# Decay of Rhenish tuffs in Dutch monuments. Part 2: Laboratory experiments as a basis for the choice of restoration stone

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**Rhenish tuffs (Eifel, Germany), have been used as building material in the Netherlands since Roman times. They were the most important natural building stone in the Netherlands in early medieval times. In addition, tuff was used as raw material for production of trass, that served as a pozzolanic addition for mortars. Rhenish tuffs, notably Römer, Weiberner and Ettringer, show remarkable differences in decay. Ettringer tuff applied during late 19th – early 20th century restorations often shows severe deterioration, whereas, for example, most 14th century Römer in rampant arches on top of St. John's cathedral, 's Hertogenbosch, resisted weathering reasonably well, as do sculptures out of the more fine-grained Weiberner tuff on top of these. In order to obtain a better understanding of the processes underlying the decay of these tuffs and the compositional factors controlling them, a research project was started that includes both on site investigations of major monumental buildings in the Netherlands (partly) built with tuff and laboratory research. Fresh quarry samples of Römer, Ettringer and Weiberner tuff were used for selected physical characterization and testing, including a.o. hydric dilation, drying behaviour and frost resistance. One type of Römer showed a remarkably high resistance against frost. The results of the laboratory experiments on quarry samples are reported. The experiments provide a sound basis for the choice of restoration stone.**

*Key words: Natural stone, tuff, Römer, Weiberner, Ettringer, damage, laboratory research, drying behaviour, frost resistance, salt crystallization*

## 1 Introduction

The use of tuff as a building stone was very widely diffused in the Netherlands, especially until the beginning of the 13th century, when brick masonry was re-introduced. Many Romanesque churches as well as other buildings at that time were built with tuff. Tuff was further used as raw material for the production of trass, which served as a pozzolanic aggregate for mortars. During the past century, tuff has been used as a restoration stone in many monumental churches, where it replaces other decayed stone, commonly original tuff, but occasionally also other types of natural stone. Nowadays, many problems are reported with the (restoration) tuff: scaling, spalling and crack formation. Conservation authorities feel that the decay, especially of the tuff stone used in restorations during the late 19th and early 20th century, is occurring much earlier than expected. Both the tuff originally applied and the one commonly used in restorations originate from the Eifel region, Germany. A still continuing research programme was started aiming at:

- assessing types of decay to tuff stone in monumental buildings in the Netherlands
- obtaining a better insight into the processes and causes of decay
- assessing quality criteria for the choice of tuff to be used for restoration purposes

In this paper, part of the laboratory research on fresh quarry samples, aiming at assessing durability of different types of tuff, is reported.

## 2 Types of tuff used in the Netherlands

Tuff stone, used in the Netherlands, was obtained from the volcanic Eifel region, and was transported from the quarries of the Laacher See area along the Rhine and its tributaries. The following types of tuff have been used: Römer, Weiberner (including the variety designated as Hohen Ley or Hohenleie), and more recently, Ettringer (including the variety called Hasenstoppler). The fourth variety, Riedener, is rare, if used at all. These names refer to topographic provenance, rather than lithological or mineralogical characteristics. The tuffs usually exhibit low unit weight and high porosity. Below, a short introduction is given to the Römer, Weiberner and Ettringer tuff; a more elaborate description of mineralogical composition and weathering patterns may be found in Nijland et al. (2004, this issue).

### *2.1 Römer tuff*

Römer tuff was the most important type of natural stone in the Netherlands from the 10th until the early 13th century (Slinger et al. 1980). Experience by the Netherlands Department of Conservation shows original Römer tuff to be very weather resistant. The colour of the matrix varies from brown to grey. The original Römer tuff does have relatively few rock fragments. The stone currently available as dimension stone has a larger amount of basaltic inclusions, which makes it more difficult to work and carve. Examples of old Römer and Weiberner tuff (probably 14th – 15th century), still in excellent condition are present in the rampant arches of St. John's in Den Bosch (cf. Nijland et al. 2004). Fresh quarry material of Römer D and Römer ZR, used for laboratory experiments, represent -at least in their visual appearance- both types, respectively.

