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# Test Report

## Testing the Resistance of MOWILITH-Modified Mortars upon Exposure to pH 1 Sulphuric Acid

Customer: Clariant GmbH
Polymerisates D 581 Research
**65926 Frankfurt am Main**
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Hamburg, 05 July 1997 Report number: 9772

This report includes 24 pages, 13 of them text pages.



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# 1. Introduction

The purpose of the tests was to determine whether the resistance of mortars to attack by pH 1 sulphuric acid can be increased through the **MOWILITH** concrete additive.

The goal was to determine how the resistance of mortar with quartzite aggregate vs. limestone aggregate is influenced through modification with MOWILITH. Furthermore, the task was to determine whether modification with MOWILITH also increased the resistance in mortar with CEM I R cements. The reason for conducting these tests is to evaluate the effect of polymer dispersion in mortar when exposed to attack by pH 1 sulphuric acid compared to mortars with $C_3A$-free cements (CEM I R HS NA cements).

The resistance of mortars to sulphuric acid was tested according to the “Guideline for Testing Mortars for Use in Sewer System Construction” **[1]**. The mortars used for reference were mortars with the same consistency and the same water/cement value as the MOWILITH-modified mortars.

# 1 . Abbreviations Used

The mortar mixtures have been labelled with the following abbreviations:

**Table 1:** Mortar samples abbreviations

| | Abbreviation | Meaning |
|---|---|---|
| 1st position | **K** or **N** | Limestone (German: *Kalkstein)* or standard sand aggregate (German: *Normsandzuschlag*) |
| 2nd position | **HS, R** or **H** | CEM I 42.5 R **HS NA,** CEM I 42.5 **R** or CEM III A 32.5 cements |
| 3rd position | **0** or **1** | without MOWILITH or with MOWILITH |
| 4th position | **-1** to **-15** | Prism number |
| 5th position | **A** or **B** | Prism half |

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# 3. Fresh Mortar Test

## 3.1. Mortar Consistency Setting and Determining the Mixture Compositions

In order to set the consistency of the mortars, a search was made for mortars with dispersion with each of the cement types (CEM I 42.5 R and CEM I 42.5 R HS NA) and with a flow spread of greater than 13 and less than 21 cm. The basic mixtures are mortars with dispersion with quartzite aggregate and with limestone aggregate that have the fresh mortar properties listed in Table 2. The MOWILITH additive was added as 15% dispersion – referring to the cement weight – and factored in with the aggregate. The water contained in the MOWILITH dispersion was factored in as mixing water.

The reference mortars (with CEM I 42.5 R HS NA) were composed in such a way to yield the same W/C value as that of the mortars with dispersion. The consistency of the reference mortars was set by adding Addiment products BV1 (liquefier) and FM6 (plasticiser) to the mortars containing MOWILITH. The grain size distribution of the limestone aggregate was composed according to the grain size distribution of the norm sand used.

The mixture compositions and the fresh mortar properties tested are listed below in Table 2.

The ability to process the MOWILITH-modified mortars was remarkably good. The known thixotropic effect of the concrete additive proved to be particularly favourable in the water/cement values determined, particularly with regard to preventing signs of separation and mixture bleeding during compressing. The workability of the reference mortars while adding the liquefier could be established with these two markers in mind.

**Table 2:** Mixture compositions and tested fresh mortar properties of the test programme mortars

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| **Mortar with CEM I 42.5 R and MOWILITH** | | | | | | | | | | |
| | Aggregate | Cement | Water | Additive | W/C | $LP_1$ [%] | $LP_2$ [%] | Raw Density [kg/dm$^3$] | $A_{01}$ [cm] | $A_{012}$ [cm] |
| **Mixture: N R 1** | | | | | | | | | | |
| | Norm sand | | | Dispersion | | | | | | |
| [g] | 1350.0 | 450.00 | 155.25 | 67.50 | 0.42 | 5.6 | 5.0 | 2.193<br>2.205 | 14 | 15 |
| [ml] | 509.43 | 145.16 | 155.25 | 64.90 | | | | | | |
| **Mixture: K R 1** | | | | | | | | | | |
| | Limestone | | | Dispersion | | | | | | |
| [g] | 1350.0 | 450.00 | 191.25 | 67.50 | 0.50 | 3.9 | 3.4 | 2.240 | 15 | 14 |
| [ml] | 509.43 | 145.16 | 191.25 | 64.90 | | | | | | |
| **Mortar with CEM I 42.5 R HS NA and MOWILITH** | | | | | | | | | | |
| **Mixture: N HS 1** | | | | | | | | | | |
| | Norm sand | | | Dispersion | | | | | | |
| [g] | 1362 | 450.00 | 155.25 | 67.50 | 0.42 | 4.5 | 4.2 | 2.158 | 15.5 | 15.5 |
| [ml] | 513.97 | 140.62 | 155.25 | 64.90 | | | | | | |
| **Mixture: K HS 1** | | | | | | | | | | |
| | Limestone | | | | | | | | | |
| [g] | 1362 | 450.00 | 186.75 | 67.50 | 0.49 | 3.1 | 3.3 | 2.164<br>2.157 | 15.25 | 14.75 |
| [ml] | 514.0 | 140.6 | 186.75 | 64.90 | | | | | | |
| **Mortar with CEM I 42.5 R HS NA and BV1 and FM6** | | | | | | | | | | |
| **Mixture: N HS 0** | | | | | | | | | | |
| | Norm sand | | | BV1/FM6 | | | | | | |
| [g] | 1432.6 | 450.0 | 180.9 | 1.8 / 6.3 | 0.42 | 2.8 | 3.0 | 2.248<br>2.242 | 14.75 | 15 |
| [ml] | 540.59 | 140.6 | 202.5 | 1.54 / 5.48 | | | | | | |
| **Mixture: K** HS **0** | | | | | | | | | | |
| | Limestone | | | | | | | | | |
| [g] | 1432.6 | 450.0 | 216.9 | 1.8 / 6.3 | 0.50 | 1.9 | 1.9 | 2.268<br>2.272 | 14.75 | 14.5 |
| [m1] | 514.0 | 140.6 | 216.9 | 1.54 / 5.48 | | | | | | |

# 4. Sulphuric Acid Resistance after 70 Days of Exposure to pH 1 Sulphuric Acid

The test specimens were left in the mould for 1 day, removed from the mould and then stored in water for 6 days. From the 7$^{th}$ day until day 28, they were stored at 23 °C and 95% rel. humidity. On the 28$^{th}$ day, they were cut in half and measured, and, after being stored in water for 2 days, 5 prism halves of each mixture were stored for 70 days in sulphuric acid (H2SO4) with a pH value of 1.

During the 70 days of storage, the pH value was kept constant through computer-controlled titration. The aggressive solution was replaced every 7 days. The surface/volume ratio was set at 20 m$^{-1}$ for each test specimen, and the solution was kept in constant motion by agitators. The test specimens were not moved during the entire time of storage, and the layer of corrosion formed was not removed when the solution was replaced each week.

In addition, the five prism halves of each mixture were stored in water during the 70 days of sulphuric acid storage. Their compression strength is used as the reference strength when evaluating the drop in compression strength in order to determine the change in relative strength.

After the time of storage, loose parts were removed from the test specimens with a scrubbing brush and, if necessary, using a wire brush, and were photographed to document the external changes. The weathering depth in the brushed-off test specimens was determined by the change in the external dimensions $\mathbf{X_A}$. Afterwards, cube-shaped test specimens were sawn out of the middle of the corroded prism half so that they were approx. 40 mm in size. The cubes were ground plane parallel and photographed, and the breaking load was determined after 2 days of storage at 23 °C and 50% rel. humidity. The corrosion depths, calculated from the change in relative compression strength $\mathbf{X_{ß,D}}$, were compared with test specimens of the same composition and age that had been stored in water.

### 4.1. Test Results

After the storage time, loose parts were removed from the test specimens with a scrubbing brush and, if necessary, with a wire brush, and were photographed to document the external changes. The weathering depth in the brushed-off test specimens was determined by means of the external dimensions. Afterwards, cube-shaped test specimens were sawn out of the middle of the corroded prism half so that they were approx. 40 mm in size. The cubes were ground plane parallel and photographed, and the breaking load was determined after 2 days of storage at 23°C and 50% rel. humidity. The two sections obtained while preparing each test specimen were used to determine the penetration depth visually and microscopically.

The corrosion depths brought about during the exposure to acid are the principle means for evaluating the behaviour of the tested mortars.

In each instance, an initial impression is provided by the visually identified **weathering depth $X_A$**, which is determined directly after the test specimens are brushed off.

The **corrosion depth $X_M$**, determined in the cross section using light microscopy, indicates how much the infusing acid has changed the material structure, with the weathering depth factored in for the purpose of a better comparison.

The extent, or depth, to which the material structure has been affected with respect to load capacity is revealed by the special compression tests conducted on the test specimens after being exposed to acid, which is then used to calculate the **corrosion depth $X_{ß,D}$**: The initial cross section of the test specimen minus the corrosion border of thickness $X_{ß,D}$ yields the non-impacted core dimensions with respect to strength, with the strength of a test specimen of the same age – but not stored in acid – used as the reference for strength. According to previous experience, the following is to be expected: **$X_A < X_{ß,D} < X_M$**.

