Sixth International Conference on Durability of Concrete Structures **Paper Number ICC-P03**
18 - 20 July 2018
University of Leeds, Leeds, West Yorkshire, LS2 9JT, United Kingdom

Absorption, Porosity, Capillarity and Chloride Diffusion in Ultra High Performance Concretes

J.M. Gandía-Romero, J.E. Ramón-Zamora and I. Gasch
IDM - Instituto Interuniversitario de Reconocimiento Molecular y Desarrollo Tecnológico,
Universitat Politècnica de València, Spain

M. Valcuende, V. Calvet and R. Calabuig,
Dpto. de Construcciones Arquitectónicas, Universitat Politècnica de València, Valencia, Spain

P. Serna
ICITECH Instituto de Ciencia y Tecnología del Hormigón, Universitat Politècnica de València, Valencia, Spain

ABSTRACT

Concrete durability performance can be assessed by a number of parameters, among which permeability properties are key. In this experimental work, the permeability to water and the diffusion of chlorides in Ultra High Performance Concrete (UHPC) are studied. To this end, three types of concrete were made: two Ultra High Performance (one with fibers and one without fibers) and a Conventional Concrete (CC) of w/c ratio equal to 0.5. The compressive strength of Ultra High Performance Concretes was 130 MPa, and that of conventional concrete was 50 MPa. All of them were cured at a temperature of 20°C and RH greater than 95% until the age of 28 days. In the case of UHPCs with fibers, some of the specimens were not placed in the curing chamber but were allowed to air dry in a laboratory environment in order to study the influence of curing on this type of concrete. The results show that UHPCs have remarkably lower water permeability than CC, with the water absorption and water porosity being in the order of 8 times lower, the water absorption by capillarity being in the order of 30 times lower, and the non-steady-state chloride migration coefficient more than 100 times inferior. The values recorded of absorption and capillarity in UHPCs with and without fibers were very similar. However, the permeability to chlorides was somewhat higher in concretes with steel fibres. With regard to the influence of curing, in air-dried UHPCs there was a significant increase in permeability to both water and chlorides. Despite this, the chloride migration coefficient registered remained very close to the values proposed by some recommendations for very high durability concrete.

Keywords: Ultra High Performance Concrete (UHPC), absorption, porosity, capillarity, durability.

1.0 INTRODUCTION

The assurance of high durability is a key parameter to ensure the service life of concrete structures. Scientific and technological advances have allowed the development of new materials for the construction of structures that provide superior properties compared to those usually used. In this matter, Ultra High Performance Concrete (UHPC) is one of the materials with more studies in recent years. The first application in civil engineering was in 1997 in a pedestrian bridge in Sherbrooke, Canada (Acker *et al*., 2004). Later on it was used in other areas such as the construction of Cattenom and Civaux power plants (Resplendido, 2004) and research studies on the behaviour of UHPC filled tubes (Tue *et al*., 2004). These concretes are made with an inferior water/binder (w/b) ratio and elevated cement contents and additions, especially silica fume. The material obtained has high mechanical performance features and a compact microstructure (Heinz y Ludwig, 2004; Herold y Muller, 2004).

UHPC has less water and gas permeability than conventional concrete (Roux *et al*., 1996; Graybeal, 2006; Pierard y Cauberg 2009; Ghafari *et al*. 2012; Tam *et al*., 2012). However, the results obtained by different researchers are disperse since they depend on different factors such as: the type of additions used (Tafraoui *et al*., 2016), the w/b ratio, the application of pressure during setting (Roux *et al*., 1996) or the type of curing performed (Yazici *et al*., 2009; Gesoglu *et al*. 2015; Gu *et al*., 2016; Chen *et al*., 2018), getting as a result UHPC with a compressive strength that can vary from 120 MPa to more than 250 MPa.

Thus, for example, according to some authors the water absorption is about 14 times smaller than that of a conventional concrete (Roux *et al*., 1996) and according to others can be up to 60 times smaller (Pierard and Cauberg 2009; Ghafari *et al*., 2012).

With regard to the chloride migration, Roux *et al*. (1996) obtained in tests carried out with UHPC of 230 MPa an effective diffusion coefficient 30 times lower than in a concrete of 90 MPa and 55 times lower than in a conventional concrete of 35 MPa.

