TREATMENT OF POROUS BUILDING MATERIAL WITH WATER REPELLENT AGENTS - RISK OR PROTECTION?
CASE STUDIES ON EFFICIENCY AND DURABILITY

Eberhard Wendler,
Fachlabor für Konservierungsfragen in der Denkmalpflege, München

1 INTRODUCTION

The corrosive action of water to porous material is known since the antiquity. However, there are several examples of stone material that has been in permanent contact with water since centuries without showing any damage. Thus, it is not the presence of water itself but its chemical and physical effects which promote destruction to the material.

Water as a polar compound is able to dissolve amounts of pollutant gases like sulfur dioxid or nitrous oxides which form aggressive acids. Capillary absorption of these acids into the pore space of stones is harmful when the material contains reactive binding material which is dissolved or transformed into different compounds.

Absorption of water to the surface of clay minerals may lead to swelling. If the expansion is transmitted to the structure, a dilatation takes place which is not always completely reversible. Wetting and drying lead to scaling damage especially on clayrich sandstones.

Water can dissolve soluble salts which can migrate along the moisture gradient, crystallizing frequently at the outermost surface as a harmful efflorescence.

Biological growth on stone surfaces can start only if a minimum amount of water is present. A biofilm once formed, however, is capable of accumulating and retaining water from air humidity, thus creating its own environment as a precondition for surviving.

Finally, a wetted stone surface acts like a fly catcher, fixing dust particles from the environment. Due to recrystallization, theses particles may be bound closely together forming a crust on the stone surface. Crusts as well as biofilms may be harmful if they interact with the surface. If the water permeability is remarkably reduced, the surface is held in a wet state so that an intense chemical reaction potential is generated with exchange of electrolytes and metabolism products in the solution phase. On the other hand, a crust (or biofilm) may protect the surface due to the reduction of capillarity and gas diffusion.

In many cases, an impregnation is carried out only for esthetical reasons, i.e., to prevent further pollution of a freshly cleaned (or fresh) facade, regardless of the absorbency and the mineralogical composition of the stone material.

2 INVESTIGATIONS ON DURABILITY OF IMPREGNATIONS ON NATURAL STONE

While impregnations in former times have been carried out by the use of plant waxes, parafin solutions, C-organic resins etc., the predominant compounds used during the past 30 years have been solutions of alkyl silanes, siloxanes or polymeric silicon resins. The final reaction product in all three cases is a silicon resin film, which coats the surface of the capillary pores of the stone.

Between 1986 and 1992 some 100 test areas at about 40 different buildings in Germany have been investigated which have been treated with Si-organic water-repellents 1 to 20 years. The capillary water absorption on the facade was measured by means of the Karsten tube, monitoring the amount of water absorbed versus the time during 1 hour. By a calculation program [1], the estimation of the water absorption coefficient w [$kg/m^2\ h^{0.5}$] and the corresponding intrusion coefficient B [$cm/h^{0.5}$] is possible. Furthermore, one can distinguish between real absorption, i.e. transport of water into the stone (which is described by the w-value) and surface parallel water spreading inside an outermost zone with a water-repellent zone behind the surface.

Comparing with the weathered, untreated stone material, a valuation of the efficiency of the former treatment can be carried out. Regarding the different age of the test areas, an evaluation concerning durability is possible.

Figure 1 shows an example from a test area on Schlaitdorfer Sandstein at the Cologne cathedral [2]. The stone has been strenthened with silicic acid ester (SAE) and subsequently impregnated by a solution of isobutylsilane in 1977. Assuming that the freshly treated stone had a w-value of $< 0.1\ kg/m^2\ h^{0.5}$ (as it is usually the case), it can be clearly seen that the w-value obtained from Karsten measurements rises with increasing age of the treatment.

