Decay of Rhenish tuff in Dutch monuments. Part 1: Use, composition and weathering

Timo G. Nijland[1], Sonja Brendle[1], Rob P.J. van Hees[1,2] & Geert-Jan L.M. de Haas[3]

[1] TNO Building & Construction Research, Delft, The Netherlands
[2] Delft University of Technology, Faculty of Architecture, Delft, The Netherlands
[3] Institutt for Geologi & Bergteknikk, NTNU, Trondheim, Norway; current address: Nuclear Research Group, Petten, The Netherlands

Rhenish tuffs from the volcanic Eifel region, Germany, have widely been used as building stone in the Netherlands. Different kinds of tuff (Römer, Weiberner, Ettringer, Riedener) show different kinds of decay, and also within each group, remarkable differences in weathering behaviour occur. In the present study, a short introduction is given to the historic use of tuff in the Netherlands, and a survey of weathering patterns is presented. Fresh quarry samples and material removed from several Dutch monuments have been studied by polarization-and-fluorescence microscopy (PFM) and X-ray diffraction analysis (XRD). So far, no relationship between mineral assemblages and durability could be established.

Key words: Natural stone, tuff, Römer, Ettringer, Hasenstopler, Weiberner, Hohenleie, weathering patterns, damage, mineralogy, zeolites, analcime, chabazite, philipsite, merlinoite

1 Introduction

Volcanic tuffs are widely distributed in the world and are either used as dimension stones or as a pozzolanic addition to cement. Zeolitic tuff has been used as building material in, among other countries, Bulgaria, Cuba, Germany, Greece, Italy, Mexico, Romania and the United States. Tuff from the German Eifel area, so-called Rhenish tuff, has been used as dimension stone in the Netherlands since Roman times.

Reconstruction of the 11,900 BC eruption of the Laacher See volcano in the Eifel region, Germany shows that material from this eruption was deposited over large parts of Europe, notably towards the northeast and south (Van den Bogaard & Schmincke 1985). Since, a considerable amount of material has been transported to the west as a building stone, not only tuff derived from this eruption, but also tuff deposited by older volcanos. Together with Drachenfels trachyte from the Siebengebirge north of the Eifel, Rhenish tuff has been used and re-used in the Netherlands since Roman times. Though original building time tuff is still present in several monuments, tuff is often considered as a building stone of questionable durability. Especially tuff used for restoration purposes during the early 20th century shows nowadays severe decay. In order to understand decay processes and compositional / microstructural characteristics of different types of tuff determining durability, a research project on Rhenish tuffs was started by TNO Building and Construction Research. Two papers in this special issue report the first results of this project. Here, results of a literature, microscopic (PFM) and X-ray diffraction (XRD) studies and site survey are reported. Laboratory investigations are reported by Van Hees et al. (2004a).

2 Use of tuff in the Netherlands

Use of tuff as a building stone in the Netherlands dates back to Roman times. The same kind of tuff, widely known as Römer tuff, was used again in the period of romanesque architecture, from the 10th til the early 13th century. It was the most common type of natural stone used in the Netherlands at that time (Slinger et al. 1980). The towns of Deventer and Utrecht were major trading centres in tuff. Römer tuff has been used only scarcely in the eastern (Twenthe) and southeastern (Limburg) parts of the country, but has widely been applied in other parts, like the romanesque churches of the northern province of Groningen (De Olde 2002, 2003) and the western provinces of Holland (Den Hartog 2002), as well as in the early 11th century churches built in Utrecht by Bishop Berend. Minor amounts of the latter tuff still survive in these churches (Fig. 1). Rhenish tuffs may also be found in romanesque or early gothian style churches in the Belgian province of Limburg, often as recycled Roman material (Dreesen et al. 2002), whereas it has also been applied in some western Belgian cities that could be reached over the river Zwin (Brugge, Damme; Slinger et al. 1980) and some churches in Denmark.

Fig. 1. Surving 11th century Römer tuff on the north façade of John's church, Utrecht.

Fig. 2. Römer and Weiberner tuff on one of the rampant arches of St. John's catherdral, s Hertogenbosch, probably dating back to the 14th – 15th century.

From the early 13th century onwards, Römer tuff was pushed out of the market by fired clay brick and other types of natural stone, like Bentheim sandstone. However, in the 15th and early 16th century, people started using tuff again, especially the Hohenleie (or Hohen Ley) tuff, a variety of the Weiberner tuff. This type of tuff has, among others, been applied in the Our Lady church, Zwolle, the Grotekerkstoren, Dordrecht, and several other church towers (Slinger et al. 1980). Weiberner tuff s.sr. has been used in the same period. Original Weiberner tuff is, together with Hohen Ley and Römer tuffs, still present in the rampant arches of St. John's cathedral, 's Hertogenbosch (Fig. 2).

During the late Middle Ages, Römer tuff from older buildings was frequently reused and applied as cladding of clay brick walls. During restoration works, but also for new buildings, during the end of the 19th and the first half of the 20th century, Weiberner (Fig. 3) and especially Ettringer (including the Hasenstoppler variety) have frequently been used. Ettringer and/or Hasenstoppler have, among others, been applied during restorations of the Grote Kerk, Dordrecht (1920's as well as 1953 – 1966), the St. Steven's church, Nijmegen, whose restoration was completed in 1969, the rebuilding of the Eusebius church, Arnhem during the period 1959 – 1964 (Fig. 4) and the Bovenkerk in Kampen (1958 – 1972) (Slinger et al. 1980). Experiences with Ettringer/Hasenstoppler tuff used for restoration purposes during the late 19th – early 20th century are bad. A siginificant amount of the applied materials nowadays shows severe decay, and has to be replaced again. In contrast, Ettringer tuff applied in newly constructed buildings during the same period performed well. The town hall of Rotterdam, built in 1916, has a tower with a façade of Ettringer tuff (Fig. 5).

