the macrolevel only the largest inclusions occur with minimum linear dimensions of the representative volume element (RVE) at least four times the maximum linear grain size i.e. around 100 mm. The adequate explanation of macrostrains or macrostresses necessitates consideration of properties from the lower levels though. The mesolevel consists of inclusions of fine aggregates embedded and bonded by mortar matrix. The typical linear dimension of the RVE is approximately 10 mm. Considering durability of composites the mesolevel porosity must be taken into account. Hardened cement paste between little inclusions is considered to be the microlevel. The typical linear dimension of the RVE is around 0.5 mm, with enclosed pores of an order of 0.1 mm. Zaitsev and Wittmann believed that the microstress/microstrain relationship is nearly linear. The lowest nanolevel is comprised of hardened cement paste enclosed between little (10^{-4} mm)–capillary pores with the typical linear dimension of the RVE is $5 \cdot 10^{-4}$ mm.

Assessment of structural properties presented in this study corresponds with the three-level model. Clear physical explanation of the origins of each category and the resultant porosity evident from MIP advocated such choice. The three-level classification was also applied in studies carried out by Beddoe and Setzer [1], and by Kukko [10]. The pore size classification employed in this model is as follows:

- ► MACROLEVEL (with inclusions of coarse aggregate) air pores are larger than 10 μm in diameter,

- ► MESOLEVEL (with inclusions of fine aggregate in cement paste matrix) pores in the range between 10 μm and 50 nm,
- ► MICROLEVEL (hardened cement paste) capillary pores with diameter range from 1-50 nm (the lower limit being usually between 4-5 nm).

Type of forces acting upon pores of different size is the criterion for classification presented by the International Union of Pure and Applied Chemistry [14]:

- ► MACROPORES $d > 50\ nm$ (with forces arising from Laplace adsorption),
- ► MESOPORES $2 < d \leq 50\ nm$ (with forces arising from Kelvin adsorption). Enclose capillary pores,
- ► MICROPORES $d \leq 2\ nm$ (with forces arising from homogen adsorption).

Concrete/mortar/cement paste consists of a solid phase and air voids totally or partially filled up with water. The solid phase is the conglomerate of cement gel paste, calcium hydroxide and residuals of unhydrated cement particles. The cement gel, believed to be the most important part of the constituents, is formed by a solid part (colloidal hydration products, mostly calcium silicate) and a non-solid part–the gel pores ($0.5 < d \leq 50\ nm$). The average size of gel pores can be expressed in terms of hydraulic gradient, which is of the order of 0.75 nm [10]. The gel pores initially filled up with water, are in equilibrium with the hydration products. The volume and size of gel pores is not influenced by water to binder ratio in contrast to capillary pores. The volume of capillary pores, in contrast is greatly dependent on the water to binder ratio and the degree of hydration. For water to binder ratio lower than 0.7 the hydration process segments the capillary pores creating isolated cavities–subject to further subdivision with age. The share of capillaries in the total porosity diminishes over time with progress of hydration processes, carbonation etc. According to classical frost action theories [19] the capillary porosity is the driving factor in frost deterioration processes. They play a major role in frost resistance estimation [10]. Gel pores do not participate in development of frost defects. They contribute, however, to the generation of shrinkage forces and consequent deformations. A few-millimetres-long meso- have an adverse effect and reduce strength and elasticity of concrete [12, 15]. Pores in the range of 300 – 3000 nm have been recognised as the most important from the point of view of damage due to freezing/thawing [11]. Nevertheless, some investigations suggest, that the capillary flow takes place mainly in pores having diameters in the narrower band of 250 – 1400 nm [20]. Because the pores with diameters greater than 1400 nm do not reach a state of full saturation, they are able to accumulate volume changes without causing any damage [8]. Pores having smaller diameters (resulting from a significant effect of the friction forces) and bigger diameters (due to the effect of gravitation) are said to affect the capillary flow to a lesser degree [2, 6]. The discontinuity of a pore system is also found to be beneficial from the point of view of frost resistance as it prevents from a deep ingress of water into the structure of concrete. Bentz and Garboczi suggested that regardless of water/binder ratio and the rate of hydration, a porosity of 18% is required to provide a discontinuous system of capillaries [2]. Useful information of the overall durability is also given by the threshold width of capillary pores. It has been found that it strongly affects the permeability and diffusion phenomena within a porous cement matrix [4]. Furthermore, O'Farrell et al. formulated a hypothesis that compressive strength is insensitive to threshold diameters greater than 200 nm [17].

