High Early Strength Gain Low-carbon Concrete: A Microstructure Study

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Abstract: Replacing part of the cement with supplementary cementitious materials (SCMs) reduces CO_2 emissions associated with cement production. High slag substitutions however may compromise early age strength which is necessary for most commercial applications. Boral's ENVISIA®, which is an engineered blend of OPC, GGBFS and a special additive, meets the early age requirements and has been shown to demonstrate equivalent or better durability properties than equivalent high-SCM concrete. This study investigates the pore solution and phase development of ENVISIA® binder system to understand the mechanism behind its faster early age strength development and high volume stability (low drying shrinkage). Microstructure investigation of mature ENVISIA® concretes (5-year old Grade 40MPa and 3-year old Grade 55MPa) and equivalent grade high-SCM blends was also carried out to assess similarities and differences. Pore solution analysis shows enhanced dissolution of aluminium and silicon in the ENVISIA® binder accelerating the formation of calcium silicate hydrate (C-S-H) at early ages which is the main cement hydrate. The faster formation of C-S-H explains the early age strength gain as well as the volume stability of ENVISIA® concretes. Microstructure of mature ENVISIA® concretes and equivalent grade high-SCM blends were found to be highly comparable. No unusual hydrates or abnormalities were observed in any of the concretes.

Keywords: strength, cement, slag/GGBFS, low carbon binder, shrinkage

1. Introduction

Cement production results in substantial amount of carbon dioxide (CO_2) emissions. Calcination of limestone in order to produce cement clinker accounts for about 60% of CO_2 emissions at a cement plant[1]. Therefore, replacing part of the cement with SCMs such as fly ash and ground granulated blast furnace slag (GGBFS or slag) offers high potential to reduce the amount of CO_2 associated with cement production. Slag, being hydraulic in nature like cement, allows higher substitutions than other SCMs. High slag substitutions are however limited by slow early age strength development which is needed for most commercial applications of concrete [2, 3].

Boral's ENVISIA®, which was first commercialized in July 2013, is an engineered blend of OPC, GGBFS and a special additive designed to accelerate early age hydration and thus, attain required early age strength [4, 5]. Several studies have been conducted to qualify ENVISIA® concretes as an alternative to conventional high SCM concretes and overall, ENVISIA® was found to have equivalent or better durability properties than high SCM counterparts [4, 6-8]. A study of ENVISIA® concretes in various grades (32, 40 and 60 MPa) showed that ENVISIA®: 1) exhibits higher early strength gain and significantly lower drying shrinkage compared to conventional concrete, 2) has improved durability in terms of water permeability, water sorptivity and chloride permeability, and 3) effectively mitigates alkali-silica reaction (ASR) [6, 7]. Similarly in another study, ENVISIA® concrete developed for marine applications showed a much lower chloride diffusion coefficient by both NT492 and NT443 tests, lower water sorptivity by ASTM C1585 method and lower water permeability by DIN 1048 test in comparison with traditional marine concrete (Shrinkage Limited Cement/GGBFS) [8]. The chloride durability of ENVISIA® has also outperformed conventional concrete designs and the requirements of Transport for New South Wales (TfNSW) Bridge Specification B80 leading to the potential for increased service life of reinforced concrete structures [4]. Overall, the studies carried out on ENVISIA® demonstrates that it is suitable for use in demanding applications where lower drying shrinkage, higher chloride resistance and resistance to sulphate or acid attack are required. It is also suitable for use to mitigate ASR when reactive aggregates are used [8].

Whereas, several tests have shown that ENVISIA® is highly reliable and meets requirements for commercial applications, there has been no study of mature ENVISIA® concretes to understand the microstructure and how the microstructure compares with high-SCM concretes of equivalent grade. This study therefore aims to examine the microstructure of mature ENVISIA® concretes (5-year old Grade 40MPa and 3-year old Grade 55MPa) in comparison with equivalent grade high-SCM blends. Pore solution as well as formation of hydrates in ENVISIA® and equivalent high-slag binder system were also investigated to better understand early age strength development and volume stability.

2. Materials and Methods

2.1 Analysis of Mature ENVISIA® Concretes (Cast Cylinders)

The concrete samples for microstructure investigation were supplied by Boral Baulkham Hills. Details of the mature concrete cylinders investigated are provided in Table 1. The mature concretes are Grades 40MPa (5-year old) and 55MPa (3-year old) and include a reference control as well as an equivalent ENVISIA® version (with ZEP®). ZEP® is GGBFS combined with a special additive. It is worth noting that the Grade 40MPa concrete (PT Control) is a ternary blend containing both slag and fly ash. The rest of the mature concretes are all cement-slag blends. No visible cracks and physical defects were observed in any of the mature concretes during visual inspection.