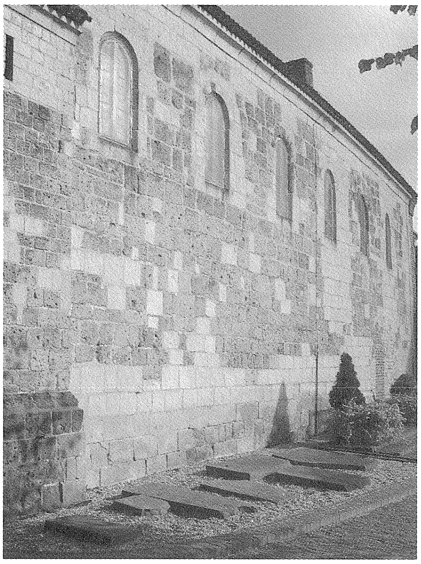


Fig. 3. Mixture of recycled Römer tuff andWeiberner tuff in the Old Church, Oosterbeek, rebuilt after serving as a Britishbridgehead in the late 2nd World War.

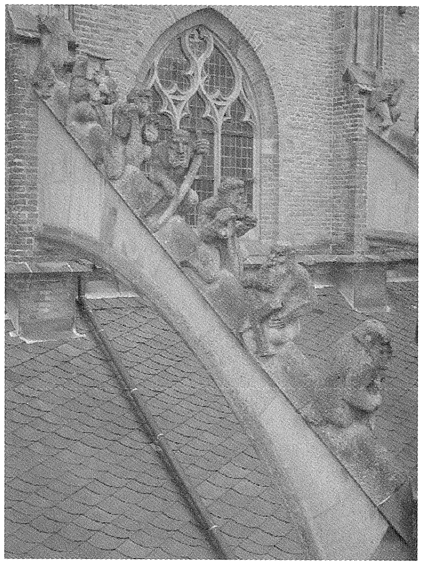
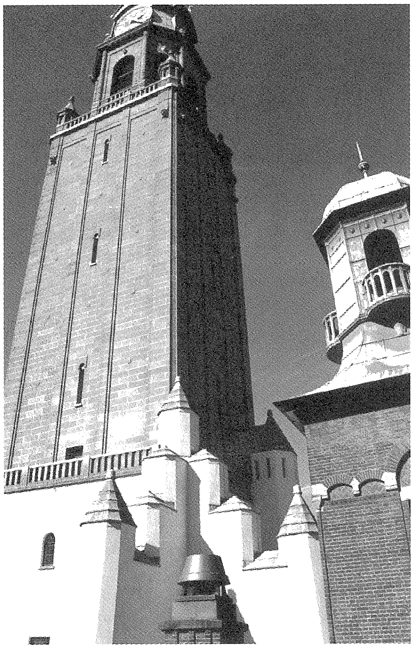


Fig. 4. Sculptures in Ettringer tuff on one of the rampant arches of Eusebius' church, Arnhem, reconstructed in the period 1959-1964. The sculptures have recently been conserved by impregnation by acrylic resin.

During recent restoration and cleaning, only subordinate amounts had to be replaced.
Other examples of application of Ettringer tuff in the construction of new buildings during this period are the former library of Delft University of Technology, Delft, and the KAS Bank in Amsterdam, completed in 1932.

Information on the use of Riedener tuff in the Netherlands is scarce. It has possibly been applied in small amounts at the St. Walburg church, Zutphen and Peter's church, Leiden.



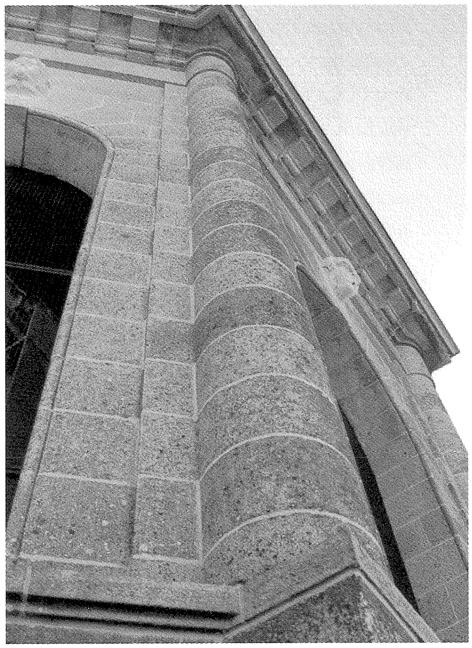


Fig. 5. Overview (left) and detail (right) of the tower of the 1916 town hall of Rotterdam with façade made with Ettringer tuff.

