Fraunhofer
UMSICHT

Report

Testing of the biogenic sulfuric acid corrosion resistance of MasterSeal 7000CR

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carried out by:
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1 Content of project

The purpose of the project was to carry out a weathering test for MasterSeal 7000CR against biogenic sulfuric acid corrosion.

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 samples is in the range of 8 up to 10. That means, a 6 month period in the chamber is comparable to a 48 up to 60 month period in a real sewer system.

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 onsusceptible materials.

The weathering test was carried out from 08.08.2013 to 12.02.2014.

Individual samples were examined for microbially growth. These examinations were conducted in cooperation with Prof. Dr. Wolfgang Sand of the University Duisburg-Essen (Biofilm Centre of the University Duisburg-Essen, Aquatic Biotechnology).

Individual samples were also examined for signs of corrosion and where possible, physical properties of the materials checked by BASF Construction Chemicals in their Global Development Laboratories at BASF Construction Solutions GmbH, Trostberg (s. Annex 1). This work was carried out additionally to the project by BASF and was on responsibility of BASF.

2 Description of the test bench and test process

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

Fig. 1 Test bench at Fraunhofer UMSICHT.

The test bench 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.

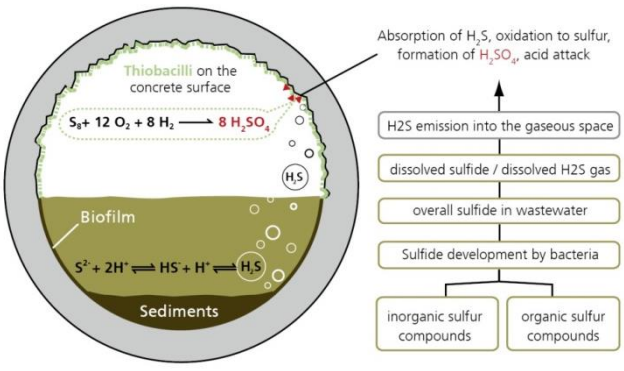


Fig. 2 Development of biogenic sulfuric acid corrosion (source: Bock, E., Sand, W., Pohl, A., Bedeutung der Mikroorganismen bei der Korrosion von Abwasserkanälen, TIS Tiefbau – Ingenieurbau – Straßenwesen, Sonderdruck zum 4. Statusseminar »Bauforschung und -technik«, 1983, s. 47-49).

The weathering is conducted by making use of the process described in figure 3. The bacteria solution is temperature controlled and pumped in circiut 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 wiht NaS_2 and the gas is flushed discontinuously in the test chamber by a pressure impuls using air. The gas is fed above the samples in the gas compartment of the test chamber.

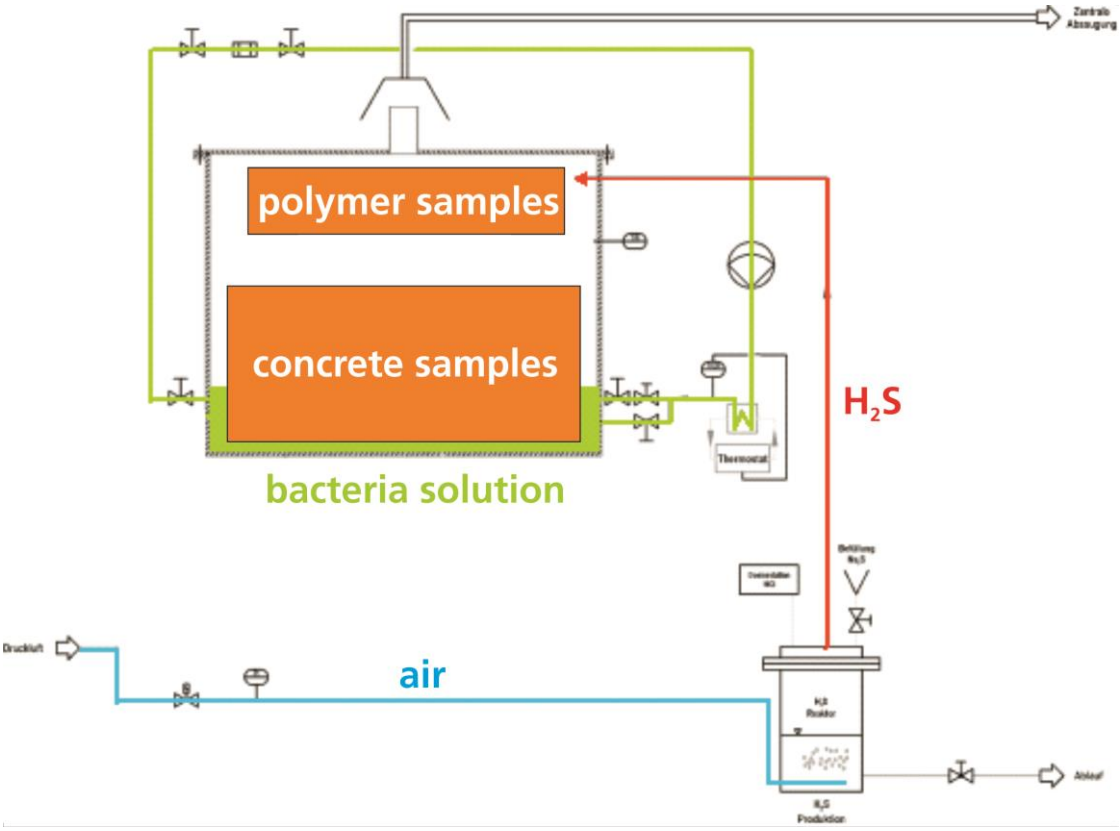
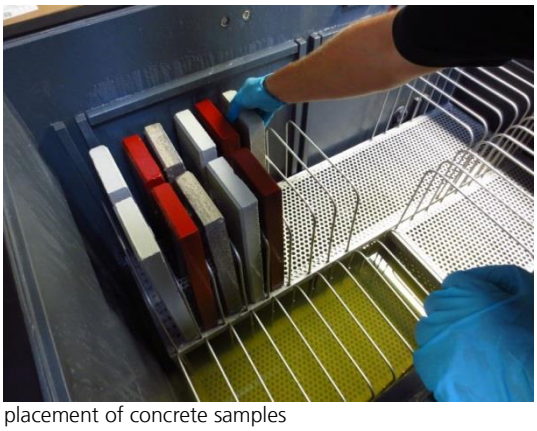


