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Nanotechnically optimized binders for the production of user-friendly high-performance concrete

Nanotechnisch optimierte Bindemittel für die Herstellung von anwendungsfreundlichem Hochleistungsbeton

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SUMMARY

It has been found that, because of the low water content, the Portland cement fraction in ultra high performance concrete (UHPC) is only slightly hydrated and consequently only exists as an inert particle fraction. In the investigations described here the Portland cement content was therefore reduced and directly replaced by pozzolanic, latent-hydraulic or inert fine powders. In contrast to the usual UHPC production with silica fume, which is used as the fine material for filling the voids in the microstructure of the binder, components with tailored particle size ranges were used here to avoid an excessive surface area caused by the void filler. This optimization of the chemistry and particle size range was carried out to meet the respective requirements in three publicly funded projects: BMBF OLAF "High-performance concrete for all", EU "Energy efficient Building H-House" and BMBF "C³ Carbon Concrete Composite, high performance concrete B2 base project". Reactive synthetic oxides, with which additional hydration reactions can be controlled during the dormant phase of Portland cement hydration, were also used. The results were essentially binder compounds that could be mixed homogeneously in a cement plant and then used with the aggregates available in a concrete plant to produce a UHPC that is easy to handle. The additional silos that would otherwise be needed in a concrete plant for storing silica fume and other fine materials for producing UHPC are no longer required as a result of the binder compounds produced in a cement plant. Compared with the usual UHPCs produced with silica fume, the optimized particle size grading with industrial homogenization has the effect that UHPC can be produced even in simple mixers. Optimization of the binder compounds leads to an extremely dense microstructure of the binder in the hardened UHPC, which, as a result, is characterized by special properties, such as durability and ASR resistance, even with particularly critical aggregates. There are descriptions of other concrete properties and the associated investigations that were carried out. Some examples describe possible applications of the UHPCs produced with these binder compounds, in which production of machine beds with these concretes has already become a commercial application. The use of less than 50 mass % Portland cement clinker in the binder compounds indicates also a way to CO_2 reduction.

(Translation by Robin B.C. Baker)

ZUSAMMENFASSUNG

Aus der Erkenntnis heraus, dass der Portlandzementanteil in einem Ultrahochleistungsbeton (UHPC) aufgrund des geringen Wasseranteils nur zu einem geringen Teil hydratisiert und dann als inerter Kornbandanteil existiert, wurde in den hier beschriebenen Untersuchungen der Portlandzementanteil reduziert und direkt durch puzzolanische, latenthydraulische bzw. inerte Feinstäube ersetzt. Im Gegensatz zur üblichen UHPC-Herstellung mit Silikastaub als Feinststoff zur Hohlraumfüllung im Bindemittelgefüge wurden hier zur Vermeidung einer zu großen Oberfläche durch den Füller auf das Kornband abgestimmte Komponenten eingesetzt. In drei öffentlich geförderten Projekten BMBF OLAF „Hochleistungsbeton für Alle", EU „Energy efficient Building H-House" und BMBF „C³ Carbon Concrete Composite, Basisprojekt B2 Hochleistungsbeton" wurden diese granulometrischen und chemischen Optimierungen entsprechend den jeweiligen Anforderungen durchgeführt. Dabei kamen auch reaktive synthetische Oxide zur Anwendung, mit denen zusätzliche Hydratationsreaktionen während der Ruhephase der Portlandzementhydratation gesteuert werden können. Die Ergebnisse waren im Wesentlichen Bindemittelcompounds, die im Zementwerk homogen gemischt und dann im Betonwerk mit den vorhandenen Gesteinskörnungen zu einem einfach handhabbaren UHPC verarbeitet werden können. Die sonst für die Herstellung von UHPC erforderlichen zusätzlichen Silos für die Bevorratung von Silikastaub und weiteren Feinstoffen entfallen durch die vorgefertigten Bindemittelcompounds. Die im Vergleich zu üblichen mit Silikastaub hergestellten UHPCs optimierte Kornabstufung mit industrieller Homogenisierung ermöglicht somit eine Betonmischung auch in einfachen Mischern. Die Optimierungen der Bindemittelcompounds führen zu einem extrem dichten Bindemittelgefüge im ausgehärteten UHPC, der sich durch besondere Eigenschaften, wie z.B. Dauerhaftigkeit und AKR-Beständigkeit, selbst mit kritischen Gesteinskörnungen auszeichnet. Über weitere Betoneigenschaften und die dazu durchgeführten Untersuchungen wird berichtet. Einige Beispiele beschreiben Anwendungsmöglichkeiten der mit diesen Bindemittelcompounds hergestellten UHPCs, wobei die Produktion von Maschinenbetten bereits zur Serienanwendung gehört. Durch den Einsatz von weniger als 50 M.-% Portlandzementklinker in den Bindemittelcompounds wird hier auch ein Weg zur CO_2-Minderung gezeigt.

Nanotechnically optimized binders for the production of user-friendly high-performance concrete – part 1

Nanotechnisch optimierte Bindemittel für die Herstellung von anwendungsfreundlichem Hochleistungsbeton – Teil 1

1 Introduction

About 850 kg/t CO_2 is generated during the production of Portland cement clinker due to the calcination of limestone from $CaCO_3$ to CaO and by the fuels used in the burning process. At this point possible ways of reducing the CO_2 output have been virtually exhausted. Replacement of Portland cement clinker by high-grade cement substitutes offers effective CO_2 reduction although Portland cement clinker will still form the basis of durable concrete structures in the future. It is well known that the mechanical properties of concrete can be selectively adjusted by varying the fineness of the cements and that the raw materials are available in sufficient quantity. Replacing Portland cement clinker by cement substitutes is not simple because of the quality and availability of suitable substitutes. The substitute material with the longest record of success is slag meal produced from granulated blastfurnace slag. After addition of water its latent hydraulic properties are activated by Portland cement clinker, resulting in a homogeneous hardened cement paste.

A method, in which cement constituents are ground individually, screened and then combined selectively to form binders with special properties, was developed about 20 years ago at Dyckerhoff (Buzzi Unicem Group). The binder properties were adjusted to meet the requirements of the applications by a combination of Portland cement clinker and blastfurnace slag meal with different particle sizes, sometimes combined with inorganic oxides. This gives them a significantly superior performance to that of pure Portland cements.

This took place initially with ultra-fine cements for injection work and increasingly also in recent years for the production of standard cements with special properties (so-called premium cements). Based on this experience, work was carried out in publicly funded projects on further optimization of the binder systems.

2 Current state of knowledge

2.1 Literature research

From the material technology aspect the cement is not fully utilized as a binder when used in UHPC in familiar compositions with water/cement ratios of 0.17 to 0.23. Not enough water is available for complete hydration of the cement and 50 to 70 % of the clinker is not utilized in UHPC, as compared to 10 % in standard concrete [1]. The unhydrated cement particles do in fact remain as high-strength components with optimum bonding to the hydrated hardened cement paste matrix but large parts of the high-grade binder only function as a filler. Production of the Portland cements used in these compositions is known to be associated with substantial CO_2 emissions, so the fact that some of the binder only serves as a filler should be avoided as far as possible.

UHPC often consists of 600 to 900 kg/m^3 cement, up to about 250 kg/m^3 very fine, reactive, silica fume, various fine stone meals and sand. Over 40 vol. % of the UHPC is made up of very fine materials with particle sizes of less than 0.25 mm. Without major modifications it is very difficult to handle these individual component compositions – if they can be handled at all – in the usual mixing plants for producing precast elements and concrete products. In their current design (weighing system, hopper design, mixer) ready-mixed concrete plants are not at all suitable for the production of UHPC. Substantial investment is needed just for dust-free handling of the unusual, very fine materials, (e.g. silica fume) [2].

There are only a few UHPC structures in Germany, not least because of the current building approval regulations. The best-known is the Gärtnerplatz bridge built in 2004 on the basis of a mix formulation from Kassel University with UHPC top booms and carriageway slabs that are only 8 cm thick on a steel tube lattice girder (❱ Fig. 1). In 2010 the company Max Bögl, Neumarkt, supplied UHPC elements based on their own mix formulation for building the WILD bridge in Kärnten, Austria (❱ Fig. 2).

Figure 1: Gärtnerplatz bridge in Kassel

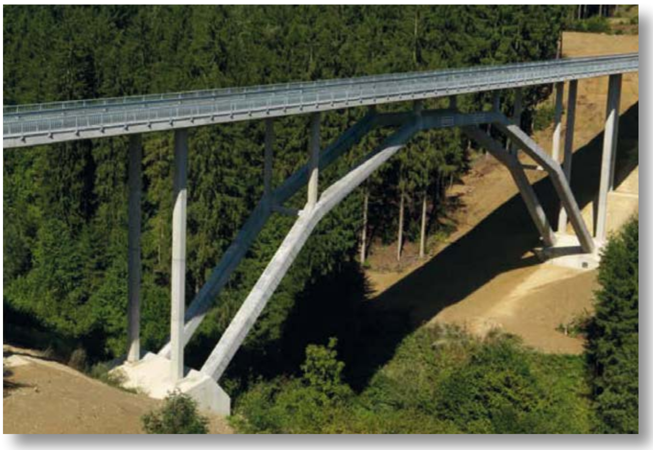

Figure 2: WILD bridge in Kärnten

Around the world there are also numerous projects based on UHPC dry premixed formulations, such as Ductal from Lafarge Holcim. The UHPC concretes produced with special high-performance mixers show impressive mechanical parameters.

2.2 Status report by the German Committee for Structural Concrete (DAfStb)

A first status report on ultra high performance concrete was published in 2008 by the German Committee for Structural Concrete [3]. In 2013 a subcommittee of the DAfStb started to draw up guidelines for UHPC with the working group AG1 Concrete Technology and Implementation and the AG2 Dimensioning and Construction working groups [4]. As before, the concrete technology deals essentially with the standard cements and compositions already known from the focal programme. The positive practical experience with premixed binders was in fact noted but so far these have not been taken into account in drawing up the guidelines. This is because, as described below, no compounds exist in the range controlled by the building inspectorate. It is up to the cement producer to obtain building approval regulations that involve a great deal of time and expense. However, the application itself is still not a regulated mode of construction so the cost of general building approvals and agreements in the individual case bears no relationship to possible sales of binders in the specific application.

2.3 Research project by the Federal Association of the Ready-Mixed Concrete Industry (BTB)

A UHPC research project was started in 2008 by the Federal Association of the Ready-Mixed Concrete Industry. Operational trials at four different locations using different procedures were intended to provide the ready-mixed concrete industry with information about the possible uses of UHPC. Different types of mixer, the capacity of plants with respect to storage and metering of the initial constituents and the metering sequence, transport and conveying of UHPCs were taken into account.

Conventional compositions with Portland cement and silica fume as well as premixed Portland pozzolanic cement and a binder compound containing fine quartz sand were used. The advantage of this binder compound was that only one empty cement silo was needed and it could be processed just with the aggregates available at the plant. All the other variants with special stone meal required additional metering and storage equipment that would have to be installed in ready-mixed concrete plants before production of large quantities of UHPC in a fully automatic process chain. For small production quantities at significantly reduced plant capacity it would be possible to use manual metering with increased demands on industrial safety because of dust exposure to silica fume. The lack of building approval regulations was cited as a constraint to large-scale production of UHPC with the pre-mixed binder compound (Nanodur® Compound 5941) from Dyckerhoff GmbH in ready-mixed concrete plants; apart from this the only negative factor was the comparative long mixing time needed for effectivity of the PCE. Not only the easier handling but also the better homogeneity of the binder for UHPC that can be achieved through the dry preliminary mixing of the very fine materials in a cement plant favour the compound variant [2].

3 Development aims

The development of UHPC that had already been carried out and its practical implementation made hardly any allowance for the existing plant situation in the concrete industry. A few specialized companies were working in cooperation with universities on individual solutions but so far these have shown little suitability for general application. An important precondition for the success of new products and/or methods of construction in the concrete industry is the widest possible utilization of existing machinery and raw materials. University approaches to UHPC often provide a good academic service without sufficient practical relevance. It begins with high-performance mixers that are essential for the dense packing, signify considerable capital investment and are of only limited suitability for routine business with large quantities. It continues via special fine quartz grains that are not without problems from the occupational healthcare point of view and extends to additions that are difficult to handle, such as silica fume. These raw materials are not in daily use in the concrete industry nor is there any suitable storage and metering equipment for them. After a development time of more than 20 years there are therefore still only a few specialist companies for the production and application of the high-tech material UHPC.

The development objectives resulting from this finding are simple processing of UHPC, i.e. production with conventional machinery and constituents that are usual in the industry, and the possibility of standardizing the binder used. Assisted by the existing production of fine cements (see Section 4.1) and the experience with dealing with synthetic oxides the first step was adjustment and optimization of the dense packing of the raw material grains in analogy with classical UHPC. The results achieved were protected by patents.

