Hydrophobe VI

6th International Conference on Water Repellent Treatment of Building Materials Aedificatio Publishers, 167 - 180 (2011)

Study on the Application of Anti-Graffiti Systems on Natural Stones and Concrete

U. Mueller¹ and K. Malaga^{1,2}

¹Federal Institute for Materials Research and Testing, Division VII.1; Unter den Eichen 87, 12205 Berlin, Germany

²CBI Swedish Cement and Concrete Research Institute, Brinellgatan 4, 50115 Boras, Sweden

Abstract

The goal of this study was to find a correlation between cleaning efficacy of substrates protected with anti-graffiti and their porosity, surface roughness, composition and as well as usability of the Technical Testing Guideline for Anti-Graffiti Systems (BASt) for natural stone and brick/clinker masonry. The results showed that the cleaning efficacy mainly depends on the porosity of the substrate and the type of antigraffiti. Also higher surface roughness contributed to a lower cleaning efficacy. The results showed also, that concrete panels and cement joints in masonry represented the worst case. The colour change of all substrate materials compared to concrete was mostly within the acceptable limits. Gloss changes were significant for a number of substrates. In particular several of the wax treated low porosity substrates exceeded the threshold value of 10. The limit of water vapour permeability of the AGS prescribed in the TP-AGS might be too high for natural stone substrates. In general the TP-AGS is useful for the determination of the efficiency factor of antigraffiti agents on various substrates.

Keywords: anti-graffiti, permanent, sacrificial, stones, concrete, cleaning efficiency

1 Introduction

Many objects in our built environment are affected by graffiti problems. Besides the aesthetical impact graffiti cause considerable costs for their removal [1] and subsequent costs for repairing damages caused by improper graffiti cleaning. Dimensional natural stones are particulary sensible towards graffiti, since their variety and variability of properties represent a real challenge for an effective graffiti removal. Crucial factors for cleaning building substrates from graffiti consist in the type of paint and the intrinsic properties of the substrate [2]. Further factors concern the duration of the paint on the surface, the type of cleaning method and agent as well as the ambient temperature. However, the important aspect with graffiti removal is the porosity, surface condition of the substrate, including surface roughness and its finish. By experience low porosity materials are known to be cleaned from graffiti much easier than highly porous materials [3] as well as flat and smooth surfaces can be cleaned much more easily than rough surfaces [4, 3].

Anti-graffiti systems (AGS) are meant to aid the cleaning process by inserting a layer between the paint and the building substrate. This layer may have a low surface energy thus making it difficult for the paint to stick to the substrate or it may be easily removed itself together with the paint. The increasing porosity and surface roughness of a substrate usually increase consumption of the agent [4]. It is however not completely clear how a substrate with its intrinsic properties is influencing the efficacy of anti-graffiti systems. Studies of behaviour of AGS on various natural building stones showed completely different results of the same system applied on different stones. This concerned not only the cleaning efficacy but also the durability of the AGS under different climatic conditions [5]. Testing methods used in Germany for determination of the cleaning efficacy and durability of anti-graffiti systems are usually based on only one or few standard substrates [6, 7]. Further studies on the factors influencing the behaviour of the same AGS on different substrates are therefore needed.

The goal of this study was to find any link between cleaning efficacy and the porosity, surface roughness as well as the type of substrate material. A second goal was to test the applicability of the Technical Testing Guide for Anti-Graffiti Systems (TP-AGS), issued by BASt for testing concrete, on natural stone and brick/clinker masonry. The methodological approach of this study consisted in the application of a permanent and sacrificial system on concrete, clinker and natural stone panels. The selected types of the stone panels had different surface finish. This approach was seen as help to correlate critical substrate properties with the behaviour of the AGS and to give hints on how to optimize the TP-AGS concerning testing the efficacy on other than concrete substrates.

