

# **Durability Properties of High Volume Mineral Admixture Cement Composite**

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Cement is used to make cement composite, produces a large amount of  $CO_2$  (870 kg/ton) during manufacturing. Hence, an approach to effectively reduce  $CO_2$  emissions in the concrete industry is to reduce the amount of cement by increasing the amount of a mineral admixture such as blast furnace slag powder or fly ash. Here, we optimized the high volume mineral admixture binder composition by investigating the strength properties of a cement mortar made using binders with various admixtures and inorganic stimulus agents. We used a cement composite mix with a water/binder ratio of 26 % or 46 % to evaluate the compressive strength and durability of the cement composite with increasing amounts of admixture. The cement composite mixture with an inorganic stimulus agent showed outstanding chloride penetration resistance over all curing times and a durability factor of 90 % or more to freezing and thawing. A higher carbonation resistance was found when increasing the curing time for the high volume mineral admixture compositions with an inorganic stimulus agent with a sufficiently long curing period, high volumes of the admixture can be used to produce concrete with suitable properties for various applications.

Keywords: High volume mineral admixture, Inorganic activator, Durability, Chloride penetration resistance, Carbonation.

### **INTRODUCTION**

At the 21<sup>st</sup> U.N. convention on climate change held in Paris in 2015, the participating countries submitted voluntary greenhouse gas reduction goals with targets to be achieved by 2025 to 2030. Korea set its reduction to 37 % of the businessas-usual level of  $CO_2$  emission, which was the highest of any country. The carbon emissions from the cement industry account for 7.5 % of the national quota (128 million ton), hence, a strategy for reducing CO<sub>2</sub> from this source is urgently needed [1]. The cement industry is highly energy intensive (emitting 870 kg of CO<sub>2</sub> for every ton of cement produced), hence, a decrease in cement production is effective in reducing greenhouse gas. It has been proposed that the most effective way of reducing CO<sub>2</sub> emissions is to reduce the amount of cement used in cement composite production by using an admixture made from industry waste products such as blast furnace slag powder or fly ash [2,3].

Cement composite made using admixtures generally has many advantages including improved fluidity, reduced hydration heat and enhanced long-term strength. However, widespread use of admixtures has been limited due to problems such as delayed setting time, reduced early strength and increased carbonation [4-6]. To resolve challenges such as delayed early hydration, various approaches have been proposed, including high pulverization of admixtures, the use of alkali activation agents to catalyze the admixture reaction and the addition of inorganic stimulus agents.

Blast furnace slag powder forms silicate-rich, dense ASH<sub>6</sub> films on the particle surfaces by eluting free calcium ions (Ca<sup>2+</sup>) when in contact with pure water. However, in the presence of an activating substance such as calcium hydroxide, the ASH<sub>6</sub> film is destroyed by adsorbed OH<sup>-</sup> or SO<sub>2</sub><sup>2-</sup> ions on the surface of the blast furnace slag particles. Here, Ca<sup>2+</sup>, Al<sup>3+</sup>, Mg<sup>2+</sup> ions are released and CSH hydrate or calcium aluminate hydrate, which are hydraulic substances like cement, are formed and hardened [4].

The surface layer of fly ash is composed of hyaline, a dense, chemically stable phase. Because the silica-alumina glassy chain containing Si, Al and Cain hyaline is strong, this bonding has to be broken for Pozzolan reaction to occur. In order to activate the reaction, the reactive inner layer of the fly ash has to be exposed by eroding the dense, strong surface layer by the addition of a sulfate or other highly basic material. Hence, the selection of a suitable alkaline activating agent is an important factor to successfully decompose silica-alumina bonding [7].

Decreasing the particle size of the blast furnace slag powder to increase the surface area and reactivity is an effective method for increasing the strength of the reaction. However, economic efficiency decreases due to the increased manufacturing cost of pulverization and constructability reduces because of the increased viscosity [8]. There are several studies regarding alkaline activating agents that induce the hydration reaction of the blast furnace slag powder by creating an alkali environment without the need for hydrating the cement. However, when using Na- or K-based alkaline activating agents, constructability of the final cement product becomes poor due to rapid hardening and alkali-aggregate reactions occurring in the concrete. In addition, it has also been reported that most alkaline activating agents are highly corrosive chemicals and hence difficult to handle [9].

