„MPA-Performance-Test“

Test method for determining the acid resistance of concrete or mineral systems

accredited according to
DIN EN ISO/IEC 17025:2018

The accreditation is valid for the attachment document D-PL-11217-01-01 listed test methods.

DAkkS Deutsche Akkreditierungsstelle

CONTENT

1 Acid resistance of concretes

1.1 General information and areas of application

Among others, the following applications require acid resistance of concretes:

Figure 1 Application areas – acid resistance of concretes

One of the main areas of application is wastewater treatment plants. Approximately one-fifth of the total of approx. 575,000 km of the public sewer network in Germany shows the damage that needs to be repaired in the short to medium term. A large number of damages are due to biogenic sulfuric acid corrosion (BSC) with a combined chemical-biological attack. The selection of suitable construction products, depending on the respective stress scenarios, is of particular importance. Descriptive building material models often reach their limits. This is especially true for projects where the performance of the products must be proven for maximum exposure scenarios and for life expectancies of up to 100 years or when the exposure class for a chemical attack is XA3 or even higher.

A variety of test methods can be used to evaluate the resistance, performance, and durability of the construction products to the above-mentioned stresses in the area of the BSK. Long-term tests or time-lapse tests in sulfuric acid with different pH values and stress scenarios are often used. The evaluation criteria are determined depending on the material and the respective test procedure.

The “MPA-Performance-Test” of Kiwa GmbH, MPA Berlin-Brandenburg, is a widely used test method in Europe for evaluating the acid resistance of concretes in wastewater treatment plants. This is a "normatively" regulated test method that is recorded in the European Technical Assessment Document EAD 180009-00-0704. Based on this document, European Technical Assessments (ETA's) are issued for acid-resistant concrete pipes in extension of DIN EN 1916:2003-04.

1.2 Major projects of Kiwa GmbH, MPA Berlin-Brandenburg

Kiwa GmbH is the leader in Germany in terms of testing, monitoring and certification services in the construction industry. With over 5,000 employees, Kiwa GmbH also has a leading position in Europe and worldwide. MPA Berlin-Brandenburg, as an institute of Kiwa, is specialized in testing, monitoring, and consulting services in the field of application of building materials in wastewater plants.

Kiwa GmbH, for example, has been involved in the planning of many major projects in this field over the past 20 years:

- The “MPA-Performance-Test” was also used in the Emscher project, the largest construction project in the field of wastewater facilities in Germany in the last 30 years (planned service life: 120 years, € 4.3 billion construction sum). We were involved in this project both as auditors and in an advisory capacity.
- The Deep Tunnel Sewerage System II (DTSS Phase II) construction project in Singapore is currently being monitored similarly.
- Other major projects were successfully implemented with the leading concrete manufacturers and operators of wastewater treatment plants (e.g., Berliner Wasserbetriebe, Port of Copenhagen HO- FOR), both in the in-site concrete and in the transport and precast concrete industry.
- The last eight cooling towers of large power plants were accompanied in terms of material technology and quality assurance, worldwide Kiwa GmbH is involved in the construction of these cooling towers, which have an acidic environment as a permanent exposure.
- During the renaturation of opencast lignite mines, a topical issue in Germany, countless investigations have been carried out. A concrete structure that comes into contact with acidic water of flooded open- cast mines has been designed, tested and implemented according to their planned service life.

In the context of such construction projects, far more than 300 concrete formulations have been included in the evaluation of durability. Countless long-term tests with almost all variations of binders are available to Kiwa GmbH, MPA Berlin-Brandenburg. The correlations between stress scenarios and the material-specific resistances have been worked out or scientifically researched.

2 "MPA-Performance-Test"

The "MPA-Performance-Test" is a procedure for testing increased resistance of mineral systems to chemicalattack (especially to acid) and is composed of:

- Acid test (part 1),
- Holistic approach - holistic description of performance (part 2),
- Lifetime assessment (part 3).

The test method is accredited according to DIN EN ISO/IEC 17025:2018 and defined within the framework of a European Technical Assessment (ETA) and thus also normatively regulated.

