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Nanotechnological improvement of structural materials – Impact on material performance and structural design

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ABSTRACT

Within the last decades, the performance of concrete has been significantly improved by applying different kinds of micro- and nanoparticles and by applying analytical methods from fundamental research disciplines that had not been used for construction materials before, e.g. atomic force microscopy. One prominent result is Ultra-High Performance Concrete (UHPC) with its steel-like compressive strength which allows for slender but nevertheless very long lasting and thus sustainable concrete structures. On top of that several research projects performed at the University of Kassel, which this contribution likes to review, aim at making concrete an impervious, ceramic-like, acid resistant multifunctional "smart" material with added values by further changing its nano- and microstructure and/or applying reactive coatings e.g. with the ability to degenerate air pollutants.

1. Introduction

Within the last decades, the performance of concrete has significantly been increased. One example is Ultra-High Performance Concrete (UHPC) originally developed by Bache in the 1980s. In [3] and [5] a worldwide survey on the state of research and application is given.

Its most notable characteristic is an extremely dense microstructure resulting in a steel-like compressive strength of about 180–250 MPa combined with a significantly improved durability. The structural density results primarily from a high packing density of fine and ultra-fine particles $\leqslant$125 μm in the cement matrix and a comparatively low *w*/*c*-ratio of about only 0.20. The first German large scale application based on an individually designed concrete mix was the "Gaertnerplatzbridge" in Kassel, built in 2007 (cf. Fig. 1). This very slender structure consists of a 3D steel truss in combination with longitudinal girders and deck slabs, both made of prefabricated, prestressed, fiber-reinforced UHPC elements. Due to the high adhesive tensile strength of the material, the slabs of the bridge deck were glued to the girders with an epoxy resin without any additional means of fixation [2,3]. The bridge is intensively monitored. Since 2007 no changes in the structural behavior or any other degradation have been noticed.

To gain the fundamental knowledge being necessary to make UHPC a commonly applicable material, a comprehensive 10 Mio. € Research Program on UHPC, funded by the German Research Foundation (DFG) and coordinated at the University of Kassel, has been performed in Germany [4] with more than 20 research institutes involved. The material oriented projects covered the suitability and performance of raw materials including artificial nanoparticles, appropriate mix designs, the rheological specifics of fresh concrete as well as the time-dependent development of the microstructure and the deformation behavior and durability of hardened UHPC. Most of these numerous projects have already been reported on in the proceedings of the Symposia on Ultra-High Performance Concrete and Nanotechnology in Constructions held in Kassel 2008 and 2012 [3,5]. This contribution intends to review some of the projects that have been performed or are currently active at the University of Kassel.

2. Microstructure

The outstanding strength and durability of UHPC is based on the very special microstructure of the cement matrix. Depending on the maximum grain size of the aggregates, UHPC contains between 550 and 800 kg cement per m^3, up to about 250 kg/m^3 of microsilica (pyrogenous SiO_2) and a significant amount of other mineral fillers to improve the packing density of the matrix, and to increase the amount of nanoscaled C–S–H cement phases densifying the microstructure [6]. A secondary effect results from a very low effective *w*/*c*-ratio of about 0.20 only (*c* = cement + microsilica). While ordinary concrete is a porous medium with a high content of capillary pores, UHPC is characterized by a very dense and homogenous structure similar to the microstructure of the aggregates used (cf. Fig. 2).

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Fig. 1. Gaertnerplatzbridge in Kassel, under construction (left) and in use (right). Girders and deck plates made of UHPC are glued with an epoxy resin. Slab thickness is only 85 mm.

Due to the absence of capillary pores the resistance to carbonation and to corrosive media including acids is remarkably improved. As an example Fig. 3 shows prisms produced from a cement mortar (REF) and an UHPC (M2Q according to [1]) both made with OPC and stored for 12,000 h in a 5% ammonium nitrate solution [7].

One of the thematic priorities of research at the University of Kassel is the rheological behavior of the fresh UHPC widely steered by the large amounts of very fine particles tending to agglomerate due to their high specific surface area and thus the high interparticle forces. To desagglomerate the fines highly efficient polymeric superplasticizers are needed. Up to now their efficiency could only be evaluated indirectly by testing e.g. mortar mixtures.