3.1 Patents

Classical UHPC compositions follow the familiar cement reaction and supplement the mineralogical two-component system comprising cement and aggregate by the use of reactive silicon dioxide for the pozzolanic reaction. However, this can only start after 8 to 12 hours when sufficient calcium hydroxide has formed. Only then the additional C-S-H phases consolidate the microstructure consisting of the phases formed initially by the hydration reactions. It was known that synthetic oxides react very much faster than the industrial by-product silica fume. This was shown by investigations at

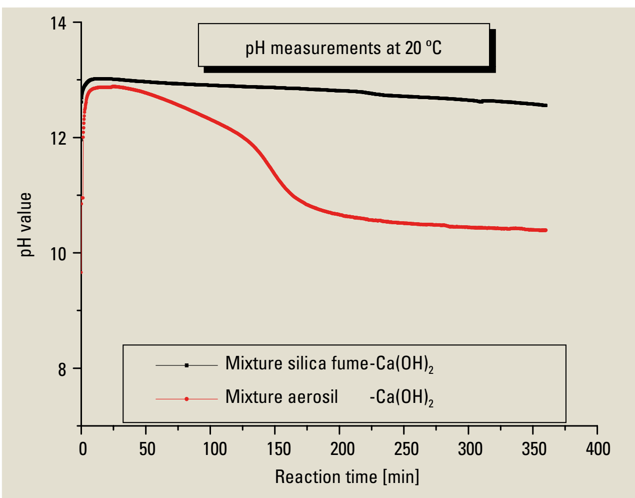

Figure 3: Time-dependant decrease of the pH of a calcium hydroxide solution with silica fume and Aerosil (synthetic oxide) [5]

Figure 4: Column structure of the Lufthansa Aviation Centre in Frankfurt

Siegen University [5] in which silica fume and a synthetic oxide were added to a saturated calcium hydroxide solution and the reduction in the pH value was measured as an indication of C-S-H phase formation (❱ Fig. 3).

In this trial the reaction of the synthetic oxide was virtually complete after only three hours. These observations gave rise to the idea for the UHPC binder of letting a pozzolanic reaction take place during the dormant phase of the cement reaction. This was implemented successfully by the use of reactive synthetic oxide powders based on silicon and lime. A patent for this idea was successfully applied for in 2007. Further protective rights were applied for, e.g. for a composite material that also contains binder compositions with several main constituents such as granulated blastfurnace slag, fly ash and limestone meal [6].

4 Development steps for optimizing the UHPC binder compound

4.1 Mikrodur®-technology

The following developments were based on the production of ultra-fine cements that is protected by patents, in which fine cements are produced by separate grinding of Portland cement clinker and blastfurnace slag meal using high-performance separators. The Portland cement clinker used in the production is produced without secondary fuels. A production plant for these fine cements had been built at the Neuwied plant more than twenty years ago. At first the ultra-fine cements produced there with d_{95} finenesses of 6, 9.5 and 16 µm were used for grouting in the geotechnical sector and for repairs of structures with very small voids. It very soon became apparent that these ultra-fine cements are also suitable for strengthening a wide variety of building materials.

The next steps were the development of high performance flowable mortars without silica fume for filling high-voids asphalt layers as semi-flexible pavement (Microfond) and Flowstone, a premixed binder for producing artificial stone for artistic and architectural applications.

The systematic strengthening of standard cements with fine cements started in 2004. Columns of high performance concrete made with Veridur® CEM II/A-S 52,5 R cement were manufactured for the first time without silica fume for the construction of the Lufthansa Aviation Centre at Frankfurt airport (❱ Fig. 4) [7].

Standard cements that have been strengthened with fine cements are designated premium cements. They have now become established in the market and are indispensable for particular requirements. The premium cements registered as standard cement have proved widely successful, from the construction of cooling towers and high performance concrete foundations, wind-power plants and wastewater units to numerous bridge reinforcements – chiefly in the Netherlands. When the exceptional durability beyond the warranty period is considered these expensive special building materials are substantially better economically than standard concrete construction.

4.2 Nanodur®-technology

Nanodur® technology is a logical progression from Mikrodur®-technology taking account of the findings from the UHPC research projects. Exceptional properties are made possible by the dense packing of the hardened cement paste developed there. After the combination of standard cements and fine cements the next stage in the development was the additional use of synthetic oxides with a particle size in the nanoscale range. The synthetic oxides are used both for optimizing the particle size range and for controlling the hydration. They are produced either in a wet process by precipitation or by pyrogenic methods, such as flame hydrolysis and pyrolysis. The processes provide primary particles in

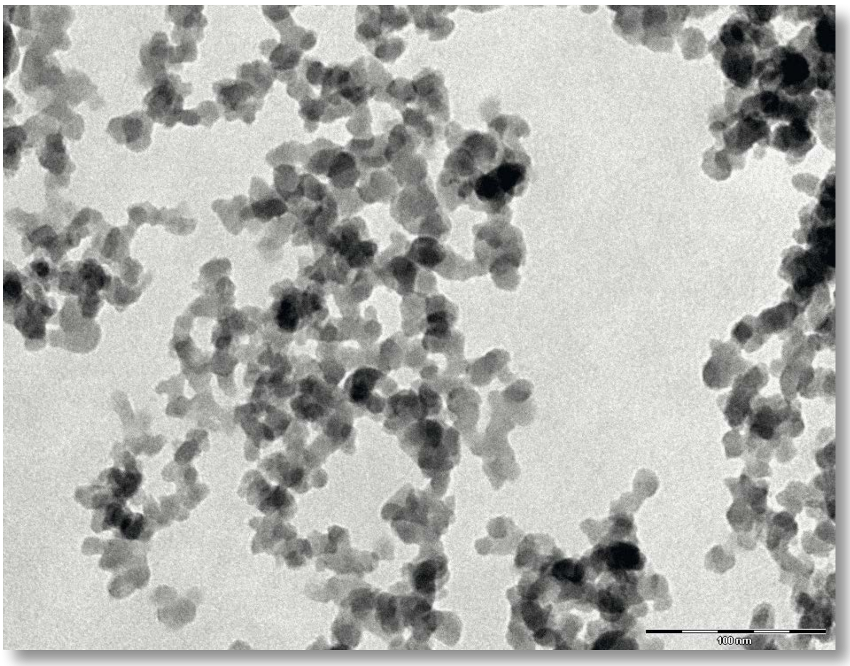

Figure 5: TEM photomicrograph of a synthetic oxide (source: Evonik)

the range of a few nanometres – 5 to 50 nm with pyrogenic production and 5 to 100 nm with wet chemical precipitation. These primary particles immediately form aggregates linked by solid bridges which agglomerate to different degrees depending on the production method (❱ Fig. 5). By shear intense mixing with other materials the agglomerates can be dispersed again into smaller clusters. With the pyrogenic synthetic oxides the aggregate size is less than 200 nm but with the precipitated synthetic oxides it lies in the micrometre range. To illustrate the order of magnitude Fig. 5 shows a TEM photomicrograph of synthetic oxides with a primary particle size of approximately 10 nm [8].

Granulometric optimization by the fine cement components from the Mikrodur®-technology and synthetic oxides is being carried out on the basis of a high grade CEM I 52,5 R cement that has already proved successful in premium cements. The individual components are homogenized in several stages in a powder mixer with cutter heads to form the final Nanodur® binder. The result is a stable binder that does not exhibit any segregation even during pneumatic conveying and long transport distances. The Nanodur® cement – standardized as CEM II/B-S 52,5 R – for simple production of UHPC was awarded the innovation prize by the concrete construction components supply industry at the 52nd Betontage Congress in Neu-Ulm in 2008 (❱ Fig. 6).


INNOVATIONSPREIS

DER ZULIEFERINDUSTRIE BETONBAUTEILE 2008

Concrete Solutions

52. BetonTage

12. – 14. Februar 2008, Neu-Ulm

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Zement „Nanodur“ zur einfachen Herstellung von UHPC

IN DER KATEGORIE

Betontechnologie

GESTIFTET VON

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Dipl.oec. Ulrich Lotz
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Figure 6: Certificate for the innovation prize of the concrete component supply industry

5 Brief descriptions of the funded projects

Since 2009 Dyckerhoff GmbH has investigated the potential of binder optimization with special emphasis on CO_2 reduction in three publicly funded projects. The first project was OLAF (see Section 5.1) in the BMBF NanoTecture calls for nanotechnology in building construction. This was followed by H-House (see Section 5.2) in the context of the initiative for Energy-efficient Building (EeB) of the 7th Framework Programme of the European Union and the B2 base project within the C^3 Carbon Concrete Composite (see Section 5.3) of the BMBF call "Twenty20".

5.1 OLAF – Nanotechnologically Optimized, Long-lasting, energy-efficient and especially Application-Friendly high performance concrete [9]

High performance concretes are increasingly capable of replacing metallic materials. The high mechanical load-carrying capacity and durability is made possible by the dense microstructure of the hardened cement paste.
As already mentioned, conventional ultra high performance concrete UHPC requires exceptionally finely divided raw materials as well as special mixing technology and curing. This makes market introduction, which anyway involves a great deal of time and cost due to expensive approvals, even harder.

5.1.1 Nanotechnological optimization

The properties of ultra high performance concrete are essentially determined by dense packing of the microstructure of the hardened cement paste. Graded aggregates and reactive binder components are optimized at low water/cement ratios to achieve minimum voids. UHPC compositions also contain SiO_2 components for the pozzolanic reactions that contribute the mineral densification of the microstructure. Unlike the situation with conventional UHPC, with BMBF OLAF the granulometric optimization of the microstructure was achieved by fine cements and fly ash from coal as well as inert fine limestone meal. The pozzolanic reaction took place through synthetic oxides as the regulating factor for the cement hydration. The project partner Evonik synthesized a large number of different nanostructured oxides during the project. During the course of the project it was established that there are no suitable test methods for UHPC that would be able to provide reproducible results for definitive selection. The brittle material properties combined with influencing factors from the storage did not

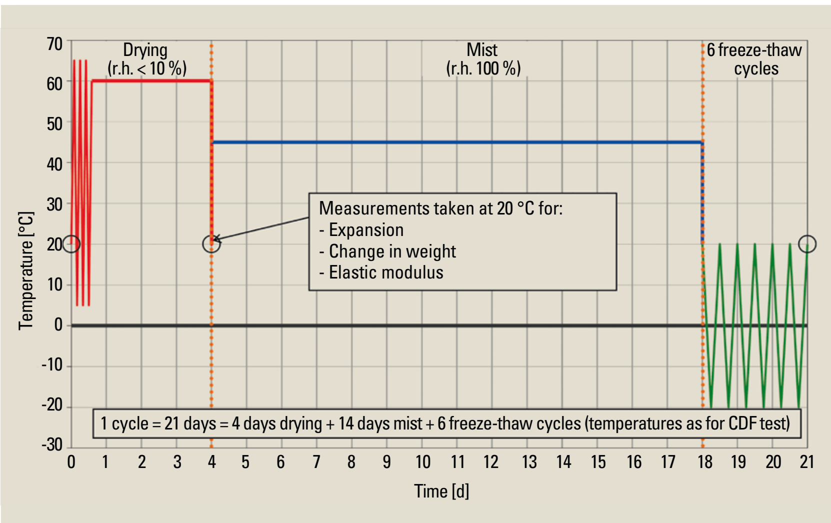

Figure 7: Climate cycles in the climatic chamber (source: Bauhaus-Universität Weimar)

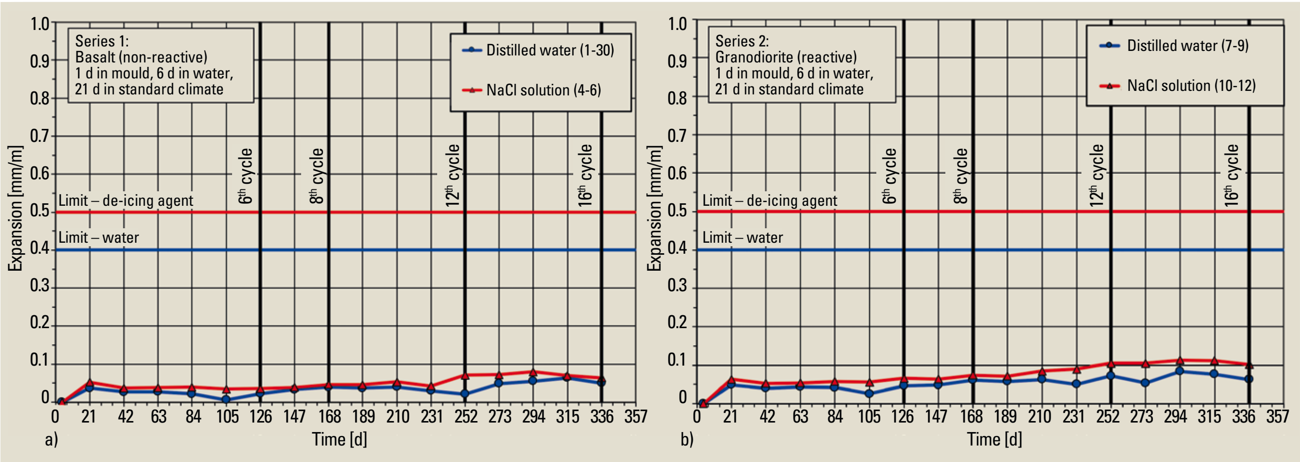

Figure 8: Expansion values for a) basalt aggregate and b) granodiorite aggregate

provide adequate differentiation in the basic compression and flexural tests. Within the framework of the project there was also a lack of sufficiently detailed and proven analytical methods for the adequate description of the precise action mechanism of nanoparticulate systems in a complicated UHPC matrix.

5.1.2 Long service life

The alkali-silica reaction (ASR) has caused numerous cases of concrete damage in recent years and is often called sensationally in public as concrete cancer. ASR is caused by alkali-reactive aggregates that contain stressed quartz. They form swellable gels through reaction with alkalis from the cement and destroy the concrete by the increase in volume. This process is assisted by climatic effects and aggressive media. In its life cycle a concrete passes through numerous climate cycles. These processes can be simulated on an accelerated time scale using alternating climate storages.

