# BEHAVIOUR OF IMPREGNATED NATURAL STONES AFTER DIFFERENT WEATHERING PROCEDURES

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## 1 INTRODUCTION

The use of suitable water repellent products can slow down the alteration processes of natural stones. In many cases damages, originally caused by water movements, can be avoided. The success of a conservating treatment with water repellents depends upon many factors.

Series of comprehensive tests were carried out to determine the durability of water repellent products and their durable efficiency on natural stone specimens, respectively. The investigations, described in this paper, were carried out with four products: Two commercial water repellent systems (one widely used in the past and one modern system), one common silica ester for strengthening of deteriorated porous materials with hydrophobic properties and one experimental product according to a new concept for polymer based impregnation materials for strengthening and hydrophobic properties /1/.

Three different types of artificial weathering procedures were carried out in a comprehensive test programme: freeze-thaw-cycles, natural weathering over three years and a complex weathering in an environmental simulation system. Information concerning the durable efficiency of the impregnations could be achieved by comparing different test results before and after the weathering procedures.

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## 2 TEST PROGRAMME

### 2.1 MATERIALS

The tests were carried out with the following products:

Material A: silica ester system

It consists of a common tetraethoxisilane with oligosiloxanes added for adopting hydrophobic properties. Such stone protecting systems are widely used since more than thirty years.

Material B: siloxane system

It consists of oligosiloxanes dissolved in mostly aliphatic hydrocarbones ("white spirit").

Material C: silane system

It consists of isobutyltriethoxisilanes as single ingredient without any solvent.

Material D: polyurethane-based system

It consists of two significant molecule parts. One is a so-called hard segment, which is built up by an isophoronediisocyanate. The other segment, the so-called soft segment, is built up by a oligodimethylsiloxane. The mixture is dissolved in buthylacetate. The main characteristics of the four tested materials are put together in table 1.

TABLE 1 Characteristics of the tested water repellents

| No. | agent | content of active agent M.-% | type of solvent |
|---|---|---|---|
| 1 | 2 | 3 | 4 |
| A | silica ester | 100 | - |
| B | siloxane | 6.3 | white spirit |
| C | silane | 100 | - |
| D | polyurethane | 30 | butylacetate |

The substrates for the water repellent materials were new samples of a German red sandstone called Ebenheider Sandstein. This type of sandstone is fine-grained with a pore volume of about 22 Vol.-%. The components are quartz (about 34 Vol.-%), different fragments (about 21 Vol.-%) and feldspar (about 8 Vol.-%). A thin argillaceous-ferritic coating of the components functions as binder with a mean content of about 15 Vol.-% /2/.

## 2.2 APPLICATION

The stone samples used had dimensions of 50 mm x 50 mm x 100 mm. The lateral faces of the specimen were sealed by a conventional epoxy-resin to prevent water or solvent from evaporation, whereas the front faces remained free. The water repellents were applied by capillary suction for 4 hours. After application, the samples were stored in laboratory climate 23 °C/50 % relative humidity. Table 2 shows the quantitative fluid uptake during application and the penetration depth of the different materials.

Table 2: Application results

| No: | fluid uptake g/m² | penetration depth mm |
|---|---|---|
| 1 | 2 | 3 |
| A | 3670 | 25 |
| B | 3110 | 25 |
| C | 2440 | >38 |
| D | 3300 | 35 |

## 2.3 WEATHERING PROCEDURES

After hardening of the impregnation materials over a period of 28 days in a climate room (23 °C/50 % r.H.) four different types of weathering were carried out.

O: Reference storage
The specimens were stored in laboratory climate 23 °C/50 % r.H. for about 6 months.

L: Freeze-Thaw-Cycling with Deicing Salt Influence
Storage in saturated sodium chloride solution (treated surfaces immersed to 5 mm depth into the solution) with a temperature T = (-15 ± 3)°C for two hours and storage in a water bath (treated surfaces immersed to 5 mm depth into the bath) with a temperature of (20 ± 2)°C for two hours.
The total amount of freeze-thawing-cycles was 40.

F: Natural weathering
The treated specimen were exposed in industrial atmosphere for a duration of 3 years.

V: Complex environmental simulation
The treated specimens were weathered in an experimental simulation apparatus called VENUS (Versuchsanlage zur Entwicklung naturnaher Umweltsimulationskonzepte) for one year. The control unit allows independent variation of the parameters: IR/UV radiation, humidity,

temperature, rain, wind, and air pollution. The aim of the tests is the distinction of the effectiveness and durability of materials under complex weathering without any unnatural increase of weather components /3/. The cycles were calibrated by evaluating the data of different climate stations at places with extreme climate conditions in Europe.

After the different weathering procedures the specimens were stored under normal climate conditions (23 °C/50 % r.H.) before starting efficiency tests.

### 2.4 EFFICIENCY TESTS

The hydrophobicity of the impregnated stones was quantified by capillary water absorption of the entire specimen and contact angle measurements in the depth profile. In addition the mechanical properties bending strength and modulus of elasticity were determined.

For the measurement of capillary water-uptake the samples were immersed into a water bath (depth about 5 mm) for 24 hours and the free capillary water uptake through the impregnated surface was measured in kg/m². For the tests concerning contact angle and mechanical properties the samples were sawn into segments with thicknesses of 4 mm. The mechanical properties were determined by biaxial bending tests to estimate strength and modulus of elasticity according to the depth of the specimen /4/.

## 3 RESULTS AND DISCUSSION

### 3.1 INVESTIGATIONS BEFORE WEATHERING

The basic aim of protection measures consisting of impregnation with water repellents is a reduction of the uptake of liquid water. The test results of free capillary water absorption (after one day) of the impregnated specimens before exposure are put together in figure 1. The water-uptake of an untreated specimen Ebenheider sandstone can be estimated with 10 kg/m².