### *2.2 Weiberner tuff*

Weiberner tuff is a rather homogenous, fine grained tuff (Hohen Ley or Hohenleie is considered a variety of the Weiberner) and has only a small amount of lapilli. Weiberner tuff has a more homogenous appearance than Ettringer and Römer tuff. The Weiberner tuff generally lacks the yellow deteriorated pumice inclusions abundant in Ettringer tuff. Rock fragments are quite small and often greenish. Weiberner tuff has been quarried since the Middle Ages. Samples denoted as Weiberner A used in laboratory experiments comes from one of the three quarries currently operating.

*2.3 Ettringer tuff*

Ettringer tuff (including the variety Hasenstoppler) was in the Netherlands mainly applied for restoration purposes during the 20th century, with some use for new buildings in the 1920's and 1930's. The bulk does have a light brown colour with different, coloured regularly distributed rock fragments; single fragments are sized up to 1 cm. Quarrying of Ettringer tuff started in the 19th century. Ettringer tuff often shows severe weathering, after a relatively short life in service. Ettringer used in laboratory studies represents the currently available material.

## 3 Laboratory research

Laboratory research comprised characterisation of the material and weathering durability of 4 different types of tuff, viz. Römer ZR, Römer D, Ettringer ZE and Weiberner A. For Römer ZR and Ettringer ZE, density, porosity, water absorption coefficient, drying behaviour and hygric and hydric dilation were determined (Table 1, fig. 1). In addition, some data are reported for samples of Römer and Weiberner tuff, deriving from St. John's Cathedral, 's Hertogenbosch and most probably original (i.e. 14th – 15th century).

As far as weathering durability is concerned, both frost resistance and salt crystallisation resistance were determined on all 4 types of tuff.

*3.1 Sample description*

Römer tuff ZR has a brown coloured matrix. Pores are visible with the naked eye. The tuff has quite large rock fragments 0.5 - 2 cm, mainly basalt, and smaller fragments 1 - 3 mm. This tuff derives from a bottom layer, lithic concentrated zone, within an ash flow deposit. Volcanic glass in matrix and pumice has been replaced by analcime, chabazite and phillipsite; minor illite was also detected by XRD.

Römer tuff D is different, as it lacks the large basalt fragments, contains quite some pumice and has more abundant macropores. The matrix contains analcime and chabazite; phillipsite, common in most Römer tuff, is absent.

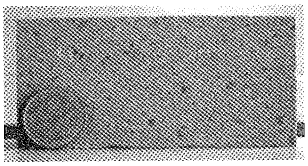
Ettringer tuff ZE does have a yellowish ground mass with regularly distributed inclusions. The size of single inclusions can be up to 1 cm, but most of them are smaller than 5 mm. The brown-yellow ground mass is harder than the yellow part. This soft part is probably altered pumice. The tuff also has yellow-orange inclusions with white dots, which indicates that most probably the variety Hasenstoppler is dealt with. Volcanic glass in matrix and pumice has been replaced by analcime, chabazite and phillipsite; minor illite was also detected by XRD.
Weiberner tuff A is fine grained; fragments of pumice and basalt (size up to few mm's) are present.

Matrix of the Weiberner consists of analcime, with accessory calcite, clinochlore and gypsum. Volcanic glass in the matrix and pumice has been replaced by analcime; chabazite and phillipsite common in most Weiberner tuff, are absent.

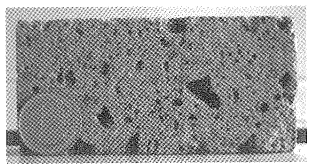
### *3.2 Porosity and density*

Apparent density and porosity were determined conform RILEM CPC 11.3 (1979) for all samples. Water absorption coefficient was determined for the four quarry materials, hygric (RH between 35 and 60%) and hydric (immersion in water) dilation and drying behaviour were determined for Römer ZR and Ettringer ZE. Properties are reported in Table 1.

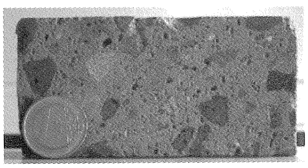
Remarkable are the properties of the restoration stone Römer D, considered for St. John's cathedral in comparison with the properties of the original Römer from that building as well as literature data (Grimm 1990): Römer D shows very low density and a very high porosity. Hygric and hydric dilation of tuff are very high, compared with literature data for sandstone (Snethlage & Wendler 1997).