Since porosity reflects on the magnitude of permeability, which in turns is crucial from the point of view of durability, its estimation is absolutely necessary.
It is widely recognized, however, that it is the pore size distribution, rather than total porosity that controls durability of cementitious materials [13, 16, 21].

The aims of this study are to identify/assess microstructural properties (porosity, pore size distribution, void ratio) of air-entrained cement-based mortar subjected to extended trials of pure freezing and thawing cycles and determine the magnitude of their influence on its mechanical properties. The primary methods of data acquisition of pore structure reconfiguration utilized in this investigation were MIP and SEM. Mechanical properties assessment (flexural and compressive strength) was carried out with application of destructive testing procedures. The above parameters are established for mortar subjected to alternated climate conditions. A corresponding set of results is also determined for samples cured in laboratory for predetermined periods of time.

EXPERIMENTAL INVESTIGATION

Materials and Applied Methodology

For the purpose of this experiment six different mixes of mortar were designed. The Ordinary Portland Cement was mixed at 1:1 ratio with fine sand (majority of particles smaller than 0.6 mm). Throughout the investigation an even water to cement ratio of 0.4 was maintained. To ensure adequate variation in the microstructure the air-entraining agent complying with BS 5075 Part 2 was used at various concentrations: 0, 4, 7, 10, 13 and 16% (by weight of cement content). The mix proportions and applied nomenclature is presented in Table 1.

Table 1. Cement mortar composition.

Mix code	**R-Reference**	**A**	**B**	**C**	**D**	**E**
Water/Cement	0.4	0.4	0.4	0.4	0.4	0.4
Sand/Cement	1:1	1:1	1:1	1:1	1:1	1:1
Air-entraining agent [%]	0	4	7	10	13	16

The mortar prisms (160 x 40 x 40 mm) after curing for 28 days in laboratory conditions (50±5% RH and 23±2deg C) were exposed to freezing and thawing cycles with ambient temperature decreasing from 20 to -20 deg C. The minimum temperature recorded in the centre of the sample was -17.8 deg. C. The programmed relative humidity in the Climate Control Chamber was maintained at the level of 80% at positive temperatures throughout the whole experimental procedure. Further modification of the microstructural characteristics, namely porosity, pore size distribution and threshold diameter was achieved

by adoption of regular assessment (every 3 months throughout 18 month period) of the samples stored in the alternated conditions concurrently with laboratory cured material.
The following results have been obtained for samples of: 28 days, 1, 3 and 6 months of age (corresponding to 122, 366 and 732 F/T cycles respectively).
The analysis of mechanical properties has been performed using standardized procedures for compression and flexural tests; BS 1881-119:1983 and BS 1881-118:1983 respectively. Microstructural examination has been carried out with the use of Porosimeter Autopore II 9230 by Micromeritics with a pressure range up to 60000 psi. The Scanning Electron Microscope - Leo 1530 further advanced the micro-scale analysis.