The concretes were subjected to scanning electron microscopy energy dispersive spectroscopy (SEM-EDS) to characterize the microstructure. The SEM images were obtained both on fractured concrete and polished concrete. Micro-computed tomography (Micro-CT) was also carried out to rule out presence of abnormalities /defects in the mature concretes.

The mature ENVISIA® concretes provided for microstructure studies have also undergone a series of tests as part of Boral strength and durability studies and some results are included in this report. These include compressive strength tests as per AS 1012.9, drying shrinkage as per AS 1012.12 and chloride ingress test as per NT BUILD 443. All performance/durability tests were carried out by Boral Materials Testing Laboratory at Baulkham Hills.

Table 1 Mix design for Mature ENVISIA® Concretes (Grades 55MPa and 40MPa)

Mix description		Marine concrete	Marine ENVISIA®	Post-Tensioned (PT) Concrete	Post-Tensioned (PT) ENVISIA®
MIX DATE:		26/07/2017		24/02/2015	
Shrinkage Limited (SL) Cement	kg/m^3	191	192	291	173
Maldon Enviroment Slag	kg/m^3	355	0	80	0
Maldon ZEP	kg/m^3	0	358	0	259
Eraring fly ash	kg/m^3	0	0	40	0
Total Cementitious	kg/m^3	546	550	411	432
Total Aggregates	kg/m^3	1624	1606	1784	1787
Slump AS 1012.3.1	mm	220	210	120	120
Water	kg/m^3	212	214	204	198
Water/Cementious material ratio	ratio	0.39	0.39	0.50	0.46

2.2 Microstructure development of ENVISIA® at early ages

Binder systems that mimic ENVISIA® and an equivalent high-slag concrete were also prepared for pore solution analysis and X-ray diffraction to characterize the changes in pore solution in relation to the formation of hydrates. Both binder systems have 50% cement and 50% slag. The ENVISIA® binder contains a special additive.

3. Results and Discussion

3.1 Early Age Strength, Drying Shrinkage and Chloride Ingress Performance of ENVISIA®

Figure 1 shows the compression test results of the mature concretes (supplied by Boral Baulkham Hills) at 1, 3, 7 and 28 days. The results demonstrate ENVISIA®'s much higher early strength gain than the control concretes (high-SCM counterpart), with about similar strength attained at 28 days.

Figure 2 shows the drying shrinkage and chloride ingress performance of Marine Control and Marine ENVISIA® respectively measured up to 2 years. From the plots, it is clear that Marine ENVISIA® demonstrates better volume stability (Figure 2a) and chloride resistance (Figure 2b) than Marine Control at all times. Marine ENVISIA® and Marine control are both below the maximum chloride ingress requirement specified in TfNSW Bridge Specification B80 for Nordtest NT Build 443 which is at 2.0 x 10^{-12} m^2/sec (Figure 2b). The chloride diffusion coefficient further decreases with time as may be expected due to continued hydration of the concrete and consequent refinement of the microstructure. The excellent chloride ingress performance of cement-slag binders is generally attributed to more refined microstructure and better chloride binding capacity than plain cement. Replacing cement with slag increases the aluminates in the system that are able to react with chloride to form calcium chloro-aluminates (Friedel's salt) which not only effectively binds chlorides but also contributes to pore blocking [9, 10].

