INFLUENCE OF NANOPARTICLES IN UHPC BY INTENSIVE (VACUUM) MIXING STUDIES

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ABSTRACT

The production of ultra-high performance concrete is made possible by a combination of an optimal packing density, a suitable mixing procedure and an effective match between a third generation superplasticizer and the binders. By increasing the level of performance, it is questionable how the robustness of the mixture evolves. What is the effect of a different silica fume and superplasticizer on the workability and the compressive strength? Also an undesirable increase in air content can alter the fresh and hardened properties. In order the control the air content a vacuum mixer can help. In case of the silica fume and superplasticizer, compatibility tests should be performed in advance. This paper reports the influence of the smallest particles in ultra-high performance concrete, how they affect the fresh and hardened properties.

The air content was decreased by lowering the pressure in the mixing pan from 1013 mbar to 50 mbar. CT-scans clearly show a reduction of the air cavities. Furthermore, six different types of silica fume from two companies were tested. The workability was checked with the mini-slump flow. Besides this, three cubes were tested to determine the compressive strength. The effect of the superplasticizer was investigated by evaluating the slump life of 5 different types of polycarboxylate ethers. In conclusion, an ultra-high performance concrete was achieved with a compressive strength of 173 MPa. This was due to the selection of a good superplasticizer and silica fume. The air content reduction also contributed to an increased strength. Further research should be focussed on the durability and service life of such a dense concrete type.

Key-words: Nanoparticles, Silica fume, Superplasticizers, Ultra High Performance Concrete, Vacuum mixing.

INTRODUCTION

Ultra-high performance concrete (UHPC) is a relatively new construction material. The dense structure and the high strength make it suitable for specific application. It can be used to protect important facilities such as nuclear plants, high rise buildings and power plants against aircraft impacts. Some connection parts in offshore constructions can be replaced by UHPC elements, making the construction more cost-efficient. Furthermore it has an important aesthetic advantage. The quality of UHPC is dependent on the selected materials, the mixing process and the way of casting and curing. One of the materials commonly used in UHPC is silica fume. This powder can improve the packing density by its filler effect, increase the

hydration by its pozzolanic activity and ameliorate the workability by its ball bearing effect. Important research has already been performed in literature concerning the characterization of this fine powder[1], its hydration process[2] and its influence on the compressive strength and the workability[3,4]. The test program of this paper comprise six different types of silica fume. Their effect on the fresh and hardened properties of an ultra-high performance concrete is tested. A new type of white silica fume is also included in this test program. Different as for the other white silica fumes SF4 is a by-product of the silicium industry and does not originate from a zirconium factory. In order to make a UHPC commercially attractive, a sufficient slump life is necessary. In general this can be prolonged by choosing a suitable superplasticizer. Therefore, five different polycarbolylate ethers are tested. Their influence on the workability and the rheology of an ultra-high performance concrete is checked. After a thoughtful selection of the raw materials, a good mixing principle should be chosen. For UHPC an intensive vacuum mixer can be profitable. This type of mixer not only reduces the mixing time[5] but also controls and reduces the amount of entrapped air. The effect of vacuum mixing will be proven in this paper by the aid of computed tomography. This selection process finally led to an UHPC with a compressive strength of 173 MPa. This strength was obtained, without any special heat curing or autoclave treatment.

EXPERIMENTAL WORK

Materials and mix proportion

The composition of the ultra-high performance concrete used in this program can be found in Table 1. The chemical composition of the cement is given in Table 2. The high binder content (947 kg/m³) is necessary to obtain a strength of 150 MPa and gives the UHPC a high stiffness.