### 4.1.1. Determination Process and Results of Weathering Depth $X_A$

The external dimensions of the test specimens after being brushed off were measured to determine the weathering depth. The dimensions of each test specimen before storage were used as the initial dimensions, yielding the values listed in Table 3. The changes in the external measurements of the mixtures are documented in Image 2 to Image 7.

**Table 3:** Corrosion depth of the mortars after 70 days of storage in pH 1 sulphuric acid, determined from the changes in external dimensions compared to the external dimensions of each test specimen and associated statistical values in mm

| **Mixture** | **K HS 0** | **K HS 1** | **K R 1** | **N HS 0** | **N HS 1** | **N R 1** |
|---|---|---|---|---|---|---|
| Mean value [mm] | 0.03 | 0.06 | 0.06 | 1.40 | 0.45 | 0.18 |
| Standard deviation [mm] | 0.07 | 0.07 | 0.05 | 0.13 | 0.11 | 0.08 |
| Percentage standard deviation [%] | 234.30 | 101.25 | 86.52 | 9.13 | 23.90 | 45.02 |

### 4.1.2. Determination Process of the Corrosion Depth $X_{ß,D}$ and Results of the Compression Test after Removal from Storage in pH 1 Sulphuric Acid

To determine the residual compression strength, the strengths of the corroded test specimen cubes were compared to the strengths of the test samples prepared the same way after being stored in water. These reference strengths were also determined for the cubes. The strengths were compared to the initial cross section surfaces of each test specimen before storage. The values are listed in the following table; the cross section surfaces can be seen in Image **8** to Image **13** appended below.

**Table 4:** Strengths of the mortars after 28 days and after 70 days of being stored in pH1 sulphuric acid or in reference water

| **Test specimen age 28 days** | | | | | | |
|---|---|---|---|---|---|---|
| **Mixture** | **K HS 0** | **K HS 1** | **K R 1** | **N HS 0** | **N HS 1** | **N R 1** |
| Mean value [N/mm$^2$] | 70.5 | 52.2 | 54.1 | 83.1 | 58.8 | 58.5 |
| Standard deviation [N/mm$^2$] | 2.1 | 1.9 | 1.3 | 4.5 | 1.8 | 0.7 |
| **70 days of storage in reference water** | | | | | | |
| Mean value [N/mm$^2$] | 71.1 | 52.5 | 54.4 | 85.8 | 57.1 | 60.9 |
| Standard deviation [N/mm$^2$] | 2.7 | 0.9 | 0.6 | 2.7 | 1.3 | 1.3 |
| **70 days of storage in pH 1 $H_2SO_4$** | | | | | | |
| Mean value [N/mm$^2$] | 70.9 | 53.5 | 54.1 | 66.9 | 47.6 | 49.9 |
| Standard deviation [N/mm$^2$] | 0.6 | 1.3 | 2.3 | 2.0 | 1.2 | 4.1 |
| | | | | | | |
| **Percentage residual compression strength [%]** | **99.6** | 101.9 | 99.5 | **78.0** | 83.4 | 81.9 |
| | | | | | | |
| **Corrosion depth from the residual compression strength $X_{ß,D}$ [mm]** | **0.0** | **-0.2** | **0.0** | **2.3** | **1.7** | **1.9** |

## 4.2. Determination Process and Results of the Corrosion Depth $X_M$ Calculated Using Microscopy

One of the sections from the preparation of each test specimen for the compression strength test was ground to determine the penetration depth visible per microscope. To do this, the test specimen was first pressed with EP resin. A cross section slice 5-10 mm thick was then sawn from this, surface-ground on one side and adhered to a microscope slide 5 x 5 $cm^2$ in size. Afterwards, the sample was ground plane parallel and polished. The damage depth was determined using a light microscope at 50x and 100x magnification (ocular) in incident light with a crossed analyser. The corrosion zones at 50x magnification for representative sample sections are documented in Image 14 to Image 19 appended below.

A clearly visible brown layer of iron oxide hydroxide can be seen with the polymer-modified **norm sand mortars** (Image 18 and Image 19), which is not the case with the unmodified norm sand mortar (Image 17). This is indicative of delayed diffusive transport – due to the polymer modification – of the dissolved iron ions out of the cement stone matrix on the one hand and of the hydronium ions into the cement stone matrix on the other.

The **limestone mortars** do not exhibit a pattern of damage that is quite as distinguishable. Nevertheless, Image 15 and Image 16 display a similar effect of MOWILITH for the polymer-modified mortars in comparison to the unmodified mortar (Image 14). The heavily darkened layer (caused by portlandite enrichment, directly to the right of the brown iron hydroxide layer) is much more pronounced and thicker in the unmodified mortar.

The average depth of damage is approx. 0.5 mm (±0.25 mm) in the modified limestone mortars and approx. 1.5 (±0.25 mm) in the modified norm sand mixtures. The unmodified reference mixtures exhibit a damaged zone with an average thickness of approx. 1.5 mm (±0.25 mm) for the limestone mortar (K HS 0) and approx. 1.75 mm (±0.25 mm) for the norm sand mortar.

The microscopically identified corrosion depth $X_M$ is calculated by adding the weathering depth $X_A$ to the average thicknesses of the corrosion crusts and damage zones. The values of $X_M$ are summarised Table 5 on the following page in the Summary section.

# 5. Summary and Evaluation of the Results

In the tests, it was calculated how the resistance to pH 1 sulphuric acid exhibited by mortar with quartzite aggregate vs. with limestone aggregate is influenced through modification with MOWILITH. Furthermore, the effect the use of CEM I R has compared to $C_3A$-free cements (CEM I R HS NA) was determined.

Resistance to sulphuric acid was tested in accordance with the "Guideline for Testing Mortars for Use in Sewer System Construction" **[1]**. Mortars with the same consistency and the same water/cement value as the MOWILITH-modified mortars were used as reference mortars.

**The fresh mortar consistency – 14 cm to 15.5 cm – is within the required consistency range of 13 cm to 21 cm for all mortars. Compared to the reference mortars, the ability to process the MOWILITH-modified mortars proved to be much better, particularly with regard to signs of separation, cohesion and bleeding.**

A summary of the individual test results following removal from storage in pH 1 sulphuric acid are shown in Table 5 below. The residual compression strengths and residual load capacities are documented on the next page in Image 1 in graph form.

**Table 5:** Mean values of the mortar test results after the test specimens were removed from storage in pH 1 sulphuric acid. In addition, the values of the reference mortar are listed in italics in this table **in accordance with the sewer system construction guideline** (W/C 0.45, CEM I 42.5 R HS NA: norm sand 1:3).

| | **Unit** | **K HS 0** | **K HS 1** | **K R 1** | **N HS 0** | **N HS 1** | **N R 1** | ***REF* 3** |
|---|---|---|---|---|---|---|---|---|
| | | | | | | | | |
| Corrosion depth $\mathbf{X_A}$ from the external dimensions | [mm] | 0.1 | 0.1 | 0.1 | 1.4 | 0.5 | 0.2 | *1.7* |
| | | | | | | | | |
| Corrosion depth $\mathbf{X_M}$ from the microscopic tests | [mm] | 1.35 | 0.6 | 0.6 | 3.15 | 2.0 | 1.9 | *3.8* |
| | | | | | | | | |
| Corrosion depth $\mathbf{X_{ß,D}}$ from the residual compression strength | [mm] | 0.0* | 0.0 * | 0.0 * | 2.3 | 1.7 | 1.9 | *3.1* |
| | | | | | | | | |
| Residual compression strength | [mm] | 99.6 | 101.9 | 99.5 | 78.0 | 83.4 | 81.9 | *71.8* |

*** The values are within the fluctuation range of the compression strength values for comparison test specimens of the same composition stored in water.**

The reference mortar **N HS 0** with norm sand selected here shows resistance that is superior to the mortars normally used for the sewer system construction test due to the reduction in the water/cement value from 0.45 to 0.42 in comparison to the standard reference mortar. The reference values for the standard reference mortar are listed in the **REF 3** column in Table 5. The residual load capacity of the standard reference mortar of approx. 6% is below that of the reference mortar N HS 0. Thus, the resistance of **all tested** systems is greater than that of the standard reference mortar.

It was confirmed for mortars with **limestone aggregate** that the resistance to sulphuric acid was improved considerably through the addition of limestone alone. The residual load capacity for all limestone mortars is approx. 100%. The polymer modification with MOWILITH resulted in a reduced damage zone compared to the reference mortar **K HS 0**. Based on the results for norm sand mortars, it can be assumed that even longer exposure to PH 1 sulphuric acid will yield much lower rates of corrosion for MOWILITH-modified limestone mortars in comparison to the limestone reference mortar.

