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Properties of Dimension (Facing) Stone from Estonian Dolostone

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In this work the hydrophobization of dimension (facing) stone from Estonian dolostone was investigated. Due to the diversity of the structure and properties of the stone from one source and the differences of dolostone mined from different areas of Estonia – Kaarma, Selgase and Orgita, certain properties of stone were investigated by chemical analysis, X-ray diffraction and scanning electron microscopy. Water absorption by DIN 52103 and frost resistance by DIN 52104 were carried out. XRD measurements showed that the composition of Estonian dolomite was nonstoichiometric for samples from all three deposits. For Selgase and Orgita dolostone, in comparison to Kaarma dolostone, typical absence of relatively large pores and smaller interval of absorption times of a water drop occurred. Comparing the ratio of water absorption time to the stated by producer norm of hydrophobic liquid (R/N) it could be concluded that commonly coating once is sufficiently suitable. After 100 freezing-thawing cycles no signs of damages on any specimen cubes or plates were discovered.

Keywords: carbonate rock, weathering of stone, degradation, prevention against deterioration.

1. INTRODUCTION

Dolostone together with limestone and marble is one of basic forms of carbonate rocks [1, 2]. Carbonate rocks have been and continue to be the major source of architectural and statuary stone. The pyramids, Sphinx, and most other Egyptian monuments were built from limestone; most Greek and Roman architecture, including the many temples at Acropolis, were built from marble. Famous pieces of statuary in dolostone are also well known, but the primary importance of dolostone has been in common construction. Finishing stone from dolostone stem from Estonia were used continually in architecture in Baltic countries and also in St. Petersburg [3, 4].

Due to sedimental formation of carbonate rocks and chemical properties of main constituent minerals durability of dolostone to weathering is much lower than of granite stones. Weathering includes processes, such as chemical influence of air and rainwater and the mechanical action of water, whereby rocks, when exposed to atmosphere, decay into products or disintegrate into fragments. Weathering includes also disintegration by mechanical forces generated within the rock. As carbonate rocks contain a network of pores and cracks, aqueous solutions penetrate into rock and damage it in variety of ways. The loss of cohesiveness between grains by wetting and bursting pressure from freezing, salt crystallization and swelling clay minerals may occur.

Deterioration of carbonate stone was noticed rather soon after beginning its usage. The problems hade rapidly became more alarming as the world became industrialized and polluted. Greek and Roman writers indicated the necessitate of treatments to forestall deterioration of stone already centuries ago. So-called scientific approaches began to appear in the 19th century. Prevention against deteriorating of stone was primarily carried out by applying different waxes, paint, or other coating what was available and might work.

After about 1960, polymeric chemicals with more suitable properties became commercially available. It is essential, before applying certain chemicals to carbonate stone against deterioration, to study properties of stone. The composition and texture of carbonate stone from different deposits may vary in a big extend. Therefore treatment effect of each chemical on stone may occur very different.

The aim of present study was to investigate some properties of Estonian dolostone and the coating effect with hydrophobic liquid chemicals of dimension (facing) stone.

2. EXPERIMENTAL DETAILS

Dolostones from Kaarma, Selgase and Orgita deposit were studied using chemical analysis, microscopic and X-ray diffraction methods. X-ray analysis on D5005 Bruker AXS diffractometer and microscopic observations in the scanning electron microscope JEOL JSM 840A were carried out. Commercial dimension (facing) stones with size 150×150×10 mm with ground upper side, and cubic form specimens with size 40×40×40 mm were used for the experiments. For coating commercial hydrofobization liquids HIDROFOBS and FUNCOSIL SNL were used.

