PRELIMINARY RESEARCH FOR THE RESTORATION CONCEPT OF MARBLE PANELS FROM THE STOCLET PALACE IN BRUSSELS

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ABSTRACT

A study was carried out to define the appropriate cleaning and consolidation of deteriorated marble panels of the Stoclet Palace in Brussels constructed at the beginning of the 20th century. Deterioration of the marble panels was triggered by the anisotropic dilatation of the constitutive dolomitic minerals creating irreversibly fissures and pores through which penetration of water and corrosion products could occur. The results from the study showed that the mechanical removal of the superficial black crust was not possible without important material loss of degraded zones. Moderately deteriorated marble panels could be effectively consolidated which was not the case for strongly degraded ones for which replacement was recommended due to the severe stability problems.

INTRODUCTION

Erected near the centre of Brussels, the Stoclet Palace was finished with polished white marble panels and richly decorated with bronze elements (Fig. 1). The marble is of a dolomitic type and probably stems from North-Europe (Norway or Sweden). This palace, recently added to UNESCO's World Heritage List, represents a unique example of architectural art of the beginning of the 20th century: "Created under the supervision of the architect and interior designer Josef Hoffmann, the Stoclet House is a masterpiece of the creative genius of the Vienna Secession through its aesthetic and conceptual programme of Gesamtkunstwerk, through its architectural vocabulary, through its originality, and through the exceptional quality of its decoration, of its furniture, of its works of art and of its garden. It is a remarkably well conserved symbol of constructive and aesthetic modernity in the west at the start of the 20th century." [1]

Figure 1: The Stoclet Palace, *Wim Robberechts* © Robberechts-Région de Bruxelles-Capitale / UNESCO

The marble panels, however, are presently suffering from diverse deterioration phenomena, such as polish loss resulting from exposure to acid rain, biological contamination, formation of black crusts (Fig. 2), anisotropic dilatation of constitutive minerals (Fig. 3) and deposition of corrosion products from the bronze sculptures and decorative elements (detail on Fig.3).

Figure 2: Black crust

Figure 3: Marble panel deformation resulting from the anisotropic dilatation of constitutive minerals; the detail shows deposition of corrosion products

The granular disintegration of marble is a well known phenomenon [2-4]. Most minerals present a dilatation that is not equal in all directions. Exposure to temperature cycles, i.e., alternating warming and cooling, results in irreversible deformations that are enhanced in the presence of moisture. During warming, pores and micro fissures between constitutive grains are formed and increase the porosity and permeability of the marble. During cooling, the micro fissures tend to close, but not completely: hence a marble panel won't return to its original dimension. The residual porosity accumulates after successive cycles through which the generation of products from bronze sculptures and decorative elements occurs. The latter are a quite common problem whenever marble and bronze are combined in one monument. When the corrosion products, composed mainly of copper oxides, hydroxides and salts, are absorbed by the material, they suffer some chemical changes that firmly fix them to the substrate and their removal is therefore quite difficult [5].

Figure 4: Optical microscopic analysis of a sample taken from the backside of the main building, a detail of the superficial layer

Optical microscopic and SEM-EDX analyses of the surface layer of a moderately deteriorated marble panel of the palace are shown in Figs. 4 and 5 illustrating granular disintegration giving rise to the deposition of copper corrosion products, including $CuCl_2$, in the micro fissures.