The addition of steel fibres to the concrete increases the ductility (Oh, 1992; Oh, 1994; Bayard y Ple, 2003; Graybeal, 2006; Wang *et al*., 2015), its load capacity also increases (Ashour *et al*., 1993), as well as the shear strength (Campione *et al*. 2008). However, a high concentration of fibers can create fiber bundling and therefore increase the permeability of the material.

Therefore, the objective of this experimental work is to study the porosity of UHPC with fibers, comparing the results with those obtained with UHPC without fibers and those registered with conventional high strength concrete. On the other hand, the influence that curing has on this on UHPCs is analysed.

2.0 EXPERIMENTAL PROGRAM

2.1 Materials

Three different types of concrete were made: an Ultra High Performance Concrete (UH), an Ultra High Fibre Reinforced Concrete (UHF) and a Conventional Concrete (CC). The Ultra High Performance Concretes were designed with a w/c ratio of 0.2, while the Conventional Concrete with a w/c ratio of 0.5. The concrete specimens were cured during 28 days in a curing chamber with controlled temperature and humidity conditions, at 20ºC and with RH 95%. In addition, some UHF specimens were air dried in a laboratory environment to study the influence of curing on this type of concrete (UHF-air).

For the concrete mixes UH and UHF, cement CEM I 42.5R (SR), limestone aggregates, silica fume and silica flour were used. Taking this mix as a reference, the Conventional Concrete was made using the same type of cement but without silica fume and silica flour. The characteristics of each mix are shown in Table 1. For each mix three batches were made and for each batch several concrete specimens were produced, which were demolded 48 hours after casting.

2.2 Test and methodology

In order to analyse the permeability to water and the diffusion of chlorides, four types of measurements were performed: water porosity, absorption, capillarity and chloride migration coefficient. Moreover, Scanning Electron Microscopy (SEM) analysis was performed during the experiment to evaluate the microstructure of concretes and Energy Dispersive X-ray spectroscopy (EDX) was used for the analysis of phase composition. In addition, the compressive strength at the age of 28 days was determined from each mix (Table 2). For this purpose 100 mm diameter x 200 mm high cylindrical specimens were used.

Table 1. Mixture proportions of concretes

Material	Unit	UHF	UHF-air	UH	CC
Cement	kg/m^3	800	800	800	450
Water	kg/m^3	160	160	160	225
Superplasticizer	kg/m^3	30	30	30	1,37
Silica fume	kg/m^3	175	175	175	-
Silica flour	kg/m^3	225	225	225	-
Coarse aggregate	kg/m^3	-	-	-	880
Fine sand	kg/m^3	302	302	302	-
Medium-sized sand	kg/m^3	565	565	565	-
Coarse sand	kg/m^3	-	-	-	880
Steel fibres	kg/m^3	175	175	-	-
Curing		20ºC	Air	20ºC	20ºC

Table 2. Compressive strength

	UH	UHF	UHF-air	CC
f_c (MPa)	129.8	128.4	137.9	49.9

<u>Water porosity and absorption test</u>
The tests were carried out at 14 days, 28 days, 2 months and 6 months, in prismatic specimens of 100x100x40 mm, according to the NF P 18-459 standard (AFNOR, 2010). First, the specimens were dried in an oven at 105ºC until constant weight (M_{dry}). Then they were introduced in a vacuum unit and after 4h, maintaining the pressure, they were submerged in water covering them 20 mm. After 44h the test specimens were removed from the vacuum unit and the hydrostatic mass (M_{water}) and the air mass (M_{air}) were obtained.

<u>Capillarity test</u>
This test was carried out in accordance with the Spanish standard UNE 83982 (AENOR, 2008) using prismatic specimens of 100x100x50 mm. During the test the specimens remained in a container with 5 mm of water and weighed at specific time intervals. The test concludes when a steady state is reached (when the difference between any two successive values, spaced 24 hours period, is less than 0.1%). Results are expressed in terms of the quantity of water absorbed per unit surface area. The tests were carried out at the ages of 28 days, 2 months and 6 months.