Water absorption by DIN 52103 and frost resistance by DIN 52104, using freezing-thawing cycles with water saturated cubes and plates in atmosphere with 100 % relative humidity were performed. For characterization of water absorption speed the time of complete absorption of 1 water drop was measured [5]. Eight plates were choosen from each deposit. To reveal the possible discrepancy in the absorption over the whole area of one sample, 35 separate areas were marked on ground surface of every plate and the absorption time of 1 drop was measured on each area separately. As a whole, in one series, 280 drops of water were dipped onto the marked areas of 8 samples

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and the absorption time was measured. Hydrophobization was performed only on 1 plate from each sample series choosen before. After the first run on uncoated plates the sample stones were dried and coated in horizontal position 1 – 3 times with hydrophobic liquid. Samples were covered until visible thin layer of liquid was uniformely spread on the surface. After complete absorption of liquid, the coating procedure was repeated. Coated plates were dried at room temperature until all solvent evaporated. For every coated plate time of one water drop absorption in the same marked areas as on uncoated plates was determined. From these parts of uncoated plates where the absorption time of water was extremely different sample pieces of 20×20 mm were cut out and studied more thoroughly.

3. RESULTS AND DISCUSSION

Commonly in all dolostones besides the base mineral dolomite there are main impurity minerals illite and quartz. The position of the highest peak in the X-ray diffraction pattern (XRD) of Estonian dolostone showed that the composition of dolomite was nonstoichiometric for samples from all three deposits (Fig. 1). In [1] it is shown that in stoichiometric dolomite (Ca : Mg molar ratio is 1 : 1) the main peak lays at $2\theta = 30.99°$ and in high-calcium dolomite (Ca : Mg molar ratio is 1.24 : 1) it is found to occur at $2\theta = 30.78°$.

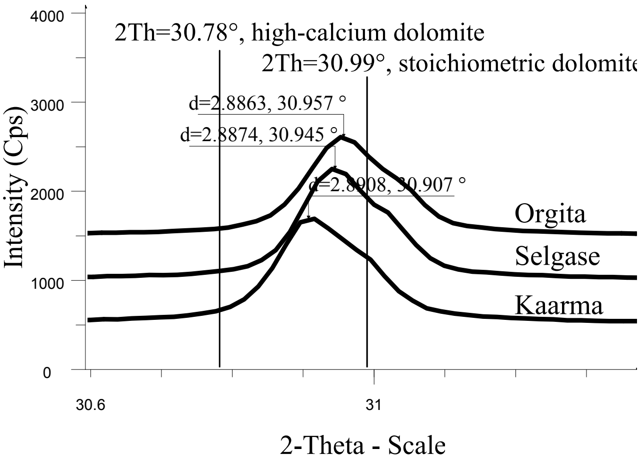


Fig. 1. XRD patterns of Kaarma, orgita and Selgase dolostones near the stochiometric peak according to [1]

All measured main peaks were shifted to the left compared to the stoichiometric peak position, but did not reach the high-calcium peak position. Histograms of absorption time on 280 areas are presented on Figure 2. These histograms showed largest for Kaarma and smallest for Orgita dolostone plates intervals between minimal and maximum water absorption times. The absorption time of water drop characterizes directly the rate of water absorption and indirectly the size of pores and cracks. Therefore it can be proposed that distribution of effective diameters of all caverns is similar to histograms on Figure 2. The average water drop absorption time on 280 areas of Kaarma dolostone plates was 5.7 ±4.6 min, Selgase – 9.6 ±6.7 min and Orgita – 26.5 ±6.6 min.

There are several properties of material what affect the water transport inside the porous stone. Dolostone properties, which have the greatest influence to the water movement in stone, are presented in Table 1.