A new approach is to use AFM techniques like colloidal probe to study these forces [8]. As a model system, silica beads fixed to a cantilever probe and to a substrate have been brought into contact and pulled apart. The measurement setup is shown in Fig. 4. The force curve while extending and the adhesive force while retracting the probe have been measured. The measurement system was submerged in a wet cell containing water, electrolytes representing the ionical composition of cement matrix water, and superplasticizers in different combinations. Fig. 4 gives the attraction forces measured in water containing the same concentrations of different polymeric SPC in nN.

The test setup is used both to identify and to improve superplasticizers or to evaluate mixtures of superplasticizers based on different types of polymers best fitting the specific surface properties of the mixture of different reactive and inert nano- and microfines used in UHPC or in self-compacting concretes and mortars. Furthermore it helps to understand the interactions between the polymers and the particles and thus to improve the rheological behavior of the fresh concrete aiming at a model allowing for a more reliable forecast of the workability of a specific mortar or concrete when applied in praxis.

AFM technique even enables to "see" and follow very early hydration reactions on the surface of cement grains in the nanoscale. Fig. 5 shows the laser based measuring device installed in the AFM cell (upper left figure) to evaluate the time depending change of the topography of the surface of a dry cement grain (upper right figure) due to the formation of a first gel-like layer (lower right figure) when coming in contact with water and the beginning of the development of C-S-H phases after about 2 h (lower left figure). As stated for the measurement of the interparticle forces the AFM technique enables to better understand and thus to influence the early hydration process e.g. by means of chemical additions.

3. Nanotechnological improvements

The performance of today's UHPC can be further improved by nanotechnological approaches. In [9] a deeper insight into the challenges and promises that nanotechnology provides for the development of high-performance concretes is given, and it also highlights the unusual characteristics and difficulties that arise and have to be overcome in the nanocosm. As an example, a further increase in both strength and resistance to corrosive media can be expected by incorporating synthetic nanosilica particles with a carefully controlled particle size distribution extending the packing optimization to the nanoscale.

Furthermore, so called "alternative binders" which are largely free of Portland cement clinker – they are based e.g. on puzzolanic fly ashes from combustion of hard coal, ground granulated slag, or mixtures of both, activated by sulfuric or alkaline accelerators [10] – yield a structure that proves stable against most acidic attacks. This is part of current research projects aiming at designing concretes that are produced under with mineral binders and behave like ceramics. Activating agents can be alkali salts (carbonates, sulfates), alkali hydroxides or alkali silicates, also known as waterglass. These binder systems form calcium free reaction products with high chemical resistance especially to acids – even against biogenic sulfuric acid – and sulfates. They are particularly suitable

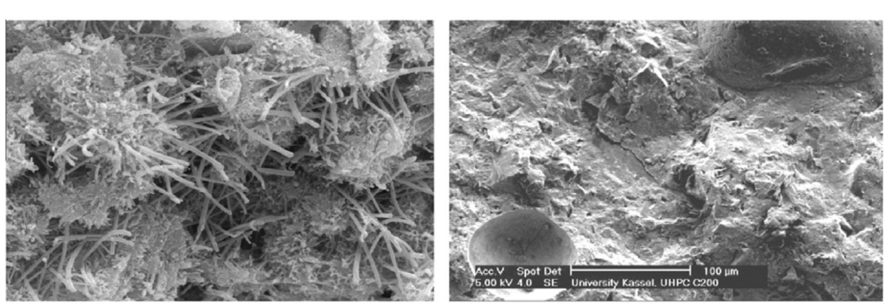

Fig. 2. Matrix of ordinary concrete C35/45 (left) compared to UHPC (right) (SEM picture, same scale).

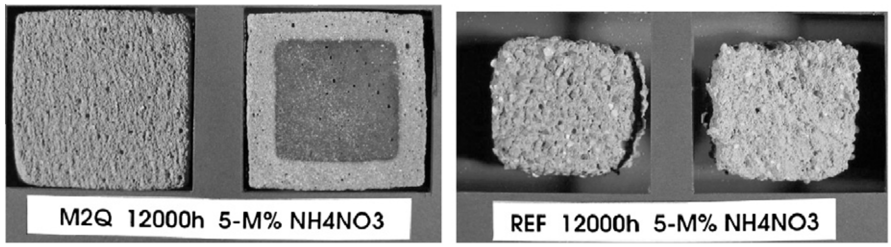

Fig. 3. Ordinary concrete (REF) and UHPC (M2Q) after being submerged in 5 mass% ammonium nitrate solution at 20 °C for 12,000 h [7].

