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# Durability assessment of industrial by-product and marine resource-based ultra-high-performance concrete

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ABSTRACT

The increasing demand for concrete and the associated environmental impacts such as depletion of natural resources (e.g., fresh water, river sand, and coarse aggregates) have prompted the development of seawater and sea-sand concrete (SWSSC). On the other hand, incorporating industrial by-products in concrete as supplementary cementitious materials (SCMs) can offset the cement carbon footprint. Utilizing seawater, sea sand, and industrial wastes in ultra-high-performance concrete (UHPC) fabrication can lead to a sustainable as well as durable construction material, especially suited for marine infrastructure development. This experimental work investigates the durability properties of ultra-high-performance seawater and sea-sand concrete (UHP-SWSSC) with partial substitution of cement by ground granulated blast furnace slag and silica fume as SCMs. Five mixes were developed with varying proportions of SCMs as cement replacement (0% as control mix, 25% and 50% by mass) and water-to-binder ratio (0.15, 0.2 and 0.25). In addition to mechanical behaviour through standard axial compression tests on cube specimens, several durability indicators such as water absorption, sorptivity, the permeability of chloride ions, and volume of permeable voids were measured over time. Results reveal that the incorporation of SCMs in UHP-SWSSC although improves the mechanical properties marginally, significantly enhances the durability performance. In comparison to the control mix, 53%, 75%, and 95% reductions in the volume of permeable voids, rate of water absorption and non-steady state chloride migration coefficient were observed in a 50% SCM replaced mix, respectively. Addition of ground slag and silica fume induced a relatively compact matrix through refinement of the microstructure, which made the resulting concrete nearly impermeable to ion movements. An optimum water-to-binder ratio of 0.2 was established, below which neither the strength nor the durability characteristics improved further.

## 1. Introduction

The ever-rising consumption of concrete leads to severe environmental impacts like added demand for naturally occurring mixing water, river sand, and coarse aggregates. For instance, New South Wales in Australia no longer has quarries to supply natural sand for concrete plants, and therefore switched towards manufactured sand from the blasting of rock masses. The production of cement, the concrete binder, is also a source of substantial $CO_2$ emissions, which impairs environmental sustainability [1]. Considering these distressing concerns, seawater and sea-sand concrete (SWSSC) manufactured from naturally abundant marine resources can be a suitable alternative to conventional concrete in the coming decades. In addition, hazardous industrial waste products (e.g., blast furnace slag, silica fume, fly ash etc.) which may pose a threat to the ecological balance [2] can be successfully recycled as supplementary cementitious materials (SCMs) in SWSSC production. These pozzolanic industrial by-products, when used as full or partial replacements of OPC, can not only curtail the carbon footprint but also enhance the mechanical as well as durability characteristics of concrete [3]. Existing literature generally agrees that incorporating sea-sand and seawater although improves the mechanical strength during the early ages of mixing due to their accelerated hydration mechanism, subsides long-term strength development as soft hydration products leach out [4]. SWSSC was found to possess lower water absorption, sorptivity, freeze–thaw and chloride penetration resistance compared to conventional freshwater based concrete, which can be further enhanced by the addition of SCMs [5].

Nowadays, ultra-high-performance concrete (UHPC) has become

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more popular as a superior alternative to normal-strength concrete due to its remarkable mechanical and durability performance as well as prolonged service life in severe exposure environments [6]. UHPC is defined by its relatively high binder content, application of very fine powders and exceptionally low water-to-binder ratio, which enable the dense material packing and subsequent compactness of the microstructure [7]. Improved microstructural features such as the homogeneous and impermeable interfacial transition zone (ITZ) lead to the enhanced durability performance of UHPC, especially in terms of resistance against chloride ingress, alkali-silica reaction, carbonation, and sulphate attack [8]. The incorporation of SCMs in UHPC facilitates the formation of secondary calcium silicate hydrates (C-S-H), which augments the durability properties by blocking the interconnected pores inside of the concrete matrix [9]. It is noteworthy that the UHPCs discussed in the abovementioned studies were developed from freshwater and conventional aggregates. The durability performance of seawater and sea-sand ultra-high-performance concrete (UHP-SWSSC) is not well investigated.

