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Evaluation of brick resistance to freeze / thaw cycles according to indirect procedures

Authors:

Assist.Prof. Ivanka Netinger, PhD. CE
University J. J. Strossmayer in Osijek
Faculty of Civil Engineering of Osijek
nivanka@gfos.hr

Martina Vračević, M.Sc. CE
Institut IGH
Regional Centre of Osijek
martina.vracevic@igh.hr

Prof. Janja Ranogajec, PhD. Tech.
University of Novi Sad
Faculty of Technology
janjar@uns.ac.rs

Snežana Vučetić, B.Sc. Tech.
University of Novi Sad
Faculty of Technology
snezanap@uns.ac.rs

Preliminary note

Ivanka Netinger, Martina Vračević, Janja Ranogajec, Snežana Vučetić

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The brick resistance was tested in the paper by direct method, and according to some indirect procedures presented in international literature and regulations. Requirements for indirect estimation of brick resistance to freeze / thaw cycles set by Canadian and U.S. standards have proven to be inapplicable, and the same applies to estimation based on pore structure. A connection between absorption/ desorption of water and brick resistance to freeze/thaw cycles was observed.

Key words:
resistance to freeze/thaw cycles, compressive strength, boiling absorption, water absorption, saturation coefficient, pore structure, absorption/desorption of water

Prethodno priopćenje

Ivanka Netinger, Martina Vračević, Janja Ranogajec, Snežana Vučetić

Procjena otpornosti opeke na cikluse smrzavanja/odmrzavanja prema indirektnim postupcima

U radu je ispitana otpornost opeke direktnim postupkom te nekim indirektnim postupcima sukladno svjetskoj literaturi i propisima. Zahtjevi za indirektnu procjenu otpornosti opeke na cikluse smrzavanja/odmrzavanja postavljeni prema kanadskim i američkim normama su se pokazali neprimjenjivima kao i mogućnost ocjene na temelju strukture pora. Uočena je povezanost sposobnosti upijanja/otpuštanja vode i otpornosti opeke na cikluse smrzavanja/ odmrzavanja.

Ključne riječi:
otpornost na cikluse smrzavanja/odmrzavanja, tlačna čvrstoća, upijanje vode pri kuhanju, vodoupojnost, koeficijent zasićenja, struktura pora, upijanje/otpuštanje vode

Vorherige Mitteilung

Ivanka Netinger, Martina Vračević, Janja Ranogajec, Snežana Vučetić

Ermittlung des Frost-Tau-Widerstands von Ziegelstein durch indirekte Verfahren

Der Widerstand des Ziegelsteins ist durch das direkte Verfahren und durch in der Literatur und in Verordnungen vorhandene indirekte Methoden ermittelt worden. Die Anforderungen der indirekten Methode des Kanadischen und des Amerikanischen Standards, sowie die auf der Porenstruktur basierte Beurteilung, haben sich als nicht anwendbar gezeigt. Ein Zusammenhang des Frost-Tau-Widerstands von Ziegelstein mit der Absorption/Desorption von Wasserbeständen ist festgestellt worden.

Schlüsselwörter:
Frost-Tau-Widerstand, Druckfestigkeit, Kochwasseraufnahme, Wasseraufnahme, Sättigungskoeffizient, Porenstruktur, Absorption/Desorption

1. Introduction

Clay brick is one of the oldest construction products highly popular even today because of its mechanical properties, availability, and a relatively low price. Clay brick has a pleasant colour and it can be produced with various surface textures, which also makes it desirable from an architectural point of view. Nowadays, when the use of concrete is dominant, clay is still the material of choice for construction of smaller structures in the eastern Slavonia, and also elsewhere for the renovation of historic buildings. Whether the brick is used as an independent material for construction of structural elements, or as a material for revetment of another structural element, deterioration may seriously jeopardise the stability of the structures. This makes durability one of main requirements that are set for brick as a construction material. Main factors leading to deterioration of brick properties are the crystallization of salt and the cycles of freezing and thawing [1]. In their structure, porous construction materials almost always contain some amount of moisture, i.e. of physically bound water. The presence of bound water directly affects brick properties such as the strength, shrinkage/expansion, water vapour transmission, and resistance to external conditions. The capacity of materials to accumulate moisture within the porous system is one of the basic parameters influencing their consistency but also their use in masonry [2].

The crystallization of salt takes place if a construction material contains soluble, hygroscopic salts in its structure. These salts are many times more hygroscopic then the brick itself, and so the moisture content in the material increases in proportion to the content of salt and the increase of moisture in the air. There are several ways in which salt can penetrate into the wall: it may be transported from soil by capillary moisture, initial salt may originate from construction material itself (before the material is placed in the wall), salt may come from Portland cement with which the brick is bound, it may arrive via aerosol from polluted air, or may also come from winter road maintenance. It may be of animal origin, or may be due to metabolic activity of microorganisms, and may also come from salts from inadequate preservation substances. Initial salts, i.e. salts contained in a construction material prior to its placing, are most frequently found in some types of brick produced from clays rich in alkaline and alkaline earth metals (young clays rich in mica). Once they reach the wall, salts migrate with water toward the surface during the wall drying process, and by the evaporation of moisture they remain on the wall surface where they concentrate and crystallize, thus forming light stains on the wall. This phenomenon is called efflorescence. During alternating drying and wetting cycles, the salt concentration increases, the volume of crystals attains the volume of pores (voids) in the material. Crystallization pressures within pores increase and are transferred onto pore walls. These pressures may attain very high values that exceed the strength of the construction material, which results in cracking, spalling and, as a final consequence the surface of the masonry structure turns into dust [3].

The freezing action in brick occurs when the temperature falls bellow zero at which point the process of water freezing in brick is initiated. The expansion of ice results in the increase of stresses within the material. The intensity of stress caused by freezing depends on the quantity of pores in the material and on the level of its saturation [1]; a greater proportion of pores causes greater stress while in case of small saturation level the stress is negligible because the free space in pores allows for water expansion during the freezing. If the stress generated exceeds the brick strength, the brick will be damaged due to repeated freezing and thawing cycles.

According to European standards, the durability of bricks is checked by verifying the initial salt content, HRN EN 772-5:2003 [4], and by verifying resistance to freezing/thawing cycles, HRS CEN/TS 772-22:2006 [5]. However, in addition to the mentioned direct method for verifying brick resistance to freezing/thawing cycles, the international literature also proposes some indirect procedures and limit/critical values for the assessment of brick resistance to freezing and thawing. The processing of raw material is specified so that a sufficient durability can be achieved. In practice, it would be advisable to use both methodologies (direct and indirect) and to correlate raw material properties with manufacturing methods [6]. These indirect procedures, and the influence of characteristics of raw materials and manufacturing methods on brick quality, are described below. In the experimental part of the paper, the resistance to alternating freezing and thawing of bricks produced by various procedures and fired at various temperatures is estimated using indirect and direct methods, and then conclusions are made regarding their applicability.

