Analysis of Ink Bottle Pores from MIP Data with the Pore-Cor Model

Peter Matthews [1], Christopher Gribble [1], Luca Lucarelli [2], Andreas Schreiber [3], Jürgen Adolphs [3]

[1] Environmental and Fluid Modelling Group, University of Plymouth, Drake Circus, Plymouth, Devon, PL4 8AA, UK.

[2] ThermoFisher Scientific, Strada Rivoltana, 20090 Rodano (Mi) Italy

[3] Porotec GmbH , Niederhofheimer Str. 55a, 65719 Hofheim/Ts., Germany

Introduction "Ink Bottle Pores"

The invoking of "ink bottle" pores, with a single small pore entrance and large volume beyond the entrance, provides a common method for explaining the overall hysteresis observed in mercury intrusion porosimetry (MIP). However, hysteresis is also caused by contact angle hysteresis, mercury snap-off, and rupture of the pore network. So the existence of ink bottles cannot be judged simply from the extent of MIP hysteresis. However, their existence can be investigated using the Pore-Cor Research Suite software (University of Plymouth, UK), which generates a three-dimensional void network with a simplistic Cartesian geometry that has the same percolation properties, in terms of MIP, as an experimental sample. Successful modelling requires very accurate experimental MIP measurements over the entire pressure region up to 400MPa, including blank runs at the same temperature to allow correction for compressibility, and values of sample density. The software then uses connectivity, as well as pore and throat sizes and a short range size auto correlation function, as a fitting parameter to match the percolation properties. The fitting is carried out with an 8-dimensional Boltzmann-annealed amoeboid simplex. Interrogation of the resulting explicit 3-dimensional network, in terms of the connectivities of individual pores, yields a range of connectivities over the permitted range of 1 to 6.

The software does not prove the existence of ink-bottles, but can demonstrate for a particular sample whether the existence of ink bottles is compatible with the shape of the MIP curve, porosity and density. A range of other properties can also be modeled, for example diffusion[1].

Samples & MIP Experiment

"OPC"

Hardened Cement Paste made of Ordinary Portland Cement CEM I 32.3R, w/c=0.4 minimum 28 days cured [2,3]

Mercury Intrusion Porosimetry (MIP) investigations were conducted at Porotec lab with PASCAL 140/440 Mercury intrusion porosimeters (ThermoFisher Scientific) up to 400MPa (UHPC) and 200MPa (OPC) with blank correction.

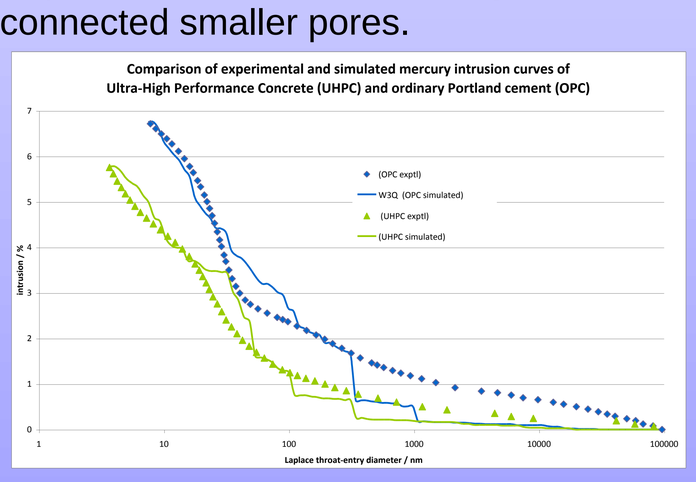
"UHPC"

Ultra High Performance Concrete made of cement CEM 52,5R HS-NA (733 kg/m³), sand (1008 kg/m³), microsilica (230kg/m³), quartz I (183 kg/m³), vol.% of fines < 0.125mm (405 l/m³), plasticiser (28.6 kg/m³), water (161 l/m³). The water cement ratio was w/c = 0.23, considering the water content of the plasticiser the water binder ratio is w/b = 0.19 minimum 28 days cured (provided by University Kassel [4])

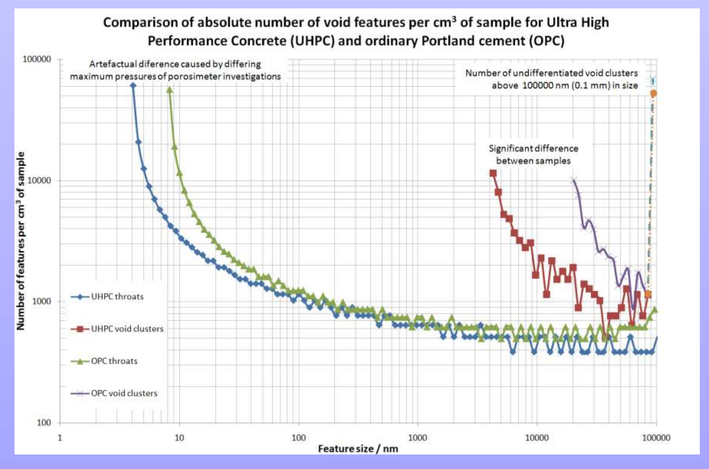
Results

Results for a specimen sample are presented as a fit to the mercury intrusion curve, the corresponding pore and throat size distributions, and the individual pore connectivities. Those **pores with connectivity of 1 are ink bottles**, although some larger ink bottles could be clusters of well connected smaller pores.