3 Petrographic and physical characteristics of types of tuff

The names used for different types of Rhenish tuffs refer to their topographical provenance, rather than petrographic characteristics. Nevertheless, the different tuffs may be distinguished petrographically, though they show considerable variation. Römer tuff has a trachytic composition and is derived from the lithified ash flows and glow avalances of the 11,900 BC eruption of the Laacher See volcano (e.g. Van den Bogaard & Schmincke 1984, 1985). This type of tuff has variously been termed *duifsteen, trastuf, lapillituf* or *Andernach tuf* in older Dutch literature. In older literature, the Weiberner, Ettringer and Riedener tuff are grouped together as *selbergitic tuff* (Frenchen 1971). These tuffs have leucitic compositions, and are lithified ashes erupted from the Riedener volcano complex (Viereck 1984, Schmincke 1988).

The tuffs have some features in common: They are macroporous rocks, with pumice and rock fragments occurring in a fine grained matrix that was originally composed of volcanic glass. Typical igneous minerals and xenocrysts are sanidine, other feldspars, clinopyroxene (Ti-augite, diopside), olivine, amphibole, biotite, ore minerals and carbonate, in addition to leucite in the Ettringer and Weiberner tuff (Fitzner 1994, this study). In all tuffs, volcanic glass has been replaced by zeolites, notably analcime, chabazite and phillipsite (Sersale & Aiello 1964, Fitzner 1994), though zeolitization may be quite variable at quarry scale (Bernard & Barth-Wirsching 2002).

3.1 Römer tuff

Macroscopically, the colour of the matrix varies from brown to grey, often with a rose huge. Generally, original Römer tuff contains only a small amount of rock fragments other than pumice. The dimension stone currently available for restoration purposes contains a larger amount of basaltic inclusions, which makes it more difficult to work and carve. This stone is apparently derived from the bottom parts of the ash flows / glow avalanches.

Original, non-weathered Römer tuff, applied to St. John's cathedral, 's Hertogenbosch during the building period (14^{th} – 15^{th} century) is a macroporous stone with a limited amount of rock fragments. Macroporosity in part arises from the selective weathering of pumice fragments (Fig. 6). Typically, the matrix makes up about 50 vol.% (Fitzner 1994). In currently available material akin to original Römer tuff, well developed zeolites occur in both the matrix and pumice fragments (Fig. 7). The pumice fragments have usually a dense rim of zeolites (Fig. 8), much denser than Ettringer tuff. According to Fitzner (1994), analcime and chabazite are dominant zeolites in the Römer tuff. Present studies on fresh quarry material (Table 1) and material from Dutch monuments (Table 2) show that assemblages of analcime + chabazite as well as analcime + chabazite + phillipsite occur, the latter being most common. In weathered samples, also the assemblages analcime, analcime + phillipsite, and phillipsite occur (Table 2); though this may be due to weathering, it is most likely an original feature, as chabazite is more resistant to acid solutions than phillipsite (De'Gennaro et al. 1984).

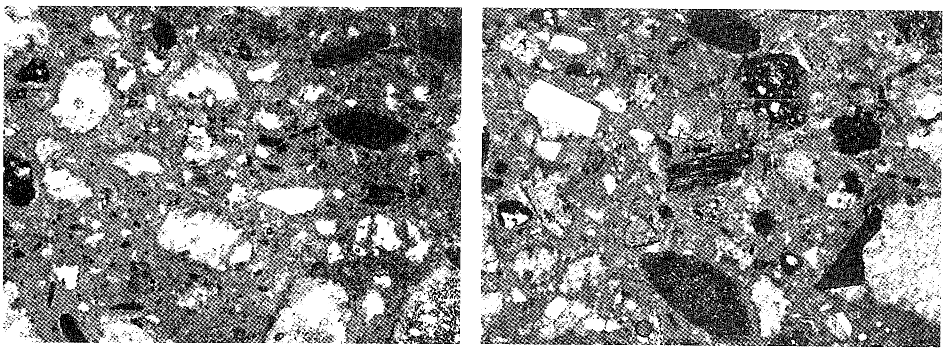


Fig. 6. Microphotographs with an overview of the microstructure of building time Römer from St. John's cathedral, 's Hertogenbosch (sample TUF 68; left) and an akin type of currently available Römer (sample TUF 72; right). View 5.4 x 3.5 mm.

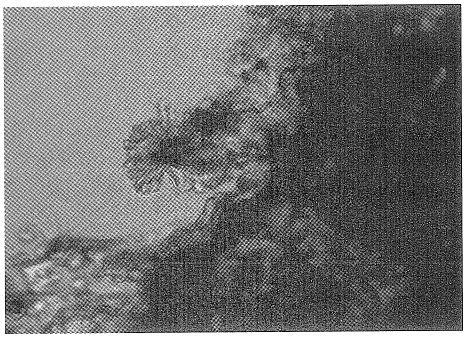


Fig. 7. Microphotograph showing well developed zeolites in the matrix of fresh quarry material of Römer tuff (sample TUF 72, view 0.7 x0.45 mm).

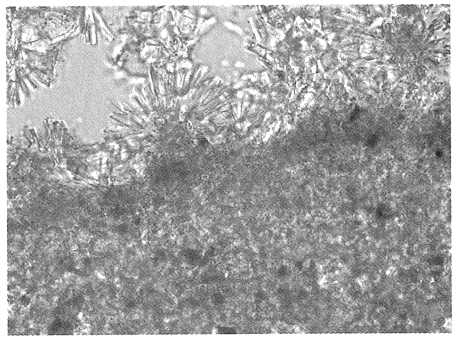


Fig. 8. Microphotograph showing detail of the rim of a zeolitized pumice fragment in original Römer tuff from an unknown monument (sample TUF 46, view 0.35 x 0.22 mm).

