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Evaluation of the Effectiveness of Protective Treatments for Limestones of Riga Brethren's Cemetery

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Abstract

Laboratory tests were carried out in order to evaluate several kind of protectives for calcareous stone materials used for construction and restoration of Riga Brethren's Cemetery. All laboratory investigation mainly were done according to *A Laboratory Manual for Architectural Conservation* [1]. Both for untreated and hydrophobised samples water absorption by capillarity, water absorption by total immersion and evaporation measurements were carried out. As the tests are still engaged definite conclusions on protectives can not be drown before setting up other experiments necessary to complete the data - pore size distribution, water vapour permeability, artificial corrosion test and *in situ* - water absorption measurements with Carsten tube of treated and untreated stone surfaces.

Keywords: Cultural heritage, freshwater limestone, restoration materials, stone conservation, protective coatings, laboratory tests

1 Introduction

For the construction of Riga Brethren's Cemetery the local freshwater limestone or so called tufa from Allazi (Riga District, Latvia) was used. However already during the construction (1920 - 1936) as the quarry was rather small the limit of stone material was finished . Thus in object the stone blocks of different quality could be observed as there were no possibilities to select more qualitative material. This particular kind of calcarenite is markedly porous and is liable to decay owing to its high water absorption capacity. The possibility to protect the consolidated and cleaned stone surfaces against the destroying environmental factors with the help of colourless water repellent treatments have frequently been discussed. The products used for stone treatment have to meet a row of requirements: chemical stability, comparable thermal and moisture expansion of treated and untreated parts, stability to UV radiation, water vapour permeability and others [2]. In order to evaluate protective treatments the laboratory tests were carried out using not only the samples of freshwater limestone, but also Langensalz travertine and Birzi dolomite as restoration materials and Italian travertine as there are some stone carvings of this material in the object.

As a result of earlier geological investigations - the observations at all the Latvian freshwater limestone deposits and the exploration in the area of the Allazi freshwater limestone quarry, it was founded that there is no freshwater limestone, suitable for the restoration, in Latvia [3]. After different laboratory analysis, as more appropriate for substitution of freshwater limestone, the travertine from Langensalz (Germany) was recommended by geologists. The Langensalz travertine is a rather expensive restoration material, so for the peripheral part of the monument - steps and floor, the small - cavernous quartzose dolomite from the Birzi (Latvia) deposit was recommended.

2 Description of materials

2.1 Stone materials

Both the Latvian freshwater limestone and travertine from Langensalz are similar in their colour, structure and texture, petrography and chemical

composition. According to chemical analyses (see Table 1) the freshwater limestone and Langensalz travertine are calcium carbonate rocks ($CaCO_3$ - 97.7 and 98.22%, $MgCO_3$- 0.56 and 0.23%). A small amount of organic substances (1.53%) and Fe_2O_3 (ca 0.1%) are responsible for their yellowish colour. Freshwater limestone consists of microcrystalline (0.001 - 0.2 mm) and macrocrystalline (0.25 - 0.7 mm) calcite ($CaCO_3$) aggregates. Though very porous, it is, however, frost resistant, because the pores never fill up with water more than 90% of the volume [5].

Both travertine and freshwater limestone are porous carbonate rocks formed under the continental conditions as a result of organic and inorganic process. travertine is a better consolidated rock as a result of the diagenetic process, and it is 4-5 times sturdier than freshwater limestone [4]. The porosity of materials is following: freshwater limestone - 33%, Langensalz travertine - 8.23%, Italian travertine - 5.28% and Birzi dolomite - 5.07%.

Table 1: Chemical composition of stone materials of Riga Brethren's Cemetery (% of Mass)

stone type	heating loss at 1000°	SiO_2	CaO	MgO	Al_2O_3	Fe_2O_3	K_2O	Na_2O	SO_3
freshwater limestone	42.96	0.71	54.74	0.27	0.16	0.10	0.12	0.07	0.18
travertine (Langensalz)	43.93	0.36	55.03	0.11	0.12	0.10	0.11	0.07	0.14
travertine (Italy)	43.34	0.66	54.94	0.21	0.11	0.08	0.07	0.03	-
dolomite (Birzi)	45.36	1.32	30.52	21.3	0.46	0.31	0.14	0.07	0.14

2.2 Protectives

The products tested are listed in Table 2.