Figure 2 shows the attempt of valuating all investigated test fields of different age. The graph is the result from some 1000 measurements on some 100 test fields, i.e., each single point is a statistical average from 10 particular measurements on one test field, respectively. The valuation number range is from 1 to 6: 1 means optimal water-repellency with $w < 0.1\ kg/m^2\ h^{0.5}$ in all points, while No. 6 is attributed to test fields which show no difference in absorbency from the untreated material, i.e., have no efficiency any more. Plotting the valuation number versus the age of treatment, a clear tendency can be seen: One year after the treatment, almost every field has a sufficient water-repellency. With rising age of the treatment, however, some 85% of all test fields show a decrease in efficiency. A remarkable drop can be recognized after five years. In contrast, there are some positve exceptions which do not show a remarkable decrease in efficiency even after 15 years. These exceptions are related to test areas on very famous buildings like the Cologne cathedral or the minster of Ulm where the treatment has been carried out by instructed personal. Thus, carefulness in application seem to enhance durability of water-repellents.

In addition, the following observations have been made:

- The decrease in water-repellency proceeds from the surface to the interiour. In most cases, a thin outermost zone of less than 1 mm is moistened again, while the inner material still shows the effect of impregnation. Thus, because rain or dew cannot be soaked into the interior of the material, the surface remains wet for a much longer period than in case of the untreated material.

- Especially on limestone surfaces, the prolonged period of wetness leads to intensive biological growth. Obviously, the suitable p_H-range of limestones (7 - 8) favours the growth in contrast to non-carbonatic sandstones.

- Cleaned and impregnated limestone facades remain light only for a period of some 3 to 5 years. After that time, a brownish or greyish crust begins to form.

- The main reason for the reduction in efficiency seems to be the deposition of hydrophilic dust particles inside the outermost grain layers. Thus, a lateral zone is formed which is able to take up water again. This zone is sharply separated from the intact water-repellent zone inside.

- Water-repellency does not equally decrease at the surface of a sqaure stone. Differences in material properties due to the stratification, differences in application quality, or geometrical factors (shape) may explain this observation:

Figure 3 shows an example from two sqare stones inside a test area from the Alte Pinakothek in Munich, which is built from Regensburger Grünsandstein, a calcareous sandstone containing glaukonite. The stone has been strengthened with SAE and subsequently impregnated by a combined water-repellent product which consists of SAE and an oligomeric siloxane (OSX). The resulting w-values obtained from different points on the stones show clear areas with higher and lower water absorption, which could be explained by either of the above mentioned reasons.

3 LABORATORY EXPERIMENTS

Investigations concerning hygric swelling and shrinking of treated and untreated material of clayrich sandstone yealded surprising results [3]:

Drillcore samples of Abtswinder Schilfsandstein from Bavaria have been fixed in a dilatometer and wetted subsequently in rising air humidity (20_C) and finally stored under water for 48 h. Figure 4 shows the moisture dilatation function of alkyl silane treated and untreated material. The dotted parts of the plots represent the hygroscopic region (air humidity), while the upper end of the curves correspond to the equilibrium value after storing in water. It can be clearly seen that the amount of water absorbed is reduced by the impregnation to some 40% of the untreated value. However, the corresponding hygric dilatation is even enhanced comparing equal moisture contents. In spite of reduced water uptake, complete wetting leads to only 20% reduction in the hygric dilatation. In changing air humidity, treated samples react with a higher amplitude in dilatation than untreated. Since the frequency of humidity changes is much higher than that of rain events, the risk for subsequent damage is greatly enhanced by the treatment in this case. The example shows clearly that the priority is not to exclude capillary water from the pore space but to reduce the damage producing effects of water. It has, however, to be emphasized that similar effects have not been measured on all silicon-organic products. Moreover, the same product performed differently on different kinds of stone.

Samples of Ebenheider sandstone, a clayrich bunter sandstone, have been capillary treated with a combined hydrophobic strengthener consisting of SAE and OSX. After a reaction time of some 6 weeks, the hygric dilatation during storing under water has been measured simultaneously at points of different depth. The side planes of the samples have been isolated by an epoxy resin so that water could only enter from the front ("rain") and the rear ("inner humidity") plane. In figure 5, the hygric dilatation of different depth zones of an impregnated core sample is plotted versus the time of wetting. It can be recognized that the dilatation of the outermost, treated zone (2 and 18 mm) is only delayed, after 45 h the same value of some 700 _m/m is reached as in the untreated zone.