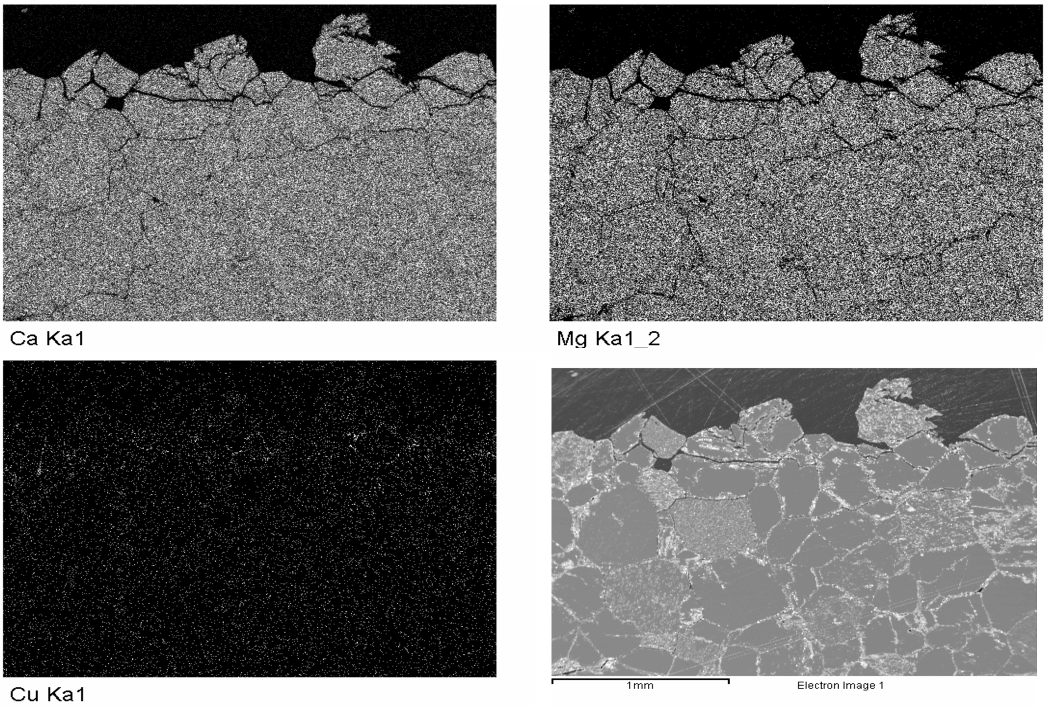

Figure 5: Mapping of calcium, magnesium and copper of the surface layer presented in Fig. 4

illustrating granular disintegration; Down, right – image of the same superficial layer obtained by backscattered electrons (SEM-EDX)

The thickness of marble panels is between 30 and 35 mm. While most of them are moderately deteriorated, some panels surrounding a terrace are highly degraded (Fig. 6), having a very low cohesion to a depth of at least 10 mm, representing about 30% loss of structural strength of the panel.

Figure 6: One of the strongly deteriorated marble panels surrounding a covered open terrace (inside part)

Atmospheric pollution contributes to another degradation phenomenon – formation of the black crusts. This occurs especially on surfaces that are protected from direct rain, so that the deterioration products do not get washed off and tend to accumulate in poorly coherent layers on the stone surface [6]. The first stage in the process is therefore the loss of high polish, followed by the gradual growth of an opaque layer containing most commonly gypsum and carbon particles. This layer eventually falls off exposing the relative intact subsurface, previously beneath the crust, to the deterioration agents [7].

EXPERIMENTAL

The research project focussed on defining a cleaning procedure and the consolidation properties of ethyl silicate based products applied on moderately and strongly deteriorated marble panels, as well as the characterisation of the marble itself.

Marble Characterisation

The mineral composition along with the structure of the stone was determined by means of petrographic analysis. Mercury Intrusion Porosimetry, *MIP* (Micromeritics Autopore II 9220) and Thermogravimetric Analysis, *TGA* (NETZSCH STA 449 F3 *Jupiter*) were used to determine the total porosity and to quantify the constitutive minerals (calcite and dolomite), respectively. *MIP* measurements were performed on a sample lifted from the backside of a moderately deteriorated panel. The grain size distribution is determined by gently grinding a sample of a highly degraded panel followed by sieving.

Cleaning

For the in situ cleaning of moderately deteriorated marble panels showing black crusts, the following cleaning techniques were evaluated:

- water vapour (150°C, 30 bar (3 MPa))
- warm water under pressure (80°C, 80 bar (8 MPa))

The cleaning effect was evaluated by visual inspection of the surface.

Cleaning with saturated water vapour was proposed because it causes significantly less material loss with respect to the other commonly used methods, such as wet sandblasting. On most unweathered materials, this technique usually causes no material loss whatsoever. Therefore it is very suitable for cleaning building materials in cultural heritage.