3.2 *Weiberner and Hohenleie tuff*

Macroscopically, Weiberner tuff is a rather homogenous, fine grained tuff. The tuff used in the Netherlands named Hohenleie, Hohen Ley or Hochlei, is considered a variety of the Weiberner which has only a small amount of lapilli (Slinger et al. 1980). Weiberner tuff has a more homogenous appearance than the Ettringer and Römer tuffs. The Weiberner tuff generally lacks the yellow deteriorated pumice inclusions abundant in Ettringer tuff. Rock fragments are quite small and often greenish, though levels with abundant, larger (10 – 15 mm) fragments are exposed in the three quarries nowadays operating in Weiberner tuff, and have also been applied in the past, as do fine grained varieties with a few, isolated, 3 – 6 cm sized pumice fragments.

Though supposed to be a leucitic tuff, leucite was not encountered by XRD in any of the investigated samples (Tables 1, 2). This may be because it occurs in amounts below the detection limit; Microscopic investigation shows that it has commonly been replaced by analcime (Fig. 9). Weiberner tuff has a matrix with considerably smaller macropores than Römer tuff (Fig. 10).

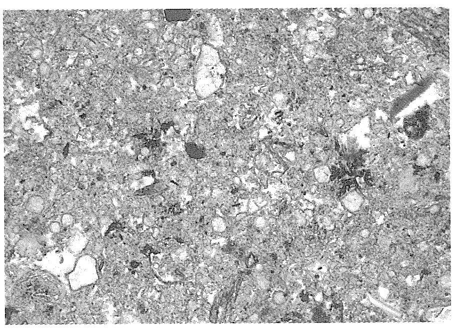


Fig. 9. Microphotograph showing numerous pseudomorphs of analcime after leucite in Weiberner tuff.

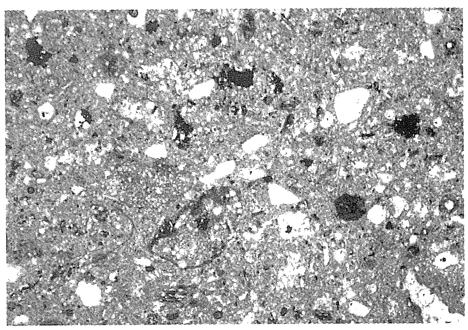


Fig. 10. Microphotograph with an overview of the microstructure of Weiberner tuff (sample TUF 69, with of view 5.4 x 3.5 mm).

Table 1. Mineralogy of fresh quarry material as determined by XRD. For mineral abbreviations, see appendix.

Type of tuff	Sample	Igneous minerals/ xenocrysts	Matrix	Other secondary
Ettringer, hard part of matrix	TUF 10	Qtz, San	Anc, Cha, Phi	Ill, Cc
Ettringer, soft part of matrix	TUF 11	San	Anc, Phi	Ill
Römer, type 1	TUF 12	Qtz, San, Aug	Anc, Cha, Phi	Ill, Gy
Römer, type 2	TUF 72	Qtz, San, Ms	Anc, Cha	Cch
Weiberner, quarry 1	TUF 69	San, Ms	Anc,	Gis
Weiberner, quarry 2	TUF 70	San, Ms	Anc	Gis, Ill, Cc
Weiberner, quarry 3	TUF 71	San, Or, Ms	Anc	

Table 2. Mineralogy of weathered samples from Dutch monuments as determined by XRD. For mineral abbreviations, see appendix.

Type of tuff	Weathering	Monument	Sample	Igneous minerals, xenocrysts	Matrix	Secondary phases	Other
Ettringer	gypsum crust	St. John's cathedral, 's Hertogenbosch	TUF 6		Anc	Ill	Gy
Ettringer	gypsum crust	Eusebius church, Arnhem	TUF 8	San, Aug	Phi	Ill	Gy
Ettringer	weathered matrix	St. John's cathedral, 's Hertogenbosch	TUF 7	Qtz, San, Aug	Cha, Phi, Mer	Ill	Cc
Ettringer	weathered matrix	Eusebius church, Arnhem	TUF 9	Qtz, San, Aug, Phl	Phi, Mer	Ill	
Ettringer	scale		TUF 32	Qtz, Mcl, Aug	Anc, Phi		Gy
Römer	grey deposit	Old Church, Delft	TUF 22	Qtz, Mcl	Anc, Cha		Gy
Römer	grey deposit	village church, Anjum	TUF 23	Qtz	Anc		Gy
Römer	grey deposit	Lebuïnus church, Deventer	TUF 29	Qtz, Ab, Aug	Anc		Gy
Römer	grey crust	Burcht, Leiden	TUF 18	Qtz	Anc, Cha, Phi	Ill	Gy, am
Römer	matrix below grey crust	Burcht, Leiden	TUF 19	Qtz	Anc, Cha, Phi	Ill	Gy
Römer	matrix showing dissolution	John's church, Utrecht	TUF 35	Qtz, Mcl, Aug	Anc, Phi		Gy
Römer	part with loss of matrix	Lebuïnus church, Deventer	TUF 28	Qtz, Ol	Phi		Cc
Römer	powdery matrix	Proosdij, Deventer	TUF 25	Qtz	Anc, Cha, Phi		Cc
Römer	powdery matrix	Lebuïnus church, Deventer	TUF 26	Qtz, Ol, Aug	Anc, Phi		Gy
Römer	powdery matrix	St. Walburg church, Zutphen	TUF 33	Qtz	Anc, Cha, Phi		Gy
Römer	weathered matrix	Old Church, Delft	TUF 21	Qtz, San	Anc, Cha, Phi	Ill	

