Optimizing the Acid Resistance of Concrete with Granulated Blast-Furnace Slag

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Abstract. Concrete for agricultural or industrial applications is often subject to intense acid attack. Most affected structures are sewage structures and biogas plants, natural draught cooling towers or silage silos. Widely independent from acid type, in most cases the acid attack on concrete runs the same way, starting with dissolution of easily soluble calcareous phases like calcium hydroxide. With ongoing attack, calcium-silicate-hydrate crystals (CSH) are also affected by acidic media. In contrast, siliceous phases like silicon-dioxide (SiO₂) are widely unaffected by acid attack. While the dissolution of the matrix is increasing with ongoing attack, quartzitic aggregates remain unchanged. Beside the use of coarse SiO₂-aggregates, the resistance against acid attack is mainly increased by a minimization of the porosity. For this purpose on one hand, a low water/cement-ratio has to be sought, on the other hand also the fines should be distributed with an optimized grading curve (e.g. Fuller-principle). In practice, this results in a combination of various fine and ultra-fine components, e.g. fly ash, GGBS, silica fume or metakaolin. Such binder compositions lead to a particularly dense microstructure, especially at pore sizes below 1 micron, and a higher chemical resistance due to a lower Ca(OH)₂ content. This paper gives an overview on typical acid-resistant concretes, most common applications as well as the effects of the related acid attack and points out the potential of granulated blast furnace slag addition to such concretes.

1 Introduction

In agriculture as well as in industrial and wastewater engineering plants, concrete structures may be exposed to various chemical attacks. One type of these attacks is based on the action of strong acids. For example, natural draught cooling towers with exhaust gases from flue gas desulphurisation and denitrification systems are subject to sulfuric and nitric acid attack. Furthermore, biogas and sewage plants can be exposed to a sulfuric acid and in silos used for agriculture acetic and lactic acid can be formed. To increase the resistance of concretes, 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 by the use of an optimized grain size distribution up to the finest aggregates. For a complete hydration of cement, a w/b-ratio of about 0.40 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 [1-4].

Another possibility besides reducing the w/b-ratio to reduce the permeability of concrete is the use of an optimized grain size distribution for the aggregate up to the finest parts and also for the binder according to the Fuller or other principles [4-6]. The individual grain fractions are composed in such a way, that the finer fractions fill the interstices of the larger ones. In addition, the porosity at the aggregate surface decreases due to a reduced distance of the finer grain fractions and the binder to the aggregate [7].

In addition to the optimization of the physical resistance, it is necessary to increase the chemical resistance of the binder matrix. Regardless of the type of acid, the dissolution of calcium hydroxide (Ca(OH)₂) is the first step in an acid attack, starting at a pH of 12.5. With decreasing pH further phases dissolve, such as aluminate hydrates, ettringite, monosulfate and finally

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the calcium silicate hydrates (CSH) [8]. The $\text{Ca}(\text{OH})_2$ forms preferentially at the areas where the water was previously located as well as at the surface of the aggregate [9]. This results in a three-dimensional interconnected structure of $\text{Ca}(\text{OH})_2$ in ordinary Portland cement (OPC). Under acid attack, the $\text{Ca}(\text{OH})_2$ is dissolved and the attacking medium can penetrate deeper into the concrete along these channels [10]. If a part of the OPC is replaced by latent hydraulic or pozzolanic additives, less OPC is available to form $\text{Ca}(\text{OH})_2$. This causes, depending on the proportion of the replacing additive, an interruption of the three-dimensional $\text{Ca}(\text{OH})_2$ microstructure. Furthermore, in latent hydraulic and pozzolanic reactions, $\text{Ca}(\text{OH})_2$ is consumed as an exciter and incorporated into newly forming CSH, which further reduces porosity. These CSH also have a lower calcium / silicon ratio (C/S) than OPC [8, 9]. As the C/S decreases, the pH required to dissolve the CSH also decreases. CSH-phases with a low C/S-ratio resist acid attacks longer than CSH with a high C/S-ratio. The C/S-ratio of OPC is > 1.5 , that of ground granulated blast furnace slag (GGBS) containing CSH ≈ 1.0 [11].

2 Methods

2.1 Materials

To optimize the acid resistance, the binder composition was initially investigated on a mortar scale. Three different granulated blast furnace slags were used for the investigations. Due to their reactivity, these GGBS can be divided into "slow" (A), "medium" (B) and "fast" (C) reacting. A characteristic value for the reactivity is the basicity. However, other chemical constituents and the glass content have an influence on the reactivity, too. With increasing SiO_2 content, the reactivity decreases, as well as with a TiO_2 content above 1.0 w.-% and a MnO content above 2.0 w.-%. An increasing proportion of CaO , MgO and alkalis increases the reactivity. A high proportion of Al_2O_3 also has a positive effect if the SiO_2 content is not too high [12-14]. Table 1 shows the chemical composition of the three GGBS.