In consideration of the review above, this paper experimentally investigates the durability characteristics of UHP-SWSSC which utilises industrial by-products (i.e., ground granulated blast furnace slag and silica fume) as SCMs by partially replacing cement. Five mixes were designed by altering the percentage of cement substitution (0% as control mix, 25%, and a maximum 50% by mass) and water-to-binder ratio (0.15, 0.2, and 0.25). The influence of these parameters on mechanical behaviour was evaluated through axial compression tests on cube specimens. Furthermore, several tests to determine the transport properties such as water absorption, volume of permeable voids (VPV), sorptivity, and resistance to chloride penetration were carried out to assess the durability performance. The impacts of Joule effect through heating up of specimens during the chloride penetration test and subsequent influence on chloride migration coefficient were monitored. Finally, a correlation between the initial intensity of current flow and the chloride migration coefficient was developed to investigate the possibility of predicting the resistance against chloride ingress in UHP-SWSSC.

## 2. Materials, mix designs, and methods

### 2.1. Raw materials and mix designs

An Australian general-purpose ordinary Portland cement (GP Cement) conforming to the specifications of AS3972-2010 [10] was procured from Cement Australia. Two types of SCMs, i.e., ground granulated blast furnace slag (GGBFS) and undensified silica fume, were sourced from Australian Steel Mill Services Ltd (ASMS) and Simcoa, plant Kemerton, Western Australia, respectively. Natural sea sand and seawater for mixing and curing concrete were collected from Malabar beach of Sydney, NSW, Australia. The chemical composition of raw binders and seawater can be obtained from the previous publication [11] by this research group. It is evident that seawater was rich in $Cl^-$, $Na^+$, $SO_4^{2-}$, $Mg^{2+}$ etc. The cation and anion compositions of seawater from Malabar beach were found to be similar to the corresponding world average values. For example, $Cl^-$ content of seawater in this study and the corresponding world average were 19131 mg/L and 19352 mg/L, respectively. Prior to using as aggregate, the sea sand was modified for particle size distribution by sieving through a 1.18 mm sieve in order to exclude the natural and man-made impurities, such as stone chips, seashells, plastics, plant remains, etc. The particle size distribution of gap-graded sea sand can be found in [11].

A polycarboxylate based high range water reducer (HRWR), MasterGlenium SKY 8700 sourced from BASF, was applied as a superplasticizer to achieve the desired workability even at a very low water-to-binder ratio. No steel fibre was incorporated in the production of UHP-SWSSC to attain an economical mix and circumvent the possibility of corrosion in a chloride rich environment.

A total of five UHP-SWSSC mixes were designed and compared in the present study. Three mixes were developed by altering the percentages of cement replacement by slag and silica fume. The UHP-SWSSC with 100% OPC was termed as “control mix”, along with “binary mix” where 25% of cement was replaced by GGBFS and “ternary mix” where 50% of cement was substituted by 37.5% GGBFS and 12.5% silica fume. Two more UHP-SWSSC mixes were prepared by varying the water-to-binder ratio of the 50% SCM-based ternary mix. These additional mixes had a water-to-binder ratio of 0.15 and 0.25, besides the water-to-binder ratio of 0.2 for the first series. The sand-to-binder ratio and superplasticizer-to-binder ratio were kept the same for all five mixes (0.83 and 0.02, respectively). The different mix ratios are listed in Table 1. The label for each concrete mix (termed as ‘mix ID’) consists of the type of aggregate used, percentage of OPC replacement and water-to-binder ratio from left to right. For example, SS-50–0.2 refers to a UHPC mix manufactured with sea sand as fine aggregate, with 50% cement replacement by SCMs, and a water-to-binder ratio of 0.2.