The principle of the **acid test (Part 1)** is based in its entirety on the general characterization of the impermeability of concrete as a material and the direct verification of resistance to attack by sulfuric acid. A major strength of the method is that the depth of damage to the concrete is made directly visible by microscopic methods and determined quantitatively in mm/stress period.

The method works with a constant pH value (pH-stat). Since a high-performance concrete was used as a reference concrete for comparison purposes in all tests, Kiwa also provides directly comparable data for the different pH values. The reference concrete is concrete with the highest possible acid resistance.

The **acid test (part 1)** in the "MPA-Performance-Test" provides for 12 weeks of exposure to sulfuric acid at pH = 3.5. Only by means of suitable optical microscopy< / polarization microscopy or scanning electron microscopy on thin sections is it possible to determine the depth of damage after the end of the exposure.Concretes in general that are damaged by acid develop two damage fronts over time, which are shown in figure 2. The total damage depth results from the removal depth determined on the ground section and the damage depth determined by polarized light microscopy or scanning electron microscopy.

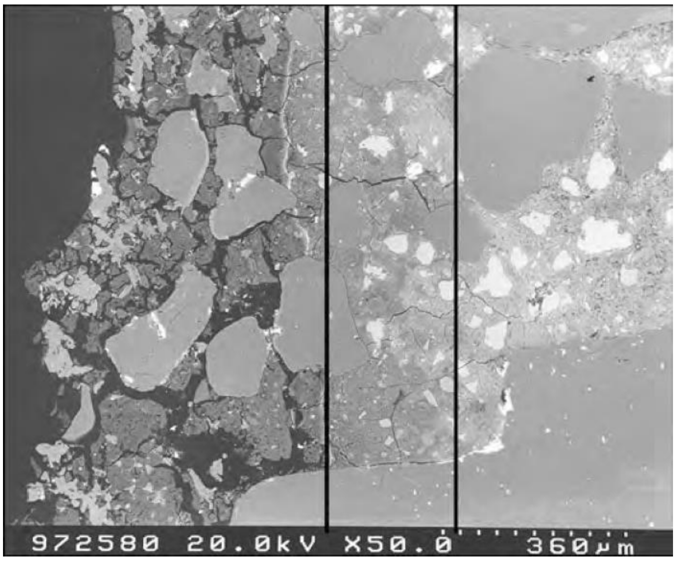

Figure 2 First and second damage front (SEM image on thin section).

The pH value of 3.5 has been introduced in Germany for the proof of optimal acid resistance of concrete and can be found in the requirements of the Additional Technical Terms of Contract (ZTV) for concretes with increased acid resistance, e.g., of the water associations *Emscher Genossenschaft* or *Berliner Wasserbetriebe*, the *Lausitzer und Mitteldeutsche Bergbau-Verwaltungsgesellschaft* (LMBV) or the *Verband der Großkraftwerksbetreiber* (VGB).

Experience shows that even high-performance concretes optimized for chemical resistance are exposed to a disproportionate increase in weathering below pH 3.5. Lower pH values (especially < 2.5) tend to level out existing resistance differences between test concretes, i.e., quality differences can no longer be differentiated so sharply.

The advantage of the method is the good reproducibility of the measurement results. The measurement series of the reference concrete make this clear:

- Mean depth of damage: 1.14 mm
- Standard deviation: 0.09 mm (CV = 8 %)

The testing part of the **holistic approach (part 2)** also provides a holistic description of the performance of the concrete; among other things, the "matrix quality" of the formulations is determined here. Matrix quality refers to the freedom from microcracks of the binder matrix, which has a decisive influence on long-term durability. The determination of the freedom from microcracking is carried out by determining the frost (de-icing salt) resistance as an auxiliary variable. In each case, the tests must comply with limit values that a concrete mix design must meet in its entirety without exception to be considered a mix design of the highest durability and impermeability. The sulphate resistance (test duration: 91 days) and the chloride penetration resistance (test duration depending on the impermeability of the microstructure) are also an- alysed as fingerprints for describing the performance of the concrete in the holistic approach.

