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WEATHERABILITY OF ROMAN TRAVERTINE

Summary of Doctoral thesis

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CONFIRMATION

I confirm that I had elaborated the given Doctoral thesis submitted for nomination of doctoral degree in engineering chemistry. Doctoral thesis has not been submitted in any other University for nomination of scientific degree.

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Doctoral thesis is written in English and involves 1) introduction and topicality of theme; 2) historical and theoretical background; 3) methodology; 4) experimental part I: state assessment of travertine objects; 5) experimental part II: study of deposition layers; 6) experimental part III: material characterisation; 7) general discussions, 8) conclusions, 9) bibliography; 117 figures; 25 tables, 134 pp.

Topicality of theme. In history, mainly local stone materials from nearby quarries with easy access and transportation were chosen as building materials and long-term exposure performance is known for local stones exposed in regional environment. Nowadays the shipment of stone materials is worldwide and the practical experience of the use of building stone in other regions can not be extrapolated to the new ones.

Prediction of durability and weatherability of stone is of great importance as only slight changes to improve durability of stone could be done. Difficulty of prediction of durability is determinate by the unique properties of stone formed up in geological processes. However, if used professionally with knowledge of material, design and maintenance, durability of stone could be improved significantly. For protection of Cultural Heritage, prediction of durability of stone is even more complicated. All stone details assessed nowadays have already changes in their structure and composition due to previous weathering [1] and predicted durability obtained for the quarried stone could not be applied in the case of Historical Monuments. The other problem predicting durability is the complexity of test methods for evaluation of durability and weatherability of stone materials, the interpretation of obtained data [2,3] and their apply for objects exposed under changing environment.

In Latvia historically local dolomites and boulders were used for construction of manors, castles and churches. From the 19th century building stone has been imported from the nearby countries (Sweden, Germany, Estonia) with regional climatic conditions comparable to Latvia; and practical experience from the use of these materials in regions of their geological origin could be analysed.

In the 1930ties Roman travertine quarried in the *Acque Albule* basin, 10 km East of Rome in Tivoli area in Italy was used for the construction of Heritage Monuments in Latvia and is the only known example of the use of Roman travertine in area of the Northern Europe.

Roman travertine is worldwide building material proved in practice to be a durable exterior cladding and sculptural material. Despite this, there are very few examples of the use of Roman travertine in exterior in the frost regions. The characteristic properties of travertine and related regional climate are often not well understood by designers who misuse travertine and by conservators who provide inappropriate conservation treatments giving raise for misleading conclusions on durability of Roman travertine. Roman travertine objects represent a unique case in the history of Latvia's Crafts, Sculpture and Architecture. Evaluation of performance of Roman travertine in frost regions is of great importance in order to safeguard Cultural Heritage Monuments.

Aim of work: characterise structural changes of Roman travertine due to exposure in Latvian climatic conditions in order to elaborate scientific background for the methodology of conservation/restoration and maintenance of Roman travertine in Cultural Heritage objects; give scientifically based guidance on the possibility of use of Roman travertine in Northern climatic conditions.

Main tasks:

- study of geology, production and use of Roman travertine;
- historical, artistically/architectural study of Monuments in Latvia constructed of Roman travertine;
- evaluation of state condition and practical experience of durability of Roman travertine projects realised in Northern and Southern climates;
- *in situ* study of the weathering of Roman travertine in Latvia's Monuments in correlation with the characteristics of environment;
- comparative study of unexposed and weathered Roman travertine's structural, physical, mechanical, chemical and durability properties;
- field tests and restoration of Roman travertine objects in Latvia.

Scientific significance and main results.

1. Identification, historical study, state assessment and documentation of Latvian Cultural Heritage built of Roman travertine were done. Roman travertine Monuments are mainly located in central region of Latvia; in total, 5 Monuments has been identified and assessed, for 3 of them conservation/restoration project has been elaborated.
2. The climate of Northern regions like Latvia is characterized by frequent freeze/thaw cycles (about 70 per year) and high relative humidity (average about 80-90%).
3. Northern climatic conditions, very different form Mediterranean regions, like Italy (estimated freeze/thaw cycles are about 21 per year), where travertine is quarried, determines an increase of open porosity (and a consequent drop of close porosity) due to development of cracks and fissures after continuous freeze/thaw cycles.
4. Weathering of travertine results in increase of capillarity in direction parallel to the bedding planes, decrease of mechanical properties and an increase in anisotropy in the direction parallel to bedding planes, which is the weakest structural part of this construction material.
5. Degree of increase of structural anisotropy of weathered travertine compared to untouched stone material of the same lithological type could be assumed as one of parameters evaluating state of weathering of travertine.

Practical application. Tests of physical/mechanical properties, accelerated durability tests, as well practical experience has showed that Roman travertine is suitable for most uses including more severe exposure conditions like frost cycles presented in Northern climatic regions. Travertine's weak bedding planes set up special problems for the design, as the structural weakening due to corrosion processes results in weakening of physical/mechanical properties that promotes water penetration and reduction of mechanical resistance imposed by the weak bedding planes. Northern climate promotes severe exposure conditions at which the weak bedding planes could determine the resistance for the whole material. Therefore if Roman travertine is used in Northern regions, higher demands on design and workmanship, regular survey and maintenance should be involved as mandatory premise.

Roman travertine used for construction of Cultural Heritage Monuments in Latvia is unique case in Latvia's craft, architecture and art. However it has been stated that in Latvia's case study already structurally damaged Roman travertine more susceptible to deterioration was used however according to its physical/mechanical properties it is still durable material to be exposed in Northern climate. Design of Monuments in Latvia for most cases is carried out in a way suggesting most appropriate exposure conditions; however lack of maintenance, humid climatic conditions and frequent freeze/thaw cycles have promoted favourable conditions for intensive bio-colonisation (especially algae, micro organisms) and deposition of soot, dust, wind-blown particles resulting in unpleasant aesthetical appearance of Monuments and increasing probability of frost damages of material. Maintenance of objects should be done after each 2 to 4 years involving surface cleaning and protection using treatment with biocides. Planning conservation/restoration projects, consolidation and surface protection of Roman travertine should be involved.

