

# LONG-TERM EXPOSURE OF TREATED NATURAL STONE - DEVELOPMENT AND FIRST RESULTS OF A TESTING CONCEPT

CHR. BRUCHERTSEIFER\*, S. BRÜGGERHOFF\*, J. GROBE\*\*,  
K. STOPPEK-LANGNER\*\*

\* Zollern-Institut beim Deutschen Bergbau-Museum/DMT,  
Herner Strasse 45,  
D-44787 Bochum (FRG).

\*\* Westfälische Wilhelms-Universität Münster  
Anorganisch-Chemisches Institut,  
Wilhelm-Klemm-Strasse 8,  
D-48149 Münster (FRG).

## SUMMARY

First results of a field exposure study on treated natural stone, started in 1986, in the FRG, are presented. The exposure program includes ten different types of natural stone representing typical building materials used in monuments in the former Western Germany and eleven types of organosilicon water repellents. The treated material was exposed at six different sites in Germany with variable climatic and immission situations within Central-Europe. The investigation started in 1994 delivers results with respect to a suitable treatment of weathered stone and implies consequences for an efficient testing procedure.

## 1 INTRODUCTION

Effectiveness and durability of water repellent treatments are a fundamental problem in building conservation. It gave rise to start a large field exposure study with different types of natural stone and water repellent agents in 1986.<sup>[1]</sup> The aim of this study was to yield a database for a tailor made treatment of weathered stone materials used in famous monuments.

Field exposure of treated natural stone allows

- elucidation of the effects of weathering factors on the hydrophobic layer: mechanisms of degradation of specific agents can be investigated by sampling without consideration of conservatory aspects,
- an optimized scientific approach based on well-defined zero condition for each sample<sup>[2]</sup>,
- development and optimization of testing procedures.

In 1994, the exposed stone material was investigated extensively.<sup>[3]</sup> This investigation aimed at the development of an efficient testing concept to evaluate the remaining quality of the hydrophobic layer on the stone surface. Regarding the concept, two ways were followed:

First, a macroscopic method should be used to elucidate the loss in hydrophobization due to weathering.

The second way should enable to identify the hydrophobic agent on molecular basis by means of surface sensitive spectroscopic techniques.

## 2 EXPERIMENTAL SET-UP

### 2.1 FIELD EXPOSURE PROGRAM

Subjects of the field exposure campaign were ten different types of natural stone, relevant under conservatory aspects in the former Western Germany. In order to get a wide material spectrum sandstones as well as limestones and clayey materials were selected:

Baumberger sandy limestone, Ruhr sandstone, Auerkalk, Burg sandstone, Rùthener green sandstone, Anröchter Dolomit with a mainly calcareous matrix, Schleeriether sandstone, Eichenbühler sandstone, Obernkirchener sandstone, Hils sandstone.

These materials, prepared as prismens (300x300x150 mm) of freshly quarried stone, were treated with commercially available water repellents and consolidants. Eleven different types of organosilicon compounds (silanes, siloxanes and silicones) and three acrylates were used. Two samples remained untreated.

The organosilicon agents were applied by soaking the samples for one minute, the acrylates by complete soaking (IBACH technique) or by coating with a brush. After application and drying under controlled conditions, the samples were exposed at six different sites in Germany with variable climatic and immission situations: Dortmund (urban situation within an industrial area, NW-Germany), Duisburg (center of heavy industry, NW-Germany), Eifel (rural situation, highlands NW-Germany), Nürnberg (urban situation within an industrial area, center of Germany), Munich (urban situation with high traffic density), and Kempten (urban to rural situation, climatic influence of the Alpes).

An obligatory five-figure code number served for identification of the extensive sample material. The first two numbers mark the type of stone, the next two numbers mark the hydrophobic agent (untreated material is marked as "00"), the last number serves for characterization of the exposure site (reference material: Nr.7); sequence as enumerated above (see Fig. 2-6).

The corresponding environmental data were taken from official measuring stations close by. One set of samples of each stone variety was stored in the lab for comparative investigations (reference samples).