It can be seen from this diagram, that the four investigated impregnation materials meet the requirement of extreme reduction of capillary water absorption. The uptake results achieved after 24 hours were between 0.07 and 0.14 kg/m². This is only about 1 % compared with an untreated reference sample.

Figure 2 shows the contact angles, which were measured on the surfaces of thin slices cut out of the impregnated specimens before weathering.

FIG.1 Capillary water absorption of impregnated Ebenheider sandstones before exposure

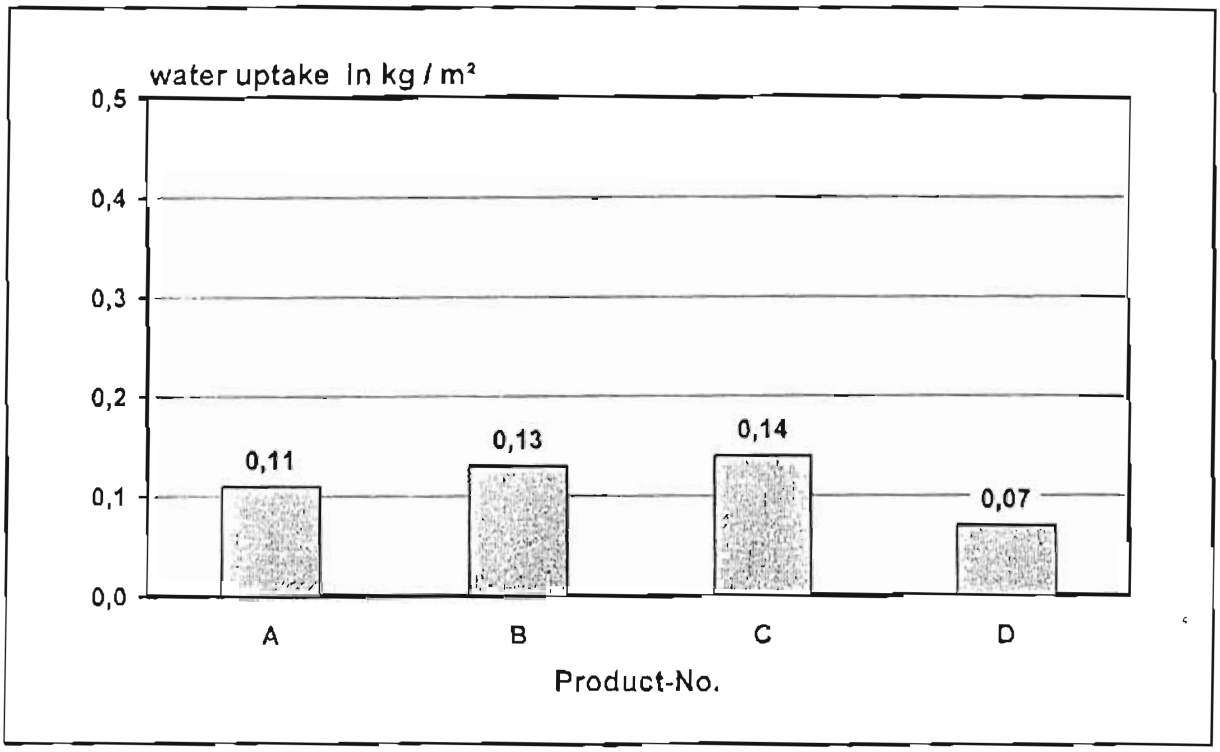
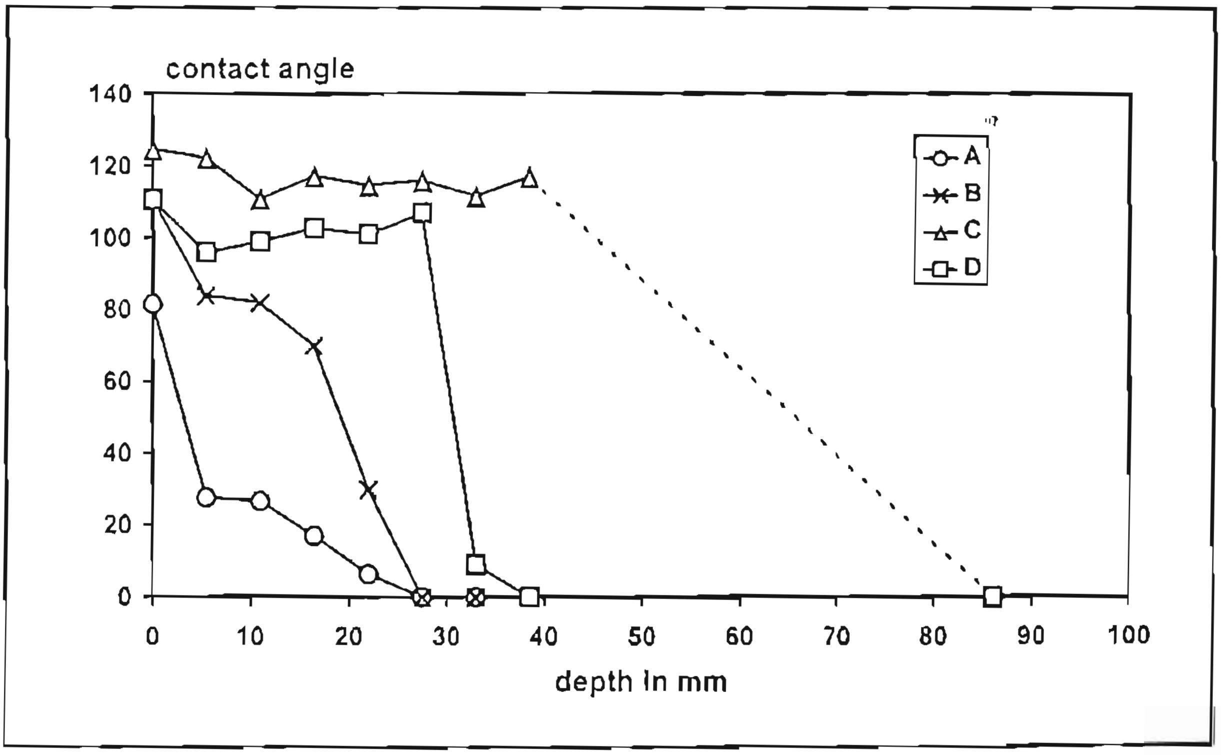