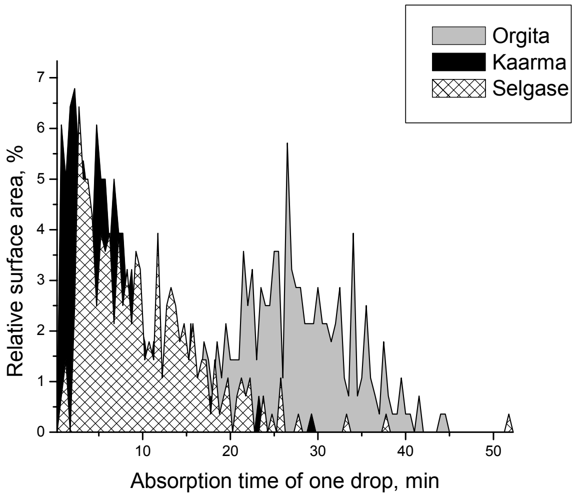


Fig. 2. Histograms of absorption time on 280 areas of Orgita, Kaarma and Selgase uncoated dolostones

Table 1. Chemical properties of studied dolostones

Property	Deposit		
	Kaarma	Selgase	Orgita
Apparent density, g/cm^{-3}	2.20 – 2.25	2.11 – 2.27	2.42 – 2.62
Insoluble part, % in acid	9.4 – 10.5	8.2 – 8.7	10.2 – 16.3
Water absorption, %	10.1 – 11.2	7.7 – 9.1	3.9 – 5.2

To reveal the main properties of stone, what are responsible in these large differences in the absorption times of water drop on different surface areas on the same plate, correlation between water drop absorption time, absolute water absorption, dolostone structure and impurity mineral composition were studied.

At first it was found that water drop absorption rate is not directly connected to absolute water absorption, as 4 sample pieces from Kaarma dolostone absorbed nearly the same absolute water quantity - 10.1 – 11.2 %, but water drop absorption times differed 38 times (0.5 – 19.1 min). Kaarma dolostone structure is characterized by relatively big amount of dolomite crystals with various sizes and numeral large pores and holes (Fig. 6, a, b). The water penetration is alikely rapid whether sample contains a small number of gross pores or a large number of small pores.

The main impurity minerals in all studied dolostones were the same – quartz and clay mineral illite. Comparing the typical XRD peak of illite at $d = 9.903$ Å in diffraction patterns of insoluble in acid residues of Kaarma and Orgita (Fig. 3), it could be concluded that the content of illite in Kaarma dolostone is couple of times higher than in Orgita dolostone. As the quantities of insoluble in acid residues are nearly the same for all investigated dolostones (Table 1), it could be stated that the whole illite content in Orgita dolostone is also few times less than in Kaarma dolostone.

Typical for all clays is relatively high porosity, what is determined by very small particles size of clay constituent minerals. Therefore the content of illite in dolostone influences water absorption more or less depending of its distribution in stone. For Selgase (Fig. 7) and Orgita (Fig. 8) dolostone, in comparison to Kaarma dolostone, was typical absence of relatively large pores and smaller interval of absorption times of a water drop (Fig. 2). Thereby differences between the biggest and smallest water absorption times for Selgase dolostone were measured 12.2 (25.7 – 2.1min) and Orgita – 3.0 (40.4 – 12.8 min) times.

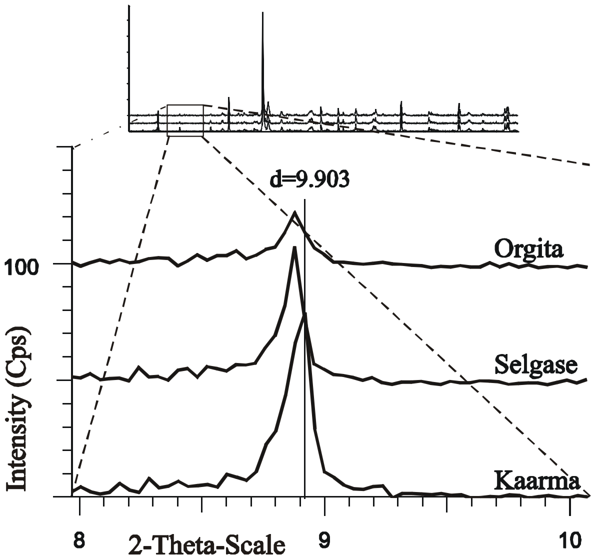


Fig. 3. XRD peak of illite at d = 9.903 Å in diffraction patterns of insoluble in acid residues of Orgita, Selgase and Kaarma