<u>Chloride migration coefficient test</u>
This test provides a measure of the resistance of the concrete to chloride penetration and it was carried out according to standard NT BUILD 492 (NORDTEST, 1999). Cylindrical specimens with a diameter of 100

mm and a thickness of 50 mm were used. An external electrical potential is applied axially across the specimen and forces the chloride ions to migrate into the specimen. At the age of test, the specimen is axially split and a silver nitrate solution is sprayed on to one of the freshly split sections. The chloride penetration depth can then be measured from the visible white silver chloride precipitation, after which the chloride migration coefficient can be calculated from this penetration depth. The test was carried out at the ages of 28 days and 6 months. For each mix, 2 batches were made and three samples were carried out for each batch, taking the arithmetic mean of the six values obtained as the result.

3.0 RESULTS AND DISCUSSION

3.1 Microstructure

Figures 1, 2 and 3 show the SEM images of the concretes used in this study. All three ultra-high performance concretes (UH, UHF and UHF-air) have a very similar microstructure. The matrix is very dense and the hydration products are mainly C-S-H, very rich in silicon in some areas, probably due to the large amount of silica fume used in the concrete (Fig. 1).

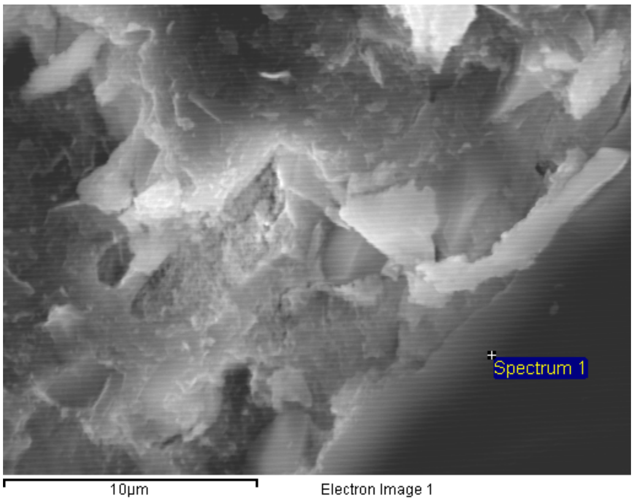

Fig. 1. SEM image of UH concrete (x 5000)

C_3S and C_2S were also found in all these mixes, giving an evidence that the hydration of Portland cement was not fully completed (Fig. 2). According to this, it should be noted that the amount of water used in the dosage has been very low (w/b = 0.16) and therefore insufficient to react with all the cement, leaving unhydrated particles. On the other hand, as other authors state (AFGC, 2013), it is noteworthy the absence of portlandite in the samples analyzed. This is justified by the high content of silica fume in the concrete, which reacts pozzolanically with the $Ca(OH)_2$ generated during the hydration of the cement.

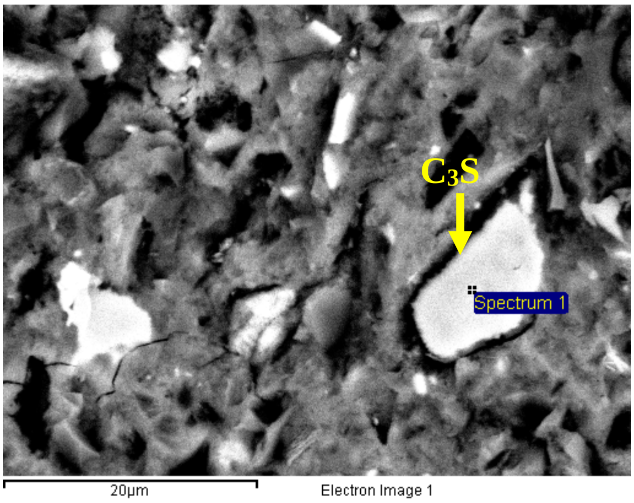

Fig. 2. Backscattered electron (BSE) image of UH concrete

As regards the Conventional Concrete, the microstructure is less dense (some voids) and less homogeneous (Fig. 3). In Figure 3 the different crystalline structures can be seen and Portland cement hydration products, such as calcium hydro silicates (C-S-H) and portlandite (hexagonal shape crystals), can be identified.