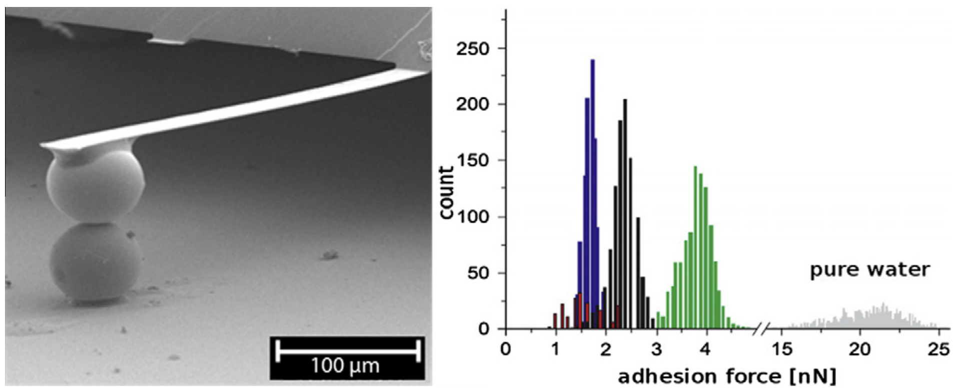

Fig. 4. SEM micrograph of the measurement setup and interpartikel forces determined in an AFM cell without and with different superplasticizer.

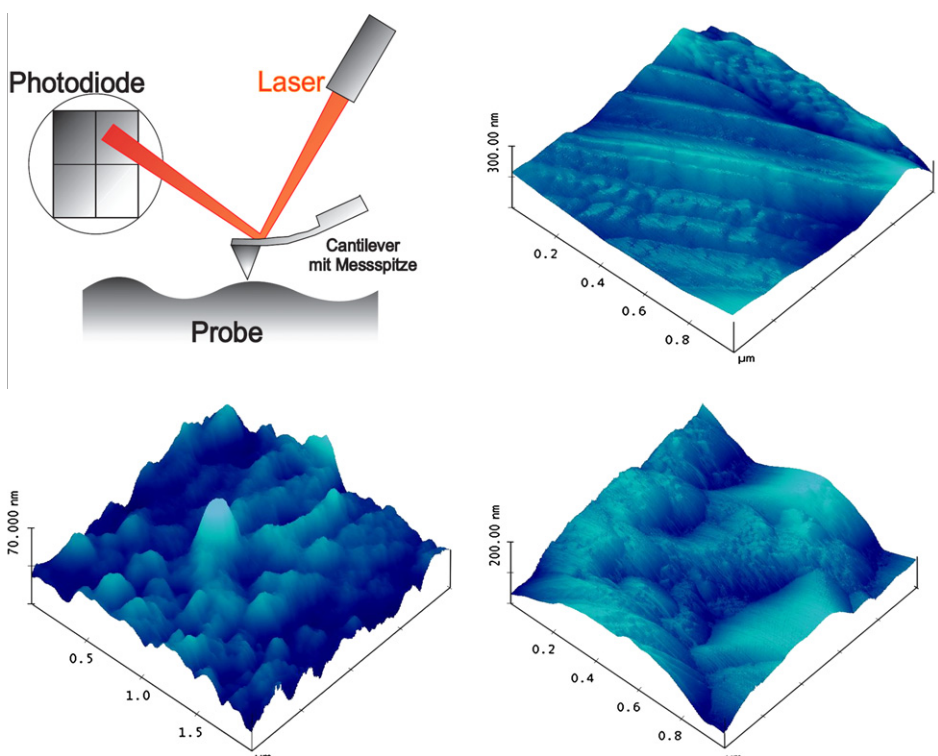

Fig. 5. AFM pictures showing the early hydration reactions on the surface of a cement grain when coming in contact with water. Base length 1 × 1 µm.

for highly stressed building elements, found in the field of industrial sewer systems, and e.g. biogas production.

Fig. 6 shows the ceramic like microstructure of a hardened alkali activated binder based on slag. Fig. 7 (right) shows a mortar based on alkali-activated GGBFS with potassium waterglass compared to a reference specimen made with OPC CEM I after 14 days storage in lactic acid (pH = 2). This comparison shows that alkali-activated systems have great resistance not only in sulfuric acids, but also in the case of exposure to organic acids.