Table 2. (Continued)

Type of tuff	Weathering	Monument	Sample	Igneous minerals, xenocrysts	Matrix	Secondary phases	Other
Römer	weathered matrix below efflor.	John's church, Utrecht	TUF 36	Qtz, Aug	Anc, Cha, Phi		Gy
Römer	detached layer	Broederenkerk, Deventer	TUF 30	Qtz, Aug	Anc, Cha, Phi		Gy
Römer	matrix below detached layer	Broederenkerk, Deventer	TUF 31	Qtz, Ol, Aug	Anc, Phi		Gy
Römer	matrix	unknown	TUF 46	Qtz, San	Anc, Cha		
Römer	scale	Old Church, Oosterbeek	TUF 2	Qtz, Ol, Aug	Anc, Cha, Phi	Ill	Cc
Römer	spalling	St. Walburg church, Zutphen	TUF 34	Qtz, Aug	Anc, Cha, Phi		
Römer	spalling	Nicolas' church, Utrecht	TUF 40	Qtz, Mcl, Aug	Anc, Phi		Gy
Römer	in shower area	Peter's church, Utrecht	TUF 37	Qtz, San, Aug	Anc, Cha, Phi		
Römer	porous, above shower area	Peter's church, Utrecht	TUF 38	Qtz, Mcl, Aug	Anc, Cha, Phi		Gy
Römer	porous, above shower area	Pandhof, Utrecht	TUF 39	Qtz, Aug	Anc, Cha, Phi		Gy
Römer	porous, above shower area	Nicolas' church, Utrecht	TUF 41	Qtz, Aug	Anc, Cha, Phi		Gy
Weiberner?	thin crust containing fungi	Old Church, Oosterbeek	TUF 1	San, Ol, Aug	Anc, Cha, Phi	Ill, Cch ?	Gy
Weiberner?	exfoliation, due to salt (?)	Old Church, Oosterbeek	TUF 3	San, Aug	Anc	Ill	Gy
Weiberner	powdery matrix	Dom tower, Utrecht	TUF 43	Qtz, San, Ol	Anc, Cha, Phi		Gy
Weiberner	spalling	Dom tower, Utrecht	TUF 42	San, Mcl, Ol	Anc, Cha, Phi		Gy

Analcime is the dominant zeolite in this tuff, according to Fitzner (1994). Present studies on material from the three quarries presently operating in Weiberner tuff confirm this (Table 1). However, material derived from Dutch monuments also shows the assemblage analcime + chabazite + phillipsite (Table 2).

3.3 Ettringer tuff

Macroscopically, the matrix has a light brown colour with abundant, regularly distributed rock and pumice fragments; single fragments are sized up to a few centimetres. The tuff denoted as Hasenstoppler is considered to be a variety of Ettringer tuff (Slinger et al. 1980), only distinguished by specific rock fragments (Fig. 11).

As with Weiberner tuff, leucite is not detected by XRD. It has largely been replaced by zeolites (Fig. 12). Phillipsite is supposed to be the dominant zeolite in Ettringer tuff (Fitzner 1994). Present XRD studies show the assemblages analcime + chabazite + phillipsite and analcime + phillipsite in fresh quarry material (Table 1), whereas the assemblages, analcime, phillipsite, phillipsite + merlinoite and chabazite + phillipsite + merlinoite are encountered in material from Dutch monuments (Table 2). The occurrence of merlinoite is remarkable, as it has not previously been reported from the Eifel area (Geuer 2001). It is, however, quite akin to phillipsite, and its crystallization may be due to small variations in the chemical environment (Passaglia et al. 1977), in particular slightly higher K/Na ratios (Colella et al. 1977, Donahoe et al. 1984).

Fig. 11. Example of rock fragmentconsidered typical for Hasenstopplertuff.

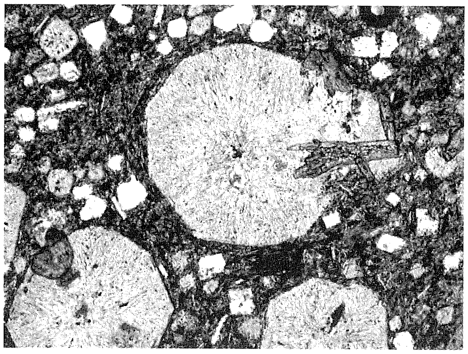


Fig. 12. Microphotograph showing zeolite pseudomorphs after leucite in fresh quarry material of Ettringer tuff (sample TUF 13, view 1.4 x 0.9 mm).

3.4 Riedener tuff

Typical Riedener tuff is a fine grained, greenish tuff, with very few rock fragments. However, material remaining in the abandonned quarry of the Riedener tuff shows a much larger variation, often being rather similar to Weiberner tuff. No samples of Riedener tuff were available for XRD or PFM studies.