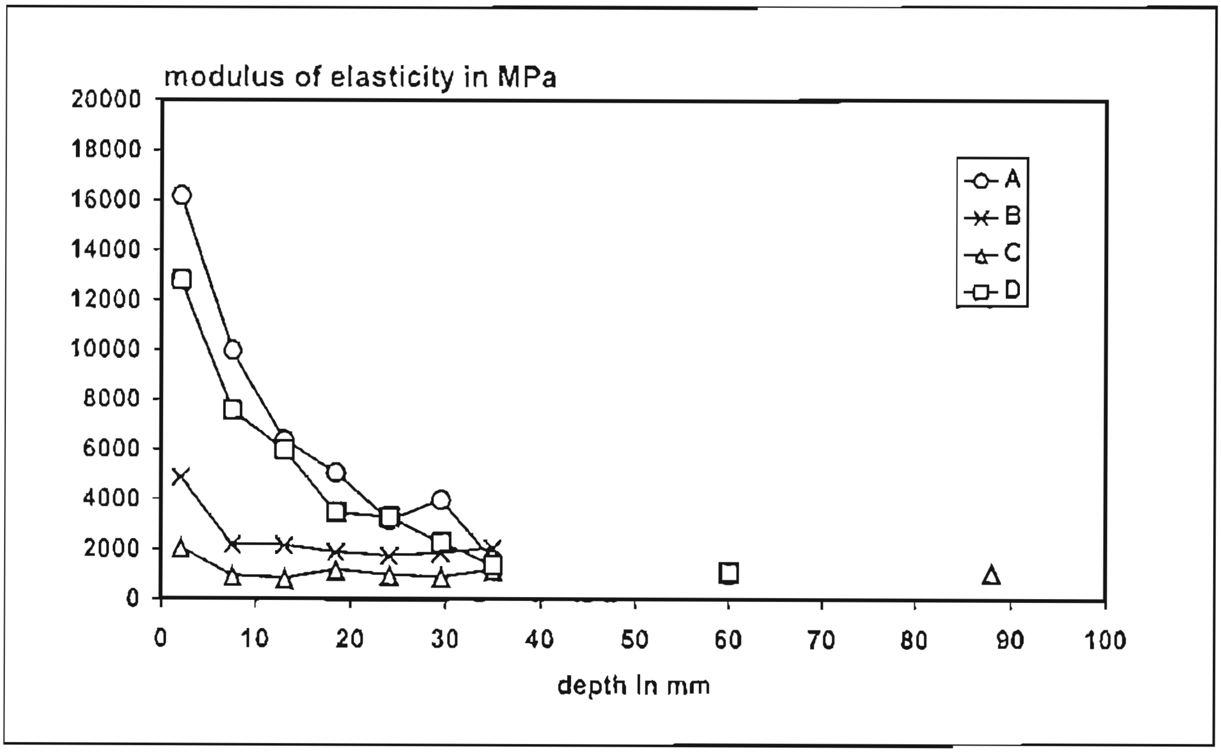

FIG.2 Contact angle according to the depth of the specimen of impregnated Ebenheider sandstone without weathering



All the investigated agents produced relatively high contact angles between 80 and 130 degree on the outer, the impregnated surface of the specimen. The values of the materials A and B decrease linear with the stonedepth. In a depth of 27 mm an angle could no longer be measured. The results of the slices cut out of sandstone treated with materials C and D differ completely. Up to a depth of about 30 mm, the measured contact angles stay constant between 100 and 120 degree. The values of material D go down to zero in a depth of 38 mm, whereas the contact angle on a slice out of the C-treated specimen still was on the same high level in a depth of 40 mm as on the outer surface. A definite penetration depth of material C could not been followed from these results. They were between 40 and 85 mm.

Extreme differences in their mechanical behaviour were obtained in the bending tests. On the one hand the water repellent materials with strengthening properties (A and D) caused a strong increase of bending strength in the treated stone area. Similar increases could not been measured in the case of B and C on the other hand. Figure 3 shows, that the modulus of elasticity had been increased by impregnation.

FIG.3 Modulus of elasticity in the depth of impregnated Ebenheider sandstone before weathering