There are various studies reporting the effects of inorganic stimulus agents on the properties of the blast furnace slag powder and cement products. Piao et al. [4] examined how different inorganic stimulus agents such as plaster, anhydrous gypsum and limestone affected the compressive strength and pore structure of blast furnace slag powder and reported that plaster was the most effective in increasing strength. Soh et al. [5] proposed a method of improving the performance of drying shrinkage, neutralization and mechanical stability under freezing-thawing cycles using anhydrite, anhydrous gypsum and limestone in blast furnace slag cement. Ryu et al. [10] studied the hydration properties of a reduced carbon emission cement blend using quicklime, anhydrous gypsum and CSA. A supply of CaO and SO<sub>3</sub> raw materials is necessary to activate the reaction with the blast furnace slag powder and fly ash. It was confirmed that the addition of an inorganic stimulus agent like plaster or quicklime in appropriate ratios to a cement blend can produce a material with comparable long-term performance compared to standard cement blends, despite the delayed strength development.

In order to reduce the use of cement and increase the proportion of admixtures, here we investigate various cement blends with high volumes of admixtures and various inorganic stimulus agents. We characterized the basic properties and durability of the cement composite made from the cement blends based on evaluation of the cement hydration behaviour with increased admixture concentration. These results are of relevance for the practical development of environmentally friendly cement to reduce greenhouse gas emission in the concrete industry.

# EXPERIMENTAL

**Experimental design:** The experimental design for this study is summarized in Table-1. Based on results of previous studies [9,10], the strength properties of blended cement (Series I) with different inorganic stimulus agents were evaluated and the basic properties and durability of the cement composites prepared with optimal binder conditions were then evaluated (Series II).

In order to identify the optimal binder, we evaluated the strength of the blended cements using different inorganic stimulus agents (IGA). We used quicklime (QL), combined heat power plant fly ash (HA) and anhydrous gypsum (AG) as IGA materials. Each stimulus agent was added singularly at a concentration of either 5 or 10 % of the total mix amount, where the samples are labeled, e.g., AG5 and AG10 depending on the IGA content. In addition, we prepared samples with a mixture of IGA materials, where equal parts of either QL or HA were mixed with AG for a total IGA content of 10 % of the total mix amount. Then, the strength of these nine different cement blends were evaluated. The strength evaluation was based on the standard for type II moderate heat Portland cement. We did not consider strength standard for the general type I Portland cement due to the low cement contents in the samples. Table-2 shows the cement composite mixtures used to evaluate the basic properties and durability. For the bonding mixtures shown in Series I and Series II, we evaluated the performance of the cement composite in terms of general strength as well as under the conditions of the class 2 cement strength standard. Two water-bonding mix ratios were used (46 and 26 %) for these tests. Three binder compositions were characterized with different amounts of admixtures: (1) a ternary blended cement (TBC) containing OPC 50 %, GGBS 30 % and FA 20 % which is generally used to produce a lowheat concrete, (2) a high volume mineral admixture blended cement (HVMC1) without an inorganic stimulus agent and (3) the optimal cement blend identified after analysis of Series I (HVMC2).

We controlled the amount of water and admixture for each composition to result in uniform performance of the cement composite directly after mixing, to satisfy the following targets: slump of  $180 \pm 20$  mm and air content of  $4.5 \pm 1.0$ % for the 46% water/binder (W/B) ratio material and target slump flow

