Increasing Durability of Building Stones to Mitigate Structural Pathology of Historic Structures

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ABSTRACT: Building materials’ durability is fundamental for architectural heritage preservation. Stones’ susceptibility to salt decay is related to structural pathology phenomena. The need for increasing materials’ durability for structures’ strengthening leads to criteria and methodology for the evaluation of conservation interventions on treated porous stones. In the present work, given the decay pathology relations in the masonries of Medieval Fortifications of Rhodes constructed by porous biocalcarenite and the use of Cyprus biocalcarenite for restitution, samples of quarry stones and consolidated – protected ones are examined. Microstructural characteristics are evaluated by Mercury Intrusion Porosimetry and mechanical characteristics through compressive - bending strength tests respectively. Crystallization pressure values are calculated and compared to compressive and tensile strength of the stone, examining the probability of stone disruption due to salt crystallization. Thermodynamic analysis is performed, indicating the most probable thermodynamic phenomenon to take place, that is salt crystallization in capillaries or stone mechanical failure.

1 INTRODUCTION

Materials’ decay can be defined as degradation of material’s properties (physical, chemical, mechanical, etc.) and characteristics (texture, mineralogical composition, etc.) over time, leading to material failure. Decay phenomena develop either at the interface between the material and the environment, or at the interface between materials. Materials’ decay is a function of intrinsic and extrinsic factors. Intrinsic factors are related to the material itself, including type, properties, mass distribution, source and processing technology of the material. Extrinsic factors refer to the environmental effect of the material and comprise factors relating to the atmosphere and to the usage of the material.

2 SALT CRYSTALLISATION

2.1 Salt decay

Salt decay is the most significant deteriorating mechanism for monuments and buildings in marine environment. Salts migrate in the form of solution through the complex capillary system of porous stones towards the surface. Crystallization of soluble salts may result in salt efflorescences, which deposit on the external surface of the stone. The phenomenon is observed when the rate of salt solution migration to the surface is higher than the drying rate. Another possibility is salt subefflorescences, which appear below the stone surface. The phenomenon is ob-
served when the rate of salt solution migration is lower than the drying rate. This case is considered the most critical for deterioration of stone, as it may lead to stress development into the pore walls.

Susceptibility of stone to soluble salts decay is highly dependent on its microstructural and mechanical characteristics. The assessment of the susceptibility of building stones to salt decay can be accomplished through two approaches. The first one involves evaluation of crystallization pressure as a function of the stone’s microstructure. The second approach involves prediction, through thermodynamic terms, of the most probable development of the deterioration phenomenon.

2.2 Direct evaluation – crystallisation pressure

In the first approach, crystallization pressure is estimated through a microstructural study, and is then compared to the mechanical properties of the material.

Critical microstructural parameters, such as the ratio of active to total porosity, the average pore radius, the specific surface area, and the bulk density are measured through mercury intrusion porosimetry. These microstructural parameters allow for a direct evaluation of stone susceptibility to decay due to crystallization.

Furthermore, another characteristic value of the crystal can be calculated, the crystallization pressure, which is the excess pressure developed due to salt crystal growth. More specifically, crystallization pressure can be calculated as a function of the microstructural characteristics of the porous stone:

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P = 2\sigma \left( \frac{1}{r} - \frac{1}{R} \right)
\]

where \( P \) = the crystallization pressure, \( \sigma \) = the interfacial crystal salt-solution tension, \( r_i \) = the sum of small pores radii of the porous stone, and \( R \) = the radius of coarse pore of the porous stone. As far as the critical radius is concerned, that is the distinguishing radius among small and coarse pores, the recommended value is 5 µm. This means that pores with radii greater than 5 µm can be classified to the category of coarse pores.

Compression and bending tests are performed for the evaluation of the mechanical characteristics of the stones. The values of the crystallization pressure are then correlated with the values of the compressive and tensile strength of the stone. When the crystallization pressure value exceeds the strength of the stone, mechanical failure is observed. Susceptibility of stone to salty decay is a function of the compression modulus and the compression strength of the stone in conjunction with the microstructural characteristics or the modulus of elasticity and the tensile strength in conjunction with the microstructural characteristics. It should be noted that tensile rather than compressive strength is considered to be the most representing factor for the comparison with the crystallization pressure values. This is due to the fact that tensile strength represents the cohesive strength of the material, in other words, the maximum load per surface area, which can be supported without material failure.

An energetic evaluation is performed, combining the crystallization pressure with the compressive and tensile strength values of the stone and estimating the probability of disruption of the stone pore walls or filling of the smaller pores.