2 Sample material and methods

For the selection of the natural stone types the requirements and application examples in the Federal Motorway System was considered. The stone were selected according to the data listed in [8], which includes low, intermediate and high porosity stones. The surface finish was cut for all types. Stones with intermediate porosity were also fractured, bush hammered and chiselled. The samples are listed in Table 1.

Table 1:	Samples used for the	study
----------	----------------------	-------

Sample	Trade Name	Color	Poros. Vol%
MG1	Flossenbürg Granite	yellow grey to blue grey	2,7
MG2	Selters Trachyte	light blue	14,7
MG3	Mayern Basalt Lava	dark brown	34,8
SSt1	Lindlar Greywacke	grey to grayish brown	6,9
SSt2	Anröchte Greensandstone	grey green	8,0
SSt3	Postaer Sandstone	yellow brown	19,3
KSt1	Treuchtlinger Limestone	blue grey to white	3,9
KSt2	Crailshaim Limestone	grey	5,1
KSt3	Thüster Limestone	brown grey	21,2
KSt3	Thüster Limestone	brown grey	21,2
MW	clinker masonry panel	red	21,2
В	Concrete paving panel (these panels have usually carbonated surfaces)	light grey	5

Two types of anti-graffiti agents were used: a permanent system (AGS1) consisting of a fluorinated silane (water based liquid) and a cleaning agent, and a sacrificial system (AGS2) based on a micro crystalline wax (water based liquid). For each of the substrates 10 panels in the size of 30 x 30 cm² were prepared: 4 panels for application with AGS1, including one coated and painted reference panel; 4 panels for application with AGS2, including one coated and painted reference panel; 2 uncoated panels each for the application of the paint. In total the amount of agents used was below 200 g/m² on the cut panels, but higher for the MG3, SSt3 and B. The panels with other than cut finish required up to 50% more of the agents. AGS1 had a mean coating thickness of 2 um and AGS2 of 4 um. Before coating with AGS the panels were stored at least 14 days at 23 °C and 50 % RH. After coating the storage of the panels was repeated for 14 days before the paint was applied. The permanent and sacrificial agent was applied with a brush on horizontally placed panels. The amount of agents used was controlled by weighing the panels before and after each application step. The paint consisted of the different types listed and required by the method TP-AGS. The paint was applied with a mask in form of circular patches. The stone substrates were characterized by petrographic analysis [9]. Other properties of uncoated and coated samples were determined on 3 to 6 specimen according to the following methods:

- Total porosity, apparent density, specific gravity [10]
- Pore size distribution by Hg-intrusion [11].
- Surface roughness by Laser scanning confocal microscopy and structured light scanning on cut and uncoated specimen and photogrammetry on fractured, bush hammered, chiselled specimen.
- Water absorption [12] on uncoated specimens and capillary water absorption coefficient [13] and water vapour permeability [14] on coated and uncoated specimens.
- Colour and gloss measurement according to TP-AGS [15] on coated and uncoated samples.

Additional analysis was performed on selected coated samples by means of Scanning Electron Microscopy (SEM). The results showed how the agent was distributed inside the pore system of the substrates and how the agents adhered to the surface.

After the cleaning procedures the cleaning efficacy was evaluated according to TP-AGS [15]. For the evaluation three panels were used. A fourth coated and painted panel was not cleaned and served as reference for the evaluation of the cleaned other three panels. The cleaning efficacy Additionally to the panels coated with AGS, uncoated panels were painted with the selected paints and cleaned. This should demonstrate the effects of the cleaning procedure itself on the efficacy of the graffiti removal, in particular for AGS1 coated panels, where a chemical cleaning agent (as part of the system) was used. The cleaning of the panels was performed according to TP-AGS.

3 Results

3.1 Gloss and colour change

Gloss and colour change due to the application of an AGS are clearly restricted in the TL-AGS but the threshold values are only valid for concrete. The values of the substrates were measured before and after application of the AGS, but only on the panels with cut surfaces.