	TABLE-1							
	EXPERIMENTAL CONDITIONS							
	Components	Details						
	Binder	OPC: 10 %, FA: 20 %, GGBS: 60-70 %						
	Inorganic activator (IA)	QL, AG, HA						
Series I		Single IA: 5, 10 %						
		Mixture: QL:AG (90:10), HA:AG (90:10)						
	Mortar	Compressive strength (3, 7, 28 day)						
	W/B	26 %, 46 %						
	Binder	TBC, HVMC1, HVMC2						
	Fresh cement composite	Slump (flow): $180 \pm 20 \text{ mm} (650 \pm 50 \text{ mm})$						
		Air content: $4.5 \pm 1.0 \% (3.5 \pm 1.0 \%)$						
Sorias II	Hardened cement composite	Compressive strength (3, 7, 28, 56 day)						
Series II		Chloride penetration resistance (3, 7, 28, 56 day)						
		Resistance of concrete torapid freezing and thawing (300 cycles)						
		Accelerated carbonation						
		- precuring (56, 84 day)						
		- 3, 7, 28, 56 day						

TABLE-2 CEMENT COMPOSITE MIXTURES									
MIX	$W/\mathbf{P}(\mathcal{O}_{n})$	$S(a_{1}(0/a))$	Unit weight (kg/m <sup>3</sup> )						
MIA	МПА W/B (%) 5/а	S/a (%)	W	OPC	GGBS	FA	IA	S	G
TBC				169	101	67	0	839	945
HVMC1	46	47.2	155	34	236	67	0	835	941
HVMC2				34	202	67	34	835	941
TBC				298	179	119	0	700	873
HVMC1	26	44.7	155	60	417	119	0	693	864
HVMC2				60	358	119	60	693	864

of  $650 \pm 50$  mm and air content of  $3.5 \pm 1.0$  % for the 26 % W/B ratio samples. The flow characteristics and compressive strength of the cement composite as it aged were evaluated, along with factors characterizing the durability, such as chloride penetration resistance, freeze-thaw resistance and carbonation resistance.

Table-3 shows the physical and chemical properties of the cement materials used in this study. Fig. 1 shows X-ray diffraction (XRD) patterns of the inorganic stimulus agents QL, HA and AG. The composition of the QL is  $\geq$  90 % CaO, mostly in form of reactive CaO. HA is a by-product of the combustion process of fuel from a cogeneration plant. Fly ash is also a by-product of a combustion process but has a different chemical composition and particle shape. The composition of HA is 27.6 % SiO<sub>2</sub> (half of that occurring in FA) and 35.3 % CO (five times that in FA due to the different fuel and combustion temperature). Both HA and FA are hydraulic and Pozzolan reactive [11,12] of the HA showed that it was mostly in the form of anhydrous gypsum and reactive CaO. As shown in the SEM images in Fig. 2, the HA consisted of a mixture of square particles and no fine micro particles were observed, where the FA sample showed spherical particles. The AG was found to be composed mostly of  $SO_3$  (50.6 %) and CaO (38.8 %), where some form of dihydrate gypsum was also identified by XRD.

Table-4 lists the physical properties of the aggregates used in the study. Sea sand was used as a fine aggregate and crushed stone with a maximum diameter of 25 mm was used as coarse aggregate. High-performance polycarboxylate AE admixture was used as a chemical admixture.

**Experimental method:** To find the optimal HVMA cementitious materials, the strength of the cement was evaluated using the KS L ISO 679 standard for each mixture. The fluidity and compression of the concrete were characterized as these are considered basic properties determining the quality of the mixture. The fluidity test includes the slump (ASTM C 143), slump flow (ASTM C 1611) and air content (ASTM C 138) tests. The compressive strength was evaluated using ASTM C 39.



Fig. 1. XRD patterns of inorganic activators



The NT BUILD 492 chloride migration coefficient from non-steady-state migration experiments [13] was used as an electrical catalytic test to compare the chloride penetration resistance of each cement composite mix as a measure of the durability. The chlorine ion diffusion coefficient was calculated