Histograms of absorption times of a water drop on dolostone plates coated once with Hidrofobs and Funcosil liquid, are presented on Figures 4 and 5 accordingly. It is seen that in all cases decreasing of water drop absorption rates takes place. The biggest water drop absorption time differs from the smallest on Kaarma dolostone plates 1.6, for Selgase – 1.5 and for Orgita – 2.0 times. Similar results were obtained when plates were coated two or three times.

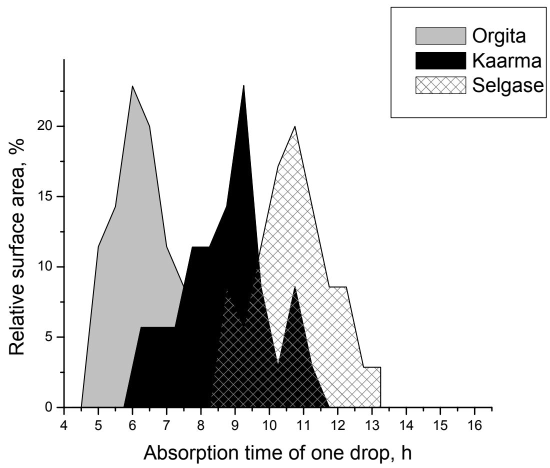


Fig. 4. Histograms of absorption time on 35 areas of Orgita, Kaarma and Selgase dolostones coated once with Hidrofobs

For determination efficiency of coating with the stated by producer norm of hydrophobic liquid used (N), ratio of water drop absorption times (R) on the same areas (center of square of surface 20×20 mm) of coated and uncoated plate, ratio of R/N and average water drop absorption times on uncoated and on the same coated plate were taken under view. Results are presented in Table 2 and 3.

Table 2. Average water drop absorption times on uncoated and coated plates

Plate	Deposit		
	Kaarma	Selgase	Orgita
Uncoated plate	4.4 min	12.0 min	29.1 min
Uncoated plate	3.9 min	8.2 min	27.0 min
∑/2	4.2 min	10.0 min	28.0 min
Coated once with Hidrofobs	8.4 h	8.7 h	6.2 h
Coated once with Funcosil	6.4 h	9.2 h	10.3 h
∑/2	7.4 h	8.9 h	8.2 h

Comparing the ratios of water absorption times to the stated by producer norm of hydrophobic liquid (R/N) it could be concluded that for the majority of cases coating once is sufficiently suitable (R/N value is maximum).

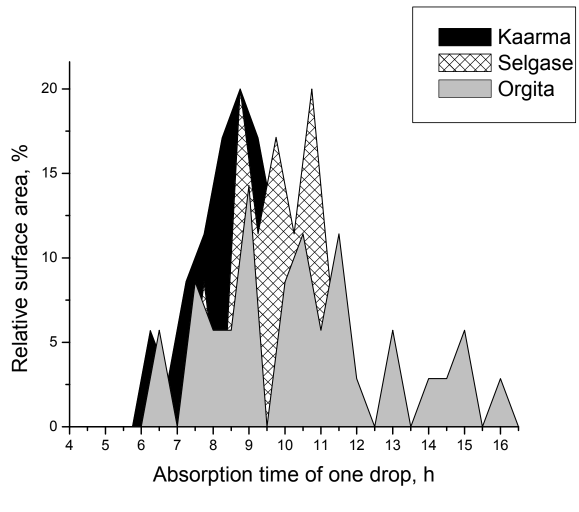


Fig. 5. Histograms of absorption time on 35 areas of Kaarma, Selgase and Orgita dolostones coated once with Funcosil