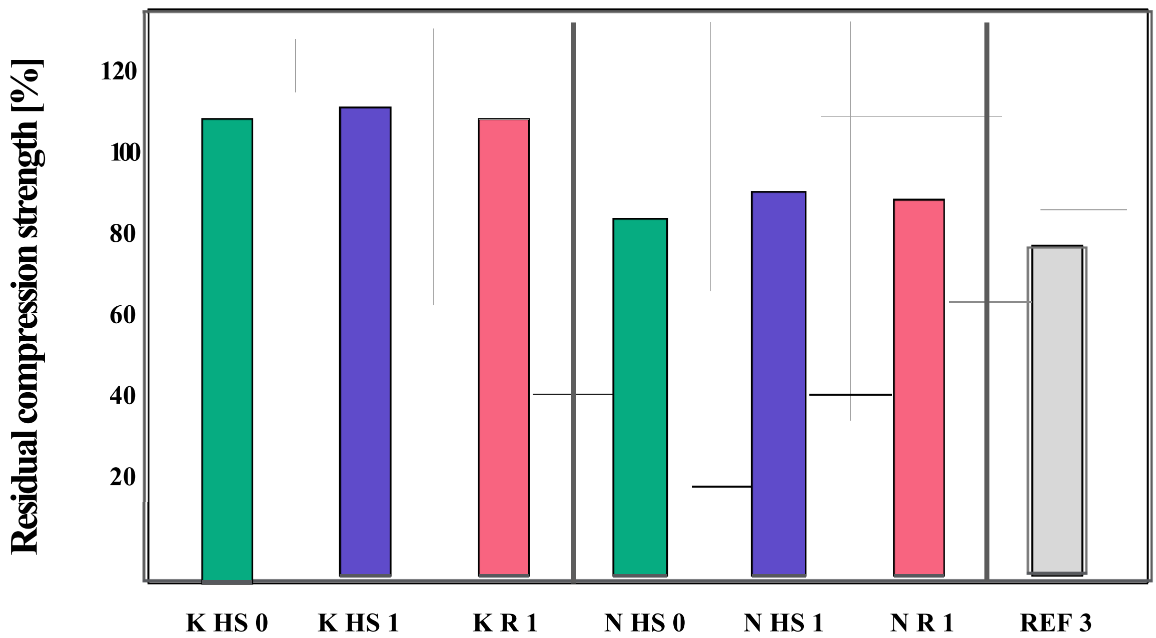


**Image 1:** Residual compression strengths of the tested mortars after 70 days of storage in pH 1 sulphuric acid at a test specimen age of 100 days, compared to the strengths of test specimens of the same age after 70 days of storage in water.
In addition, the value of the **reference mortar according to the test guideline** (W/C 0.45, CEM 1 42.5 R HS NA: norm sand 1:3) is shown **(REF 4)**.

The polymer modification with MOWILITH obviously has the effect that, regardless of the aggregate used, mortars made of CEM I 42.5 R cement are more resistant to pH 1 sulphuric acid than polymer-modified mortars made of $C_3A$-free CEM I 42.5 R HS NA cement.

**All systems tested – including the improved reference mortars – passed the test for corrosion resistance to pH 1 sulphuric acid in accordance with the Hamburg “Guideline for Mortars in Sewer System Construction”.**

**The polymer modification with MOWILITH, particularly for mortars with quartzite aggregate, increased the resistance to sulphuric acid compared to reference mortars without MOWILITH.**

## 6. Signature

21073 Hamburg, 5 July 1997

[signature]

Prof. Dr.-Ing. L. Franke

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# 7. Appended Images

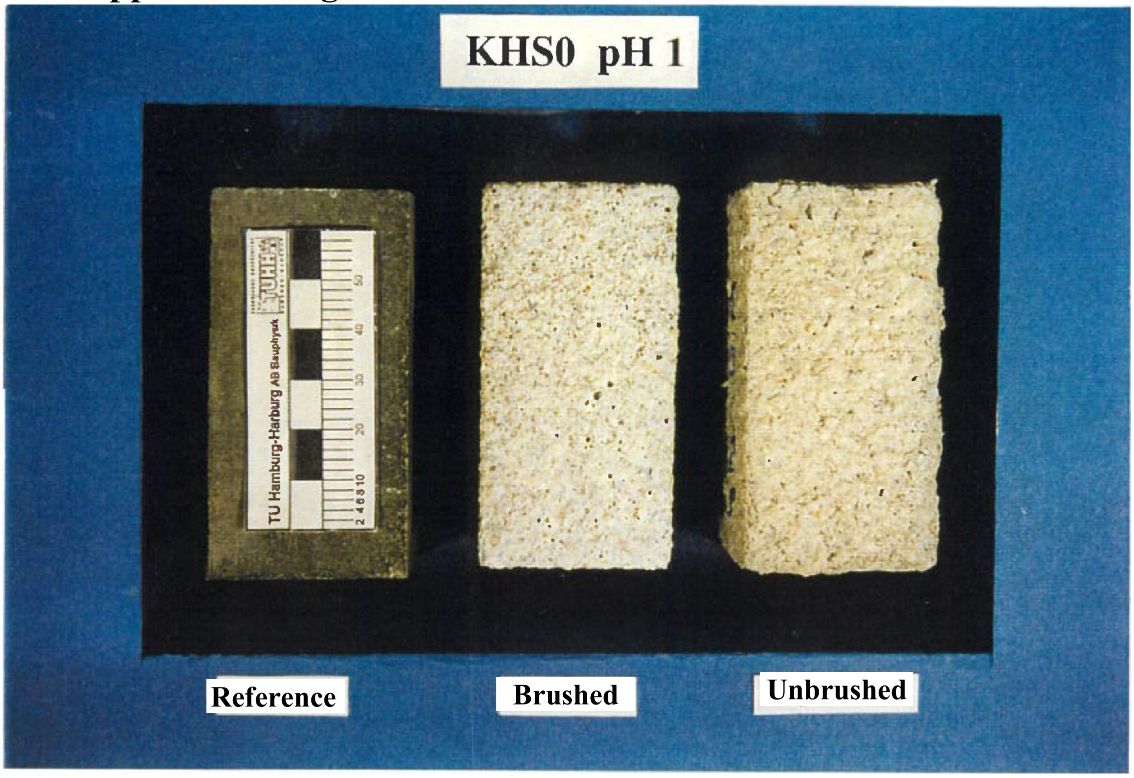


**Image 2:** Mortar prisms after the end of storage. Mixture with limestone and CEM I 42.5 R HS NA **(unmodified)** after 70 days of storage in pH 1 sulphuric acid.

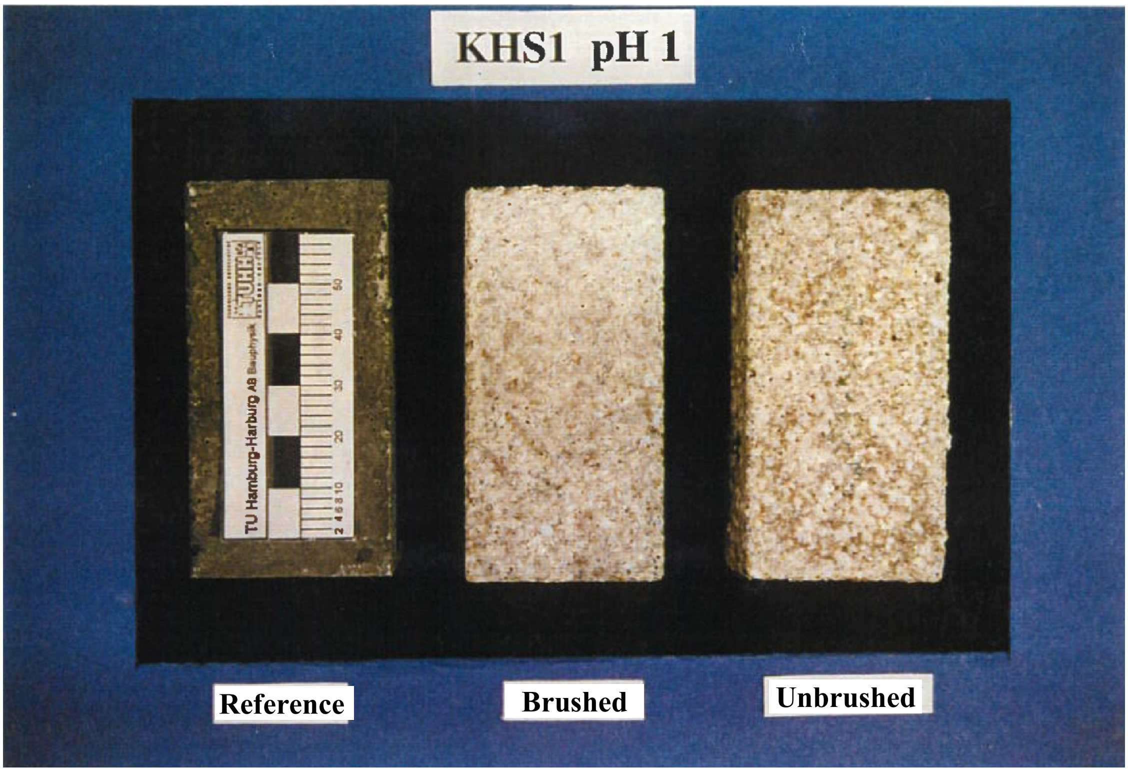


**Image 3:** Mortar prisms after the end of storage. Mixture with limestone and CEM I 42.5 R HS NA **(MOWILITH-modified)** after 70 days of storage in pH 1 sulphuric acid.