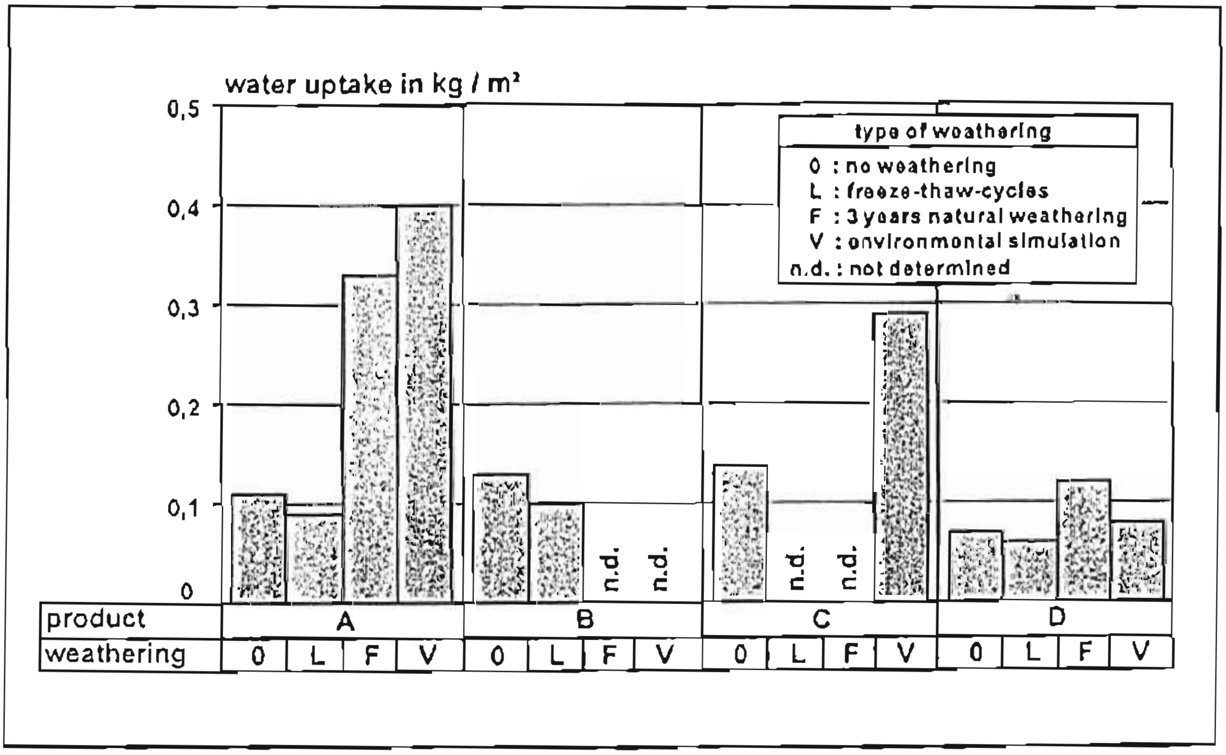
It can be stated, that a look at an increasing strength cannot be sufficient for assessing suitable mechanical behaviour. The possible change in the modulus of elasticity has to be considered. The modulus should not be increased extremely. A surprise in our test series was the modulus rise in the outer slices of the products B and C, which were not made for stone strengthening. Nevertheless at least the product B caused a significant increase of the modulus of elasticity.

## 3.2 INFLUENCE OF WEATHERING

All the tests carried out before weathering (presented in chapter 3.1 - reference storage 0) were carried out in the same way after finish of the different natural or artificial weathering procedures. The measured properties after weathering are shown in the following figures in comparison with the reference data.

Figure 4 shows the capillary water uptake of impregnated Ebenheider sandstone due to different types of weathering.

FIG.4 Change of water-uptake of impregnated Ebenheider sandstone due to different types of weathering.



In some cases the weathering causes a degradation of the hydrophobic effect of the stone. Generally it can be stated, that the freeze-thawing-cycles with deicing salt influence did not change the adsorption results of the tested agents. The highest rate of degradation could be detected on the specimen, treated with product A after complex weathering V. The uptake was four times as high as before weathering. An increasing factor three was achieved in case of product A and weathering type F and in case of product C and weathering V. The effect of degradation was very low after all weathering types in the case of stones, treated with product D. The figures 5, 6 and 7 show the contact angle (according to the depth of the specimen ) on slices cut of the treated stone samples and the changes due to weathering. For clearing up the behaviour of the materials the results with three tested materials are presented separately: product A in figure 5, product B in figure 6 and product D in figure 7. Generally it can be stated, that we achieved some single values of small contact angles on the outer surface. Possible reasons may be contaminations of the stone faces due to dust or due to chemical or biological pollution.

FIG.5 Change of contact angle due to different types of weathering (Product A, Ebenheider sandstone)