Consolidation

For consolidation, two products based on ethyl silicate (tetra ethyl ortho silicate, TEOS) were selected. One was a simple consolidant while the second one was an elastified product. The choice of TEOS is based on its widespread application as a consolidant, even on marbles suffering from granular disintegration [8-10]. For many years it has been used in Belgium with very good results.

Moderately as well as highly deteriorated marble panels were lifted from the construction and cut so as to obtain samples of 180x120 mm. Some of these were consolidated two or three times with the simple TEOS formulation (FTB-Remmers, SH 75, dry weight: 51%), while another group of samples was treated in a similar way with the elastified TEOS formulation that contains elastomeric fragments to reduce the brittleness of the formed gels (FTB-Remmers KSE 300, dry weight: 33 %). All tests were carried out in duplicate.

The consolidant was sprayed, at low pressure, on to vertical surfaces in a wet-on-wet manner. The time between two successive treatments was one day. Consolidated samples were conditioned at 20°C/55 % relative humidity (RH) for one month.

The consumption of strengthening product was measured by the weight difference before and after treatment.

The impregnation depth of the treatment was determined two weeks after the last application by sprinkling water drops on a lateral surface of the sample.

The mass return or dry weight of the products was determined by conditioning 0,5g of product in an aluminium cup at 20°C and 55% RH to constant weight. The values determined are the average of three measurements.

The consolidation effect was evaluated by means of hardness profiles obtained by a portable DRMS-device (Drilling Resistance Measurement System, SINT Technology DRMS Cordless 2006). On each sample, at least three DRMS measurements were carried out from which an average hardness profile is calculated. For each type of treatment, an overall average hardness profile is calculated from the average curve obtained per sample.

Colour variations were monitored using a BYK Gardner colour-guide 45/0 colorimeter. Overall changes in the colour of the surface (treated minus untreated sample) are expressed as:

$\Delta E^*= [(\Delta L^*)^2+(\Delta a^*)^2+(\Delta b^*)^2]^{0.5}$, where L*, a*, and b* are the luminosity and colour parameters of the CIE lab system [11]. On each sample, 10 colour measurements were carried out from which an average L*, a*, and b* was calculated. For each type of treatment, an overall average ΔE* was calculated from all the ΔE* obtained per sample.

RESULTS & DISCUSSION

Substrate

The petrographic analysis showed that the marble is composed of relatively equigranular crystals of calcite (~23%) and dolomite (~77%) having a pseudohexagonal to interlobate form with no privileged orientation. The size of calcite grains varies from 60 to 500 µm, with the majority of around 200 µm.

Fig. 7 illustrates the grain size distribution of the dolomitic marble after gently grinding a sample of the panel presented in Fig. 6.