In the frame of elaboration of thesis, conservation/restoration of 2 Roman travertine Monuments has been done.

Theoretical background. Building stone is durable, when the weathering of rock does not appreciably modify its structure, compositional, physical, mechanical and aesthetical properties. *Durability* [4] refers to the measurement of the ability of natural building stone to endure and to maintain its essential and distinctive characteristics of strength, resistance to decay and appearance with relation to a specific manner, purpose and environment of use. *Weather ability* is used to describe stones long-term withstand in object under all weathering factors for the given case study and are expressed as changes in stones aesthetic and structural properties during exposure. The weathering properties of a stone material are best judged by the examination of buildings in which it has been used - *practical experience.* However practical experience is not available if it is required to estimate the durability of a new material or of a material used under new conditions [5]. It should be considered that stone used successfully on a similar project in the past may not have the same physical or mechanical properties for current project [2].

Laboratory durability tests. All limestones (like travertines) have broadly similar chemical composition and it is the internal structure of a limestone, rather than its composition, that gives the clue to its durability [6]. It also should be considered that the stone can vary from quarry to quarry, from one area within a single quarry to another, and possibly within a single quarry block.

A number of indirect rock durability estimation methods have been developed, which are based on the hydric properties: water absorption, capillarity and porosity. One of the fundamental properties of limestones is porosity: laboratory tests have shown that low porosity stones (< 5%) and high porosity stones (> 30%) are resistant to salt and frost damage [6]. Saturation coefficient is another parameter for classification of building stones in the order of their relative durability [5]. Values > 0.85 represents stone with a high proportion of fine pores allowing to be absorbed by capillary action thus indicating a stone of rather low durability. Saturation coefficient and porosity should be used in conjunction with each other because saturation coefficient is only of any use if the sample contains a significant amount of pore space [7].

Building Research Establishment recommends the complex of three tests for limestones: crystallisation test using 14% solution of sodium sulphate; saturation coefficient; porosity [7]. The crystallization test is a comparative one in that stones of known durability are included as internal reference samples to ensure that the test is giving consistent results.

Pore size distribution has been found to be an essential parameter in assess of durability of porous inorganic materials. It has been experimentally demonstrated that bricks (as well as other construction materials such as stone or mortar) with a high porosity and a high percentage of pores with diameter < 5 - 2 ^im are most susceptible to weathering, particularly due to salt crystallisation and freeze/thaw phenomena [8-11].

Methodology. Weatherability of Roman travertine was studied by:

■ *visual state assessment* of travertine objects in Northern climatic regions in Latvia and in New York (USA) and in Southern climatic region in Rome (Italy);

- *analyses of surface deposition layers* on travertine in objects in Latvia was done using X-ray diffraction (XRD; Philips PW-1710 diffractometer), chemical compositional analyses, fourier transform infrared spectrometry (FTIR), scanning electron microscopy (SEM/EDX; Zeiss DMS 950 equipped with Microanalysis Link QX 2000) and analyses of bio-contamination;
- *material characterisation* and *comparative test of physical, mechanical/properties and accelerated durability* of two types of Roman travertine: 1) travertine of 60 years exposure in Latvian environment, further in text - weathered travertine and 2) fresh travertine, quarried in 1998, of 2 years seasoning, further in text - quarried travertine. Material characterisation was done by inductively coupled plasma mass spectrometry (ICP-MS; PERKIN ELMER Sciex-Elan 5.000); optical microscopy (OM; stereomicroscope MBS and LEICA WILD MAKROSKOP M420, polarized optical microscope Olimpus BX-60 and LEICA DMLP); mercury intrusion porosimetry (MIP; Porosimeter Auto Pore III); hydric tests (free water absorption: NORMAL 7/81; water absorption by capillarity: prEN 1925:1988; drying: NORMAL 29/88, saturation by boiling: EN 772-7:1998); mechanical tests (compressive strength: LVS 156:2000, flexural strength).

Accelerated durability tests involved salt crystallization test according to LVS EN 12370:2000 and 2 types of frost resistance: 1) test by free saturation of samples before freezing comprising cycles of freezing in air and thawing in water executed manually. Each cycle consisted of 8 hours freezing period in air (in the range from -15 to -20°C) followed by 16 hours thawing period in water by total immersion at room temperature (+ 20±5°C); 2) test by maximal saturation of samples before freezing by boiling in water for 5 h. After the frost test the hydric properties of the sound samples were done according to the previous methodology and compared with the results of hydric properties before frost test.

Experimental part I: state assessment of travertine objects. The visually detectable performance of exposure of Roman travertine in exterior in Southern climatic region - in Rome, Italy and Northern climatic region - in Latvia and in Northeast region in USA (New York) was studied. Criteria for choose of objects abroad was: 1) location in Southern and Northern climate in order to compare climatically different and similar exposure conditions with Latvia; 2) approximately the same construction time and geological origin of Roman travertine as for Monuments in Latvia.

In Latvia Roman travertine has been used for construction of 5 Cultural Heritage Monuments: 1) *Freedom Monument* (sculptor K. Zāle, arhitect E.

Štālbergs; 1935; Riga); 2) sculpture *Fallen Brothers* (sculptor K. Zāle, arhitect E. Štālbergs; 1936; Ensemble of Riga Brethren's Cemetery; Riga); 3) *Smardes Brethren's Cemetery* (sculptor K. Zāle, 1936; Tukuma district, Smarde parish); 4) *Monument devoted to soldiers of Rigas 6th unmounted regiment* (sculptor M. Šmalcs, architect N. Voits, 1937; Jelgava district, Cenas parish); 5) *Tomb stone devoted to family of K. Skalders* (unknown author, 1930-ties; Bauska, Plosta Cemetery).