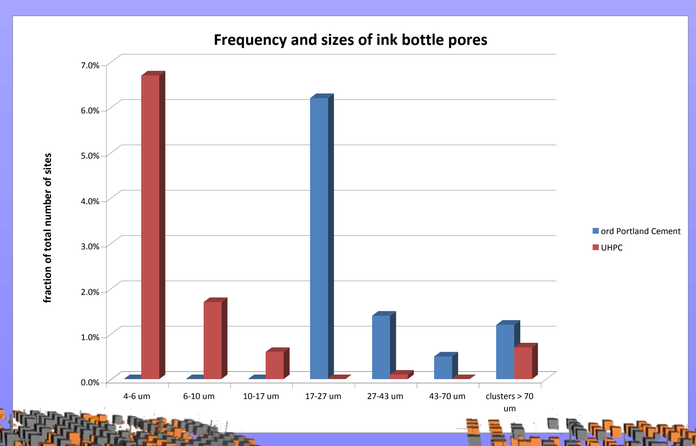
Intrusion curves, experimental and modeled with Pore-Cor



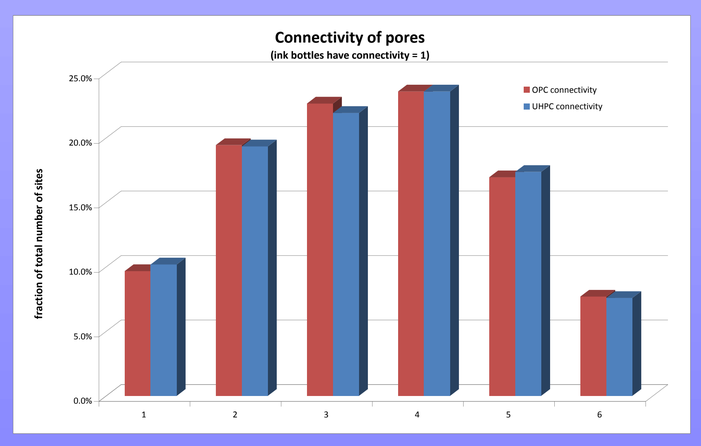
Number of void features

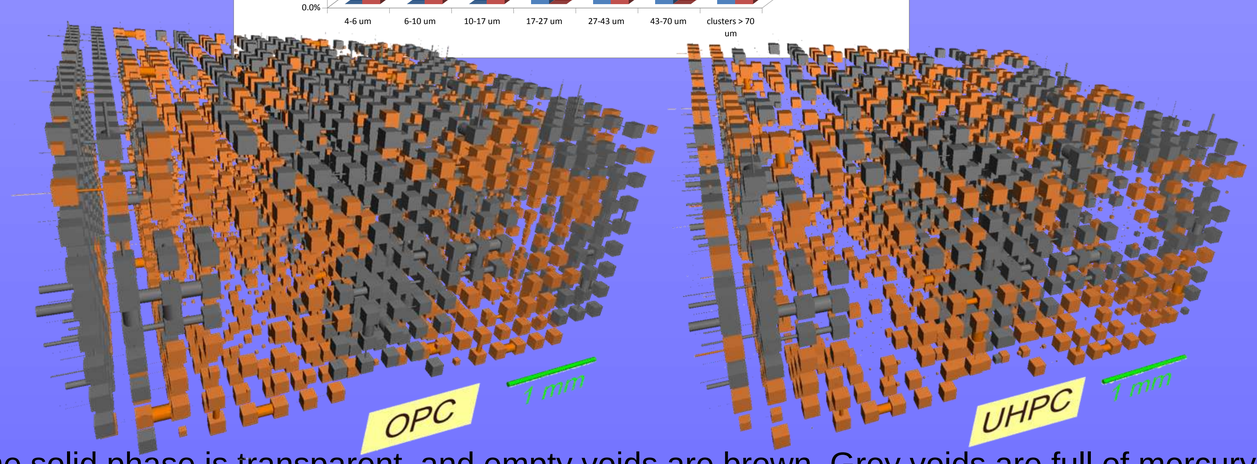


Ink Bottle Pores



Connectivity





The solid phase is transparent, and empty voids are brown. Grey voids are full of mercury intruded at a pressure of 37.5 MPa – note that the UHPC is much less intruded.

Much of the nanoporous structure is invisible in the pictures, but can be toured in virtual reality.

Conclusion

The Pore-Cor results show a clear difference in size and frequency of ink bottle pores between OPC and UHPC, which is realistic in the context of the known high density and strength of UHPC. The connectivity of pores is similar.

References:

1. Laudone, G.M., Matthews G.P., and Gane, P.A.C. Modelling diffusion from simulated porous structures, Chemical Engineering Science, 63 , 1987-1996 (2008).
2. Adolphs, J. "Physico – Mechanical and Chemical Properties of Hardened Cement Paste Interacting with Moisture" RILEM Proceedings 5th International Essen Workshop - Transport in Concrete 11.-13. June 2007, 181-193 (2007).
3. Adolphs, J., Heine, P., Setzer, M.J.: „ Changes in Pore Structure and Mercury Contact Angle of Hardened Cement Paste Depending on Relative Humidity", *Materials and Structures* Vol. 35, 477-486 (2002).
4. Adolphs, J., Schreiber, A.: „Microstructural Characterisation of Ultra-High Performance Concrete" Proceedings *International Symposium on Ultra High Performance Concrete* (eds. M. Schmidt, E. Fehling, C. Geisenhanslüke), Kassel, Germany September 13-15 2004, 265-272 (2004).