Table 1 - Mix proportion UHPC

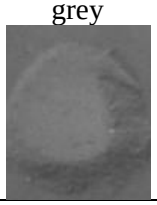
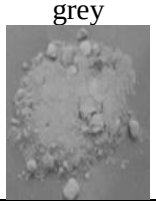
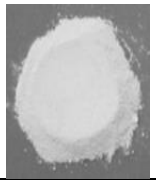
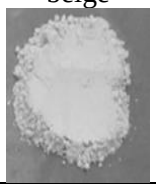
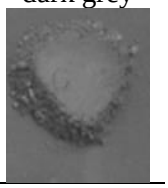
Materials	**Mass/volume ratio (kg/m³)**	**Material/cement ratio**
CEM I 52.5 N HSR/LA	721	1.000
Silica Fume (SF)	226	0.314
Sand 0/0.5	992	1.375
Flour	180	0.250
Superplasticizer solids (SP)	/	0.0136
Water	157	0.240
W/B	0.185	

Table 2 – Chemical composition of the cement

	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	SO_3
CEM I 52.5 N HSR/LA	20.90	3.64	5.19	63.68	0.77	0.17	0.62	3.03

The quartz sand 0/0.5 had a d_{50} of 342.0 µm. This value is determined with a dry laserdiffractometer, Mastersizer 2000. The CEM I 52.5N HSR LA had a d_{50} of 11.88 µm, a Blaine fineness of 4322 cm²/g and a density of 3137 kg/m³. The quartz flour had a d_{50} of 13.43 µm. The d_{50} of the powders were determined with the same laserdiffractometer but with a wet unit. Isopropanol was used as dispersant. Before the measurement, the powders were submitted to a sonification bath during 5 minutes. Six silica fumes have been used which differed in their apparent color, their BET specific surface, their chemical composition and particle size distribution. A summary of the characteristics can be found in Table 3.

Table 3 – Characteristics of the tested silica fumes

	SF 1	SF 2	SF 3	SF 4	SF 5	SF 6
SiO_2 [%]	94.73	95.07	94.97	96.53	97.88	96.10
Fe_2O_3 [%]	0.71	1.29	1.88	1.11	1.11	1.37
Al_2O_3 [%]	0.36	0.95	0.35	0.32	0.08	0.05
CaO [%]	0.20	0.19	0.19	0.19	0.36	0.64
MgO [%]	0.39	0.44	0.62	0.30	0.13	0.28
Na_2O [%]	0.20	0.37	0.41	0.26	0.14	0.29
K_2O [%]	0.90	1.52	1.45	0.84	0.18	0.94
Alkalis [%]*	0.79	1.37	1.36	0.81	0.26	0.91
C [%]	0.46	0.57	0.56	0.19	0.25	0.80
SO_3 [%]	0.27	<2	NA	NA	0.35	<2
Cl [%]	NA	<0.3	NA	NA	0.01	<0.1
LOI [%]	1.86	<4	<3	NA	2.00	<4
SSA_{BET} [m²/g]	15.51	18.0	20.64	18.9	21.98	19.65
ρ [kg/m³]	2232	2187	2128	2204	2084	2192
	densified	densified	undensified	densified	densified	densified
Age at testing in §2.1 [months]	18	2	2	2	7	7
Color [-]	grey 	grey 	grey 	white 	beige 	dark grey 

*Alkalis equivalent: (Na_2O + 0.658 K_2O); NA= not available measurement

The particle size distribution was determined by a nano zetasizer, based on the Brownian movement of the silica fume particles the distribution can be defined[6]. Distilled water was used as dispersant. Before the test, the samples were dispersed in a sonification bath for 5 minutes. The results are an average of 5 successive measurements. Figure 1 and Table 4 give the particle size distribution of the different silica fumes.

Table 4 – Characteristics values of the particle size distribution of the tested silica fumes

	d_{10} [nm]	d_{50} [nm]	d_{95} [nm]
SF1	137	316	5270
SF2	125	292	1081
SF3	244	659	5347
SF4	223	479	1155
SF5	174	533	1291
SF6	118	211	5678