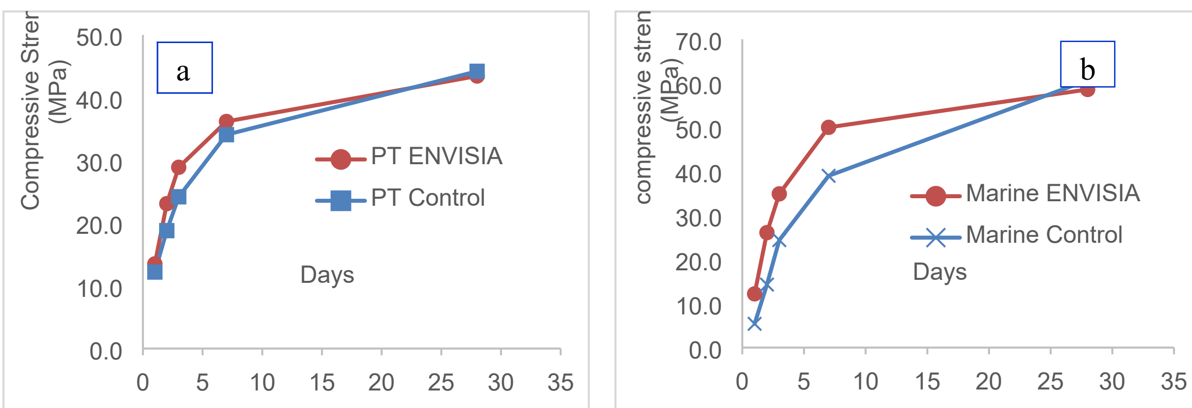

Figure 1 Early age compressive strength results of the a) 3-year old (Grade 40MPa) and b) 5-year old cylinders (Grade 55MPa)

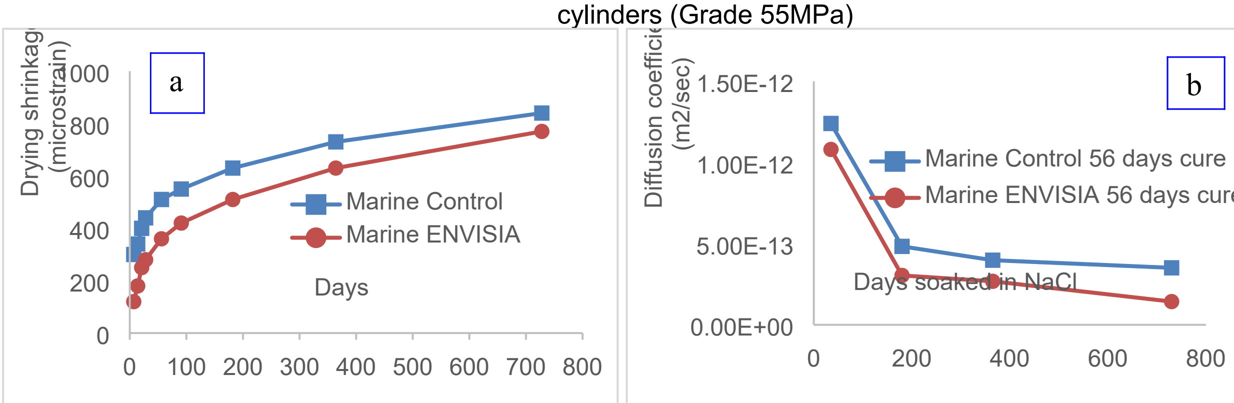

Figure 2 Volume stability and chloride ingress performance of Marine ENVISIA® and Marine Control: a) Drying shrinkage and b) Chloride Ingress Test Results

3.2 Pore solution of ENVISIA® concrete and Formation of Hydrates

In order to better understand the early age strength development of ENVISIA® concretes, binder systems at early ages (ENVISIA® and high-slag equivalent) were subjected to pore solution analysis and X-Ray diffraction. Results of the pore solution analysis in Figure 3 show the massive increase in the concentration of both silicon and aluminium in the pore solution indicating higher solubility of the reactive phases of cement and slag in the ENVISIA® system. This results in significantly higher amount of calcium silicate hydrate (C-S-H) formed at early ages (Figure 4) which is the main phase contributing to the strength development of cement and cement-based binder systems. Slight increase in ettringite can also be observed. The drastic increase in the amount of C-S-H likely explains the high early age strength gain of ENVISIA®. Ettringite like any other cement hydrate contributes to microstructure densification and strength development. From Figure 4, the faster consumption of portlandite in the ENVISIA® system is also notable which confirms increased slag hydration. Slag from point of view of cement hydration is calcium deficient, hence takes some calcium from portlandite (by-product of cement hydration and the most soluble calcium source in the binder) to form C-S-H.