4 CONCLUSIONS

The goal of an impregnation of natural stone should not be simply the reduction of capillary water uptake. Damage producing factors like hygric swelling and shrinking should be considered as well as effects induced by the aging of the water-repellent, i.e., enhanced biological growth or subsequent frost damage due to a sharp separation of wet and dry zones.

During the last 5 to 10 years, efforts have been made in the developement of new or modified protective agents with the aim to avoid the disadvantages of marketable agents [5, 6]. However, a long period of tests is necessary to test these agents under long term conditions. Therefore, with the view to the next years, some general suggestions for the use of common impregnation agents should be given. A useful application should have the following assumptions:

- High capillary absorbency ($w > 1$ kg/m² $h^{0.5}$), combined with
  a) the presence of raective compounds in the structure and/or
  b) sensitivity to hygric swelling processes.
- The possibility of repetition of the treatment without alteration of the mechanical properties in the treated zone. An alternative could be the developement of highly durable agents (» 20 years).
- The absence of moisture pathways from the ground or the interiour.
- The absence of soluble and hygroscopic salts.
- A joint network without fissures or defects.

FIGURE 1:
Capillary water absorption coefficients (w) from Karsten measurements. Cologne Cathedral, Schlaitdorfer Sandstein, Test area (1977), treated with SAE and subsequently impregnated with isobutyl silane. Measurement 1986 (9 years) and 1992 (15 years). The value of the freshly treated material is estimated from the experience on other test fields.