Table 2: ectives applied on stone samples

Code	Products, company (country)	characterisation of composition
K501	Masonry Waterproofing Solution K501 - Liquid Plastics Ltd (England)	water based silane-siloxane compound
SNL	Funcosil SNL - Remmers (Germany)	siloxane based with biocidal additives (siloxane ca 7 M%)
WS	Funcosil WS - Remmers (Germany)	water based silane emulsion (alkylalkoxysiane ca 10% m/m)
OW	Funcosil OW - Remmers (Germany)	silicon based emulsion
NA6	NaAl6 - product investigated by the Academy of Sciences of Latvia (Latvia)	sodiumalumomethilsilanolate (Si - 4.9% by vol.)
Seal	Premium Waterproofing Sealer - "House Beautiful" (USA)	light petroleum solution of modified and cyclopenta resins (less than 750 g/l VOC)

3 Experimental

3.1 Preparation of samples

Cubes measuring on all sides ca 5cm were sawed from test stones -freshwater limestone, Langensalz travertine, Italian travertine and Birzi dolomite. The cubes were cleaned with destilled water and dried in a 60° C oven for 24 hours. Prior to weighing, the stones were cooled in a desiccator. In each series a total of 21 samples were used, 3 as references and 3 for treatment with each product - masonry Waterproof, Funcosil, NaAl6 and Sealer. Samples with all protective products, except NaAl6 were treated by total immersion completely covered for 3 x 10 sec with protective product up to 1 cm over the samples surface. The samples were then dried for 1 week at rooms temperature. Such a treatment sets were repeated, altogether 3 times for

Table 3: Amount of absorbed product, % of mass (determined 1 month after the last application)

protective product	freshwater limestone	travertine (Langensalz)	travertine (Italy)	dolomite (Birzi)
Sealer	1.943	0.197	0.136	0.056
Funcosil WS	0.779	0.143	0.004	0.034
Funcosil SNL	1.704	0.306	0.097	0.065
Funcosil OW	0.730	0.128	0.038	0.019
K501	0.585	0.251	0.068	0.027
NaAl6	0.297	0.191	0.061	0.050

each sample. Product NaAl6 was used by brushing in similar way as described above. The amount of protective product absorbed by the samples was determined calculating the difference between dry weights before and after treatment. The weghing were made 1 month after application of the product. The quantities of absorbed products are summarised in Table 3.

3.2 Water absorption by capillarity

The test was carried out according to *A Laboratory manual for Architectural Conservation* [1]; weight readings were taken as for high-porosity materials with a high water absorption rate, respectively after 1′, 2′, 3′, 4′, 5′, 10′, 15′, 20′, 25′, 30′, 1h, 2h, 3h, 4h, 5h, 24h, 48h, and 72h. The results are showed in Figure 1.-4., for each stone type separately.

Freshwater limestone (Figure 1). The products Sealer, Funcosil OW, Funcosil SNL and NaAl6 perform outstandingly in that they prevent any water absorption even after 72 hours. The Waterproof K501 product performs well during only the first 30 min of testing, then the water absorption capacity increases almost linearly and after 48 hours of exposure reaches its maximum approaching the value of Funcosil WS treated samples but still keeping the protective capacity on a half lower than untreated materials. Funcosil WS treated samples absorbs water very fast during the first 30 min, then at the second hour of testing reaches it maximum and stays at the same level until 72 h of exposure. Also this product like K501 shows protective capacity between untreated and Funcosil, NaAl6 and Sealer treated tufa. As regards untreated tufa the water absorption capacity is very high and high value - almost maximum is reached already during the 25 - 30 min of testing, what is due to the extremely high porosity of stone material.