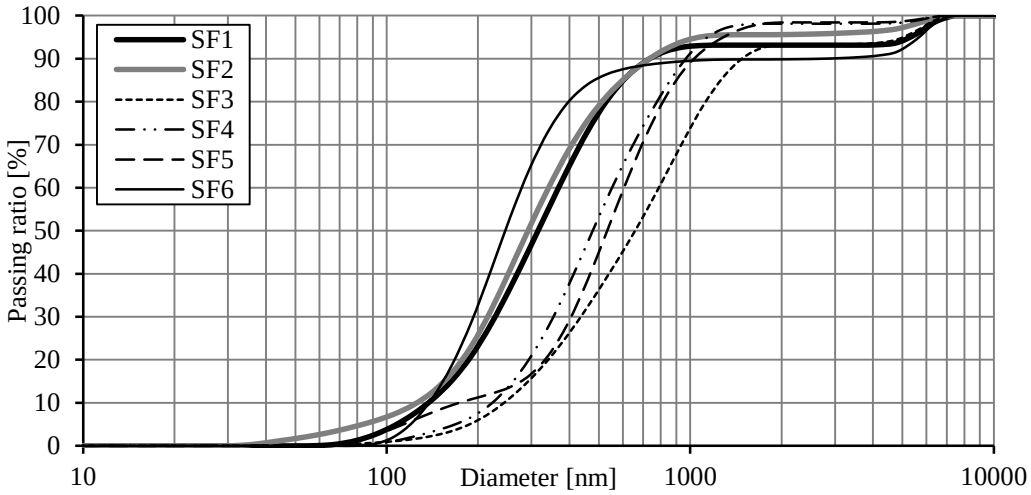


Figure 1 – Particle size distribution determined with a nano zetasiezer

The silica fumes were delivered by two different companies. Silica fume SF 1-2-3-4 came from another distributor than silica fume SF 5-6. SF 4 was obtained by removing the carbon content as much a possible from SF 3. All the silica fumes were densified for transport, except SF 3 which was undensified.

Five different polycarboxylate ethers (PCE) were checked on their influence on the slump life of the ultra-high performance concrete. Different types of PCE's were selected in order to examine whether they behave as a slump keeping, slump controlling or water reducing superplasticizer[7]. Their characteristics are found in Table 5.

Table 5 – Characteristics of the tested superplasticizers

	SP1	SP2	SP3	SP4	SP5
ρ [g/l]	1100	1080	1090	1100	1090
pH	6-8	3-5	4	3.5-5.5	3.5-5.5
Structure	No information given	PCE with mixed side chains (short & long)	No information given	PCE with high charge density	PCE with long side chains
Dosage according to supplier [%wt.cement]	0.44-1.32	0.2-1.5	0.2-4	0.05-0.8	0.2-2

Mixing procedure

A 5 liter intensive vacuum mixer was used to mix the ultra-high performance concrete, Figure 2. First the dry powders were mixed during 15 s. In the next 20 s, the water immediately followed by the superplasticizer were manually added to the mixture at a mixing speed of 1.6 m/s. This is followed by an intensive mixing period. The duration was determined based on the powercurve[5], for which the agitator speed was kept constant at 6 m/s. The stabilisation time was considered to be reached when the curve had a gradient of -0,0006. The authors chose a hybrid mixing procedure, consisting of an intensive phase for 150 s at a speed of 6 m/s until the maximal power is reached and a slow phase for 120 s at a speed of 1.6 m/s until stabilisation. In case of vacuum, a reduction from 1013 mbar to 50 mbar was established at the moment of the intensive phase until the end of the mixing procedure.

Figure 2: A 5 liter intensive vacuum mixer with inclined mixing pan. A: the pin-agitator; B: the vacuum pump; C: mixing pan and outer protection ring.

Methods and sample preparation

Workability and rheology

For the workability, a Haegerman cone was filled with concrete 7.5 minutes after the addition of the water. Next the cone was lifted and the spread was measured in two perpendicular directions. For the slump life, the spread was measured every ten minutes after an intensive mixing period of one minute. A four vane rheometer was used to examine the influence of different superplasticizers on the viscosity and the yield value of the mixure. The vane blade had a length of 30 mm, a height of 40 mm and a thickness of 2 mm. It rotated in a cylindrical cell with diameter 70 mm. This cell was provided with small vanes, to prevent wall slippage. The rotating vane is positioned 20 mm above the bottom of the cell, which is filled with UHPC to the same height of the vane, 60 mm. In this way a top effect is prevented, however a bottom effect is still present. The resulting flow resistance in the reservoir is measured at the inner vane. The UHPC was subjected to a preshear period of 40 s at a speed of 40 rpm. Together with a decreasing rotational velocity profile it removed the thixotropic behavior in the sample. The rheological properties were determined controlling the rotational speed in 15 s steps, with a measuring point every second. The speed varied from 40 rpm to 15 rpm in steps of 5 rpm, from 15 rpm to 2.5 rpm in steps of 2.5 rpm and from 2.5 rpm to 0.5 rpm in steps of 0.5 rpm. At each step, when the torque and the rotational velocity have reached equilibrium, an average value of both parameters is calculated from the last five measuring points. The UHPC behaved as a shear thinning material. For this the yield stress was determined with the Herschel-Bulkley model. In order to have an idea about the viscosity at low shear rates, the plastic viscosity of the Bingham model is used.