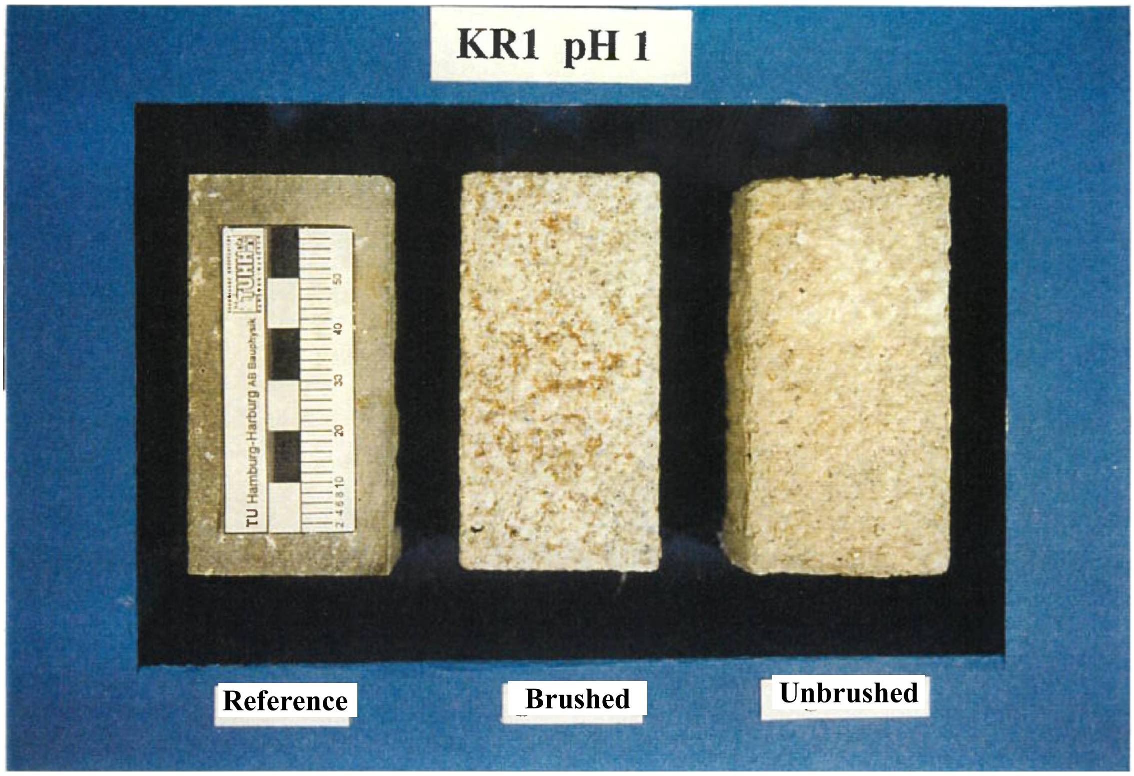


**Image 4:** Mortar prisms after the end of storage. Mixture with limestone and CEM I 42.5 R **(MOWILITH-modified)** after 70 days of storage in pH 1 sulphuric acid.

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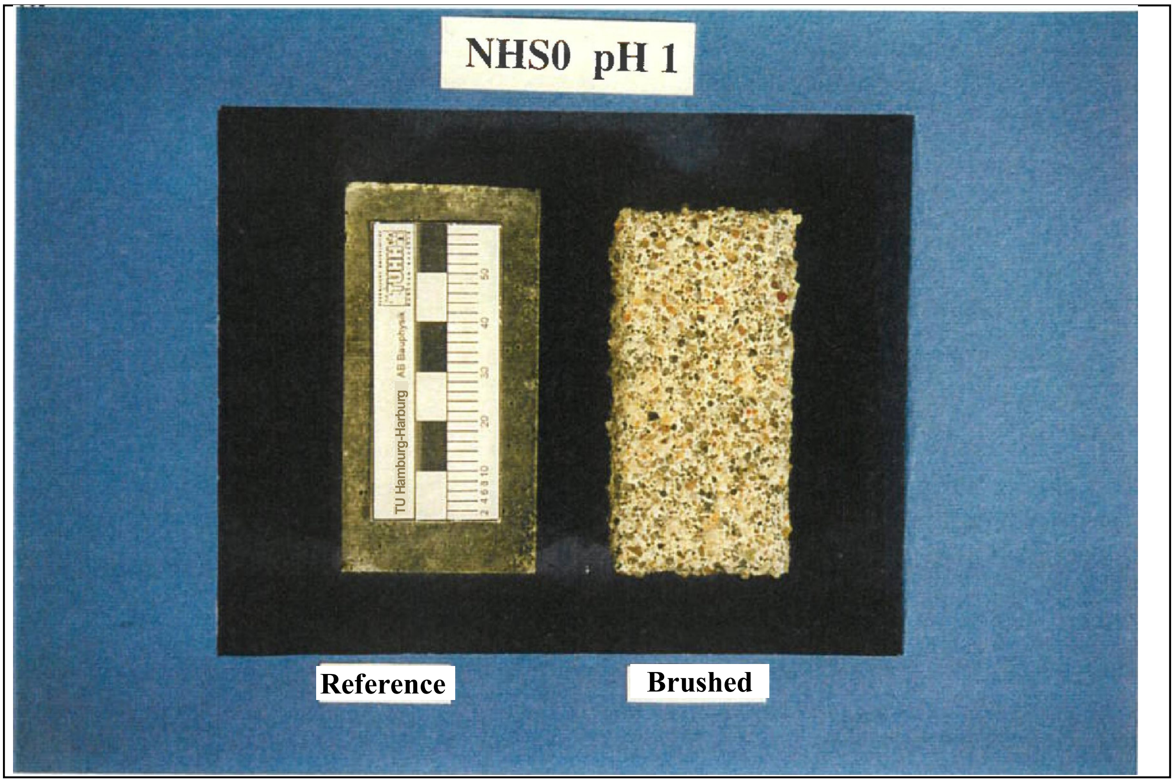



**Image 5:** Mortar prisms after the end of storage. Mixture with norm sand and CEM I 42.5 R HS NA **(unmodified)** after 70 days of storage in pH 1 sulphuric acid.

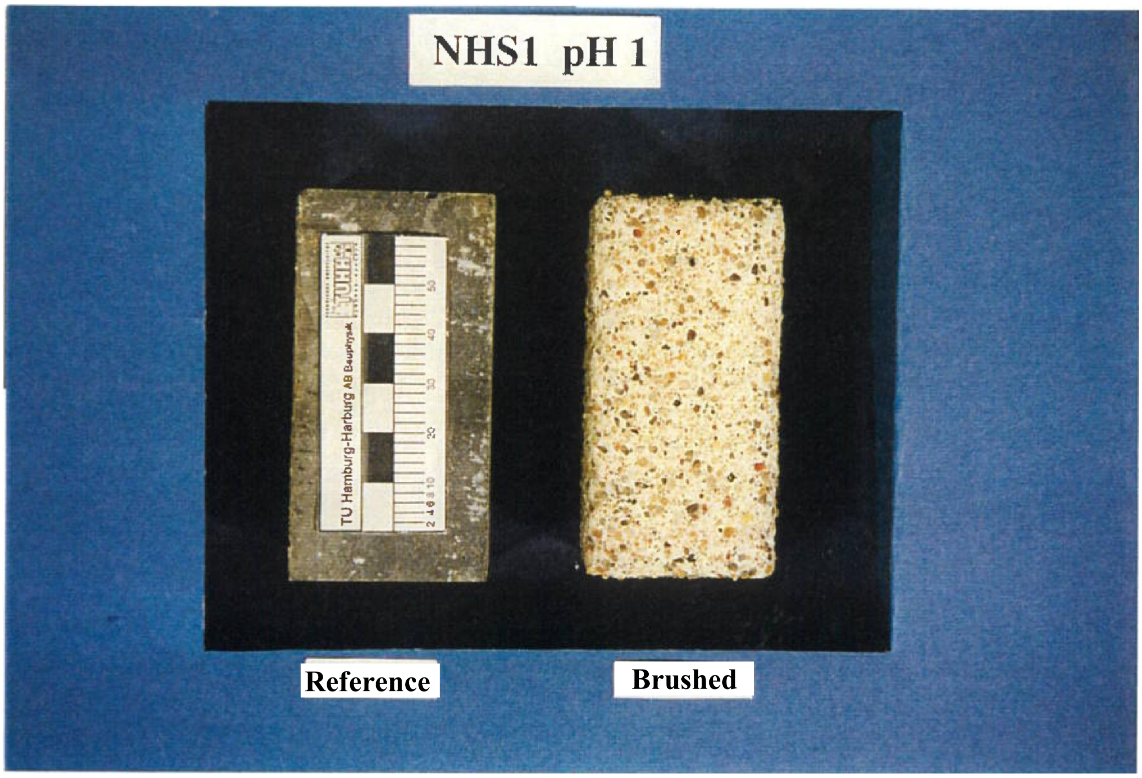



**Image 5:** Mortar prisms after the end of storage. Mixture with norm sand and CEM I 42.5 R HS NA **(MOWILITH-modified)** after 70 days of storage in pH 1 sulphuric acid.