The batching of UHP-SWSSC was done in a 70-litre stainless steel Bennet pan mixer. First, the cement, SCMs and fine aggregate were dry-mixed for 10 min at a low speed (50 rpm). Water and HRWR were mixed separately and later added to the dry materials over a course of 30 s. Afterwards, the mixing continued for a further 10 min (5 min at 50 rpm low speed and 5 min at 100 rpm medium speed). Subsequently, the concrete was cast in the respective cube and cylinder moulds in a single layer conforming to the recommendations of ASTM C1856/C1856M–2017 [12]. After casting, the concrete-filled moulds were stored at a fixed temperature of 23 °C and a relative humidity of 50% for 24 ± 2 h. After the specified time, the concrete specimens were demoulded and submerged in 23 °C water for curing. Although specimens under both tap water and seawater curing were evaluated for strength, all transport property tests were carried out on specimens cured in seawater.

### 2.2. Test procedures

The mechanical and durability tests were carried out after a curing period of 28 days. All the test results for this study are obtained from the mean of three identical specimens. Axial compressive strength tests of UHP-SWSSC were conducted according to ASTM C109/C109M-2020 [13] on 50 mm × 50 mm cubes. All the transport property tests were performed on 100 mm dia. × 50 mm thickness concrete discs cut from typical 100 mm dia. × 200 mm height cylinders. Water absorption and VPV tests were conducted as per ASTM C642-2013 [14]. A drying period of 96 h in a ventilated oven at 110 ± 5 °C and a water absorption period of 72 h was determined upon trials. Subsequently, the specimens were vacuum saturated to evaluate the VPV. Sorptivity tests of UHPC were conducted according to the instructions in ASTM C1585-2013 [15], where the rate of water absorption was measured through a singular surface of the internal concrete cross-section. The tests were continued until the 14th day since the initiation of water absorption to better understand the nature of sorptivity in relatively less porous UHPC. The NT Build 492 Nordtest method [16] was adopted to determine the non-steady state chloride migration coefficient. During the chloride migration test, the temperature of the anolyte NaOH solution was continuously monitored to evaluate the possibility of heating up the specimens, which can accelerate chloride ion movement due to the Joule effect.

## 3. Results and discussion

### 3.1. Compressive strength

Figure 1 depicts the axial compressive strength of UHP-SWSSC cube specimens cured under both tap water and seawater environments. It is evident that seawater when used in curing has a detrimental effect on compressive strength. Formation of expansive reaction products (e.g., ettringite, Friedel’s salt etc.), leaching of soft compounds [4] and

**Table 1**
Mixture proportions of materials for UHP-SWSSC.

| Mix ID | Replacement of OPC (%) | | Water to binder ratio | OPC (kg/m$^3$) | Slag (kg/m$^3$) | Silica fume (kg/m$^3$) | Sand (kg/m$^3$) | C/A (kg/m$^3$) | Water (kg/m$^3$) | HRWR (kg/m$^3$) |
|---|---|---|---|---|---|---|---|---|---|---|
| | Slag | Silica fume | | | | | | | | |
| SS-0–0.2 | 0 | 0 | 0.2 | 1200 | 0 | 0 | 1000 | N/A | 240 | 24 |
| SS-25–0.2 | 25 | 0 | 0.2 | 900 | 300 | 0 | 1000 | N/A | 240 | 24 |
| SS-50–0.2 | 37.5 | 12.5 | 0.2 | 600 | 450 | 150 | 1000 | N/A | 240 | 24 |
| SS-50–0.15 | 37.5 | 12.5 | 0.15 | 615 | 461.3 | 153.7 | 1025 | N/A | 184.5 | 24.6 |
| SS-50–0.25 | 37.5 | 12.5 | 0.25 | 585.7 | 439.3 | 146.4 | 976.2 | N/A | 292.9 | 23.43 |

SS: sea sand, C/A: coarse aggregates.