## 2.2 MACROSCOPIC TESTING PROCEDURES

The examination in 1994 was started with a selection of three varieties of stones. Due to mineralogic aspects (mineral bonding) a sandy limestone (Baumberger sandy limestone, BKS), a clayey type of stone (Schleeriether sandstone, SRS) and a silicate material (Obernkirchener sandstone, OKS) were chosen. BKS is known to undergo material corrosion very easily, SRS, due to its high content of clay minerals, is classified as susceptible for humidity and frost, whereas OKS represents a strong material in general.

The investigation were carried out mainly on exposed prismens from the sites in North Rhine Westfalia (NW-Germany).

At first, the exposed samples had to be investigated in terms of characteristic trends in damage signs depending either on the material characteristic, the exposure site or the applied hydrophobic agent.

Documentation of the sample weight was secured by weighing the material after climatization.

Water absorption measurements (diving of complete samples) as an indirect method to characterize the effectiveness of the hydrophobization were a main part of the experimental work. The all-side water contact should yield an average value for the remaining hydrophobic effect. For these tests, performed as long-term diving experiments, careful pre-work was necessary. Outbreaks of material at edge and corner positions of the prismens as well as faces of the prismens at which a thin slice of ca. 2cm had been cut off after an exposure of 2,5 years were sealed with a special colourless epoxy resin. This was necessary for securing water transport through the impregnated zone exclusively.

Because water desorption is one of the most important criteria for the weathering behaviour, long-term water diving of the samples was connected with subsequent water desorption measurements.

Selected sides of some samples were additionally investigated by the KARSTEN-method.

Penetration depths of the organosilicon agents were determined optically. In addition, contact angle measurements in the border zones of the exposed samples were carried out.

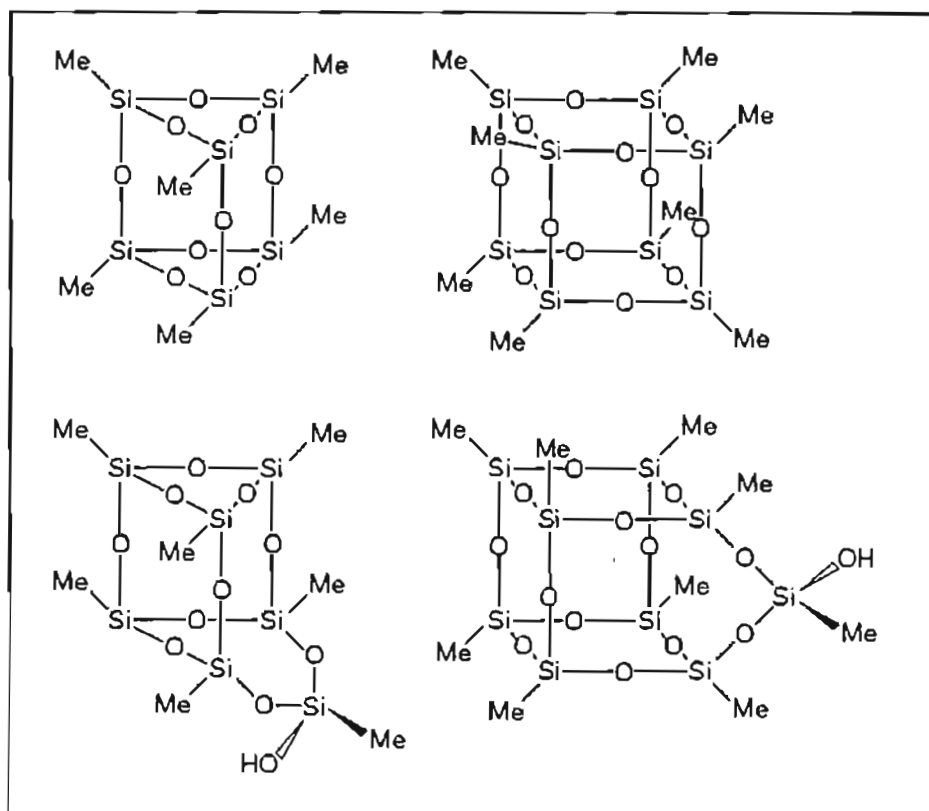
## 2.3 TOF-SIMS INVESTIGATIONS OF SILYLATED SUBSTRATES

Static SIMS is a powerful tool for analyzing polymeric surfaces, such as silylated mineral substrates. The time-of-flight method (TOF-SIMS) allows to obtain molecular information from the uppermost monolayer.<sup>[4]</sup> Large mass range, the quasi-simultaneous ion detection, and high sensitivity secure the power of this technique.