2. Parameters for estimating brick resistance to alternating freezing and thawing

Parameters for estimating brick resistance to alternating cycles of freezing and thawing can be either direct or indirect. Indirect parameters for estimating durability of bricks are: compressive strength, pore structure, saturation coefficient, initial rate of water absorption, and water absorption. The direct parameter, which is the only parameter for estimating brick durability according to European standards, is its direct resistance to freezing and thawing cycles. The testing of the brick's direct resistance to freezing and thawing cycles is specified in HRS CEN/TS 772-22. It implies the construction of a test wall (0.25 square meters in area) made of bricks, with joints made of foam rubber of rapid hardening mortar. The test wall is immersed in water until full saturation. Then it is taken out of water and placed into a testing device where the wall is subjected to alternating freezing and thawing. In the testing device, the wall is sprinkled with water for one minute at the temperature of 0 °C, and then the temperature in the testing device is reduced to -15 °C and the sample is kept 90 minutes at that temperature. This constitutes one freezing/thawing cycle which is repeated for 100 times. The objective

Table 1. Criteria for acceptance of brick resistance to freezing/thawing cycles in severe conditions of exposure [8]

Standards		Lowest required compressive strength [MPa]	Maximum allowed absorption at the 5-hour boiling [%]	Maximum allowed saturation coefficient	Maximum allowed 24-hour water absorption [%]
CSA – Canadian standards	individual bricks	17,2	17,0	0,78	8,0
	mean value for five bricks	20,7	-	-	-
ASTM – American standards	individual bricks	17,2	20,0	0,80	-
	mean value for five bricks	20,7	17,0	0,78	-

is to test brick resistance to freezing/thawing cycles in severe conditions. After the end of this testing, the level of damage, if any, is estimated. This verification of resistance to freezing/thawing cycles according to HRS CEN/TS 772-22:2006 is a time-consuming and demanding procedure. For that reason, some faster indirect procedures for estimating this property of bricks are presented below.

2.1. Compressive strength

The compressive strength of material is indirectly related to its resistance to freezing/thawing cycles [7]. In fact, a stress is generated in material during conversion of water into ice, and the material uses its own tensile strength to withstand such stress. A high tensile strength of material also implies a high compressive strength, and so it can be concluded that the greater the compressive strength of material, the higher its resistance will be to freezing/thawing cycles. As the compressive strength is inversely proportional to the total porosity of material, a low strength brick will also be characterized by greater porosity, which will make it susceptible to damage during the freezing/thawing cycles. The lowest required compressive strength of brick, as specified in the US and Canadian standards [8], is presented in Table 1.

According to the US and Canadian standards, the brick that does not meet the requirements specified in Table 1 (water absorption, absorption after 5 hours of boiling, and saturation coefficient), can be subjected to direct testing to check its resistance to freezing/thawing cycles. One freezing/thawing cycle lasts about 24 hours. Bricks are exposed to 50 freezing/thawing cycles, or are tested until full destruction. If the loss of brick mass after 50 cycles is within allowable limits, and if no cracks have occurred, the brick is considered resistant to freezing/thawing cycles.

2.2. Porosity and pore structure

It is known that durability is considerably affected by pore size and spacing between pores [9, 10]. According to the cited literature, pores larger than 1 μm (large pores) are easily filled with and emptied of water. That is why they improve the durability of bricks [9, 11]. According to [9] small pores (less than 0.1 μm in size) do not significantly affect the brick's resistance to freezing/thawing cycles as water freezes in such pores only at very low temperatures. However, during formation of ice nucleus water may move from small pores toward the nucleus and the size of the ice can increase in large pores and pore walls may be affected by stress (ice-lens mechanism) [12]. This mechanism is based on the difference in free energy between unfrozen water in small capillary pores and ice in large pores, which enables transfer of water toward the zone in which the ice already exists. Medium size pores (from 0.1 μm to 1 μm) are most susceptible to the freezing/thawing action and to soluble salt action. It can therefore be concluded that the porosity and distribution of pore sizes constitutes a critical factor for the durability of construction materials, and hence also of bricks [7, 13]. Consequently, during production of bricks, the objective is to obtain the smallest proportion of medium size pores, and the maximum proportion of large pores.

2.3. Saturation coefficient

The term saturation coefficient is used for denoting the quantity of absorbed water which will not cause damage to material due to the freezing/thawing action. The saturation coefficient shows the relationship between the quantity of absorbed water when the sample is gradually immersed in water under normal atmospheric pressure in the period of 24 hours, and the quantity of water that has been absorbed by the sample after 5 hours of boiling. In simpler terms, the saturation coefficient defines the ratio of pores that are easily filled with water to the total volume of pores. Taking all this into account, the saturation coefficient can be regarded as the first indicator of durability properties, i.e. it is the indication of the free space in pore volume that remains once the pores are filled with water, which can be used to accommodate water volume created by freezing. According to [9], the saturation coefficient can be related to the size of pores, and is proportional to the quantity of pores of medium radius. In addition, in case of a structure with a great number of large pores, the saturation coefficient increases while with a great number of fine pores it decreases. Although the maximum allowed saturation coefficient, the so called "critical" saturation coefficient, by which the resistance to freezing/thawing cycles is ensured, depends on the characteristics of used raw material and on the method of brick manufacturing (and consequently ranges between 0.75 and 0.8 [9, 10]), the US and Canadian standards [8] specify uniform values (as shown in Table 1). Considering the mathematical connection between the saturation coefficient and water absorption, bricks have to meet only one of these two criteria.

2.4. Initial rate of water absorption

Although the European method for determining the initial rate of water absorption is specified in HRN EN 772-11:2011 [14], it does not define - in relation to this property - the limit that will ensure sufficient resistance of brick to freezing/thawing cycles. The relationship between the initial rate of water absorption and saturation coefficient is studied in [9] and it was determined that an increase in saturation coefficient is proportional to an increase in initial rate of water absorption. The level of correlation between these two parameters is a function of homogeneity of raw material and is therefore more pronounced in case only one raw material is used, than in case when several raw materials are mixed. In addition, the correlation of saturation coefficient and water absorption is more pronounced for the duration of one hour than the correlation of saturation coefficient and water absorption for the duration of one minute, as the latter correlation can be affected by the surface texture of the sample. Greater water absorption rate over time should point to a greater proportion of large pores, and hence to a greater resistance to freezing/thawing cycles. Consequently, a greater drying rate should also point to a greater proportion of large pores.

2.5. Water absorption

The European method for the determination of water absorption is described in HRN EN 772-21:2011 [15]. However, the limit that will ensure sufficient resistance of brick to freezing/thawing cycles is not defined for this property. The water absorption value for bricks greatly depends on the raw material used for their fabrication, and so this value is larger in case of bricks made of clay containing a higher proportion of CaO [9, 16]. A greater water absorption should point to a higher proportion of greater pores that are more easily filled with water, and hence also to a greater total porosity of brick. The resistance to freezing/thawing cycles is a function of distribution of pore sizes and their spacing.

