OPTIMIZING THE ACID RESISTANCE OF CONCRETE WITH GRANULATED BLAST-FURNACE SLAG

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ABSTRACT. Concrete structures exposed to high levels of chemical attacks are assigned to exposure class XA3, which recommends separate concrete protection or a special expert solution to ensure durability. Due to the partial substitution of Portland cement by blast-furnace slag, an increased resistance to acid attacks could be achieved within the framework of a research project. The technical and ecological advantages of cements containing granulated blast-furnace slag were exploited through chemical, granulometric and concrete technological optimizations. Despite extensive parameters, a statistical test design (DoE) was able to limit the experimental effort, thus defining principles for the conception of binder systems with increased chemical resistance. Mortar prisms indicated that the use of (ultramine) blast-furnace slags (up to 13,000 cm²/g according to Blaine) with a broad particle size distribution can have a positive effect both on the capillary/gel pore ratio and on the calcium hydroxide content in the cement stone. Furthermore, the chemical composition of the blast-furnace slag as well as the water-binder ratio are decisive influencing factors for the acid-resistance, which was confirmed in accelerated acid resistance tests on concretes (pH-stat method). After 13 weeks of storing concrete specimens in sulfuric acid (H₂SO₄, pH 3.5), reduced damage depths and lower weight losses were observed compared to conventional binder compositions. The results serve as a basis for the development of highly acid-resistant concretes using blast-furnace slag-containing binder systems. Currently, the acid resistance of those concretes is being investigated in a long-term study by outsourcing representative test specimens into the Emscher sewer.

KEYWORDS: Blast-furnace slag, concrete, durability, sulfuric acid.

1. INTRODUCTION

Concrete structures in agriculture as well as in industrial and wastewater engineering plants may be exposed to various types of chemical attacks. Even though concrete is known for its high durability, the material is susceptible to acid attacks [1, 2]. Acidic media can diffuse through the porous binder matrix and dissolve it. To increase the acid resistance of the binder, priority is given to reducing the porosity. This is done on the one hand by the choice of a low w/b-ratio and on the other hand using an optimized grain size distribution up to the finest aggregates. For a complete hydration of cement, a w/b-ratio of about 0.4 is required. The larger amount of water is chemically bound in the calcium silicate hydrates (CSH), a minor part remains in the gel pores < 30 nm. With increasing w/b-ratio, more and more capillary pores are formed, causing a connected network of capillary pores at a w/b-ratio of approx. 0.60 [2, 3]. Especially the usage of ordinary Portland cement (OPC) lowers the resistance of concrete towards acidic attack because it releases readily soluble calcium hydroxide (Ca(OH)₂) and large portlandite crystals while hydration [4]. The Ca(OH)₂ preferably develops where water is located as well as on the surface of the aggregates [5], which results in a three-dimensional interconnected structure of Ca(OH)₂ [6]. The substitution of OPC by granulated blast-furnace slag (GGBFS) reduces those effects due to a reaction of the GGBFS with the surplus Ca(OH)₂ forming further CSH. In addition, these CSH are less soluble because of an increased silicate amount and the porosity of the binder matrix decreases which thus, obstruct harmful media from penetration into the material [5, 6]. The main objective of the research project is to optimize the acid resistance of commonly used concretes while at the same time maintaining good workability with the greatest possible avoidance of costly additives. The potential of GGBFS to strengthen the acid resistance is being evaluated by means of a comprehensive research programme involving a wide range of parameters.

2. RESEARCH PROGRAM

2.1. BINDER OPTIMIZATION

Due The research program was divided into two parts. In a first step, the binder was optimized on a mortar scale before a series of binder com-
positions, based on the results of the mortar tests, got examined with coarse grain on a concrete scale. To evaluate a wide range of GGBFS, three granulated blast-furnace slags with different reactivities were considered. The reactivity is defined as the ratio of calcium and magnesium to silicon ((C+M)/Si)). Before the blast-furnace slag was used to produce concrete, it has been grounded into four degrees of fineness, resulting in two GGBFS (4,200 cm²/g and 7,000 cm²/g) and two fine GGBFS (10,000 cm²/g and 13,000 cm²/g). To investigate the characteristic values for the acid resistance, the w/b-ratio was varied between 0.30 and 0.44 and the percentages of OPC and GGBFS got amended.

Due to the huge quantity of parameters, a statistical Design of Experiments (DoE) with 45 different binder compositions was able to limit the experimental effort, thus defining principles for the conception of binder systems with increased chemical resistance. The testing area of the DoE is shown in Figure 1.

2.2. ACID RESISTANCE TEST SETUP

The acid resistance of the concretes was tested in an acid test rig, which is based on the pH-Stat method according to the MPA-Berlin-Brandenburg testing procedure [7]. The test stand consists of a reservoir, which is connected to multiple storage tanks via acid-resistant hoses. The reservoir features a magnetic stirrer as well as a titrator and a pH-electrode, which continuously measures the oxonium ion concentration of the test medium. Sulfuric acid (H₂SO₄) has been used as the test medium, which was constantly maintained at a pH value of 3.5 ± 0.05 (automatic endpoint titration). When the pH-value of the sulfuric acid exceeded an equivalence point, concentrated sulfuric acid (H₂SO₄, 2.0 molar) was automatically titrated and distributed by the magnetic stirrer. In order to prevent a high concentration of dissolved substances in the storage tanks, the sulfuric acid was also completely replaced every 14 days. The sulfuric acid was transported via pumps with a flow rate of approx. 15 dm³/h into the storage tanks, which always contained at least 34 litres of acid. Via a built-in overflow, the test medium is returned to the reservoir. The overall structure of the acid test rig is shown schematically in Figure 2.