The test method permits the inclusion of aggressive media (water, de-icing salts, sulfate solutions) in realistic climate cycles (❱ Fig. 7).

The alternating climate storage was carried out over a period of 1 year with basalt, as having little sensitivity to ASR, and granodiorite as a particularly ASR-sensitive aggregate. The measured expansions lay far below the limits for water and de-icing agents (❱ Figs. 8a and b).

5.1.3 Energy efficiency

Particular energy efficiency is achieved if the binder contains finely divided composite constituents, such as granulated blastfurnace slag, fly ash and limestone meal, in excess of the quantity permitted by the current cement standard (❱ Fig. 9). The saving in CO_2 was demonstrated in a life cycle analysis carried out by the project partner Evonik. The binder concept developed in the project with less than 50 % of the CO_2-intensive Portland cement clinker contains nanostructured oxides based on synthetic silicon oxide as well as lime components for controlling the pozzolanic reaction in the early hydration periods.

In comprehensive comparative concrete investigations with the binder concept in a practically proven mix composition with Nanodur® Compound 5941 and aggregates comprising pit sand, hard stone chippings and micro steel fibres it was demonstrated that with the new OLAF binder concept not only the mechanical properties, such as elastic modulus, compressive strength and flexural strength, but also the impermeability, durability and resistance to freeze-thaw with de-icing salt are comparable.

OLAF coarse-grained mix formulation:

- 1 050 kg/m³ binder compound 5941
- 812 kg/m³ basalt chippings 2/5
- 377 kg/m³ quartz sand 0/2
- 60 kg/m³ micro steel fibres
- 160 kg/m³ water
- 15 kg/m³ PCE superplasticizer

Creep loading and alternating climate storage also showed that with selected composition of the binder and hydration control by nanostructured synthetic oxides it is possible to produce a high grade concrete with exceptional properties even though this binder contains less than 50 mass % Portland cement clinker.

5.1.4 Ease of application

An application-friendly high performance concrete was achieved in the OLAF project by a pre-mixed binder in which all the fine materials needed to achieve the densest possible

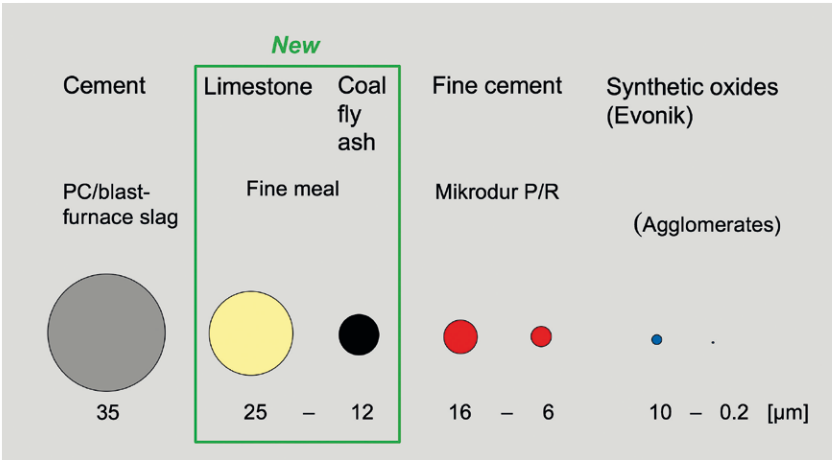

Figure 9: Size comparison of the binder components of ultra-fine cement

packing were homogenized in a dry state in the cement plant in a special powder mixer. The mixer elements rotate in the range from 100 to 500 rpm and the cutting heads positioned in the material flow rotate at 1 000 to 5 000 rpm. This therefore involves a combination of mixing and grinding (= shattering of aggregates and agglomerates). A binder compound (OLAF Compound 5941) that is ready for use was produced in the cement plant with 59 mass % cement and 41 mass % fine quartz sand.

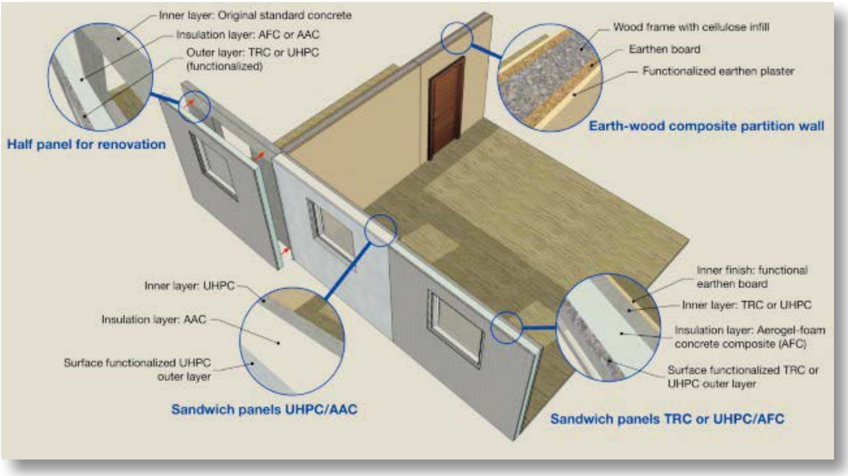

Figure 10: H-House structure

The binder, which has been intensively mixed under dry conditions, also ensures trouble-free UHPC production in concrete pan mixers with little shearing intensity in combination with the usual aggregate available in concrete plants. Compared with conventional UHPCs made with standard cements and pozzolans like silica fume it means that no sophisticated and expensive mixing technology is needed to ensure the homogeneity of the binder and the fresh concrete. Through the preparation of a binder with special composition in a high performance powder mixer with all the necessary fine materials there is no need for high investment in sophisticated concrete mixing technology in the concrete plant. Not only large but also smaller companies can therefore have access to the UHPC technology.

According to the current situation the binder concept based on less than 50 mass % Portland cement with three other main constituents, namely blastfurnace slag meal, fine limestone meal and fly ash, is a CEM X cement and therefore cannot yet be covered by a standard [9].

5.2 H-House project [10]

The project, funded by the EU, covers the development of various eco-innovative building systems for energy-efficient structures and healthier dwellings. The latter comprises essentially internal walls made of wood and earthen building materials that are not discussed in this article.

Designs based on UHPC in a sandwich structure with mineral insulating materials are possible strategies for repairing external walls and building new ones (❱ Fig. 10).

The task of the German partners in the concrete technology sector was essentially the development of building material concepts for combinations of load-bearing UHPC and mineral, thermally insulating, aerated concrete. The companies involved were Dyckerhoff and Xella coordinated by the Federal Institute for Materials Testing (BAM).

In utilizing the results from the OLAF project the first step was to check the suitability of raw materials from various cement plant locations. Limestone and trass meal as well as fly ash were designated as the clinker replacements. The Nanodur® Compound 5941 had by now become internationally established for machine beds and tool stands so this pre-mixture of 59 mass % cement and 41 mass % fine quartz sand was also chosen for the production of UHPC in the H-House project.

The first step consisted of staged replacement of the Portland cement by the individual clinker replacement materials, namely fly ash, limestone and trass. Standard prisms were produced and the compressive and flexural strengths were tested after 2d, 7d and 28d as specified in DIN EN 196-1. In each case three standard prisms were also removed from the mould after 24 hours and autoclaved at 12 bar and 180 °C for 6 hours.

The hydrate phase development was examined using the Rietveld analysis and individual selected samples were examined by scanning electron microscopy. The tests showed that autoclaving significantly increased the strengths compared with normal storage. This confirmed that autoclaving of UHPC is basically possible and therefore sandwich elements consisting of a load-bearing UHPC precast component and the insulating aerated concrete mass can be autoclaved together. A detailed view on the test results will follow in part 2.

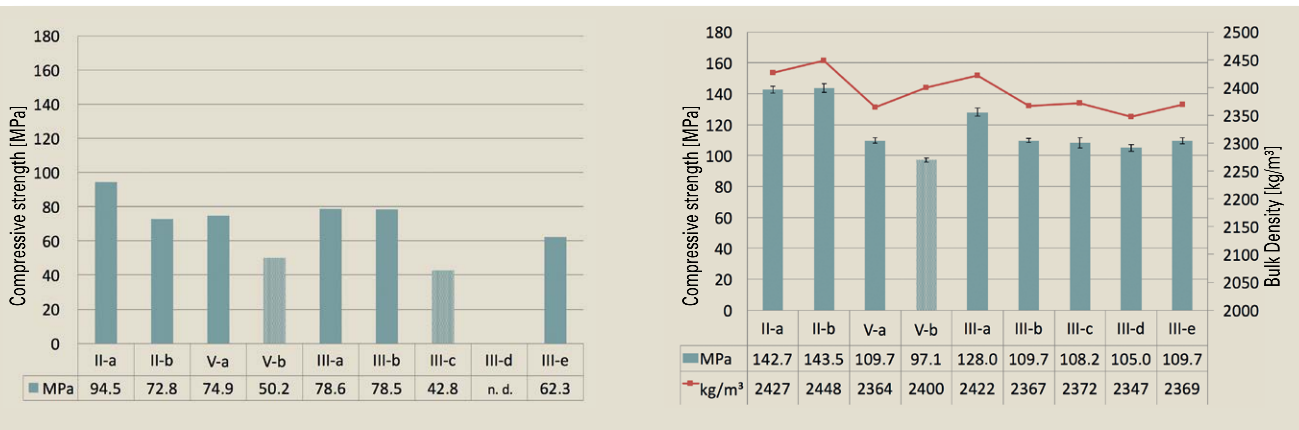

Figure 11: Compressive strengths of the UHPC concretes, after 2d (left), after 28d (right), bulk density (red line)

Table 1: Binder mixes used for UHPC

No.	Type	Specific surface area acc. to Blaine [cm²/g]	Characterization
1	CEM I 52,5 R	~ 5300	Rapid strength development
2	CEM I 42,5 R	~ 3900	High sulfate resistance
3	CEM I 52,5 R	~ 5200	Normal strength development
4	CEM I 42,5 R	~ 4000	White cement

Cement/Binder	No.	Composition [mass %] (rounded to 5 mass %)				
		OP Cement	BFS A	BFS B	FA	LS meal
CEM II/B-S	II-a	70 (1)	30	–	–	–
	II-b	70 (2)	30	–	–	–
CEM V/A	V-a	55 (3)	–	30	15	–
	V-b	55 (2)	–	30	15	–
CEM III/A-M (S-LL)*)	III-a	55 (1)	10	20	–	15
	III-b	55 (4)	20	10	–	15
	III-c	40 (2)	30	–	–	30
CEM III/A-M (S-V-LL)*)	III-d	50 (3)	30	–	15	5
	III-e	50 (3)	–	30	15	5

*) Not defined in EN 197

The structural design of the H-House elements were part of the other partner's working packages. A so-called fine-grained mix formulation was used for producing the UHPC slabs:

H-House fine-grained mix formulation:

- 1 050 kg/m³ binder Compound 5941
- 1 150 kg/m³ pit sand 0/2 mm
- 168 kg/m³ water
- 18 kg/m³ PCE superplasticizer

The most promising of the different binder mixes were selected for the durability investigations. For operational reasons trass was no longer considered as a clinker replacement. Mixtures of limestone meal and fly ash were chosen instead (❱ Table 1).

In the strength testing after 2 and 28 days the mixes containing fly ash (III-d, III-e, V-a and V-b) tended to be worse than those containing different limestone meals (III-a-c) when compared with the reference mixes (II-a, II-b) based on Nanodur® Compound 5941. The performance of the binder variant III-a containing very fine limestone meal came closest to that of the reference mix II-a (❱ Fig. 11). Mix III-b based on white cement also safely reached the compressive strength requirement of at least 100 MPa.

Slight scaling up to a maximum of 90 g/m² after 28 freeze-thaw cycles only occurred in the CDF test with the fly ash variants. The other binders exhibited almost no loss of material (❱ Fig. 12). The chloride migration was very low with all the variants. The limit of $5 \cdot 10^{-12}$ m²/s was not reached by a wide margin (❱ Fig. 13).

Dark fly ash is unsuitable for façade elements for visual reasons so only the binder variants III-a based on grey and III-b based on white cement were used and then tested in, operational trials at Strängbetong in Sweden using local aggregate.

A filigree folded structure (❱ Fig. 14) for an exhibition stand was also produced to demonstrate the flow properties of TP-H-House Compound 5941.