Observed travertine objects in Rome, USA and Latvia differs significantly by design, specification and craftsmanship that lead to individualities of weathering patterns of each case study. One of the significant difference characteristic for Monuments in Latvia is that non-seasoned (saturated by quarry moisture) Roman travertine was used that has resulted in frost damages due to shipment via cold sea and exposure under frost in Riga. Latvian case-study is an example that it is never too many to postpone properties of natural rocks in order to improve their performance in objects and to avoid creation of unreasoned opinions on material durability.

Soiling and bio-contamination of travertine is characteristic for all observed objects in Rome, New York and Latvia, while frost caused damages could be detected only for objects exposed in Northern climate - New York and Latvia [6, 13**],** However Latvian case study of Roman travertine used in exterior should be regarded as specific due to non-seasoning of travertine material and its further damage under frost. It could be concluded that in Latvia's case already damaged Roman travertine more susceptible to deterioration was used.

Experimental part II: Study of deposition layers. Surface layers on stone Monuments are the product of interaction between stone material and atmospheric deposition. Surface layers formed on travertine Monuments in Latvia have the form of: 1) black crusts of thickness up to 1-2 mm mainly localized on the stone surface of sheltered exposure; 2) intensive black and grey soiling, uniform thin layer of soiling covering the whole exposed area of travertine. Sampling and study of deposition layers was done at 3 subsequent levels according to the schema shown in Figure 1.

Petrographic investigations showed that the dissolution of calcite could be detected that in the early stage shows as flattening of the walls of the open pores. Further studies showed that the infiltration of soiling could be observed in the whole depth of exposed travertine blocks (deposition layers from 2nd and 3rd sampling levels, see Figure 1).

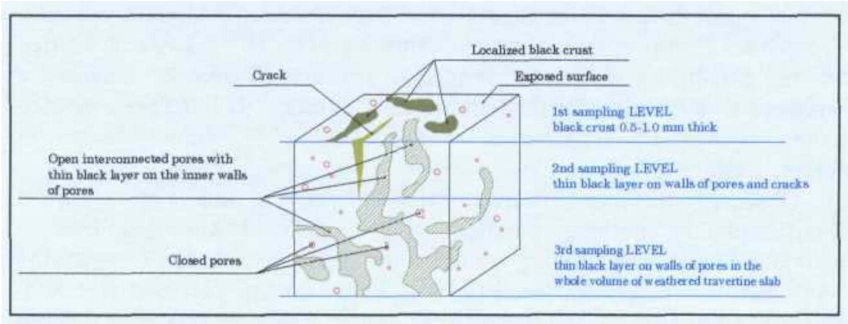


Figure 1. Schematically drawing of sampling levels of deposition layers from weathered Roman travertine from Freedom Monument in Riga.

Compositional analyses of deposition layers. XRD and FTIR analyses showed that calcite, quartz and gypsum are presented in surface crusts, while for 2nd and 3rd sampling levels only calcite could be detected. SEM/EDS analyses showed that 2nd and 3 rd deposition layers consist of variously shaped solid particles deposited on the crystals of calcite (Figure 2) with wide range of elements presented (Figure 3) related to presence of quartz (origin -windblown dust, adjacent materials -granite cladding), halite (origin - sea-salts, de-icing salts), mineral and rock fragments, clay minerals (origin - windblown dust), feldspars and ferromagnesian silicates (origin - windblown dust, adjacent materials - granite cladding).

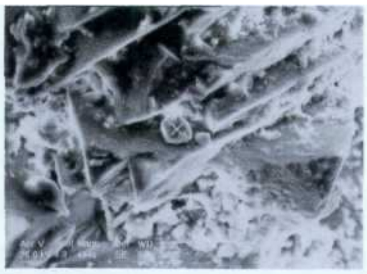


Figure 2. SEM/EDS analysis (point marked by "X"). Dolomite ($CaCO_3MgCO_3$) deposited on the cleavage planes of calcite crystal.

It was found that open pores of travertine has deposition layers similar by composition as found on exposed surface suggesting the infiltration of deposition in the depth of fabric. Soiling has passed through the open and connected porous system suggested that whole volume of exposed travertine slabs have been subjected to environmental agents during exposure and changes in open porosity could be prospective.

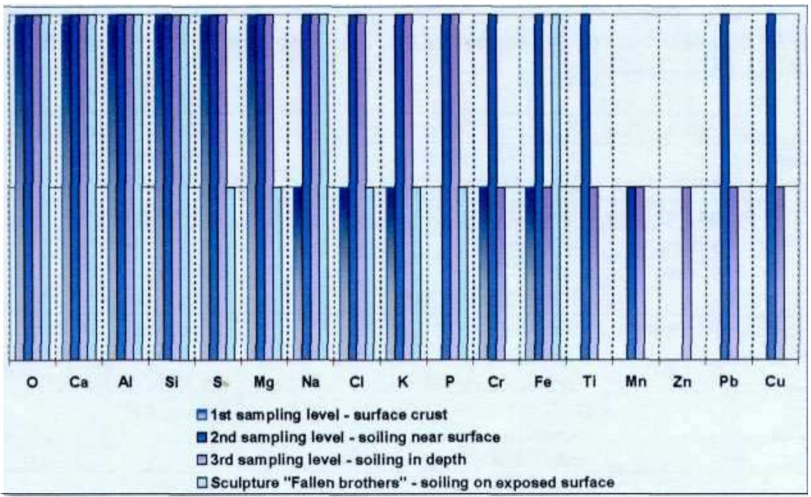


Figure 3. Summary of EDS results from qualitative element analyses of soiling levels from travertine.

