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Concrete with high resistance to acids

based on Dyckerhoff VARIODUR® Premium Cement

... with Mikrodur Technology
Concrete with a high resistance to acids

Experience shows that the requirements for the durability of wastewater systems are fulfilled by the use of normal concrete only if they carry normal municipal wastewater. However, if the wastewater contains media that attack concrete in higher concentrations, or if operationally-related biogenic sulphuric acid forms in the sewer atmosphere, signs of severe corrosion often appear after just a few years of operation. This can result in considerable limitations in the serviceability and stability of the wastewater system. Nevertheless, in comparison with other building materials used in wastewater technology, concrete exhibits decisive technical and economic advantages, so that network operators in wastewater areas with a particularly high potential of attack demand concretes with a high resistance to acids.

Concretes that are highly resistant to acids have a particularly high microstructure density, which is achieved on the one hand by means of a low water/binder ratio and on the other by the use of reactive concrete additives. The microstructure density can be increased still further with an optimally matched binder granulometry. Besides that the binder volume and, hence, the proportion of potentially acid-soluble constituents in the concrete are reduced as far as possible, as a result of which the resistance to acids can additionally be increased. However, at the same time the durability properties must be optimised in such a way that the hardening characteristic of the binder/concrete fulfils the requirements with regard to manufacturing.

The measures mentioned can lead to difficulties in the manufacture and processing of the concrete, however. For practically usable concretes, therefore, optimisation is necessary between the raising of the resistance to acids on the one hand and sufficient processability on the other. Highly effective superplasticisers matched to the binder in combination with a grading curve rich in coarse grains are purposeful measures for this.

From the experiences gained through development work over several years, the above-mentioned requirements can best be fulfilled if the binder components are combined purposefully in high performance mixers following separate grinding and sieving. The separate optimisation takes place both for reasons related to chemical reactions and also according to granulometric criteria. The premium cements developed as a result by Dyckerhoff AG also make a contribution, as CEM II and CEM III, to the preservation of resources and the reduction of CO₂ emissions. As with other high performance concretes, very high homogeneity must also be ensured during the manufacture of concretes with high resistance to acids. To this end it is necessary to intensively monitor the raw materials and the fresh concrete, which sometimes significantly exceed the specifications given in standards.

The development of the high performance binder ≥ XA 3 began at Dyckerhoff AG as early as the late 1990s, with the aim of permanently and adequately resisting an acidic chemical attack down to a pH value of 3.5 with no additional protection of the concrete surface. Even in the initial experiments, cements containing blast furnace slag were used, in which blast furnace slag and Portland cement cinder were separately ground, granulometrically optimised and subsequently manufactured in high performance mixers with the addition of a sulphate carrier.

### Tab. 1: Concrete recipes

<table>
<thead>
<tr>
<th></th>
<th>Concrete 1</th>
<th>Concrete 2</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Cement</strong></td>
<td>Variodur 40 CEM III/A 52,5 R</td>
<td>Sulfadur CEM I 42,5 R-HS/NA</td>
</tr>
<tr>
<td></td>
<td>350 kg/m³</td>
<td>245 kg/m³</td>
</tr>
<tr>
<td><strong>Fly ash</strong></td>
<td>-</td>
<td>77 kg/m³</td>
</tr>
<tr>
<td><strong>Microsilica</strong></td>
<td>-</td>
<td>56 kg/m³</td>
</tr>
<tr>
<td><strong>Water</strong></td>
<td>147 kg/m³</td>
<td>127 kg/m³</td>
</tr>
<tr>
<td><strong>w/b value</strong></td>
<td>0.42</td>
<td>0.42</td>
</tr>
</tbody>
</table>
Comparative study of two concretes with high resistance to acids

Initial situation
A comparative study of two concretes was carried out on behalf of Dyckerhoff AG at the Professorship of Building Materials Technology at the Ruhr University in Bochum. A characteristics profile was created for each concrete that included the essential fresh and hardened concrete properties. One of the main items of the study was to compare the resistance to acids of the concretes examined.

The concretes have different binder compositions. Concrete 1 was manufactured with a blast furnace cement using ultra-fine blast furnace slag from a separate grinding. Concrete 2 on the other hand was manufactured using Portland cement with a high resistance to sulphates, plus fly ash and silica dust [1]. Both concretes exhibit a w/b ratio of 0.42 and were manufactured with quartzitic aggregates [largest grain 16 mm]. Alongside the laboratory concretes, additional samples from a large-format pipe made of concrete 1 were included in the acid tests.