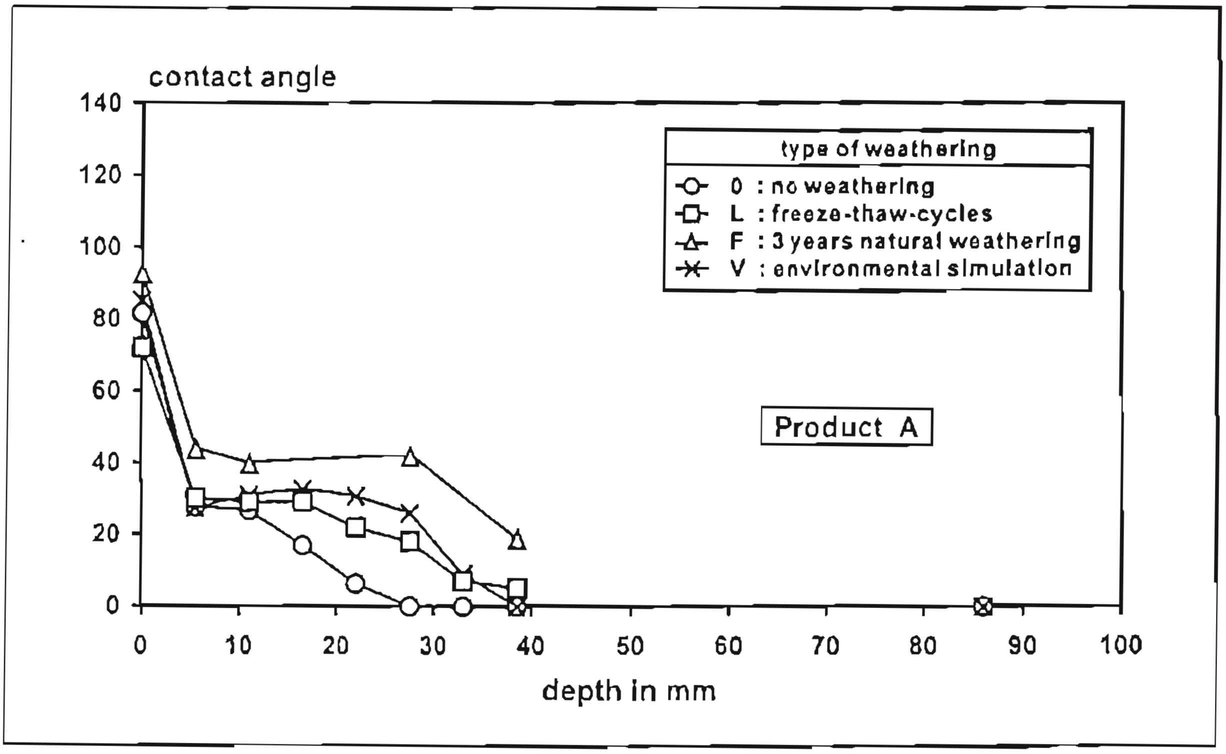


FIG.6 Change of contact angle due to different types of weathering (Product B, Ebenheider sandstone)

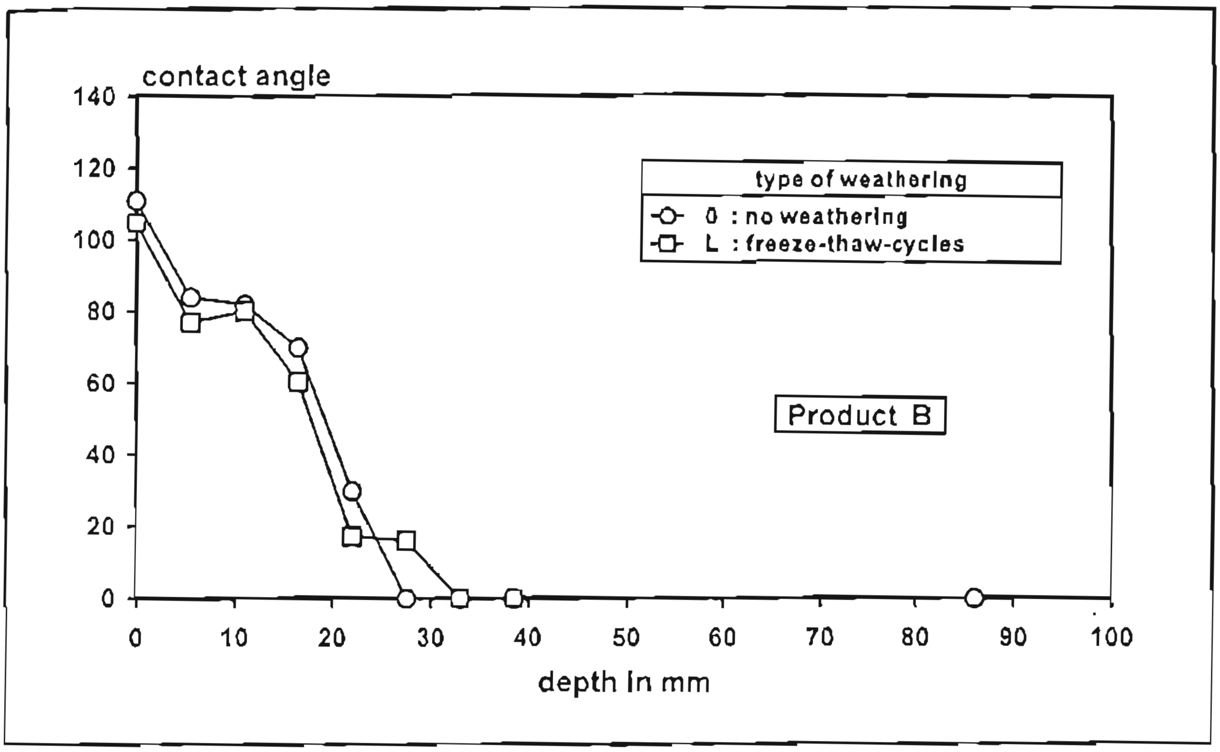
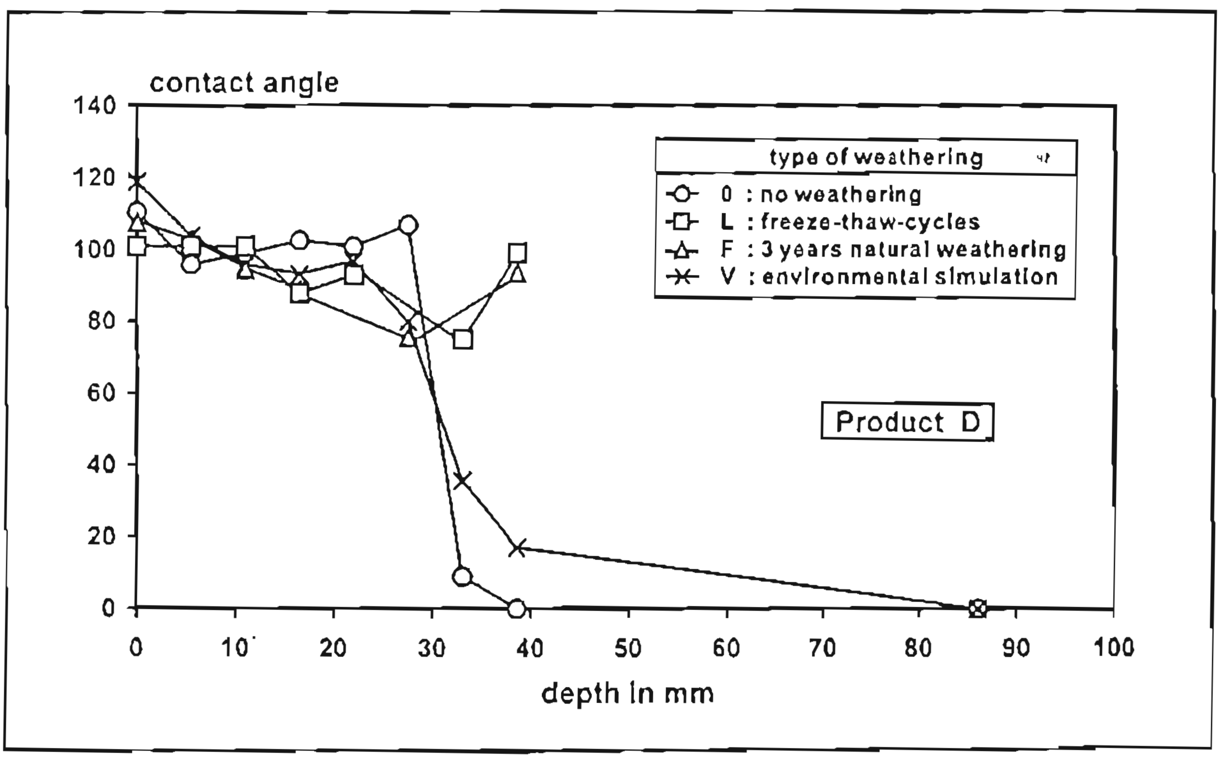