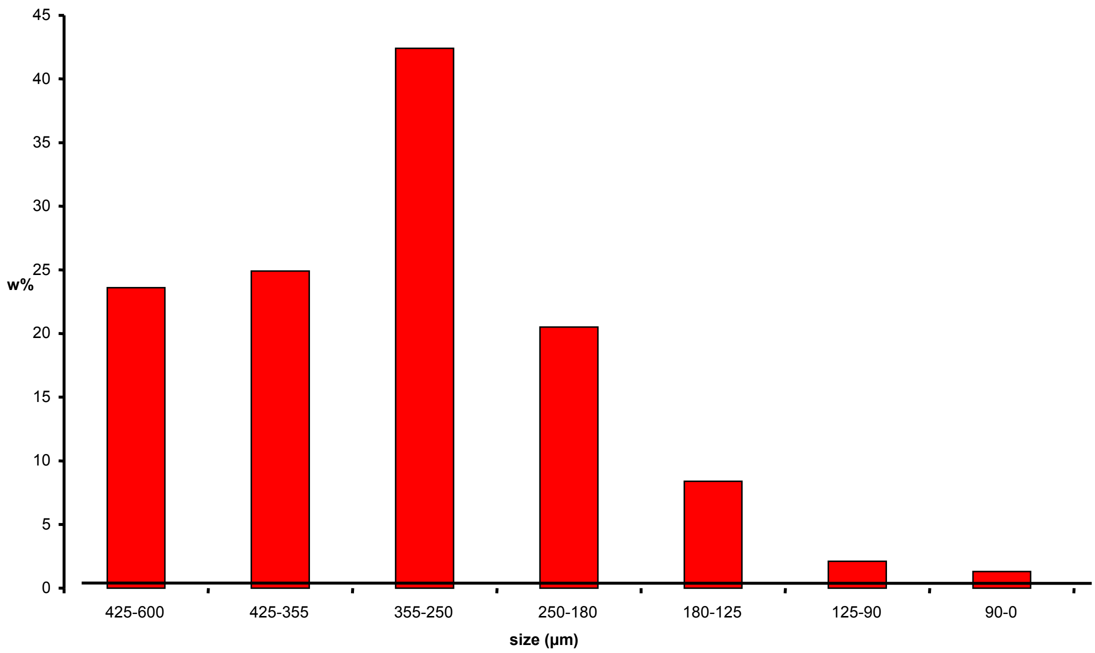

Figure 7: Grain size distribution of the ground dolomitic marble from a sample of the panel shown in Fig.6

Two types of porosity were noted from petrographic analysis:

1. intragranular, reflected in the calcite cleavages and
2. intergranular, marked around calcite grains, composing the main part of the total porosity. This type of porosity depends on the degree of alteration.

The total porosity is low, about 2%, and is therefore at the very measurement limit of the instrument.

Cleaning of Moderately Deteriorated Marble Panels

The cleaning using water vapour (150 °C) at a pressure of 30 bar (3 MPa) is a slow and soft procedure that only results in the removal of superficial dust. The surface of the marble panel showed almost no mechanical damage after cleaning even on zones presenting a low cohesion (Fig. 8). Black crusts could not be removed by means of this soft cleaning technique (see detail on Fig. 8) and hence the original aspect of the marble could not be regained. Even the addition of a non ionic tensio-active agent did not improve the cleaning efficiency.

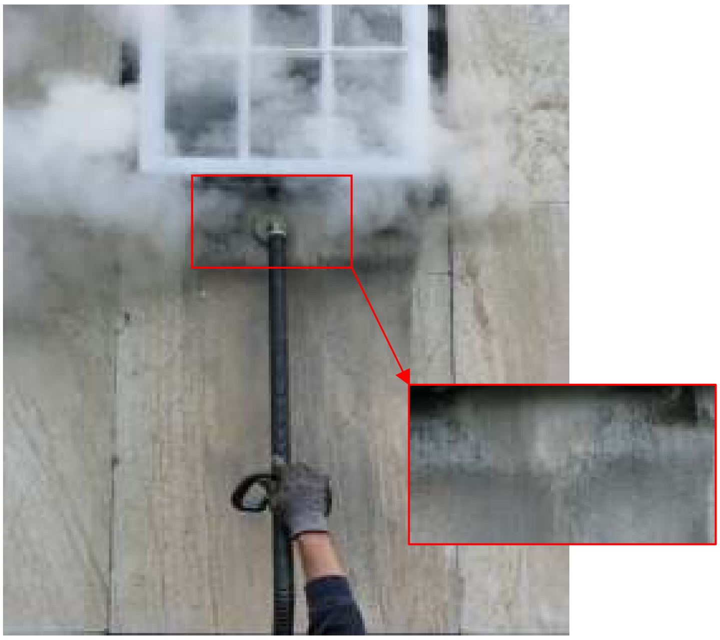

Figure 8: Cleaning of a marble panel with water vapour (150°C, 30 bar (3 MPa))

Detail: a degraded zone of the marble panel in between undegraded zones showing a black crust after cleaning

Warm water (80°C) at a projected pressure of 80 bar (8 MPa) enabled a fast and moderately efficient removal of the black crusts (Fig.9). However, due to the high pressure, important material losses at zones of the marble panel showing surface degradation could not be avoided (see detail on Fig. 9).

Figure 9: Cleaning of a marble panel with warm water under pressure (80°C, 80 bar (8 MPa))

Detail: material loss on a degraded zone of the marble panel after cleaning

Consolidation of Deteriorated Marble Panels

Consolidation of Highly Degraded Panels

According to the literature, TEOS gels have a bridging capacity of 50 µm (0.05 mm), and hence can bridge gaps formed by loose grains having a maximum grain size of 0.325 mm [8,12]. However, some marbles may have a wider range of grain sizes.