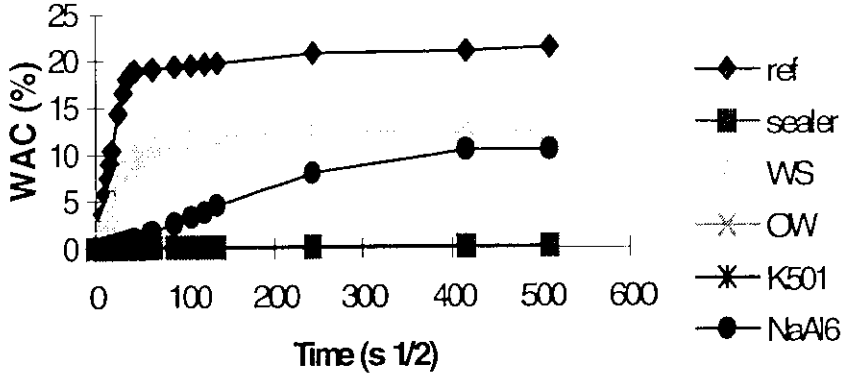

Figure 1: Water absorption by capillarity. Freshwater limestone.

Travertine (Langensalz) (Figure 2). For this type of stone perfect protective capacity shows all products tested except Funcosil WS, although as from Figure 2 could be seen, for Funcosil W.S treated samples quite small quantities of water are absorbed. Thus the samples are with good water - repellent properties if to compared with untreated ones.

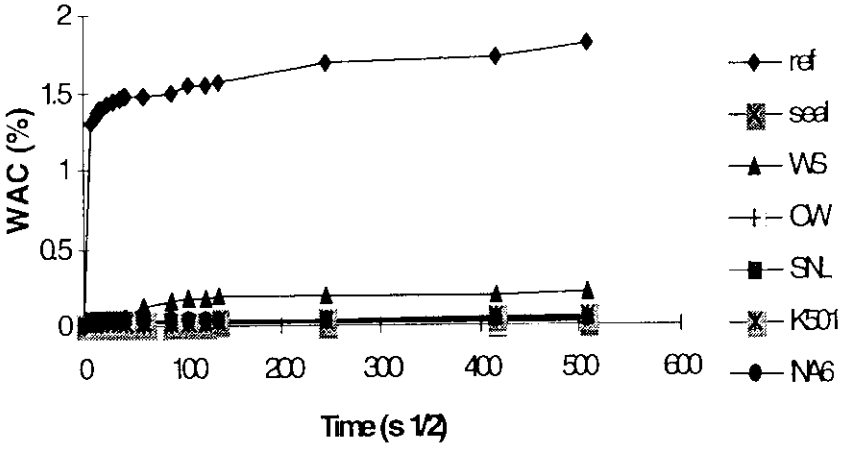

Figure 2: Water absorption by capillarity. Travertine (Italy)

Travertine (Italy). All products used for the treatment of Italian travertine performed good results (Figure 3) inhibiting the water absorption during

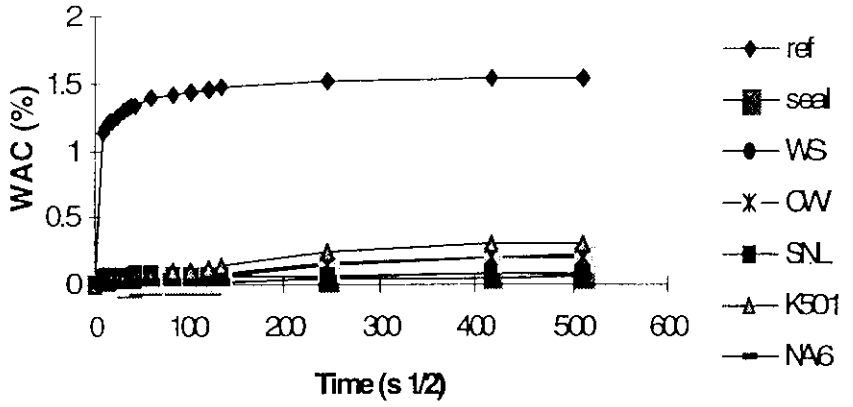

Figure 3: Water absorption by capillarity. Dolomite (Birzi).

the whole period of testing - 72 hours. The water absorption capacity of Funcosil WS treated samples is very low after 30 min of exposure but it increases for following 5 hours, then the maximum is reached and absorption stays constant still very low for 72 hours

Dolomite (Birzi). Also for this lithotype all the products decrease water absorption very significantly in comparison to untreated samples (Figure 4).