Computed Tomography

The tomographic scans were performed at UGCT, the Ghent University Centre for X-ray Tomography. For the measurements an X-ray CT scanner called HECTOR was used[8]. This device scans a rotating small sample, with a fixed X-ray source, a XWT 240-SE microfocus with a focal spot size of 4 µm and PerkinElmer 1620 CN3 CS flat panel detector. An UHPC core with a diameter of 1 cm and height of 1 cm was scanned. With the applied source-to-object distance and source-to-detector distance a pixel resolution of 6.5 µm was obtained.

Using the software Morpho+[9], in use at the UGCT, the air voids were separated from the UHPC matrix. The 3D visualization of the air cavities and larger capillary pores was done with Volume Graphics VGStudioMax 2.1. This technique was chosen over standard methods as the ASTM C457 as these techniques are not able to give a three dimensional representation of the air bubbles in the concrete.

TEST RESULTS AND DISCUSSION

Effect of different silica fumes on the workability and compressive strength of UHPC

The effect of different silica fumes on the workability of UHPC can be seen in Figure 3. SF 4 performed remarkably well compared with the other five types. A possible reason for this is the low BET specific surface and carbon content of this silica fume[3]. The latter leads to a lower consummation of superplasticizer than the other types. This phenomena strongly depend on the origin of the silica fume. Depending on the electric arc furnace used in the Silicium production, the carbon may have more or less unsaturated bonds. These bonds are able to form charge-transfer-complexes with PCE, which lead to a larger need of dispersion. A possible reason why SF 5, with a low carbon content, did not lead to a good workability is the high specific surface of this type of silica fume, leading to a higher water demand.

Figure 3: Effect of different types of silica fume on the workability of UHPC.

For each silica fume, cubes with side 100 mm were cast and tested at the age of 28d and 91d. For each age three cubes were compressed. Between casting and testing, the specimens were stored in a climate room with relative humidity of 95%±5% and 20°C±2°C. The results of the compressive strength can be seen in Figure 4. In conclusion, SF 3 and SF 4 gave the highest strength at both ages. The highest value was obtained with SF 4, namely 169 MPa. SF 3 was the only type that was undensified. Despite the presence of some agglomerates as can be seen in Table 4, it was clearly beneficial for the strength not to densify the silica fume. One of the reasons why SF 4 performed well can be attributed to the lack of agglomerate and a better packing density. The latter can be demonstrate by a simple packing calculation[10], Figure 5. The solid concentration of the granular material (denoted as Ø), is determined with the mass and the dimensions of the hardened cubes tested on their compression strength.