Figure 1 illustrates the results of the gloss measurements. It clearly shows the impact of the coatings but with AGS 1 all values are below the threshold value of 20. For AGS2 in total 5 substrates are exceeding the threshold value of 10. Despite the fact that B, MG3 and SSt3 consumed the highest amount of agents they exhibited almost no change in gloss. This was due to the fact that the agent penetrated the pore system and was not coating entirely the surface in contrast to the denser substrates.

The colour change of the panels due to the application of the AGS is depicted in Figure 2. Minor changes were only detected on the AGS1 treated panels. Surprisingly no major changes in colour occurred despite the sometimes strong coloration of the substrates and the fact that the threshold values were designed for concrete panels with a defined a*-, b*- and L*-values.

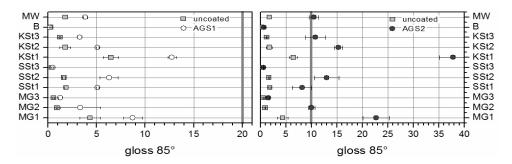


Figure 1: Results of gloss measurements for uncoated and coated specimens with AGS1 and AGS2. The threshold values for gloss according to TL-AGS are indicated by grey vertical lines

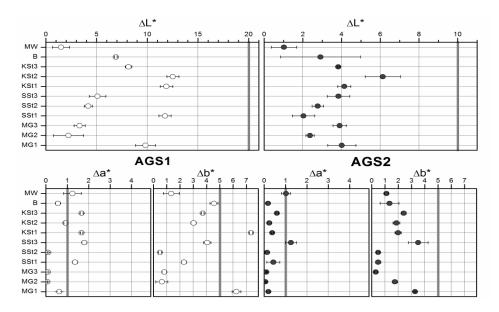


Figure 2: Color change of cut stones and the masonry (MW) and concrete panel (B) due to the application of the AGS. The threshold values for color changes according to TL-AGS are indicated by grey vertical lines

3.2 Influence of AGS on water transport properties

The results showed that the capillary water absorption coefficient (C) was reduced by both AGS. However, AGS1 exhibited 50% smaller reduction of C compared to AGS2. Both systems could therefore be characterized as water repellent. The results for the water vapour permeability were less distinctive. The μ -values exhibited high standard deviation for both agents under wet bulb as well as dry bulb conditions. Best to interpret were the results gained under wet bulb conditions. AGS1 coated specimen showed up to 1.5 higher μ -values and AGS2 coated specimen showed up to 3 times higher μ -values compared to uncoated samples.

3.3 Cleaning efficacy of AGS1

For AGS1 coated panels the cleaning efficacy was measured after every cleaning cycle. Efficacy coefficients were formulated for each paint patch and added to a panel coefficient. The mean efficacy coefficient F_{AGS} was calculated from three panels. In total 10 cycles were performed including paint application, cleaning and determination of cleaning efficacy.

Figure 3 illustrates the results of the cleaning efficacy tests where the cleaning cycles are plotted versus the efficacy coefficients. If a substrate exceeded the threshold value of ten (10) three additional cleaning cycles were performed and then the substrate was taken out of the test. The results show the influence of the substrates on the cleaning efficacy of AGS1. The cut natural stone substrates MG3 and SSt3 exceeded already after 1 or 2 cycles the threshold value of 10 (Fig. 4). The concrete panels passed only 4 cycles below 10. Furthermore the panels with the fractured, bush hammered and chiselled finishes exceeded the threshold value for F_{AGS} after 4 and 10 cycles, respectively. Interestingly the cut limestone all passed the tests with KSt1 showing the second best performance of all the substrates. This is in particular interesting since the system is based on a fluorinated silane where one could expect a better performance on a siliceous substrate. The best performance exhibited actually the clinker of the masonry panels, where the paint could be removed almost completely but not from the cement mortar joints, which showed only an inferior cleaning effect, exceeding the threshold value clearly after 10 cycles. The uncoated concrete panels reached almost the same low efficacy coefficient as the coated specimens. With the uncoated substrates of lower porosity (MG1, SSt1, SSt2, KSt1, KSt2) F_{AGS} oscillated around 10. This showed a strong effect of the cleaning agent. The more rough surfaces exhibited also more residuals of the paint.