Significant cause of surface deposition and further discoloration of Roman travertine in Monuments in Latvia is bio-contamination. According to chemical analyses about 50%, up to 70% of deposition could be related to colonisation of biology. Biological analyses show that the growth of mosses, algae, microscopic fungi and bacteria could be detected. Micro-organisms can change the colour of stone material, especially fungi of family *Dematiaceae (Altenaria, Cladosporium)* that content dark pigments - *melanine* and *melanoid* [13] both detected for travertine monuments in Latvia. Roman travertine Monuments in Latvia are related to intensive formation of biological colonisation. The microbial contamination acts as a preliminary precursor for the development of crusts: increases adsorption of airborne particles on the stone surface; enforcing alterations in the capillary water uptake and water vapour diffusion in the rock material.

Experimental part III: Material characterisation. Material characterisation involves testing of weathered and quarried Roman travertine in order to give comparative characterisation of travertine's physical/mechanical, compositional and durability properties.

Information of type and origin of weathered and quarried travertine are summarised in Table 1. Comparative study of petrography, composition and amount of trace elements by ICP-MS showed that both weathered and quarried travertine could be referred to the same type of travertine.

Table 1. Denomination of weathered and quarried Roman travertine used in Latvian Monuments.

Criteria	Weathered travertine	Quarried travertine
Name of the natural stone	Travertino Romano Chiaro Barco	Travertino Romano Chiaro Barco
Petrological family	Travertine	Travertine
Typical colour	Yellowish grey	Yellowish grey
Place of origin	Bagni di Tivoli (Roma, Lazio), Italy	Bagni di Tivoli (Roma, Lazio), Italy
Name and address of supplier	Mariotti Carlo & Figli S.p.A., Via Tiburtina 287, 00011 Tivoli Terme, Rome – Italy *(in 1930ties, when travertine was supplied to Latvia, company work under name of Luigi Bartolini)*	Travertini Giansanti, via Tiburtina - km 25,350 Guidonia, Rome, Italy

Physical properties. *Pore size distribution.* Weathered travertine has increase in macroporosity for 6% and for about 3% higher capillary porosity and hygroscopic porosity resulting in increase of capillary water uptake and water condensation in pores. Weathered travertine (Figure 4) has almost similar distribution of pores in the range of pores < 1.5 µm, while quarried travertine has higher amount of pores in the range 0.4 - 0.1 µm with decrease in range of 0.1 - 0.005 urn compare to weathered travertine. From the point of frost resistance it could be seen that weathered travertine has slightly lower amount of pores sensitive to frost resistance compare to quarried travertine leading to conclude on higher frost resistance.

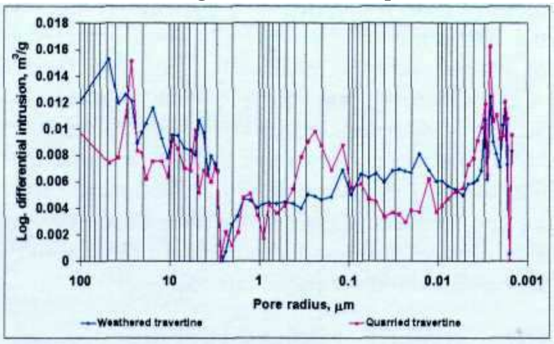


Figure 4. Pore size distribution of quarried and weathered travertine by MIP.

It could be assumed that frost action has resulted in mechanical corrosion of pore system of weathered travertine due to freeze/thaw cycles resulting in deterioration or crushing of pore walls, formation of new capillaries or widening radii of existing ones in the range of pore size 0.4 - 0.1 µm (Figure 4).

Capillarity. Curves of capillarity for weathered and quarried travertine (Figure 5) shows remarkable differences compare quarried and weathered travertine and compare capillarity in different directions according to the bedding planes. Impact of sedimentation to physical properties is clearly visible from capillarity curves. For weathered travertine capillarity in direction parallel to the bedding planes are 2 times higher than in direction perpendicular to bedding planes. This leads to conclude that weathering results in higher differentiation according to bedding planes and confirms that placing in bed of stone blocks in objects is of great importance of all porous stone materials.

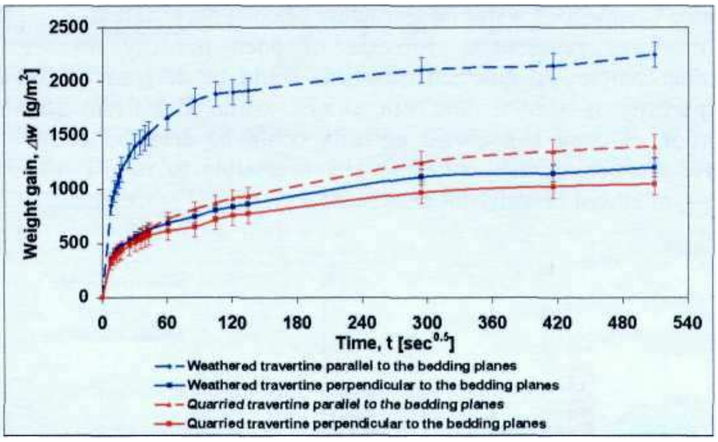


Figure 5. Capillarity of quarried and weathered travertine, weight gain [g/m^2] vs time [sec^{0,5}].

Deterioration along the bedding planes occurs when weather exposure creates internal fissures and delimitations that further reduce strength in the weak direction [12]. These cracks behave like pores, especially with respect to water suction and to occurrence of internal stress and could be the reason for higher capillarity for weathered travertine. Higher capillarity of weathered travertine is confirmed by MIP results showing higher amount of capillary pores for weathered travertine.

From the results of water absorption by capillarity it could be concluded that weathered travertine presents 2 times anisotropy of water absorption according to bedding planes, while quarried - only 1 time suggesting that due to weathering increase of anisotropy of weathered stone material could be prospective.