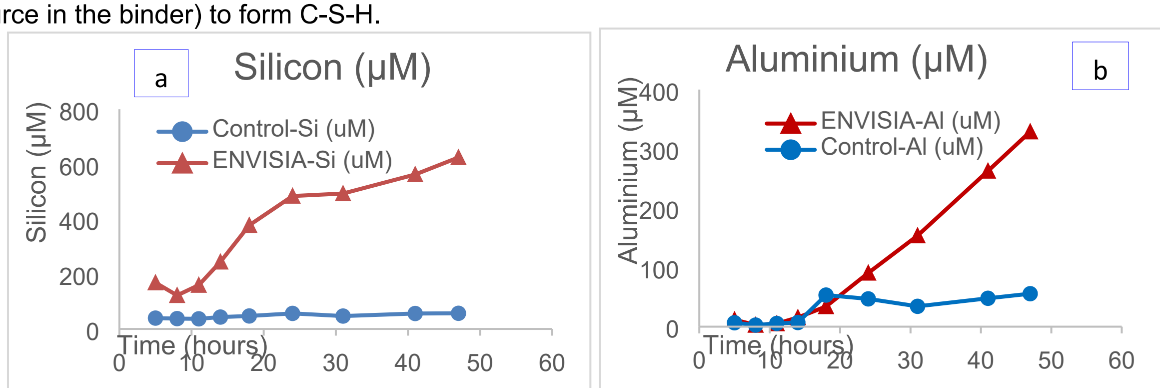

Figure 3 Pore solution analysis results of High-Slag Control and ENVISIA® at early ages (50:50 cement to slag): a) silicon and b) aluminium

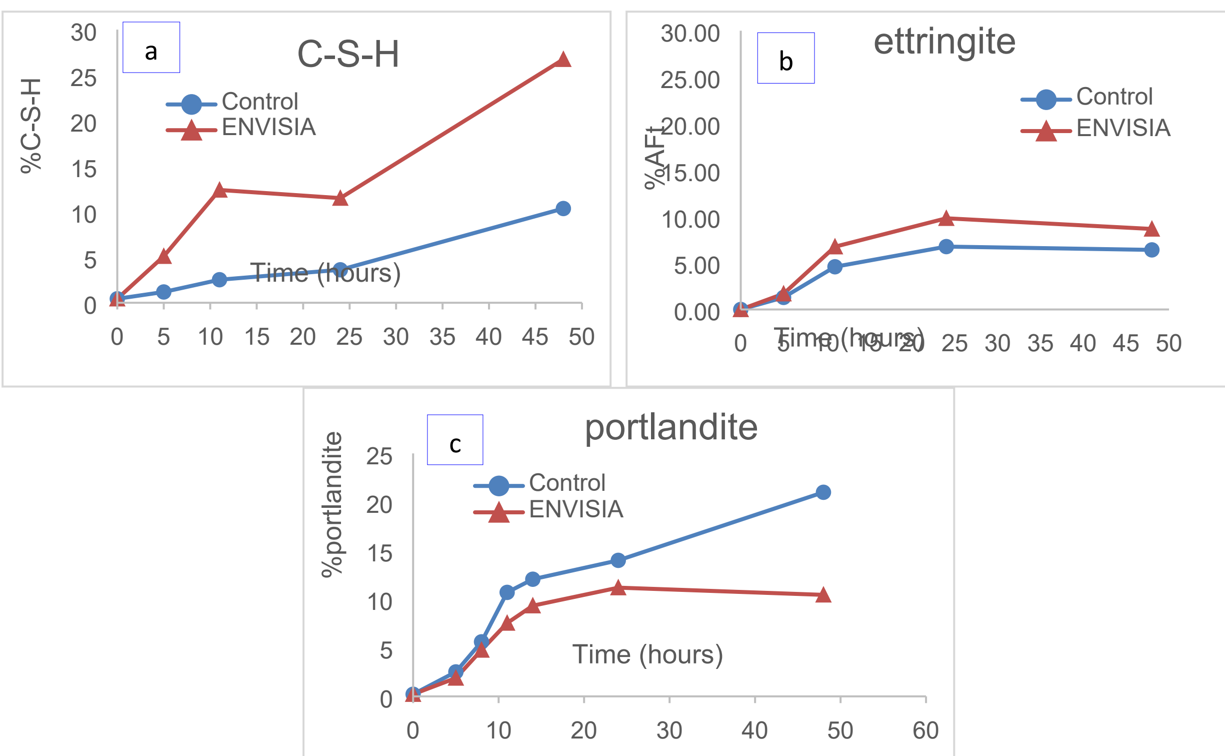

Figure 4 XRD analysis of the phase development of the main hydrates in High-Slag control and ENVISIA® at early ages (50:50 cement to slag): a) calcium silicate hydrate (C-S-H), b) ettringite (AFt) and c) portlandite ($Ca(OH_2)$) reported at % of total hydrates