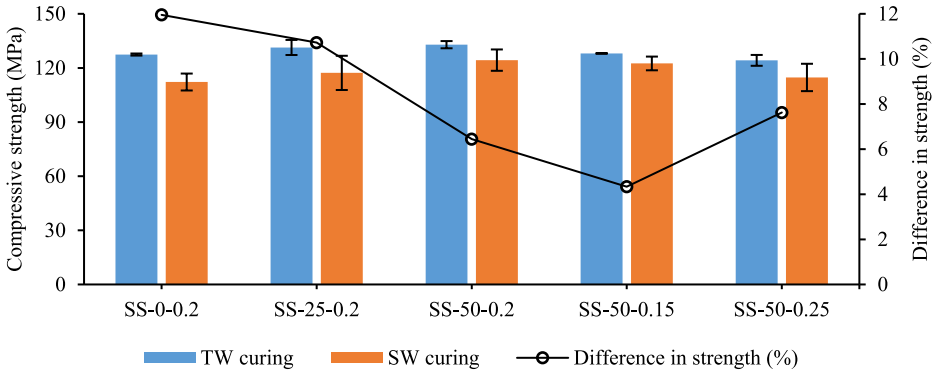


**Fig. 1.** Compressive strength of UHP-SWSSC mixes under different curing environments.

development of microcracks as a result of chloride and sulphate attack under seawater exposure [11] inhibit the development of strength, especially in concrete with high cement content. However, the negative impact is more noticeable in the control mix compared to SCM incorporated mixes, especially the OPC-slag-silica fume based ternary UHPCs. While seawater curing degrades compressive strength by 12% in the control mix, 50% SCM based ternary mix with the same water-to-binder ratio loses a mere 6.4%. Application of SCMs enhances the pozzolanic reactivity and densifies the microstructure, which hinders the penetration of seawater into the concrete matrix and leads to a marginal strength loss.

Substitution of cement by SCMs can produce slightly higher strength in both tap water and seawater curing regimes. The strength data in Figure 1 are after 28 days of water curing and the following discussions will limit to that. A slight strength increase of 4.3% and 10.8% in SS-50–0.2 compared to control was noticed under tap water and seawater curing conditions, respectively. According to the finding reported in Du et al. [9] and Sakir et al. [17], SCMs, especially silica fume is highly pozzolanic, which converts the Portlandites into secondary C-S-H. This chemical transformation facilitates an enhancement of the microstructure, resulting in improved interfacial bond strength and ultimately leading to a more homogeneous interfacial transition zone (ITZ) and superior strength. Additionally, significantly smaller, and spherical particles of silica fume act as filler, improving the particle packing density. Lothenbach et al. [18] concluded that SCM particles, especially silica fume, generates additional nucleation sites where hydration products can accumulate, which ultimately accelerates hydration reactions and produces a compact microstructure. The densified microstructure of silica fume incorporated UHP-SWSSC is also the reason behind its inconsequential strength loss under a harsh marine curing environment.

It is generally accepted that lowering the water-to-binder ratio decreases the porosity of the microstructure, which eventually leads to higher strength. However, UHP-SWSSC with a water-to-binder ratio of 0.20 yielded slightly greater strength compared to the mix with a lower water-to-binder ratio of 0.15 (3.8% and 1.5% under tap water and seawater curing, respectively). Zhang and Zhang [19] reported that strength development in UHPC matrix with an extremely low water content is inhibited if the water present is lesser than a minimum margin due to the unavailability of water to continue the hydration reaction. A higher water-to-binder ratio of 0.25 in 50% SCM based UHP-SWSSC decreased the strength by 6.5% and 7.7% compared to SS-50–0.2 in tap water and seawater curing, respectively. Water-to-binder ratio of 0.20 was found to achieve the maximum strength regardless of the curing regime.

### 3.2. Water absorption and porosity

All the UHP-SWSSC mixes evaluated in this study have a final water absorption of less than 5%, and thereby fall under the category of 'high quality concrete', as categorised in [20]. Nonetheless, the addition of SCMs significantly reduced the water absorption of UHP-SWSSC (Figure 2). A 51.9% reduction in water absorption was observed in the 50% SCM based ternary mix compared to the control (2.05% and 4.26%,

