Report

Biogenic sulfuric acid corrosion resistance of MasterSeal 7000 CR

Report no. 20220927A

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carried out by:
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Contents

1 Content of project

The purpose of the project was to carry out a weathering test for the waterproofing and concrete protection system MasterSeal 7000 CR against biogenic sulfuric acid corrosion. The duration of the weathering test should be 72 weeks.

The test chamber used leads to an acceleration of weathering because of the optimized conditions for the bacteria regarding H_2S concentration, nutrient content, moisture, and temperature. Based on experiences of the University of Duisburg-Essen (Biofilm Centre, Prof. Wolfgang Sand) the acceleration factor concerning concrete specimens is in the range of 8 up to 10. That means, a 17 month period (72 weeks) in the chamber is comparable to a 136 up to 170 month period in a real sewer system (more than 11 to 14 years).

Biogenic sulfuric acid corrosion (BSA) is a chemical attack to surfaces of different materials such as concrete, iron and polymers. It is caused by sulfuric acid producing bacteria e.g. from the genus *Thiobacillus* and others. It mainly occurs in waste water systems, where sulfur compounds are degraded by microorganisms. Gaseous sulfur compounds are released and accumulate in the head space. Chemical oxidation of H_2S to elemental sulfur and the following biological oxidation via thiosulfate and other polythionates cause a decrease of pH (< 7). The reduced sulfur compounds are oxidized to sulfuric acid yielding energy for the growth of thiobacilli (*T. neapolitanus*, *T. intermedia*), which further decrease the pH. Below pH 5.5 *A. thiooxidans* colonizes the surface. Between pH 2.0-3.0 this organism will find optimal growth conditions. Result is a successive colonization of surfaces by different thiobacilli. Sulfuric acid is produced as a metabolite of these organisms causing an attack on susceptible materials.

The weathering test was carried out from 1 October 2020 to 24 February 2022.

Individual specimens were examined for microbially growth. These examinations were carried out in cooperation with Brill+Partner GmbH, Bremen.

Individual specimens were also examined for signs of corrosion and physical properties of the materials by Master Builders Solutions Deutschland GmbH in their laboratories at Master Builders Solutions Deutschland GmbH, Trostberg (s. Annex 1). This work was carried out additionally to the project by Master Builders Solutions Deutschland GmbH and was on responsibility of Master Builders Solutions Deutschland GmbH.

2 Description of the test bench and test process

The test facility used for the weathering is located at Fraunhofer UMSICHT and operated by Fraunhofer UMSICHT. Figure 1 shows the test facility and the connected test chambers. In this project the chamber on the left-hand side was used to carry out the weathering test.

Figure 1 Test facility at Fraunhofer UMSICHT.

The test facility simulates the attack of biogenic sulfuric acid in a sewer system. The emergence of hydrogen sulfide and the resulting corrosion caused by sulfuric acid in a sewer system is schematically described in figure 2.

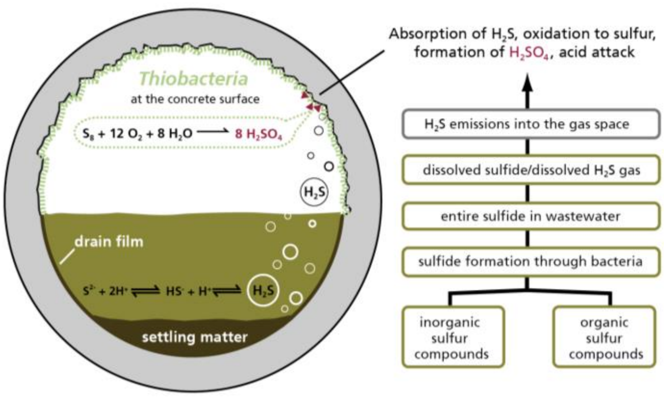


Figure 2 Development of biogenic sulfuric acid corrosion (source: Bock, E., Sand, W., Pohl, A., Bedeutung der Mikroorganismen bei der Korrosion von Abwasserkanälen, TIS Tiefbau – Ingenieurbau – Straßenwesen, Sonderdruck zum 4. Statusseminar »Bauforschung und -technik«, 1983, s. 47-49).

The weathering is carried out by making use of the process described in figure 3. A bacteria solution is temperature controlled and pumped in circuit through the test chamber sump. This leads to a moisture saturated atmosphere in the test chamber. The H_2S gas is produced in a reactor by a reaction of HCl with NaS_2 and the gas is flushed discontinuously in the test chamber by a pressure impulse using air. The gas is fed above the specimens in the gas compartment of the test chamber.