3.3 Morphology of the Hydrates in Mature ENVISIA® Concretes

Microstructure investigation of Mature ENVISIA® concretes was carried out and results were compared to that of equivalent grade High-SCM concretes. SEM images of the 5-year old 40MPa concretes (Control and ENVISIA®) are shown in Figure 5. The most notable hydrates in the fractured concrete are portlandite (hexagonal plates) and ettringite (needle-like structures). The rest of the hydrates do not have very defined morphology. C-S-H fibrils are likewise hard to see at older ages due to the more dense packing of the paste as a consequence of continuous hydration and space filling.

All hydrates observed in Control and ENVISIA® concretes were as expected in a portland cement+slag binder (i.e. no unusual products were noted). There is also no notable difference in the microstructure other than the presence of slightly more ettringite in PT ENVISIA® than in PT Control. The ettringite observed in the mature concretes (PT Control and PT ENVISIA®) is finely intermixed with the hydrates (which means formed during cement hydration) and in fact, filling empty spaces.

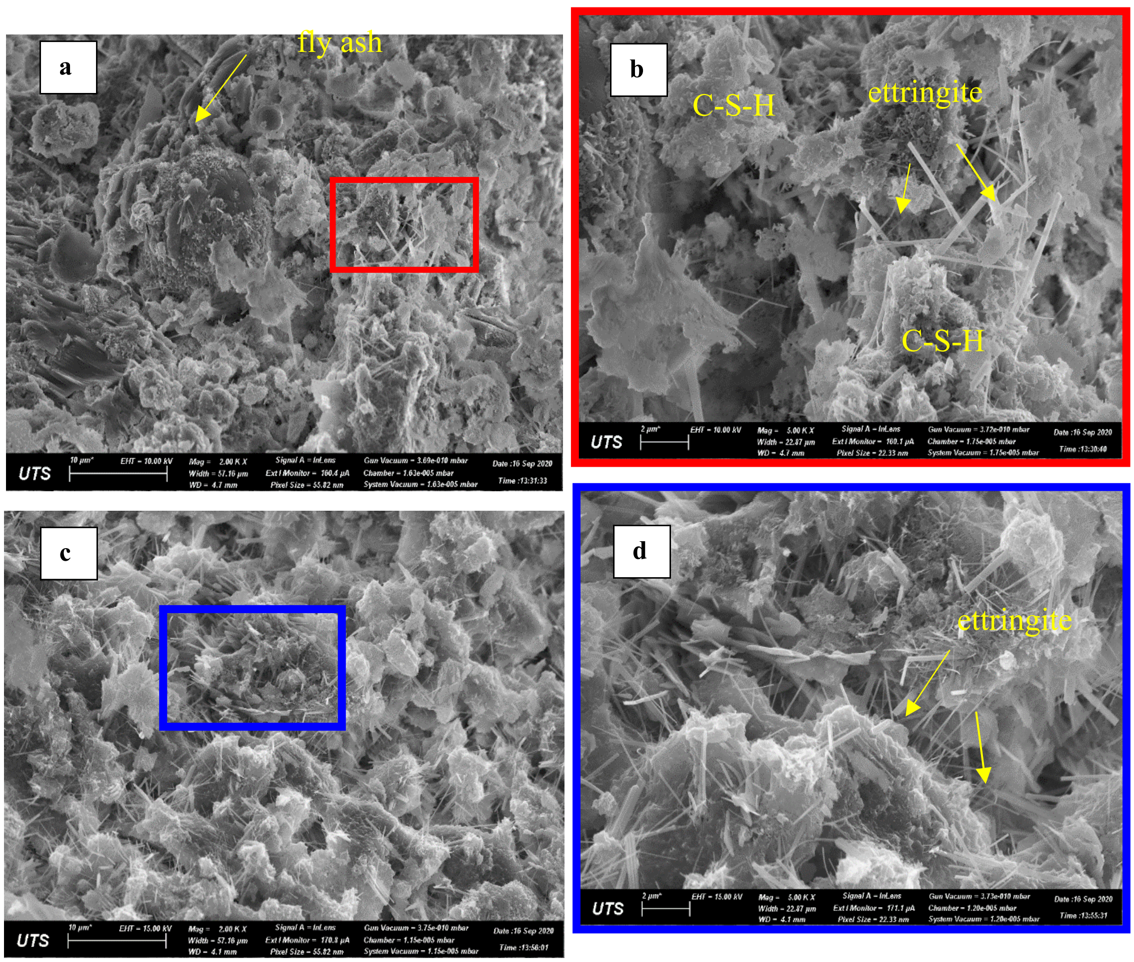

Figure 5 SEM images of the 5-year old Grade 40MPa PT Control (a and b) and Grade 40MPa PT ENVISIA® (c and d)