3. Influence of Manufacturing method on the resistance of bricks to freezing/thawing cycles

3.1. Influence of raw material

According to proportion of mineral components, clays can be divided into: non-carbonate clays, with small proportion of carbonates and great proportion of quartz (over 50 %), and carbonate clays, with the proportion of carbonates between 15 % and 30 %, and with a small proportion of quartz (less than 15%). Non-carbonate clays contain a greater proportion of SiO_2 and Al_2O_3 in their chemical composition, while carbonate clays have a higher proportion of Ca and Mg [17]. The limit by which clays are described as either carbonate or non-carbonate according to their CaO content greatly varies depending on literature consulted. Thus for instance in [18] carbonate clays are clays containing more than 6 % of CaO, while according to [19] carbonate clays are those with more than 16 % of CaO. Some conclusions about the resistance of bricks to freezing/thawing cycles can already be made on the basis of their mineralogical or chemical composition. Thus clays with a smaller proportion of $CaCO_3$ in their mineralogical composition will enable greater resistance to freezing/thawing cycles [20]. If the resistance is estimated according to chemical composition, then better resistance will be enabled by clays with a smaller CaO content [21]. In fact, in case of clay with a higher CaO content, carbonates disintegrate at higher temperatures thus increasing overall porosity and reducing resistance to freezing/thawing cycles [10]. In the presence of water, the calcium oxide that did not enter into reaction with the alumino-silicate phase will convert into the portlandite $Ca(OH)_2$, which can later be converted into $CaCO_3$ due to presence of CO_2 in the atmosphere. This will in turn result in the increase in volume of this product and in efflorescence of lime which will additionally increase the level of porosity. In order to prevent lime efflorescence, the brick made of carbonate clay should be immersed in water for a period of two hours immediately after firing [22]. It is assumed that an abundant quantity of water will rinse the CaO and reduce local appearance of portlandite. Despite smaller resistance of bricks made of carbonate clays to freezing/thawing cycles as related to bricks made of non-carbonate clay, it should be noted that carbonate clays provide bricks with greater compressive strength at lower firing temperatures [22]. In addition, it is much easier to control the firing temperature of carbonate clays as the carbonate clay morphology does not change over a wide range of temperatures. Furthermore, the temperature and atmosphere in the kiln exert a smaller influence on the final colour of bricks made of carbonate clay, as compared to non-carbonate clay [22]. Besides the influence of chemical/mineralogical composition of clay, the dwell time of clay after excavation has also proven to be important for brick resistance to freezing/thawing cycles. According to [23], longer dwell time results in better brick resistance to freezing/thawing cycles.

3.2. Influence of manufacturing method

Normal bricks used for construction of buildings and other man-made structures are mechanically made by extrusion. However, by their dimensions and shape these bricks are not appropriate for the repair of historic buildings which is why smaller series of hand-made bricks are made for this purpose in specialized manufacturing units. The basic difference between the industrial and hand-made production is in the porosity of

Table 2. Results obtained by testing particle size distribution of raw materials

Raw material	Description of particles (shape, hardness)	Particle size [mm]	C_u	C_c	G [%]	S [%]	M [%]	C [%]
● Grabovac (Kuševac) - **D**	rounded, hard and durable	0,85	-	-	0,00	4,27	51,38	44,35
○ Dren (Jarmina) - **V**	rounded, hard and durable	0,43	-	-	0,00	3,29	50,36	46,35
■ Mixture - **M**	rounded, hard and durable	0,85	-	-	0,00	2,79	51,35	45,86
Marks used: C_u - coefficient of uniformity, C_c - coefficient of curvature, G - gravel, S – sand, M – silt, C – clay								

the resulting brick. The total pore volume is greater in case of industrial-made bricks as compared to hand-made bricks. In addition, pores varying from 0.1 μm to 1 μm (medium pores) are generally formed in case of industrial production [24]. Pores obtained in this way are parallel to the direction of extrusion of the raw material, they are horizontal and are not visible at the surface of the product, converting the homogenous raw material into an anisotropic final product. The result is a product characterized by poorer resistance to freezing and thawing processes. In case of manual production, the distribution of pore generally varies from 0.1 – 10 μm [25] (with smaller proportion of pores between 0.1-1 μm interval compared to machine-produced bricks). The pores are uniformly distributed along the cross-section, which results in smaller deviations of properties of the final product, and hence in greater durability.

3.3. Influence of firing temperature

In addition to manufacturing procedure, the pore size and pore system to be formed in the brick is also affected by the brick firing temperature. According to [21], the greatest quantity of pores 0.1-0.5 mm in radius and pores 100 mm in radius are formed in samples fired at 900 °C. Mostly pores 1-2 mm in radius are formed at 1000 °C, with the simultaneous reduction in the quantity of pores 100 mm in radius. At 1100 °C, the growth of pores 1-2 mm in size suddenly reduces, while at 1200 °C the quantity of pores measuring 0.1-0.5 mm in radius increases. The influence of firing temperature on the pore structure also depends on the chemical composition of materials. In case of clay with a higher CaO content the total porosity increases with an increase in temperature, while in case of clay with a lower CaO content the situation is quite the opposite due to presence of alkali components [10]. According to [22], carbonate clays will generate the highest proportion of large pores (and hence the best resistance to freezing/thawing cycles) at the temperature of 1100 °C, while non-carbonate clays will obtained this at the temperatures from 1000 to 1100 °C. Bricks produced with clay of a higher $CaCO_3$ content will have greater water absorption at the same firing temperature [16].

4. Experimental analysis

In the experimental part of the paper, bricks were produced of the locally available raw material using two different shaping methods (manual and mechanical), and the firing was conducted at two temperatures (1000 and 1050 °C). Considering the previously described effect of the size of pores on the resistance of bricks to freezing and thawing cycles, different manufacturing methods and different firing temperatures were used so as to obtain different size and structure of pores, and to establish the relationship between the pore structure and other parameters that are used in estimating resistance of bricks to freezing/thawing cycles. This approach was adopted in an attempt to find alternative ways for estimating brick resistance to freezing/thawing cycles that would be less time consuming, simpler, and less costly compared to the direct procedure.

4.1. Properties of raw material

Raw material from clay pits situated in eastern Slavonia was used for the preparation of the samples: Grabovac (Kuševac), sample designation "D", Dren (Jarmina), sample designation: "V", and the 50:50 mixture of these two materials, sample designation: "M". The raw material is mechanically-homogenized, and "prepared" in order to obtain sufficient quality for a uniform shrinkage and required plasticity. Properties of raw material are presented in Figures 1 and 2 and in Tables 2 and 3. The particle size distribution of raw material was determined according to ASTM D 422.