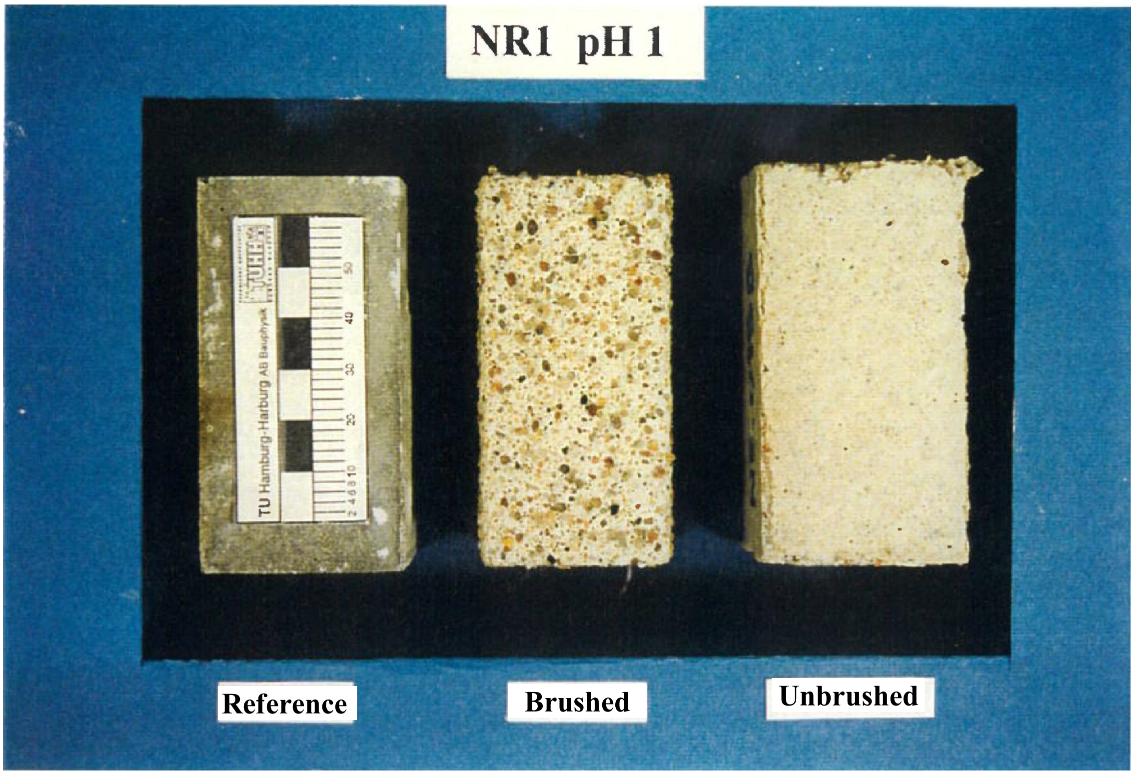



**Image 7:** Mortar prisms after the end of storage. Mixture with norm sand and CEM I 42.5 R **(MOWILITH-modified)** after 70 days of storage in pH 1 sulphuric acid.

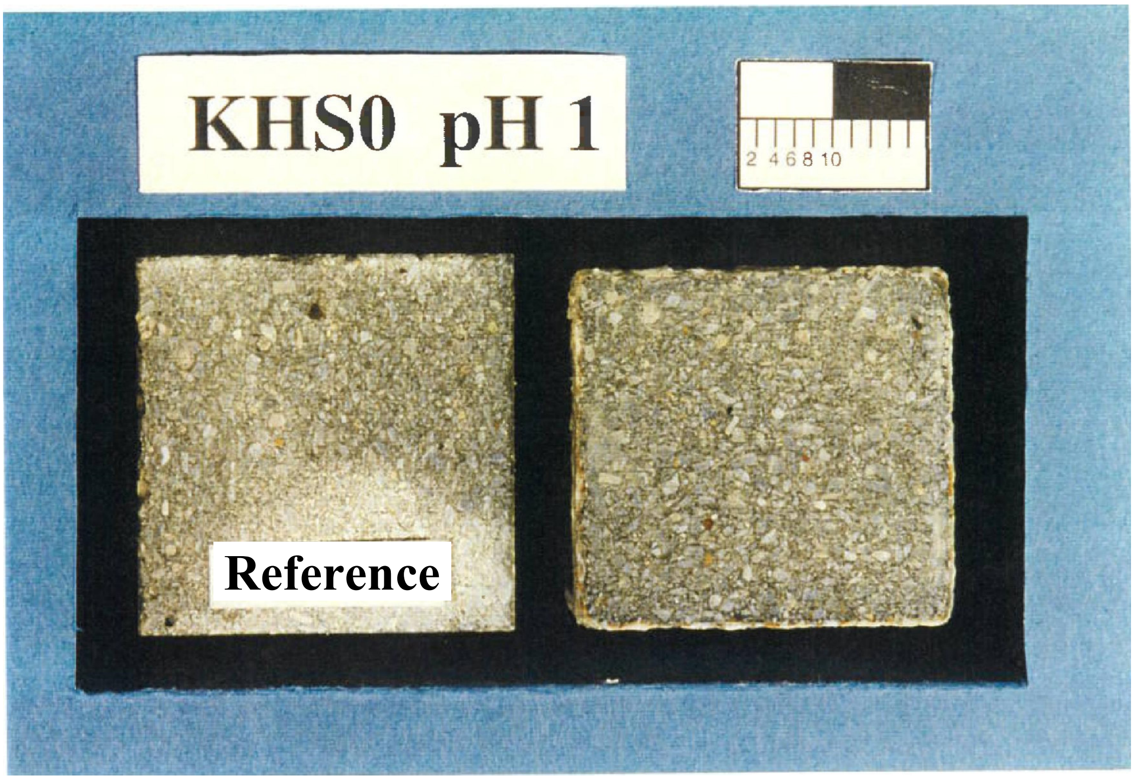



**Image 8:** Cross section surfaces of the mortar prisms before the compression test. Mixture with limestone and CEM I 42.5 R HS NA **(unmodified)** after 70 days of storage in pH 1 sulphuric acid.

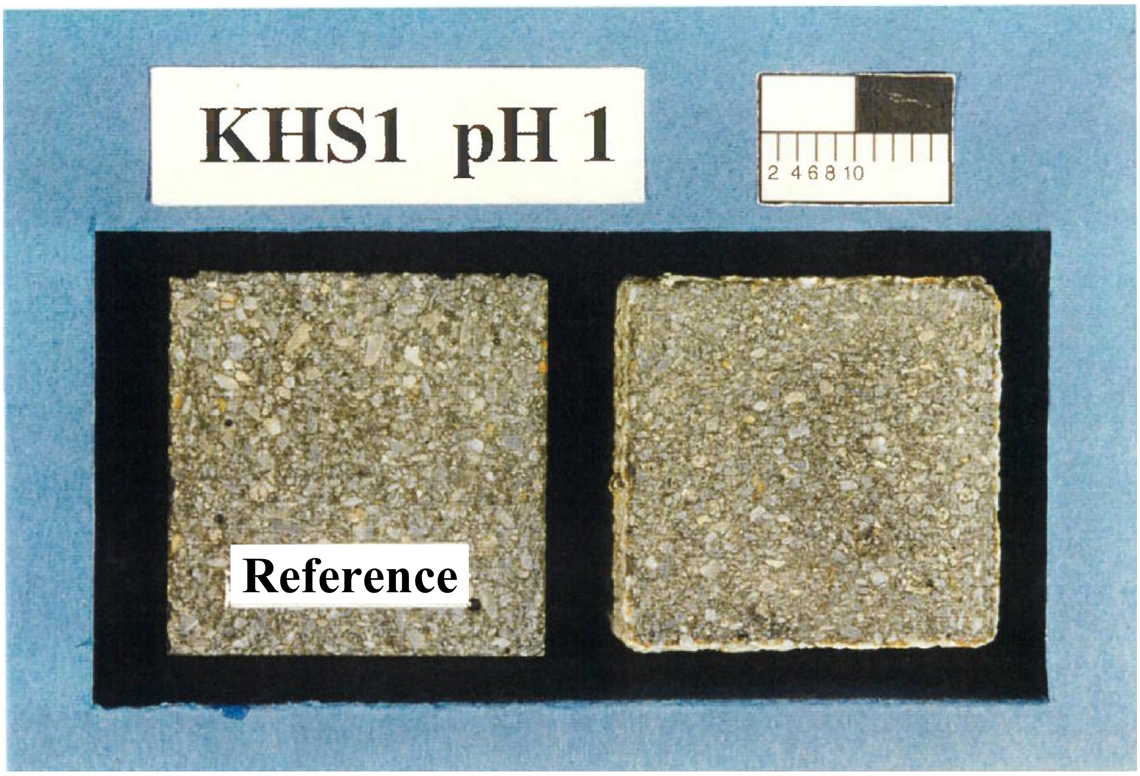



**Image 9:** Cross section surfaces of the mortar prisms before the compression test. Mixture with limestone and CEM I 42.5 R HS NA **(MOWILITH-modified)** after 70 days of storage in pH 1 sulphuric acid.