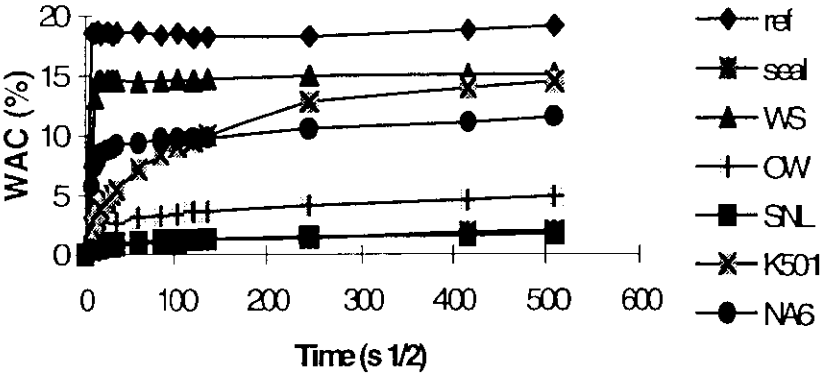

Figure 4: Water absorption by total immersion. Freshwater limestone.

There is no difference in protective capacity during the first two hours then water absorption absorption for K501, Funcosil WS and OW treated samples increases but still stays low while for other products it is almost close to zero.

3.3 Water absorption by total immersion

The test was carried out in accordance with *A Laboratory manual for Architectural Conservation* [1]. Weight measurements were taken after 1′, 2′, 3′, 4′, 5′, 10′, 15′, 20′, 1h, 2h, 3h, 4h, 5h, 24h, 48h and 72 h. The results are shown in Figure 5-8.

Freshwater limestone. The products Funcosil SNL, OW and Sealer offered the best performance (Figure 5) confirming the previous capillary absorption test (Figure 1). Initial phase of absorption for untreated, Funcosil WS and NaAl6 treated samples is very similar during the first 1-2 minutes when absorption occures very fast, thus for untreated samples the maximum of water content is already during the first 2-3 minutes absorbed. Although products Funcosil WS, K501 and NaAl6 inhibits absorption well. Noticeably that the product NaAl6 which performed almost no water absorption by capillarity, during total immersion absorbs quantities of water comparable with products Funcosil WS and K501.

Travertine (Langensalz). In test of travertine samples different products show different results (Figure 6). The same tendency to absorb more

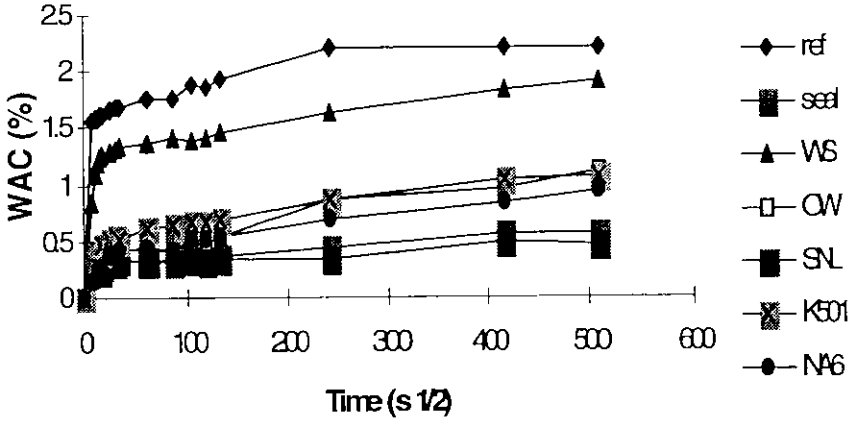

Figure 5: Water absorption by total immersion. Travertine (Lagensalz)

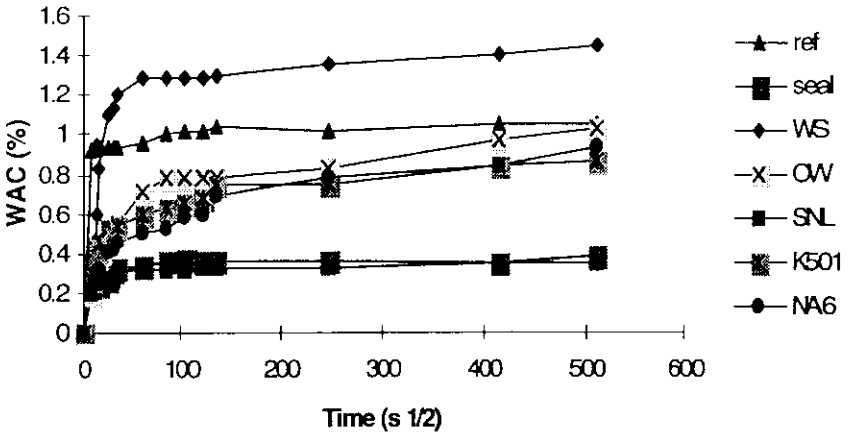

Figure 6: Water absorption by total immersion Travertine (Italy)