2.3 Energetic evaluation – thermodynamic scenario

The most probable scenario is determined by thermodynamic factors by the following susceptibility index:
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\Delta G_1 - \Delta G_2 = (\Delta G_{bulk} + \Delta W) - (\Delta G_{bulk} - \Delta G_{surf}) = \Delta W - \Delta G_{surf}
\]

\[
\Delta W > \Delta G_{surf} \Rightarrow \text{Propagation of the salt crystals along the capillaries}
\]

\[
\Delta W < \Delta G_{surf} \Rightarrow \text{Growth of bulk crystal and mechanical failure}
\]

where \(\Delta G_1\) = the free energy change which corresponds to the progressive crystal growth originating in coarse pores, leading to an increase of the crystallization pressure and eventually leading to pore walls rupture, \(\Delta G_2\) = the free energy change which corresponds to propagation of the salt crystals along the capillaries after filling the coarser pores, \(\Delta W\) = the work needed to rupture the pore walls (estimated to equal to \(\frac{1}{2} \sigma_c \Delta V\) for compression), \(\Delta G_{surf}\) = the surface change contribution to the free energy of the salt crystal formation.

3 EXPERIMENTAL PROCEDURE

Various conservation materials have been used in the past, according to the demands of the case under examination. Inorganic materials have been widely used, due to their chemical relevance to the authentic building material. Their use is confined nowadays, because they usually form undesirable crusts and by-products after their application to the stone. Organic materials lead to the increase of stone’s mechanical strength values. However, they tend to form crusts and degrade during their exposure to oxygen and ultraviolet radiation. Alkoxysilanes are the preferred materials for the treatment of siliceous sandstones, due to the formation of chemically relevant materials to the binder during polymerisation.

The examined Cyprus porous stone from Limassol quarry was a calcareous sandstone, which consisted mostly of calcium carbonate (approximately 94%), with extremely small amounts of quartz and plagioclases. The consolidation material used was ethyl silicate dissolved in ethyl alcohol 20% w.w. to SiO\(_2\) 70% w.w. in the form of transparent liquid (codename RP). It is a non-filmogenic material, penetrating, with chemical relevance to siliceous sandstones. The protection material consisted of a polysiloxane binder dissolved in white spirit (codename GP). It is a colourless, penetrating waterproofing agent for mineral or exterior surfaces, which adheres to the surface without forming a film and affecting the vapour transmission properties of the stone.

A combination of the above consolidation and protection materials was also applied (codename RG). The porous stone samples were treated by the above mentioned consolidation and / or protection materials by immersion. The materials were applied until the weight of the treated stone remained practically invariable, i.e. the variation between the two last weighs of the stone didn’t exceed 5%. Three kinds of treated samples were used, consolidated (codename RPL), protected (codename GPL), consolidated and then protected after 15 days (codename RGL). Regarding protection material, its drying time was 2 hours and the whole effect appeared after 24 hours.

All types of samples along with the untreated ones (codename NTL) were submitted to the experimental tests of Mercury Intrusion Porosimetry (performed by a Fisons Porosimeter 2000) for the evaluation of microstructural characteristics and compression and bending tests (performed by a Wykeham Farrance Model 55662 Ho3 machine based on prEN 772-1 standard test method) for the evaluation of mechanical characteristics.

Based on the obtained results, NaCl crystallization pressure was calculated and the most probable development of the deterioration phenomenon, that is disruption of the stone pore walls or filling of the smaller pores was estimated.
4 RESULTS AND DISCUSSIONS

Mercury Intrusion Porosimetry measurements revealed that the examined untreated stone presented values of total porosity approximately 30%, active porosity 7-9% and average pore radius 3-4 µm. A great percentage of pores presented radius size between 1-5 µm.

Results indicated that after the treatment there was an alteration of the stone’s microstructural characteristics for all types of specimens. The ratio of active to total porosity, which represents the percentage of pores communicating with the environment, was decreased compared to the untreated specimens. Average pore radius was also decreased, indicating deposition of the conservation materials into the pores of the stone. As far as specific surface area is concerned, the values were reduced after the treatment, indicating a decrease in the percentage of fine pores. Reduction of fine pores is desirable. Water in fine pores tends to be absorbed and retained for long periods. Therefore, condensation is more likely to occur in them. In the same way, bulk density values presented an increase after the treatment, indicating amelioration of stone’s cohesion.