The surface structure of  $\text{CH}_3\text{Si}(\text{OEt})_3$  condensates on various substrates (e.g.  $\text{SiO}_2$ , feldspars, calcite and clay minerals) is well investigated by TOF-SIMS. Bulk properties of the polysiloxane formed can be elucidated by means of DRIFT- and  $^{29}\text{Si}$ -NMR-spectroscopy.

The fully condensed uppermost layer is characterized by silsesquioxanes  $(\text{CH}_3\text{SiO}_{1.5})_n$  ( $=T_n$ ) and homosilsesquioxanes  $(\text{CH}_3\text{SiO}_{1.5})_n\text{OSi}(\text{OH})\text{CH}_3$  ( $=T_nD$ ) where  $n$  is an even number  $\geq 4$ . These exhibit cage-like molecular structures and appear in form of typical quasi-molecular ions in the SIMS spectra  $(\text{M-CH}_3)^+$ ,  $(\text{M-OH})^+$ .<sup>[6]</sup>

FIG. 1 Structures of silsesquioxanes (upper half) and homosilsesquioxanes (lower half)



These "chemical probes" should give the opportunity to investigate the surface properties of the organosilicon compounds used in the exposure project - investigation of the freshly soaked material and the exposed stone including depth profiling of the water repellent agent. The stone material chosen for SIMS analysis was OKS. It is a suitable material because of its relatively smooth surface and its homogeneous texture.

Surface investigation of the organosilicon compounds were performed on thin stone slabs (19x10x2 mm). After cutting the slabs from cubes and drying they were soaked for 1 h with the water repellent agent prior to a reaction time of four weeks and TOF-SIMS measurements.

Samples of the exposed and reference material, were taken from that area of the prismens showing the highest degree of degradation of the protecting agent (lower edge of the prismens).

The material was investigated with the TOF-SIMS-I instrument, built at the Physics Department, University of Münster.<sup>[6]</sup>

### 3 RESULTS AND DISCUSSION

Petrographically, BKS is a biomicritic carbonate mudstone which contains, in addition to calcite, 30 vol% quartz and 10 vol% of different sheet silicates (clay minerals, among them typically glauconite). The SRS is a fine sandstone with a high content of clay minerals which causes a storing of water implying frost susceptibility (hygric swelling and frost sprinkling). The OKS is a very pure quartzitic sandstone. Thus, chemically the three varieties are very different materials. Table 1 gives an overview on porosity, pore radii maximum and the specific surface.

TABLE 1 Petrophysical data of BKS, SRS and OKS

	BKS	SRS	OKS
Porosity [vol. %]	20.6	17.8	18.3
Pore radii maximum [ $\mu\text{m}$ ]	0.3	3.7	2.2
Specific surface [ $\text{m}^2/\text{g}$ ]	10.5	7.9	0.9

#### 3.1 WATER ABSORPTION MEASUREMENTS

The prepared prismens were dried at 60°C and then climatized at 20°C to reach weight constance. Diving in big water-filled plastic buckets followed by putting the prismens on the sealed face. The water stand was kept at 5 cm above the samples.

OKS samples (code-Nr. 09) were stored for 768h (= 32d), BKS (code-Nr. 01) and SRS (code-Nr. 07) samples for 192h (= 8d), for here a water content of > 50 rel.% is achieved much faster for the BKS and SRS samples.

The figures below show the course of water uptake (expressed as relative value to the maximum water absorption of the untreated material) and desorption (expressed as the relative water content in the sample) versus time. Results for OKS samples treated with a silane mixture ( $\text{C}_3/\text{C}_8$  silanes + catalyst, code-Nr. 01, Fig. 2), a combination product (consolidant and siloxane, code-Nr. 05, Fig. 3) and a siloxane mixture ( $\text{C}_1/\text{C}_8$  siloxanes + catalyst, code-Nr. 09, Fig. 4) all exposed in Dortmund (DO, code-Nr. 1) and Duisburg (DU, code-Nr. 2) are presented.