water than other products Funcosil WS treated samples show both during previous test by capillar absorption and by total immersion, in later one the quantity of absorbed water approaches the untreated stone samples. Absorption dynamic is comparable for untreated and Funcosil WS treated samples during first 4 minutes of testing. The best protective capacity inhibits Funcosil SNL and Sealer, then follows NaAl6, K501 and Funcosil OW, showing very close results.

Italian travertine. The results in Figure 7 show that the best protective capacity have Funcosil SNL and Sealer while Funcosil OW, K501 and NaAl6 keep water inhibition only at the first 5 hours of testing and the result after 72 h approaches untreated samples. Noticeably that product Funcosil WS offers no protection at all; in this respect, it is worth noting that, as shown in Figure 7, the oucome of treatment with this product is actually increasing in total absorption, while during previous test by capillarity, all products show similar results.

Dolomite (Birzi). For this lithotype different products provide very different results (Figure 8). If during capillar absorption all products increased water uptake then in this case - by total immersion NaAl6, Sealer and Funcosil SNL treated samples shows absorption decrease; for Funcosil OW treated samples absorption is decreased only during initial phase, then it ap-

proaches untreated samples. Funcosil WS and K501 even increases the water absorption capacitty.

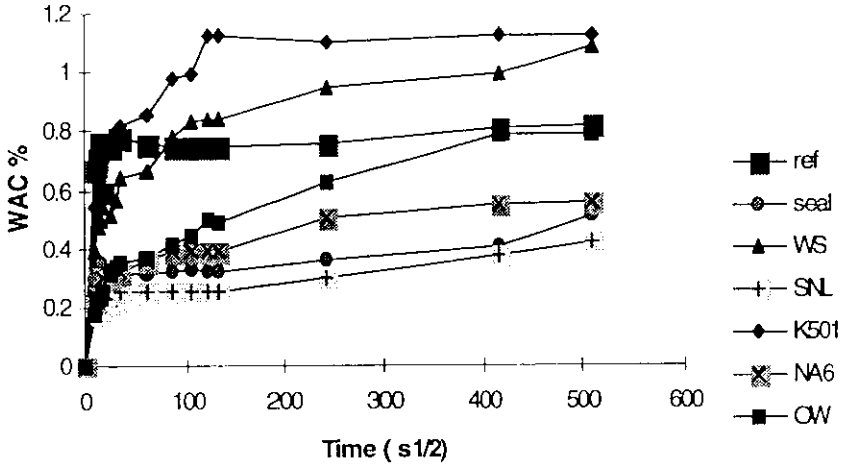

Figure 7: Water absorption by total immersion. Dolomite (Birzi)

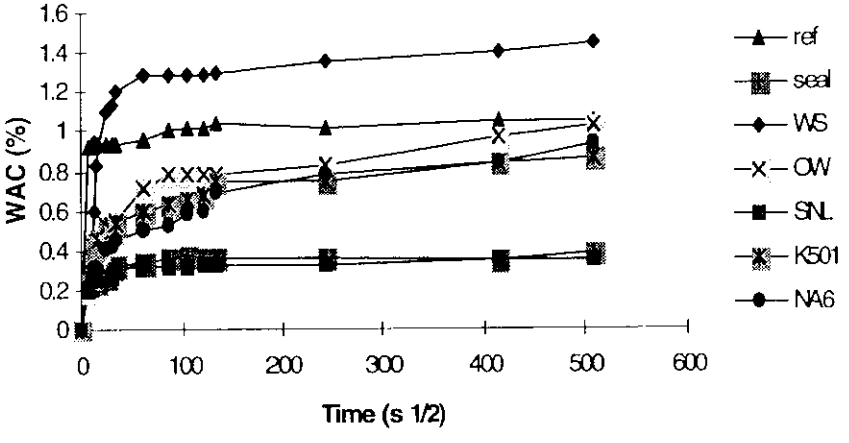

Figure 8: Water absorption by total immersion Travertine (Italy)