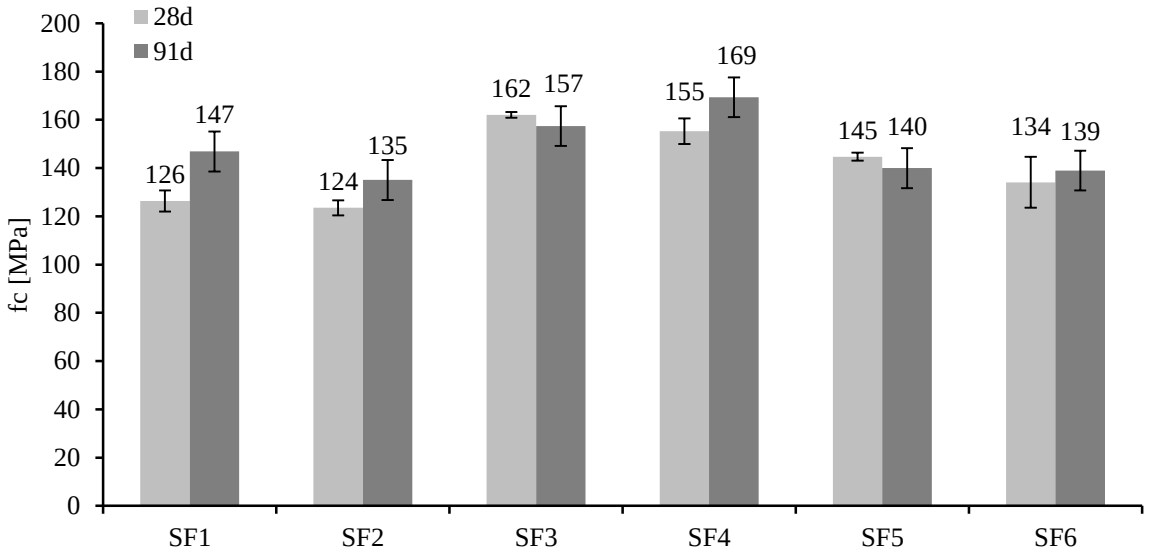


Figure 4: Effect of different types of silica fume the compressive strength of UHPC.

In conclusion, Figure 5 shows the highest solid concentration for SF 4 and the lowest for SF 1 and SF 2. The ability of the silica fume to fill the interstices of the matrix clearly influences the compressive strength of the mixture. Nevertheless, a good pozzolanic activity is equally important. This can be seen by SF 3, which has a lower solid concentration (Ø) and thus a lower particle packing but an equal strength as SF 4. Test methods as thermogravimetry and X-ray diffraction are currently performed to have a better insight on the hydration process[11].

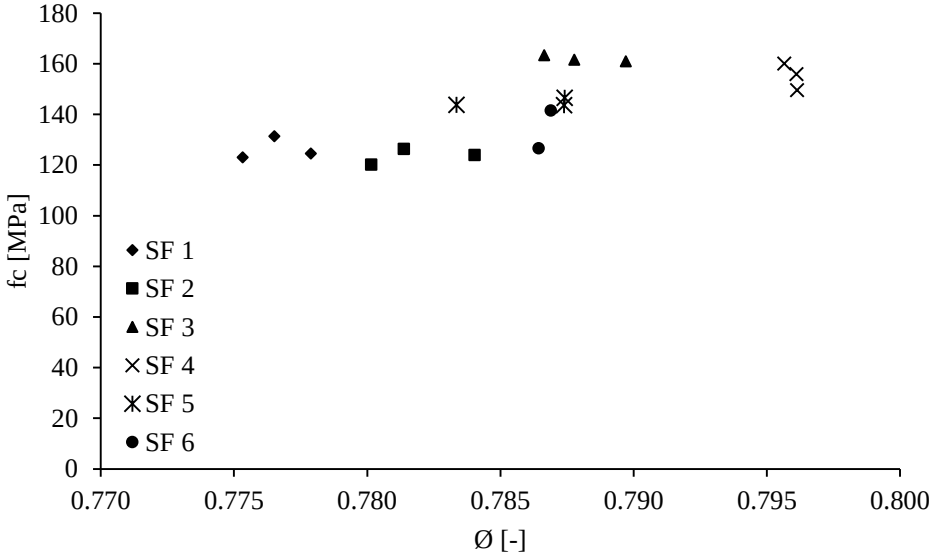


Figure 5: Influence of different silica fumes on the solid concentration of the mixture and its effect on the compressive strength at 28 days.

At 91 days the compressive strength of SF 4 kept increasing, indicating that the packing density is not the only governing factor. In general, the densified silica fumes SF 1-2-4 delivered by the first distributor, showed an important increase between 28 days and 91 days. This was not the case for SF 5-6 delivered by the second distributor.