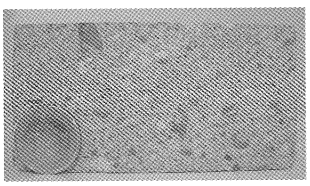
*Weiberner A*



*Römer D*



*Römer ZR*



*Ettringer ZE*

*Fig. 1. Overview of the different types of tuff.*

*Table 1. Properties different types of tuff (dimensions quarry specimens 5 x 10 x 5 cm).*

| Type of tuff | Apparent density $e_{ap}$ = [g/ cm$^3$] | Porosity P = [vol.%] | Water absorption coefficient [kg/m$^2$s$^{0.5}$] | Hygric dilation [μm/m] 20°C and 35-60% RH | Hydric dilation [μm/m] 20°C and 35% RH – immersion in water |
|---|---|---|---|---|---|
| Römer ZR | 1.55 | 41.5 | 0.17 | 235 | 740 |
| Ettringer ZE | 1.53 | 42.3 | 0.05 | 280 | 730 |
| Weiberner A | 1.32 | 47.4 | 0.26 | - | - |
| Römer D | 1.13 | 53.9 | 0.32 | - | - |
| Römer St. John's | 1.57 | 37.7 | - | - | - |
| Weiberner St. John's | 1.34 | 45.9 | - | - | - |

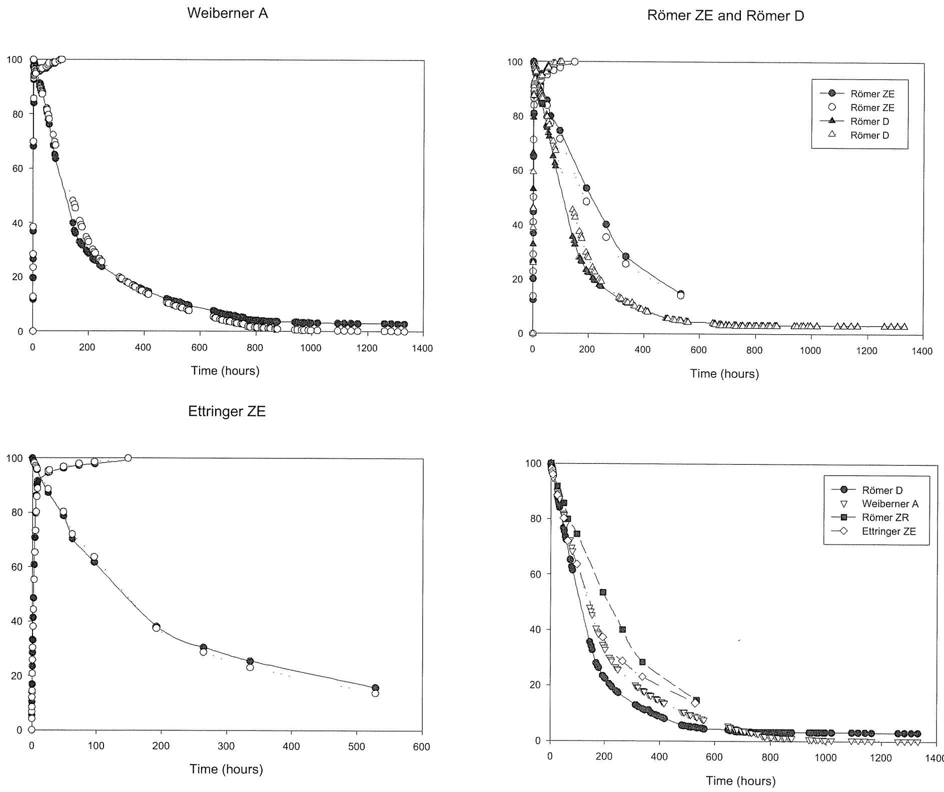



*Fig. 2. Drying behaviour of 4 types of (quarry) tuff. Conditions 20 °C / 50 % RH. In the graphs for the single tuff types, water absorption is also shown, on the same time axis: Drying clearly takes a very long time. Difference in drying rate for stone with the same (topographical) provenance may be considerable.*

### 3.3 *Drying behaviour*

Drying behaviour was determined for all four different types of tuff. Specimens (size 5 x 5 x 10 cm) were sealed on four sides, in order to ensure drying in one direction (via a 5 x 10 cm surface). Free water absorption during 72 h was allowed, although generally after 24 h, constant weight was reached. Drying conditions were 20 °C / 50 % RH, without forced air movement. Drying is shown in Fig. 2, where the free water absorption after 72 h is defined as 100 %.