SEM images of the 3-year old 55MPa concretes are shown in Figure 6. The 55MPa concretes are notably denser and less porous that the 40MPa concretes as may be expected from much lower water/cement ratio and higher binder content (resulting to higher strength). Similar to the 40MPa concretes, there is also no notable difference in the microstructure of the Marine concretes other than the slightly higher amount of ettringite observed in the Marine ENVISIA®. The enhanced stability of ettringite in ENVISIA® as confirmed in both Grade 40 and Grade 55MPa concretes likely contributes to its better drying shrinkage performance. Drying shrinkage refers to the volume contraction due to loss of capillary water. Ettringite has more bound water than other cement hydrates and therefore occupies bigger volume. Table 2 summarizes the water content of various hydrates.

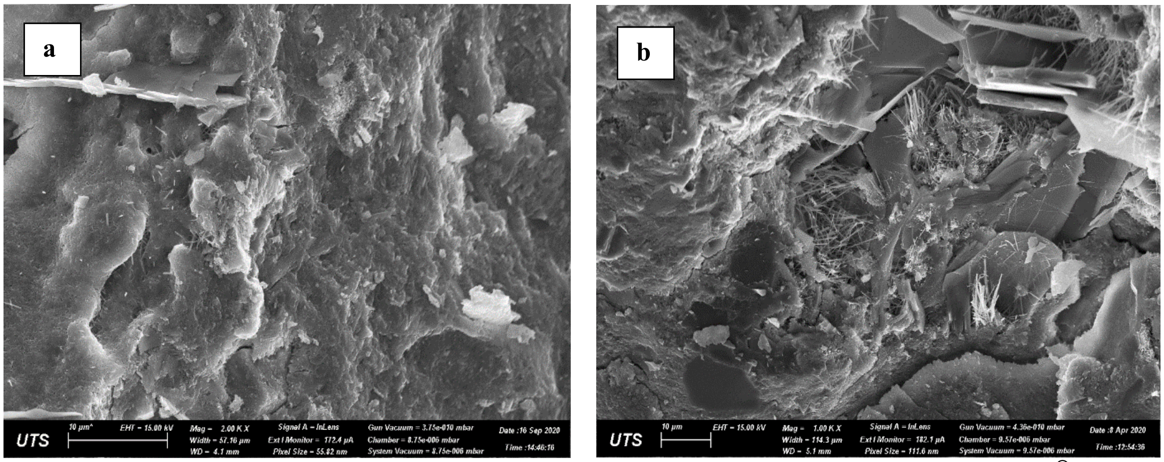

Figure 6 SEM images of the 3-year old a) Marine Control and b) Marine ENVISIA®

Table 2 Percentage of water in various hydrates

Phases	**Formula**	**%H_2O**
ettringite	$3CaO.\ Al_2O_3.\ 3CaSO_4.32H_2O$	46
C_3AH_6	$3CaO.Al_2O_3.6H_2O$	28
CSH	$1.7CaO.SiO_2.4H_2O$	30
Portlandite	$Ca(OH)_2$	24

3.4 Polished sections and micro-CT to check for Defects and Abnormalities

Polished sections were prepared to better observe any unusual feature in the microstructure. Figures 7 and 8 show backscattered electron images (BSE images) and secondary electron (SE) images respectively of the polished sections respectively. BSE images of PT Control and PT ENVISIA® in Figure 7 show the presence of different phases in the concrete. Some unreacted components (fly ash, slag, cement clinker and limestone) are still notable. The presence of fly ash in the PT control confirms that it's a triple blend. Secondary electron (SE) SEM images of the polished sections of the PT and Marine concretes in Figure 8 show that the aggregates are intact, there is a good aggregate-paste bonding in the concrete matrix and no unusual features in both concretes.