Evaporation and drying. It was stated that drying rate of weathered and quarried travertine proceed without drying stage I, when the rate of evaporation is limited or controlled by the external conditions rather than by the rate of transport within the material, but only thought stage II - controlled by the porosity and pore system of material. Therefore it means that drying rate of travertine strongly depends on structure of material, particularly on capillary and hygroscopic porosity.

Free sorption. The dynamic of water absorption under atmospheric pressure shows that weathered travertine has 2 times higher water absorption. Weathered travertine has more rapid water absorption explained by the elevated capillary and hygroscopic porosity that promotes further migration of absorbed water into structure of open pore system.

Calculated parameters. Increase of open porosity for weathered travertine compare to quarried travertine could be determined. Estimated total porosity is similar for both stones, while significant changes in proportion of open and closed porosity could be detected - there is an increase of open porosity (the porosity accessible to water) with related decrease of closed porosity for weathered travertine (Figure 6).

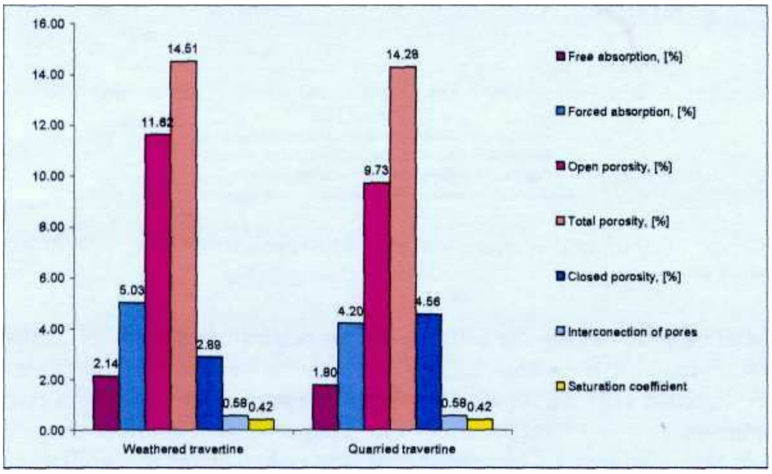


Figure 6. Calculated parameters of physical properties for weathered and quarried Roman travertine.

The elevated water absorption and porosity of the weathered travertine is resulted from alteration processes of travertine during the exposure of 60 years. In the case of weathered travertine used in Monuments in Latvia the freeze damages (cracking) of non-seasoned travertine could increase the porosity and water uptake. By further exposure due to corrosion action of water migration in open pore structure (freezing/thawing, condensation/evaporation cycles) open porosity has increased.

Mechanical properties. *Compressive strength.* Test of compressive strength (Figure 7) was done in two directions according to the bedding planes of travertine - with the load applied parallel and perpendicular to the bedding planes. Obtained results of test values for compressive strength have high area of standard errors about 20% due to the high heterogeneity of travertine structure and prohibit data analyses in regard to structural weathering. In summary it could be concluded that:

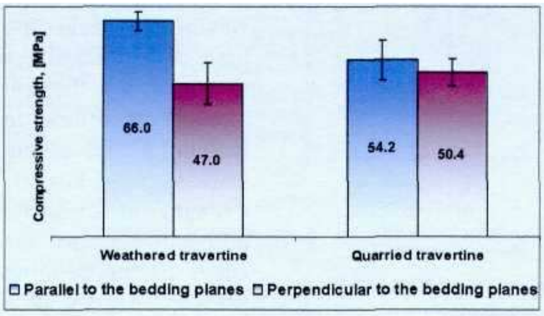


Figure 7. Compressive strength of weathered and quarried travertine parallel and perpendicular to the bedding planes.

- both weathered and quarried travertine meets the necessary requirements for cladding slabs;
- quarried travertine has structural anisotropy of compressive strength according to bedding planes of 1,1 times;
- weathered travertine has structural anisotropy of compressive strength according to bedding planes of 1,4 times;
- it could be marked that quarried travertine is more homogeneous stone than weathered travertine.

Flexural strength. Test of flexural strength was done in two directions according to the bedding planes of travertine - with the load applied perpendicular to the bedding planes and perpendicular to the edges of the bedding planes. Results of flexural test (Figure 8) shows that both weathered and quarried travertine have flexural strength appropriate for external stone cladding. Weathered travertine has for 20 to 30% lower flexural strength than quarried travertine. Reduction of tensile strength of weathered travertine suggests on structure weakening due to corrosion processes and increase in anisotropy according to bedding planes. Travertine's weak bedding planes pose special problems for the design of anchorage systems that avoid water penetration and tensile stresses imposed by the weak bedding planes.

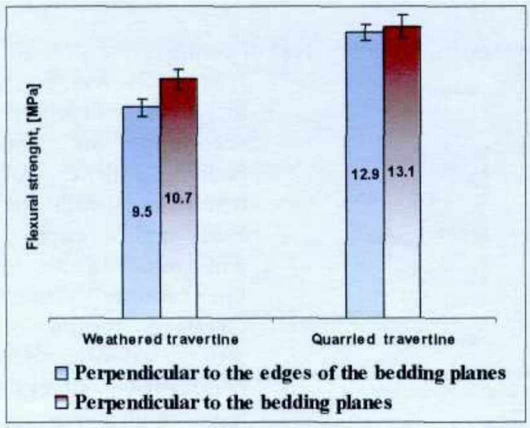


Figure 8. Flexural strength of weathered and quarried Roman travertine perpendicular to the bedding planes.

Quarried travertine performs very slight anisotropy (it is more homogeneous), while weathered travertine have difference of 1,1 times of flexural strength according to bedding planes having lower flexural strength in direction perpendicular to the edges of the bedding planes. This suggests that if travertine is laid on its natural bed in object it will perform higher flexural strength.