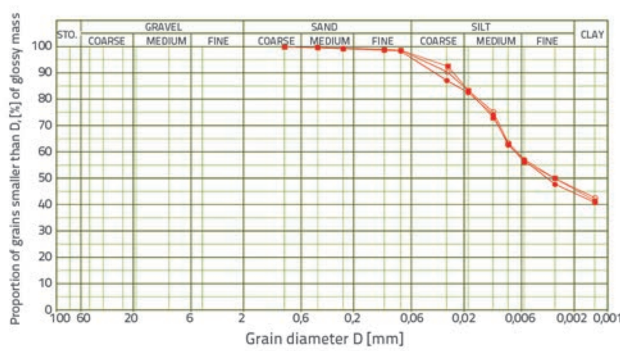


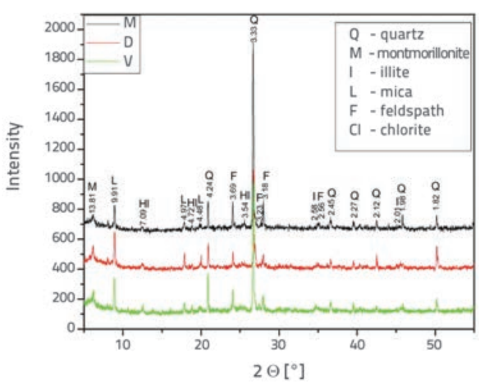
Figure 1. Particle size distribution of clay materials

The small percentage of CaO and MgO in chemical composition (Table 3) shows that these are non-carbonate clays of the type that is usually encountered in eastern Slavonia. The high content in potassium oxide is due to the presence of illite which is characterized by low melting temperature. The high content in iron is most probably due to the presence of mica and chlorites. Chlorites contain Fe^{3+} ions which are separated already at 550 °C and are converted into hematite. Chlorites with a high Mg^{2+} content shift the melting temperature toward higher values. This, however, did not happen with regard to tested properties as the MgO content determined by chemical analysis amounted to approximately 2 %.

Table 3. Results obtained by chemical analysis of raw materials

Element	Percent by mass [%]		
	Sample "D"	Sample "V"	Sample "M"
Na_2O	0,54	0,47	0,51
MgO	1,98	2,24	2,08
Al_2O_3	24,65	21,14	21,72
SiO_2	55,12	56,80	57,24
SO_3	0,10	0,17	0,06
Cl	0,04	0,02	0,07
K_2O	4,22	3,79	3,48
CaO	1,17	1,29	1,27
TiO_2	0,52	0,64	0,72
Fe_2O_3	11,66	13,45	12,85
Ignition loss [%]	16,7	13,00	14,50
Total:	**100,00**	**100,00**	**100,00**

Based on mineralogical analysis of the tested raw materials (Figure 2), it can be concluded that these raw materials are in fact systems based on quartz, feldspath, chlorite, montmorillonite, mica and illite. Thus the analysis has confirmed once again that these are non-carbonate systems. It can be seen by comparing radiographs of raw materials from Grabovac (Kuševac), sample mark: "D" and Dren (Jarmina), sample mark: "V" that the raw material marked "V" is richer in mica and quartz compared to the Grabovac raw material. Typical features of the system with this composition are: great sensitivity to drying, and occurrence of liquid phase at lower temperatures.



Figue 2. XRD analysis of raw materials

4.2. Manufacturing of bricks

Brick samples measuring 12.5/6/3 cm were shaped both mechanically and manually and protected with sand in order to prevent sudden loss of moisture from the raw material. The samples were dried for about 45 days on a flat surface covered with sand. This flat surface was placed on the floor of the test room to avoid reduce air circulation so that the samples form sudden moisture loss and excessive sun. During the drying the shrinkage of brick samples was monitored and a greater shrinkage of the final product was observed in case of manually manufactured brick compared to the mechanically produced brick. In case of mechanically manufactured brick, a greater shrinkage was observed due to drying in the direction of brick extrusion through the outlet, as compared to the perpendicular direction. In case of manually produced brick, the shrinkage value during drying was not influenced by the direction of the manufacturing of the product. After drying, brick samples were fired in electric kiln with an increase in temperature of 45 °C per hour, until the target temperature was reached (1000°C or 1050 °C). Once the target temperature was reached, the samples were kept in the kiln for additional 30 minutes. The brick shrinkage after firing was monitored and it was observed that the higher temperature of firing causes greater shrinkage in both manually and mechanically produced bricks. Once again, in case of mechanically shaped brick, a greater shrinkage was observed in the direction of brick extrusion through the outlet compared to the perpendicular direction. The influence of direction of manufacturing of manually produced bricks on its shrinkage was not observed during the firing process.
The brick sample manufacturing process is presented in Figures 3 to 8. Since, three raw materials were used, two methods of manufacturing and two different firing temperatures, the total of 12 types/series of bricks were prepared. A total of forty samples were made for each brick series.