Acid tests
The testing of the resistance to acids took place in a separate storage bath for each concrete. Sulphuric acid with a pH value of 3.5 was used as the test solution. The sulphuric acid was circulated by pumps over the entire duration of the test. The test solution in the reservoir and the storage baths was completely exchanged every two weeks. The complete acid test rig is illustrated in fig.1.

During the storage time of 15 weeks, the loss of mass was determined for three unbrushed and three brushed test specimens from the concrete samples. Phenolphthalein tests on the fresh breakage surfaces provided information about the depth of damage. The non-discoloured area of the breakage surface was microscopically photographed and measured. Following the end of the storage in acid, thin sections were manufactured from one unbrushed and one brushed concrete disc from each of the two concrete sorts and microscopically examined.

Fresh and hardened concrete properties
With regard to the factory manufacture of concrete pipes, it was possible to achieve processing-friendly and practically usable fresh concrete properties with both concrete recipes. After one day concrete 1 exhibited a higher compressive strength than concrete 2. In contrast to that, the mechanical properties of the two concretes no longer differed significantly after 28 and 56 days (Table 2).

Change of mass
The unbrushed specimens of both concretes exhibited significant gains in mass after just a few days of storage in sulphuric acid (fig. 2). The initial gain in mass decreased continuously over the further course of the acid storage, whereby the gain in mass was somewhat higher in the case of concrete 1. This behaviour has already been observed in earlier studies and has been attributed to the new formation of reaction products from concrete and acid constituents that remain in the microstructure of the concrete [2, 3].

In the case of the brushed samples, the overlaying of reaction products and the loss of mass due to acid attacks is less noticeable, since the lightly adhering reaction products on the immediate surface are mechanically removed. An actual loss of mass compared to the initial mass before the acid storage was first determined in the case of concrete 2 after 73 days and in the case of concrete 1 only after 107 days of storage in sulphuric acid. There was no visibly recognisable difference in the specimens of the two concretes. The gain in mass is markedly higher for the pipe samples than for the laboratory concrete with the same composition.

Depth of damage (phenolphthalein test)
A damage front on the fresh breakage surfaces sprayed with phenolphthalein could be observed via the colour contrast under an optical microscope. As expected, the course of the depth of damage was unevenly distributed over the extent of the specimens. Even after just 31 days of storage in sulphuric acid, concrete 1 exhibited a somewhat smaller depth of damage than concrete 2. The pipe concrete exhibited a
greater depth of damage throughout than laboratory concrete 1 [4].

**Pipe jacking – Gelsenkirchen Zoom**

In the Gelsenkirchen close to the Ruhr Zoo ‘Zoom Erlebniswelt’ (Zoom World of Adventure), a wastewater sewer comprising two jacking sections in a curve with a radius of 470 m was driven from a double pressure pit in the Emscher Marl. The building company W. Epping Spezialtiefbau used a pipe jacking machine with an open heading face and a controllable cutting shoe. The main pressing station in the start shaft consisted of 4 hydraulic telescopic cylinders with a pressing force of 3,000 KN per cylinder. Corresponding pressure relief valves were installed in order to avoid impermissible pressing forces.

The soil at the heading face was broken up by a roadheader fixed in the machine pipe and was transported to a mining cart with the aid of a conveyor belt. Cable winches pulled the mining cart through the pressurized airlock chamber to the start shaft, where it was emptied by a cable excavator. In order to seal the annular gap and reduce the friction caused by rock pressure, bentonite suspension was used during jacking. The heading face itself, which was freely walkable at all times, was supported by air overpressure, which displaced the in-situ groundwater and prevented unstable soil from flowing in.

**Requirements for the jacking pipes**

The jacking pipes had to be produced as follows on the basis of DIN EN 1916 and DIV V 1201, as well as the client’s - the Emschergenossenschaft - contractually agreed specification sheets and additional technical contract conditions:

- jacking pipes DN1600/DA2240
- standard face-to-face length 4.00 m
- weight 19.5 t
- with stainless steel sleeves, like all other built-in parts also
- concrete with increased resistance to acids

**Pipe manufacturer**

The pipes were manufactured in the Hünxe works of E+F GmbH Rohrwerk Epiton. Before pipe manufacture commenced, a QA plan had to be drawn up with the collaboration of everyone involved and in consultation with the Professorship of Building Materials Technology at the Ruhr University in Bochum. The extensive initial testing was carried out in April 2007 under the supervision of the Emschergenossenschaft and the Ruhr University in Bochum. In conjunction with this, numerous specimens were manufactured, among others for the analysis of the chemical resistance.