As shown in Fig. 7, the dolomitic marble has, apart from small grains below the 325 µm limit, a rather large proportion of dolomite crystals that are significantly larger in size. These larger grains are beyond the limit of grain sizes that, in case of a powder, can be effectively consolidated with TEOS. However, an experimental approach is needed to confirm that marbles having this grain size distribution may not be consolidated since the space between the crystals is a critical parameter.

Fig. 10 presents the hardness profiles of the highly degraded marble panel presented in Fig. 6 before and after consolidation with the simple TEOS formulation. The untreated marble panel as such shows a low hardness, which is even more pronounced for the surface layer of at least 10 mm depth. The consolidation effect of two or three applications with TEOS, for which the consumption was respectively 1300 and 2200 $g \cdot m^{-2}$, was considered insufficient since the mechanical strength of the surface layer hardly increased. Handling the consolidated samples made the presence of loose material evident. This was also the case after consolidation with the elastified TEOS formulation. This poor result can be attributed to the significant fraction of large crystal sizes in this marble as discussed above (Fig. 7).

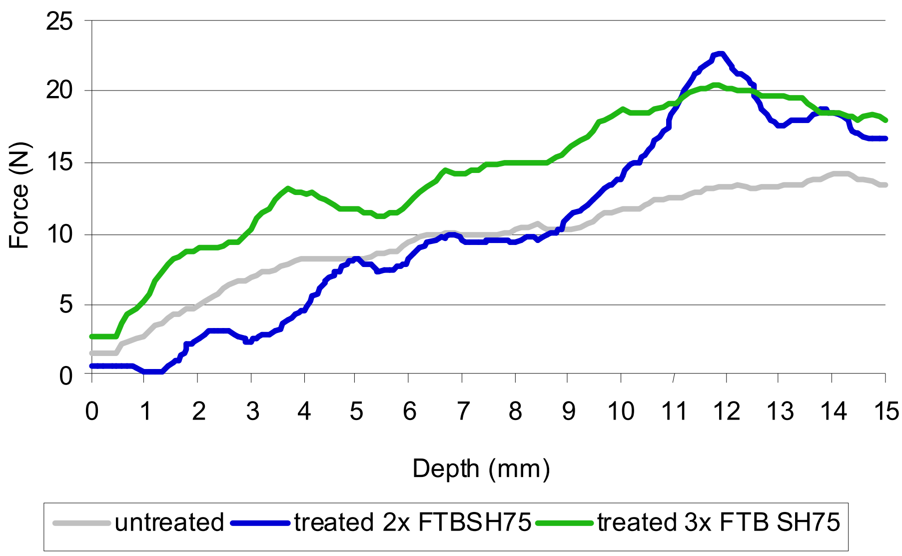

Figure 10: Average hardness profile of samples taken from the highly degraded marble panel presented in Fig. 6 before and after consolidation with a simple TEOS formulation.

Other types of consolidants were considered but not recommended, due to the risks arising from their poor performance or negative effects. For example, lime water (saturated calcium hydroxide solution) was excluded because of the slow rate of carbonatation, the different mineralogical properties and lower mechanical resistance of the formed calcium carbonate compared to the original one [13, 14]. Organic consolidants like epoxies and acrylic resins were excluded because of their high viscosity and/or colour changes after exposure to oxygen and UV-light [14].

Hence, an effective and long lasting conservation of the highly degraded panels of the palace is considered impossible at this time and since their stability is seriously compromised, replacement is recommended.

Consolidation of Moderately Deteriorated Panels

Table 1 summarizes the application methodology, i.e., number of applications, average consumption of the applied TEOS consolidating products and the results of the subsequent evaluation of the consolidation, i.e., impregnation depth and colour variations, for the case of moderately deteriorated marble panels.

Table 1: Average consumption and impregnation depth of the two tested consolidants and ΔE* of the consolidation of moderately deteriorated marble panels.