The silane mixture (Fig. 2) shows a nearly unchanged effect in hydrophobization for the exposed prismens. After 768h, the water uptake for the exposed prismens is even lower compared to the reference sample. This could be due to further polycondensation reaction of the initial monomeric silane molecules but also - at least partially - due to pore sealing caused by biological impact and load of dust. Obviously, no reduction of the hydrophobic effect depending on the exposure site occurred. Drying for 85h, the water desorption curve of the untreated sample (Fig. 2b) slopes below that of the treated material. This typical phenomenon when comparing hydrophobized and untreated materials is due to the reduction of capillary water transport in the hydrophobization zone.

FIG. 2 Water uptake (left) and desorption (right) for the OKS samples treated with the silane mixture

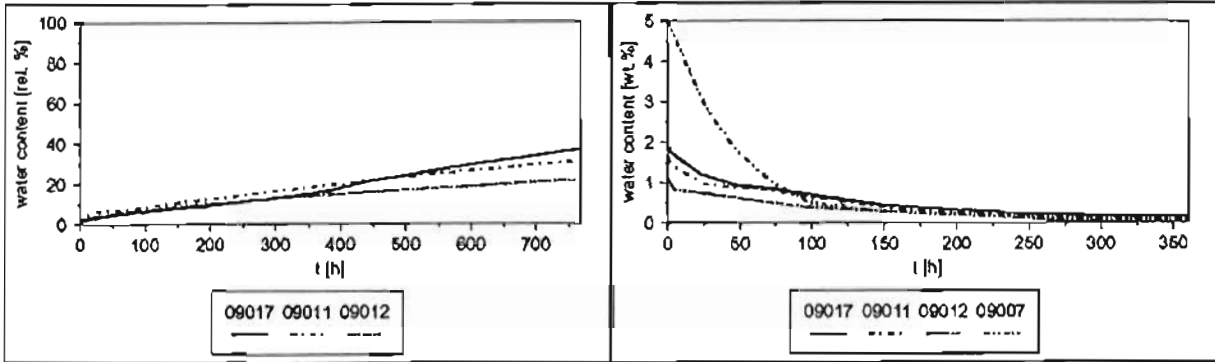


FIG. 3 Water uptake (left) and desorption (right) for the OKS samples treated with the combination product

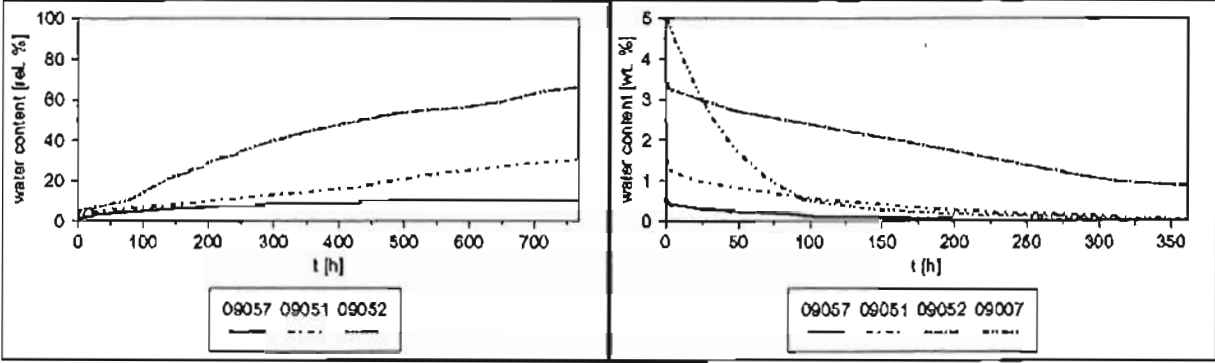
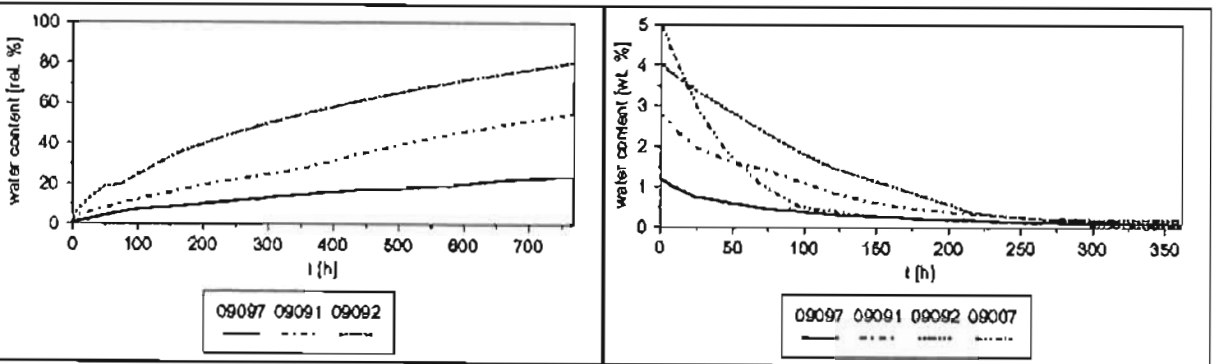