Weathering parameters were: 30 °C, 100 ppm H_2S, near 100 % RH.

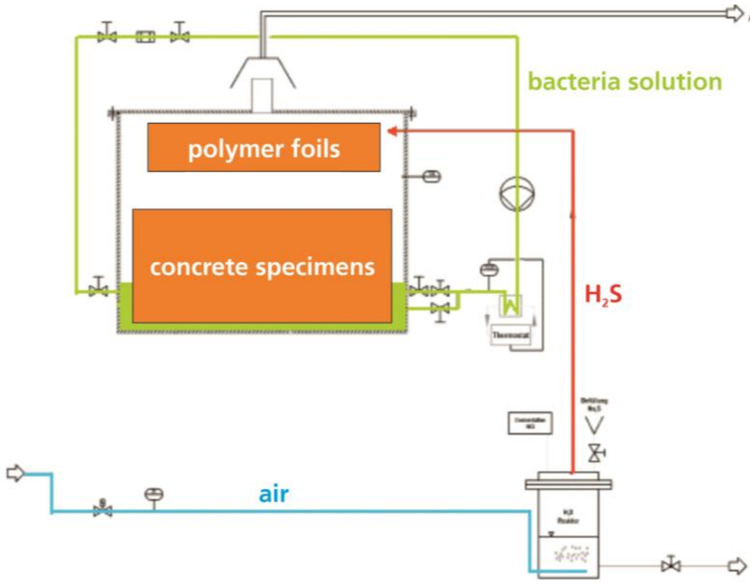
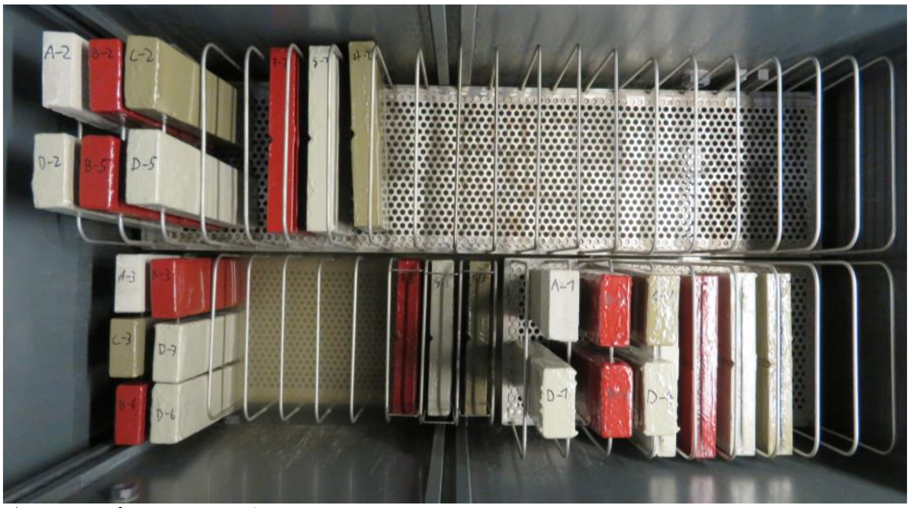


Figure 3 Schematic flow diagram of the process.

The concrete specimens were placed in the bottom of the chamber using a rack made of stainless steel. In figure 4 the placement of the concrete specimens is shown.

The polymer films were placed above the concrete specimens in a rack made of PVC (s. figure 4). The films were placed on sheets of artificial turf (polypropylene) to avoid an all-area contact with the PVC rack and were covered with small frames made of polycarbonate to avoid movement.



Placement of concrete specimens

Platform with polymer foils with frames of carbonate

Figure 4 Placement of concrete specimens and polymer films. Specimens of MasterSeal 7000 CR are the ones in red colour. The specimens in other colours have been provided by Master Builders Solutions Deutschland GmbH for additional testing and comparison.

The position of each specimen in the chamber was documented.

Concrete specimens were subjected to three separate cycles of weathering. The first set of specimens remained permanently in the gas phase, a second set was cycled in and out of the bacteria solution (15 cm height) on a two weekly basis to simulate the effect of the varying water line in sewer environments, and a third set was permanently placed in the bacteria solution (15 cm height).

3 Weathering test

3.1 Timetable and parameters

The weathering was carried out from 1 October 2020 to 24 February 2022. On 1 October 2020 the concrete specimens and polymer films were placed in the chamber. On 24 February the specimens were taken out from the chamber. The specimens were finally given to Master Builders Solutions Deutschland GmbH.