Product	Number of applications	Consumption ($g.m^{-2}$)	Impregnation depth (mm)	ΔE* [(a)]
FTB-Remmers SH75	2	1320	5-6	4,2
	3	1810	5-6	1,8
FTB-Remmers KSE 300	2	1480	5-6	2,6
	3	1710	5-6	2,7

(a): $\Delta E^* = (\Delta L^{*2} + \Delta a^{*2} + \Delta b^{*2})^{1/2}$, $\Delta L^* = L^*_{after\ consolidation} - L^*_{untreated}$; $\Delta a^* = a^*_{after\ consolidation} - a^*_{untreated}$; $\Delta b^* = b^*_{after\ consolidation} - b^*_{untreated}$

The consumption as well as the impregnation depth of both tested consolidation products are quite comparable. After treatment, the colour variations, and hence the aesthetic impact, are rather low (between 1,8 and 4,2; only values above 5 can be detected by the human eye) [15].

Fig. 11 illustrates the average DRMS-results obtained on samples from moderately deteriorated marble panels. Before treatment, the marble shows a deteriorated surface layer up to 5-6 mm depth, hence corresponding with the impregnation depth of the consolidants (Table 1). A remarkable difference in hardness compared to the highly degraded panels (Fig. 10) is noticed. Two applications with FTB-Remmers SH75 result in an increase of the surface layer hardness quite comparable to that of the underlying sound zone (Fig. 11). A third application does not improve significantly the strengthening properties. Similar results were obtained after treatment with the elastified TEOS product. Fig. 12 compares the hardness profiles of moderately deteriorated marble after two applications with both types of strengthening products and one before treatment. This shows that a slightly better consolidation effect is obtained with FTB-Remmers KSE 300. Moreover, water absorption tests with the Karsten pipe according to [16] revealed no water uptake during 15 minutes, whereas the samples treated with the simple TEOS consolidant still showed some water uptake (0,05 ml), that already is low compared to the average one measured on the untreated sample (0,30 ml).

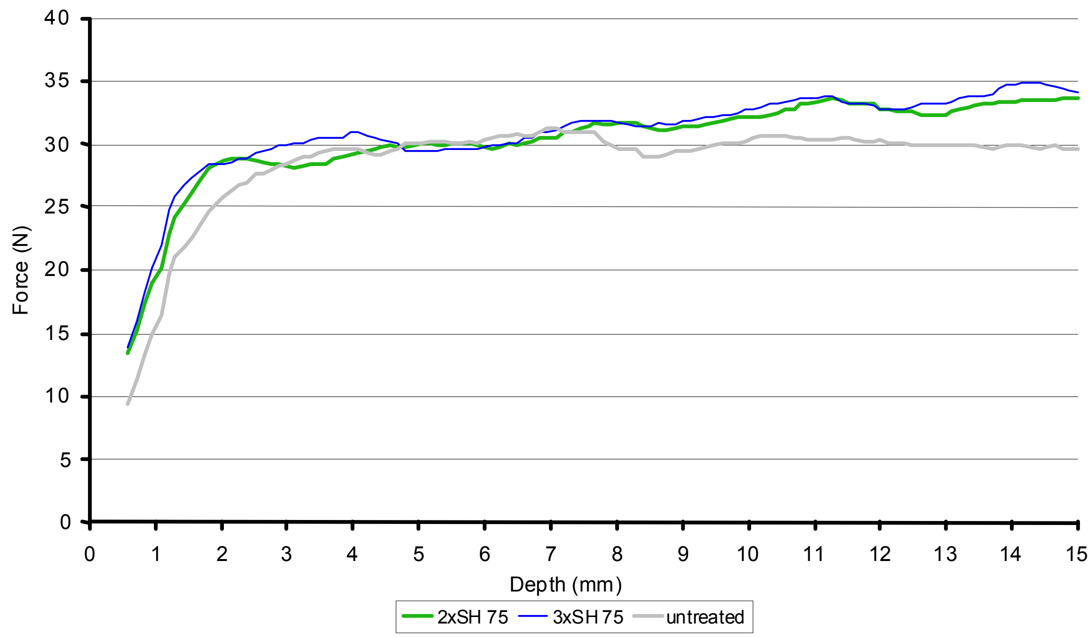

Figure 11: Average hardness profile of moderately deteriorated marble panels before and after two or three applications, wet-on-wet, with a simple TEOS formulation.