TABLE-3 PHYSICAL AND CHEMICAL PROPERTIES OF THE CEMENT MATERIALS									
Chemical composition (%)									
Iviaterrar	SiO <sub>2</sub>	$Al_2O_3$	Fe <sub>2</sub> O <sub>3</sub>	CaO	MgO	SO <sub>3</sub>	L.O.I	$(g/cm^3)$	
OPC	21.6	5.6	3.8	60.8	2.1	2.4	2.2	3.1	
GGBS	34.1	15.4	0.5	41.6	4.2	3.2	0.3	2.9	
FA	60.0	22.7	5.9	7.1	0.0	0.2	3.7	2.3	
QL	1.5	1.3	0.5	90.5	0.6	0.7	4.5	3.3	
HA	27.6	13.0	6.9	35.3	6.0	5.6	4.5	2.8	
AG	3.0	1.4	0.4	38.8	1.6	50.6	3.9	2.8	

TABLE-4 PHYSICAL PROPERTIES OF AGGREGATES								
Classification	TypesG <sub>max</sub> (mm)Density (g/cm³)Absorption (%)FM							
Fine aggregate	Sea sand	5	2.58	0.70	2.72			
Coarse aggregate	Crushed stone	25	2.61	0.78	6.93			

after the cement composite has been aged for 3, 7, 28 and 56 days.

To evaluate the freeze-thaw resistance for each cement composite mixture, the ASTM C 666 standard test was used to measure the mass change and relative dynamic elastic modulus of the specimen after every 30 cycles.

The KS F 2584 accelerated carbonation test was used to evaluate the carbonation resistance. This standard test method includes 28 days of standard curing followed by 28 days of air-dry curing prior to the accelerated carbonation test. In this study, both a standard and increased curing period were used to further examine the influence of design conditions of the cementitious materials and curing period on carbonation. First, standard curing (56 days) was carried out for accelerated carbonation testing with 28 days of standard water curing followed by 28 days of air-dry curing. The extended curing period test involved 56 days of standard water curing followed by 28 days of air-dry curing for another accelerated carbonation test. The progression of the concrete carbonation was characterized by measuring the carbonation depth and velocity coefficient of carbonation using the KS F 2596 cement composite carbonation depth method after 7, 14, 28 and 56 days.

#### **RESULTS AND DISCUSSION**

**Compressive strength of mortar:** Table-5 shows the mixtures with different binder compositions along with the compressive strength values of the prepared mortars. Fig. 3 shows the compressive strength development ratio of HVMA mortar compared to PL for each binder sample.

In the case of the mixture using QL, the sample with 5 % QL (Q5) had reduced 3-day strength compared to PL, but the strength development ratio increased after 7 days of aging. The sample with 10 % QL (Q10) showed lower strengths compared to PL over the entire period tested. It was determined that the slow reaction of the QL cement with water resulted in lower strength development in the early stage, but in the long term the influx of CaO from the QL increased the strength.



Fig. 3. Compressive strength development ratio of HVMA mortars at different ageing times

The hydrating and catalytic Pozzolan effect of the cement has been shown to decrease with high levels of QL, decreasing the strength over all time periods [14].

The mixture with HA showed high strength compared to PL over all the entire measurement time and in particular, the strength development was favoured during early aging. This was due to the mixed reaction of CaO and SO<sub>3</sub> from the HA with water, increasing the early strength and 28-day strength. We observed that as the concentration of HA increased, the strength development in early stage was comparable with that over the long term.

The samples prepared with AG showed a tendency for increased compressive strength in the early ageing period and the strength development dropped over time. This change in strength development increased with increasing AG content. The AG reacts with water to generate ettringite, supplies SO<sub>3</sub> and also catalyzes the latent hydraulic property of blast furnace slag powder which improves early strength development. However, for long-term ageing, strength development is slowed as the supply of CaO occurs less readily in AG compared to QL and HA [5]. The excessive supply of SO<sub>3</sub> from AG10 compared to AG5 triggered delayed early hydration and prevented strength development in AG10.