FIG.7 Change of contact angle due to different types of weathering (Product D, Ebenheider sandstone)



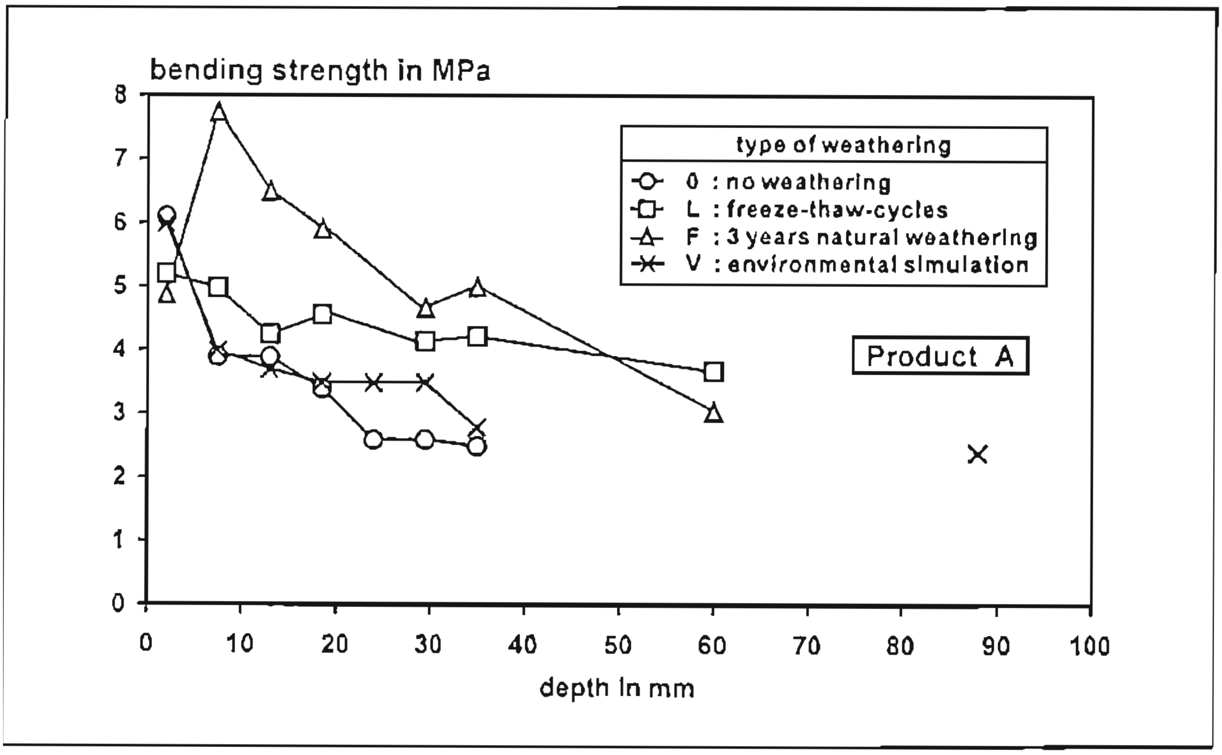
Looking at the hydrophobic properties of the agent A (fig. 5), contact angle measurements on impregnated Ebenheider sandstone, it can be seen, that there are increases of contact angles after the three weatherings in depths higher than 10 mm. An assumption is, that the chemical reaction had not been finished in the stone at the end of the reference storage 0. The loss of hydrophobicity, measured by the change of water uptake (see figure 4) could not be varified by the contact angle results.

Sandstones treated with product B were only weathered according L (Freeze-Thawing). 40 of such cycles did not influence the contact angle on slices cut out of the specimens. This corresponds with the results of the water-uptake, shown in figure 4.

As shown in figure 7, also the contact angles of specimen, treated with product D, does not change after different types of weathering (natural and artificial). It can be seen, that the contact angle stays on a level between 90 and 120 degree up to a depth of about 30 mm independent from the type of weathering.