3.4 Cleaning efficacy of AGS2

All substrates coated with AGS2, even the ones with rough surfaces, were far below the threshold value for the panel cleaning efficacy coefficient (F_{AGS}) of 30. Only one substrate was above F_{AGS} = 10. The uncoated panels showed clearly values above 30 with the exception of the clinker masonry panels. But here the limit of the efficacy coefficient for the individual paint patches was exceeded two times. Otherwise, there was a clear difference between the cleaning effect of the coated and uncoated panels.

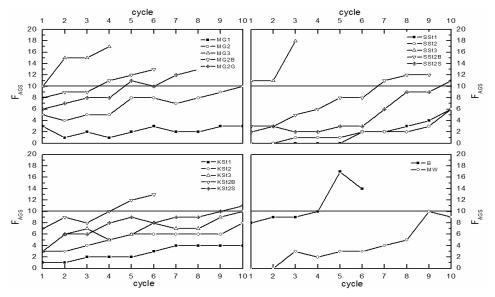


Figure 3: Cleaning effects of AGS1 in form of efficacy coefficients F_{AGS} vs. the number of cleaning cycles. The threshold value $F_{AGS} \le 10$ is indicated by a grey horizontal line. Natural stones with extensions B = fractured finish, G = bush hammered; S = chiselled

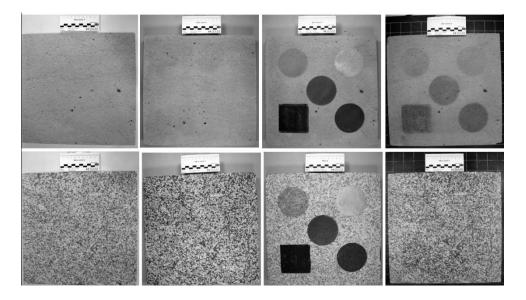


Figure 4: Cleaning results for the AGS1 treated SSt3 (upper row), and MG1 (lower row).

The four pictures for each series are, from left: uncoated sample, coated, coated and with applied graffiti paints, cleaning effect after five cleaning cycles

Table 2: Results of the cleaning efficacy test for uncoated and the coated (AGS2) panels. The grey shaded areas exceed the threshold value for $F_{AGS2} \le 30$. MW-0 failed because it exceeded the threshold value for the coefficient $F_i \le 3$ of a single paint patch two times

Sample	Uncoated	AGS2	Sample	Uncoated	AGS2
MG1	45	3	KSt2	49	4
MG2	49	8	KSt3	49	6
MG2B	33	7	SSt2B	47	5
MG2G	36	1	SSt2S	47	2
MG3	50	9	KSt2B	35	8
SSt1	50	4	KSt2S	49	9
SSt2	49	3	В	44	1
SSt3	44	2	MW 1	20	3
KSt1	49	13			

3.5 Scanning Electron Microscopy (SEM)

Analysis by SEM was performed on only two different coated and painted substrates: the low porosity sandstone SSt1 and the high porosity sandstone SSt3 (Tab. 1).

The dense sandstone SSt1 showed a clearly distinctive coherent coating layer of AGS1 below the paint layer (Fig. 5a). Even the two application layers of AGS1 could be discerned. The paint layer was adhering only selectively on the layer consisting of the anti-graffiti agent. The porous sandstone SSt3 showed a higher penetration of the agent into the pore system. A coherent layer of AGS was not observed on this substrate despite that the paint layer was clearly discernable and coherent (Fig. 5b).

But also here, the paint layer was only selectively adhering to the AGS1 showing the water repellency and oleophobic effect of the agents. SSt3, however, showed also paint within pores close to the surface, even though the pore walls were coated with AGS1.