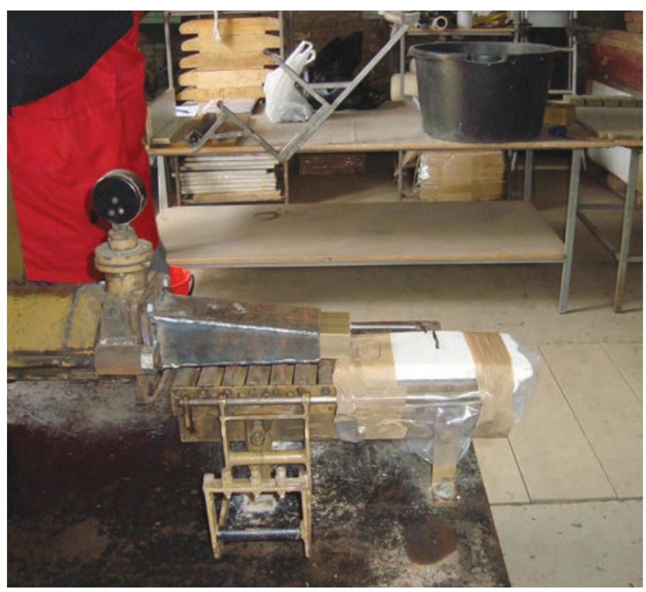


Figure 3. Mechanical fabrication of bricks

Figure 4. Mould for manual fabrication of bricks

Figure 5. Covering fresh bricks with sand

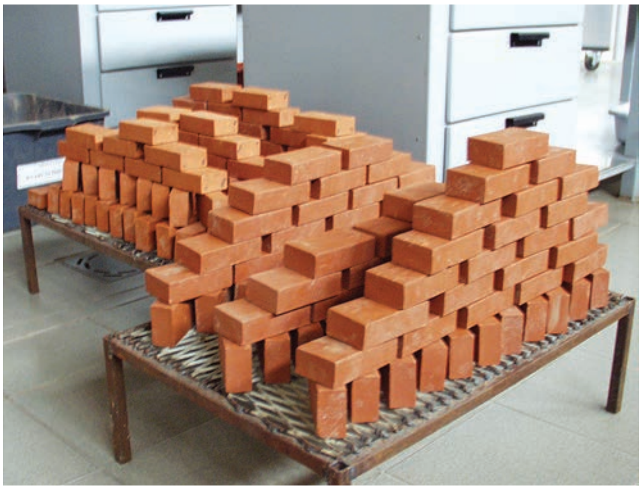


Figure 6. Bricks after firing

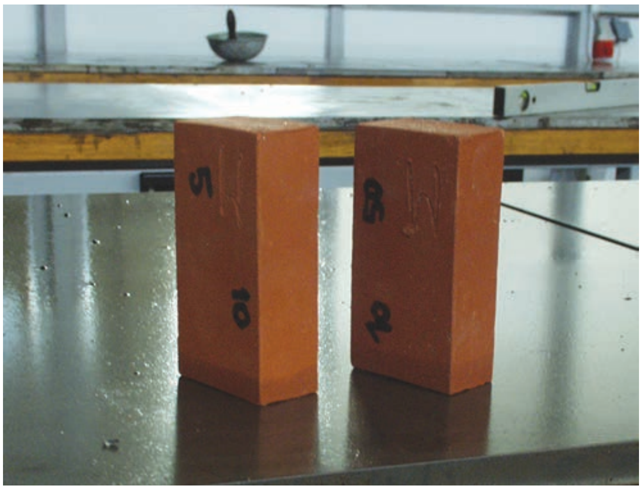


Figure 7. Mechanically produced bricks (by extrusion)

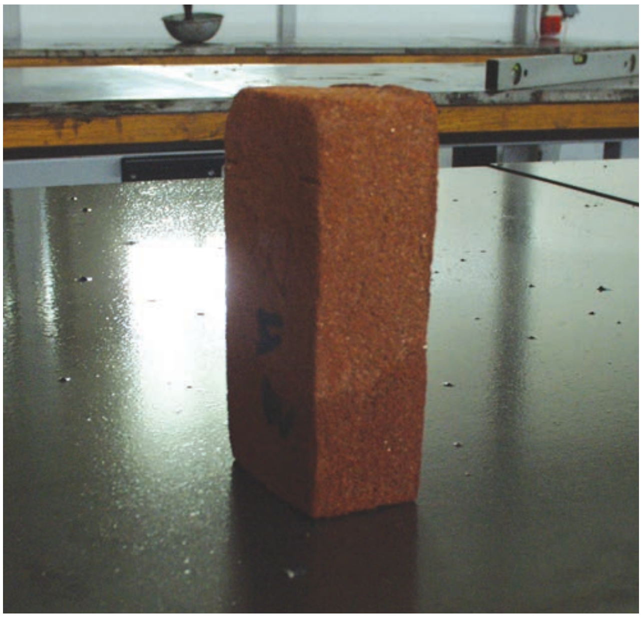


Figure 8. Manually produced bricks

4.3. Testing of brick properties

Although European standards specify that the resistance of bricks to freezing/thawing cycles should be checked according to HRS CEN/TS 772-22:2006 due to insufficient number of bricks for the manufacturing of the test wall, another method, HRN B.D8.011: 1987 [25] was used. Direct parameters such as compressive strength and water absorptions were tested according HRN EN 772-1:2011 and HRN EN 772-21:2011 [15, 26]. In addition, saturation coefficients were determined for each brick series, water absorption by boiling during the period of five hours was determined according to HRN EN 772-7:2003 [27], water absorption for one hour (cold water), and the water desorption during the time that is needed to attain a fully dry mass was also determined. The proportion of open pores was determined according to HRN EN 772-3:2011 [28], and the total proportion of pores and the distribution of pore sizes was determined using the mercury porosimeter. Table 4 shows the sample testing plan and number of samples tested per property for each series of the brick samples.

Table 4. Sample testing plan and number of samples tested for each property

Property tested	Standard/procedure according to which testing was conducted	Number of tested samples
Direct resistance to freezing/thawing cycles	HRN B.D8.011: 1987	5
Compressive strength	HRN EN 772-1:2011	10
Absorption during 5-hour boiling	HRN EN 772-7:2003	10
Saturation coefficient	ratio of water absorption to 5-hour boiling absorption	
Water absorption	HRN EN 772-21:2011	
Proportion of pores per size	mercury porosimeter, pore radius class 0.03-360 µm	3
Total porosity	mercury porosimeter, pore radius class 0.03-360 µm	3
Water absorption during the time	the bottom side of the completely dry sample was immersed in water down to 5 ± 1mm in depth, and the water absorption over time was monitored	10
Water desorption during the time that is needed to achieve a completely dry mass.	completely saturated sample was placed into the drying oven at 105 °C, and water desorption was monitored until the fully dry mass was attained	

Test results are presented below for each property, as the mean values of all measured values (Figures 9 to 22), and their standard deviations (Figures 9 to 18).

4.3.1. Test results and analysis of results

The samples saturated with water were placed in the refrigerator and exposed to the temperature of -20±2 °C for four hours. After that the samples were immersed in water where they were kept for four hours at the temperature of +15 to +20 °C. This cycle was repeated twenty-five times, and sample condition was checked after each cycle. The brick is considered resistant to freezing/thawing cycles if the signs of damage are not visible on any of the tested samples after 25 cycles of freezing and thawing in water. The condition of brick samples after exposure to freezing/thawing cycles is shown in Figures 9 and 10.

Figure 9. Appearance of manually produced brick "V" after exposure to freezing/thawing cycles

According to the method used, bricks produced in both ways and fired at both temperatures exhibited resistance to 25 freezing/thawing cycles as envisaged in [25] for brick exposure to severe conditions. Here it should be noted that it was observed that – after exposure to freezing/thawing cycles – initial cracks actually widened in case of mechanically produced bricks while the crack width remained unchanged in case of hand-made bricks.

Figure 10. Appearance of mechanically produced brick "V" after exposure to freezing/thawing cycles

Compressive strength values (Figures 11 and 12) are higher in case of mechanically produced bricks as compared to hand-made bricks. In addition, compressive strength values are generally higher in case of bricks fired at higher temperatures. According to Table A.1 from HRN EN 772-1:2011, compressive strengths shown in Figures 11 and 12.a were normalised, and their normalised values are presented in figures 11 and 12.b. The strength of mechanically produced bricks exceeds the strength of hand-made bricks by 42 to 57 %. If temperature is increased for 50°C the strength increases by 26 to 36 % for mechanically produced bricks and by 36 to 41 % for manually produced bricks. According to [8], bricks produced in both ways and fired at both temperatures meet the minimum compressive strength specified from the resistance to freezing/thawing cycles (Table 1).