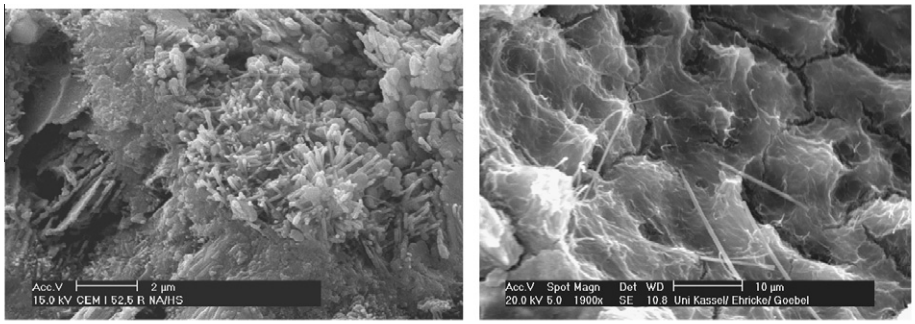

Fig. 6. Left: hydrated Portland-cement: C–S–H-phases and acid solubel portlandit. Right: GGBF-Slag + nanosilica + alcaline accelerator: stable cement-like phases.

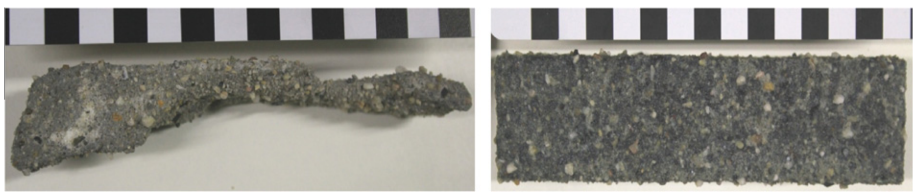

Fig. 7. Left: cementitious mortar with OPC CEM I. Right: alkaline-activated mortar of GGBS with potassium waterglass, both after 14 days storage in lactic acid (pH = 2).

The presently achievable compressive strength of about 200 MPa for UHPC can be increased even further by using of nanoscale silica and adapted production processes. It was found that the UHPC mixture that was used for the Gaertnerplatzbridge in Kassel (max. grain size 0.5 mm, 733 kg OPC, 230 kg SF, 183 kg quartz - powder/m^3; effective *w*/*c* 0.20) could be further increased up to 500 MPa when the fresh concrete had been consolidated under a constant uniaxial pressure of 50 MPa for the first 4 h after moulding, and subsequently stored at 250 °C for 7 days. Along the way, due to the evaporation of free water the *w*/*c*-value sank to only 0.14. Extrapolating from recent experiences it may be possible to produce precast concrete elements for special applications (e.g. prestressed girders, highly-loaded columns, truss joints) that can bear much higher loads than recent UHPC. It might even replace high-strength steel or cast steel in many applications.

4. Smart materials

Until today, concrete has primarily been seen as a structural material. Nanotechnology helps to make it a multipurpose ''smart'' functional material. Nanoscale titanium dioxide is one of the materials that have already been used for several applications. When concrete is treated or coated with thin layers containing TiO_2 particles, it can be used as self-cleaning and air-purifying surface. In view of the enormous facades and roof areas that are available on all the buildings in existence, the application of a thin transparent ''reactive'' surface layer containing nano-TiO_2 could make a lasting contribution to air purification. The potential and the practical execution is the subject of one of the research projects on smart concrete materials performed at the University of Kassel [11,12].

The well known photocatalytic function of titanium dioxide described in [11] is based on its semiconductor properties. One essential precondition for photocatalytic degradation besides UV light is the presence of oxygen and humidity. Photons can be absorbed if the titanium dioxide is exposed to sunlight and if they have a sufficiently high energy. This is the case when the energy of the irradiating light, which is inversely proportional to the wavelength (typically ultraviolet (UV) light), is greater than the band gap (the energy required to transfer an electron from the valency band (VB) of the semiconductor to its conductivity band (CB)) of the titanium dioxide. As the solar radiation spectrum extends into the UV range, part of the absorbed photons possesses sufficient energy to raise electrons from the valency band to the conductivity band. This produces electron holes (h^+) in the VB and an excess of electrons (e^-) in the CB. These electron-hole pairs can then either recombine within or at the surface of the titanium dioxide (a,b) or else react with electron acceptors (e.g. O_2) (c) or donors (e.g. OH^-) (d) adsorbed on the surface. The resulting hydroxyl ($OH^\cdot$) or superoxide (O_2^-) radicals are some of the strongest oxidizing agents and can oxidize and completely decompose almost any organic material.