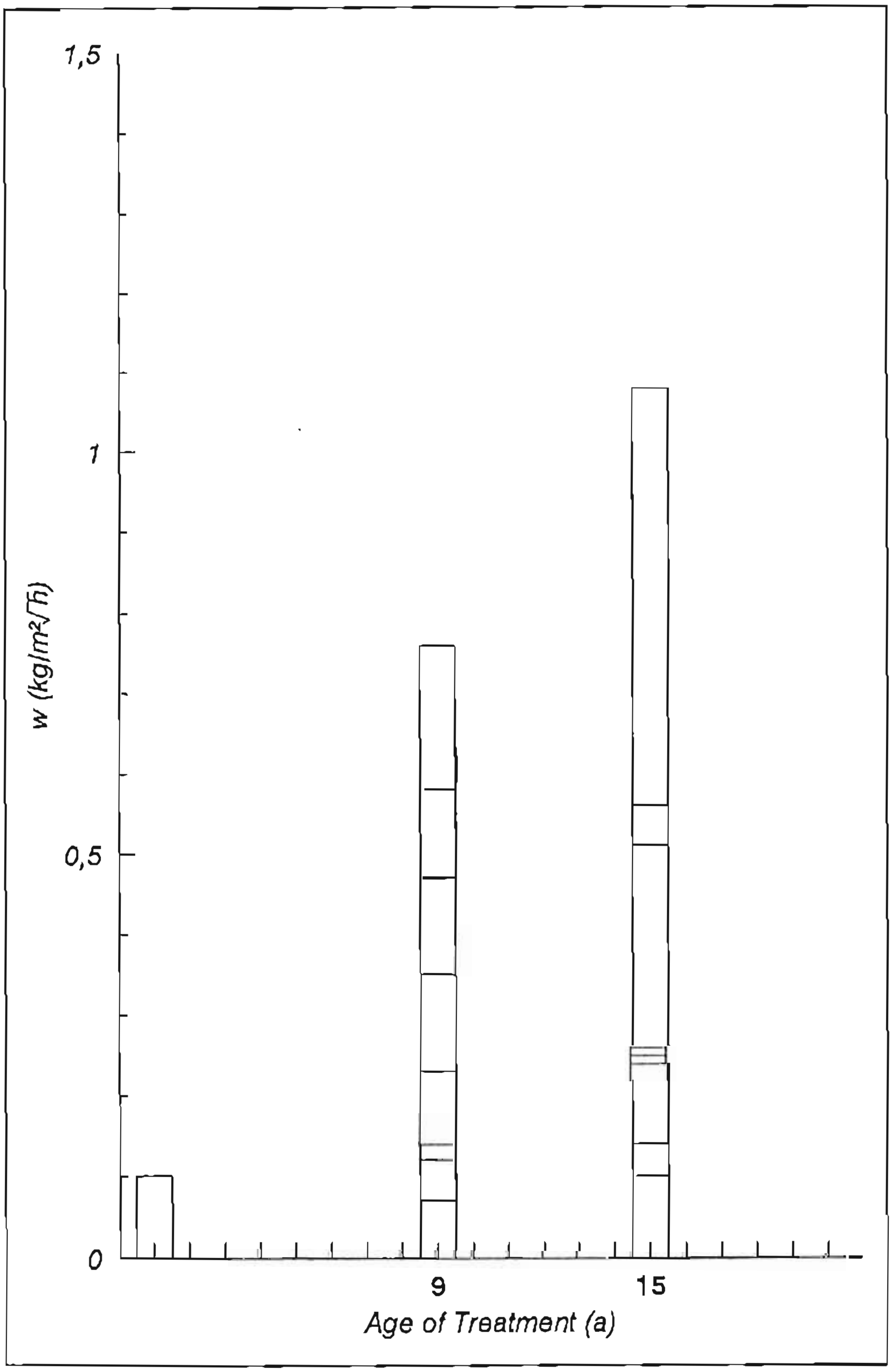


FIGURE 2:
Durability of hydrophobing treatments. Karsten Measurements on some 40 different buildings. The w-values of 10 particular measurements on each test field are transformed into a valuation number:
1: optimally water-repelling properties in all points to
6: no difference in absorbency to the untreated material on either point.
The valuation number is plotted against the treatment age. Each point represents the result of 10 Karsten measurements. 85% of all values are located inside the grey bar.