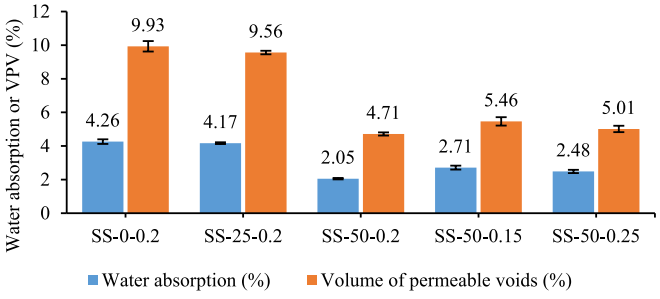


**Fig. 2.** Water absorption and volume of permeable voids of different UHP-SWSSC mixes.

respectively). Highly pozzolanic silica fume can refine the pore structure by forming secondary C-S-H, thereby decreasing the volume of larger-sized capillary pores and increasing smaller-sized gel pores [21], leading to a very dense microstructure. It is noteworthy that the decrease in water absorption of seawater and sea sand based UHPC upon a 12.5% silica fume addition was notably higher than a 39% decrease reported by Sabet et al. [20] for a comparable silica fume dosage in freshwater and river sand based conventional UHPC. In a chloride rich environment, alumina ferrite monosulphate (AFm) phase of cementitious binder can convert into Friedel's salt, which can disconnect the larger capillary pores and densify the microstructure, ultimately reducing water absorption [22]. However, the addition of only GGBFS did not achieve a noticeable improvement in water absorption (4.17% and 4.26% in the binary and control mixes, respectively) due to its slower pozzolanic reactivity, as indicated by Lothenbach et al. [18] and Prakash et al. [23].

Figure 2 also demonstrates a comparison of porosity in terms of VPV, indicating a marginal reduction of 3.7% in the OPC-slag binary mix, whereas the SS-50–0.2 ternary mix experienced a substantial 52.6% improvement compared to the control. UHP-SWSSC mixes with water-to-binder ratios 0.15 and 0.25 showed higher water absorption and VPV compared to their SS-50–0.2 counterpart. While it is well known that the cementitious matrix becomes denser with the reduction of the water-to-binder ratio, UHPC with an extremely low water-to-binder ratio can be so viscous that the entrapped air voids cannot be eliminated even after vibration [11].

Overall, as shown in Figure 3, water absorption and VPV demonstrated a linear correlation ($R^2 = 0.98$) for the mixes compared in this study. As VPV is known to be governed by capillary pores, it is understood that water can access only the larger capillary pores of the UHPCs after a relatively prolonged immersion period. The impermeable nature of the dense UHPC matrix did not allow water to penetrate the gel pores during the testing timeframe.

### 3.3. Sorptivity

It is evident from Figure 4 that the inclusion of silica fume as SCM considerably decreases the rate of capillary water absorption. Sorptivity represents the uptake of water into concrete matrix through capillary suction and also depends on effective porosity as well as pore structure [24]. Initial (during the first 6 h of the test) and secondary (until test termination) rates of water absorption are obtained from Figure 4, where excellent correlation coefficients ($R^2 > 0.95$) were achieved for both coefficients. OPC-slag binary mix has a similar initial (0.004 $mm/\sqrt{sec}$) and slightly improved secondary sorptivity coefficients compared to the OPC only control mix (0.0007 and 0.011 $mm/\sqrt{sec}$ for SS-25–0.2 and SS-0–0.2, respectively). The insignificant pore refinement can be attributed to the slower pozzolanic reaction of slag and its contribution primarily as a physical filler. Silica fume infused ternary mixes exhibited significantly lower initial and secondary sorptivity coefficients (0.0008 and 0.0004 $mm/\sqrt{sec}$, respectively) compared to control and binary mixes. Martys and Ferraris [25] found the capillary pores to dominate the initial rate of absorption, whereas the secondary

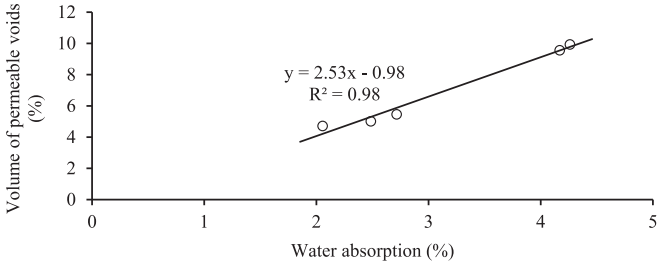


**Fig. 3.** Correlations between volume of permeable voids and water absorption of UHP-SWSSCs.

absorption rate was limited by the gel pores. Silica fume not only filled up the large pores physically but also disconnected the pores by forming secondary C-S-H through its pozzolanic activity leading to around 75% reduction in the rate of initial and secondary water absorption. This mechanism is regarded as silica fume's dual pozzolanic-filler effect by Tahwia et al. [26].