RESULTS AND DISCUSSION

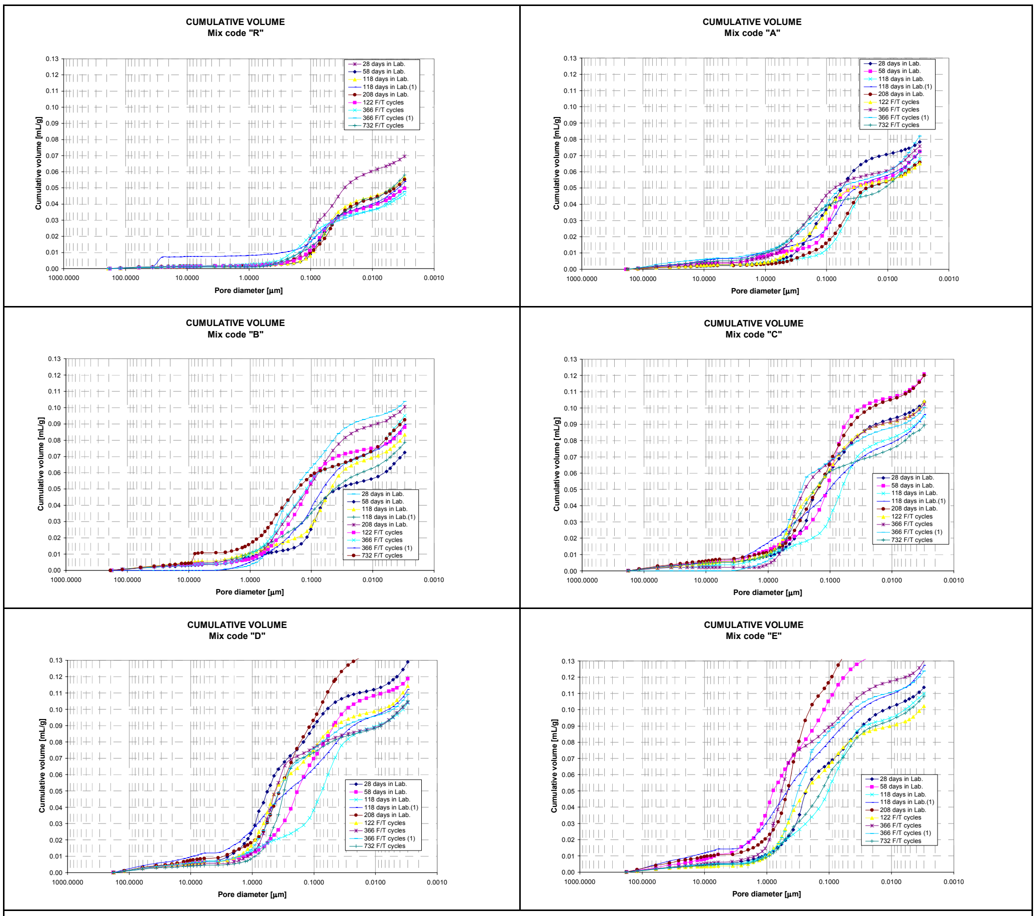
Figure 1 documents the alterations which occurred in the structure of the air-entrained cement mortar subjected to a total number of up to 732 F/T cycles. Significant alterations due to differentiated levels of air-entrainment and curing regimes are apparent from cumulative intrusion curves. The trends of pore reconfiguration are not uniform however. The total porosity obtained for mortar coded as: R, A, B (without air-entrainment and with the lowest applied dosages) is subject to gradual reduction after initial curing in laboratory conditions for 28 days. The other mixes, with considerably higher content of air-entrainer performed in completely opposite manner. An increase in total porosity was observed over time. An overview of porosity accompanied by adjustments at the microlevel level–spacing between C-S-H gel surfaces–synonymous to hydraulic diameter is presented in the Figure 2.

An important feature consistent for mortars of all kinds, regardless of curing conditions, is the boundary of 3 μm beyond which there is no substantial traces of the air-entraining agent. It is important to notice that there are very little changes observed for all types of tested mortar in pore size distribution above 3 μm.

Higher content of air-entraining admixture tend to promote formation of finer pore system, with higher volumes of pores especially with diameter below 100 nm. As a result, considerable reduction in mechanical properties is observed for samples containing artificially entrained pores (see Fig. 4). The higher the concentration of air-entraining admixture the greater appears to be the volume of voids in the range from 1000 to 100 nm. A clearly pronounced peak corresponding with diameter band breadth 600-200 nm is noticeable in the total volume intrusion curves obtained for samples D and E (see Fig. 1). Presented in Figure 3 evaluation of pore size distribution derived for samples of all kinds suggests considerable fragmentation of capillary pores. Following reduction in total porosity (approximately 40%), recorded for samples subjected to freezing and thawing, can be translated as an outcome of much more advanced hydration, when compared with laboratory cured material due to presence of extra moisture.