Effect of different superplasticizers on the workability and rheology of UHPC

The influence of different PCE's on the spread of UHPC, is shown in Figure 6. For these tests, silica fume 1 was used. The highest initial spread was obtained with SP 5, which reached a maximum value at 20.5 minutes and loses his workability after that. This behavior is typical for a water reducer. The lowest initial spread was noted for SP 4, nevertheless this superplasticizer reached the highest spread value after 40.5 minutes and then started to decrease. This behavior indicates a spread controlling superplasticizer. SP 1 and SP 3 had a similar behavior. An average initial spread that keeps increasing in time. This evolution is inherent for a spread keeping superplasticizer. SP 2 had a stable spread during the test period but did not increase in this 65.5 minutes.

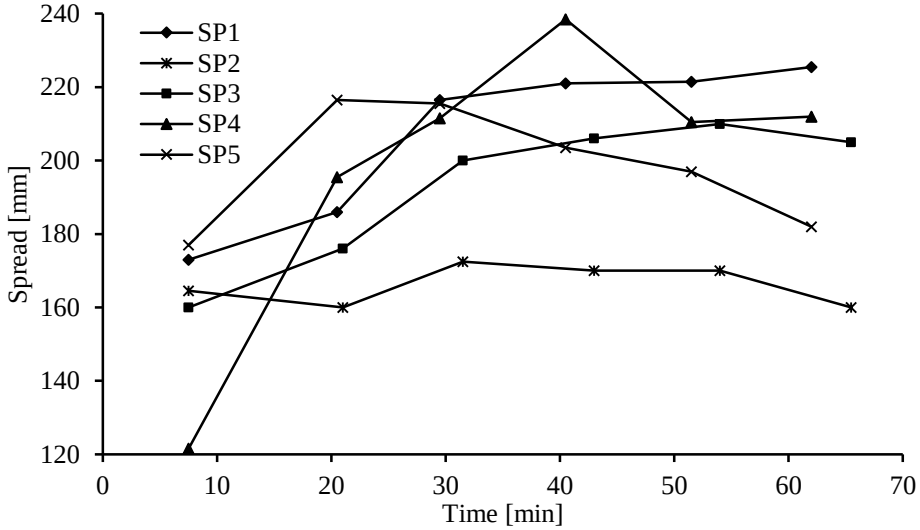


Figure 6: Effect of different superplasticizers on the slump life of UHPC.

The influence of the different superplasticizer on the time evolution of the yield value and the plastic viscosity is illustrated in Figure 7. Similar conclusions can be drawn as in Figure 6. SP 1 and SP 3 perform the best, namely an improved rheology during the test period. The other superplasticizers show at some point an increase in yield value and/or plastic viscosity. In conclusion, SP 3 leads to the lowest plastic viscosity. Consequently, this type of PCE is preferable in an ultra-high performance concrete.

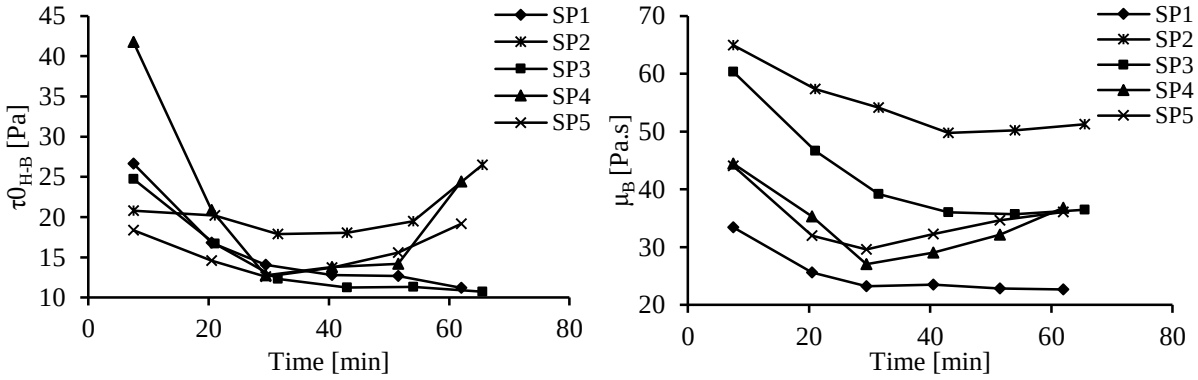


Figure 7: Effect of different superplasticizers on the time evolution of the yield value (left) and the plastic viscosity (right) of UHPC.