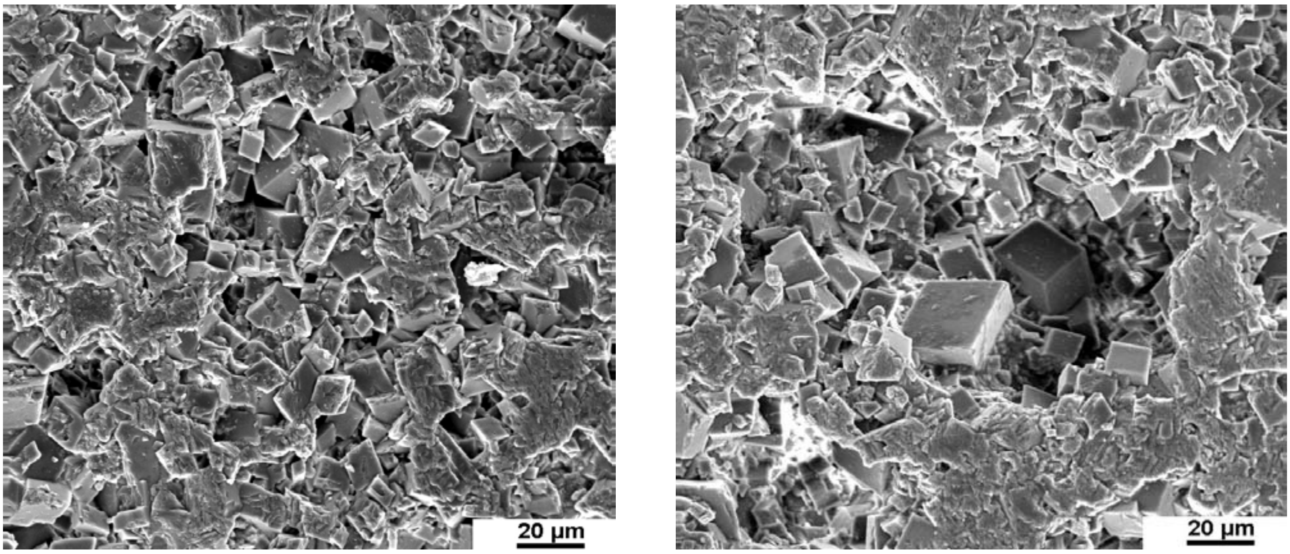
From economical viewpoint considering norms of both hydrophobic liquids, it is rational to coat all types of dolostone only one time. With increasing the repetition of coating there is no considerable effect in the water absorption time, only the quantity of used hydrophobic liquids increases.

Drawing a comparison between water drop absorption times on uncoated and coated plates it is obvious that in result of hydrophobization rate of water absorption is similar in all cases. As the ratio of the biggest water drop absorption time to the smallest for uncoated plates is 29.1 min / 3.9 min = 7.5, then the same for coated plates is 10.3 h / 6.2 h = 1.7.

20 cubic form specimens and 10 plates of dolostones, coated once with Hidrofobs and Funcosil, and 10

Table 3. Average ratio of water drop absorption times of coated and uncoated plates

Hydrophobic liquid and number of coating times	Kaarma			Selgase			Orgita		
	N	*R*	*R*/*N*	*N*	*R*	*R*/*N*	*N*	*R*	*R*/*N*
Hidrofobs									
Once	275	155	0.56	120	62	0.52	115	14	0.12
Two time	550	219	0.40	240	65	0.27	220	27	0.12
Three time	825	136	0.17	360	53	0.15	325	27	0.08
Funcosil									
Once	275	197	0.72	135	106	0.79	110	24	0.22
Two time	550	272	0.49	270	217	0.80	200	35	0.18
Three time	825	194	0.26	405	225	0.55	290	42	0.14



a b

Fig. 6. Chemically etched surface of Kaarma dolostone shows large crystals. SEM microphoto