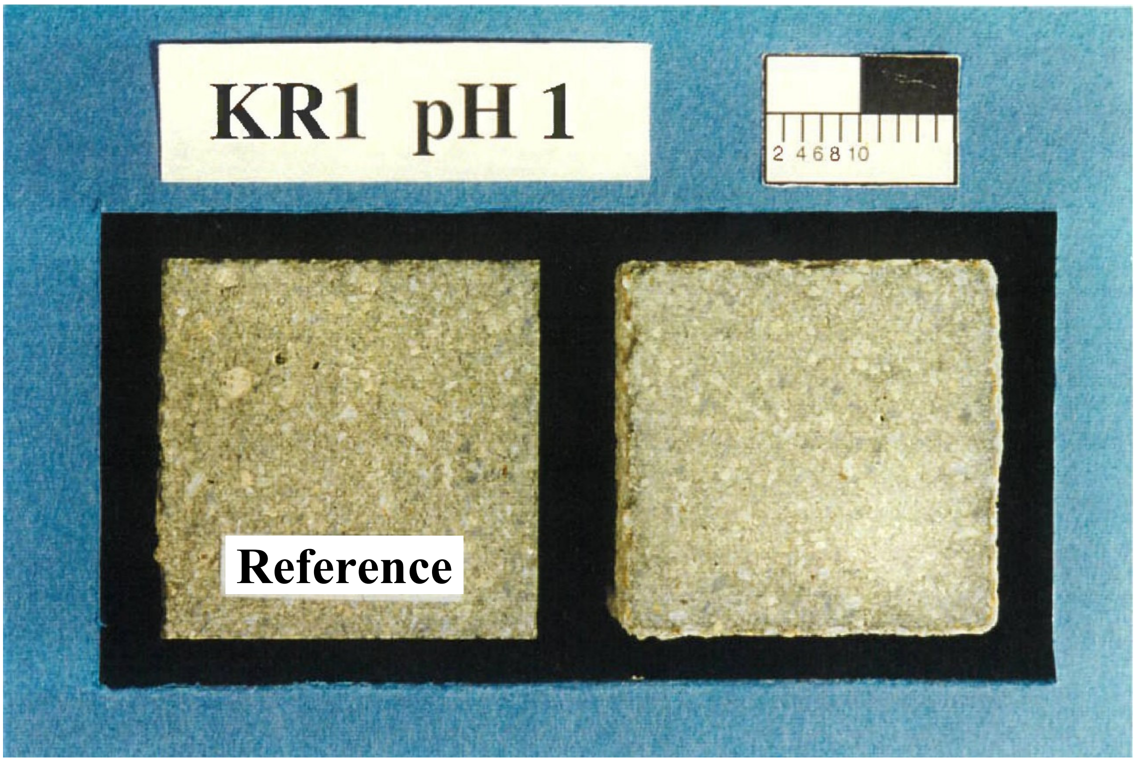



**Image 10:** Cross section surfaces of the mortar prisms before the compression test. Mixture with limestone and CEM I 42.5 R **(MOWILITH-modified)** after 70 days of storage in pH 1 sulphuric acid.

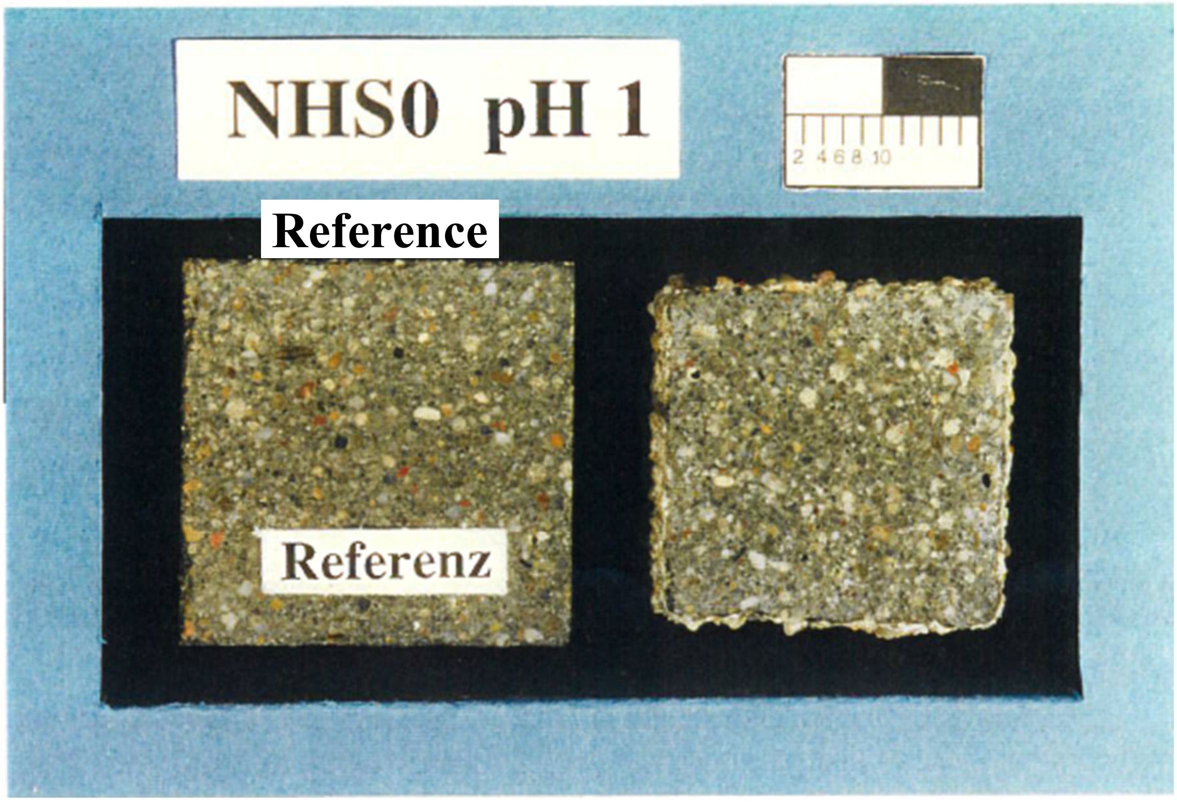
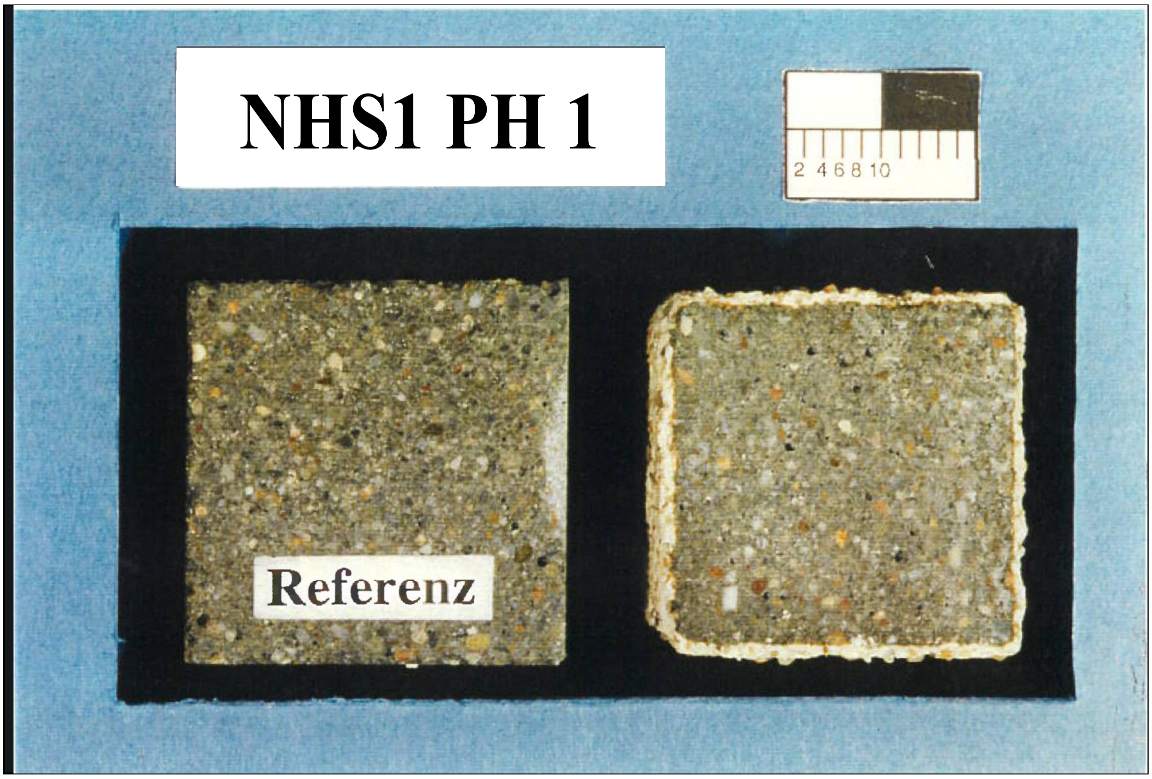



**Image 11:** Cross section surfaces of the mortar prisms before the compression test. Mixture with norm sand and CEM I 42.5 R HS NA **(unmodified)** after 70 days of storage in pH 1 sulphuric acid.

**Reference**

**Image 12:** Cross section surfaces of the mortar prisms before the compression test. Mixture with norm sand and CEM I 42.5 R HS NA **(MOWILITH-modified)** after 70 days of storage in pH 1 sulphuric acid.