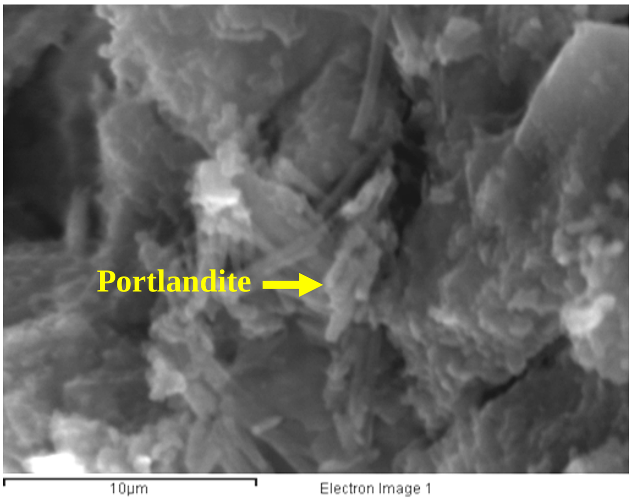

Fig. 3. SEM image of CC concrete (x 5000)

3.2 Water porosity and absorption

From the measurements made, the water porosity and absorption were obtained.

To calculate the water porosity, equation [1], provided by the standard NF P 18-459 (AFNOR, 2010), has been used.

$$\varepsilon = \frac{M_{air} - M_{dry}}{M_{air} - M_{water}} \cdot 100 \qquad (1)$$

where:
M_{air} is the air mass
M_{water} is the hydrostatic mass
M_{dry} is the dry mass

Figure 4 shows, for each type of concrete, the average water porosity.

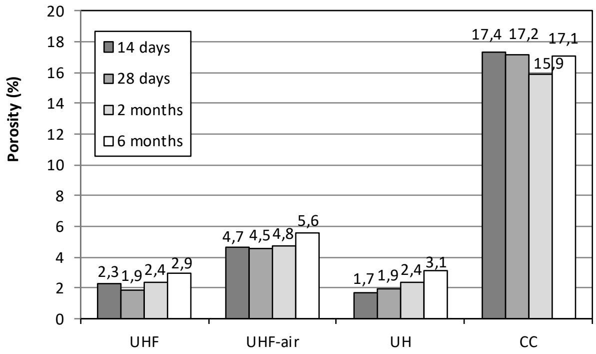

Fig. 4. Water Porosity

The absorption has been calculated with equation 2, given by the standard UNE 83980.

$$A = \frac{M_{air} - M_{dry}}{M_{dry}} \cdot 100 \qquad (2)$$

where:
M_{air} is the air mass
M_{dry} is the dry mass

Figure 5 shows the average absorption for each type of concrete.

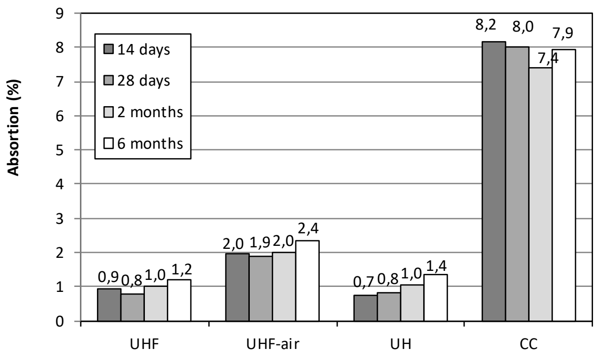

Fig. 5. Water absorption

The results show that for Ultra High Performance Concretes that have the same curing (UHF and UH), regardless of whether they have fibers or not, the porosity and absorption obtained are very similar. On the other hand, those concretes that were air-dried, have a greater absorption and porosity than those that were cured at a controlled temperature of 20ºC.

The values of porosity and absorption obtained for Ultra High Performance Concrete are within the ranges proposed by other authors (Söylev and Özturan, 2014; Wang *et al.*, 2014; Fallah and Nematzadeh, 2017).

It was also observed that UHPC shows very low porosity and water absorption capacity, which are approximately 9 times less than that of CC.