The tests must comply with the limit values that a concrete mix design must meet in its entirety without exception to be considered a mix design of the highest durability and impermeability.

Based on the results of the MPA performance test, a **lifetime assessment (Part 3)** can be carried out according to a probabilistic approach, for example, if the performance of the products has to be proven by testing for maximum stress scenarios and life expectancies of up to 100 years. In this way, maintenance work can be reliably planned in the long term and downtimes can be reduced.

2.1 Specimen / Specimen fabrication

Cubes (150 x 150 x 150) mm³ aged 56 days are used for the tests. The number of specimens required for each test method is listed in Table 1.

Table 1 Tests and number of cubes required

Testing		Number of cubes
Acid-Testing (part 1)	Acid resistance after storage for 12 weeks at pH = 3.5	5
Holistic Approach (part 2)	Total porosity and pore radius distribution	1
	Residual alkalinity	1
	Chloride migration	3
	Test for absence of microcracks via determination of freeze-thaw and de-icing salt resistance(CDF)	5
	Sulphate resistance	*
Total		15 Cube (edge length= 150 mm)

*) For the determination of the sulphate resistance of the binder
Flat prisms (160x40x10) mm³ are produced according to DIN EN 196-1 (w/c = 0.5).

The approach, as well as the test conditions for part 1 (acid test) and part 2 (holistic approach) in the "MPA-Performance-Test", are described below.

2.2 Acid test (part 1)

As test specimens for the determination of the acid resistance via the microscopic determination of the total damage depth, plates with dimensions of (100 x 150 x 40 mm³) are sawed out from the concrete cubes with an edge length of 150 mm using diamond technology. The exact dimensions are recorded with the caliper gauge before storage to be able to determine the exact material removal after acid exposure. Four plates are used for acid storage. Furthermore, two similar slabs are stored in tap water. A control concrete mix of known damage depth is tested.

The further steps of the preparation are summarized in the following:

1. measuring and weighing the test specimens as received,
2. water saturation of the test specimens over three days and subsequent weighing,
3. placing in the racks (e.g., made of PE-HD),
4. placing the racks in the containers with acid in the order of numbering,
5. set the controller for continuous electrometric checking of the pH value.

The test facility for determining acid resistance consists of an acid-resistant container with a volume of at least 45 l and a reservoir tank with a volume of at least 80 l (see figure 3). The acid is constantly circulated by a centrifugal pump and homogeneously distributed in the container via nozzles distributed at regular intervals in the container. To compensate for possible inhomogeneities between the containers, the samples are transferred within the containers at weekly intervals.

Figure 3 **Test facility for storing the specimens in acid**

Acid resistance is determined by storage in sulfuric acid at pH = 3.5 for 12 weeks. The pH value is continuously monitored; if the pH value increases, sulfuric acid is immediately added. Every two weeks, the entire sulfuric acid is replaced, including readjustment of the pH value.

After one week, any growth on half of the test specimens is removed under running water with a brush under slight pressure. The remaining test specimens of a formulation are briefly rinsed with water without pressure and then carefully dabbed dry with a cloth. After the drying step, the mass of the test specimens is determined by weighing.

Finally, stereomicroscopy and polarization microscopy are used to determine the removal rate and the damage depth of the specimens with the simulation of an additional abrasive attack. The optically detectable maximum concrete erosion of the respective acid-bearing concrete mix (binder matrix) is first determined with the aid of stereomicroscopy on polished sections. For this purpose, a segment of approx. 4 cm x 5 cm is cut off from one specimen (brushed specimens in each case) of the concrete mixtures by precision cutting with a diamond disk. Each of the six ground segments produced in this way is thus stressed or tested both from the upper side of the specimen and from two narrow sides (see figure 4).