The analysis of the total volume intrusion (TVI) curves conveys transitions of microstructure occurring over the time. It is then apparent that the TVI curves attain the

"***S***" shape which is even more transparent for samples subjected to a greater number of freezing and thawing cycles/more mature. Despite the fact, that the analysis needs further validation (with results obtained for samples subjected to over 2100 freezing and thawing cycles) a preliminary formulation of a generic pore size distribution curve has been attempted. The suggested boundaries of pore size distribution of a frost resistant mortar are presented in Figure 6. Such conclusions were drawn on the basis of available up to date results and are subject to further evaluation. Nevertheless, considering that most currently used tests evaluate the frost resistance on the grounds of only 300 F/T cycles the authors believe that only some aspects of the proposal might need amendments. The width of the ***S***-shaped curve, as well as the angle of the tangent are of great importance. The maximum pore diameter corresponding to the cross with an upper limit tangent should also be carefully considered. It is assumed that in order to provide adequate resistance to F/T cycles, it should be below, rather than above the diameter of 1 μm.



CUMULATIVE VOLUME
Mix code "R"

CUMULATIVE VOLUME
Mix code "A"

CUMULATIVE VOLUME
Mix code "B"

CUMULATIVE VOLUME
Mix code "C"

CUMULATIVE VOLUME
Mix code "D"

CUMULATIVE VOLUME
Mix code "E"

Figure 1. Cumulative Volume and Total Volume Intrusion curves acquired for individual mixes at varied stage of maturity/number of F/T cycles.

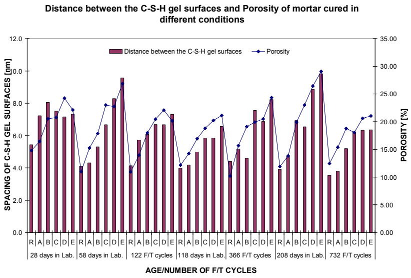


Figure 2. Total porosity and spacing between C-S-H gel surfaces determined for air-entrained mortar at different stages of maturity.

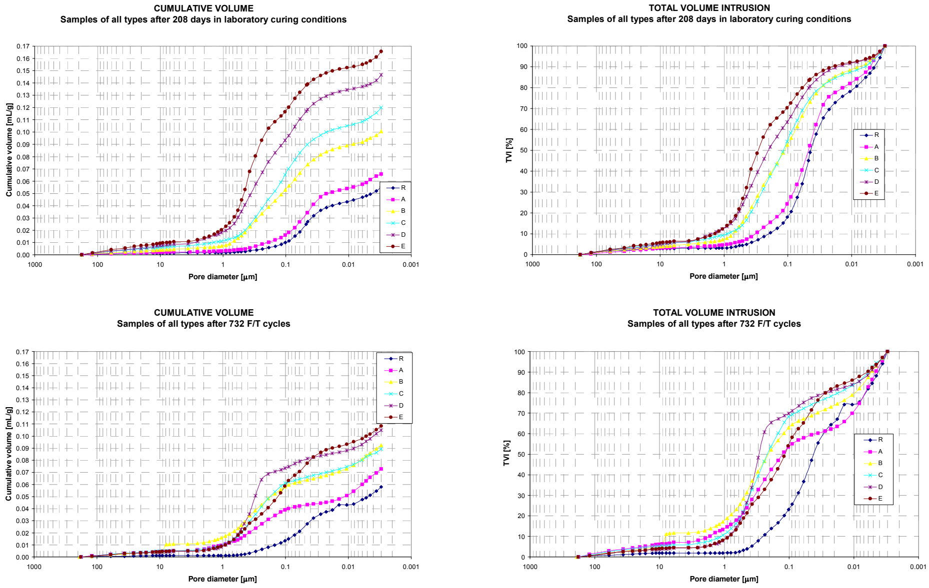


Figure 3. Cumulative Volume curves acquired for samples of all types (R, A, B, C, D, E) at the age of 208 days/after exposure to 732 F/T cycles.

Although an absolute statement on the role of gel pores (*d<3 nm*) in the propagation of frost deterioration is impossible in the light of the presented results, their contribution, if any, may emerge to be irrelevant. It is believed that rearrangements in the pore structure at greater scale results in frost defects. Considering threshold diameter (Figure 5) it is apparent that compressive strength is insensitive to it above approximately 250 nm. The obtained value is very close to that found by O'Farrell (200 nm). An attempt to find correlation between flexural strength and the threshold diameter was unsuccessful. There is no evident relationship between flexural strength and the threshold diameter which shapes permeability of porous materials.