TABLE-5 BINDER COMPOSITION AND COMPRESSIVE STRENGTH OF MORTAR									
Mix decign _			Compressive strength (MPa)						
with design -	OPC	GGBS	FA	QL	HA	AG	3 day	7 day	28 day
		Type II Por	rtland cement (	KSL 5201)			7.5	15.0	32.5
PL		70					9.4	15.4	30.2
Q5		65		5			8.9	17.7	34.4
Q10		60		10			5.1	11.6	23.6
H5		65			5		9.9	16.3	31.3
H10	10	60	20		10		10.3	17.2	30.8
A5		65				5	16.1	24.1	29.8
A10		60				10	11.2	19.4	26.7
Q5A5		60		5		5	9.1	23.9	38.5
H5A5		60			5	5	13.2	27.2	36.0

The use of a single IGA showed that AG is effective in increasing early strength and QL and HA are effective in increasing long-term strength. Considering this, we evaluated mixtures of 5 % QL or HA as a CaO supplier with AG as a SO<sub>3</sub> supplier. For Q5A5, we observed excellent strength development over the long-term ageing due to the CaO supplied by QL, but strength development in early age was rather low due to the effect of the QL. However, the strength development of H5A5 (a mixture of HA and AG) improved in the early stages compared to Q5A5 and the continuous Pozzolan reaction of reactive CaO from HA also enhanced strength over the entire ageing period. This composition also showed the best strength development of the binder mixtures analyzed and therefore was selected as the optimal binder mix proportion for further experiments.

**Properties of fresh cement composite:** Table-6 shows the basic properties (including slump, flow, air content, PC concentration and compressive strength) of the cement composite mixtures with different water-binder ratios. The PC concentration was controlled for the target slump and air contents in W/B 46 %. Ternary blended cement used a PC content of 0.85 % of the binder, whereas HVMC1 and HVMC2 with high volumes of admixtures achieved equivalent fluidity using only 0.60 % PC. This is due to the increased use of GGBS, where HVMC2 using inorganic stimulus agent had a relatively low fluidity compared to HVMC1, mainly due to the effect of HA with less favourable particle morphology. In the high-strength area of W/B 26 %, the fluidity of the concrete showed the same trend as the general strength, with excellent fluidity even with the use of high volume admixture.

**Compressive strength of concrete:** Fig. 4 shows the compressive strength of the concrete for each binder composition as a function of ageing time. Ternary blended cement is composed of 50 % OPC, 30 % GGBS and 20 % FA, which can generate more CaOH (a hydration product of cement) than the HVMC mix with high admixture contents. Therefore, TBC had the highest strength development after 7days of ageing from the latent hydraulic behaviour of GGBS and active Pozzolan reaction of FA.

For the samples with the high volume admixtures, HVMC1 shows the lowest strength development in all stages, as well as the smallest strength increase after 7 days. This was attributed to the significantly delayed early hydration of the cement due to the large volumes of admixture, as well as the low amount of calcium hydroxide produced affecting the hydration of GGBS and FA resulting in less strength development over the long term. HVMC2 showed a low degree of strength development over the entire time period investigated



Fig. 4. Compressive strength of concretes prepared with different binder compositions at various ageing times

compared to TBC. On the other hand, compared to HVMC1 it showed a large strength increase starting at day 3. The supply of SO<sub>3</sub> ions from the AG catalyzed the latent hydraulic property of GGBS and improved the early strength development performance. In addition, the continuous calcium ion supply from the CaO in HA also activates the Pozzolan reactions of GGBS and FA, with the expected strength improvement at the later stages of ageing.

Chloride penetration resistance: Fig. 5 shows the results of the chloride ion diffusion coefficient test for the cement composite samples with different W/B ratios and binder compositions for various ageing times. It can be seen that the chloride ion diffusion coefficient tends to decrease as W/B decreases and age increases and the diffusion coefficient drops in the order of HVMC2, HVMC1 and TBC over the whole time period studied. In particular, in the case of TBC and HVMC1, the chloride ion diffusion coefficient significantly increases with the higher W/B of 46 %. Whereas in case of HVMC2, the chloride ion diffusion coefficient was low for both water-binder ratios, due to the effect of the binder containing both GGBS and FA. The chloride ion penetration resistance improved with an increased amount of admixtures, similar to the results of a previous study that demonstrated outstanding chloride ion penetration resistance at a low compressive strength [15].