Table 1. Chemical composition of the GGBS (w.-%).

GGBS	A	B	C
SiO_2	38.7	38.95	33.3
Al_2O_3	10.9	10.1	15.1
FeO	0.32	0.37	0.35
TiO_2	0.60	0.55	1.33
MnO	1.67	0.30	0.45
CaO	35.6	42.4	38.8
MgO	10.1	5.13	9.61
$\text{Na}_2\text{O-eq}$	1.29	0.62	0.83
(C+M)/S	1.18	1.22	1.45

In order to be able to produce a dense structure using granulometric optimization, each blast furnace slag was ground to four different finenesses: Two GGBS with a

fineness of about 4.200 cm^2/g (X1) resp. 7.000 cm^2/g (X3) and two fine GGBS with about 10.000 cm^2/g (X4) resp. 13.000 cm^2/g (X6). The fineness was determined as well by the Blaine value (EN 196-6) as by the particle size distribution. In table 4 the "X" is replaced by the terms of the GGBS "A", "B" and "C". For the early strength development despite the latent hydraulic reaction, a CEM I 52.5 R was used. Furthermore, 4.0 w.-% anhydrite (referring to the blast furnace content) was used for the sulphatic excitation. CEN standard sand according to EN 196-1 and PCE-based superplasticizer were also used for the subsequent production of mortar prism, based on which the relevant characteristic values have been determined. Later mortar prisms were also made for testing the acid resistance. In addition, mortar prisms made of CEM III/B 42.5 N-LH/SR/NA were used for comparison for acid storage.

2.2 Composition of the binder

Based on a statistical design of experiments the contents of OPC, GGBS and fine GGBS were varied and different w/b-ratios (0.30, 0.37 and 0.40) were used. The OPC-content was varied between 15 and 40 w.-% of the binder. The slag-containing fraction of the binder was composed of GGBS and fine GGBS with varying proportions. Table 2 shows the proportions of OPC, GGBS and fine GGBS of the binder compositions.

Table 2. Binder compositions (w.-%)

Mixture-no.	OPC	GGBS	fine GGBS
1	15	35	50
2	15	80	5
3	27.5	45	27.5
4	40	10	50
5	40	55	5

Table 3. Variations for the 5 binder compositions

Attempt-no.	w/b-ratio	GGBS	fine GGBS
M-1	0.30	A1	A4
M-2	0.44	A1	A6
M-3	0.44	A3	A4
M-4	0.30	A3	A6
M-5	0.44	C1	C4
M-6	0.30	C1	C6
M-7	0.30	C3	C4
M-8	0.44	C3	C6
M-9	0.37	B2	B5

2.3 Characteristic values for the acid resistance

For each binder composition 9 variations were used depending on the reactivity of different GGBS, the fineness of GGBS and fine GGBS, and the w/b-ratio (Table 3). In Experiment No. M-9, the fineness of GGBS

and fine GGBS were adjusted by combining GGBS with different finenesses. With the GGBS X1 and X3 a fineness of 5.600 cm²/g (X2) and with X4 and X6 a fineness of 11.500 cm²/g (X5) was produced.

Mortar prisms were produced from a total of 45 compositions, on the basis of which significant parameters for the acid resistance were determined. In addition to the determination of flexural and compressive strength after 7 and 28 days, the porosity and the calcium hydroxide content were evaluated as significant parameters regarding acid resistance.

The porosity was measured after 28 days using mercury pressure porosimetry. The capillary pore fraction depended on the w/b-ratio and the fineness of the binder. Both at a low w/b-ratio and at a greater fineness of the binder, the proportion of capillary pores decreased. At a w/b-ratio of 0.44, the content of capillary pores was at a specific surface area of about 5000 cm²/g approximately 9%, at w/b-ratio of 0.30 approximately 6.5%. At a specific surface area above 9.000 cm²/g, the proportion dropped to 4.0% (w/b-ratio 0.44) or 3.5% (w/b-ratio 0.30) (Fig. 1).

Fig. 1. Capillary porosity after 28 days

The calcium hydroxide content was also determined after 28 days by thermogravimetry. The calcium hydroxide content was low at 1.2% to 2.5 w.-%. When Portland cement was used, the Ca(OH)₂ content is up 15 to 25 w.-%. For compositions of 25 % OPC and 75 % GGBS, Ca(OH)₂ contents of about 2.9 w.-% were determined after 28 days [15]. As the fraction of GGBS decreased, the content of Ca(OH)₂ increased. At the w/b-ratios of 0.44 there was a higher Ca(OH)₂ content than at w/b-ratio of 0.30. This can be explained by the fact that at a low w/b-ratio of 0.30, the cement grains do not hydrate completely and thus less Ca(OH)₂ is formed [9]. The variable GGBS did not exert any significant differentiated influence on the Ca(OH)₂ content. There were no significant differences between the binder compositions with slag A and slag C.