Fig. 3 Schematic flow diagram of the process.

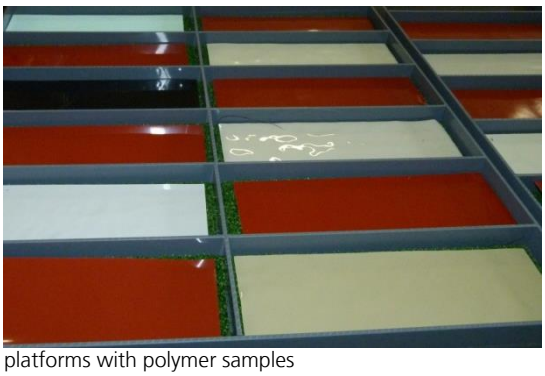
The concrete samples were placed in the bottom of the chamber using a rack made of stainless steel. In figure 4 the placement of the concrete samples is shown.

The polymer films were placed above the concrete samples in two racks 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.

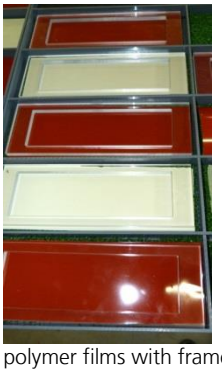


placement of concrete samples

concrete samples placed in chamber



platforms with polymer samples



polymer films with frames of carbonate

Fig. 4 Placement of concrete samples and polymer films.

The position of each sample in the chamber was documented and is listed in annex 1 concerning the concrete samples and annex 2 concerning the polymer films.

Concrete samples were subjected to two seperate cycles of weathering. The fist set of samples remained permanantly in the gas phase while a second set was cycled in and out of the bacteria solution on a weekly basis to simulate the effect of the varying water line in sewer environments.

3 Weathering test

3.1 Timetable and parameters

The wethering was carried out from 01.08.2013 to 12.02.2014. At 01.08.2014 the concrete samples and polymer films were placed in the chamber together with BASF using a defined nomenclature. On 13.11.2014 BASF inspected the test and documented the samples by taking photos. On 12.02.2014 the samples were taken out from the chamber together with BASF and given back to BASF.

The bacteria solution was heated up to 30 °C and the temperature was controlled during the test. The concentration of H_2S was between 30 und 60 ppm. Therefore H_2S is produced continously and fed in the test chamber every 10 minutes by a pressure impuls using air. The inoculations of the samples were carried out by hand using a spray pump and were started on 08.08.2014. The concrete samples were inoculated once a week for 4 weeks and the polymer films were inoculated once a week for 3 weeks.

The weathering test was accompanied by a microbiological analysis that was carried out by the University of Duisburg-Essen (Biofilm Centre, Prof. Wolfgang Sand) to confirm bacterial growth. The results are listed in table 2 and table 3.

Sample	**Chemoorganotrophic bacteria** [cfu/cm²]	**Fungi** [cfu/cm²]
MasterSeal 7000CR + primer	1E+03	u.d.
MasterSeal 7000CR	u.d.	u.d.
concrete no coating	3E+03	1E+02

Tab. 2: Cell numbers of chemoorganotrophic bacteria and microscopic fungi in [cfu/cm²], cfu= colony forming unit; u.d.= under the detection limit of 3 cells/cm², The tests for neutrophilic and acidophilic sulfur-oxidizers were qualitatively positive, but were not quantifiable due to less than 1 cell per mL (comparable with cm²).