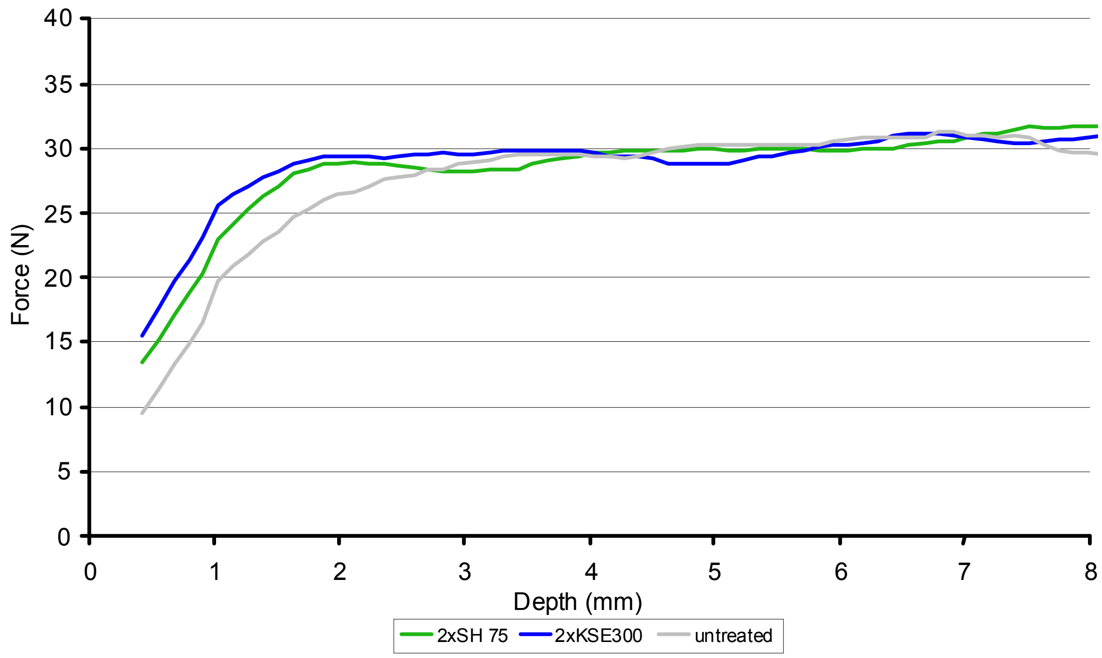

Figure 12: Average hardness profile of moderately deteriorated marble panels before and after two applications with the simple TEOS consolidant (FTB-Remmers SH75) and with the elastified TEOS formulation (FTB-Remmers KSE 300)

CONCLUSIONS

A study was carried out to evaluate cleaning and consolidation for the marble panels of the

Stoclet Palace, constructed in the early 20th century. Corrosion of bronze sculptures and elements decorating the palace resulted in the deposit of copper corrosion products on the marble panels. The anisotropic dilatation of the constitutive minerals resulted in the irreversible creation of pores and micro fissures through which moisture and pollutants as well as copper corrosion products could penetrate.

Black crusts formed by the chemical transformation induced by air pollutants could not be completely removed without important material loss in degraded marble zones. Hence it was recommended to use a soft technique that removes superficial dirt of moderately deteriorated panels, such as warm water at 30 bar (3 MPa).

Some highly degraded marble panels that surround a terrace show a loss of cohesion to a depth of at least 10 mm, representing about 30% loss in structural strength of the panel thickness. Since the consolidation effect of up to three applications with either of the two TEOS based products was not sufficient to restore the cohesiveness of the sugaring marble, and other types of consolidants were not appropriate, replacement of these highly degraded panels was recommended for safety reasons. The results of the study showed that the TEOS formulations tested were not able to bridge the intergranular gaps formed between the crystals in the decohesioned area. This was attributed to the significantly large grain sizes present in the marble that are beyond the recognized bridging capacity of these products.

Most of the marble panels were moderately deteriorated up to 5-6 mm depth. Two applications of either of the two tested consolidants generally resulted in an increase of the hardness of the deteriorated surface layer to values comparable to that of the underlying sound stone. A third application did not significantly improve the consolidation effect of these panels. A slightly improved consolidation effect was obtained for the elastified TEOS product.

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