Among the mixes with 50% cement replacement and varying water content, the rate of water absorption in SS-50–0.2 was the lowest, suggesting the optimum water-to-binder ratio of 0.20 to produce an impermeable microstructure. Both the initial and secondary sorptivity coefficients in SS-50–0.2 were smaller than 0.15 and 0.25 water-to-binder ratio alternatives, indicating a lower volume of capillary as well as gel pores.

### 3.4. Resistance to chloride penetration

Similar to other transport properties, resistance to chloride transport significantly improves with the incorporation of SCMs. As illustrated in Figure 5, the non-steady state chloride migration coefficient dramatically decreased in 50% SCM based trinary mix compared to the control mix ($0.2\times10^{-12}$ $m^2/s$ and $3.8\times10^{-12}$ $m^2/s$ in SS-50–0.2 and SS-0–0.2, respectively), which is indicative of the substantial increase in the resistance against chloride ingress. All the SCM infused UHP-SWSSCs in this study had 28-day migration coefficients lower than $2.5\times10^{-12}$ $m^2/s$ and therefore, can be classified as 'extremely high' chloride resistant according to the criteria developed by Teng et al. [27]. Also, they fall well within the chloride migration coefficient limit of $12\times10^{-12}$ $m^2/s$ prescribed in the Transport for New South Wales (TfNSW) QA Specification 3201 for special class early high-strength concrete [28]. As such, marine resource based UHPC can potentially be utilised (or at least trialled for confidence) in concrete pavement maintenance projects that require quick strength gains. Another reason behind attaining an extremely high chloride transport resistance might be the already available chloride content in UHP-SWSSCs. As the mobility of ions under an externally applied potential gradient is facilitated in the chloride migration test, a reduced difference in the chloride concentration between the pore solution and the NaCl catholyte can inhibit the migration of external chloride into the concrete matrix. The chloride penetration depth in SS-50–0.2 was found to be less than 3 mm, which is significantly lower than the control and OPC-slag binary mixes. The depth of chloride penetration observed in the current study is comparable with the penetration depths reported by Vincler et al. [29] for fresh water based UHPCs manufactured without steel fibres. Chloride migration coefficients in the trinary mixes with water-to-binder ratios of 0.15 and 0.25, although very low ($0.37\times10^{-12}$ and $0.26\times10^{-12}$ $m^2/s$, respectively), were slightly higher than SS-50–0.2, confirming the optimum water-to-binder ratio of 0.2 to achieve a durable UHPC. It is noteworthy that the degree of improvement in chloride penetration resistance in SCM based UHP-SWSSC was much higher than what was obtained in water absorption, porosity and sorptivity tests. Due to the dense microstructure of UHPCs, water can access only the larger capillary pores during natural water absorption tests. On the contrary, chloride ions are forced into concrete in the chloride migration test by an external potential gradient, accessing the gel pores and capturing their pore size distribution. Therefore, chloride migration tests can be considered more accurate to evaluate the durability behaviour of UHP-SWSSCs.

It is acknowledged that applying higher voltage in chloride migration tests can cause heating of the specimens and the corresponding anolyte solution, known as 'Joule heating' [30]. The increase in temperature can accelerate the chloride diffusion by decreasing the resistivity of concrete. To avoid the Joule heating effect, a potential difference of 10–15 V was recommended by Andrade [31] to facilitate migration of chloride ions. However, such a small voltage was insufficient to drive chloride into the compact microstructure of UHP-SWSSCs. Nonetheless, it is evident from Figure 6 that although a very high voltage of 60 V was applied for a relatively long duration of up to 96 h, it did not