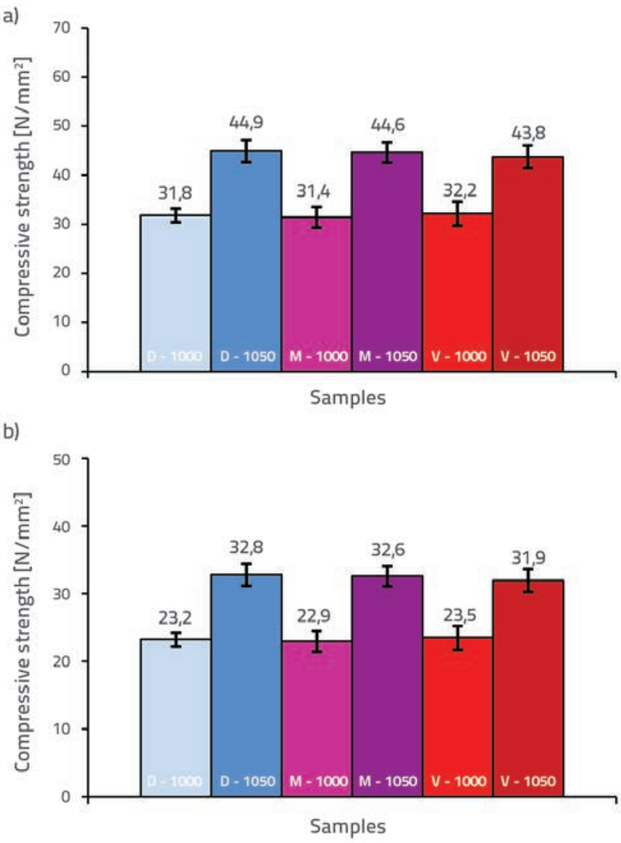


Figure 11. a) Compressive strength for manually-produced bricks; b) Normalised compressive strength for manually fabricated bricks

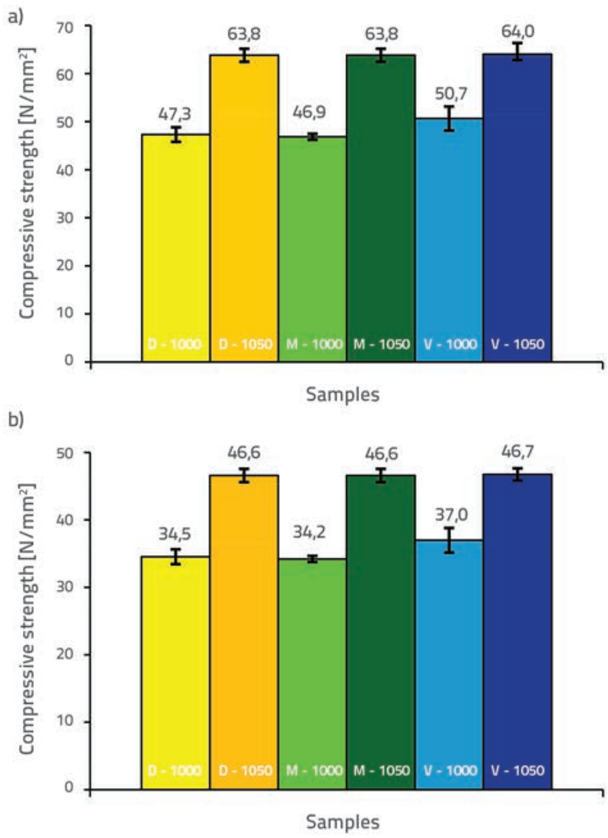


Figure 12. a) Compressive strength for mechanically-produced bricks; b) Normalised compressive strength for mechanically fabricated bricks

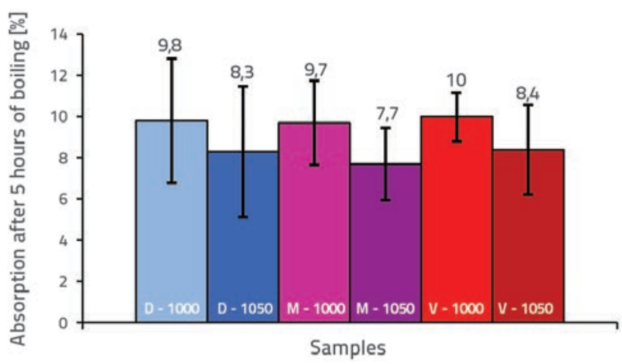


Figure 13. Water absorption after 5 hours of boiling, for manually prepared bricks

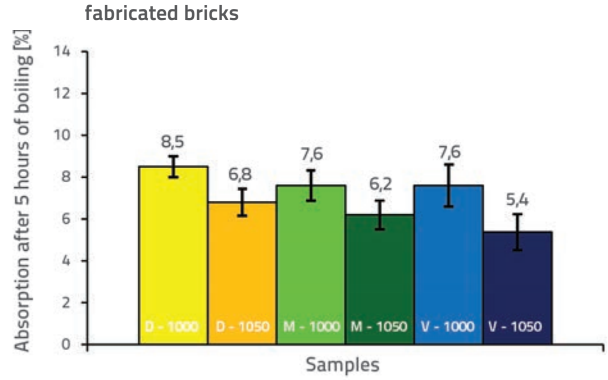


Figure 14. Water absorption after 5 hours of boiling, for mechanically produced bricks

It can be seen from Figures 13 and 14 that the water absorption after 5-hour boiling time for manually produced bricks is higher by 15 to 56 %. According to [8], bricks produced in both ways and fired at both temperatures meet the maximum allowed water absorption values after 5-hour boiling time (Table 1) as prescribed for the resistance to freezing/thawing cycles. By increasing the temperature for 50° the water absorption reduces at 5-hour boiling for 19 to 26 % in case of manually produced bricks, and for 23 to 41 % in case of of mechanically produced bricks.

No regular behaviour relating to firing temperature and production method was observed for saturation coefficients (Figures 15 and 16). It was however, registered that values

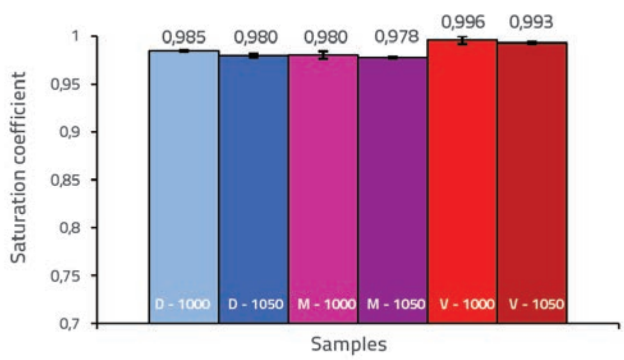


Figure 15. Saturation coefficient for manually-produced bricks

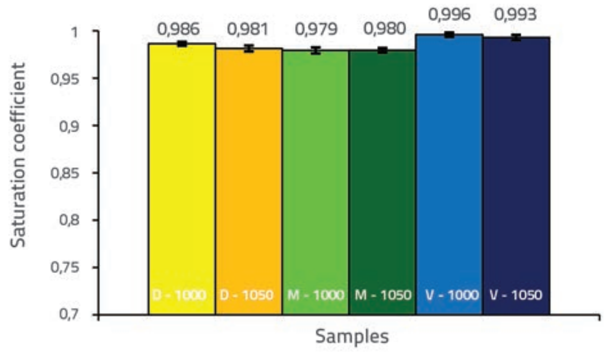


Figure 16. Saturation coefficient for mechanically-produced bricks

are significantly above the limit (Table 1) that ensures brick resistance to freezing/thawing cycles [8].