The results of AGS2 showed a good adhesion of the coating on the low porosity sandstone SSt1 (Fig. 5c). The paint, however, was only selectively adhering to the AGS2 layer with partially large gaps between AGS2 and paint layer. The different application layers of AGS2 were clearly visible. SSt3 exhibited also a deep penetration of AGS2 into the pore system of the sandstone (Fig. 5d), similar to the effect observed with AGS1. As with SSt1 the paint layer was laying on the agent only selectively.

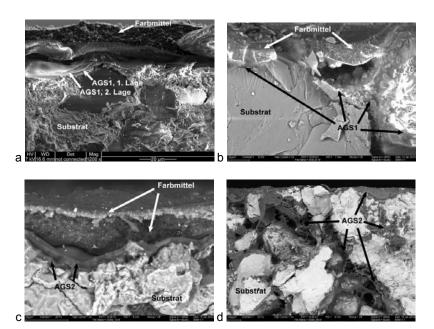


Figure 5: Paint and AGS1 on the substrate SSt1 (a) and SSt3 (b). Paint and AGS2 on the substrate SSt1 (c) and SSt3 (d)

4 Discussion of the results

4.1 Gloss and colour change

In the TP-AGS changes of the substrate colour due to the application of an AGS is determined on a concrete substrate with a defined $L^*a^*b^*$ range. Surprisingly, the colour change of the substrates other than concrete was within narrow limits even though some of them were distinctively coloured and showed also textural patterns. For AGS1 few samples resulted in higher than accepted in TP-AGS Δa^* - and Δb^* values (Figure 2).

For AGS2 almost all the colour changes were within the allowably tolerances according to [15]. The gloss measurements showed for concrete (coated with AGS1 and AGS2) almost no change occurred and all other substrates coated with AGS1 were within the limit defined in TP-AGS. The panels coated with AGS2 (except for concrete), however, exceeded the gloss threshold for several substrates (Figure 1). The gloss differences were not significantly influenced by surface roughness but mainly by the total porosity.

4.2 Water transport data

The data for the water transport properties of the substrates (water absorption coefficient and water vapour permeability) before and after coating with the agents do not reveal any clear correlation with the substrate type. Both agents strongly reduced the coefficient. The water absorption coefficient exhibited a stronger reduction with the porous substrates due to the coating with AGS1 or AGS2. The water vapour permeability was stronger reduced by AGS2 than by AGS1.

4.3 Substrate properties and cleaning efficacy of AGS

Three of the specific substrate properties were considered when evaluating the cleaning efficacy of anti-graffiti systems: total porosity, average pore radius and surface roughness. These characteristic substrate values were plotted versus the maximum cleaning efficacy coefficient F_{AGS} and two of them are illustrated in Figure 6 and 7.

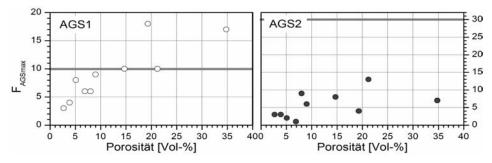


Figure 6: Correlation between cleaning efficiency and porosity. The grey lines designate the threshold values F_{AGSmax}

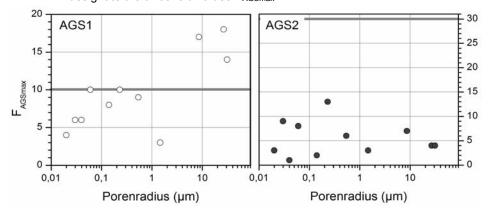


Figure 7: Correlation between the cleaning efficiency and pore radius of the substrate. The grey lines designate the threshold values F_{AGSmax}

Figure 6 shows a clear correlation between F_{AGS} of AGS1 and the total porosity: The higher the porosity the higher the efficacy coefficient. This correlation is still visible with AGS2 treated substrates but not as clearly. A similar pattern was found when plotting the mean pore radius vs. F_{AGS} (not shown here). With AGS1 treated substrates showed lower F_{AGS} when the pore radius was small and a higher coefficient when the pore radius was high. AGS2 treated samples did not reveal this correlation so clearly.