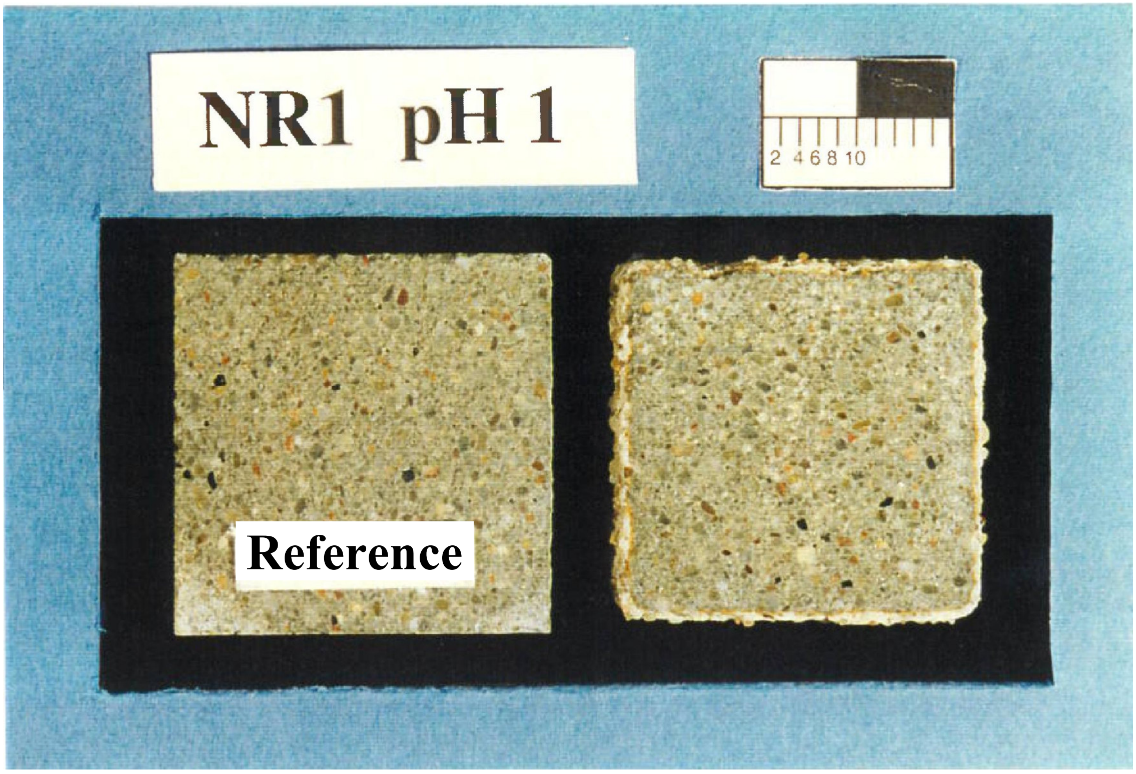



**Image 13:** Cross section surfaces of the mortar prisms before the compression test. Mixture with norm sand and CEM I 42.5 R **(MOWILITH-modified)** after 70 days of storage in pH 1 sulphuric acid.

**Image 14:** Corrosion border zone of mortar **K HS 0** with limestone and CEM I 42.5 R HS NA **(unmodified)** after 70 days of storage in pH 1 sulphuric acid, ground, under the microscope. The image width is 2.7 mm (55x magnification).

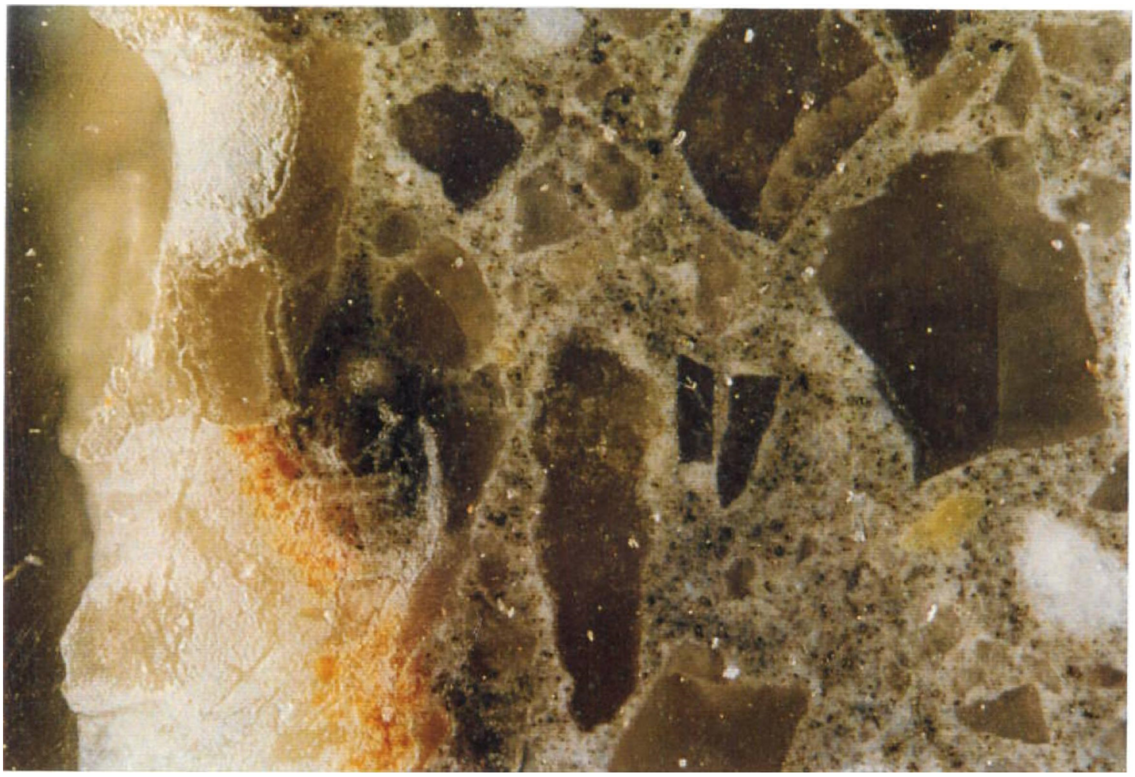


**Image 15:** Corrosion border zone of mortar **K HS 1** with limestone and CEM I 42.5 R HS NA **MOWILITH-modified)** after 70 days of storage in pH 1 sulphuric acid, ground, under the microscope. The image width is 2.7 mm (55x magnification).

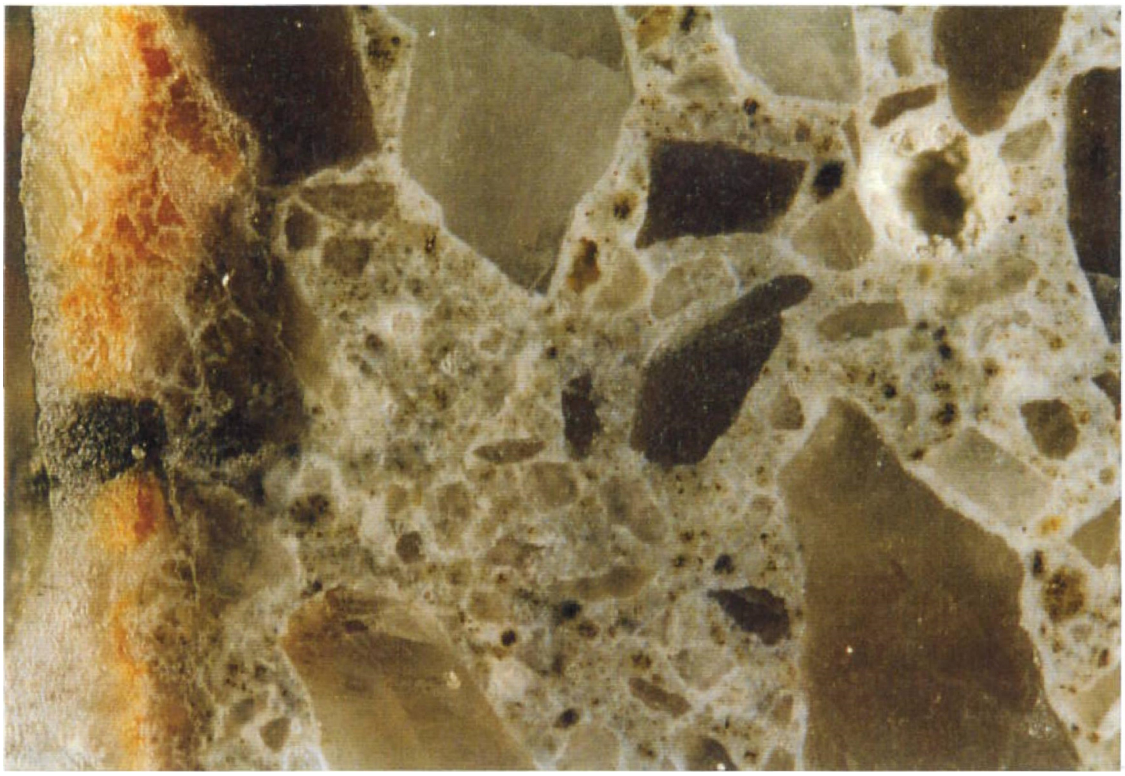


**Image 16:** Corrosion border zone of mortar **K R 1** with limestone and CEM I 42.5 R **MOWILITH-modified)** after 70 days of storage in pH 1 sulphuric acid, ground, under the microscope. The image width is 2.7 mm (55x magnification).