It can be seen from Figures 17 and 18 that manually produced bricks are characterized by greater water absorption. However, here it should be noted that the standard deviation for manually produced bricks is significant, and so the results presented can not be considered relevant. According to [8], bricks mechanically manufactured meet the maximum allowed water absorption value (Table 1) set for the resistance to freezing/thawing cycles. By increasing the temperature for 50 °C the water absorption reduces by 18 to 29 % in case of industrial bricks. The comparison of the values obtained accordingly to the requirements contained in the US and Canadian standards is presented in Table 5.

The assumption is that larger pores are developed at lower firing temperature and that these pores will be filled with water at a faster rate but that they are also susceptible to faster desorption of water, which would be favourable for the brick resistance to freezing and thawing cycles. The bricks tested in this paper exhibit resistance to freezing/thawing cycles according to [25] for severe conditions of use, but not according to Canadian and the US standards. Indirect parameters for estimating brick resistance to freezing/thawing cycles according to Canadian and the US standards have proven to be inadequate for use and so attempts are made below to find the relationship between water absorption and desorption, distribution of pore sizes, and resistance to freezing/thawing cycles for bricks produced (manually/mechanically) from various raw materials thermally treated at two temperatures (1000 °C and 1050 °C).

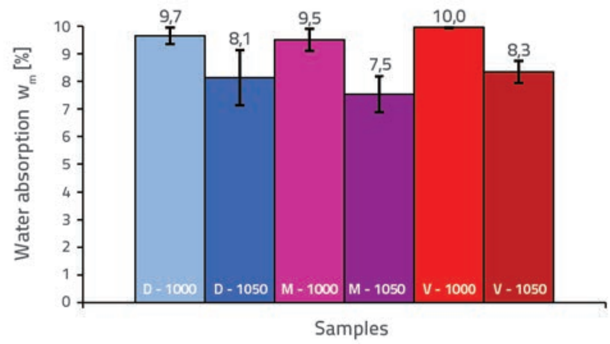


Figure 17. Water absorption of manually produced bricks

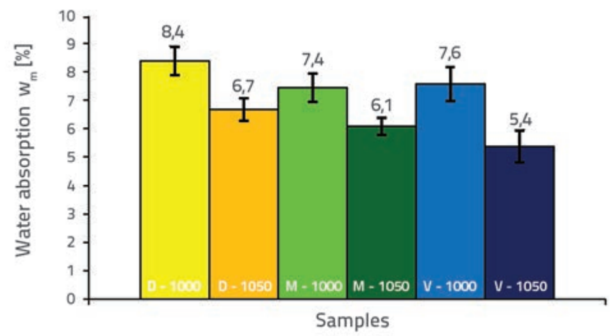


Figure 18. Water absorption of mechanically produced bricks

Table 5. Comparison of results with the requirements contained in Canadian and the US standards

Type of brick / property	Compressive strength [MPa]		Absorption at 5-hour boiling time [%]		Saturation coefficient		Water absorption during 24 hours [%]	
	Tested (*/**)	Minimum requirement	Tested (*/**)	Maximum allowed	Tested (*/**)	Maximum allowed	Tested	Maximum allowed
D1000-manual	20,9/23,2	Canadian and the US standards: -individual value: 17,2 - mean value: 20,7	12,9/9,8	Canadian standards: - individual value:17,0 US standards: - individual value: 20,0 - mean value: 17,0	0,987/0,985	Canadian standards: - individual value: 0,78 US standards: - individual value: 0,8 - mean value: 0,78	10,1	Canadian standards: - individual value: 8,0
D1050-manual	30,9/32,8		11,6/8,3		0,984/0,980		9,1	
M1000-manual	20,4/22,9		11,8/9,7		0,985/0,980		10,2	
M1050-manual	30,7/32,6		9,5/7,7		0,984/0,978		8,3	
V1000-manual	20,7/23,5		11,5/10,0		0,998/0,996		10,1	
V1050-manual	29,5/31,9		10,6/8,4		0,995/0,993		8,8	
D1000-mechanical	32,4/34,5		9,1/8,5		0,990/0,986		8,9	
D1050-mechanical	44,5/46,6		7,6/6,8		0,982/0,981		7,2	
M1000-mechanical	32,6/34,2		8,5/7,6		0,986/0,979		7,9	
M1050-mechanical	44,1/46,6		6,9/6,2		0,986/0,980		6,3	
V1000-mechanical	34,9/37,0		8,7/7,6		0,997/0,996		8,2	
V1050-mechanical	44,9/46,7		6,3/5,4		0,997/0,993		5,9	