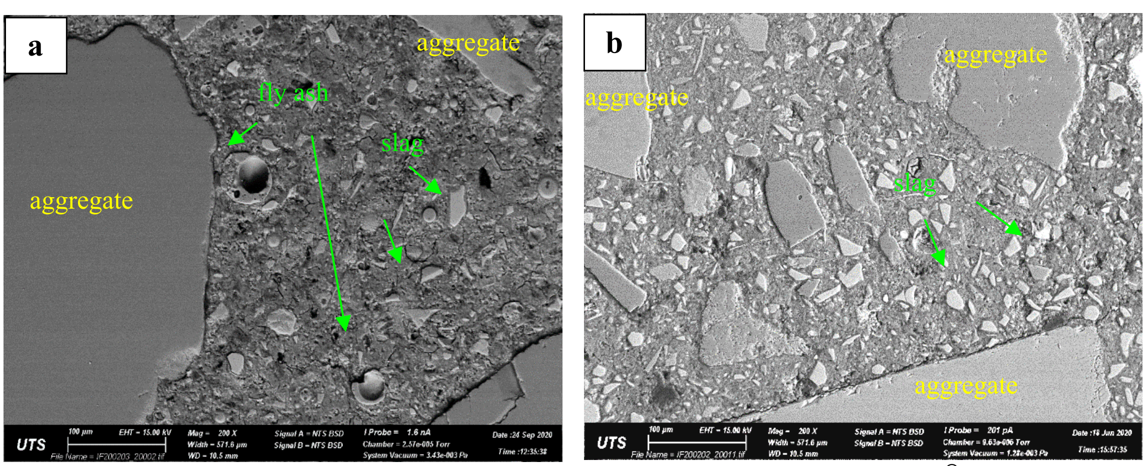

Figure 7 BSE SEM images of a) PT Control and b) PT ENVISIA®

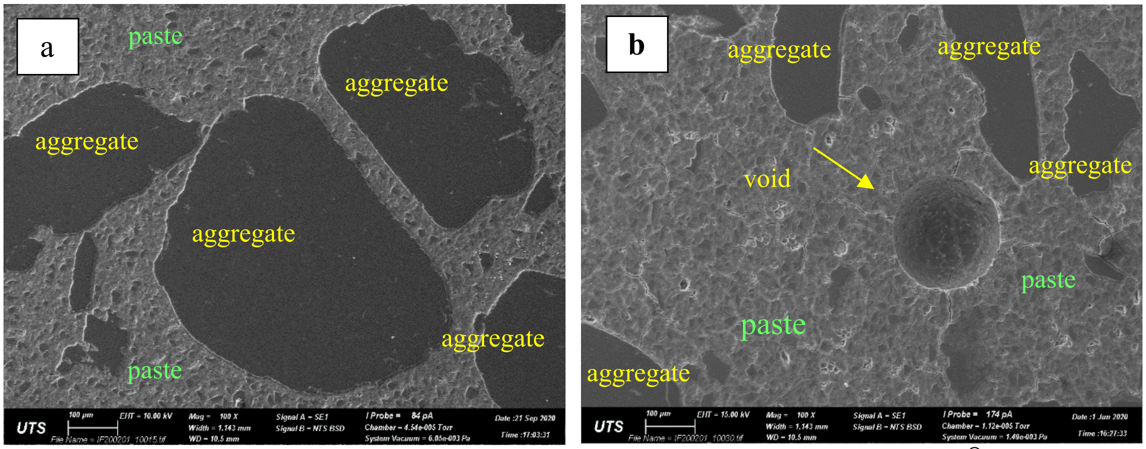

Figure 8 SE SEM images a) Marine Control and b) Marine ENVISIA®

Micro-CT has been conducted to further verify the absence of cracking or any abnormalities in the mature concretes. Micro-CT allows much more thorough investigation of the structure since it obtains multiple slices of the concrete allowing to check for presence of defects in the entire volume. The results show absence of cracking in the paste or aggregates in all the micro-CT slices. Representative 2-D slices of the concretes are shown Figure 9. Less aggregate and higher binder content per volume can be observed in the Grade 55MPa concretes in comparison with the Grade 40MPa concretes as expected.