3.4 Evaporation

The test was carried out in laboratory environment immediately after the total immersion test on the same samples, recommended by *A Laboratory manual for Architectural conservation* [1]. The weight readings were taken after 1′, 2′, 3′, 4′, 5′, 10′, 15′, 20′, 25′, 30′, 1h, 2h, 3h, 4h, 5h, 24h, 48h and 72 h. The results are shown in Figure 9-12.

Freshwater limestone. The products Funcosil OW, SNL and Sealer actually seem to foster evaporation (Figure 9). In reality this is only apparent, as the test actually verifies the capacity of evaporation of water absorbed during the total immersion test (Figure 5). During the latter test samples permitted a reduced quantity of absorbed water, and hence the evaporation rates are not so much related to the absorbed water content which probably is not inside the samples, but stayed on their surface and can of course easily evaporate. The group of products Funcosil WS, K501 and NaAl6 proves to reduce the evaporation rate of stone during first 24 hours of testing, but then approaches the untreated samples and at the end of experiment - after 72 h, all water absorbed evaporates for all samples.

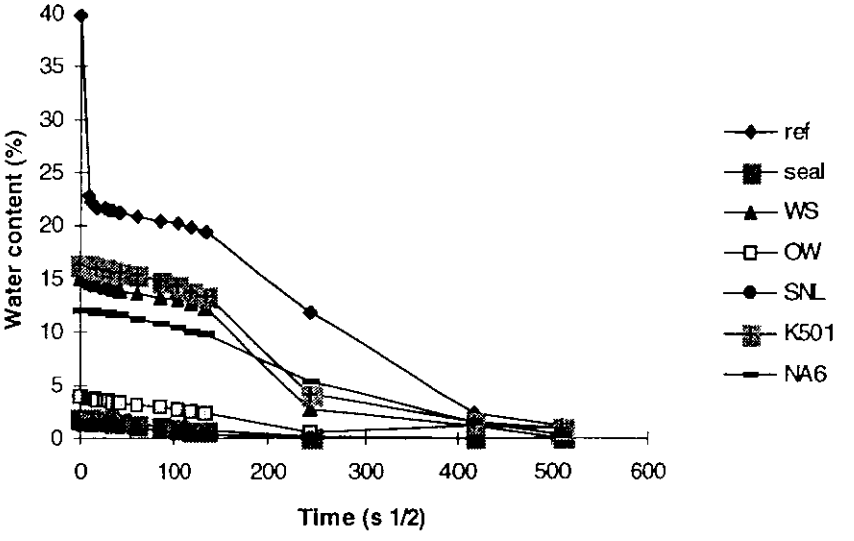

Figure 9: Evaporation. Freshwater limestone

Travertine (Langensalz). As shows the Figure 10, all the products are not reducing evaporation rate, initially the material's surface dries rapidly, subsequently the small amount of water absorbed is released gradually. The curve of untreated sample shows how slowly evaporation from untreated samples occurs - even after 72 h of drying material still keeps quite large moisture content.

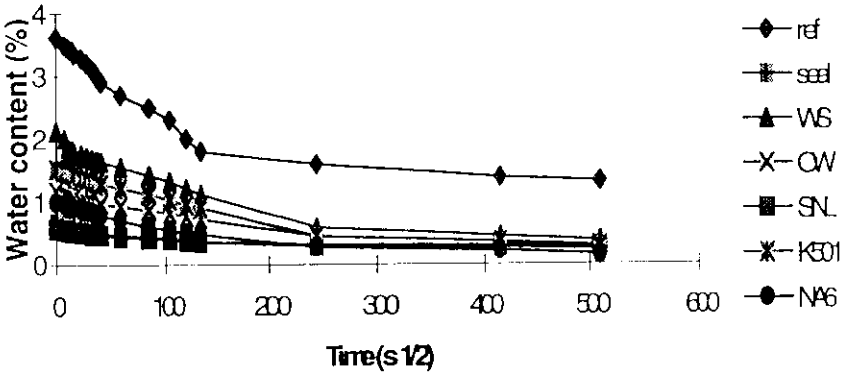

Figure 10: Evaporation Travertine (Lagensalz)