4 Weathering of Rhenish tuff

4.1 Typical weathering forms

Though several weathering forms may occur on all types of tuff, several of them are typically for specific kinds of tuff:

- Spalling is common on Römer tuff (Fig. 13), in contrast to Weiberner (on which it is rare) and Ettringer (on which it has not been observed).
- Aveoli are also common, due to the selective weathering of pumice fragments. They are common on Römer and Ettringer tuff (Fig. 14), not on Weiberner tuff.
- Exfoliation (or scaling) is common on Weiberner tuff, and appears to be related to rising moisture and salt crystallisation (Fig. 15).
- Salt efflorescence is common (see below)
- Powdering of the matrix occurs over large surfaces of tuff masonry, in particular those of Römer tuff (Fig. 16).

- Dissolution of matrix occurs at all types of Rhenish tuff, especially where accumulation of water occurs and drying conditions are slow.
- Grey deposits can be found on all Rhenish tuffs, and usually contain gypsum.
- Large cracks occur in Ettringer and Hasenstoppler tuff in particular, often resulting in the loss of extending parts of sculptures and worked stones (Fig. 17).
- Biological growth easily develops on all kinds of Rhenish tuff, which are apparently more bioreceptive than other types of natural stone (Fig. 18).

Fig. 13. Spalling of Römer tuff, church tower at Tienhoven.

Fig. 14. Aveoli on Ettringer tuff, Old Church, Delft.

Fig. 15. Exfoliation of Weiberner tuff, Old Church, Oosterbeek.

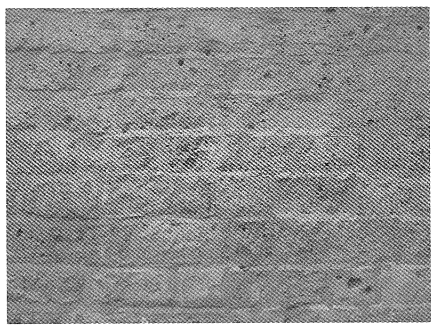


Fig. 16. Powdering of Römer tuff masonry, Lebuïnus church, Deventer.

Fig. 17. Cracking in Ettringer tuff, left a plint at the St. John's centre, 's Hertogenbosch, right a sculpture at St. John's cathedral, 's Hertogenbosch.

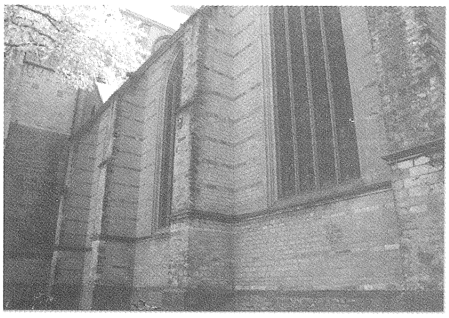


Fig. 18. Growth of algae on the north façade of the Laurens Church, Alkmaar. Note that algae developed on the tuff masonry, whereas the heads of the buttresses and layers within the tuff masonry out of Gobertange sandy limestone and Bentheim sandstone are free of growth.

Fig. 19. Römer tuff with hard, glassy surface at street level below Gobertange sandy limestone of the St. Lambertus tower, Vught.

In general, weathering and decay are most severe in zones with a high, frequent exposure to moisture. However, in addition to the weathering forms described above, which are expressions of negative effects on durability, one particular form of aging of Römer and Weiberner tuff was observed, which apparently preserves this tuff from further weathering, even at positions where the tuff is exposed to high moisture levels. The surface of the tuff becomes hard, sometimes with an glassy appearance, in which a fine mazed craquélé crack pattern occasionally developed. This type of aging has been observed at street level in the church towers of the St. Lambertus church (Fig. 19), Vught, the Old Church, Oosterbeek, the church at Tienhoven and the Lebuïnus church, Deventer as well as on the rampant arches of St. John's cathedral, 's Hertogenbosch. In case of the latter, the tuff dates back to the original building period. In case of the St. Lambertus tower, this tuff was apparently left in place during restoration works in 1954, when tuff at higher levels was replaced. Since, it did apparently not decay. Research into the nature of this type of aging is in progress.

4.2 Rate of decay

In churches, original Römer tuff has mainly been preserved on the northern façades (Kramer & Feenstra s.a.). This is, however, due to subsequent re-styling of the churches rather than decay (Kramer & Feenstra s.a.). In church towers, original Römer tuff is present on all sides. In most monuments, severely deteriorated blocks occur directly adjacent to almost unaltered blocks. If Römer tuff is present in the south façade, it is in similar condition as their counterparts in corresponding northern façades. Comparison of photographs taken with a time span of 30-40 years shows no visual increase in deterioration at most localities (Kramer & Feenstra s.a.).

With respect to decay of Weiberner tuff, a comparison of photographs could be made for only 3 objects (Kramer & Feenstra s.a.). For two objects, there is no increase of damage. In case of the other, the increase of damage is probably related to the use of blocks of lesser quality during the 1940 restoration. During the general inventarisation of decay of natural stone performed in the 1950's, 10 objects with Weiberner tuff were inspected (anonymous 1956; Table 3).

The pumice fragments present in Ettringer tuff are less prone to weathering than those in Römer tuff (Kramer & Feenstra s.a., Slinger et al. 1980). In several quarries of Ettringer tuff, layers of less cemented tuff occur, which are more prone to weathering. During the general inventarisation of decay of natural stone performed in the 1950's, 13 objects with Ettringer tuff were inspected (anonymous 1956; Table 3).

Table 3. Results from the 1950's inspection of natural stone objects in the Netherlands (anonymous 1956).