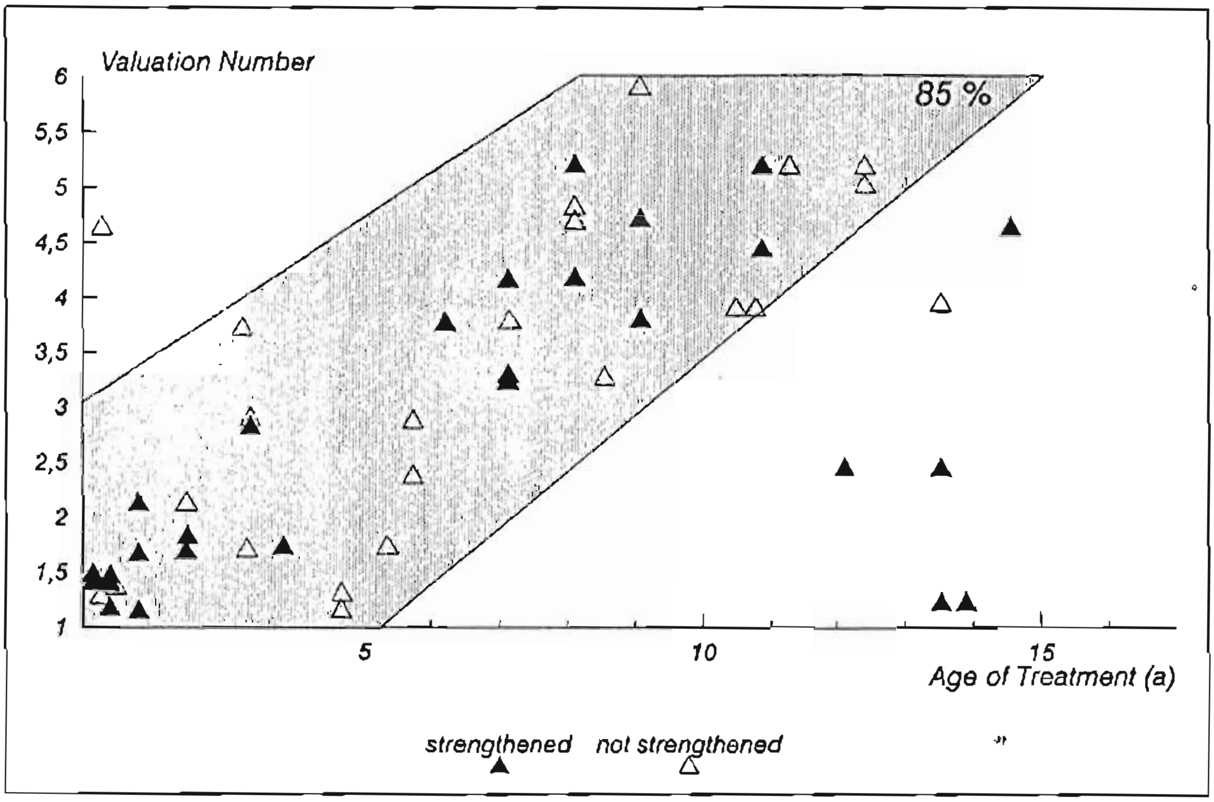
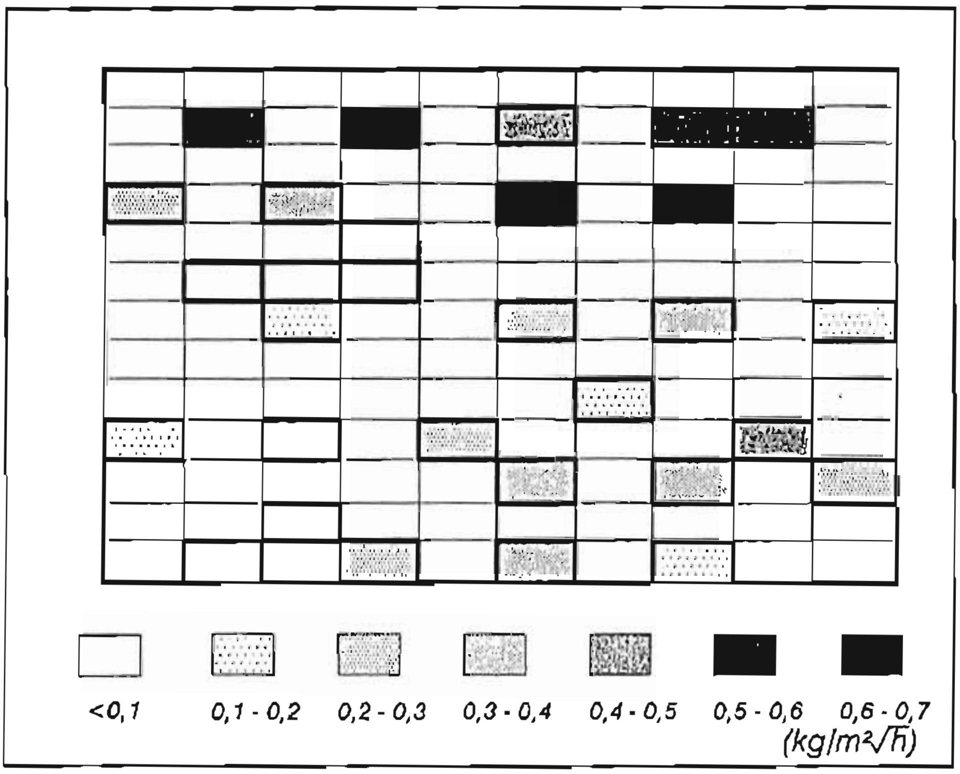


FIGURE 3:
w-values from Karsten measurements on two square stones of Regensburger Grünsandstein from the Alte Pinakothek in Munich. Test field, treated with SAE and subsequently impregnated with a combined SAE/OSX-product in 1978. Measurement: 1988. It can be assumed that w was < 0.1 kg/m² $h^{0.5}$ at all points on the freshly treated stone. The differences in absorbency after 10 years may be due to material inhomogenities (stratification), carelessness in application or geometrical effects (different intensity of dust or moisture input).