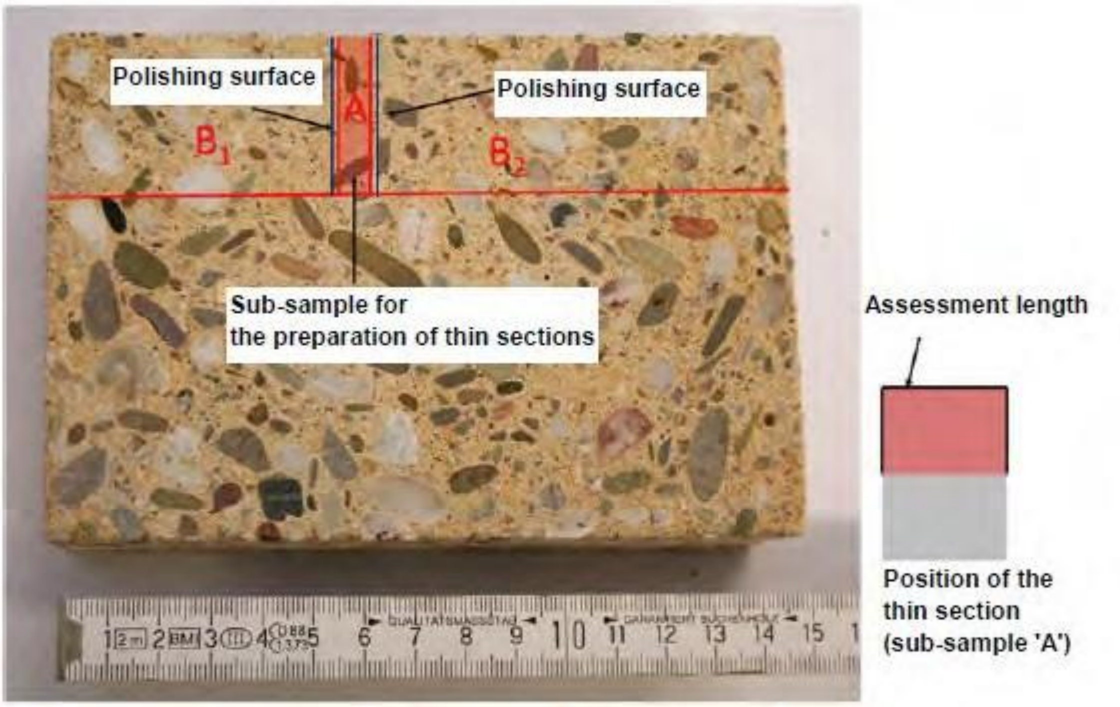

Figure 4 **Schematic representation of how the specimens are obtained for the thin sections (A) andthe ground sections (B1 and B2)**

While stereomicroscopy reveals the maximum depth of erosion, only the examination of the concrete thin sections with the aid of a polarized light microscope or a scanning electron microscope reveals the exact type and depth of damage (see figure 2). The respective thin sections are produced, for example, in an area of approx. 2 cm x 4 cm with a thickness of 30 µm and evaluated in the transmitted light method with darkfield illumination in polarized light.

The total damage depth, which is composed of the removal depth determined on the ground joint and the damage depth determined by polarized ion microscopy, must be less than 1.3 mm.

2.3 Holistic approach (Part 2)

2.3.1 Total porosity and pore radius distribution

The porosity is decisive for the impermeability of the concrete to dissolved pollutants. The total porosity of the concretes used is determined from the raw and solid densities, the determination of cumulative pore volume of the concretes used and the pore size distribution in the pore range < 100 µm (0.1 mm) by means of mercury pressure porosimetry.

The total porosity is determined according to DIN EN 1936:2007-02 and must be less than 11 % by volume. The cumulative pore volume of the concrete in the pore range < 100 µm (0.1 mm) is determined bymercury pressure porosimetry according to DIN 66133:1993-06 and must be smaller than 40 mm³/g. In addition, the mean pore volume must be less than 0.1 µm.

2.3.2 Chloride migration coefficient

For the investigation, the chloride migration method is used as described by Tang[1] und Schießl[2] or in the BAW Code of Practice "Chloride Penetration Resistance of Concrete" by the Federal Waterways Engineering and Research Institute (BAW) (see figure 5).