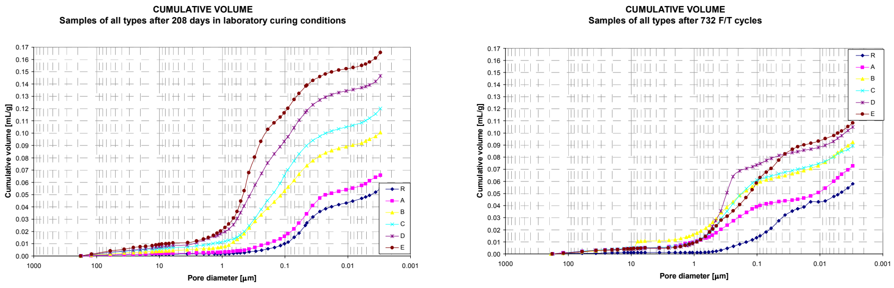


Figure 3. Cumulative Volume curves acquired for samples of all types (R, A, B, C, D, E) at the age of 208 days and after exposure to 732 F/T cycles.

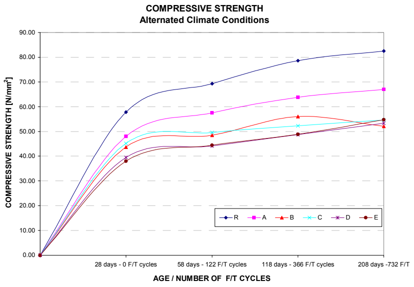


Figure 4. Mechanical characteristics of all types samples exposed to F/T cycles.

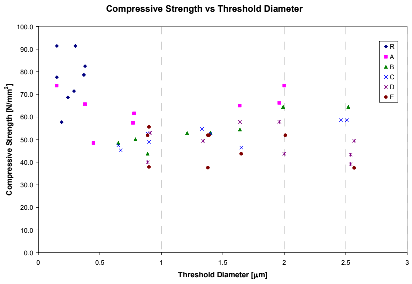


Figure 5. Relationship between Threshold Diameter and Compressive strength for air-entrained mortars.

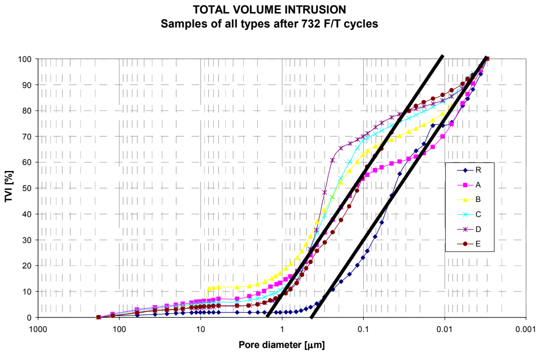


Figure 6. Lower and Upper limits of pore size distribution curve of mortars of increased frost resistance.

CONCLUSIONS

On the grounds of the presented results and analyses the following conclusions can be drawn:

- Alterations induced into the structure due to pure freezing and thawing are concentrated in the micro and mesolevel. There is no evidence suggesting spread over onto the macrolevel.
- The influence of air-entraining admixture is negligible above diameters of 3 µm.
- Pore diameters below 250 nm (threshold diameter) impose an effect on compressive strength. No relationship between threshold diameter and flexural strength, however, has been found.
- A model facilitating an increased resistance to pure freezing and thawing cycles has been formulated. It is believed that the reengineering of pore size distribution curve to comply with the set up limits shall increase resistance to freezing and thawing cycles.

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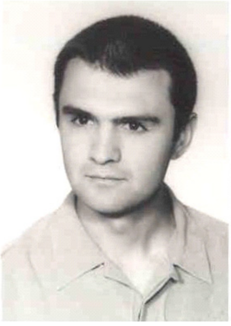

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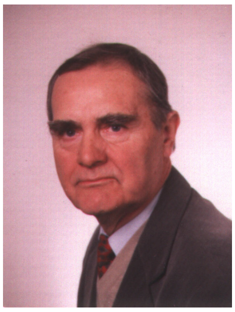

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