Frost resistance of rock materials

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HIGHLIGHTS

- Volumetric strain of rock material due to ice formation is presented.
- The coefficient α_r defining the relative content of freezing water is determined
- A potential range of rock frost resistance is determined on the basis of coefficient α_r and volumetric capillary absorption.

ARTICLE INFO

ABSTRACT

A precise classification of rock raw materials with respect to frost-resistance is still an issue. The knowledge of the rock's origin and its mineral composition and structure is not an effective diagnostic tool. This paper discusses the possibility of applying the capillary absorption and volumetric strain of a frozen rock sample for diagnostic purposes. Twenty one different volcanic, metamorphic and sedimentary rocks were used in the study. The strain caused by the phase change of water into ice was determined by the Differential Analysis of Volumetric Strains (DAVS). The following basic physical properties were also examined: porosity, absorbability, density, capillary absorption and frost resistance determined by the freeze-thaw testing. The mineral composition and microstructure of rocks were investigated using the X-ray method, derivatographic test, and microscopic observation. The (α_r) coefficient has been proposed, which in certain circumstances can be considered as a material constant, defining the ratio of the mass of water causing the rock strain during the phase change to the total volume of water in the material pores. The diagnostics criteria enabling the frost-resistance prediction have been presented.

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1. Introduction

Rock durability during freezing is affected by: the total water content of the material, the ratio of water volume to the total pore volume, the ratio of water volume to the volume of water determined under maximum absorption conditions, and the ratio of the freezable water volume to the total water content of the material. The intensity and extent of destructive processes are modified by other factors: rock mineral composition, skeletal strength, presence of ions dissolved in water as well as pore geometry and interconnections. The genesis of rocks and the extent of their transformations in time resulted in considerable rocks diversity in terms of the above mentioned factors. They, in consequence, have possibly the most varied properties with regard to water absorption and freezing effects among the classical materials used in construction. Water-soaked rocks may behave differently from each other during cooling, despite similar general absorbability,

or the freezing effects may be similar in rocks of varied absorbability. Authors believe that a special role in determining rock frost-resistance is played by the freezable water content at operating temperatures and its ratio to the total water content of the material. The operating temperatures are thought by the authors to be those below 0 °C, ranging to −10 °C for milder regions, and to −20 °C for colder regions. In this context, it is interesting to compare various capillary-porous building materials. Table 1 shows the estimated values of the ratio of the frozen water weight to the total evaporable water content determined for different materials.

Table 1 provides a specific array of different materials. Materials with cement matrices are characterized by the lowest values of the m_i/m_e index. This group of materials has been the subject of intensive research for many years. It is known that in addition to the extremely developed surface area these materials are significantly sensitive to curing conditions, especially to changes in humidity and temperature. The transformation of their microstructure is a well-known phenomenon, including important pore characteristics such as the size and connections. It is manifested in the form

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Table 1
Samples of the estimated values of the m_i/m_e index Table 1.

Material	Approximate relative amount of ice (m_i/m_e), %	Temperature, °C	Test method	Source of information
Concrete w/c = 0,4–0,5 (virgin)	10–15	−20	DSC	Johannesson [1] (2010)
Concrete w/c = 0,4–0,5 (dry + vacuum saturated)	25–35	−20	DSC	Johannesson [1] (2010)
Concrete w/c = 0,4–0,5 (virgin)	9–15	−15	–	Vuorinen [2] (1973)
Concrete w/c = 0,4–0,5 (dry + vacuum saturated)	60	−15	–	Vuorinen [2] (1973)
Cement mortar (28 days) w/c = 0,3–0,45 (dry + vacuum saturated)	4–38	−20	DAVS	Rusin et al. [3] (2007)
Cement mortar (180 days) w/c = 0,37–0,53 (virgin – stored in water)	9–25	−25	DAVS	Świercz [4] (2012)
Cement paste (500 days) w/c = 0,4–0,5 (virgin – stored in water)	0–8,6	−20	DSC	Carl le Sage de Fontenay, Sellevold [5] (1980)
Ceramic brick	90	−20	DAVS	Rusin et al. [6] (2013)
Silicate brick	77	−20	DAVS	Rusin et al. [6] (2013)
Rocks (21 types)	18–94	−20	DSC	Rusin et al. [7] 2014

*) m_i/m_e – a unit of freezable water weight to the total evaporable water weight.

of the changes in general absorbability, the freezable water content etc. In contrast to cement matrices, most rock materials with generally lower overall porosity contain more pores capable of retaining freezable water under operating conditions. It can be assumed that the role of nanopores in rocks is smaller or considerably smaller than in cement matrices. Only in the case of rocks with the finest pores the value of m_i/m_e index is comparable to that of cement paste. Majority of rocks are characterized by a much higher m_i/m_e index, often close to that of ceramics. At the same time the rock materials are stabilized in terms of microstructure and the strength of their skeletons is generally higher than that of the cement matrix skeleton.