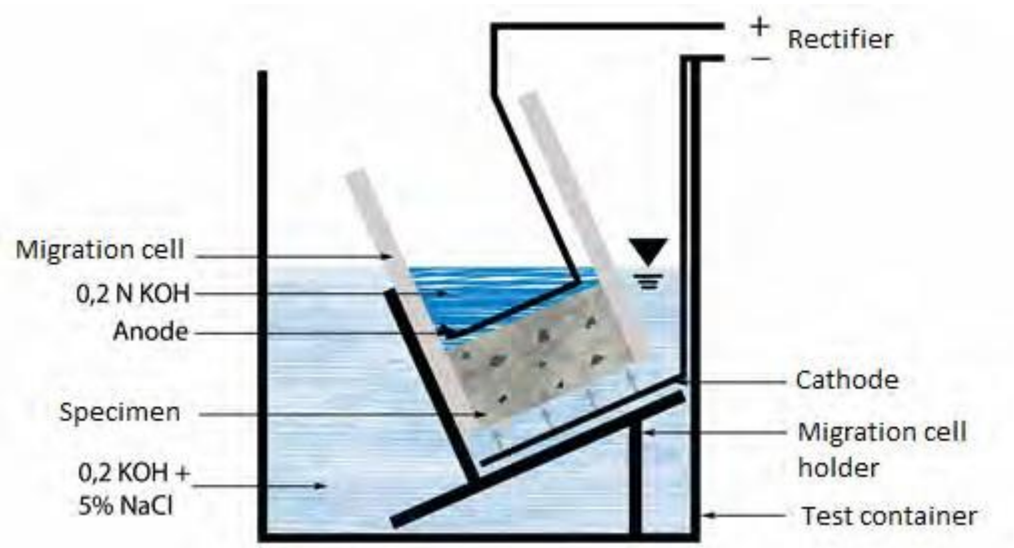

Figure 5 **Schematic diagram of the measurement setup (taken from the working instruction Quick determination of chloride diffusion coefficients for concrete test specimens, ibac) and photo of the measuring cell with power supply unit and distributor box.**

The principle of the method is based on the acceleration of ion transport by applying a DC electrical voltage (migration). The cathode chamber contains a chloride solution from which the chloride ions migrate into the concrete to be tested under the effect of the applied voltage. The migration rate depends, among other things, on the applied voltage, the chloride ion concentration, the dimensions of the test specimens, the temperature and, as an essential variable to be evaluated, the diffusion resistance of the concrete used.

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[1] Tang, L.; Nilsson, L.-O.: Chloride Binding Capacity, Penetration and Pore Structures of Blended Cement Pastes wtih Slag and Fly Ash. London: Elsevier Applied Science, 1991. - In: International Conference on Blended Cements in Construction, held at the University of Sheffield, 9-12 September 1991; Ed.: Swamy, R. N.

[2] Schießl, P., Wiens, U.: Neue Erkenntnisse zum Einfluß von Steinkohlenflugasche auf die chlorinduzierte Korrosion von Stahl in Beton. In: ibausil Tagungsbericht - Band 1; Hrsg.: F. A. Finger-Institut für Baustoffkunde, Stark, J.

The migration times, initial and final voltage and current at the individual measuring cells, the temperatures of the solutions and the penetration depth of the chloride front are measured at a total of 12 points on the two halves of the core.

The chloride front is detected after exposure by spraying with fluorescein and silver nitrate solution. Under the effect of UV light, a sharp migration front is formed, recognizable by its pink, violet colour. The chloride migration coefficient determined in this way must be less than 1.0 * 10-12 mm²/s.

2.3.3 Sulfate resistance

The sulfate resistance of the binder composition used is tested after 91 days on mortar flat prisms with the dimensions (10 x 40 x 160) mm³ of the planned binder composition, standard mortar and a w/zeq value of 0.5 using the SVA method [3].