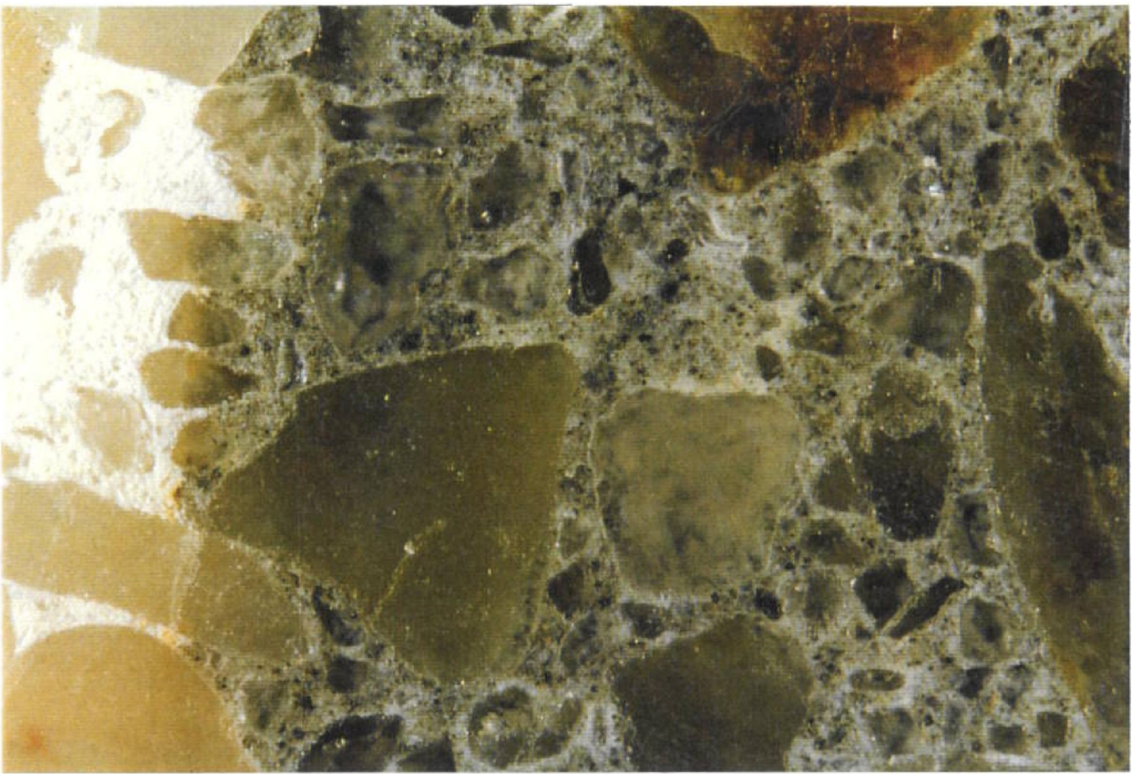


**Image 17:** Corrosion border zone of mortar **N HS 0** with norm sand and CEM I 42.5 R HS NA **(unmodified)** after 70 days of storage in pH 1 sulphuric acid, ground, under the microscope. The image width is 2.7 mm (55x magnification).

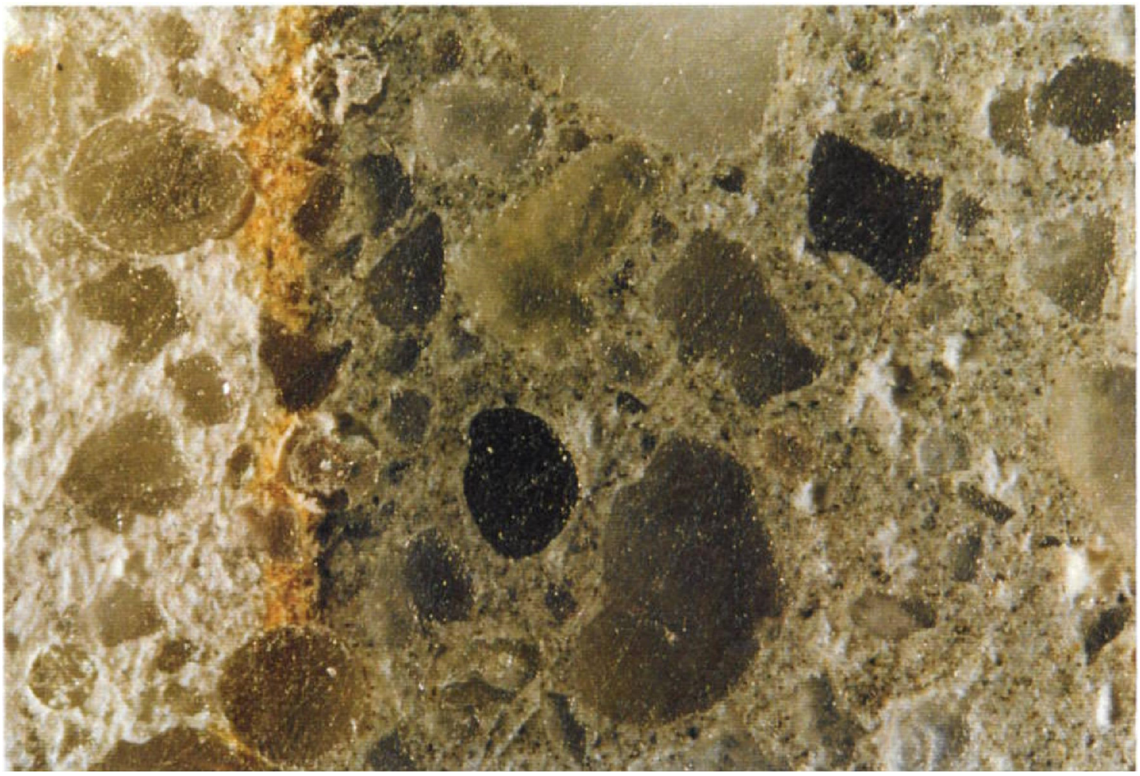


**Image 18:** Corrosion border zone of mortar **N HS 1** with norm sand and CEM I 42.5 R HS NA **(MOWILITH-modified)** after 70 days of storage in pH 1 sulphuric acid, ground, under the microscope. The image width is 2.7 mm (55x magnification).

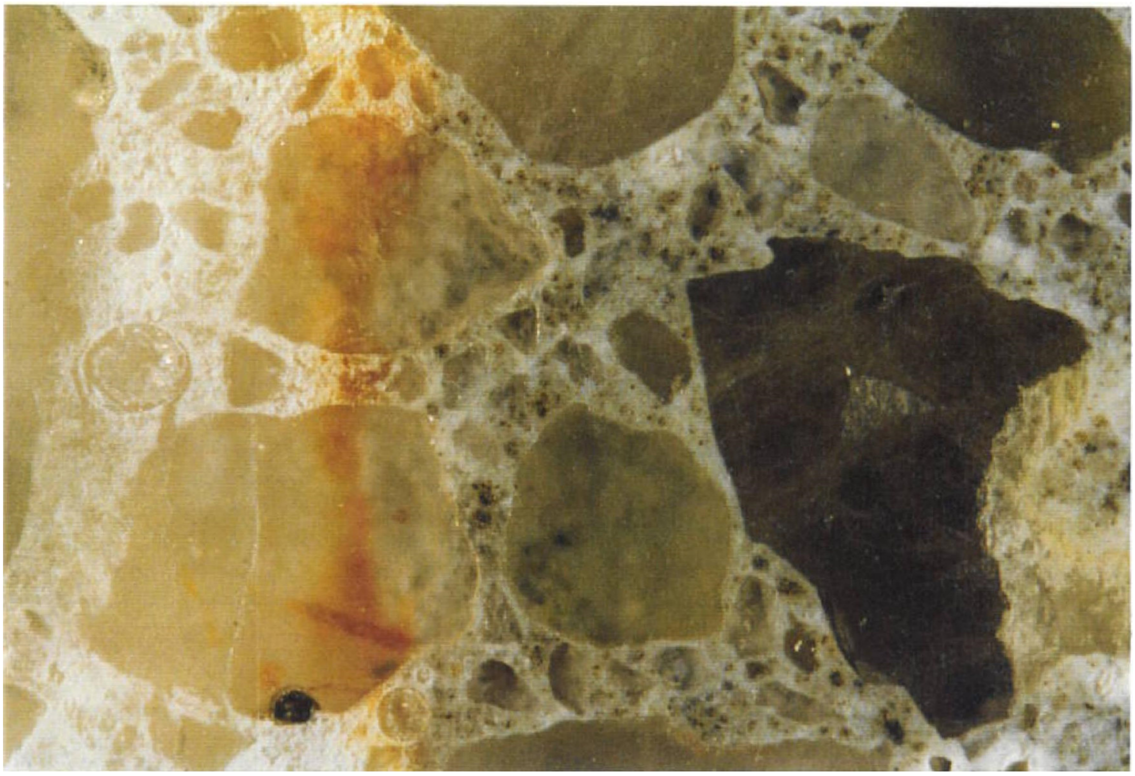


**Image 19:** Corrosion border zone of the mortar **N HS 1** with norm sand and CEM I 42.5 R HS NA **(MOWILITH-modified)** after 70 days of storage in pH 1 sulphuric acid, ground, under the microscope. The image width is 2.7 mm (55x magnification).

# 9. Literature

1 Franke, L., Oly, M. and Pinsler, F.: *Richtlinie für die Prüfung von Mörteln für den Einsatz im Sielbau.* Tiefbau Ingenieurbau Strassenbau, 4, **1997,** 19-23