Many studies have been devoted to the behavior of water dispersed in the pores of capillary-porous materials. It is known that in the pores with a cross-sectional dimension exceeding 50 nm (macropores as defined by IUPAC), the majority of the water volume behaves like bulk water, apart from the film remaining in direct contact with the pore walls. The relative physical contribution from interfacial energy increases as the pore size becomes smaller and causes the phase equilibrium temperature to decrease as the pore size diminishes (Gibbs–Thomson formula). Approximately the temperature of −25 °C corresponds to the pore radius of approx. 0.004 μm. For pores above 50 nm water-ice phase equilibrium temperature depending on the radius of curvature between non-freezable water and ice, ranges from 0 °C to approx. −2.5 °C. In fact, the initiation of freezing starts after certain supercooling, which may account to several degrees Celsius. As a result, the water in the macropores freezes almost simultaneously. As mentioned before, due to the interaction of surface forces the adsorbed water adhering immediately to the surface of the pore walls is to a large extent physically restructured and differs from free water. Its molecules are not subject to phase change into ice at operating temperatures. For pure water, the thickness of the unfrozen layer on the pore surface is estimated to be app. 0.8 ± 0.1 nm, but it rises to 1.0–1.2 nm for limewater [8].

The additional effect of decreasing the m_i/m_e index during freezing is related to the behaviour of water in interconnected mesopores (pores with cross-sections below 50 nm according to IUPAC) of various dimensions. The analysis of the heat flux hysteresis associated with the formation of ice in the rock pores during cooling and its melting during heating, recorded by DSC, shows

that significant differences in the weight of the water undergoing the phase change can occur at certain comparable temperatures – Fig. 1.

It is believed that, unlike in macropores, water cannot freeze due to spontaneous nucleation in isolated pores with a cross-section smaller than 50 nm. The contact with the formed ice is necessary, which is only possible when the water freezes in the connection pores of smaller diameter. In order for this to occur the temperature must drop to the level corresponding to the freezing temperature specific to the pores with a smaller cross-section. During thawing this phenomenon does not occur. Ice melts gradually starting with the smallest pores and then in increasingly larger ones. This results in the differences in the recorded values of the heat fluxes of the frozen and thawed samples (Fig. 1).

It can be assumed that the described effects jointly determine the ratio of freezable water to the total content of water evaporable at specified operating temperatures. As long as the picture of the relations between the phenomena occurring on the inner surface of the pores and the stability of capillary-porous materials during freezing is not clear, the methods based on the generalized observations of the measurable effects of the water phase change are useful for diagnostic purposes and practical classification of rocks. The m_i/m_e index seems to be a potentially interesting tool. According to a study published by Sun and Scherer [8], the calorimetric
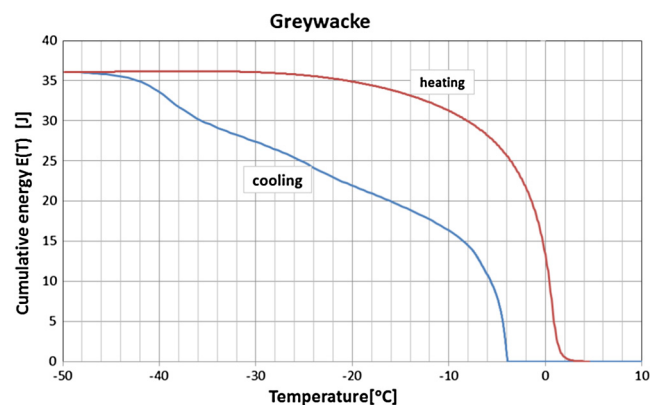
Fig. 1. Hysteresis of the heat flux associated with ice formation and thawing [7].