1. Production of flat mortar prisms according to DIN EN 196-1:2016-01, w/c = 0.5
2. Storage in the mold for two days in a humid environment, after removal from the mold further storage in a saturated $Ca(OH)_2$ solution for another 12 days // Two days of moist storage in the mould, after demoulding a further 12 days of storage in a saturated $Ca(OH)_2$ solution.
3. Storage in 4.4% Na2SO4 solution at 20 °C or in saturated $Ca(OH)_2$ solution as comparative storage. The solutions are renewed monthly.
4. Assessment of the sulfate resistance based on the strain difference ($\Delta\varepsilon \leq 0.5$) after 91 days.

2.3.4 Testing the absence of microcracks by determining the resistance to freezing and deicingsalt (CDF)

The test of microcrack resistance of the binder matrix is performed by determining the freeze-thaw resistance of the concretes used, following CEN/TS 12390-9:2017-05 with 56 freeze-thaw cycles. In addition, the test specimens are not manufactured with Teflon inserts but are cut out (halved) from cubes with the dimensions (150 x 150 x 150) mm³ in the middle, so that the concrete matrix and not the formed surface is tested.

The test procedure includes the following three steps:

1. Dry storage,
2. Pre saturation due to capillary action,
3. Freeze-thaw change with a de-icing salt attack (56 freeze-thaw changes).

Before starting the freeze-thaw cycles, loosely adhering particles and dirt are removed from the test surface of the specimens by treatment in an ultrasonic bath as described in Figure 6.

3 Deutsches Institut für Bautechnik: Prüfplan für die Zulassungsprüfung eines von DIN 1045 abweichenden Betons mit hohem Sulfatwiderstand, DIBt, Berlin, Februar 1998

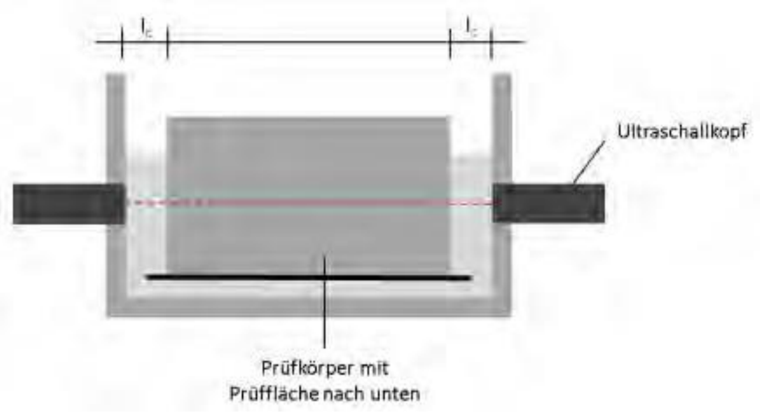

Figure 6 **Messaufbau zur Bestimmung der Ultraschalllaufzeit**

The fluid absorption, weathering and dynamic modulus of elasticity are determined after 0, 8, 14, 28, 42, 50 and 56 freeze-thaw cycles. The test liquid is a de-icing salt solution consisting of 97 wt.% demineralized water and 3 wt.% NaCl.

After 56 cycles, the weathering must be less than 1,500 g/m² and the drop in dynamic modulus of elasticity must not be more than 40 % compared to the initial condition.

2.3.5 Residual alkalinity related to the binder content

The determination of the residual $Ca(OH)_2$ content of the concretes used to check the corrosion protection of the steel reinforcement is carried out by thermogravimetry following DIN EN ISO 11358-1:2014-10.

The residual $Ca(OH)_2$ content in the concrete is determined after 91 days of hydration. For the test, a test cube is crushed under the hydraulic press and material is removed from the center of the cube. The removed concrete is crushed, triturated twice with 25 ml of isopropanol each in a mortar, the isopropanol is filtered off through a frit and then washed with 25 ml of acetone in two parts. The sample is then dried at max. 40 °C for one hour and stored in a desiccator over sodium hydroxide solution (CO_2 free) until analysis.