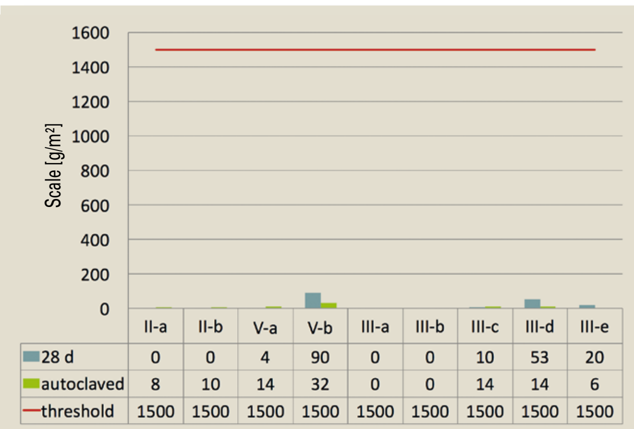

Figure 12: Results of the CDF test

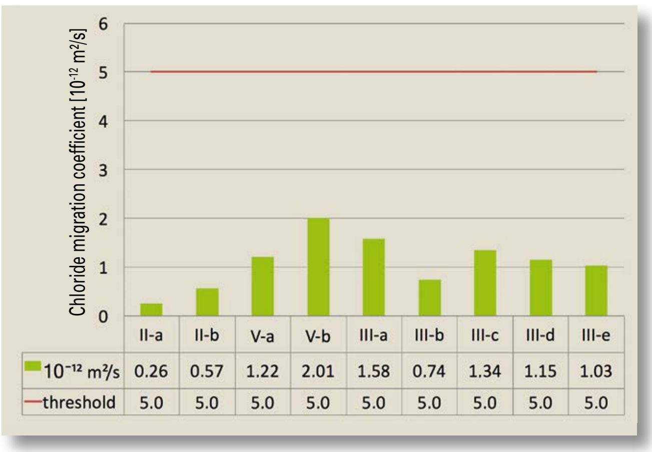

Figure 13: Results of the chloride migration test

Figure 14: Filigree folded structure made of UHPC in the mould (left) and free-standing (right)

After adoption of prEN 197-1:2014 (D) the 59 mass % cement in the compound would be covered by the standards with the designation CEM II/C-M (S-LL).

5.3 Carbon Concrete Composite project (C3) / B2 base project: high performance concrete [11]

The aim of the B2 base project was to develop high performance concretes that, when compared with the concretes currently available on the market, should exhibit greatly increased durability, optimized bond with carbon reinforcement and significantly improved energy and CO_2 balances. The high performance concretes to be developed should make a contribution to improving the mechanical properties and longevity. New binder concepts had to be developed that were particularly suitable for use as high performance concretes in precast elements and for reinforcing and repairing components with carbon reinforcement. Use was naturally also made of the results from the OLAF and H-House projects described above.

5.3.1 Selection and optimization of the binder

Two dry plant mixes based on Nanodur® and OLAF Compound 5941 were tested and evaluated by the project partners. It was apparent that because of the adhesiveness in conjunction with coarse crushed aggregate it was very difficult for the high-fines UHPC concretes to penetrate the structures of the textile scrim uniformly. For application of the binders in textile-reinforced concrete it was therefore necessary to reduce the adhesiveness, viscosity and yield value.

The great adhesiveness of the OLAF/Nanodur® concretes is caused partly by the great fineness of the fine cements and oxide components and partly by the fine quartz sand used in Compound 5941. The latter was remedied by changing over to a modified fine grain composition in which a proportion of the fine quartz component was replaced by a coarser one. Gradations were also carried out in the very fine range. Instead of the CEM II/B-S 52,5 R Nanodur® binder a comparatively "coarser" C3 Nanodur®, which corresponded to a CEM III/A 52,5 R cement, was used by the project partners as the reference cement for further trials. Blastfurnace slag meal and fine limestone meal were also used as well as fly ash. The investigations were carried out with a practically proven fine-grained mix:

Fine-grained mix for binder comparison:

- 713 kg/m^3 binder (modified cement)
- 430 kg/m^3 quartz meal
- 1 150 kg/m^3 quartz sand
- 185 kg/m^3 water
- 18 kg/m^3 PCE superplasticizer

All the binder modifications containing three different blastfurnace slag meals, fly ash from coal and fine limestone meal reached the compressive strengths required in the project with 40 mm x 40 mm x 160 mm prisms of > 100 MPa and flexural strengths > 15 MPa.

5.3.2 Granulometric optimization of the high performance concrete

Combination of the results of granulometric UHPC optimization by Dresden Technical University and the experience gained with the binder raw materials from the projects discussed above led to UHPC binder compositions that were easy to use. The resulting binder concept (BMK-D5-1) contains the necessary standard and ultra-fine cements (Mikrodur®) for granulometric optimization.

The compressive and flexural strengths of three selected UHPC compositions (› Table 2) are shown in the graphs in › Fig. 15.

However, the first two compositions have a significantly less favourable CO_2 footprint with proportions of Portland cement of 360 and 370 kg/m^3 respectively when compared with the "BMK-D5-1" binder containing 255 kg/m^3 cement. The significantly lower Portland cement content used there in combination with granulated blastfurnace slag and ultra-fine cement as well as limestone meal still generates good flexural strengths and adequate compressive strengths through integrated granulometric coordination with aggregates that are used in practice. The binder is currently designed especially for C[3] concretes and is always used in combination with carbon reinforcement.

6 Final comment

As a result of the investigations in the projects described above it should be noted that optimized composition of the binders made of high-grade raw materials in combination with suitable fine cement components always produces a very dense hardened cement paste that, with test pieces stored under water, achieves compressive strengths in the range from 120 to 150 MPa and flexural strengths between 15 and 20 MPa. This is in fact comparable with conventional UHPC compositions where the higher mechanical characteristic values are mainly the result of special processes, such as heat treatment, and special additives, such as fibres. Further test results will follow in part 2.

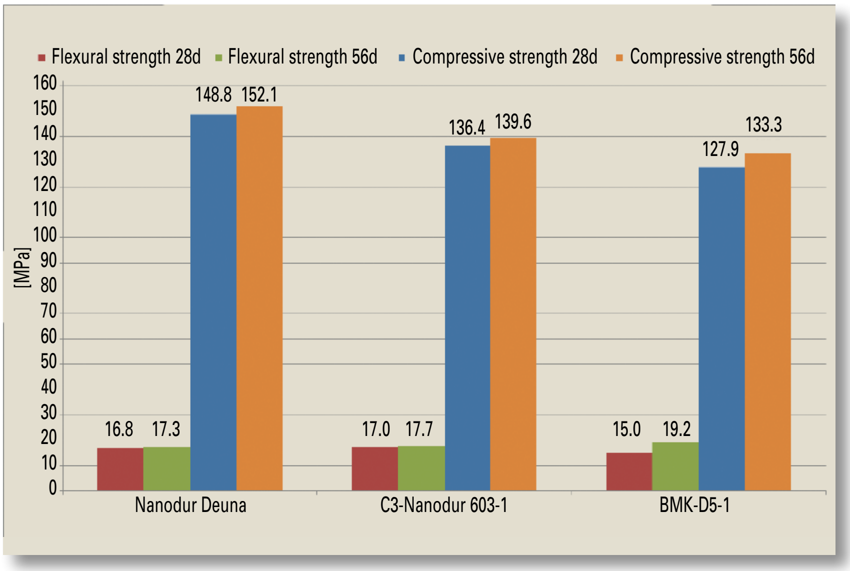

Figure 15: Characteristic mechanical values of the coarse grain mixes

Table 2: Composition of the coarse grain mixes

	Unit	Nanodur® Deuna	C3 Nan. 603-1 Neuwied	BMK-D5-1 Deuna
Binder	kg/m³	619	669	621
CEM I 42,5 R	kg/m³	370	–	255
CEM I 52,5 R	kg/m³	–	360	–
Granite chippings 2/5	kg/m³	880	419	837
Sand 0/2	kg/m³	430	669	530
Fine sand	kg/m³	–	267	250
Quartz meal 1	kg/m³	430	101	–
Quartz meal 2	kg/m³	–	67	–
Water	kg/m³	163	194	145
w/b	–	0.26	0.29	0.23
PCE	kg/m³	15.5	16	16
Bulk density	kg/dm³	2.549	2.415	2.470

Acknowledgement

The authors would like to express their thanks for the financial support of the Federal Ministry of Education and Research (BMBF) in the context of the OLAF project (FKZ 03X0066A) and the C[3] carbon concrete composite B2 base project (FKZ 03ZZ0303E) and of EU Commission in the context of the H-House project (GA 608893).

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SUMMARY

Part 1 of this article described the development of a nano-technically optimized binder for producing high-performance concretes and the special properties of them during the work in three public funded projects. The description of the tests and the results that were obtained are continued in part 2. The attempt is also made to explain the dependence of the flexural strength on the type of storage using a special experimental test rig. The performance of the binders developed in part 1 is described by application tests supplemented by mineralogical investigations and microscopical methods. The global warming potential of the different binders and their sustainability in UHPC in comparison to standard concrete are considered. It was established that the proportion of Portland cement clinker in the UHPCs could be reduced by about 50 mass % when compared to a standard concrete made with Portland cement while still maintaining the high performance. The high performance of these UHPCs enables special applications and a description is given of some practical examples.

ZUSAMMENFASSUNG

In Teil 1 dieses Artikels wurde die Entwicklung nano-technisch optimierter Bindemittel zur Herstellung von Hochleistungsbetonen sowie die Eigenschaften beschrieben, die damit produzierte Hochleistungsbetone (UHPC) bei der Erprobung in drei öffentlich geförderten Projekten zeigten. Die Beschreibung der Tests und ihrer Ergebnisse wird in diesem Teil fortgesetzt. Außerdem wird mit Hilfe einer speziellen Versuchsanordnung die Abhängigkeit der Biegezugfestigkeit von der Lagerungsart aufgezeigt. Die Leistungsfähigkeit der in Teil 1 entwickelten Bindemittel wird anhand anwendungstechnischer Tests beschrieben und die Untersuchungen durch mineralogische und mikroskopische Methoden ergänzt. Dabei werden auch das Treibhauspotenzial der verschiedenen Bindemittel und deren Nachhaltigkeit in UHPC im Vergleich zu Standardbeton einbezogen. So konnte festgestellt werden, dass sich der Anteil von Portlandzementklinker in den UHPCs um etwa 50 M.-% im Vergleich zu einem Standardbeton bei gleichbleibender hoher Leistung reduzieren ließ. Beispiele verdeutlichen die Möglichkeiten, die sich aus der hohen Leistungsfähigkeit dieser UHPCs in der Praxis ergeben.

*) Part 1 of this article was published in CEMENT INTERNATIONAL 16 (2018) No. 1, pp. 58–69.

(Translation by Robin B.C. Baker)

*) Teil 1 dieses Beitrags wurde in CEMENT INTERNATIONAL 16 (2018) No. 1, pp. 58–69 veröffentlicht.

Nanotechnically optimized binders for the production of user-friendly high-performance concrete – part 2*)

Nanotechnisch optimierte Bindemittel für die Herstellung von anwendungsfreundlichem Hochleistungsbeton – Teil 2*)

1 Introduction

Conventional UHPC is produced from standard cements, predominantly finely divided aggregates and reactive silicon components – usually silica fume as a by-product of the production of ferrosilicon. The number of applications in Germany is negligible, not least because of the current building approval regulations, but worldwide there are impressive structures made with the UHPC high-tech material, especially on the basis of ready-to-use dry mixes. Among others, the current state of the technology in Germany has been documented in the research report DFG FE 497/1-1 (2005) [1], the assessment report by the DAfStb (2008) [2], the results of the BTB research project UHFB (2013) [3] and part 1 of this publication [4].

For more than 20 years Dyckerhoff has been producing specially separated ultrafine cements (Mikrodur®) based on Portland cement clinker and granulated blastfurnace slag for grouting in the geotechnical sector and for strengthening of structures. Derived from this there were special products like Microfond – mortar for filling high void asphalt layers as semi-flexible pavement – as well as the Flowstone premixed binder for producing artificial stone for architectural applications. The next step was the development of premium cements, i.e. standard cements supplemented with Mikrodur®, with exceptional performance for making concretes for high-strength columns, foundations, cooling towers, wind turbines, sewage structural elements and bridge reinforcements.

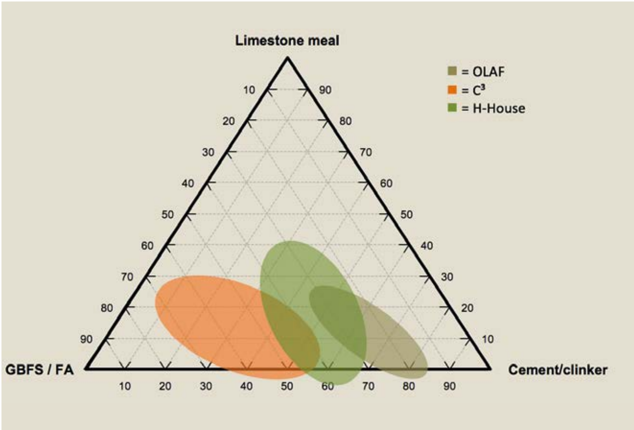


Figure 1: Classification of the binder designs used in the projects in a Rankin diagram

By combining these structure-optimized binders with reactive synthetic oxides Dyckerhoff developed the Nanodur® technology in 2007 and got patents granted for binders and methods of production.

Cement raw materials combined with synthetic oxides were investigated in three public funded projects, namely "OLAF – high performance concrete for all" (BMBF), "Energy efficient buildings: H-House" (EU) and "C³ Carbon Concrete Composite: base project B2 high performance concrete"

Table 1: Summary of the binder designs investigated in the projects

Cement in accordance with prEN 197-1:2014 (D)	OPC clinker [mass %]	Blastfurnace slag [mass %]	Fly ash [mass %]	Limestone [mass %]
(Nanodur®)1) CEM II/B-S	65...79	21...35	–	–
(H-House)1) CEM II/C-M (S-LL)	50...64	16...44	–	6...20
(OLAF)1) CEM X (S-V-LL)2)	< 50	6...20	6...20	6...20
(C³ BMK-D5-1) CEM VI (S-LL)	35...49	31...59	–	6...20

1) Used as compound 5941 containing 59 mass % cement and 41 mass % fine quartz sand
2) Not currently scheduled for standardization

Table 2: Summary of the UHPC compositions used

Constituent	Unit	Coarse grained	Fine grained	Paste
Binder compound 5941	kg/m³	1 050	1 050	1 000
Pit sand 0/2 (air dry)	kg/m³	430	1 150	–
Double-crushed chippings 2/5 (air dry)	kg/m³	880	–	–
Water	kg/m³	168	167	138
PCE superplasticizer	kg/m³	13.7	17.9	13.6

(BMBF). Binder designs were developed for different application fields (❱ Fig. 1).