FIG. 4 Water uptake (left) and desorption (right) for the OKS samples treated with the siloxane mixture



Water absorption behaviour of the samples treated with the combination product is different (Fig. 3). The DU-sample curve shows a break through the water repellent zone and a much higher maximum value than the DO-sample (difference 37 rel%). This observation is most likely due to the formation of micro-cracks in the hydrophobized and consolidated zone during exposure.

With respect to the hygric behaviour in general, these cracks, probably caused by dryness and different properties of natural and artificial binder matrix (consolidant), lead to a loss of hydrophobization. The still remaining effect however prevents a fast drying of the high loaded DU-sample resulting in an unfavourable hygric behavior for the system.

Fig. 4 reveals a massive degradation of the applied siloxane mixture, however, much stronger for the DU-sample. The drying curves show different slopes than in the above case. In both cases, the initial water uptake is larger compared to the unweathered reference sample and reflects on the degradation of the hydrophobic layer caused by environmental influences. However, the water desorption behavior is less favourable for the consolidating mixture. As indicated in Fig.3b, the water desorption proceeds much slower to give residual water contents of about 1 wt.% even after a drying period of 360h. Under the same conditions the siloxane mixture treated DU-sample contains less than 0,3 wt.% moisture after 250h (Fig. 4b).

The hygric behaviour of the SRS samples treated with the silane mixture is given in Fig. 5. In addition to the DO- and DU-site the Eifel site (highlands, code-Nr. 3) had been taken into consideration. While the water repellent effect of the silane treated OKS samples is not reduced during exposure, loss of hydrophobization for SRS must be classified as dramatically. For this material a significant reduction of the hydrophobic effect independent of the exposure site is observed.

The material strain is most extreme at Eifel site due to relatively high temperature fluctuation and high amounts of rain, leading to frost-dew-stress to the stones.

FIG. 5 Water uptake (left) and desorption (right) for the SRS samples treated with the silane mixture

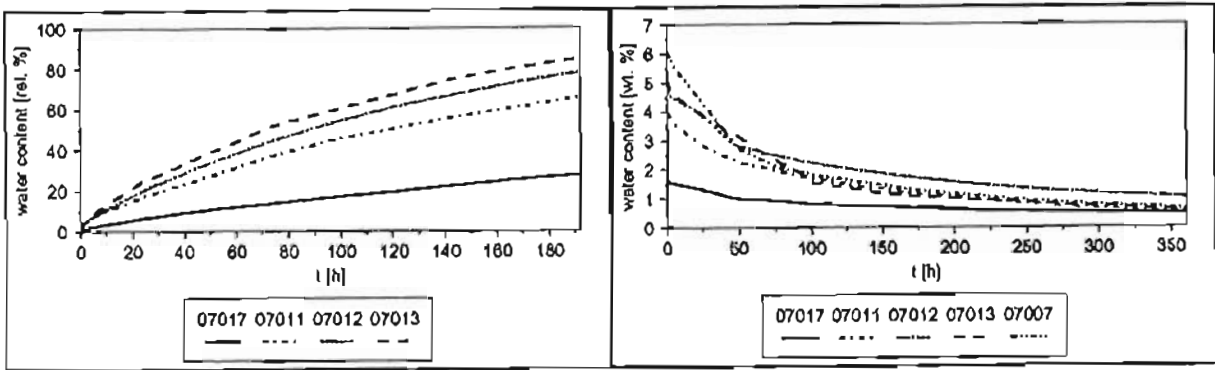


FIG. 6

Water uptake (left) and desorption (right) for the SRS samples treated with the combination product