Travertine Italy (Figure 11). The product Funcosil WS and K501 showed no alteration to the evaporation capacity of the travertine samples. Sealer and Funcosil OW offered little variation to the evaporation rates. Actually all water amount absorbed during total immersion test evaporates after 72 hours of drying from all samples in accordance with the quantity of water absorbed. Figure 11 shows also that even after 72 hours of evaporation untreated samples keep comparable high moisture content.

Dolomite (Birzi). From Figure 12 could be concluded that the products Sealer, Funcosil WS, OW, SNL, NaAl6 and K501 showed no alteration to the evaporation capacity of dolomite sample. Untreated material keeps high moisture content even after 72 hours of evaporation

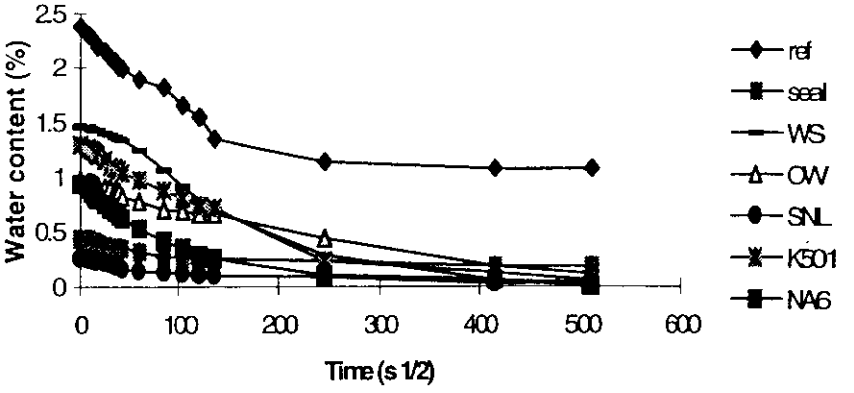

Figure 11: Evaporation Travertine (Italy)

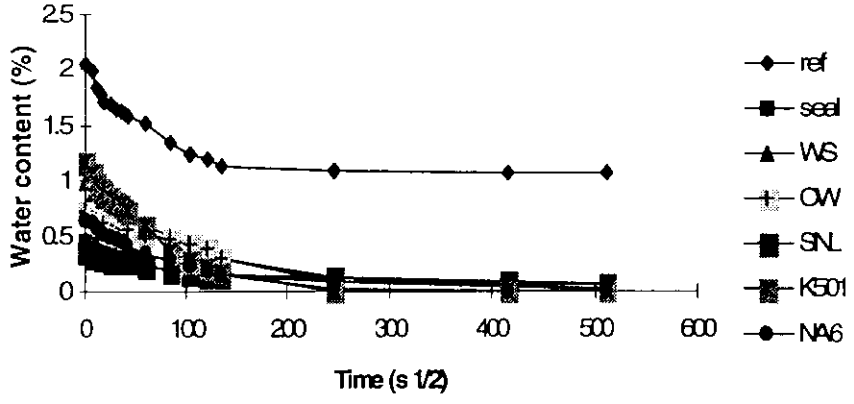

Figure 12: Evaporation (Birzi)

4 Conclusions

From the point of view of water repellence the most effective products were following: Sealer and Funcosil SNL for freshwater limestone; Sealer and Funcosil SNL for travertine (Langensalz); Sealer SNL and NaAl6 for Dolomite (Birzi); Sealer and Funcosil SNL for travertine (Italy). K501 and Fun-

cosil WS can't be used for dolomite (Birzi) as the water absorption increases. Funcosil WS and OW can't be used for Italian travertine as it increases water absorption.

However definitive conclusions on tested protectives can't be drawn before setting up other experiments necessary to complete the data. More important experiments necessary to make a better evaluation would be - pore size distribution test, water vapour permeability test and artificial corrosion tests. Water vapour permeability test being an important test will complete the results obtained in evaporation test and will show if the treated stone can freely ''breath'' - i.e. that no moisture evaporation from inside the stone is hindered.

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