Supplementary cementicious materials such as granulated blastfurnace slag, fly ash and limestone meal were used. In some cases they were also combined with different particle size distributions. The aim was to reduce the proportion of clinker to improve the ecobalance. However, the intention was to reach a compressive strength of at least 100 MPa and a flexural strength of ≥ 15 MPa.

For application in a concrete plant it should be possible to use the aggregates and mixing technology available there. For this reason, several binder compounds have been produced successfully by preliminary dry mix and homogenization processes of the components in special mixers in the cement plant. The mixing ratio of binder to fine quartz sand is 59:41. ❱ Table 1 provides a summary of the binder mix formulations developed in the projects in comparison to the Nanodur® Compound 5941, which was used as a reference material.

2 Investigation of the material properties

2.1 Compressive and flexural strengths

Mortar prisms (40 mm x 40 mm x 160 mm) were produced with the different binder mixes for testing the mechanical parameters and removed from the mould after 24 h. They were stored under water at 20 °C until examination. The compressive and flexural strengths were tested after 2 and 28 days. Not only cement paste but also fine grained mixes were used for the investigations (❱ Table 2). In each case three paste prisms were autoclaved for six hours at 12 bar and 180 °C after they had been removed from the mould.

The compressive strengths of the investigated fine grained mixtures (❱ Fig. 2) laid between 100 and 140 MPa after 28 days' water storage. Naturally, that depended on the clinker content of the binder used. With a proportion of supplementary cementicious materials of more than 50 %, compressive strengths of more than 100 MPa could still be achieved because of the density of the matrix. This value represented the target strengths for the intended applications in the projects.

The flexural strengths of the investigated fine grained compositions (❱ Fig. 3) also depended on the reactive constituents of the binder used. On average, the limit of 15 MPa which is important for designing

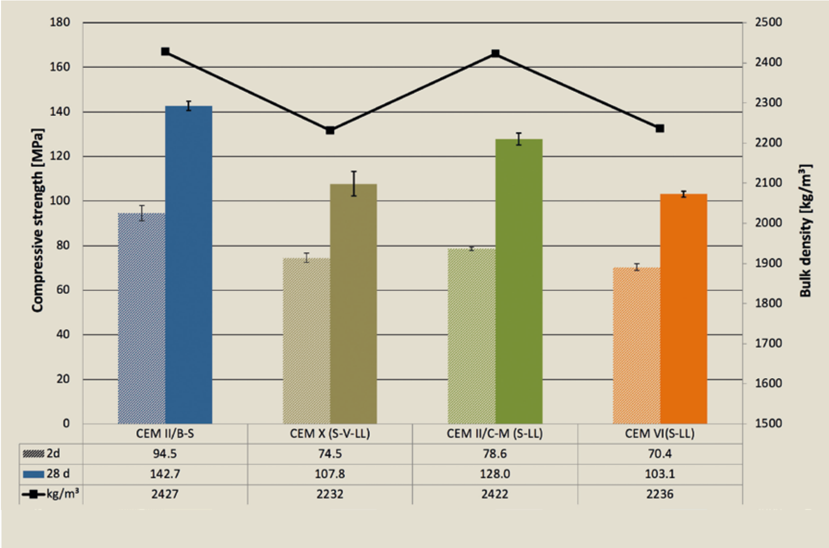


Figure 2: Prism compressive strengths and bulk densities of the fine grained mixes

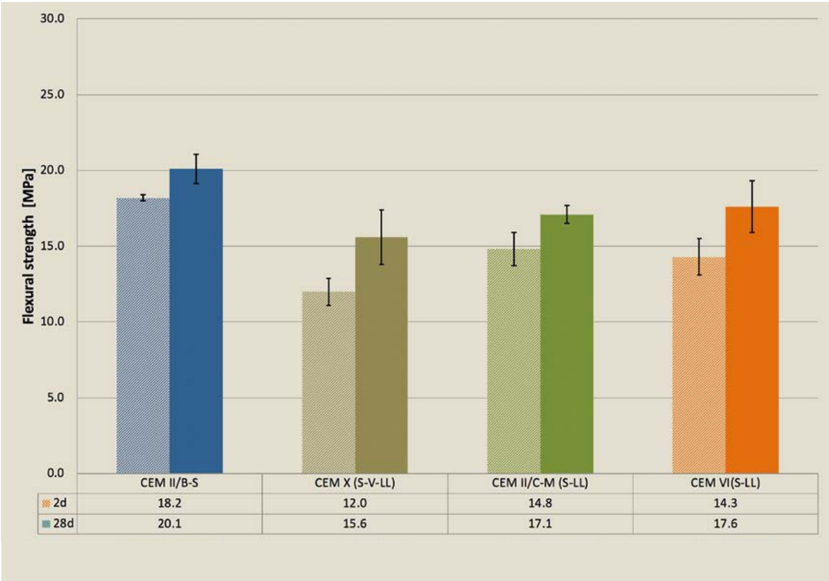


Figure 3: Prism flexural strengths of the fine grained mixes

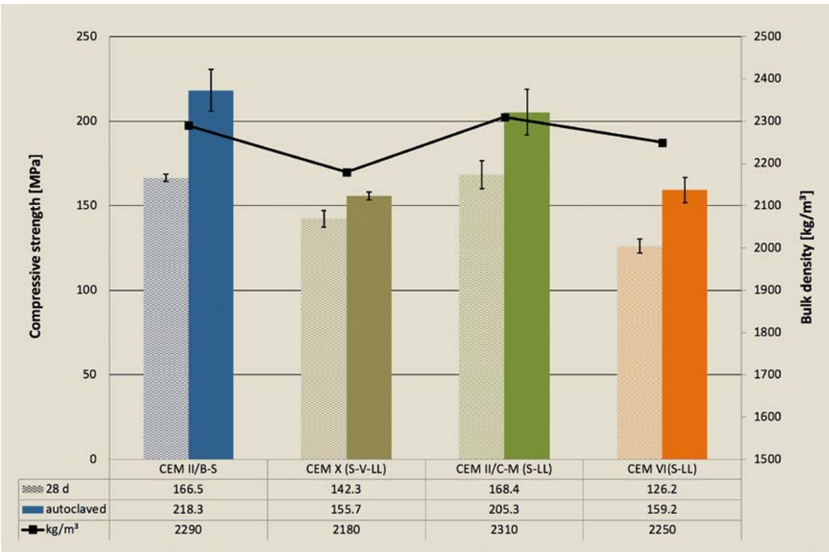


Figure 4: Compressive strengths and bulk densities of the autoclaved paste prisms (the compressive strengths of the paste prisms after 28 days' water storage are shown for comparison)

façade elements was also achieved by the binders with a high content of other main constituents. However, the characteristic value of the flexural strength was lower because of the greater test scatter.

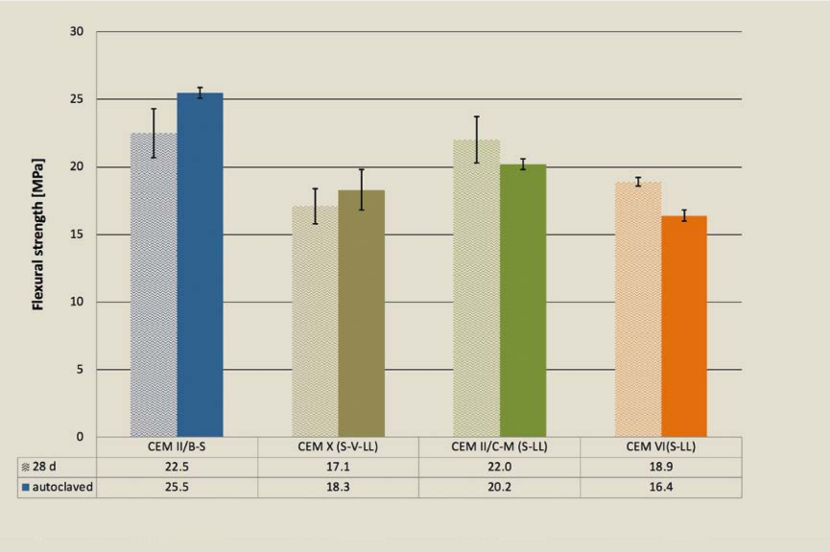
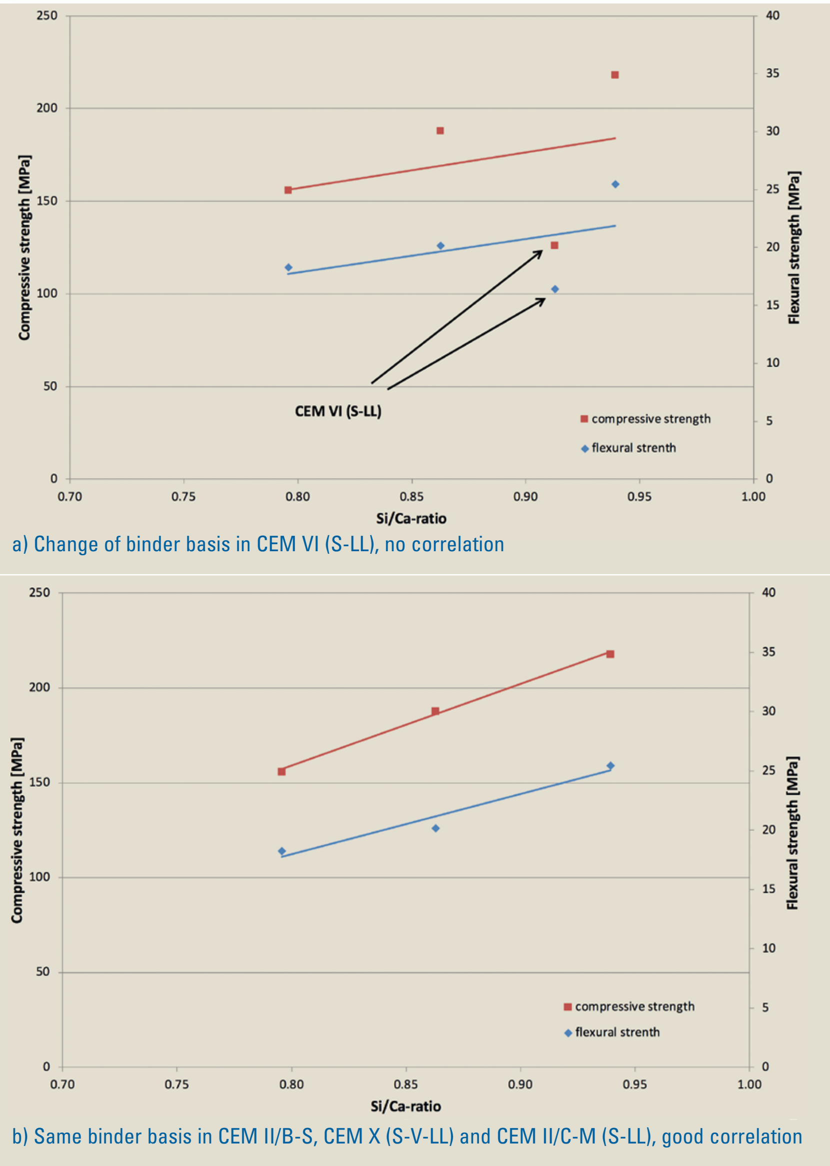


Figure 5: Flexural strengths of the autoclaved paste prisms (the flexural strengths of the paste prisms after 28 days water storage are shown for comparison)



a) Change of binder basis in CEM VI (S-LL), no correlation

b) Same binder basis in CEM II/B-S, CEM X (S-V-LL) and CEM II/C-M (S-LL), good correlation

Figure 6: Dependence of the compressive and flexural strengths of autoclaved paste prisms on the Si/Ca ratio of the binder compounds

The autoclaved paste prisms gave consistently higher compressive strengths than the samples stored in water after 28 days' hardening (❱ Fig. 4). This confirms previous observations [5, 6]. The matrix was brittle and the fracture characteristics resembled those of ceramics.

On the other hand, the flexural strengths were not always increased by the autoclaving. Sole replacement of clinker by limestone meal had a strength-reducing effect. The change in the C-S-H composition produced by the limestone apparently meant that the microstructure reacted more stably to the pressure stressing but less stably to the flexural stressing. The Si-rich fly ash contained in the CEM X (S-V-LL) sample in addition to the limestone meal appeared to offset this negative effect. An increase in the flexural strength due to the autoclaving process can be detected again (❱ Fig. 5).

Lehmann [6] mentions that limestone meal works not very effective during autoclaving. In his dissertation he describes how Ca-rich raw materials lead to Ca-rich C-S-H phases. In contrast to that, materials containing Si raise the proportion of Si in the C-S-H phases. In his autoclaving tests a high Si/Ca ratio in the C-S-H phases generally had a strength-increasing effect. In the tests described here it was found that the Si/Ca ratio in the binder compound correlated with the compressive and flexural strengths of the autoclaved paste prisms (❱ Fig. 6b). However, this only applies for observations with the same reactive raw materials. This relationship no longer holds if the cement components are changed (❱ Fig. 6a).