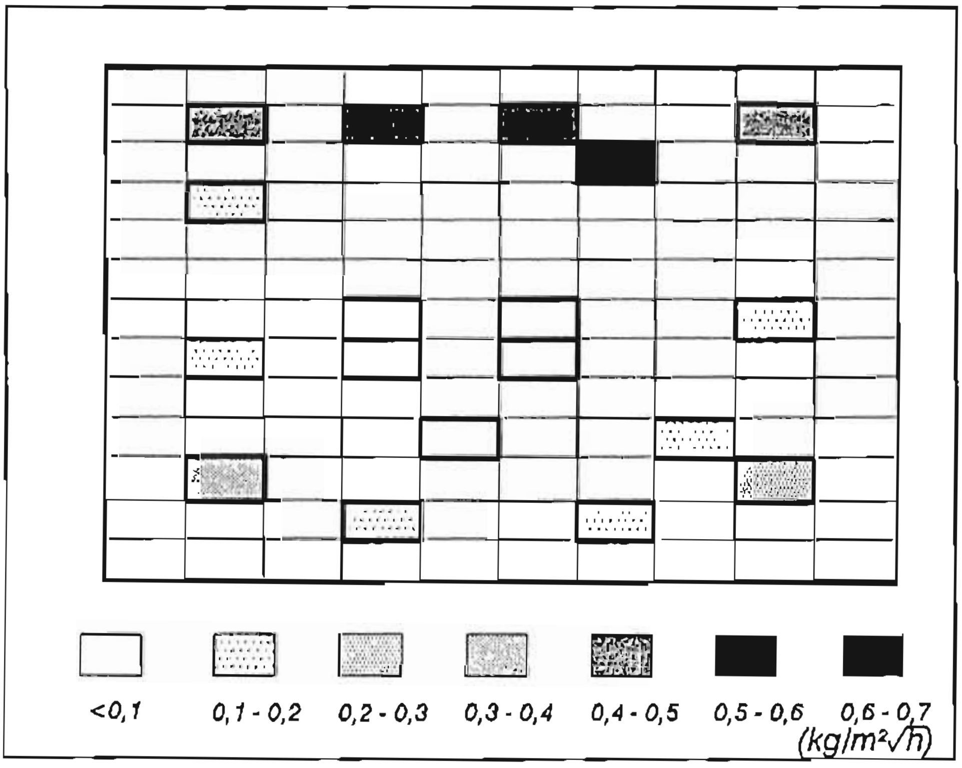


FIGURE 4:
Moisture-dilatation-function of impregnated (HI) and untreated (U) Abtswinder Schilfsandstone. Equilibrium value. Dotted lines: Measurement in air with rising humidity. Final point of the graphs (right): Moisture/Dilatation after subsequent storing under water.