The $Ca(OH)_2$ content is then determined thermogravimetrically on the "stopped" sample. Approx. 0.5 g of the sample material is placed in the thermobalance and subjected to a temperature program from 25 °C to 900 °C with a heating rate of 5 K/min. The mass loss of the mass removal step at 450 °C, which is assigned to the dehydration of the $Ca(OH)_2$, is evaluated. From the mass loss, the $Ca(OH)_2$ content is calculated back stoichiometrically.

The residual $Ca(OH)_2$ content relative to the binder content must be at least 3 wt.%.

2.4 Lifetime assessment (part 3).

As part of a research project funded by RWE, the acid resistance of concrete with increased acid resistance was tested at different pH values (2.5 / 3.5 / 4.5) over 12 months. The erosion and damage depths of the test specimens determined with the aid of a stereo and polarisation microscope are shown in Figure 7.

The difference between pH 4.5 and pH 3.5 is small compared to the high difference between pH 3.5 and pH 2.5. These results again prove the above-mentioned critical value of pH 3.5 for concrete with increased acid resistance.

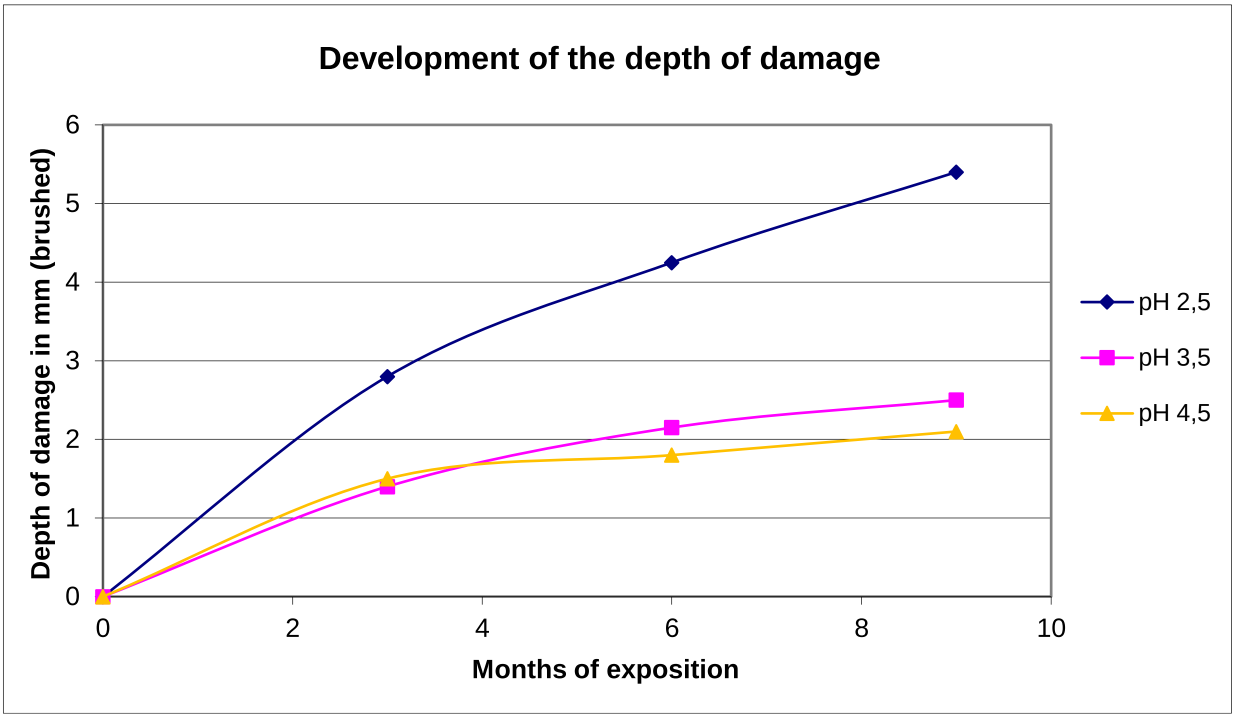

Figure 7 **Erosion and damage depths of concrete with increased acid resistance depending on the duration of exposure**

The erosion and damage depths can be characterised with good approximation by a square root from the time equation. Thus, the depth of thr damage can be calculated and evaluated as a function of pH and time, as explained below by way of example for pH 4.5:

Curvature fitting, e.g. for pH 4.5 gives:
$d=0.5348\sqrt{t}+0.0414$
d: depth of damage, t: Time in months

For t = 1200 months (100 years):
$d = 0.5348 \sqrt{1200} + 0.0414 = 18.6$ mm

d = 18.6 mm < 25 mm = cnom

The results of long-term tests already carried out are consistent with practical experience: Concrete specimens stressed with low pH values in a Berlin wastewater pumping station show comparable erosion and damage depths. The results of the specimens tested in our "MIC-Performance-Test" (previously called ODOCO-Pilot-Plant) also correspond to the calculated erosion and damage depths of the long-term test.

3 Summary

The "MPA-Performance-Test" was designed for testing high-performance concretes (including concrete with increased acid resistance), but also for testing other mineral systems. The procedure is accredited according to DIN EN ISO/IEC 17025:2018 and defined within the framework of a European Technical Assessment (ETA) and thus also "normatively" regulated. The test method has been used in countless construction projects for the best possible evaluation of concrete formulations.

The „MPA-Performance-Test" is divided into three parts, as follows:

- Part 1 Acid test (storage at pH = 3.5 for 12 weeks),
- Part 2 Holistic approach (holistic description of the performance),
- Part 3 Lifetime assessment (probabilistic approach).

The tests must comply with the limit values that a concrete mix design must meet in its entirety without exception to be considered a mix design of the highest durability and impermeability. The limit values are described in the respective test sections in chapter 3 and summarized in the following Table 2 as follows:

Table 2 Test methods and limit values for the determination of a concrete formulation highest possible durability and impermeability

Test method	Requirements (limit values)
Evaluation by depth of damage	≤ 1,3 mm
Test to evaluate the microcracking tendency via determination of the freeze-thaw resistance (CDF) after 56 cycles.	Reduction of the modulus of elasticity: 40%. Mass loss: 1,500 g/m²
Sulfate resistance via the SVA process	< 0,5 mm/m
Total porosity	< 11 Vol.-%
Cumulative pore volume in the range < 110 µm Average pore radius	< 40 mm³/g < 0,1 µm
Chloride migration coefficient	$< 1,0*10^{-12}$ mm²/s
Residual alkalinity, based on the binder	> 3 g $Ca(OH)_2$/100 g Bindemittel

The requirements (limit values) are specified in the Additional Technical Terms of Contract (ZTV) for concretes with increased acid resistance, e.g., by the Emscher Genossenschaft water board or the Berliner Wasserbetriebe, the Lausitzer und Mitteldeutsche Bergbau-Verwaltungsgesellschaft (LMBV) or the Association of Large Power Plant Operators (VGBPowerTech) specified.

For the overall "MPA-Performance-Test", a processing time of max. five months (incl. documentation) can be assumed after receipt of the sample in our laboratory.

Literature

1 Rieck, C.; Hüttl, R.: Beton mit erhöhtem Säurewiderstand für Rohre und Schächte – Prüfung, Entwicklung und Anwendung – BWI BetonWerk International, 2011

2 Röben, R.; Hüttl, R.; Waschnewski, J: Beständigkeitsuntersuchungen von Betonen für Abwasserrohre und -schächte. BWI – BetonWerk International, issue 5, 2014; pp. 12-15.

3 Rieck, C.; Hüttl, R.: Concrete with increased acid resistance for pipes and manholes – testing, development and application. CPI – Concrete Plant International, issue 3, 2011; pp. 138-144.

4 Bergmeister K., Wörner J.D.: Beton Kalender 2006, 2006, pp. 521 – 534

5 Rieck, C.; Hüttl, R.; Busch, D.: Quality Assurance and Durability of Concrete with Increased Acid Resistance for Cooling Towers. Proceedings of the International Association for Shell and Spatial Structures (IASS) Symposium 2013. 23. bis 27. September 2013, Wroclaw University of Technology. Tagungsband herausgegeben von Obrębski, J.B. und Tarczewski, R.

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