Effect of air content on the compressive strength of UHPC

The UHPC mixture, Table 1, was mixed at two different air pressures. The first batch was mixed under a pressure of 1013 mbar, the second under a pressure of 50 mbar. This vacuum technology was applied to reduce the amount of entrapped air, which can have a negative effect on the compressive strength of UHPC[12]. For these tests silica fume 1 was also used. An increase in compressive strength from 144 MPa to 162 MPa at 28 days was obtained when the amount of air bubbles was reduced from 3.29% to 0.42%. this is logical, as more material is available to withstand the compressive force. Notice the higher strength at atmospheric pressure in this section compared with the results in Figure 4. In the latter the silica fume was already aged 18 months at the moment of testing. The silica fume used in this section was younger of age and probably contained less agglomerates which could impede the hydration. To visualize the effect of an air content reduction on the microstructure of UHPC, two specimens were scanned by the CT scanner HECTOR. Each of the specimens was mixed under a different pressure. The 3D visualization is given in Figure 8.

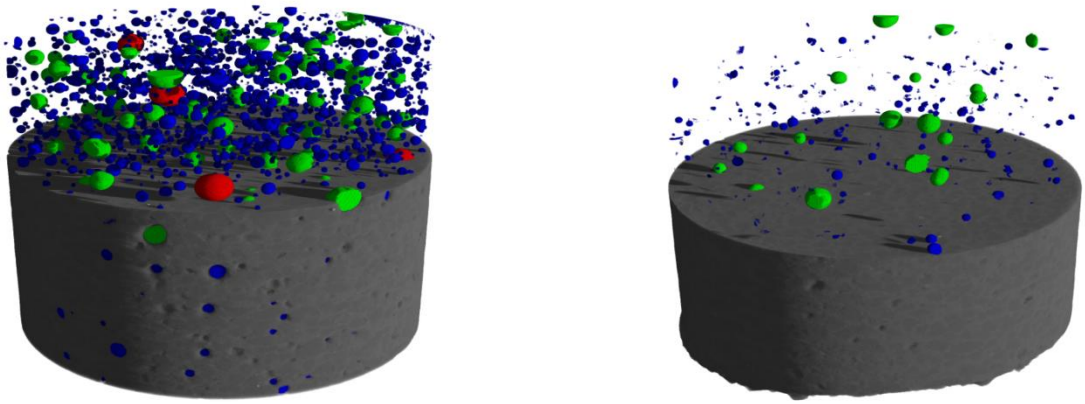


Figure 8: 3D visualization of a CT-scan from an UHPC core made under 1013 mbar (left) and 50 mbar (right).

In Figure 8, the equivalent diameter of the pores is visualized. It is clear that the air cavities and the larger capillary pores (resolution = 6.5 µm) are reduced by the vacuum technology. Moreover the larger air bubbles are removed and the smaller air bubbles are significantly reduced. This change in microstructure caused the increase of the compressive strength.

CONCLUSION

Out of this investigation follows that, a silica fume SF 4 with a low carbon content, an average BET specific surface and the capability to increase the solid concentration of the mixture gives the best workability and compressive strength for UHPC. Besides this a PCE with a high spread retention, creating a mixture with a low yield value and plastic viscosity is preferable for UHPC. This was the case for superplasticizer SP 1. After a thoughtful selection of the nanoparticles an air content reduction can lead to an even higher compressive strength, as shown in this paper. When silica fume 4 and superplasticizer 1 are used in the UHPC mixture of Table 1 and prepared in a vacuum mixer, a final strength of 173 MPa was obtained. This strength was reached without the stitching effect of small fibers, without a heat treatment or an autoclave curing. Concrete with such elevated mechanical properties, has also a superior durability[13]. As a consequence, this concrete could be used in offshore structures, reparation of bridge decks, protection of nuclear waste or nuclear facilities, production of sewer pipes, etc.

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