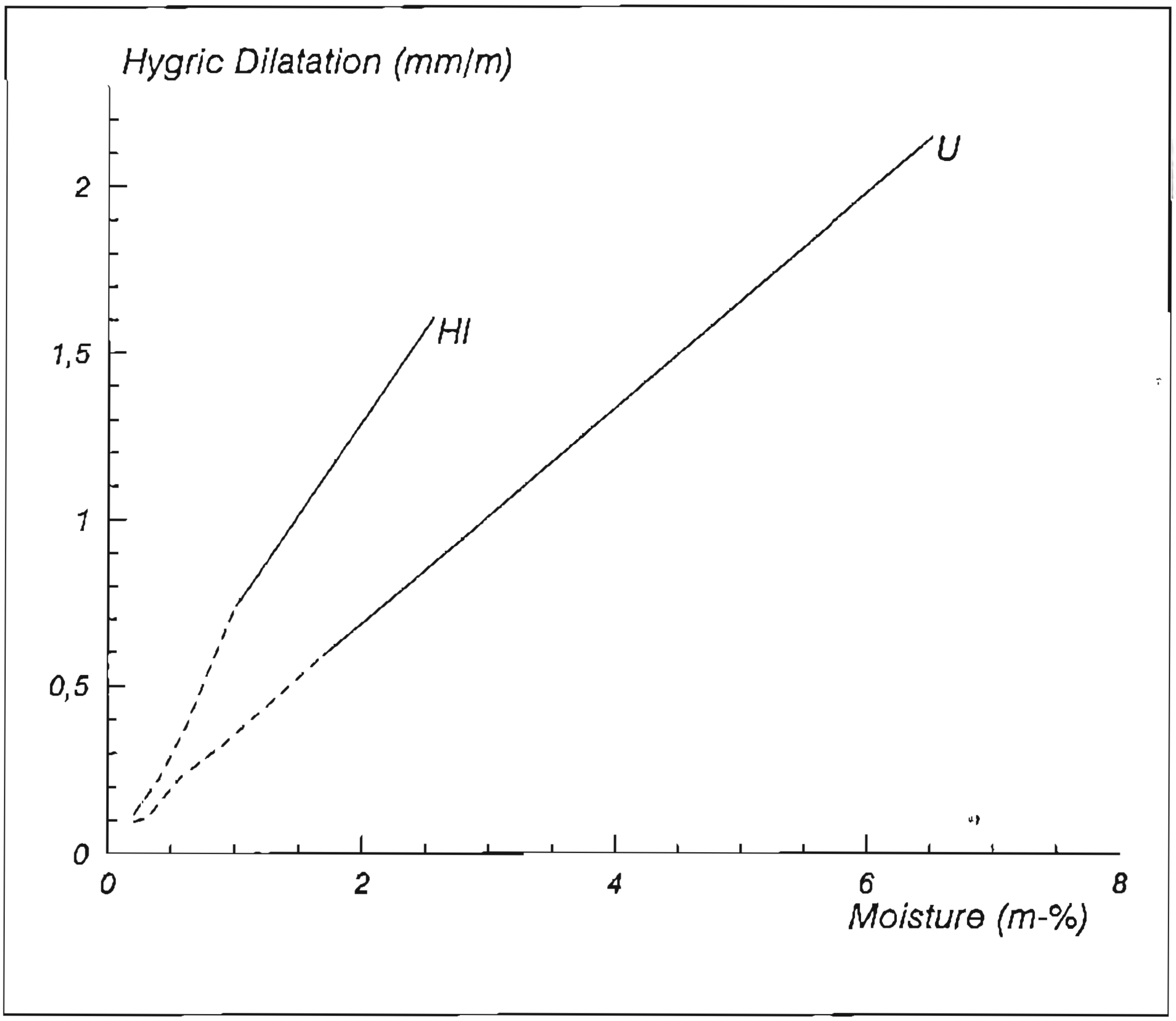
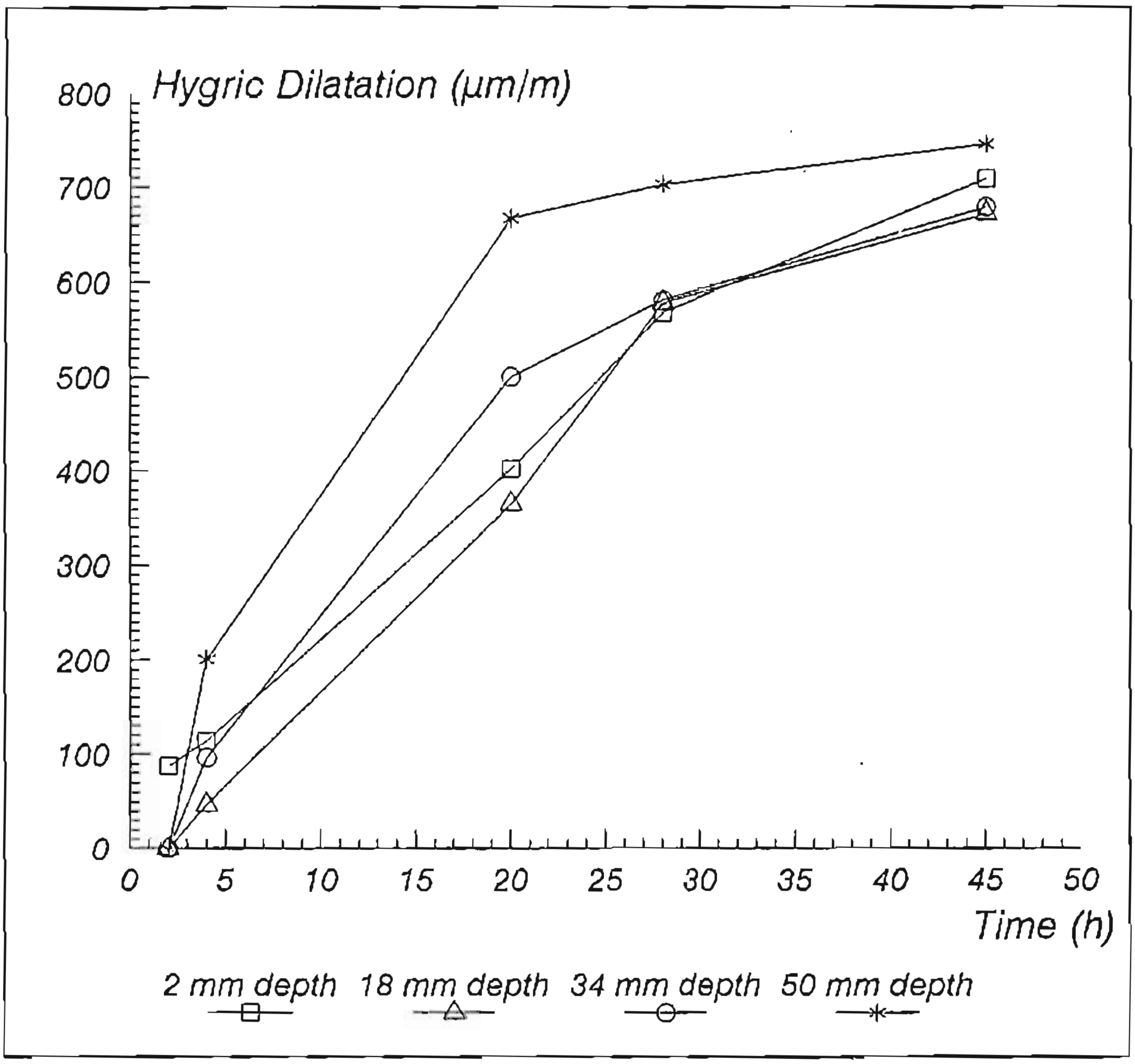