The test specimens were stored for 91 days in the storage tanks of the acid test rig starting at a preliminary age of 28 days as shown in Figure 3. The mass of the specimens was determined every two weeks in the process of the acid exchange. Figure 4 shows two mortar specimen after 91 days of storage, one in water and the other one in sulfuric acid with a pH-value of 3.5.

2.3. CONCRETE SCALE

After the binder optimization with mortar prisms, the acid resistance was tested on concrete specimens with optimized binder compositions in sulfuric acid. Again, use was made of the DoE with a statistical evaluation. For an optimal grain size distribu-
Concrete Acid Resistance Optimization

The fuller principle with a maximum aggregate size of 16 mm was applied to achieve a high packing density [8]. The concrete specimens were cut out of cubes with 150 mm edge length as shown in Figure 5. Figure 6 shows a cuboid-shaped concrete specimen (150 mm × 100 mm × 50 mm) with a high packing density of the coarse grain after preparation for the acid resistance test.

The experimental programme for the acid tests consisted of 14 binder compositions were multiple parameters got changed to each other. The results were evaluated in comparison to reference samples with CEM I 42.5 R and CEM III/B 42.5 N-LH/SR/NA. To quantify the acid attack, the depth of damage to the specimens was determined three times (after 28, 56 and 91 days) under a stereo microscope during the 91-day acid storage period. To determine the depth of damage, two different specimens were split off. The fresh fracture surfaces were sprayed with an indicator (1% phenolphthalein solution) and evaluated microscopically. The area with a pH value of 0 to 8.2 and above a pH value of 13 remains colourless, while the area between 8.2 and 13 turns pink-violet. Figure 7 shows an example of a fresh fracture surface after spraying on the phenolphthalein solution.

The depth of damage was determined at each fragment at four equally spaced measuring points, each with 4 individual measurements (see Figure 7). The average damage depth was then calculated from two different fragments (thus 32 individual values). Figure 8 shows one of those microscopic images of the acid-exposed concrete edge zone of a test specimen after 91 days of acid storage. To establish a reference line for the measurement, the acid-resistant aggregates lying on the concrete surface were used as reference point.

3. RESULTS

3.1. Binder Optimization

A statistical evaluation of the test results was used to determine the influencing parameters that significantly affect the respective target values. The specimens were tested for capillary porosity, compressive strength after 7 and 28 days and for their Ca(OH)₂ content. As shown in Figure 9, not only the w/b ratio but also the fineness of the binder (specific surface) decreases the capillary porosity of the specimens.

Regarding this and the results of the other target values, 15 binder compositions with a high potential...
of an increased acid resistance were chosen for acid-tests in order to evaluate the correlation between the binder granulometry and the acid resistance of the mortars. Figure 10 shows the location of the optimized binder compositions in the defined testing area.

3.2. CONCRETE TESTS

After the acid resistance tests, mathematical models have been created which allow the target values to be forecast within the selected system boundaries. The models were subsequently verified by separate experiments that were not part of the original experimental design.

These models provided the basis to create further optimized binder compositions for the tests with concrete specimen. Given the variation of multiple parameters of the test series, the evaluation is carried out by a statistical test assessment. Figure 11 shows the output of the analysis by means of a contour chart. The chart consists of the calculated estimated damage depth after 91 days of storage in sulfuric acid, regarding the w/b ratio, the reactivity of the GGBFS and the parameter ‘n’, which represents the RRSB slope according to DIN 66145 [9] to embody the particle size distribution (PSD) of the finest particles.

The contour chart shows that all three parameters have a massive impact on the acid resistance. In order to design an acid-resistant concrete, high reactivity should already be taken into account when choosing the blast-furnace slag. Comparing the two diagrams, damage depth under 500 µm can only be achieved with a high (C+M)/S ratio of 1.45. The PSD in the finest particle range is also of great importance. The modification from a narrow PSD (n = 1.25) to a broad PSD (n = 0.95) is about as effective as adjusting the w/b ratio from 0.4 to 0.3.

4. CONCLUSION

The main objective of the research project was to achieve the highest possible resistance of mortars or concretes against sulfuric acid attack in combination with sufficient strength development and suitable workability by using (ultra-fine) granulated blast furnace slag in the binder. It has been shown that a high (ultra-fine) granulated blast furnace slag content and a broad PSD down to the finest particle size has a favourable effect both on the capillary/gel pore ratio and on the calcium hydroxide content in the hardened cement paste.
The results presented serve as a basis for the design of highly acid-resistant concretes. The optimized concrete compositions developed in this project were able to undercut the damage depths of concretes currently regarded as extremely acid-resistant by more than 50%. It is shown that the choice of material and the preparation of the granulated blast furnace slag play a decisive role when it comes to the acid resistance of concrete.

ACKNOWLEDGEMENTS

The IGF-Project 18949 N / 2 of the Steel Institute VDEh research association was funded by the Federal Ministry for Economic Affairs and Energy on the basis of a decision by the German Bundestag as part of the program to promote Industrial Collective Research (IGF).

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