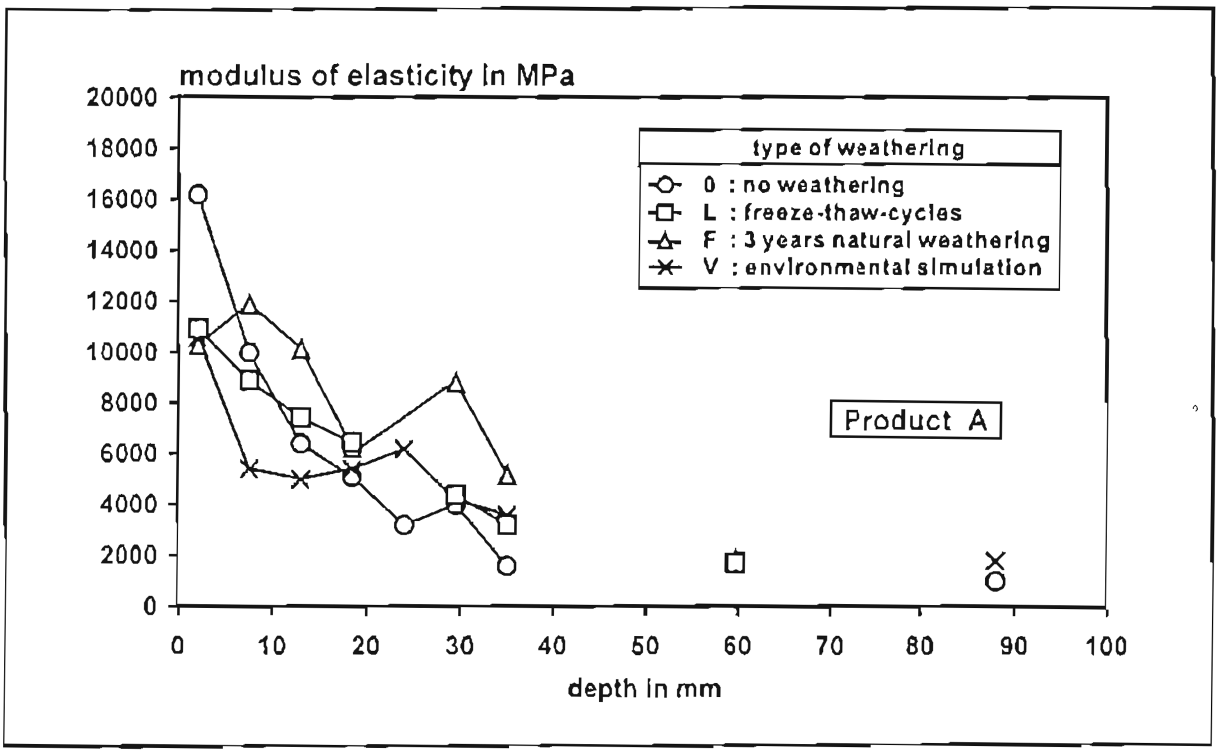
The figures 8 and 9 show the mechanical values (bending strength and modulus of elasticity) of the specimen, which were treated with product A, before and after different types of weathering.

FIG.8 Bending strength according to the depth of the specimen of impregnated Ebenheider sandstone (product A) before and after different types of weathering



The curves show a quite similar tendency, a linear decrease with the stone depth. It was surprising, that the strength level was increased due to the different weathering procedures. Additional research work is necessary to clarify these developments.

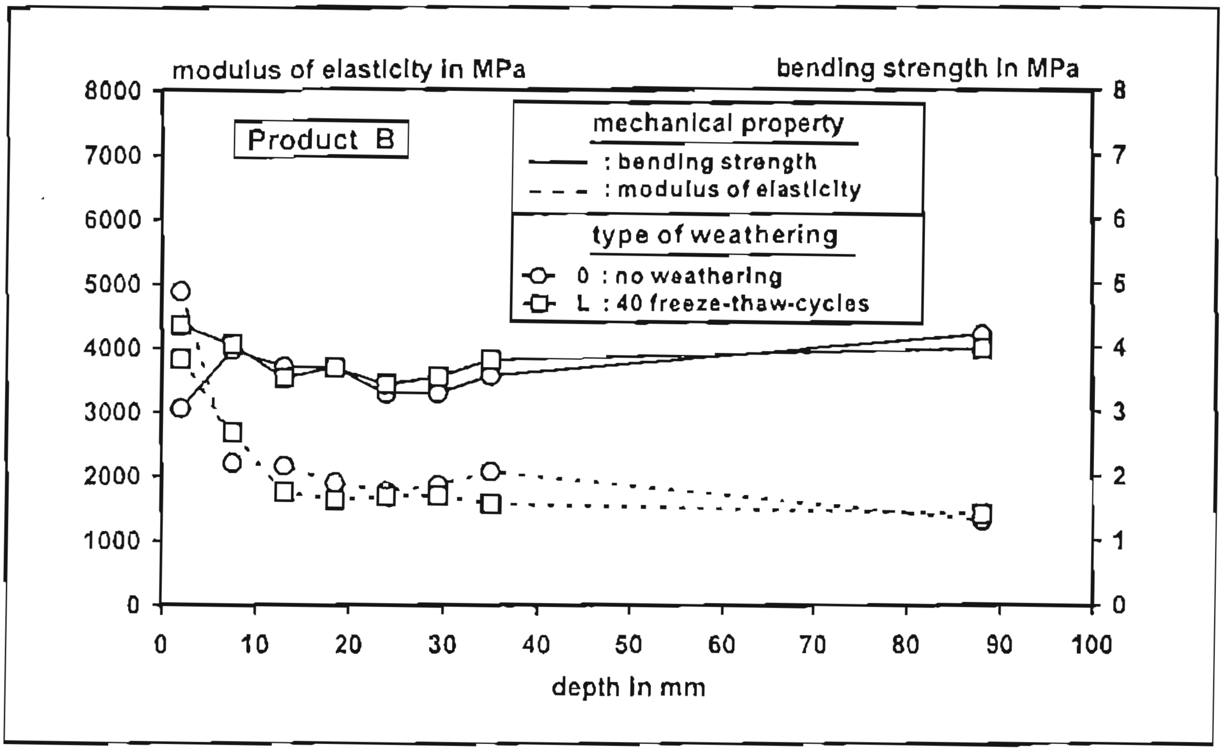
FIG.9 Modulus of elasticity according to the depth of the specimen of impregnated Ebenheider sandstone (product A) before and after different types of weathering




In case of this water repellent materials with hydrophobic properties the influence of the different weatherings on the modulus of elasticity showed a positive trend. The very steep increase from the inner stone material to the impregnated surface after the reference storage generally had been reduced.