One of the largest cage welding machines in the world, made by MBK – Maschinenbau GmbH, was used for the manufacture of the reinforcement cages. This machine manufactured the inner and outer reinforcement cages separately and fully automatically in accordance with the static calculations or the reinforcement plans respectively. The finished cage had to be checked and the data entered in the pipe data sheet. The Emschergenossenschaft requested a maximum deviation of only ± 5 mm for the concrete covering. The pipes were poured standing up in centred steel moulds. Two jacking pipes were manufactured per day with one mould set from June to December 2007.

**Concrete manufacture and QA measures**

For the manufacture of the jacking pipes, the Emschergenossenschaft had specified...
the following very high requirements for the concrete with increased resistance to acids:

- Concrete compressive strength class: C50/60 (upper limit of the compressive strength after 28 days = 90 N/mm²)
- Exposure classes: XC4, XD3, XM2, XA3*
  * additional protective measures in accordance with requirements from exposure class XA3 were dispensed with on account of the special concrete technology applied
- Largest aggregate grain size: 16 mm (no calcitic aggregates)
- Water-cement or water-binder ratio: ≤ 0.42
- Binding agent content (cement + concrete additives): ≤ 350 kg/m³

<table>
<thead>
<tr>
<th>Designation</th>
<th>kg / m³</th>
</tr>
</thead>
<tbody>
<tr>
<td>CEM III / A 52,5 R</td>
<td>320</td>
</tr>
<tr>
<td>Crushed stone sand 0 / 2 mm</td>
<td>701</td>
</tr>
<tr>
<td>Gravel 2 / 8 mm</td>
<td>301</td>
</tr>
<tr>
<td>Gravel 8 / 16 mm</td>
<td>1.002</td>
</tr>
<tr>
<td>Water</td>
<td>133</td>
</tr>
<tr>
<td>Concrete plasticiser (PCE)</td>
<td>2</td>
</tr>
</tbody>
</table>

Tab. 3: Acid-resistant concrete composition

Tab. 4: Properties of Variodur 40, CEM III / A 52.5 R

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Location parameter d'</td>
<td>8.20 μm</td>
</tr>
<tr>
<td>Slope n</td>
<td>0.99</td>
</tr>
<tr>
<td>H₂O standard stiffness</td>
<td>31.5 M.-%</td>
</tr>
<tr>
<td>Start of setting</td>
<td>200 min</td>
</tr>
<tr>
<td>End of setting</td>
<td>230 min</td>
</tr>
<tr>
<td>False setting</td>
<td>12.8 cm</td>
</tr>
<tr>
<td>Le Chat.</td>
<td>0.0 mm</td>
</tr>
<tr>
<td>Compressive strength N/mm²</td>
<td></td>
</tr>
<tr>
<td>N 1</td>
<td>21.0</td>
</tr>
<tr>
<td>N 2</td>
<td>37.6</td>
</tr>
<tr>
<td>N 7</td>
<td>63.2</td>
</tr>
<tr>
<td>N 28</td>
<td>78.0</td>
</tr>
<tr>
<td>N 56</td>
<td>80.1</td>
</tr>
<tr>
<td>SO₃ content</td>
<td>1.72 % by mass</td>
</tr>
<tr>
<td>Heat of hydration</td>
<td></td>
</tr>
<tr>
<td>0 to 0.5h</td>
<td>12.2 J/g</td>
</tr>
<tr>
<td>0 to 1 d</td>
<td>173 J/g</td>
</tr>
<tr>
<td>0 to 2 d</td>
<td>259 J/g</td>
</tr>
<tr>
<td>0 to 3 d</td>
<td>305 J/g</td>
</tr>
<tr>
<td>0 to 7d</td>
<td>358 J/g</td>
</tr>
</tbody>
</table>

Pipe concrete, acid resistant C 50 / 60
Test age 28 days

Fig. 6: Concrete compressive strengths – pipe concrete
The following was selected from the two variants in the tendering text:

a. Cement type: CEM III / A 52.5 R according to DIN EN 197-1
b. Blast furnace slag content: 40 % by mass 3 % by mass
c. Separate grinding of cement clinker and blast furnace slag
d. Requirements for ground Portland cement clinker:
   - Grinding fineness according to Blaine: 5,000 cm²/g ± 500 cm²/g
   - Location parameter d´: 11 μm ± 1.5 μm

e. Requirements for ground blast furnace slag:
   - Grinding fineness according to Blaine: 8,000 cm²/g ± 500 cm²/g
   - Location parameter d´: 6 μm ± 1.5 μm

The comprehensive initial tests on the concrete included:

- Determination of the resistance to sulphuric acid in accordance with the acid test method after Hüttl
- pH value of the sulphuric acid 3.5
- Determination of the chloride migration coefficients
- Determination of the total porosity

These tests were performed at the client’s request at the MPA (Institute of Material Testing) Berlin-Brandenburg. The Emschergenossenschaft assumed the costs for the performance of the tests. Concrete manufactured using the binder variant A was used for the implementation. The concrete mixture is given in Table 3.