Sample	Chemoorgano-trophic bacteria [cfu/cm²]	Fungi [cfu/cm²]	Neutrophilic sulfur-oxidizer [cells/ cm²]	Acidophilic sulfur-oxidizer [cells/ cm²]
MasterSeal 7000CR + primer	8E+02	2E+04	5E+01	3E+03
MasterSeal 7000CR (a)	3E+03	5E+03	3E+02	3E+02
MasterSeal 7000CR (b)	3E+03	1E+04	3E+02	3E+02
concrete no coating	3E+03	2E+03	3E+02	3E+03

Tab. 3: Overview results of sampling after 6 months of incubation in the Fraunhofer UMSICHT cabinet, cfu= colony forming unit; u.d.= under the detection limit of 3 cells/cm².

3.2 Measurement of pH-value

To determine the pH-values on surfaces of the pH strips were used. In the test period at 21 days measurements were carried out. The results are listed in figure 5.

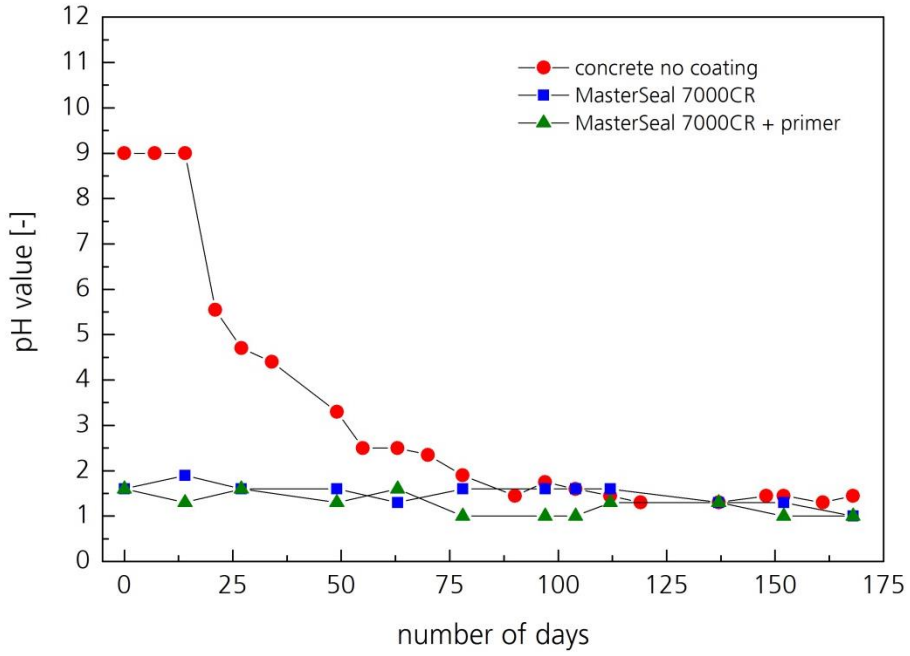


Fig. 5 pH-values of samples during the weathering test.

4 Annex

Annex 1 Results obtained after the weathering test.

5 Contact data

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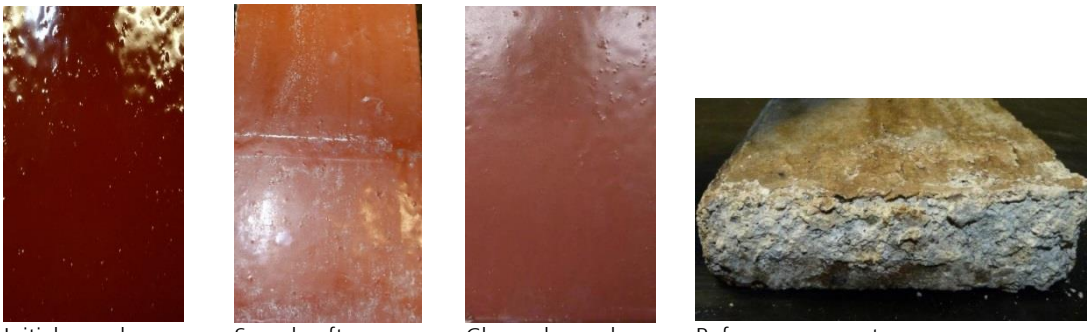
Annex 1

Results obtained after the weathering test. The tests were carried out by the Global Development Laboratories at BASF Construction Solutions GmbH, Trostberg.

This work was carried out additionally to the project by BASF and was on responsibility of BASF.

1. Images of MasterSeal 7000CR samples after testing



Initial sample | Sample after 6 months testing | Cleaned sample | Reference concrete

Fig. 1 Images of MasterSeal 7000CR samples after testing.

2. Adhesion testing in accordance with EN1542:1999

Fig. 2 Samples after adhesion testing.

All tests failed in concrete showing no reduction in adhesion and no attack of the concrete that was affecting adhesion.

3. Tensile strength and elongation in accordance with En ISO 527-1b:1996

The free film samples were tested for tensile strength and elongation in comparison with un weathered reference materials.

	Un weathered	Weathered
Tensile strength [MPa]	23.1	26.6
Elongation at break [%]	17.1	18.7

Results show no significant change in properties.

4. Vapour permeability in accordance with ASTM E96

	Un weathered	Weathered
Permeability [US Perms]	0.95	1.22
Permeability [ng/s/m/Pa]]	0.013	0.017

Results show no significant change in properties.