2.2 Influence of the storage conditions on the flexural strengths of the UHPCs

Previous investigations showed strong scatters between the individual values in the flexural strength of UHPC prisms. The resulting high standard deviations are particularly unfavourable as the flexural strength, in particular, plays an important role when assessing the properties of UHPC. Specific analysis of the influence of different storage conditions showed that the moisture level and therefore the storage conditions, have a significant influence, especially with high performance concretes (❱ Fig. 7).

Every step in the flexural strength testing procedure from sampling to loading of the prisms are in fact regulated basically. But with UHPCs even very slight variations

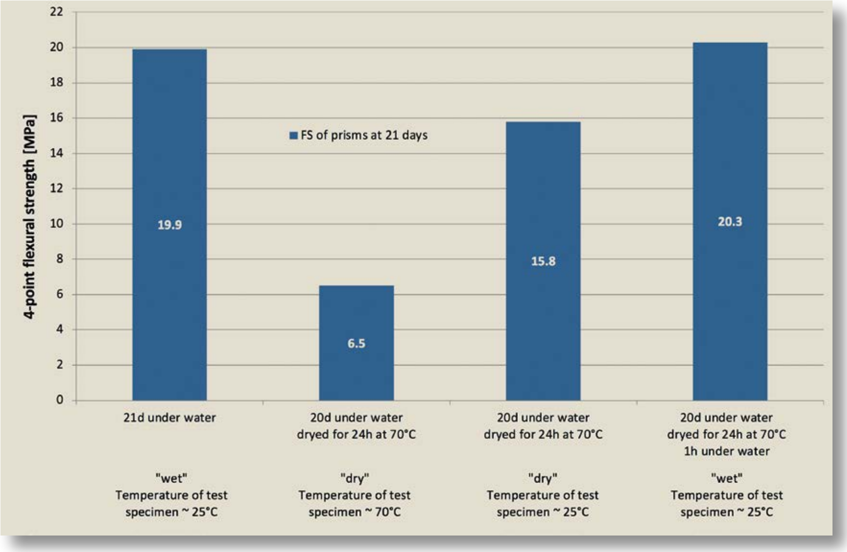


Figure 7: Flexural strengths in relation to storage conditions of the test pieces, measured on 160 mm x 40 mm x 40 mm prisms (n = 3)

gradients was measured with a test outlined in ❱ Fig. 8. A dry test piece positioned on two supports was half immersed in water. Then an axial deformation of around 11 µm was observed within two hours by the swelling and measured with extremely sensitive electro-optical measuring equipment. The mechanical load that could have resulted the same deformation was calculated and the order of magnitude lay in the range of the usual flexural strengths. This simple test demonstrated that the moisture content can have an extreme influence on the flexural strength [7].

can cause substantial differences in the measured values. In fact this phenomenon is also known with normal concrete but more pronounced with high-performance concrete. The explanatory models for concrete technology are not sufficient to explain this observation.

So investigations were commissioned at the Fraunhofer Institute for Silicate Research (ISC) in Würzburg to explain the reasons for the sharp fluctuations in flexural strength. The tests were carried out on dry and water stored samples.

The moisture distribution showed a strong gradient in the surface region of 0 to 5 mm. The effect of these moisture

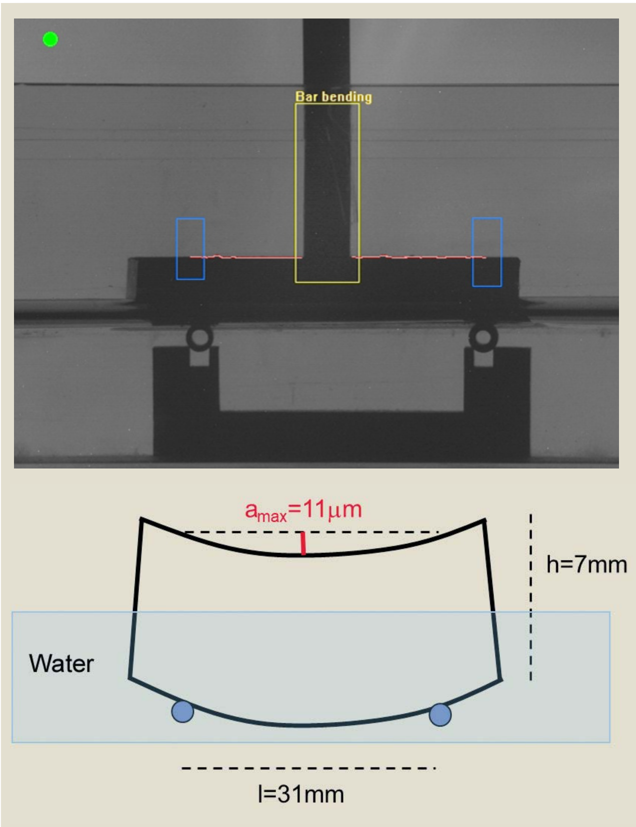


Figure 8: Test rig (top): 40 mm x 20 mm x 7 mm mortar prism, half-immersed in water, top surface coated with waterproof varnish, test piece on supports; schematic diagram of deflection test (bottom)

2.3 Durability investigations

2.3.1 Freeze-thaw resistance by the CDF method

In the CDF method the concrete surface to be tested is fully immersed in a 3 % NaCl solution and exposed to 28 freeze-thaw cycles between -20 and +20 °C. Afterwards the quantity of the scaled material is determined. The coarse grained mixes from Table 2 were used for the tests.

The scaling loss of all the UHPC samples tested after 28 cycles lay far below the CDF test limit of 1 500 g/m^2 [8]. It even met the required limit of 200 g/m^2 for the scaling loss from tactile slabs of the implementation regulations for footpaths and cycle lanes stipulated by the Berlin Senate [9]. Water or salt solutions hardly penetrate into the microstructure because of its high level of impermeability, as is also shown by the low water absorption (❱ Fig. 9). The freeze-thaw resistance of UHPC is therefore not determined by the proportion of air voids [10]. This means that normally a high freeze-thaw resistance of UHPC can be expected.

2.3.2 Chloride migration

Chloride migration is tested by measuring the penetration depth of a NaCl solution into a defined concrete body connected to a voltage of 30 V. The samples are then split and the penetration depth of the chloride ions is measured using silver nitrate solution as an indicator. The chloride migration coefficient, which is a degree for the penetrating capability of the chloride solution, is calculated from the applied voltage, the measured current strength and other parameters. The lower the coefficient the more impermeable is the microstructure and the weaker is the penetration of the chloride solution into the concrete matrix.

The test is based on the BAW code of practice "Chloride penetration resistance of concrete (MCL)" [11]. It was carried out on test pieces made with the fine-grained mix formulation in Table 2. The measured migration coefficients of all the samples tested lay significantly below the limit of $5 \cdot 10^{-12}$ m^2/s. The CEM II/C-M (S-LL) sample had the highest value. In this case the replacement of granulated blastfurnace slag by limestone meal affected the penetration resistance. However, even this binder easily complied with the limit (❱ Fig. 10).

Similar results are also described in [12] in which pure Portland cement systems containing silica fume were tested. The results confirm that, because of the impermeable microstructure, the chloride migration is very low regardless of the binder composition and the risk of steel corrosion in UHPC is extremely low.

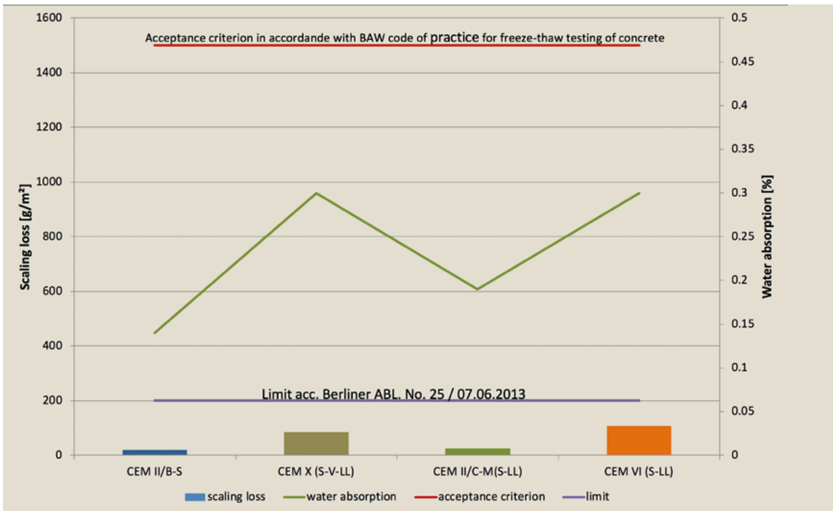


Figure 9: Scaling loss and water absorption of the test pieces in the freeze-thaw cycle test after 28 cycles (fine grained mix given in Table 2)

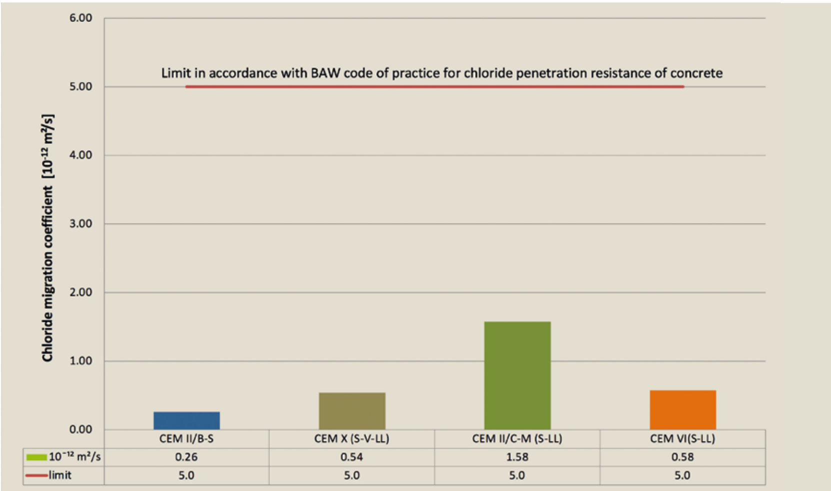


Figure 10: Results of chloride migration test (test piece: fine grained mix given in Table 2)

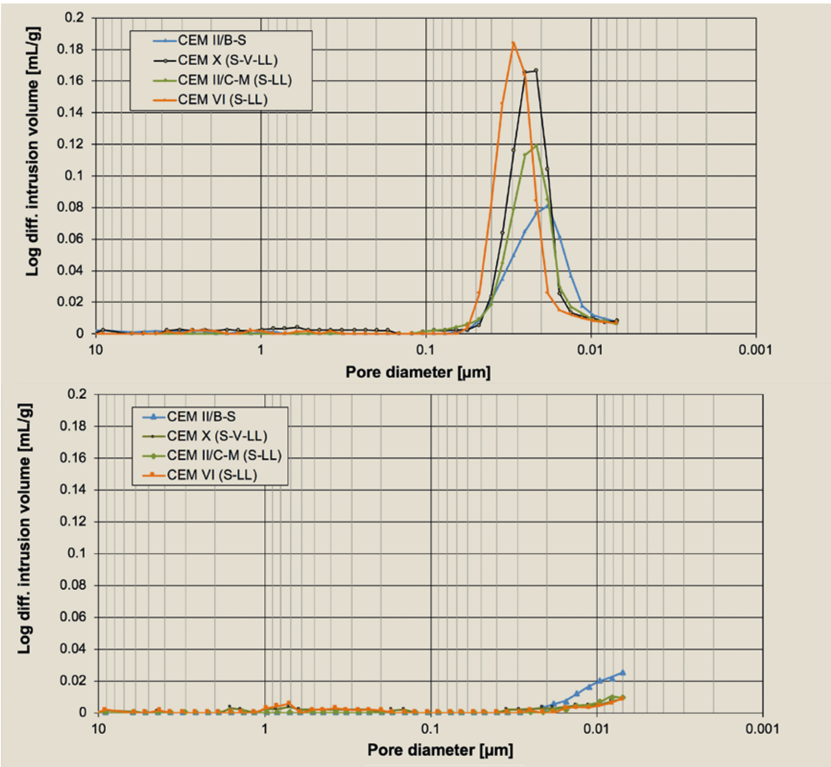


Figure 11: Pore size distribution in the UHPC paste prisms after 28 d hydration (top) and after autoclaving (bottom)

2.4 Microstructural investigations

2.4.1 Mercury intrusion porosimetry

With the mercury intrusion method the pore size distribution is determined. First the specimens are evacuated. Then the pores are filled by mercury at increasing pressure. The higher the pressure the smaller the pores which are filled. The AutoPore IV 9505 model from Micro-metrics was used. The tests were carried out on paste samples. For these investigations pieces with a size of about 10 mm were dried for 24 hours at 105 °C and then measured. ❱ Fig. 11 shows the pore size distributions of the UHPC pastes at 28 days (top) and the distribution in the equivalent samples that had been autoclaved (bottom). There are practically no capillary or air voids present after 28 days of hydration, which is the aim with UHPCs. In all the samples examined there were pores in the upper gel pore range of 0.01 to 0.05 µm. The lowest proportion of pores was exhibited by the Nanodur® (CEM II/B-S) used as a reference. The UHPC mixes with reduced clinker fractions had a significantly higher proportion. The maximum in the distribution was also displaced towards larger pore diameters with increasing proportion of pores. Comparison with the results from the CDF tests shows a correlation between the two parameters – the lower the proportion of pores the lower is the scaling loss.