The cement was supplied by Dyckerhoff AG, Neuwied works, and the concrete by Elskes Transportbeton GmbH & Co. KG, Hünxe works. The manufacture of the concrete was supervised by Melius Baustofftechnik. The strength testing of the supplied concrete was performed by the Kondor Wessels testing centre on behalf of E+F GmbH, Rohwerk Epiton.

QA measures taken in advance and during production:

- Drawing up of a QA plan in consultation with the client and the Ruhr University in Bochum, Professorship of Building Material Technologies
- Training of employees and subcontractors by the Ruhr University in Bochum, Professorship of Building Material Technologies
- The acid-resistant concrete was to be classified in monitoring class 3
- Laser granulometry of the raw materials
- Laser granulometry of the cement
- Chemical composition of the cement
- Start and end of setting
- Fresh concrete temperature between 10 °C and 30 °C

Table 4 shows the data for the selected cement CEM III / A 52.5 R (Variodur 40) by Dyckerhoff AG, Neuwied works.

The cement was mixed to order in a high performance mixer from the separately ground individual components cement and blast furnace slag and subsequently always ‘freshly’ produced directly in the silo vehicle. During the production procedure samples were taken of the cement, analysed in Dyckerhoff AG’s works laboratory and finally released for loading to the silo vehicle. During the journey of the silo vehicle from the cement to the ready-mix concrete factory, the determined cement data (laser granulometry and SO3 content) was transmitted to the recipient by email, so that the verifications demanded by the client were already available even before the silo vehicle arrived at the ready-mix concrete factory. Table 5 shows the data determined over a delivery period of around 11 months.

<table>
<thead>
<tr>
<th></th>
<th>Variodur 40</th>
<th>CEM III / A 52.5 R</th>
</tr>
</thead>
<tbody>
<tr>
<td>Location parameter d´</td>
<td>9.3 1.00</td>
<td>8.2 0.93</td>
</tr>
<tr>
<td>n</td>
<td>1.81</td>
<td>1.72</td>
</tr>
<tr>
<td>SO3 M.-%</td>
<td>1.89</td>
<td></td>
</tr>
</tbody>
</table>

The figures show the high homogeneity of the manufactured cement, which complied with the specified range of fluctuation of the location parameter d´ not only as regards the individual components blast furnace slag and Portland cement clinker, but also in the finished cement.

The concrete was produced in consistency class F3 and tested according to the QA plan both in the ready-mix concrete factory and the concrete precast factory. Following visual assessment of the consistency, the concrete was fed evenly to the formwork via a distributor plate. Compaction was performed by annularly arranged internal vibrators (spud vibrators), which were raised according to the concrete fill level. The spigot end was concreted over and recompacted with the internal vibrators. The pipe face was drawn off to height in order to ensure the right-angledness and flatness of the front surface, which is important for jacking pipes. The spigot...
end socket was covered over and the pipes had to harden for at least eight hours in the mould.

Fig. 6 shows the concrete compressive strengths at a test age of 28 days from E+F GmbH, Rohwerk Epiton’s own monitoring. The required C 50 / 60 was safely achieved at every point in time in production. For the 3-day post-treatment, a hood was placed over the pipe immediately after demoulding. Through the feeding of water under the hood, a relative humidity of at least 85 % was achieved. The pipe could not be pulled off the steel pallet until at least three days had elapsed, after which the pipes had to be stored in a standing position for at least six days. A pipe data sheet was created for each pipe in order to document the manufacturing steps, dimensions, built-in parts, building material details etc. The pipes were not delivered until at least fifteen days had elapsed. Before loading to the vehicle, each pipe underwent a final check and the result was entered to the respective pipe data sheet.

Niersverband outplacement tests

Since not all chemical attacks on wastewater systems can be simulated in the laboratory, Dyckerhoff AG strove to carry out outplacement tests in parallel to the laboratory tests. It was possible to enroll the Niersverband to carry out a comprehensive outplacement programme. To this end, mortar prisms with various cements were placed at exposed points in specially manufactured outplacement baskets at the Mönchengladbach Neuwerk wastewater treatment plant (figs. 7 to 10).

Technical data from the Mönchengladbach – Neuwerk wastewater treatment plant

The outplacement test started in May 2006 is the most comprehensive of its type in the German wastewater network.