3.3 Capillarity

This parameter is an indirect indicator of the durability since is closely related to the resistance of the concrete against the penetration of aggressive agents and the resistance to freezing/thawing.

As it was expected, in all concretes the water absorption by capillarity is lower the greater the age of the concrete, due to the progressive hydration of the cementing material (Fig. 6). This absorption is also much lower in the three types of Ultra High Performance Concretes analysed (UH, UHF and UHF-air) than in Conventional Concrete (CC) as a result of a denser microstructure. Thus, for example, the amount of water absorbed (weight increase) per unit area ΔP/S in UH and UHF is, on average, around 3% of that absorbed in the CC at the three studied ages.

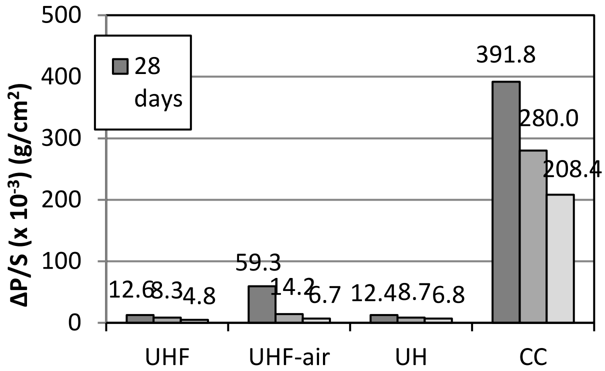

Fig. 6. Water absorption by capillarity per unit area

The values obtained in the UHPC, with and without fibers, cured in the same conditions (UHF and UH) have been very similar, with no differences observed between them. Thus, the presence of fibers does not seem to influence, significantly, the porous structure of the material.

Regarding the influence of the curing, in UHPC air-dried (UHF-air) there is a significant absorption increase, being this one significantly higher at early ages (28 days). However, as the hydration progresses, the differences with the concrete cured in the chamber decrease, obtaining values very similar to those of the UHF and UH concretes at the age of 6 months. Since poor curing have not affected the compressive strength of these concretes (Table 2), it is most likely that a small increase in porosity has occurred only in the uppermost layers of the concrete.

3.4 Chloride migration coefficient

Figure 7 shows the non-steady-state chloride migration coefficient (Dnssm) obtained at the ages of 28 days and 6 months.

Consistent with the results obtained in the other tests carried out, the chloride diffusion in the three types of UHPC analyzed (UH, UHF and UHF-air) is much lower than in Conventional Concrete, being the differences between the two of them of two orders of magnitude.

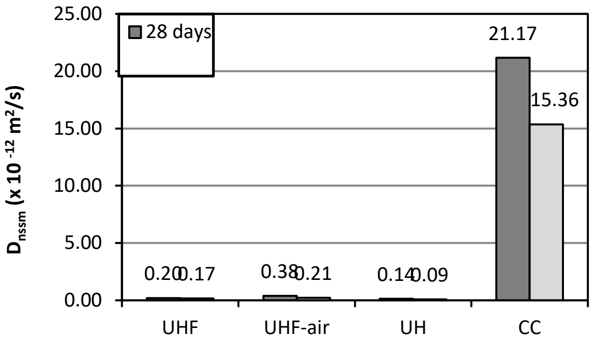

Fig. 7. Chloride migration coefficient (D_{nssm})

These results are consistent with the ones obtained from researchers as Graybeal and Tanesi (2007) or Jaafar *et al*. (2017). Other authors reported that the UHPC has a discontinuously capillary porosity and that is the reason why they have a significantly decreased of chloride permeability (Bonneau *et al*. 2000).

However, this fact is not only due to the low porosity of the UHPC, but also due to the high content of cement used in the dosage and, therefore, of calcium aluminate, since chlorides react chemically with tricalcium aluminate or its hydrates form calcium chloro-aluminate (Friedel's salt) (Diamond, 1986; Taylor, 1992) and consequently the free chloride content decreases.