Autoclaving of the samples led to a significant reduction in the proportion of pores and a displacement into the lower gel pore range of < 10 nm. It was no longer possible to detect any significant differences here between the different clinker-reduced UHPC mixes and their proportions of gel pores were even somewhat lower than with the Nanodur® mix. Apparently sufficient new formation and transformations of hydrate phases occurred to densify the compact UHPC microstructure even more in spite of the low water content of the concrete recipes.

2.4.2 Scanning electron microscopy

A Stereoscan 360 from Cambridge Instruments was used for the scanning electron microscope investigations, which were carried out on paste samples in the secondary electron mode. The samples were freshly crushed and the surfaces sputtered with platinum.

In the scanning electron microscope (SEM) the UHPC mixes containing fly ash and limestone meal exhibited a very impermeable microstructure when compared with normal concrete. The hydration products and unhydrated phases form an impermeable and structureless matrix

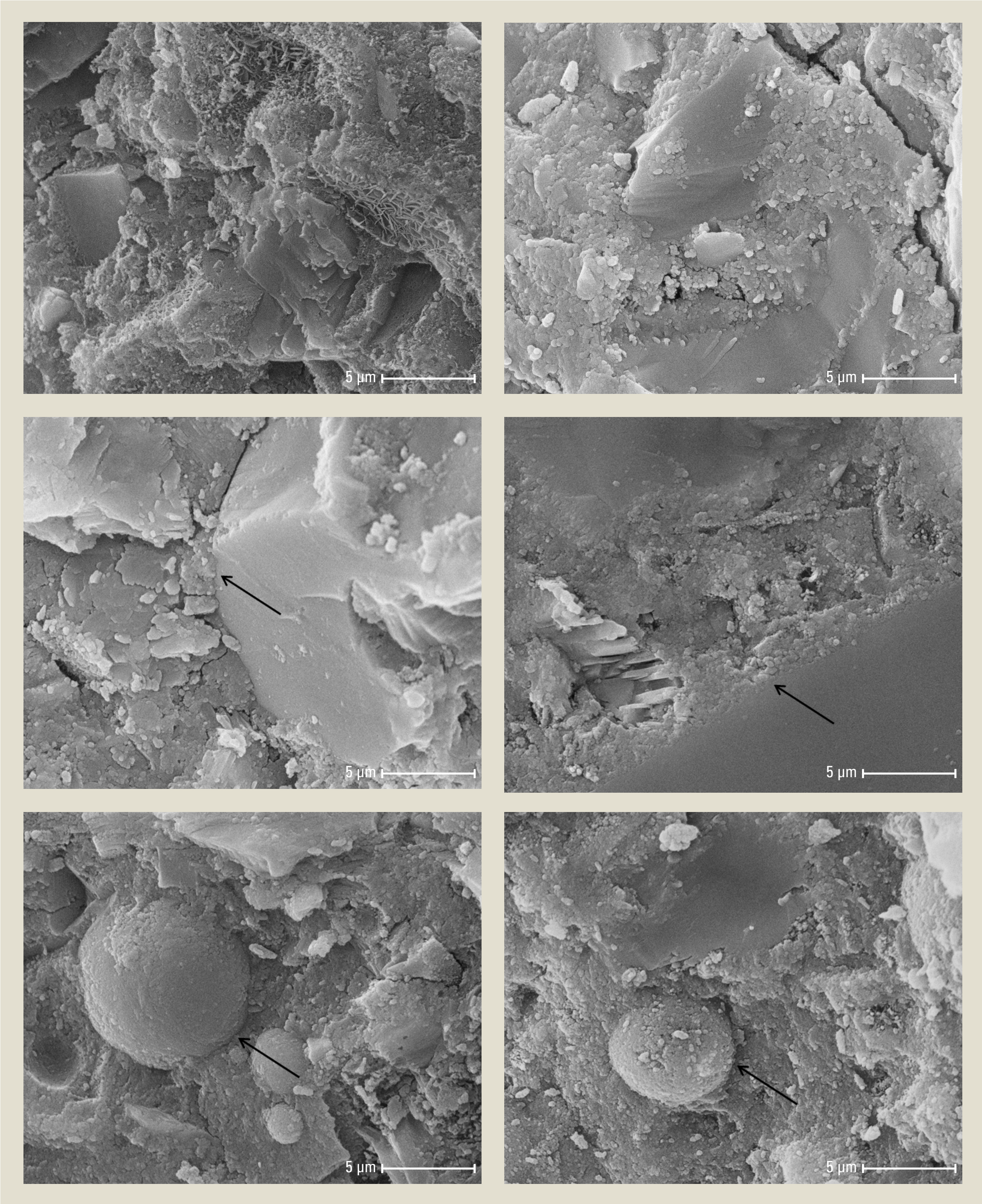


Figure 12: Scanning electron microscopy: top row: comparison of 28 days old normal concrete (left) with Nanodur® (right); middle row: quartz grain in matrix hydrated for 28 days (left) and in autoclaved matrix (right); bottom row: fly ash in matrix hydrated for 28 days (left) and in autoclaved matrix (right)

(❱ Fig. 12, top). Individual hydrate phases could no longer be detected in the SEM. The superficially hydrated granulated blastfurnace slag particles were closely combined with the binder matrix. In the samples that had been stored in water the quartz meal particles emerged smoothly from the binder matrix. On the other hand, the autoclaved samples exhibited a close bond of the cement matrix both with the granulated blastfurnace slag and with the quartz particles (Fig. 12, middle). The quartz and granulated blastfurnace slag are compactly interlocked with the binder matrix as further reaction between both had taken place during the autoclaving process in spite of the low water content.

With coal fly ash the autoclaving did not apparently produce this kind of intensive improvement of the bond with the binder matrix as in this case most of the fly ash particles had emerged from the matrix just as with the samples stored in water (see ❱ Fig. 12, bottom). However, hydration fringes could be detected on the surfaces.

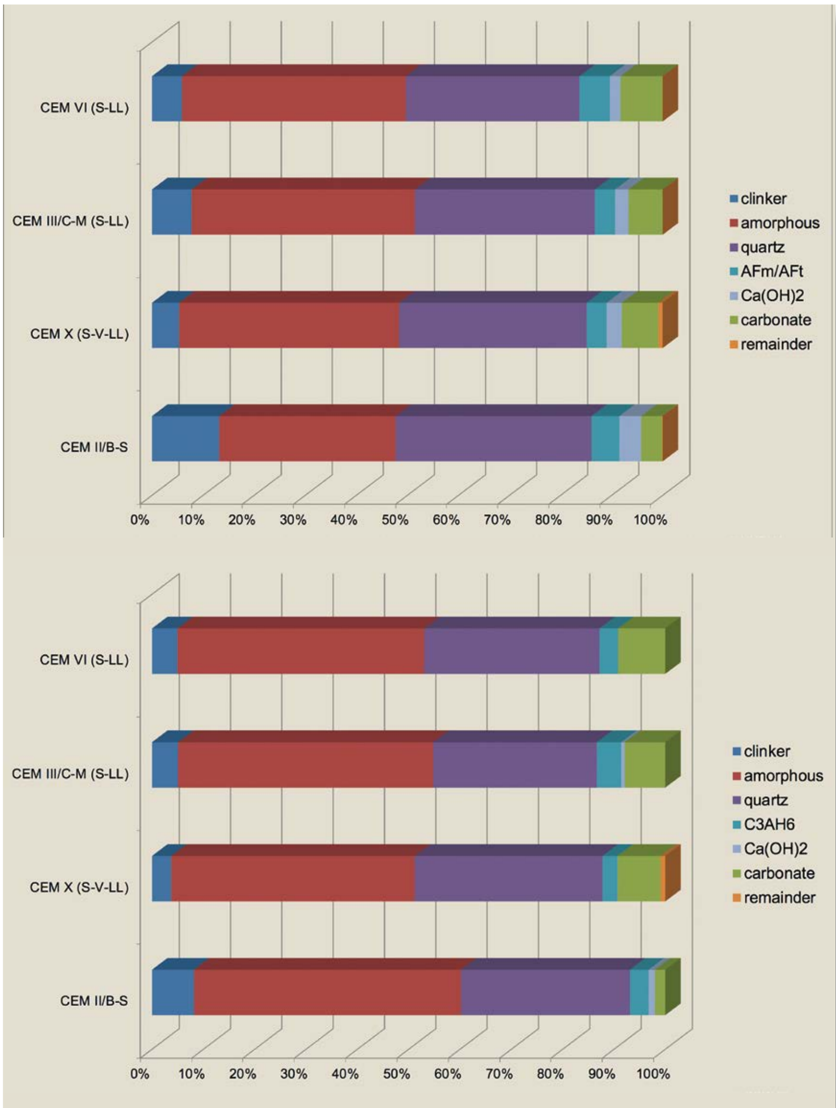


Figure 13: Mineralogical composition of the paste prisms a) after 28 days' hydration (top), b) after autoclaving (bottom)

2.4.3 X-ray diffractometry

The paste samples were ground and examined using X-ray diffractometry to determine the mineralogical composition. A D4 diffractometer from Bruker was used.

Not only ettringite but also the AFm phases monosulfate and monocarbonate were formed in the pastes hydrated for 28 days. It was not possible to differentiate between the fraction of C-S-H phases and the amorphous fractions of granulated blastfurnace slag and fly ash.

The autoclaving process led to the conversion of the aluminates to hydrogarnet C_3AH_6. In contrast to the investigations in [5, 6] it was not possible to detect any tobermorite or xonolite in the binder mixes examined here. Apparently, X-ray-amorphous silicate hydrates are formed. Their proportion increased more or less significantly with the autoclaving. Nevertheless, according to [5] crystalline C-S-H phases are formed that generate a stable, tightly cross-linked, structure that is intensified by a higher autoclaving temperature. However, these crystals could only be detected in the transmission electron microscope and had sizes of several 10 to 100 nm. In spite of their crystalline structure such small hydrate phase can only be detected in the diffractometer as an X-ray-amorphous fraction.

Because of the low water content it is always possible to identify unhydrated clinker phases in the materials being investigated, even after autoclaving. Residual clinker and the quartz fraction are reduced by further hydration while the proportion of amorphous phases increases (❱ Fig. 13). The hydration of the granulated blastfurnace slag cannot be recorded with the diffractometer.

The investigations have shown that the other reactive main constituents are partially converted into C-S-H phases and in this way densified the cementicious matrix. The mineral composition of the resulting concrete does not differ in any way from that of standard concrete. It is just that the cement matrix has a higher degree of densification through the phase conversions. Unknown risks from high addition levels of silica fume, such as with conventional UHPC where the pozzolanic reaction has not run its full course, do not occur here.

3 Observations on sustainability

Not only the global warming potential of the binders tested but also the sustainability potential of the high-performance concretes were evaluated in the consideration of the sustainability of the UHPCs.

In modern high-performance concretes the cementitious binder contributes up to 85 % of the CO_2 balance. The remaining 15 % is essentially accounted by the superplasticizers used and the material transport. To reduce the global warming potential the obvious course is therefore to reduce the proportion of Portland cement clinker in the high-performance concrete. These investigations have shown that durable UHPCs with strengths of 100 to 140 MPa can be produced with granulometrically and nanotechnically optimized binders using high proportions of other main constituents.

Ecobalances for the binder designs that had been developed were drawn up in all three projects. They relate to the production of 1 m^3 fresh concrete in the plant. A high-strength concrete composition (C55/67) with 475 kg/m^3 CEM I 52,5 R cement and a w/c ratio of 0.40 was used as the reference mix.

Comparison of the global warming potential of the considered binders systems showed variations of +10 % to -20 % relative to the reference system (❱ Fig. 14).

Because of the high binder content the UHPC concretes generally exhibit higher global warming potentials than conventional reference concretes but by selecting suitable alternative main constituents the CO_2 equivalent of the binder can be lowered without adversely affecting the durability properties of the concretes.