- 420 specimens
- 6 outplacement points (4 in the gas-filled compartment of the pipe / 2 in the water exchange zone)
- 1 control placement
- Test duration 5 years

Laboratory examinations - Niersverband / Wilhelm Dyckerhoff Institute

The outplacement was accompanied at close intervals by a carefully balanced programme of examinations with the following tests:

- Wastewater analyses
- Gas analyses
- E-modulus
- Weathering
- Weight
- Compressive strength
- Examinations of the cement microstructure with a scanning electron microscope
- Rietveld analyses
- Mercury pressure porosimetry

The chemical gas and water analyses are carried out as standard by the Niersverband’s laboratory. The further examinations are carried out as comparisons with the reference samples stored at the Wilhelm Dyckerhoff Institute in order to gain knowledge about the changes in the cement stone microstructure of the outplaced samples, among other things.

In the case of an acid attack (pH value ≥ 3.5), the blast furnace cements manufactured from separate grindings with granule-metrically optimised ultra-fine blast furnace slag exhibit clear advantages over optimised recipes with Portland cements and additives. The potential of soluble constituents is very much lower and the examinations with the scanning electron microscope show extremely dense, almost ceramic-like structures of the cement stone microstructure (figs. 11 and 12).

Natural draught cooling tower without a coating

A further area of application for the new cements arose almost at the same time in the course of the building of new brown coal and hard coal power stations. Nowadays power stations do not discharge flue gases via chimneys, but rather via high natural draught cooling towers. The first power station with this type of plant was the RWE brown coal power station Niederlaussem (BOA 2), completed in 2002. The concrete concept is based on the principle of the densest packing and makes highly resistant concretes possible for chemical attacks with very low pH values. The recipe, which has since been patented, consists of around 228 kg/m³ highly sulphate-resistant Portland cement, 65 kg/m³ hard coal fly ash and 33 kg/m³ silica dust [5]. Hence, for this solution hard coal fly ash and silica dust were also assessed in addition to Portland cement. Since the minimum cement content of 270 kg/m³ for steel reinforced

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Tab. 5: Technical data from the Mönchengladbach – Neuwerk wastewater treatment plant

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>total number of inhabitants</td>
<td>635.000 PT</td>
</tr>
<tr>
<td>and population equivalents</td>
<td></td>
</tr>
<tr>
<td>Dry weather influx Qt</td>
<td>150.000 m³/d</td>
</tr>
<tr>
<td>Mixed water influx Qm</td>
<td>288.000 m³/d</td>
</tr>
<tr>
<td>Biological cleaning stage</td>
<td>12.000 m³/h</td>
</tr>
<tr>
<td>Mechanical cleaning stage</td>
<td>38.000 m³/h</td>
</tr>
</tbody>
</table>

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Fig. 9: Outplacement in the gas-filled compartment

Fig. 10: Positions of the outplacement points

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concrete structures is not complied with, this recipe requires building authority approval.

On the basis of the positive results of the numerous laboratory and field tests, it was an obvious step to also try cement with granulometrically optimised ultra-fine blast furnace slag for resistant concretes at low pH values ≥ XA 3. This was carried out with Variodur 30 CEM II/B-S 52.5 R, a standard cement according to DIN EN 197-1, which can be used for steel reinforced and prestressed concrete structures without building authority approval. The acid resistance was verified at the Material Testing Institute MPA Berlin-Brandenburg, so that EON agreed to the concrete concept with Variodur 30 CEM II/B-S 52.5 R for the natural draught cooling tower of the new Datteln power station.

Prospects

There is an ever growing demand for increased durability, not only of the structural elements described here, which are subject to great stresses through aggressive media, but also of normal structural elements. Building materials of the future, such as UHPC, Ultra High Performance Concrete, derive their characteristic profiles from a particularly dense cement stone microstructure. Currently this can only be achieved through silica dust, which is in increasingly short supply, in conjunction with standard cements poor in C3A, sometimes only with building authority approval. These binder systems additionally require a high expenditure for dosing and quality assurance, since the raw materials cement and silica dust have to be checked both individually and in combination.

It is simpler to achieve a particularly dense cement stone microstructure through the granulometric optimisation of the cement constituents themselves. As shown in the article, this can take place with ultra-fine blast furnace slag from a separate sieving and later mixing with a basic Portland cement. The result is a standard cement which, like any other binder, can be dosed and processed in the ready-mix concrete factory with no additional expenditure. For quality assurance, only one binder component needs to be checked without interactions with others. The new binder concept is variable, i.e. other combinations with graded blast furnace slag and also fine clinker meal are possible [5]. In this way, processing-friendly standard cements are created with specifically adjustable characteristics for the reliable manufacture of high performance concretes.

References


FURTHER INFORMATION

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