With regard to the UHPC, only the air-cured concrete (UHF-air) shows a worse behaviour than the others, especially at an early age. For example, at the age of 28 days the Dnssm coefficient is twice as high in UHF-air concrete as in UHF concrete, although at the age of 6 months the chloride permeability in both concretes tends to be similar. In any case, the chloride migration coefficients obtained in the UHF-air remain very close to the ranges proposed by some authors and codes for very high durability concretes, such as the recommendations of the AFGC (AFGC, 2013) that establish values of Dnssm of 10^{-13} m^2/s.

Finally, Fig. 7 also shows a lower chloride permeability in the Ultra High Performance Concretes without fibers (UH) than in the concretes with fibers (UHF), being on average the D_{nssm} coefficient in UH 60% higher than the one obtained for UHF. This fact may be because when large quantities of fibers are used, bundles can be formed that generate weak points through which chlorides diffuse more easily.

4.0 CONCLUSIONS

The results of this research work show that the Ultra High Performance Concretes (130 MPa) have a denser microstructure and consequently a remarkably lower water permeability than the Conventional Concrete (50 MPa). The water absorption and the water porosity is approximately 8 times lower, the water absorption coefficient by capillarity was 30 times lower, and the non-steady-state chloride migration coefficient was 100 times smaller.

The values recorded of absorption and capillarity in UHPCs with and without fibres were very similar. However, the permeability to chlorides was somewhat higher in concretes with steel fibres. This fact may be because when large quantities of fibers are used, bundles can be formed that generate weak points through which chlorides diffuse more easily.

With regard to the influence of curing, in air-dried UHPCs there was a significant increase in permeability to both water and chlorides. This increase was approximately 100% in the absorption, porosity and chloride migration tests carried out at the age of 28 days. Despite this, the chloride migration coefficient registered remain very close to the ranges proposed by some recommendations for very high durability concrete.

Acknowledgement

The authors would like to express their gratitude to the Spanish Ministry of Economy and Competitiveness for the financial support from the national program of oriented research, development and Innovation to societal challenges (ref. BIA2016-78460-C3-3-R) and also to Spanish Ministry of Science and Innovation for the pre-doctoral scholarship granted to José Enrique Ramón Zamora and to Ana Martínez Ibernón (FPU 13/00911 and FPU16/00723, respectively).

References

Acker, P., Dehloul, M., 2004. Ductal® Technology: a large spectrum of properties, a wide range of application. In Proceedings of the International Symposium on Ultra-High Performance Concrete Kassel, Germany; 11-23.

Ashour, S.A., Wafa, F.F., Kamal, M.I., 2000. Effect of the concrete compressive strength and tensile reinforcement ratio on flexural behavior of fibrous concrete. Engineering Structures, 22(9):1145-1158.

Association Française de Génie Civil (AFGC), 2013. Ultra high performance fibre-reinforced. Recommendations. Documents scientifiques et techniques.

Bayard, O., Ple, O., 2003. Fracture mechanics of reactive powder concrete: Material modeling and experimental investigations. Engineering Fracture Mechanics, 70(7–8):839–851.

Bonneau, O., Vernet, C., Moranville, M., Aïtchin, P.C., 2000. Characterization of the granular packing and percolation threshold of reactive powder concrete, Cement and Concrete Research, 26(11):1639-1648.

Campione, G., Mangiavillano, M.L., 2008. Fibrous reinforced concrete beams in flexure: Experimental investigation, analytical modelling and design considerations. Engineering Structures, 30(11):2970-2980.

Chen, T., Gao, X., Ren, M., 2018. Effects of autoclave curing and fly ash on mechanical properties of ultra-high performance concrete. Construction and Building Materials, 158:864-872.

Diamond, S., 1986. Chloride concentrations in concrete pore solutions resulting from calcium and sodium chloride admixtures. Cement Concrete and Aggregates, 8(2):97-102.

Fallah, S., Nematzadeh, M., 2017. Mechanical properties and durability of high-strength concrete containing macro-polymeric and polypropylene fibers with nano-silica and silica fume. Construction and Building Materials, 132:170–187.

Gesoglu, M., Güneyisi, E., Nahhab, A.H., Yazıcı, H., 2015. Properties of ultra-high performance fiber reinforced cementitious composites made with gypsum-contaminated aggregates and cured at normal and elevated temperatures. Construction and Building Materials, 93:427-438.