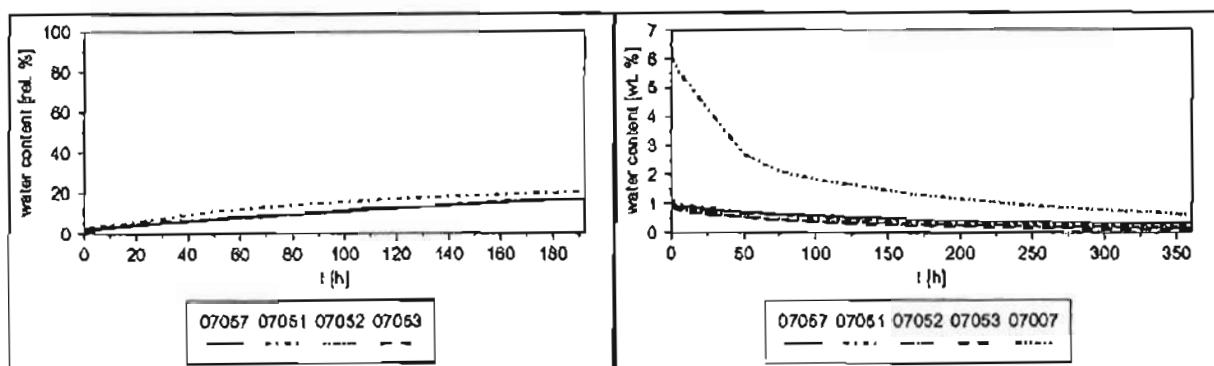


Fig. 6, presenting the results for the combination product, shows a complete turn-around in the hygric behaviour of the SRS prisms. Maximum values of water absorption are similar for the exposed and reference samples, respectively (17 to 21 rel.%). Thus, long-term hydrophobization is stable against weathering.

It is remarkable that very similar results are obtained from the investigation of the BKS samples treated with the corresponding agents. We think, that the addition of the consolidant leads to an improved bonding of the water repellent agent in the case of limy or clayey materials, whereas the effect for the silicate material is neutral.

The results imply consequences in terms of an efficient testing concept. It is obvious that quality control renders more difficult for the SRS and BKS samples than for OKS using the diving method. Locally orientated measurements, concentrated on one side of a sample (KARSTEN method) turn out to be more reliable.

Investigation with the KARSTEN-tube offered different effects on opposite sides of the prisms (side areas) probably due to climatic influences (main wind direction). This effect was very distinct for the BKS and SRS samples, less distinct for the OKS samples (long-term measurements necessary for OKS due to obvious pore sealing caused by biology and pollution).

### 3.2 TOF-SIMS MEASUREMENTS OF TREATED AND EXPOSED STONE

TOF-SIMS-studies were carried out on samples treated with the silane mixture ( $C_3/C_8$  silanes + catalyst, DU-site, low water uptake) and the siloxane mixture ( $C_1/C_8$  siloxanes + catalyst, DU-site, high water uptake), respectively.