Accelerated durability tests. *Frost resistance. Test by free absorption.* In total 150 freezing/thawing cycles were done and results are summarised in Figure 9. There is no mass decrease or decrease in apparent volume during the tests for weathered and quarried travertine. Both travertines resist 150 cycles and could be classified as frost resistant. During frost resistance test visual observation of travertine samples was done.

Although at the end of test after 150 cycles both types of travertine could be classified as frost resistant visual changes of travertine samples were observed. According to data from visual inspection following conclusions could be drawn:

- both weathered and quarried travertine performed frost damages during frost test, however the degree and severity of damage is insignificant to influence total frost resistance of series of travertine samples;
- first signs of frost damage occurs faster for weathered travertine. Quarried travertine resists more frost cycles without any damages, but when deterioration starts, it disintegrates in less time than weathered travertine.

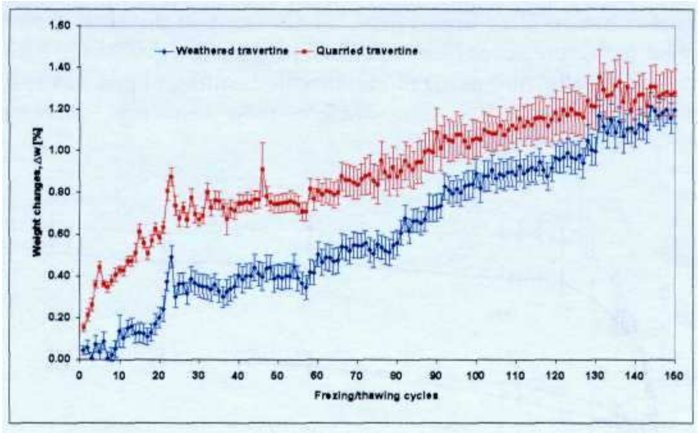


Figure 9. Weight changes of weathered and quarried travertine during freezing/thawing cycles.

As both travertines during the test are subjected to similar conditions, the properties of porosity remains as the only factor influenced material behaviour under frost. Physical/mechanical tests have shown that weathered travertine has suffered from severe frost damage occurred on saturated material.

On the other hand, MIP results showed that quarried travertine could be slightly more sensitive to frost damages compare to weathered travertine. In order to characterise theoretical way of damages caused by frost, evaluation of physical properties of weathered and quarried travertine samples was done.

Hydric properties after frost test. For weathered travertine no significant changes were observed in capillarity after the frost test (Figure 10). The increase of capillarity in direction parallel to the bedding planes after 150 cycles of freezing/thawing is only for about 10% and this confirms that weathered travertine is a resistant material for further exposure in Latvian climate. Accelerated frost test increased anisotropy for weathered travertine for 12 %.

Controversially for quarried travertine (Figure 11) another results were observed:

- water absorption by capillarity after accelerated frost test was increased in both direction according to the bedding planes of travertine; water absorption by capillarity in direction parallel to the bedding planes were increased for 68%; in direction perpendicular to the bedding planes - for 37%;

frost damage has resulted in increase of anisotropy of physical properties of quarried travertine according to the bedding planes, difference between water uptake parallel and perpendicular to the bedding planes has reached 1,6 times compare to 1,3 times before frost test, e.g., increase in anisotropy for 0.3 times or 23%.

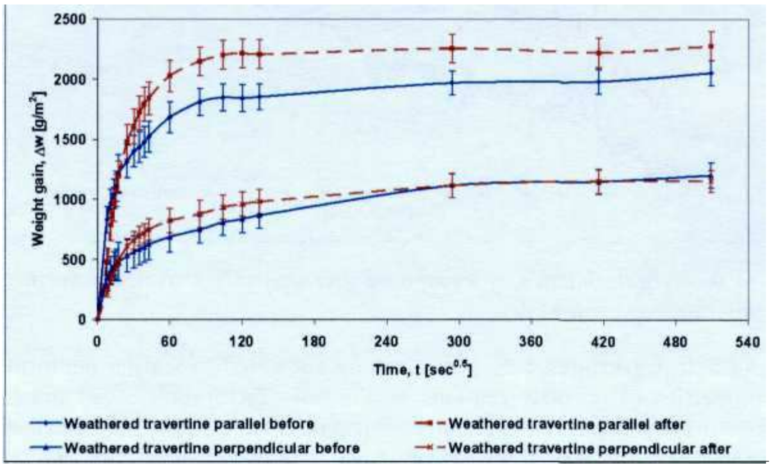


Figure 10. Water absorption by capillarity parallel and perpendicular to the bedding planes of weathered Roman travertine before and after frost test.

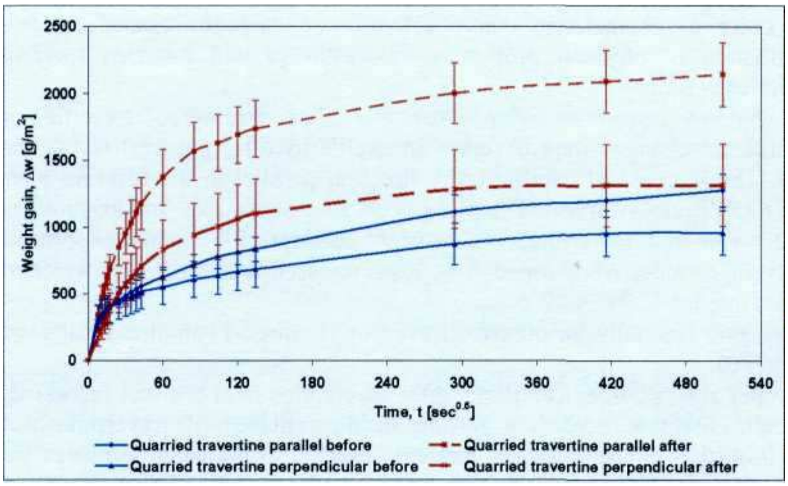


Figure 11. Water absorption by capillarity parallel and perpendicular to the bedding planes of quarried Roman travertine before and after frost test.