Ghafari, E., Bandarabadi, M., Costa, H., Julio, E., 2012. Design of UHPC using artificial neural networks. In 10th International Symposium on Brittle Matrix Composites, Warsaw, Poland (p. 9)

Graybeal, B., 2006. Material property characterization of ultrahigh performance concrete. In FHWA-HRT-06-103, U.S. Department of Transportation (p. 176).

Graybeal, B.E., Tanesi, J., 2007. Durability of an ultrahigh-performance concrete. Journal of Materials in Civil Engineering, 19:848-854.

Gu, C., Sun, W., Guo, L., Wang, Q., 2016. Effect of curing conditions on the durability of ultra-high performance concrete under flexural load. Journal of Wuhan University of Technology-Mater, 31:278-285.

Heinz, D., Ludwig, H., 2004. Heat treatment and the risk of DEF delayed ettringite formation in UHPC. In Proceedings of the International Symposium on Ultra-High Performance Concrete, Kassel, Germany; 717-730.

Herold, G., Muller, H., 2004. Measurement of porosity of ultra-high strength fibre reinforced concrete. In Proceedings of the International Symposium on Ultra-High Performance Concrete Kassel, Germany; 685–694.

Jaafar, M.F.M., Saman, H.M., Sidek, M.N.M, Ismail, N., Ariffin, N.F., 2017. Chloride Resistance Behavior on Nano-Metaclayed Ultra-High Performance Concrete. International Symposium on Civil and Environmental Engineering (ISCEE 2016). MATEC Web of Conferences, 103, article number 01023.

Oh, B.H., 1992. Flexural analysis of reinforced concrete beams containing steel fibers. Journal of Structural Engineering, 118(10):2821-2836.

Oh, B.H., 1994. Closure of “Flexural analysis of reinforced concrete beams containing steel fibers”. Journal of Structural Engineering, 120(6):1934

Pierard, J., Cauberg, N., 2009. Evaluation of durability and cracking tendency of ultra-high performance concrete. In Creep, shrinkage and durability mechanics of concrete and concrete structures (pp. 695–700). London, UK: Taylor and Francis Group.

Resplendino, J., 2004. First recommendations for ultra-high-performance concretes and examples of application. In Proceedings of the International Symposium on Ultra High Performance Concrete, Kessel, Germany; 79-90.

Roux, N., Andrade, C., Sanjuan, M., 1996. Experimental study of durability of reactive powder concretes. Journal of Materials in Civil Engineering 8(1):1-6.

Söylev, T.A., Özturan, T., 2014. Durability, physical and mechanical properties of fiber-reinforced concretes at low-volume fraction. Construction and Building Materials, 73:67–75.

Tafraoui A, Escadeillas G., Vidal T., 2016. Durability of ultra high performances concrete containing metakaolin. Construction and Building Materials, 112:980-987.

Tam, C.M., Tam, V.W.Y., Ng, K.M., 2012. Assessing drying shrinkage and water permeability of reactive powder concrete produced in Hong Kong. Construction and Building Materials, 26:79-89.

Taylor, H.F.W., 1992. Cement Chemistry, 2nd Edition, Academic Press Ltd, London.

Tue, N.V., Küchler, M., Schenck, G., Jürgen, R., 2004. Application of UHPC filled tubes in buildings and bridges. In Proceedings of the International Symposium on Ultra High Performance Concrete, Kessel, Germany; 807-817.

Wang, W., Liu, J., Agostini, F., Davy, C.A., Skoczylas, F., Corvez, D., 2014. Durability of an Ultra High Performance Fiber Reinforced Concrete (UHPFRC) under progressive aging. Cement and Concrete Research, 55:1–13.

Wang, D., Shi, C., Wu, Z., Xiao, J., Huang, Z., Fang, Z., 2015. A review on ultra high performance concrete: Part II. Hydration, microstructure and properties. Construction and Building Materials, 96:368-377.

Yazici, H., Yardimci, M.Y., Aydin, S., Karabulut, A.S., 2009. Mechanical properties of reactive powder concrete containing mineral admixtures under different curing regimes. Construction and Building Materials, 23:1223-1231.