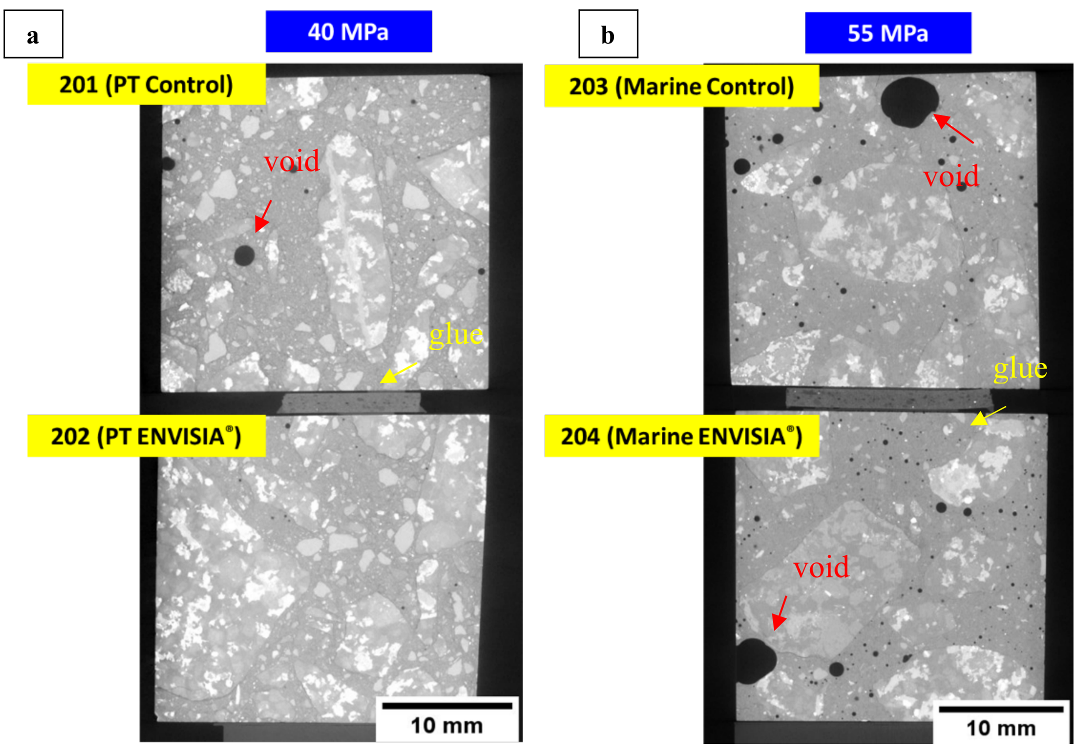

Figure 9 Representative slices of the micro-CT scan of a) Grade 40MPa and b) Grade 55MPa concretes

4. Conclusions

This study has investigated the microstructure and phase development of ENVISIA® concretes (Grades 55MPa and 40MPa) in comparison with high-SCM concretes of equivalent grade. Below are the summary of results and generated conclusions:

1. Marine ENVISIA® demonstrates faster early age strength development and lower drying shrinkage than Marine Control. From the investigations carried out on ENVISIA® and equivalent high-slag binder, the faster early age strength development of ENVISIA® may be attributed to the higher dissolution rate of cement and slag (as confirmed by the presence of higher silicon and aluminium in the pore solution), resulting to accelerated hydration and formation of much higher amount of C-S-H. A larger decrease in portlandite was also observed in the ENVISIA® system which further confirms enhanced hydration/reactivity of slag. Slag, although primarily a hydraulic material like cement, consumes portlandite during hydration to make up for its much lower calcium content.

2. All hydrates found in the 3-year old and 5-year old High-SCM control and ENVISIA® concretes were as expected in an OPC+GGBFS binder. The Marine concretes (High-SCM control and ENVISIA®) both demonstrate well-formed C-S-H phases and dense microstructure. Moreover, there is no notable difference in the microstructure of the Control and ENVISIA® concretes (both PT and Marine) other than the presence of slightly more ettringite in ENVISIA®. The ettringite observed in the concretes is finely intermixed with the hydrates which means it was formed during cement hydration and was stabilized in the binder. Ettringite like any other cement hydrate contributes to microstructure densification and strength development. The faster formation of C-S-H as well as higher stability of ettringite in ENVISIA® may explain its high volume stability (i.e. much lower drying shrinkage). Drying shrinkage results from either loss of water due to evaporation or formation of hydrates that have much lower volume than the original reactants (i.e. water and cementitious materials). Ettringite has capacity to bind more water than C-S-H and therefore occupies much bigger volume.

3. Polished sections and Micro-CT confirm no presence of cracking or any internal defects in the concretes that may lead to premature deterioration.

5. Acknowledgements

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6. References

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