Drying is fastest for Römer D, but slowest for Römer ZR. Weiberner A and Ettringer ZE are in between. Note for example the differences at 200 h. Slow drying may indicate a higher risk of frost damage. Topographical provenance clearly cannot be considered a guarantee for a certain quality and variation within a single tuff deposit may be considerable.

### 3.4 *Mercury intrusion porosimetry (MIP)*

Mercury intrusion porosimetry was performed on Römer ZR, Römer D, Ettringer ZE, and Weiberner A. The pore size distributions are given in Fig. 3. Pore size distributions do not agree with literature data. The amount of fine pores, smaller than 0.1 μm, is much less than according to Grimm (1990). This difference is especially evident for both Weiberner and Römer.

Further in this study, except for Weiberner A, the difference in total porosity as determined according to RILEM CPC 11.3 (1979, Table 1), is considerable. The most remarkable difference exists for Römer D (33.7 versus 53.9 vol.%). This can be explained by the ratio of macropores to capillary pores, which is very high for the Römer D and very low for Weiberner A, as is also shown in the microphotographs in Fig. 4. The macropores are taken into account by the RILEM method, but not by MIP.

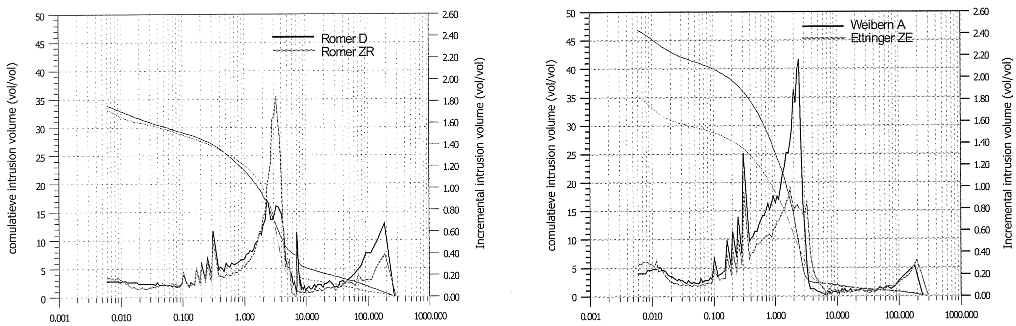



*Fig. 3. Pore size distribution for four types of tuff stone. Note the relatively high amount of small pores for Weiberner A and Ettringer ZR (increase of the cumulative curve in the left part of the graph). This could be an indication for a lower frost resistance.*