Building period	1911-20	1921-30	1931-40	unkown
	Ettringer tuff			
Good	1	3	1	
Minor to intermediate decay	1	3		1
Severe decay			2	1
	Weiberner tuff			
Good		2		3
Minor to intermediate decay		2		
Severe decay		1	1	1

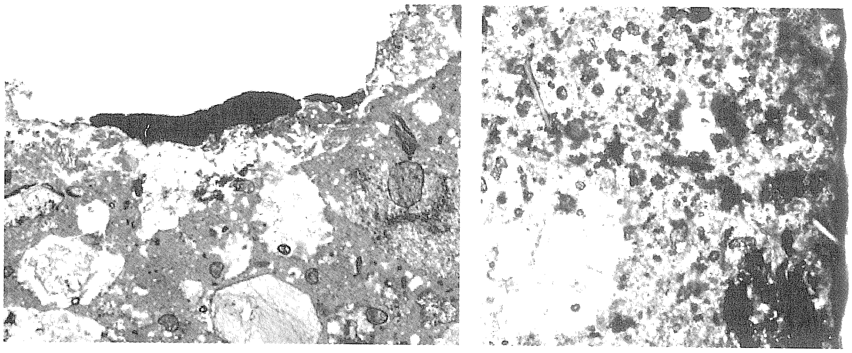


Fig. 20. Microphotograph showing deposits of Fe-rich material at the surface of Hasenstoppler tuff removed from St. John's cathedral, 's Hertogenbosch (left, sample TUF 15; Fe-rich material on top) and fresh quarry Ettringer tuff after acid rain testing (right, sample TUF 49; Fe-rich material to the right). View 5.4 x 3.5 mm.

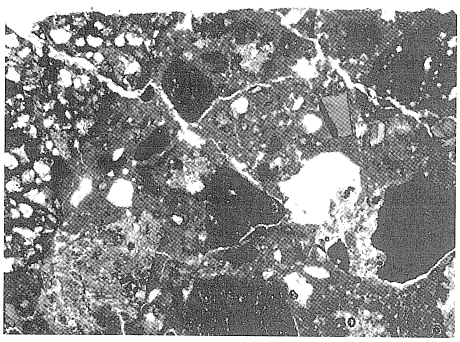


Fig. 21. Microphotograph showing internal fragmentation below the surface of Hasenstoppler tuff removed from St. John's cathedral, 's Hertogenbosch (sample TUF 15, view 5.4 x 3.5 mm).

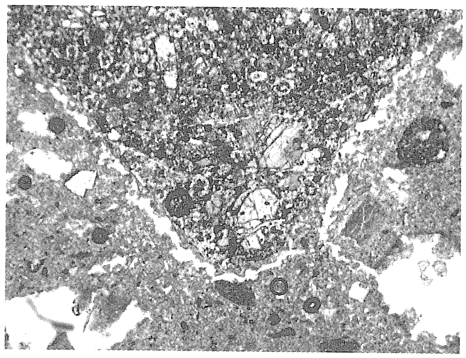


Fig. 22. Microphotograph showing debonding of rock fragment from the matrix in fresh quarry Römer tuff (sample TUF 50, view 5.4 x 3.5 mm).

4.3 Changes in microstructure during weathering

Rhenish tuffs are rocks with, at a microscale, large macroporosity. This makes it difficult to evaluate dissolution processes by microscopy. These nevertheless occur, as is manifested by the development of Fe-rich precipitates on the surface of both Hasenstoppler (Fig. 20) and Römer tuff removed from Dutch monuments; similar deposits were observed on specimens of fresh quarry material subjected to acid rain testing. Also, several tuffs contain phases relatively soluble in acid rain, like carbonates. PFM microscopy shows that the amount of interstital calcite has been reduced after acid rain testing; their dissolution may result in a development of porosity during weathering, i.e. time-dependent porosity development. Dissolution of analcime may also be a factor influencing time-dependent porosity development (see below). The preferent weathering of pumice fragments also results in an increase in macroporosity in the zone subjected to weathering processes.

Weathered specimens from monuments show development of microcracks parallel to their surface, as well as internal fragmentation of the matrix in the zone below the surface (Fig. 21). Debonding of rock fragments from the matrix was also observed in fresh quarry material after acid rain testing (Fig. 22).

4.4 Mineralogy of weathered samples

Mineralogically, no clear difference is present in the assemblages of zeolites in the matrix between fresh quarry material of Römer, Weiberner and Ettringer tuff (Table 1) and material collected from Dutch monuments (Table 2). The most prominent difference is the common occurrence of gypsum in the latter (Table 2), though it has also been encountered in one sample of fresh quarry material (Table 1); the latter may have been lying on the yard for some time. The widespread occurrence of gypsum fits well with experimental data, showing that gypsum rapidly develops in all Rhenish tuffs when exposed to atmospheric SO_2 (Fitzner & Lehners 1990).

Efflorescences on tuff are composed of gypsum and/or thenardite (Table 4). In several cases, these salts are accompanied by X-ray amorphous matter. As this has not been encountered in fresh quarry material, nor in weathered material from Dutch monuments (Tables 1, 2), it is considered to be part of the efflorescence. Most likely, it is either a residue from the incongruent dissolution of matrix zeolites, or an amorphous precipitate. It may be speculated that in particular the Na necessary for the formation of thenardite is derived from the tuff stone itself. In the present case, mineral contents have not been determined quantitatively. However, XRD results by Koch et al. (2001) for samples of Weiberner tuff from St. John's cathedral, 's Hertogenbosch, show a decrease of analcime contents in the outer zone; this may be due to (partial) dissolution of analcime, which liberates Na into solution.