Both mechanical values of the water repellent materials without strengthening properties are put together in the following figures. Product B (siloxane) was weathered only artificially, the results are put together in figure 10.

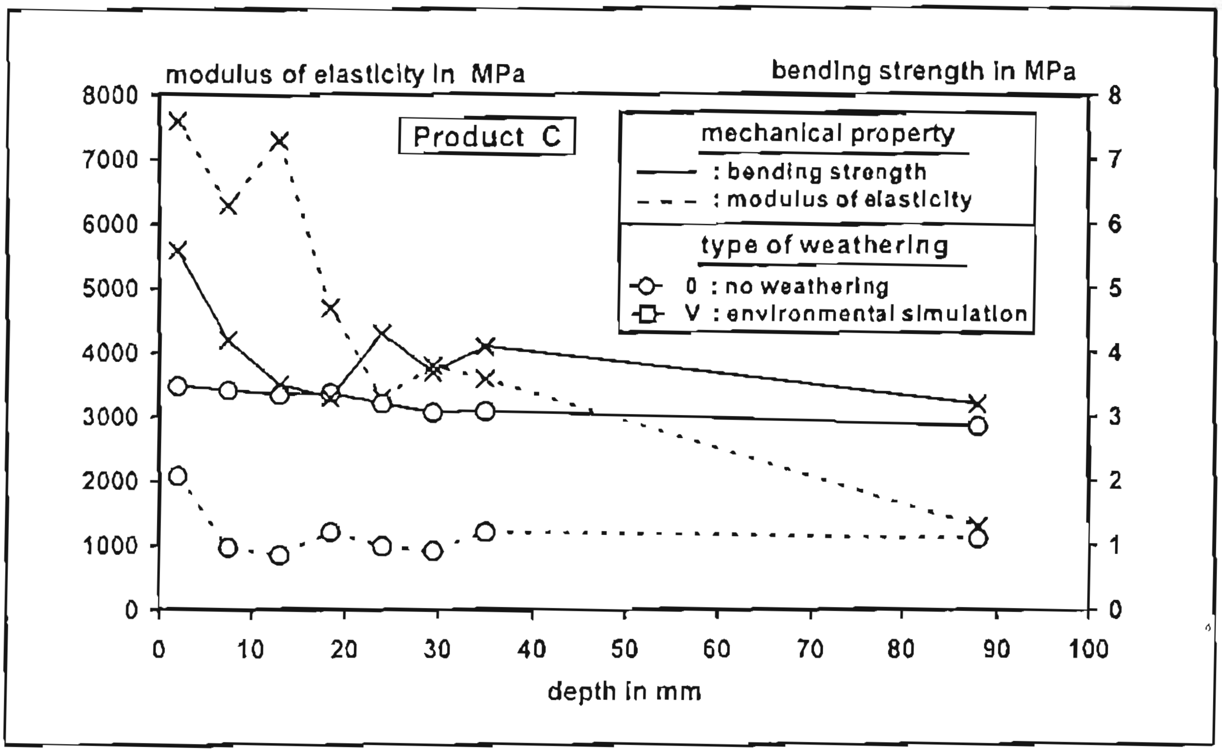
FIG.10 Mechanical properties of the specimen, treated with product B before weathering and laboratory weathering (L)




The strength of the outer slice had been increased by the laboratory weathering, the values of the inner slices did not change significantly. Overall we obtained a very modest linear increase of strength from about 3.5 MPa (depth d = 25 mm) to 4.5 MPa of the outer slice. The modulus results were similar to those before weathering. We measured an extreme increase of the modulus of elasticity in the outer 15 mm. The value rose from about 2000 MPa in a depth d = 12 mm to about 4000 MPa near to the surface.

Similar results were achieved with the specimen, which had been treated with product C. In these cases the environmental simulation (V) had been carried out. The results are shown in figure 11.

FIG.11 Mechanical properties of the specimen, treated with products C before weathering and after environmental simulation (V)




Both, bending strength and modulus of elasticity, have been increased due to the environmental simulation. A significant strength increase is limited on the outer slices whereas the modulus of elasticity increased in the entire penetrated area to a four to seven times higher level. It can be assumed, that the reason for this extreme increase might be a chemical reaction of the penetrated material at the presence of different gases at special climatic conditions. Additional intensive research is necessary to clarify the correlations between a lot of possible parameters.

# 4 CONCLUSIONS

The basic goal of hydrophobic impregnation is the reduction of capillary water uptake. Four different water repellent materials were applied onto sandstone surfaces. The tested materials reduced the absorption capacity of the natural stones on a level of about 1 %. Due to different weathering procedures the maximum water uptake was four times higher. In the tests of capillary water suction similar changes, which were obtained after natural weathering, could not been measured after freeze-thaw cycles. Generally no influence of weathering on the water uptake capacity of the polyurethane-based impregnation was found out.The curves of contact angles showed different characteristics according to the stone depth. It can be concluded from the results, that no significant change of contact angle in the stone will occur due to weathering, with the only exception of the outer face. Here contaminations by dust or pollution can cause single reductions. Contact angle measurements always have to be accompanied by water uptake investigations.Concerning the mechanical behaviour bending tests before and after weathering showed on the one hand, that reductions of increased strengths due to exposition seen unlikely, and on the other hand, that the modulus of elasticity, which might be increased after the impregnation, in some cases can be reduced due to weathering. Also with water repellents without strengthening properties increases of strength and modulus of elasticity were measured in the outer impregnated zone.Generally, it can be stated from the comprehensive tests carried out after different kinds of weathering, that the properties water uptake, contact angle in the penetrated stone and mechanical stiffness will not be deteriorated extremely by weathering conditions.

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