FIGURE 5:
Hygric dilatation as a function of time during storing under water on a prismatic (5x5x10cm) sample of Ebenheider Buntsandstein, treated with a combined SAE/OSX-product. Intrusion depth of the agent: ca. 20 mm. Simultaneous measurement on different positions. Water is able to enter the sample only from the front and rear plane (100 mm).



5 REFERENCES

1 Wendler, E., Snethlage, R.: Durability of Hydrophobing Treatments of natural Stone Buildings. In: Marinos, P.G. & Koukis, G.C. (eds.): The Engineering Geology of Ancient Works, Monuments and Historical Sites. Vol. 2 (Proc. Intern. Symp., Athens, 19.-23.9.1988), 945 - 951. Rotterdam, Balkema, 1988.

2. Wendler, E., Rückert-Thümling, R., Klemm, D.D. , Snethlage, R.: Zur Dauerhaftigkeit von Hydrophobierungsmaßnahmen auf Naturstein. Vergleichende Fallbeispiele am Kölner Dom und am Ulmer Münster. In: R. Snethlage (ed.): Jahresberichte aus dem Forschungsprogramm Steinzerfall-Steinkonservierung, Band 4 (1992), Ernst & Sohn, Berlin, 197 - 204.

3. Möller, U., Schuh, H., Wendler, E.: Längenänderungsverhalten hydrophobierter Sandsteine. Bautenschutz und Bausanierung, 4, 46 - 49 (1992).

4. Wendler, E., Lotzmann, S., Schwamborn, B.: Quell- und Schwindverhalten als Wirksamkeitskriterium zur Beurteilung von Steinschutzstoffen. In: R. Snethlage (ed.): Jahresberichte aus dem Forschungsprogramm Steinzerfall -Steinkonser-vierung, Band 6 (1994), Ernst & Sohn, Berlin, in press.

5. Sasse, H.R., Honsinger, D., Schwamborn, B.: PINS - New Technology in Porous Stone Conservation. London: E & FN, Spon, 1993, in: Proc. Int. RILEM & UNESCO Congress Conservation of Stone and Other Materials (29.6. - 1.7.1993), Thiel, M.J. (ed.), Vol. 2, 705 - 716.

6. Hilbert, G., Wendler, E.: Zielgerechte Natursteinkonservierung. Zur Reduzierung des hygrischen Quellens. Bautensch. & Bausan. 3 (18. Jhrg.), 60 - 64 (1995).

ACKNOWLEDGEMENT

The investigations presented in this paper have been supported by the German ministry of research and technology (BMBF).