* critical value, **mean value

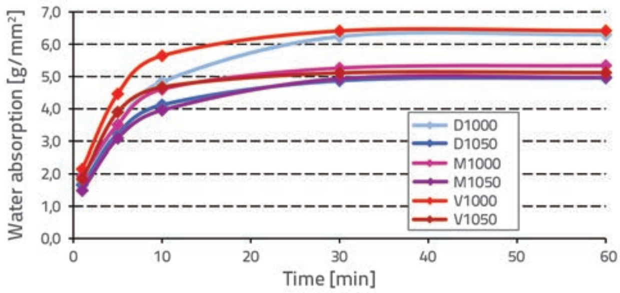


Figure 19. Water absorption for manually produced bricks

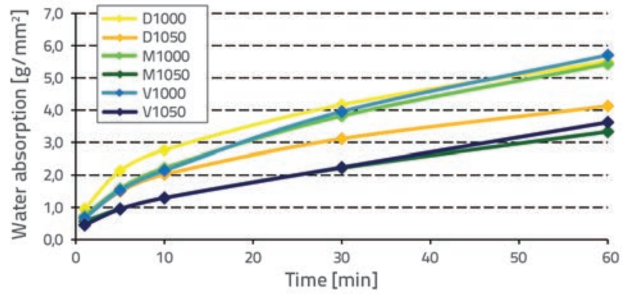


Figure 20. Water absorption for mechanically produced bricks

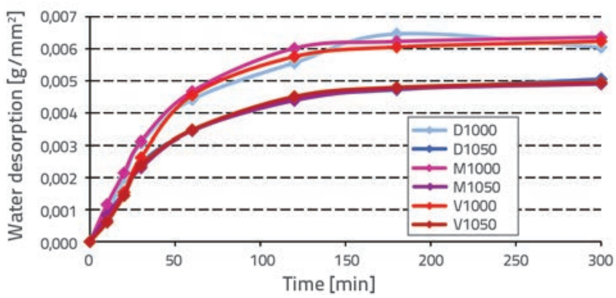


Figure 21. Water desorption for manually produced bricks

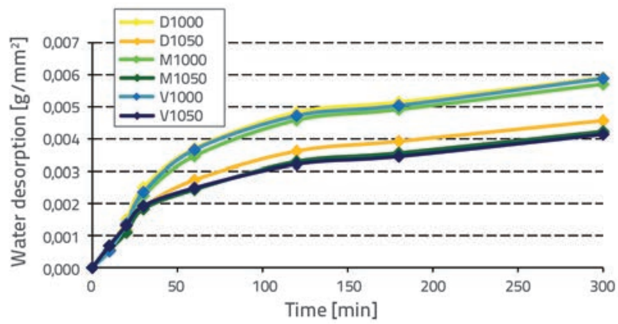


Figure 22. Water desorption for mechanically produced bricks

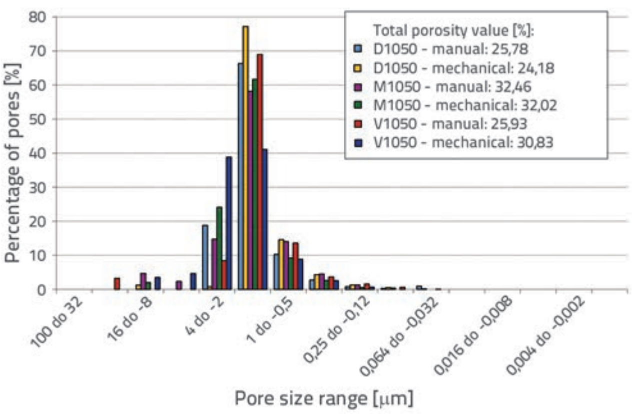


Figure 23. Distribution of pore sizes (radii) for bricks fired at 1000 °C, Hg porosimetry

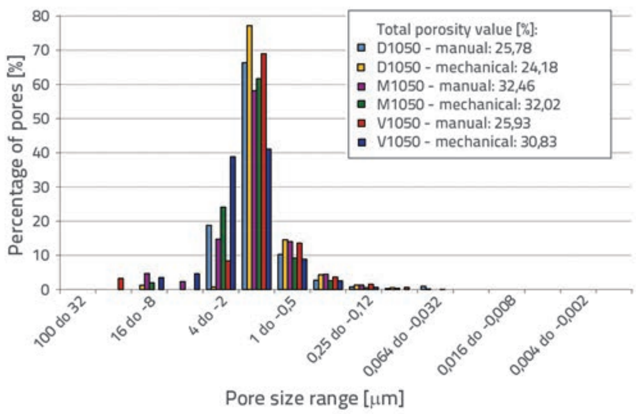


Figure 24. Distribution of pore sizes (radii) for bricks fired at 1050 °C, Hg porosimetry

It can be seen in diagrams 19 and 20 that manually produced bricks exhibit greater initial rate of water absorption capability (water absorption over time t = 1 minute) and that these bricks generally have greater water absorption capability over time when compared to mechanically produced bricks. In addition, it can be seen in both brick manufacturing methods that their capability of absorbing water over time reduces with an increase in temperature. The water desorption capability (Figures 21 and 22) is analogous to the water absorption capability – the water desorption capability is greater in case of manually produced bricks compared to mechanically produced bricks, and the water desorption is more pronounced in case of bricks fired at lower temperature. Figures 23 and 24 show reduced proportion of large pores (pore radius > 4 μm) with an increase in temperature in samples fabricated using (non-carbonate) clays. It is evident for these types of clay that the thermal treatment at higher firing temperature is inadequate as it resulted in the occurrence of a liquid phase, and in the reduced proportion of large pores and total porosity (with the exception of clay M-1050), with a simultaneous increase in capillary pores (pore radius 4-2 μm and 2-1 μm). These results are compliant with the water absorption/desorption rate results, where the values reduce with an increase in temperature (Figures 19-22). More favourable micro-structural properties and more resistant product would most probably be obtained by adding a small quantity of calcium carbonate to the raw material, and by maintaining temperature at maximum during firing to enable formation of calcium silicate.

The fact that smaller propagation (widening) of initial cracks in case of manually produced bricks was registered, after these bricks were subjected to freezing/thawing cycles, could be related here with the obtained results, and could be an indication that a greater water absorption/desorption rate leads to a better resistance of bricks to freezing/thawing cycles. The results obtained are the consequence of the relationship between the thermal treatment and the used raw material. A higher temperature is probably not adequate for geologically younger clays, and the corrections have be made with regard to raw material composition including addition of a carbonate clay. However, in addition to the size of pores, the shape and interconnection of pores are also significant for the resistance of bricks to freezing/thawing cycles. That is why the authors of the paper consider that the indirect estimation of brick resistance to freezing/thawing cycles, involving measurement of the water absorption/desorption rate, is a rapid and low-cost continuous method for checking quality of bricks. In fact, the comparison of a significantly greater number of results of the direct measurement of brick resistance to freezing/thawing cycles and water absorption/desorption capabilities, would enable the establishment of the "critical" absorption/desorption curve, Similarly, the "critical" absorption/desorption rate, which would ensure brick resistance to freezing/thawing cycles.

5. Conclusion

The possibility of defining an indirect method for estimating brick resistance to freezing/thawing cycles is analysed in the paper. Brick resistance is tested by direct procedure and some indirect procedures in accordance with international literature and select foreign standards. It is demonstrated in the paper that the requirements for indirect estimation of brick resistance to freezing/thawing cycles set according to Canadian and the US standards are inacceptable, and the same applies to the possibility of estimation based on pore structure. The fact that the Canadian and the US standards place indirect requirements to be met by bricks before the direct method for estimating brick resistance to freezing/thawing cycles shows that the indirect parameters are much stricter than the direct ones. The failure to fulfil these requirements does not automatically exclude brick as product resistant to freezing/thawing cycles. The connection between the water absorption/desorption capability, pore size distribution, and brick resistance to freezing/thawing cycles was also observed by direct procedure. The comparison of a significantly greater number of direct measurements of brick resistance to freezing/thawing cycles and water absorption/desorption capabilities, would enable the establishment of the "critical" absorption/desorption curve. It would also enable the "critical" absorption/desorption rate, which would ensure bricks resistance to freezing/thawing cycles. The proposed method for indirect estimation of brick resistance to freezing/thawing cycles would be easier to implement, less demanding with regard to the testing apparatus, less-time consuming, and less costly than the direct procedures. It would enable manufacturers, after proving validity of initial production by direct method, a rapid estimation of brick resistance to freezing/thawing cycles.

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