The comparison of surface roughness with F_{AGS} was made only with material of the same porosity but different surface finish. The results for AGS1 (Fig. 7) showed a clear increase of F_{AGS} with an increase of surface roughness. AGS2 treated samples did not reveal this trend in all cases. For two of the three substrate materials no correlation was observed.

The results showed an influence of the type of agent used on the cleaning efficacy on the particular substrates. In the case of AGS1 highly porous substrates and with a large mean pore radius a reduced cleaning efficacy can be expected as with substrates of lower porosity and smaller pore radius. With AGS2 the pore data of the substrate were less influential on the efficacy of the agent. From this and the previous results the following can be concluded:

- The application of AGS1 on low porosity substrates causes the agent to form a more or less coherent coating layer on the surface, which conveys hydrophobic and oleophobic properties.
- The application of AGS1 on porous substrates causes an impregnation of the surface and subsurface. The agent penetrates the pores and coats the pore walls but does not form a coherent coating layer on the surface.
- AGS2, however, forms with all substrate types a coherent coating layer on the substrate surface. In highly porous substrates the pores are filled down to several millimetres by the agent.

A comparison of the mineralogical and chemical data with the cleaning efficacy reveals no easy to comprehend pattern except that with the silane agent of AGS1 best results were achieved with the limestone and not with the siliceous substrates. Obviously the physical properties have a much higher influence before the mineralogical or chemical composition of the substrate materials.

5 Conclusions

Based on the results of the presented study the following conclusions can be derived for the applicability of the testing method TP-AGS and TL-AGS, respectively, on stone and clinker/brick masonry:

Cleaning efficacy: Main influential factors on the cleaning efficacy of substrates treated with AGS are the porosity (total porosity and mean pore diameter) and to a lesser degree, surface roughness. The latter factor

depends more on the type of anti-graffiti system used but generally higher surface roughness is correlated to a lower cleaning efficacy. The results showed also, that concrete paving panels, as defined in the TP-AGS, represents well the 'worst case' of a substrate and encompassing even highly porous substrates with a rough surface finish and cement joints in masonry.

Colour change due to the application of AGS: The colour change of all substrate materials compared to concrete was mostly within the limits for $\Delta(\text{Lab})$. A number of substrates showed even a lower change in values than the concrete panels. Only view substrates exceeded the limits for Δa^* and Δb^* . Here a moderate increase of the limits could be considered in order to accommodate the broader variety of colour values for natural stone.

Gloss change due to the application of AGS: Gloss changes were significant for a number of substrates. In particular several of the AGS2 treated low porosity substrates exceeded the threshold value of 10. Here, one or two low porosity reference substrates could be included into the testing procedure in order to exclude a major change of appearance on stone masonry or stone clad facades due to the application of anti-graffiti agents.

Influence on the water vapour permeability: The limit of water vapour permeability of the AGS prescribed in the TP-AGS might be too high for natural stone substrates. As the results have shown, the application of an AGS can reduce the water vapour permeability of a substrate considerably but not equally and predictably for all substrate materials. It is therefore strongly recommended to abstain from the utilization of permanent film forming anti-graffiti systems (AGS1-1, according to TP-AGS). One important aspect was not regarded in the present study. This concerns the durability of anti-graffiti systems on substrate materials other than concrete. It was also shown by others [5, 16, 17], that the durability of an AGS is not only influenced by the environmental conditions but also by the type of substrate. In order to evaluate if the Technical Testing Guideline for AGS can be applied to natural stone and clinker/brick masonry more has to be known on the influence of the substrate on the durability of AGS.