2.4 Optimized binder compositions

Based on the results of the preliminary investigations, optimized binder compositions were prepared by means of statistical evaluation. These compositions were adjusted for granulometry and w/b-ratio. The share of the OPC was between 15 and 30 w.-%, w/b-ratios 0.30, 0.35, 0.37 and 0.40 were used.

Table 4. Optimized binder compositions

Attempt-no.	w/b-ratio	OPC	GGBS	fine GGBS
6-1	0.30	15 %	70 % C3	15 % C6
6-2	0.30	30 %	50 % C1	20 % C4
6-3	0.37	25 %	60 % B3	15 % B4
6-4	0.30	25 %	60 % A1	15 % A4
6-5	0.37	25 %	65 % A3	10 % A4
7-1	0.35	15 %	75 % A3	10 % A6
7-2	0.35	20 %	65 % A1	15 % A4
7-3	0.35	25 %	55 % C3	20 % C4
7-4	0.35	30 %	50 % C1	20 % C4
7-5	0.35	15 %	70 % B3	15 % B4
8-1	0.30	15 %	70 % B1	15 % B4
8-2	0.30	20 %	70 % A1	10 % A4
8-3	0.40	15 %	70 % B3	15 % B4
8-4	0.40	15 %	70 % A3	15 % A4
8-5	0.40	20 %	65 % A3	15 % A4

The relevant parameters of these compositions, such as flexural and compressive strength after 1, 2, 7 and 28 days, as well as the Ca(OH)₂ content and porosity were also determined after 28 days.

2.5 Test method

From the optimized binder compositions mortar prisms were prepared, which were stored in an acid test rig at the age of 28 days. The test rig included several storage tanks connected to a reservoir with automatic titration. Sulfuric acid with a pH of 3.5 was used as the medium. The automatic titration allowed a pH-static test to be run. The pH was thus permanently pH 3.5 ± 0.05 (Fig. 2).

Fig. 2. Drawing test rig

The mortar prisms were stored for a total of 13 weeks. Every 14 days the sulfuric acid was exchanged and the prisms were subjected to mechanical abrasion by brushing and the loss of mass was documented. After 28, 56 and 91 days, three prisms per mixture were tested for their flexural and compressive strength. The strengths were compared with those of water-based reference prisms. Furthermore, after 28, 56 and 91 days, the damage and penetration depths were determined by means of stereomicroscopy. From selected compositions, thin sections were prepared for evaluation under the scanning electron microscope (SEM) after the 91 day acid storage.

3 Results

To test the effect of acid attack damage, flexural and compressive strength after 28, 56 and 91 days of acid storage were compared with those of undamaged water-bearing samples. The determination of the strength characteristics showed no significant change between the acid storage and the reference storage. Although the flexural strength of the acid-stored ones was lower than that of the water-bearing ones in some mixtures, the difference was less than 1 N/mm² (Fig. 3).

Fig. 3. Flexural strength of mortar specimens after 91 days in sulfuric acid or water

The compressive strength showed a similar picture. The compressive strengths of the acid-stored samples are sometimes lower, partly at the same level as the compressive strengths of the water-stored test specimens. Overall, the differences are small (Fig. 4).

Fig. 4. Compressive strength of mortar specimens after 91 days in sulfuric acid or water

In addition to the strength parameters, the $\text{Ca}(\text{OH})_2$ content was determined after 28 days. With higher w/b-ratio and above all a higher OPC content, as well as with decreasing fineness of the binder, the $\text{Ca}(\text{OH})_2$ content increases. The lowest $\text{Ca}(\text{OH})_2$ content is found in mixtures 6-1, 7-1 and 7-5, slightly above 1.0 w.-%. The maximum value reaches the mixtures 6-2 and 6-5 with over 1.9 w.-%. The commercial CEM III/B contains about 2.1 w.-% after 28 days.

The capillary porosity ranged from 3.7% to 7.3% by volume. It was largely dependent on the w/b-ratio, whereby the fineness of the binder exerted an influence.

During the acid storage, the specimens were subjected to simulated mechanical abrasion every 14 days. The mass of the specimens was measured at the beginning of storage and after each brushing operation. Based on the loss of mass, the deterioration could be reproduced. The loss of mass depends, among other things, on the GGBS used, whereby the influence of the GGBS can be superimposed by other influences. Mixtures 7-1, 7-3 and 7-5 have comparable conditions as regards the fineness of the binder (7.100 – 7.300 cm²/g) and the w/b-ratio (0.35). 7-1 was prepared with GGBS A, 7-3 with GGBS C and 7-5 with GGBS B (Fig 5.).