However the efficiency of TiO_2 nano-particles is restricted due to the fact that they tend to agglomerate, which leads to a reduction of the active surface area and a higher dosage has to be employed. Composite particles consisting of a core and a nanostructured, photoactive titania shell can be used as an alternative material for the photocatalytical modification of building materials [12,13]. Such systems can be tailored according to the purpose of their application by adjusting the size of the particles, as well as the thickness of the shell. By using cores beyond the nanoscale, agglomeration can be reduced to a great extent. It is also possible to use other materials for the core and the shell respectively to yield other characteristics.

As an example Fig. 8 shows as a result of another research project silica particles prepared via the Stoeber process [14] and coated with a photoactive titania shell via hydrolysis of tetrapropylorthotitanate [13]. The photoactivity was determined via degradation of nitrogen monoxide in the presence of UV light as described in ISO 22197 [15]. The particles contained only 5.5 wt% titania and showed a sufficient photonic efficiency of 0.4%. In comparison, the photonic efficiency of 100% industrial P25 nano titania powder (Evonic), measured under the same conditions, was 0.5%.

In addition to its photocatalytic properties, titanium dioxide also develops a superhydrophilic surface under irradiation by UV light. This behavior is based on the fact that irradiation by UV light reduces the angle of contact between the surface and the water droplets to significantly less than 10° – a value that is otherwise only achieved by water-adsorbing surfactants. Thus water can infiltrate under the dirt and wash it away effectively. In [12] this phenomenon is explained in terms of the creation of ''oxygen-deficient sites'' on the titanium dioxide surface. These occur

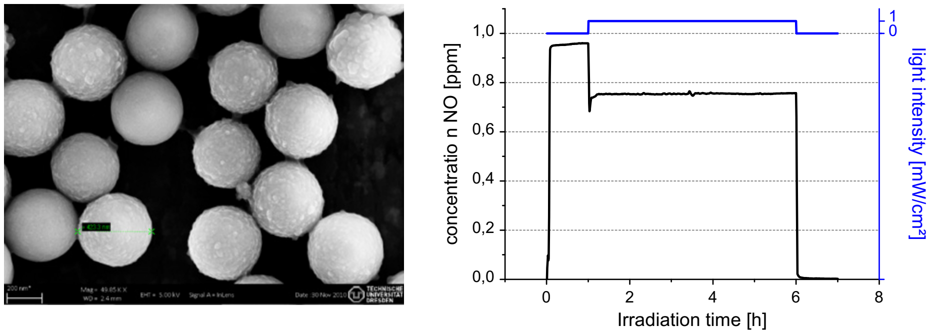

Fig. 8. Core–shell particles with silica cores and titania shells prepared via sol–gel method. Right: the degradation of nitrogen monoxide in the presence of UV light.

because during the irradiation, oxygen is eliminated from the surface and the titanium atoms that then have free binding sites are reduced from oxidation stage +4 to +3. Water can now bind onto these free binding sites, which leads to hydrophilic hydroxyl groups on the surface.

Superhydrophilicity is a reversible phenomenon, so this effect dies out about 24 h after the end of irradiation. The surface then adopts hydrophobic properties again.

5. Conclusions

Within the last decades the performance of concrete has been significantly improved by applying different kinds of micro- and nanoparticles and/or by the use of analytical methods allowing for seeing at the nanoscale like AFM technique. One of the results is Ultra-High-Performance Concrete (UHPC) with its steel-like compressive strength of about 200 MPa which allows for slender but nevertheless very long lasting and thus sustainable concrete structures. Due to the dense microstructure, its resistance to corrosive media is much higher than for ordinary concrete as well. The strength of UHPC can further be improved up to 500 MPa e.g. by incorporating nanosilica into the binder matrix and by the use of calcium free alkali-activated binders based on GGBS aiming at a ceramic like structure and behavior.

Furthermore, concrete can become a real "smart material" by adding additional values like thin surface layers of special tailor made nanoscale titanium dioxide core shell particles which can enhance structural concrete elements with self-cleaning properties and the ability to reduce air pollutants.

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