Results confirms assumption that weathering of Roman travertine results in increase of structural anisotropy of physical/mechanical properties by lowering strength of material in the weakest direction - parallel to the bedding planes.

For weathered travertine increase of free water absorption for ca 30% was detected, while for quarried travertine increase of free absorption has reached about 45%, which is for 15% more than for weathered travertine (Figure 12.)- Changes for forced water absorption was also detected, which has resulted in increase of saturation coefficient from 0.4 to 0.5, as well in decrease of interconnection of pores from 0.6 to 0.5. This means that open pore structure of materials has change by increasing of interconnected porosity facilitating water transport in material.

For quarried travertine increase of open porosity for about 10% and decrease of closed porosity for about 30% could be observed (Figure 12). The change of ration of open and closed porosity is showed in Figures 13. and 14., where open porosity is put versus apparent density of material. The changes for weathered travertine are almost undetectable, while quarried travertine performs considerable decrease of closed porosity. This leads to conclude that pore size range in radius > 3 µm and from 0.4 to 0.006 (am in radius, where weathered and quarried travertine had remarkable differences, is of great significance for frost durability.

Weathered travertine has higher amount of pores in the range of radius > 3 µm promoting more space for ice crystals to grow. Ice crystals may also formed in the finest pores, when the temperature drops below a critical point determined by the radius of curvature of the supercooled water meniscus. Quarried travertine has higher amount of pores in the range with radius from 0.4 to 0.1 µm, which is still in the size of capillary porosity and due to water absorption by capillarity could be saturated by water. At this range of pores water freezes already at temperature below zero. Therefore it could be concluded that frost damage of accelerated frost test could occur in this region.

The test of hydric properties after accelerated frost test and recalculated physical properties of porosity showed that frost attack has left a stone apparently unharmed, but internally weakened. The natural process that gives rise to porosity produces a fine pore system in the early stages and then proceeds by breaking down the pore walls, thus increasing the mean pore radius. This phenomenon was observed from study of porosity and hydric properties of naturally weathered travertine and is confirmed by results from physical properties after frost test.

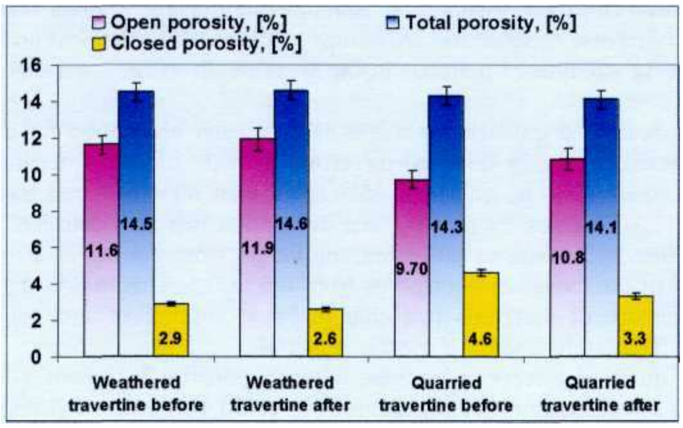
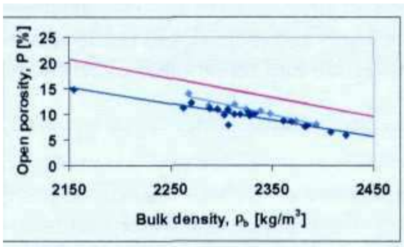


Figure 12. Recalculated values of porosities for weathered and quarried travertine after frost test.



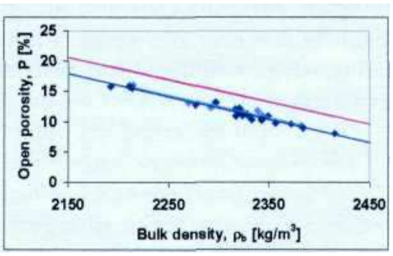


Figure 13. Open porosity versus bulk density for quarried Roman travertine before frost test (deep blue line) and after frost test (light blue line).

Figure 14. Open porosity versus bulk density for weathered Roman travertine before frost test (deep blue line) and after frost test (light blue line).

The solid red line is the total porosity for Roman travertine, where for calculation the crystallographic density of mineral calcite was used as solid density for travertine (2710 kg/m^3) [14].

Frost resistance. Test by saturation. Frost test carried out on maximally saturated travertine samples was done in order to simulate conditions of freshly quarried non-seasoned travertine saturated by quarry moisture and exposed under frost as it was during construction of Freedom Monument in Riga.

Already after the first cycle of frost test loss of weight was detected for both weathered and quarried travertine samples (Figure 15.) suggesting that travertine are susceptible to frost damage when maximally saturated. In the case of maximal saturation there is no space for ice crystals to grow as well there is no space for unfreeze water to migrate thought capillary. Therefore frost damage could occur already at the first cycle of frost test.

It could be concluded that the main damage to travertine structure of material used for construction for Monuments in Latvia was done during frost damage of saturated, non-seasoned travertine slabs.

Quarried travertine is more susceptive to frost damage by saturation compare to weathered travertine. Quarried travertine is classed as failed after 20th cycle while weathered travertine only after 37th cycle, e.g., weathered travertine has almost 2 times higher frost resistance. This confirms the previous test results that quarried travertine is slightly more susceptible to frost damage compare to weathered travertine due to lower amount of pores > 3 μm and higher amount of pores in the range with radius from 0.4 to 0.1 μm

Experimentally obtained data suggests that weathering of travertine due to frost damage proceeds at a faster degree at the first period under exposure to frost and the rate of deterioration decreases by time.