Fig. 5. Mass loss of mortar specimens after 91 days in sulfuric acid subject to the reactivity of GGBS

The fineness of the binder appears to exert less influence on mass loss. Thus, the blends 7-1 (7300 cm²/g) and 7-2 (5.230 cm²/g) showed only a small difference. While the mixture with the finer binder had a mass loss of about 2.0%, mixture 7-2 lost more than 2.1% (Fig. 6).

Fig. 6. Mass loss of mortar specimens after 91 days in sulfuric acid subject to the fineness of the binder

The w/b-ratio is of great importance for the mass loss. The lower the w/b-ratio, the lower the mass loss. Mixtures 8-2 and 8-5 differ in the fineness of the binder besides the w/b-ratio. Mixture 8-2, with a specific surface area below 5.000 cm²/g, is coarser than 8-5 at over 7.000 cm²/g, but has a lower w/b-ratio (0.30 to 0.40). While mixture 8-2 had a mass loss of about 1.9%, mixture 8-5 lost almost 2.4% mass (Fig. 7).

Fig. 7. Mass loss of mortar specimens after 91 days in sulfuric acid depending on fineness of the binder and the w/b ratio

For comparison of the optimized binder compositions with commercially available CEM III/B, mortar prisms having a w/b-ratio of 0.30 and 0.40 were also stored in sulfuric acid for 91 days. The mass loss for the CEM III/B was about 11% higher than that of the optimized blends at both w/b-ratio of 0.30 and 0.40 (Fig. 8 and 9).

Fig. 8. Mass loss of mortar specimens after 91 days in sulfuric acid in comparison with CEM III/B (w/b-ratio 0,30)

Fig. 9. Mass loss of mortar specimens after 91 days in sulfuric acid in comparison with CEM III/B (w/b-ratio 0,40)

After 28, 56 and 91 days of acid storage, in the course of the strength tests, fragments of the prisms were sprayed with phenolphthalein and examined under the stereomicroscope. The results for the damage depths correlated with the results for the mass losses. It also showed that the w/b-ratio exerted the greatest influence, while fineness and reactivity were of secondary importance (Fig. 10).

Fig. 10. Damage depth of mortar specimens after 91 days in sulfuric acid

After 91 days of storage in sulfuric acid, microsections were made from selected mixtures. On the basis of these microsections, the damage front was examined under the SEM. It was noticeable in the case of mixtures 8-1 and 8-2 that the hydrated binder had increased microstructural disturbances. Along these defects, the acid could penetrate deeper into the specimen and probably cause greater damage than with an undisturbed microstructure (Fig. 11).

Fig. 11. SEM picture of 8-2

The surface of the mortar prism is located at the top of the picture. The damage front of the sulfuric acid is clearly visible there. On the left under the aggregate, air pores and insufficient bonding of the binder matrix and the aggregate can be seen. The bad bond can also be seen in the right part of the picture. These microstructures are not only close to the surface, but are present throughout the cross section. Excluded from these points, a dense structure seems to prevail, as shown by the results of mercury pressure porosimetry. There the mixture 8-2 has a capillary pore content of 3.68%.

4 Summary and forecast

By means of granulometric optimization and a reduction in the w/b-ratio, it has been possible to improve the acid resistance of slag-containing binders over commercial cements. In the preliminary investigations, the influences of the fineness of grinding, the w/b-ratio, the reactivity of ground granulated blast furnace slag as well as the proportion of GGBS and fine GGBS were pointed out to characteristic parameters of the acid resistance.

It could be shown that with increasing fineness of the slag sands the capillary porosity decreases, whereby with the fine GGBS with a specific surface according to Blaine of 13.000 cm²/g no commensurate reduction of the porosity could be achieved. Above all, a low w/b-ratio has a positive effect. With different reactivity of the GGBS, no significant changes in porosity were observed.

The Ca(OH)₂ content was largely determined by the proportion of CEM I. With greater substitution by GGBS, the content could be lowered. Subordinate influence on a sinking Ca(OH)₂-content had an increasing fineness of GGBS and a decreasing w/b-ratio.

In the acid tests, the results coincided with those of the preliminary investigations. Significant contribution to increasing acid resistance appeared to be low w/b-ratio and fineness. Decisive for a dense structure and thus for a higher acid resistance is not the fineness per se, but a coordination of the particle sizes with each other in order to achieve a dense packing up to the finest aggregates.

Subsequently, the findings from the acid storage of mortar prisms are applied to recipes for concrete specimens. In this case, it is important to further optimize the mixture, in particular at a w/b-ratio of 0.30 and thus to reduce the imperfections in the cement stone structure. Thus, the potential of acid resistance can be further exploited. With different binder contents and an optimized packing density according to the Fuller principle for the aggregate but also for the binder, the acid resistance should be further increased. In addition, previously used formulations for acid-resistant concretes, with fly ash and silica fume, were included in the test series.

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