References

- [1] Hilgers, H. A. (2005): Graffiti, Wissenschaftliche Dienste des Deutschen Bundestages: Der aktuelle Begriff, 05(18), 2
- [2] Historic Scotland: Graffiti and its safe removal. Inform: Information for historic building owners, Historic Scotland, Edinburgh, UK, 8 S., 2005
- [3] Urquhard, D.: The treatment of graffiti on historic surfaces. Technical Advise Note 18, Historic Scotland, Edinburg, 55 S., 1999

- [4] Goretzki, L.: Graffiti-Schutzsysteme für Fassadenbaustoffe. Baupraxis und Dokumentation 10, Expert Verlag, 64 S., 1998
- [5] Gardei, G., Garcia, G., Riedl, M., Vanhellemond, I., Strupi SUPUT, J., Santarelli, M.-L., Rodríguez-Maribona, I. and Müller, U.: Performance and Durability of a New Antigraffiti System for Cultural Heritage The EC Project GRAFFITAGE. In, 11th International Congress on Conservation and Deterioration of Stone, Torun, Poland, S. 889-897, 2008
- [6] WTA Merkblatt 2-8-04/D: Bewertung der Wirksamkeit von Anti-Graffiti-Systemen (AGS). 2-8-04/D, Wissenschaftlich-Technische Arbeitsgemeinschaft für Bauwerkserhaltung und Denkmalpflege e.V., München, 14 S., 2004
- [7] Malaga, K. and Bengtsson, T.: The Nordic Method: Performance Tests for Protective Sacrificial Coatings on Mineral Surfaces. In: DeClercq, H.and Charola, A. E. (eds.), Hydrophobe 5, Brussels, Belgium, Aedificatio Publishers, S. 169-180, 2008
- [8] Grimm, W.-D.: Bildatlas wichtiger Denkmalgesteine der Bundesrepublik Deutschland. Arbeitshefte des Bayrischen Landesamtes für Denkmalpflege, 1990
- [9] DIN EN 12407: Prüfverfahren für Naturstein. Petrographische Prüfung. Deutsche Norm, Beuth Verlag, Berlin, 5 S., 2007
- [10] DIN EN 1936: Prüfung von Naturstein Bestimmung der Reindichte, der Rohdichte, der offenen Porosität und der Gesamtporosität; Deutsche Fassung EN 1936:1999. Deutsche Norm, Beuth Verlag, Berlin, 2007
- [11] DIN 66133: Bestimmung der Porenvolumenverteilung und der spezifischen Oberfläche von Feststoffen durch Quecksilberintrusion. Deutsche Norm, Beuth Verlag, Berlin, 1991
- [12] DIN EN 13755: Prüfverfahren für Naturstein Bestimmung der Wasseraufnahme unter atmosphärischem Druck. Deutsche Norm, Beuth Verlag, Berlin, 2008
- [13] DIN EN 1925: Prüfverfahren von Naturstein Bestimmung des Wasseraufnahmekoeffizienten infolge Kapillarwirkung. Deutsche Norm, Beuth Verlag, Berlin, 1999

- [14] DIN EN ISO 12572: Wärme- und feuchtetechnisches Verhalten von Baustoffen und Bauprodukten - Bestimmung der Wasserdampfdurchlässigkeit. Deutsche Norm, Beuth Verlag, Berlin, 2001
- [15] BAST TP-AGS: Technische Prüfvorschriften für Anti-Graffiti-Systeme. Technische Lieferbedingungen und Technische Prüfvorschriften für Ingenieurbauten, Bundesanstalt für Straßenwesen (BASt), Bergisch Gladbach, 9 S., 2009
- [16] García, O., Rodriguez-Maribona, I., Gardei, A., Riedl, M., Vanhellemont, Y., Santarelli, M.-L. and Strupi-Suput, J.: Comparative study of the variation of the hydric properties and aspect of natural stone and brick after the application of 4 types of anti-graffiti. Materiales de Construcción, 60, 297, S. 69-82, 2010
- [17] Malaga, K and Mueller, U.: Validation and improvement of procedures for performance testing of anti-graffiti agents on concrete surfaces. Concrete Under Severe Conditions. Environment and Loading Castro-Borges at al. (eds). Taylor & Francis Group, London, 2010