Ternary blended cement had a high chloride ion diffusion coefficient at early ages, which degraded by day  $56^{\text{th}}$ .

HVMC2 showed the highest chloride penetration resistance of all mixtures as a dense inner structure of concrete was quickly formed, resulting in the relatively high strength observed at the early stages, where the large amounts of GGBS and FA immobilized the chloride, as for HVMC1 [16].

TABLE-6 SLUMP, FLOW, AIR CONTENT, PC CONCENTRATION AND COMPRESSIVE STRENGTH OF DIFFERENT BINDERS									
W/P(0/r)	MIV	Slump and flow (mm)	Air (%)	PC (B×wt. %)	Compressive Strength (MPa)				
W/D (%)	IVIIA				3	7	28	56	
	TBC	175	4.4	0.85	12.7	20.0	33.8	40.5	
46	HVMC1	185	4.8	0.60	8.2	13.3	18.5	21.2	
	HVMC2	170	4.6	0.60	10.5	20.6	29.7	33.9	
	TBC	660	3.5	1.10	30.4	46.9	68.0	80.0	
26	HVMC1	690	3.6	0.95	13.8	28.1	35.6	37.0	
	HVMC2	670	3.8	0.95	25.4	40.4	58.3	65.2	



Fig. 5. Diffusion coefficients for different binder compositions and ageing times

These results have shown that for all binder compositions, the chloride ion diffusion coefficient was smaller for small W/B ratios and longer times. In particular, the binder with large amounts of GGBS and FA and inorganic stimulus agents densified the cement composite by a catalyzed hydration reaction and improved the chloride resistance by immobilization of the chloride ions by the admixtures. Thus, it is concluded that the HVMC2 composition could be suitable for concrete structures in marine and coastal environments that require chloride resistance.

**Freeze-thaw resistance:** Figs. 6 and 7 show the relative dynamic modulus of elasticity for freezing and thawing for samples with different binder compositions and W/B of 46 % or 26 %. In the case of the W/B 46 % samples, the relative dynamic modulus of elasticity was more than 60 % for all binder compositions, with the order of HVMC2 > TBC > HVMC1 at 300 cycles of freezing and thawing. No change in the mass was observed due to separation phenomenon on the concrete surface from repeated freezing and thawing.

The HVMC2 sample with added IGA material seemed to have high strength, around 50 MPa of cement composite strength development, at the moment of freezing and thawing testing, which demonstrates sufficient durability for freezethaw cycles. Therefore, once the concrete has achieved a certain level of strength with sufficiently low air content, even cement composite with a high volume of admixtures can have a safe level of durability to freezing and thawing, regardless of the W/B.



Fig. 6. Relative dynamic modulus of elasticity during freezing and thawing cycles for samples with a W/B of 46 %



Fig. 7. Relative dynamic modulus of elasticity during freezing and thawing cycles for samples with a W/B of 26 %

**Carbonation resistance:** Figs. 8 and 9 show the results of accelerated carbonation with the standard curing time of 56 days and the long-term curing of 84 days for each binder composition to analyze the carbonation properties as a function of the water/binder ratio. For the standard curing period, the carbonation depth of TBC was 4 mm until the end of the test at day 56. However, carbonation of the HVMC mixtures with a high volume of stimulus agent was further advanced at this time; the HVMC1 sample showed carbonation into the center of the sample.



Fig. 8. Carbonation depth for different ageing times and compositions with W/B of 46 %



Fig. 9. Carbonation depth for different ageing times and compositions with W/B of 26 %

The pH of the concrete affects carbonation and is lowered by  $Ca(OH)_2$  and the hydration of the cement. Therefore, TBC,

which has a higher amount of generated  $Ca(OH)_2$  than HVMC and a highly dense inner structure, was much more stable than the HVMC-type cement composites that suffered from rapid carbonation due to the lack of  $Ca(OH)_2$  for immobilizing the  $CO_2$  penetrating into the calcium carbonate on the cement composite surface [5]. Here, HVMC2 showed a lower carbonation depth than HVMC1, mainly due to the differences in the inner structure due to the higher strength and the relatively high amount of CaO supplied from the inorganic stimulus agent.