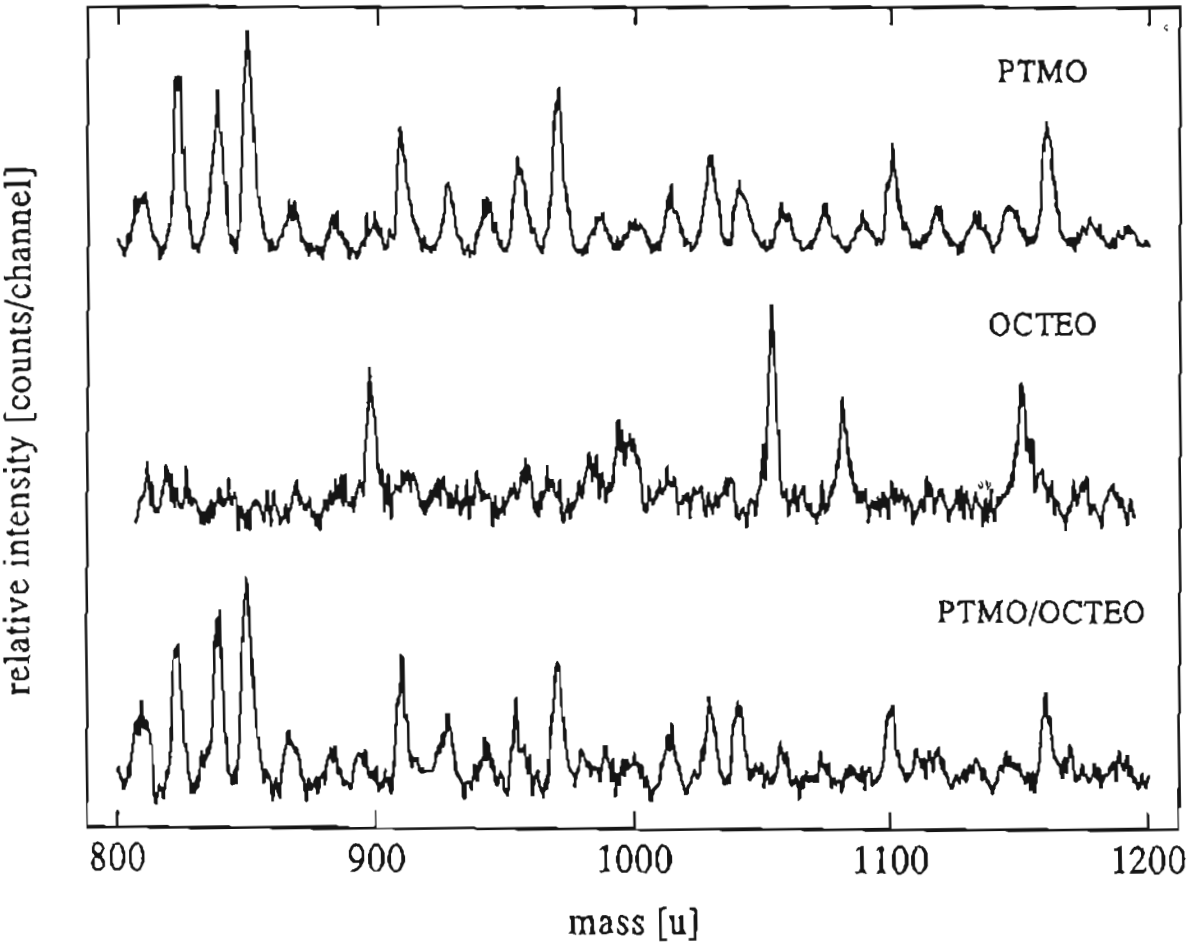
SIMS analysis of the stone material freshly soaked with the siloxane mixture showed the same peak pattern as the pure methylsilane<sup>(7)(18)</sup>, therefore suggesting the formation of silsesquioxanes and their homoderivatives. Condensation products formed by the Octyl component were not detected. The same result was obtained from further  $C_1/C_8$  siloxane mixtures.



Similarly, in the SIMS analysis of the C<sub>3</sub>/C<sub>8</sub> silane mixture only mass peaks due to fragmentation of the C<sub>3</sub> silsesquioxanes were found. These results indicate that the more reactive component (shorter alkyl chain) is concentrated in the uppermost layer. More work on this interesting aspect is in progress.

In order to get more information on the condensation process of this mixture analogous SIMS measurements of a) C<sub>3</sub> silane, b) C<sub>8</sub> silane, c) C<sub>3</sub>/C<sub>8</sub> silane mixture were performed. The mass spectra (positive mode) are shown in Fig. 7. Surprisingly, the TOF-SIMS spectrum of the C<sub>8</sub> silane reveals highly molecular condensation products, not detected in TOF-SIMS studies so far.<sup>[6]</sup> This observation could be due to catalytic effects of the stone surface which increases the degree of polycondensation.