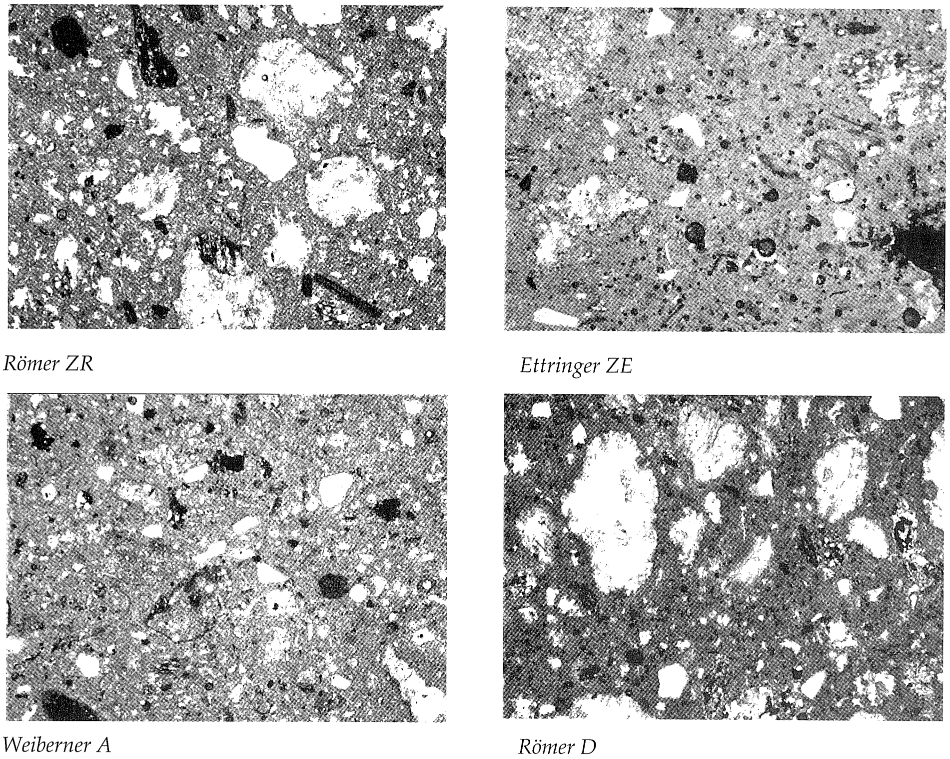



*Fig. 4. Micrographs, showing the microstructure of 4 different types of tuff. Both Römer tuffs show a high amount of macropores (view 5.4 x 3.5 mm).*

### *3.5 Frost resistance*

The frost resistance was determined according to the Dutch Standard NEN 2872 (1989). Testing the frost resistance, according to NEN 2872, is characterized by unidirectional freezing. 24 freeze-thaw cycles are performed, the freezing phase lasting 16 h, the thawing phase lasting 8 h. The temperature during freezing is alternately –5 °C (even cycles) and –15 °C (uneven cycles). Thawing is performed by submersion of the specimens in water of 20 °C.

In order to gain as much as possible information on the to be expected performance of tuff under different practice situations, for the testing pre-wetting under 0.5, 0.75 and full vacuum were chosen. These three different pre-conditionings represent different situations in practice.
Results of the frost test are given in Table 2. Fig. 5 gives an overview of the specimens after the test. Typical frost damage is shown in fig. 5 for Weiberner A. Remarkably, specimens of Römer D resisted even the most severe condition.

*Table 2. Results frost – thaw resistance test.*

| Pre-conditioning with water | | 100% vacuum | 75% vacuum | 50% vacuum |
|---|---|---|---|---|
| Weiberner A | 1 | Strong exfoliation | No damage | No damage |
| | 2 | Strong exfoliation | No damage | No damage |
| Römer D | 1 | No damage | No damage | No damage |
| | 2 | No damage | No damage | No damage |

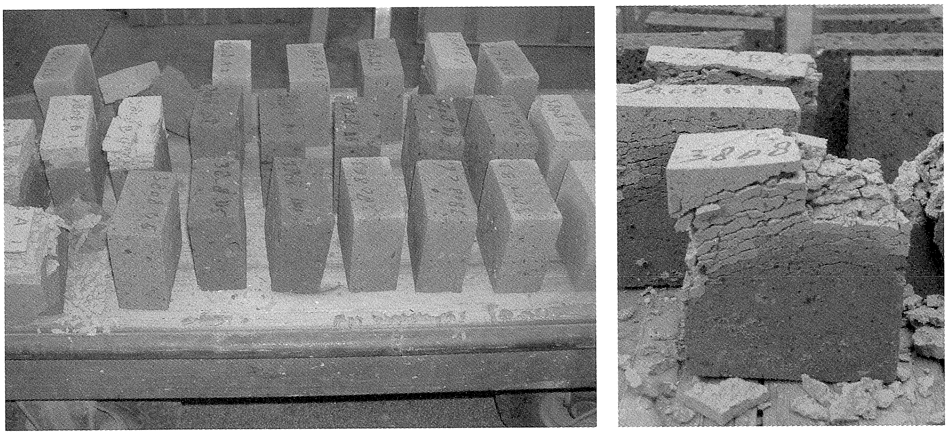


*Fig. 5. Left: overview specimens after frost - thaw test. Darker (redish) specimens in the middle are Römer D tuff, lighter coloured (grayish) are Weiberner A. Right: example of Weiberner A, showing severe frost damage.*