However, this consideration covers only a partial aspect of the ecobalance. Another aspect is the sustainability of the different

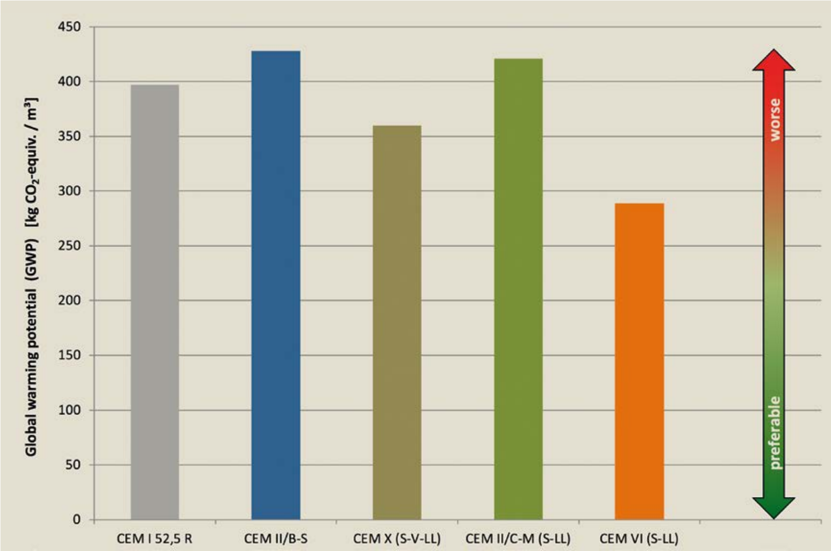


Figure 14: Global warming potential (GWP) of the individual binders, relative to 1 m³ concrete with low content of Portland cement (reference) and high binder content (UHPC)

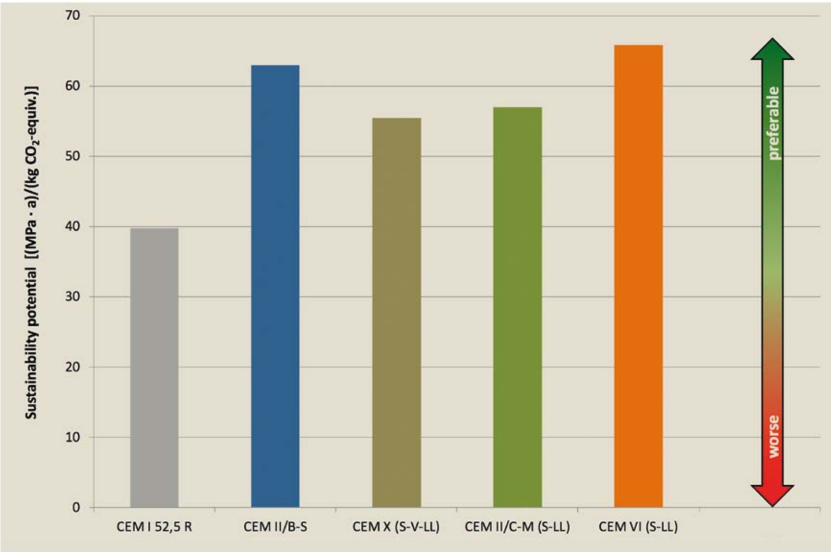


Figure 15: Sustainability of the UHPC fine grained mixes made with high content of UHPC binders in comparison with a reference concrete with low content of Portland cement

methods of construction. Substantially more durable and more slender components can be produced with UHPC than with normal concrete. The resulting lower consumption of material reduces the global warming potential of construction with UHPC compared with the reference system, in some cases substantially. This inevitably also improves the sustainability.

One approach to evaluating the sustainability at the building materials level is described in [13]. This approach considers not only the CO_2 balance but also other factors such as the efficiency and durability of the building materials used.

Based on [13] the concrete sustainability potential Ω is defined in simplified form in accordance with the following equation using the service life of the concrete, the efficiency – expressed as a characteristic compressive strength – and the global warming potential (GWP):

$$\Omega = \frac{\text{service life} \cdot \text{characteristic strength}}{\text{GWP}}$$

The binders under investigation were all tested in a high-performance mix, so they all exhibited very good durability properties (see section 2.3). A maximum service life of 200 years was assumed in conformity with the literature. The characteristic compressive strength was taken as the specific performance feature of the binder system. ❱ Fig. 15 shows the sustainability potentials of the UHPC concretes made with high amount of the different individual binders in comparison with a standard concrete produced with low amount of CEM I 52,5 R. The sustainability potential can be increased by up to 40 to 65 % when compared with the standard concrete.

However, a building approval regulation is needed to make this potential usable in practice (see section 7.2). So far, expensive and time-consuming agreements have been needed for each individual case, which has deterred designers and employers from making greater practical use of the advantages of the construction with UHPC .

4 Mixing technology

Particularly shear-intensive high-performance mixers are recommended for processing UHPC because of the large number of very fine constituents that are difficult to mix. Nanodur® Compound 5941 is already being homogenized in high-performance powder mixers in the cement plant with the result that UHPC can be produced reliably in normal pan mixers. When compared with usual UHPC applications with silica fume this demonstrates the exceptional user-friendliness of the UHPC designs developed in the projects. For example, UHPC can also be produced with the Nanodur® Compound 5941 in simple drum mixers.

Nanodur® concrete containing 60 kg/m³ micro steel fibres was used for the tests. It was produced in a drum mixer (❱ Fig. 16). All the dry starting materials were first mixed for one minute. The water-PCE mixture was then added slowly.

Depending on the type of superplasticizer the usual consistency (❱ Fig. 17) is reached after a total mixing time (wet + dry)

Table 3: Compressive strengths of the UHPC test specimen produced in different mixers after storage under water (coarse grained mix as shown in Table 1 containing 60 kg/m³ micro steel fibres)

	Drum mixer	Pan mixer
Mixing time [min]	8	
Prism compressive strength after 28 d [MPa]	188.0	177.3
Cube compressive strength after 28 d [MPa]	155.0	149.1

Figure 16: Addition of dry mix with NC 5941 (left) and micro steel fibres dosage (right)

of 8 minutes. The fresh concrete temperature lies between 21.8 and 23.2 °C (for a starting temperature of 20 °C).

The compressive strengths after 28 days all lay at a comparable level (❱ Table 3). As a future perspective, this procedure can definitely be of interest for ready-mix concrete in the case of larger quantities in which the material is homogenized briefly in the plant and the final mixing is then carried out in the truck mixer. For mechanical engineering this can be an interesting alternative for fairly small companies, especially abroad, as current drum mixers with filling volumes of up to 320 l are available as standard.

5 Examples of applications

5.1 Mechanical engineering

The early use of concrete in mechanical engineering goes back to 1917 when for the first time the engineer Georg Schlesinger replaced cast iron for tool machine beds by cement concrete. Applications then occurred more regularly from 1940 but the material did not gain acceptance in the long run because of high wear and lack of accuracy. However, the better damping of mass concrete than metal materials was attractive in principle. In the 1980s VDF Böhringer (now MAG IAS GmbH) then used a B55 concrete for producing the lower parts of beds in conjunction with bonded cast iron blocks [14].

Concrete has experienced a renaissance in the field of mechanical engineering with the development of UHPC and since then has replaced the widely used polymer concrete or "mineral casting". When compared with this material bonded with reactive resin, which has to be compacted in massive steel moulds, simple wood formwork is adequate for self-compacting UHPC. Another advantage is its greater dimensional stability with respect to creep at fairly high temperatures. An essential requirement in the production of machine beds is the crack-free production of geometrical shapes through the high strength of the hardened cement paste. A linear-elastic behaviour is required. After the end of the millennium the Homag Group used UHPC on a fairly large scale to make beds for woodworking machines (❱ Fig. 18).

Figure 17: Slump of the UHPC mixed in the free-fall mixer

The UHPC coarse grained composition containing Dyckerhoff Nanodur® Compound 5941 was used for the first time on a large scale in 2010 at the Sudholt-Wasemann special precast component plant and since then has remained unchanged:

- 1 050 kg/m³ Nanodur® Compound 5941
- 880 kg/m³ chippings 2/5
- 430 kg/m³ sand 0/2
- 158 kg/m³ water
- 15 kg/m³ PCE
- 6 kg/m³ shrinkage reducer

A flexural strength of 5 MPa is taken as the basis for the dimensioning and at least 15 MPa must be reached after 7 days in the production check on 4 cm x 4 cm x 16 cm prisms.

The self-compacting concrete mix is extremely robust and is now used successfully by various manufacturers around the world with local aggregates.

In addition to the Homag Group, world market leaders of tool machines in the metal processing sector are now using UHPC as a cost-effective and technically very attractive material. A new plant for the production of machine beds made of Nanodur® UHPC was opened in China in 2016. However,

Figure 18: Production of machine beds for woodworking machines; left: UHPC machine bed; right: finished machine

the first elements of a large portal milling machine were manufactured in Germany at Sudholt-Wasemann (❱ Fig. 19).

The Young's modulus of UHPC, which is already very high at about 50 000 MPa, can be increased to over 80 000 MPa by replacing the sand and chippings aggregate in the coarse grained mix described above by industrially processed heat-treated material, which means that it is higher than that of aluminium at 70 000 MPa.

This material property is of particular interest for machine components with very high requirements for stiffness and vibration damping. A first application was a measuring table with a special steel working surface embedded in concrete for the Spanish Research Institute Leit-IK4. Nanodur® concrete E80 used in conjunction with the bonding technique described later was awarded the 2016 innovation prize for the supply industries at the 60th Concrete Conference in Neu-Ulm.

Nanodur® Compound 5941 is now firmly established in the quality assurance plans of numerous tool machine beds and is therefore essential for the service life of the respective models. It is suitable, in principle, for use in mechanical engineering but also for all the other binder designs described above. Further reduction of the Portland cement clinker would also have a beneficial effect on the shrinkage of the UHPC that is crucial for the dimensional stability of machine beds and the positioning of fixtures.

5.2 Fish farming basins with special bonding technology

Based on the prototype of a bonded basin as a trade fair exhibit at Eurotier 2012 Benno Drössler GmbH together with Green Aqua Farming GmbH started to develop fish farming systems as modular structures with individual UHPC elements of any size that are bonded together (❱ Fig. 20). A 35 m long by 5 m wide double-level shrimp farming plant was then built for the first time at Grevesmühlen with the coarse grained UHPC mix described above containing Nanodur® Compound 5941. The elements with a wall thickness of only

Figure 19: Portal milling machine of Chinese production (Yonghua, China, photos Rottler)

Figure 20: Fish farming basins made of UHPC slabs bonded together

6 cm were produced without any reinforcement – the lower ones contained integral supports for the upper ones. After the lower basin elements had been positioned on prepared concrete beams the upper elements were placed on girders and crossbeams made of high-strength normal concrete. After completion of the installation the joints were closed by gluing cover plates in place with reactive resin adhesive. A hydraulic mortar approved for drinking water was used for sealing the joints between the cover plates and the basin elements [15].

5.3 Structural bridge strengthening

The practical feasibility of strengthening bridges with UHPC was tested successfully in 2013 in a pilot project at the initiative of Graz Technical University. 40 m^3 UHPC made with Nanodur® Compound 5941 were prepared in a ready-mixed concrete plant and placed as in-situ concrete. The aim was to raise the load-bearing capacity and at the same time to provide a seal to replace the bituminous covering (› Fig. 21). Unlike the applications described above the self-compacting coarse grained mix formulation was not used here as the grading curve had to be optimized for a placement at slopes of up to 4.5 %.

In 100 mm cubes compressive strengths of 146 MPa after 28 d and 172 MPa after 98 d were achieved with this mix as well as a flexural strength in 150 mm x 150 mm x 700 mm beams of 11.5 MPa in the 4-point test. The Young's modulus reached 52 000 MPa [16].

- 950 kg/m^3 Nanodur® Compound 5941
- 1 420 kg/m^3 quartz sand 0.6/1.2 and basalt chippings 2/4
- 90 kg/m^3 steel fibres 13/20
- 146 kg/m^3 water
- 14 kg/m^3 superplasticizer and retarder

6 Final comment

6.1 Application in construction

UHPC has hardly been used so far in Germany as a structural material because of the very expensive agreements needed in each individual case although in the long term it would be very interesting from the economic point of view due, in particular, to its great durability. This means that currently only special applications based on the specific properties of UHPC can be implemented cost-effectively.

6.2 Standardization – monitoring for standard designation

According to current standards the strength classes end at a C100/115 and it is only permissible to work up to C80/95 without time-consuming and expensive agreement in the individual case. This means that UHPC is not at present

Figure 21: Work on bridge strengthening with UHPC at the Steinbach bridge, Austria

covered by building approval regulations and compilation of the DAfStb guidelines is in progress but not yet completed.

On the binder side, compounds made of cement and fine aggregate are also not covered by the regulations and unfortunately at present no attempts are being made in this direction. However, this would be absolutely essential as it is only possible to achieve homogeneous distribution of the fine constituents that are essential for UHPC by intense dry mixing in a cement plant. Only in that way there is no need for a special mixing technology in the subsequent wet concrete mixing. Testing of Nanodur® Compound 5941 as a cement complying with EN 196 at a w/c of 0.5 with standard sand has been practiced successfully since 2010 for quality assurance in mechanical engineering. The strength targets of 15 MPa after 2 d and 40 MPa after 28 d are reliably met with the "mortar" consisting of 59 mass % cement and 41 mass % fine quartz sand. The strengths of the UHPC coarse grained mix in 4 cm x 4 cm x 16 cm prisms after 7 d always lie above 15 MPa flexural strength and 120 MPa compressive strength with Young's moduli of more than 45 000 MPa.

For UHPC with an extremely impermeable microstructure and the demonstrably higher quality than normal concrete these parameters should actually be sufficient for the monitoring and in this way facilitate the introduction of this new material. Only cement main constituents that had proved themselves over the years were used in the case of Nanodur® Compound 5941 and the binder designs developed in the projects. The synthetic oxides are only used in the early hardening phase for controlling the hydration of the ultrafine cement components to achieve an impermeable packing.

According to the draft prEN197-1:2014(D) [17] all the cements and proportions of cement in the compounds described above fulfill the requirements on the composition:

- Nanodur® Compound 5941 as CEM II/B-S 52,5
- TP H-House Compound 5941 as CEM II/C-M (S-LL) 52,5
- C^3 BMK-D5-1 as CEM VI (S-LL) 52,5 (C^3 project)

However, because of their high price as a result of the advanced production process and their special properties these products are only used where there are extraordinary demands in the contracts. As mixed products are concerned they are always only produced directly before delivery and no reserves are held in silos. The necessary monitoring could therefore only take place without great expense in case of a continuous dispatch process. However, ongoing monitoring is necessary for continuous adherence to the standard designation.

It is therefore understandable that the producers are not interested in the technically feasible registration of standard designations for new products with initially very low dispatch quantities. However, without a standard designation there can be no use of the new binders in the sector relevant to the building approval. This is an extra hurdle in the use of high-performance concrete that is also not covered by the building approval regulations. There is urgent need for action here to bring the high-performance materials, which were developed at great expense by the public funding institutions and by industry, into use more rapidly.

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