FIG. 7 TOF-SIMS spectra of the silanes PTMO, OCTEO and PTMO/OCTEO

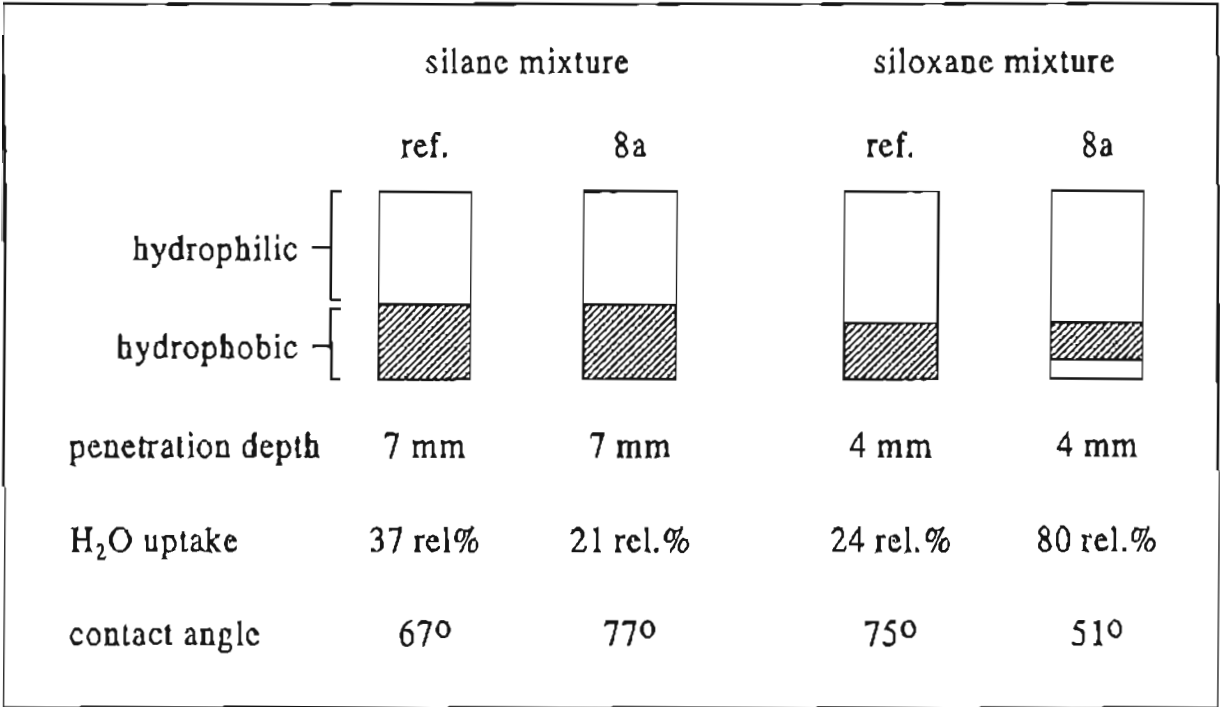


In order to evaluate the influences of weathering in the depth profile of the protective agent, samples from the most affected side of the exposed prisms were taken. Qualitatively, the penetration depth can be visualized by wetting the slabs with water; depending on the impregnation system, values between  $d = 4\text{ mm}$  (siloxane mixture) and  $d = 7\text{ mm}$  (silane mixture) are obtained.

This behaviour is generally attributed to molecular size effects of the organosilicon compounds.

However, the penetration depths measured by the wetting technique are not representative for the protective properties of the hydrophobic layer. Fig. 8 compares the penetration depths  $d$ , the water uptakes and the contact angles of the reference samples mentioned above to the corresponding exposed material.

FIG. 8 Stone slabs for depth profiling by TOF-SIMS: penetration depths  $d$ , water uptakes and contact angles of the corresponding samples



In case of the silane system, the hydrophobization, even after exposure of eight years, is improved. This interesting effect most likely results, as mentioned above, from further polycondensation reaction of the initial monomeric silane molecules. In contrast to this, water uptake and contact angle measurements on the siloxane system indicate a significant loss of hydrophobization, additionally underlined by a hydrophilic zone covering the outmost part of the sample.

Molecular information concerning this degradation process can be derived from the TOF-SIMS spectra taken directly from the stone slabs. The typical silsesquioxanes are observable only for the exposed silane system, whereas similar peak groups for the siloxane are absent.

In how far silsesquioxanes enable to monitor the water repellent properties of protective organosilicon coating has to be addressed in future studies, using larger sample numbers and higher sample rates.

## 4 ACKNOWLEDGEMENT

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