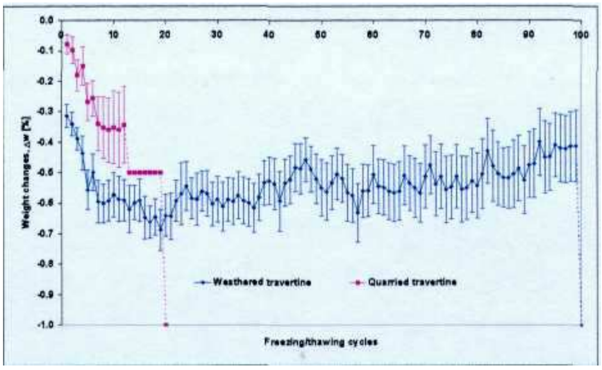


Figure 15. Weight changes of weathered and quarried travertine during freezing/thawing cycles in frosts test by saturation.

Crystallisation test. Crystallization test was done until total failure of travertine samples (Figure 16) in order to estimate differences in weathering resistance of weathered and quarried travertines. Failure of weathered travertine started already at 17th cycle, while for quarried travertine - at 36th cycle, e.g., it could be concluded that weathered travertine has 2 times lower resistance than quarried travertine. After 15 cycles of crystallisation test weight loss of both weathered and quarried travertine samples was < 1% and material should be regarded as durable and suitable for all exposure conditions [7],

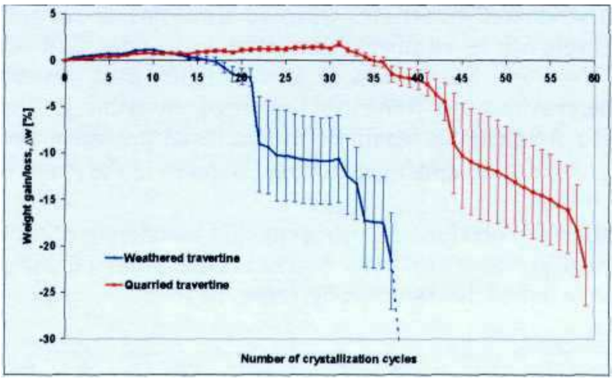


Figure 16. Crystallization test of weathered and quarried Roman travertine.

Conclusions.

1. At the second half of 1930ties Classical Light Roman travertine was used in exterior for construction of five Cultural Heritage Monuments in Latvia the region with Northern climatic conditions characterized by frequent freeze/thaw cycles (about 70 per year) and high relative humidity (average about 80-90%).

2. During exposure in Monuments in Latvia open interconnected porosity inside the material of Roman travertine has been subjected to throughout continuous infiltration of water that has resulted in dissolution and recrystallization of calcite and deposition of soiling consisting of quartz, mineral and rock fragments, clay minerals, feldspars and ferromagnesian silicates originated from windblown dust and adjacent materials - granite cladding, and halite originated from sea and de-icing salts.

3. After 60 year exposure in Monuments in Latvia Classical Light Roman travertine performs following properties: *I) free water absorption - 2.1% (range 1.3-3.4); 2) open porosity -11.6% (range 8.1-15.9); 3) saturation coefficient - 0.42 (range 0.31-0.52); 4) compressive strength - 56.5 MPa (range 15.7-86.4), 5) flexural strength -10.1 MPa (range 7.6-13.4); 6) frost resistance >150 cycles; 7) salt crystallisation - 0% weight loss after 15 cycles;* which leads to conclude that travertine is still durable building stone suitable for severe exposure conditions.

4. Unweathered Classical Light Roman travertine performs following properties: *1) free water absorption - 1.8% (range 0.9-3.2); 2) open porosity - 9.7% (range 6.0-14.8); 3) saturation coefficient - 0.42 (range 0.33-0.51); 4) compressive strength - 52.3 MPa (range 12.9-86.4), 5) flexural strength - 13.0 MPa (range 12.9-86.4); 6) frost resistance > 150 cycles; 7) salt crystallisation - 0% weight loss after 15 cycle;* which leads to conclude that travertine is building stone suitable for most uses including more severe exposure conditions like frequent frost cycles presented in Northern climatic regions.

5. Northern climatic conditions of Latvia has determined weathering of Classical Light Roman travertine resulted in: 1) increase of open porosity for 16 % with a consequent drop of closed porosity; 2) increase of capillarity in direction parallel to the natural bedding planes for 50 %; 3) decrease of flexural strength for 23 %; 4) increase in anisotropy in the direction parallel of bedding planes for about 0.4 times.

6. Accelerated frost tests in laboratory has resulted in following changes of physical properties of Roman travertine: 1) increase of open porosity for 12 % with a consequent drop of closed porosity; 2) increase of capillarity in direction parallel to the natural bedding planes for 40 %; 3) increase of coefficient of saturation from 0.4 to 0.5; 4) increase in anisotropy in the direction parallel of bedding planes for about 0.3 times and is comparable to the changes due to natural weathering observed for Roman travertine used Monuments in Latvia.

7. For Roman travertine used in Northern climatic regions higher demands on design, workmanship, regular survey and maintenance should be involved as mandatory premise due to the weak bedding planes of travertine determining travertine's durability and weatherability.

8. Main factors for weathering of Roman travertine in Monuments in Latvia are faults in workmanship of use of non-seasoned travertine and lack of maintenance of Monuments during exposure that in combination with Northern climatic conditions has caused aesthetical and structural damages to travertine.

9. In order to safeguard Cultural Heritage Monuments built of Roman travertine in Latvia maintenance of objects should be done after each 2 to 4 years involving surface cleaning and protection using treatment with biocides.

10. Based on the results of thesis, conservation/restoration projects for 3 Roman travertine Monuments in Latvia have been elaborated. Conservation/restoration of 2 Roman travertine Monuments have been done.

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