The phenomena were more intense for the consolidated samples compared to the protected ones, due to the different activity between conservation materials. The deposition mechanism of a consolidant leads to more pronounced changes of microstructural characteristics of the stone, whereas a protection material leads to hydrophobic behavior of the stone. In general, results could indicate a probable trend for lower susceptibility of stone to salt decay.

Compression strength measurements revealed that the stone’s strength was increased after the treatments and especially after protection. Such an increase was desirable. It could be considered though insignificant, avoiding any serious problems caused by great and incompatible modifications of the mechanical properties of the stone after the treatment. The examined stone was quarried and therefore didn’t present serious signs of decay due to exposure to the environmental conditions.

Moreover, bending strength measurements were performed. The corresponding bending strength values were used for the calculation of the tensile strength of the specimens. This is due to the fact that tensile strength measurements are difficult to materialize, because samples of great length are required. In the case under examination, this could not be possible. The results are in accordance with those of the compression strength measurements, i.e. protection treatment leads to the greatest increase of the mechanical strength of the porous stone.

Crystallization pressure values were increased after the treatment. These values were not the expected ones after the application of the treatment, due to the pore structure of the inhomogeneous stone. The stone under examination consists of pores, which cannot be simulated by a cylindrical model in a realistic way. Even though the examined stone presents high crystallisation pressure values after the application of the treatment, salt decay may not result in stone disruption, due to its mechanical characteristics (modulus of compressibility, modulus of elasticity).

Crystallization pressure values are correlated with the corresponding compressive, \( \sigma_c \), and tensile, \( \sigma_t \), strength values of the untreated and treated stone, combining this way microstructural and mechanical characteristics of the stone. Crystallization pressure values are significantly lower than those of the compressive strength in each case, showing that treatments didn’t cause significant changes on the stone characteristics. In the same way, crystallization pressure values are compared to the experimentally measured tensile strength values.
Figure 1: Active to total porosity ratio values, AP/TSP, for untreated and treated porous stone.

Figure 2: Pore radius average values, PRA, for untreated and treated porous stone.

Figure 3: Specific Surface Area values, SSA, for untreated and treated porous stone.
Figure 4: Bulk Density values, BD, for untreated and treated porous stone.

Figure 5: Crystallization pressure values, P, for untreated and treated porous stone.

Figure 6: Comparison between crystallization pressure values, P, and compressive strength values, $\sigma_c$, for untreated and treated porous stone.
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Figure 7: Comparison between crystallization pressure values, $P$, and tensile strength values, $\sigma_t$, for untreated and treated porous stone.

Figure 8: Free energy difference values, $\Delta G_1 - \Delta G_2$, of untreated and treated porous stone as a function of compressive strength.

Figure 9: Free energy difference values, $\Delta G_1 - \Delta G_2$, of untreated and treated porous stone as a function of tensile strength.
5 CONCLUSIONS

Susceptibility of stone to salt decay is a function of mechanical and structural parameters, i.e. compressive strength, modulus of compressibility, tensile strength, modulus of elasticity, pore size distribution. Consolidation treatments aim to the modification of the above characteristics of the stone, in order to achieve reduction of the decay phenomena caused by soluble salts.

In the present work, porous stone from Cyprus was consolidated and protected with certain conservation materials. Mercury Intrusion Porosimetry measurements revealed micro-structural modifications and a porous shifting towards smaller pore radius, due to the treatments. These phenomena were more intense for the consolidated than the protected samples. Results indicated lower susceptibility of the examined stone to salt decay after the treatment.

Compression and tensile strength values both of treated and especially of protected samples were increased compared to that of the untreated ones. The combined treatment led to the slightest increase. All changes were considered to be within compatible limits.

Crystallization pressure values, which were increased after the treatments and especially after protection, were not the expected ones after the application of the treatment, due to the pore structure of the inhomogeneous stone. Comparisons between the crystallization pressure and either, the compressive strength or the tensile strength showed that mechanical failure of the treated stone didn’t seem to be probable.

Thermodynamic analysis showed that the most probable scenario after the salt precipitation in the stone was filling of the smaller pores with salt crystals and not disruption of the stone pore walls. Protected samples presented the highest free energy difference values, indicating the strongest probability of the above mentioned thermodynamic scenario validity.

Conservation materials succeeded to reduce salt accumulation phenomena, which occur during the marine spray simulation tests. Weight gain of treated samples presented the lowest values.

The Limassol porous stone was found to present high mechanical strength values, which were intensified by the conservation treatments, indicating physico-mechanical compatibility between the stone and the conservation materials. Total evaluation of results indicated that the combined conservation treatment gave the best results.

REFERENCES