The bacteria solution was heated up to 30 °C and the temperature was controlled during the test. The concentration of H_2S was 100 ppm. Therefor H_2S is produced continuously and fed in the test chamber every 10 minutes by a pressure impulse using air.

From 1 October 2020 to 8 October 2020 the concrete specimens and polymer foils were preconditioned by moistening with the liquid from the chamber sump by spraying once a day. The inoculations of the concrete specimens and polymer foils were carried out by hand using a spray pump and were started on 9 October 2020. The concrete specimens and polymer foils were inoculated once a week for 6 weeks (s. chapter 3.3).

The weathering test was accompanied by a microbiological analysis that was carried out in cooperation with Brill+Partner GmbH, Bremen.

3.2 Measurement of pH value

To determine the pH values on the surfaces of the specimens a pH meter was used (Hanna Instruments Deutschland GmbH, type HI 99171).

Date	**Time of weathering**	**pH value**	
dd/mm/yyyy	[days]	Surface of ref. concrete	Surface of MasterSeal 7000 CR
29/10/2020	28	7	2.4
07/01/2021	98	1.2	2.2
15/04/2021	196	1.5	2.5
22/07/2021	294	1.4	1.4
11/11/2021	406	0.8	1.2
24/02/2022	511	0.7	1.1

Table 1: Results of pH values.

3.3 Microbiological investigation

Test specimens and experimental set-up

The specimens were used to quantitatively and qualitatively determine the amount of settled bacteria as well as to estimate the amount of deposited sulfur on the surface.

Several strains of sulfur/-compounds oxidizing bacteria of the species *A. thiooxidans* (K6), *A. ferrooxidans* (R1, R7, ATCC 23270), and *T. intermedia* (K12), some of which originating from samples of corroded municipal sewers, were grown as mass cultures in the laboratory, harvested, and sprayed as an aerosol into the simulation chamber. A part of the aerosol settled on the surface of the test specimens. The inoculation was done six times during a period of 6 weeks (each time with about 1.0E+12 cells in total) beginning with the moderately acidophilic strains (*T. intermedia*), following by the strong acidophiles *A. thiooxidans* and *A. ferrooxidans*. Own investigations of sewer systems made from concrete revealed that by this inoculation method, cell densities of more than 1.0E+06 cells cm^{-2} are usually achieved. Compared with natural conditions this equals a cell count that occurs only at highly endangered parts of the sewage system (Milde et al., 1983, Thiobacilli of the corroded concrete walls of the Hamburg sewer system, J. Gen. Microbiol. 129, 1327-1333). Thus, a start of the simulation experiment without a lag-phase was expected. During the subsequent weathering of the microbially contaminated concrete specimens at a temperature of 30 °C and a pollutant gas load of 100 ppm H_2S a mineral solution containing trace elements, nitrogen, and phosphate was added regularly.

Microbiological and chemical analysis

Cell counts (of living SOB) were determined via the MPN-technique using dilution series and standardized, selective culture media. The media were incubated at 28 °C for a maximum period of 4 weeks. In addition to microbiological analysis the quantity of elemental sulfur in the sample materials was determined by inductively coupled plasma optical emission spectrometry (ICP-OES) after extraction with ethanol.

Results

The highest cell numbers of the remaining strongly acidophilic sulfur oxidizers were detectable on uncoated test specimens exposed in the gas space of the test, which appeared visually heavily corroded after completion of the test with comparatively low sulfur loads on the surfaces (approx. 115 µg cm^{-2}).

In contrast, the apparently intact specimens coated with MasterSeal 7000 CR performed best under these weathering conditions and allowed only negligible cell counts (1.0E+01 cm^{-2} as the maximum) on the surface despite the respective high sulfur load that merely accumulated over time by autoxidation of the sulfide sulfur present in gaseous form as H_2S (approx. 2578 µg cm^{-2}).

Specimen	FeOx		sa SOx		ma SOx		total SOx	
Gaseous phase	S1	S2	S1	S2	S1	S2	S1	S2
Ref. concrete	7.5E+04	1.8E+02	3.7E+06	8.8E+06	1.3E+02	1.0E+02	3.7E+06	8.8E+06
Coated with MasterSeal 7000 CR	0.0E+00	0.0E+00	8.0E+00	4.8E+00	0.0E+00	0.0E+00	8.0E+00	4.8E+00

Table 2: Results of cell number analysis.
FeOx: Strongly acidophilic iron and sulfur oxidizing bacteria. sa SOx: Strongly acidophilic sulfur oxidizing bacteria.
ma SOx: Moderately acidophilic sulfur oxidizing bacteria. total SOx: Total cell count of sulfur oxidizing bacteria.
S1: Sampling no. 1, after 175 days of weathering. S2: Sampling no. 2, after 511 days of weathering.