### *3.6 Resistance to salt crystallization*

Römer ZR and Ettringer ZE, Römer D and Weiberner A were subjected to a salt crystallization test using Na2SO4. Testing was preformed according to internal TNO procedures, which is briefly described below. Specimens of 5 x 5 x 10 cm are sealed on four sides, in order to allow water absorption and evaporation in one direction. Dry weight and capillary moisture content (quantity of absorbed water at the moment that the moisture front reaches the upper surface) are determined. At the start of the test, the specimens will have to absorb a salt solution, with a quantity of 90 % of the capillary moisture content. Salt concentration is chosen on the basis of experience; for Na2SO4, an amount of 1.2 % of the dry weight of the specimen was added to the solution.

Specimens are placed in a container, leaving the bottom of the specimen free from the bottom of the container. After conditioning the specimens at 20 °C, 50 % RH, the salt solution is added. The upper side of the container is sealed, in order to prevent evaporation of the salt solution. After absorption of the solution, the effective amount of absorbed solution is determined. Specimens are placed in a climate room with constant ambient conditions of 20 °C, 50 % RH, where drying takes place. After reaching constant weight, distilled water is added from the bottom side in a quantity of 90 % of the capillary moisture content and a second evaporation and crystallization cycle is started.

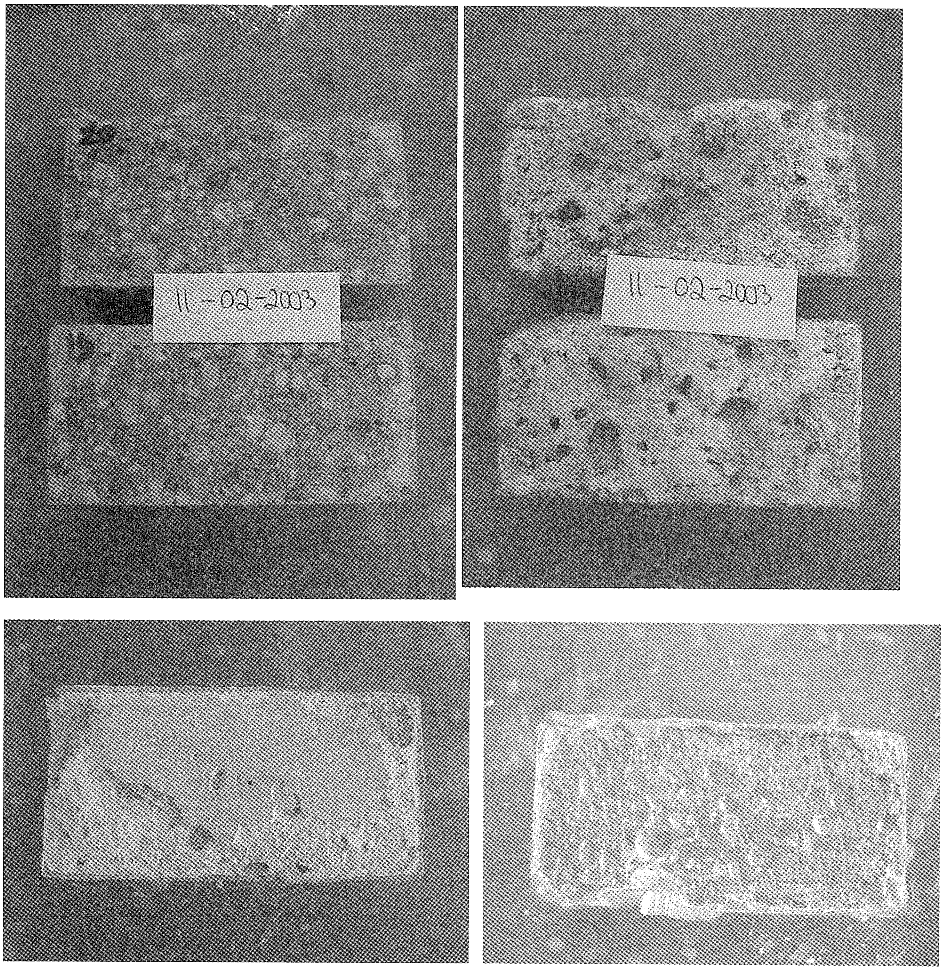



*Fig. 6. Surface of Ettringer ZE (top left), Römer ZR (top right), Weiberner A (bottom left) and Römer D (bottom right) after the 2nd cycle of the crystallization test using $Na_2SO_4$.*

For the Ettringer, only a small amount of tiny crystals was found near the margin of the specimen (Fig. 6). No loss of cohesion was observed.