Table 4. Mineralogy of efflorescences on Rhenish tuff from Dutch monuments as determined by XRD. For mineral abbreviations, see appendix.

Type of tuff	Monument	Sample	Efflorescence	Other (substrate)
Hohenleie ?	St. John's cathedral, 's Hertogenbosch	TUF 5	Gy, Thn, am	Anc, San, Ill
Römer	Old Church, Oosterbeek	TUF 4	Gy, Thn	Anc, San, Ill, Pp, Pg, Phi
Römer	Burcht, Leiden	TUF 17	Gy	Qtz, Anc, Cha, Phi
Römer	village church, Anjum	TUF 24	Thn, am	
Römer	Lebuïnus church, Deventer	TUF 27	Thn, am	Qtz, Anc
Römer	quarry material	TUF 45	Thn	Qtz, Anc, Cha, Phi
Weiberner	Dom tower, Utrecht	TUF 44	Gy, Thn	Qtz, Anc, San

5 Discussion and conclusion

Rhenish tuffs have quite variable petrographic characteristics, also within each type. These have been invoked to explain the variable weathering behaviour of these rocks (e.g. Fitzner & Lehners 1990, Fitzner 1994). Nevertheless, inspection of many monuments in the Netherlands shows that several weathering forms are common for one type of tuff, and rare for another. Microscopic debonding of rock fragments (as observed after acid rain testing) is obviously more likely to occur in tuffs rich in such fragments. Comparative microscopic investigation of material subjected to laboratory tests simulating one specific external control on weathering (acid rain, frost, etc.) and material collected from monuments evidently offers possibility in unraveling actual mechanisms of decay. On the basis of the presently available mineralogical and petrological data, weathering forms could not yet be related to the original mineralogy and microstructure. The current data set does not allow for evaluating the role of different zeolite assemblages with respect to durability. This may in part be due to the fact that moisture transport and hence weathering behaviour is controlled by submicroscopic capillary pores (cf. Van Hees et al. 2004ab). These are, however, also quite variable, even within one kind of tuff, as becomes evident comparing data given by Fitzner (1994) and Grimm (1990) and demonstrated for Römer tuff by Van Hees et al. (2004ab). Submicroscopic capillary pores are, however, not the only control on durability. In addition to the distribution of submicroscopic capillary pores, hygric behaviour of tuffs will be controled by the presence of zeolites, which easily absorb and desorb water; here the zeolite assemblage present may be a factor of yet unknown importance. Also, macropores, which occur more abundantly in the original Römer tuff than in most currently available Römer, play a role, especially in frost resistance.

Tuffs clearly show a time-dependent porosity development, i.e. progress of weathering processes with time, notably dissolution and precipitation processes, influence their microstructure and porosity. These processes are controlled by mineralogical composition and type of the rock fragments, in particular pumice. The increase in water absorption with time, as observed for Ettringer and Römer tuff (Brendle 2003), reflects this changing microstructure. Similarly, Cioffi et al. (1991) showed changes in linear strain and shrinkage for grey Campanian tuff with successive cycles of wetting and drying being related to changes in microstructure (porosity). Such coupled chemical – mechanical – hydraulic processes may exert a major control not only on the deformation of zeolitized tuffs (e.g. Kranz et al. 1989, Blacic 1993), but also on their durability as a building stone.

The development of self-protecting surface layers observed at several places is likely controlled by the original (mineralogical) composition and deserves further study.

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Appendix

List of mineral formula

am	amorphous matter	
Ab	Albite	$NaAlSi_3O_8$
Anc	Analcime	$Na(AlSi_2O_6)\bullet H_2O$
Aug	Augite	$(Ca,Mg,Fe^{2+},Al,Ti)_2(Si,Al)_2O_6$
Cc	Calcite	$CaCO_3$
Cha	Chabazite	$Ca_2(Al_{14}Si_8O_{24})\bullet 12H_2O$
Cch	Clinochlore	$(M_9,Fe^{2+})_5Al(Si_3Al)O_{10}(OH)_8$
Gis	Gismondine	$Ca_2Al_4Si_4O_{16}\bullet 9H_2O$
Gy	Gypsum	$CaSO_4\bullet 2H_2O$
Ill	Illite	$(K,H_3O^+)(Al,Mg,Fe)_2(Si,Al)_4O_{10}((OH)_2,H_2O)$
Lc	Leucite	$K(AlSi_2O_6)$
Mcl	Microcline	$KAlSi_3O_8$
Mer	Merlinoite	$(K,Ca,Na)_7Si_{23}Al_9O_{64}\bullet 23H_2O$
Ms	Muscovite	$KAl_2(Si_3AlO_{10})(OH)_2$
Ol	Olivine	$(Fe,Mg)SiO_4$
Or	Orthoclase	$KAlSi_3O_8$
Pg	Paragonite	$NaAl_2(Si_3AlO_{10})(OH)_2$
Phi	Phillipsite	$K_2(Ca_{0.5},Na)_4(Al_6Si_{10}O_{32})\bullet 12H_2O$
Pp	Pyrophyllite	$Al_2Si_4O_{10}(OH)_2$
Qtz	Quartz	SiO_2
San	Sanidine	$KAlSi_3O_8$
Thn	Thenardite	Na_2SO_4