Specimen	pH value [-]		Sulfur [µg cm^{-2}]	
Gaseous phase	S1	S2	S1	S2
Ref. concrete	1.0	0.7	779	115
Coated with MasterSeal 7000 CR	1.5	1.1	1134	2578

Table 3: Results of pH values and sulfur amounts.
S1: Sampling no. 1, after 175 days of weathering. S2: Sampling no. 2, after 511 days of weathering.

4 Investigation of mechanical properties and water permeability of the polymer films

4.1 Mechanical properties

The mechanical properties of the polymer foils were analysed according EN ISO 527-1 (tensile test). Therefor samples (5 samples per specimen) were cut out of the polymer foils and were measured with a tensile test apparatus (Instron, velocity tensile modulus 1 mm/min, further mm/min, temperature 23 °C).

Specimens after sampling 2 (511 days of weathering)

Every measurement was carried out with 5 foils per specimen.

Specimen	**Tensile modulus** [MPa]	**Tensile strength** [MPa]	**Elongation at break** [%]
MasterSeal 7000 CR	631 ± 62	29.2 ± 1.5	28.8 ± 1.4

Table 4: Results of tensile testing (511 days of weathering).

4.2 Water permeability

The water permeability was analysed according to DIN 53122-1 (gravimetrical method) at a temperature of 23 °C and a gradient of the relative humidity of from 85 % to 0 %. These measurements were carried out in cooperation with Fraunhofer IVV[1]. In deviation from DIN 53122-1, the surface-related mass of the specimens was not determined. In deviation from the standard, screw trays with mechanical locking were used.

[1] Fraunhofer Institute for Process Engineering and Packaging IVV, Freising

Specimens after sampling 2 (511 days of weathering)

The time of measurement was from 21 March 2022 to 1 August 2022. The measurement was carried out with 3 foils per specimen.

Specimen	**Water-vapour transmission rate (mean)** [g m^{-2} d^{-1}]	**Thickness** [mm]
MasterSeal 7000 CR	0.584 ± 0.050	1

Table 5: Results of water permeabilty (511 days of weathering).

Holger Wack

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5 Annex

Annex 1 Additional results obtained after the weathering test.

6 Contact data

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Annex 1

Results obtained after the weathering test on specimens stored 511 days in the gas phase.

The tests were carried out additionally to the project and were on responsibility of Master Builders Solutions Deutschland GmbH.

1. Images of MasterSeal 7000 CR

Specimen after 511 days testing.

Specimen after 511 days testing and cleaning.

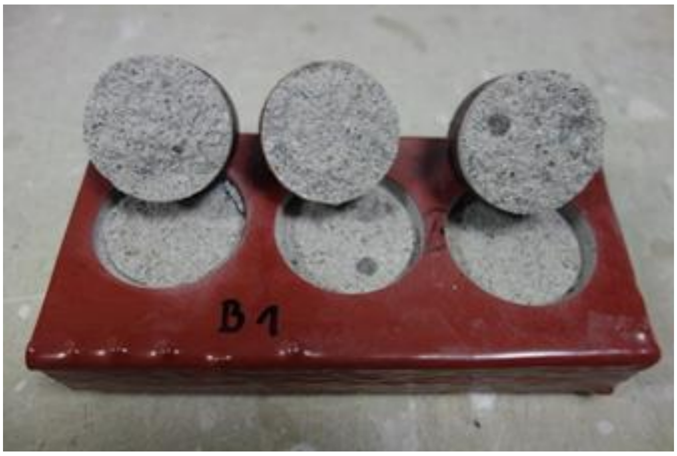
2. Image of concrete reference (CEM I)

Specimen after 511 days testing.

3. Abrasion resistance of MasterSeal 7000 CR: Taber test – after 511 days testing

Testing in accordance with EN ISO 5470-1
Weight loss after 1000 cycles: 220 mg (Required: < 3000 mg)

4. Adhesion of MasterSeal 7000 CR after 511 days testing



Testing in accordance with EN 1542
Adhesion to concrete: 3.1 MPa – failure in the concrete

After visual inspection, abrasion resistance test and adhesion test on specimens stored 511 days in the weathering chamber at the Fraunhofer UMSICHT, no reduction of properties of MasterSeal 7000 CR were observed.