For the Römer ZR, a thin surface layer was pushed up and clear efflorescence (of 1 – 3 mm height) had developed already after the first cycle; this process was repeated in the second cycle: A thin surface layer of 1-2 mm was pushed up (Fig. 6). In practice, thenardite efflorescence is quite common, especially on Römer and Weiberner tuff, and similar damage was observed (Nijland et al. 2004, this issue). It may be suggested that $Na_2SO_4$ is derived from (partial) dissolution or leaching of analcime from the stone itself, although that may be a quite slow process.

For Weiberner A, scaling occurred; a surface layer with a thickness of 1 mm, was completely lifted (Fig. 6). The material surface underneath this layer was remarkably smooth.

On Römer D, efflorescence occurred; the surface underneath was looking slightly weathered, (Fig. 6); in the matrix, however, no loss of cohesion had occurred.

## 4 Discussion and conclusions

In previous research, it was concluded that weathering forms of tuff developed under laboratory frost - thaw experiments are similar to those observed at buildings, all tuffs being susceptible to frost - thaw stress. Freeze / thaw resistance was found to decrease in the order Römer > Weiberner > Ettringer (Fitzner 1994). According to this author, the observed sequence is the result of various pore radii distributions of the three types of tuff and their related water absorption and evaporation (drying) behaviour. This is not confirmed by the current experiments. It is clear that the quality of tuff cannot just be attributed to the topographical provenance of the stone, and significant differences exists between different tuffs all denominated as Römer, or Weiberner, or Ettringer. The internal variation that may arise from both volcanic processes and subsequent diagenesis, is considerable. Within one section in one quarry, zeolitization may be quite variable at different levels, obviously leading to a different pore structure of the tuffs (e.g. Bernhard & Barth-Wirsching 2002). The choice on the basis of the provenance alone is evidently not reliable and very risky. Quality indicators based on simple material properties like water absorption coefficient or total porosity cannot be given yet.

The four investigated types of tuff show a different crystallization behaviour and resistance. Ettringer ZE and Römer D clearly suffer less from $Na_2SO_4$ crystallization damage than Weiberner A and Römer ZR. This may be related to differences in pore size distribution that are also reflected in a different drying behaviour (Fig. 2). Nevertheless, crystallization behaviour cannot be completely understood on the basis of the presently available material properties. Considering drying behaviour, the faster drying tuffs, i.e. Römer D and Weiberner A, are expected to show no or less efflorescence, whereas the slower drying tuffs Ettringer ZE and Römer ZR are expected to show a clear efflorescence. In reality, for example, Weiberner A indeed showed cryptoflorescence, eventually leading to damage, but Römer D (the fastest drying material in the test) showed a clear efflorescence. More research on the transport process during drying is clearly necessary. The use of NMR in the future is expected to give valuable additional information (Pel et al. 2003).

Hydric dilation of tuff seems extreme and is expected to be partially responsible for damage observed in practice (exfoliation, spalling). Hydric dilation could be important as part of the explanation of typical damage phenomena like spalling and scaling (together with chemical and mineralogical factors and physical mechanisms like frost - thaw cycles and or crystallization cycles).

For the time being, testing of the real damage mechanism (i.e. for example frost – thaw cycles) appears to be a more realistic approach for the prediction of durability and thus as a basis for the choice of restoration stone than assessing single material characteristics.

It is interesting to note that Römer D shows a very good frost – thaw resistance. This tuff showed to be frost resistant even under the most extreme conditions, even though its apparent density and total porosity do not resemble those of classical (durable) Römer tuff (Table 1).

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