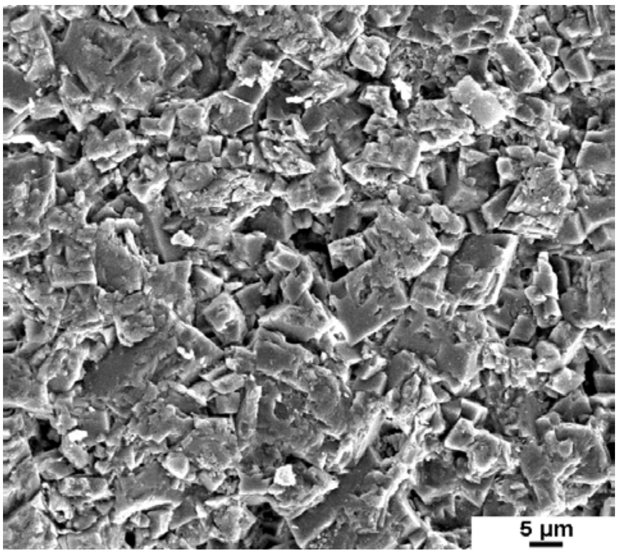


Fig. 7. Chemically etched surface of Selgase dolostone shows uniform structure. SEM microphoto

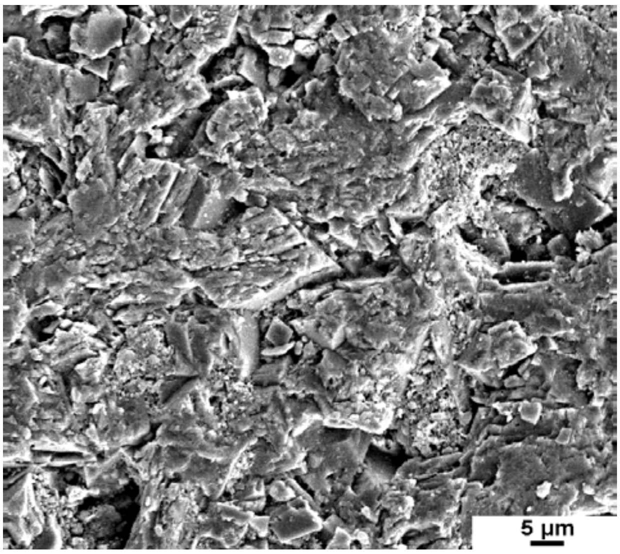


Fig. 8. Chemically etched surface of Orgita dolostone shows a dense structure. SEM microphoto

noncoated cubes from each deposit, were used for determining frost resistance. After 100 freezing-thawing cycles no signs of damages on any specimen cubes or plates were discovered.

4. CONCLUSIONS

1. By coating dolostone facing stones from Kaarma, Selgase and Orgita deposits with hydrophobic chemicals it is possible to decrease water absorption rate up to 200 times.
2. Direct dependence between water absorption rate of dolostones and efficiency of hydrophobic coating agent was found.
3. Coating of facing dolostone surface once is suitable for common practical application.
4. Hydrophobization of dolostone surface allows also using lower quality dolostone (higher water absorption) in facades.

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REFERENCES

1. **Gauri, K. L., Bandyopadhyay, J. K.** Carbonate Stone. John Wiley & Sons, 1999: 284 p.
2. **Oates, J. A. H.** Lime and Limestone. Chemistry and Technology, Production and Uses. Wiley – VCH, Weinheim, 1998, 455 p.
3. **Bulah, A. G., Abakumova, N. B.** Stone Decorations on Main Streets of Leningrad, St. Petersburg University Publ. House, 1993: 184 p. (in Russian).
4. Estonian Science History VII. Tallinn, Valgus, 1989: 176 p.
5. **Teutomico, J. M.** Laboratory Manual for Architectural Conservators. Iccrom, Rome, 1998: 168 p.