To investigate the progression of carbonation at different curing times before the start of the accelerated carbonation, TBC and HVMC2 showed delayed carbonation with time compared to the standard curing method. HVMC1 also showed fully advanced carbonation at day 56<sup>th</sup> under accelerated carbonation, which was also delayed with increasing curing time. Therefore, if a cement composite with a high volume admixture is used, the curing method is important to ensure carbonation resistance, where an increased curing period is required to improve the carbonation resistance of concrete largely substituted with admixture.

Fig. 10 shows the coefficient of carbonation rate as a function of W/B at 56 days. When the carbonation velocity coefficients of standard curing (56 days) and long-term curing (84 days) were compared at the 56<sup>th</sup> day of carbonation aging, HVMC1 with W/B of 46 % was fully carbonated and hence the carbonation velocity coefficient plateaued. However, HVMC2 showed a reduced carbonation rate at this time. HVMC1 with W/B of 26 % showed a small decrease in the carbonation velocity, but HVMC2 showed a large decrease of 46 %.

In summary, if a high volume of admixture is used, the stimulus agent that can enhance early strength and carbonation resistance due to low cement usage is necessary, along with a sufficient curing period, which is more effective in the high strength area.



Fig. 10. Carbonation velocity coefficient for different water/binder ratios and compositions after 56 and 84 days

In general, as W/B decreases, the drying shrinkage reduces and the cement composite has less porosity and pore solution amount of cement composite. This decrease in porosity limits the absorption of CO<sub>2</sub> and reduces the carbonation of the concrete. The diameter of the capillary allowing CO<sub>2</sub> to diffuse into concrete is statistically within the range of  $8 \times 10$  nm – 0.013 mm, but the minimum diameter is known to be 2-5 × 10 nm [5]. This means that for lower W/B values the total volume of the capillary tubes decreases along with the probability that the diameter of the capillary connected to the surface of the concrete structure is too small to allow diffusion of CO<sub>2</sub>, effectively decreasing the depth of carbonation. Thus, it is concluded that in order to reduce the carbonation of cement composite with large volumes of admixtures, the W/B must be lowered, an inorganic stimulus agent must be used to activate reaction with the admixtures and finally, sufficient curing is necessary during manufacturing to ensure reaction between the inorganic stimulus agent and admixtures.

#### Conclusion

Here we evaluated cement mixtures and composites with high volume admixtures in order to study the durability of environmentally-friendly cements. We analyzed HVMA binders using high volume admixtures, including the properties of fresh cement composite before curing and the compressive strength, chloride penetration resistance, freeze-thaw resistance and carbonation resistance during curing. The conclusions from this study are as follows:

• In the case of samples with a high admixture volume, fluidity greatly increased for most compositions, meaning that the amount of water in the mixture should be reduced to achieve the same wet properties as standard cement composite mixes.

• Compressive strength measurements showed that HMVC2 achieved an equivalent level of compressive strength at an early stage due to the activation reaction of the inorganic stimulus agent for both water-binder ratios and showed stable strength behaviour over all curing times compared to HVMC1.

• The chloride penetration resistance improved with high volume admixtures. A high level of chloride resistance was observed from short curing times regardless of W/B due to a high proportion of dense cement composite being formed and a high binding ratio of chloride ions in the admixtures.

• The HVMC2 showed an equivalent resistance to freezing and thawing to that of a standard mixture for all W/B values.

• The progression of carbonation was rapid for the concretes with large volume of admixtures, which was effectively slowed down when using inorganic stimulus agents due to early curing.

• When using a high volume of admixtures (low cement usage), a stimulus agent can enhance early strength and carbonation resistance is necessary, along with a sufficient curing period. Further evaluations of the durability of different binder compositions within the same strength range will be performed as future work to facilitate practical development of such concretes.

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