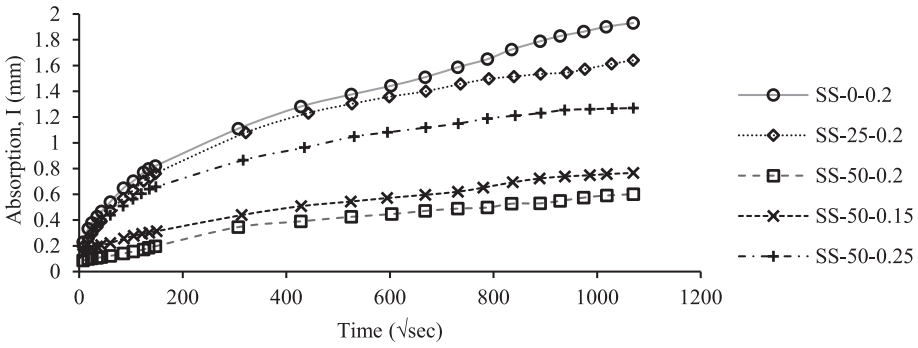


**Fig. 4.** Effect of SCMs and water-to-binder ratio on sorptivity of UHP-SWSSCs.

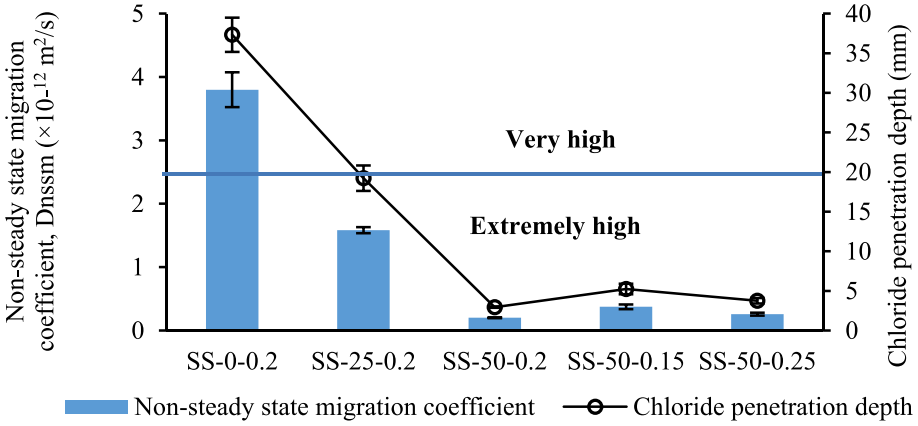


**Fig. 5.** Chloride migration coefficients and penetration depths of UHP-SWSSC mixes.

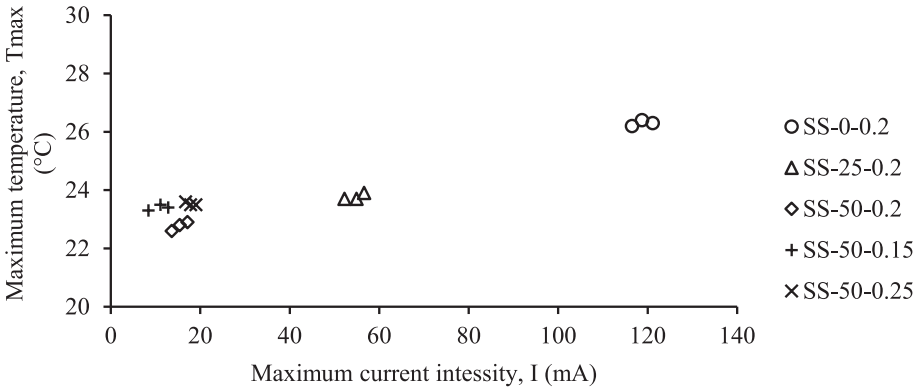


**Fig. 6.** Maximum temperature vs. maximum current intensity measurements for UHP-SWSSCs.

influence the temperature of the specimens. The maximum temperature was between 22 and 27 °C during the migration tests, which does not induce the Joule effect [29]. However, the maximum current intensity due to the applied voltage varied significantly among the mixes. The possibility of utilising the initial current intensity during the chloride migration test as a quick indicator of chloride transport resistance is investigated in Figure 7. An excellent correlation between the non-steady state migration coefficient and the initial current intensity is obtained with a correlation coefficient of 0.99.

## 4. Conclusion

The following conclusions can be drawn based on the limited scope of this study:

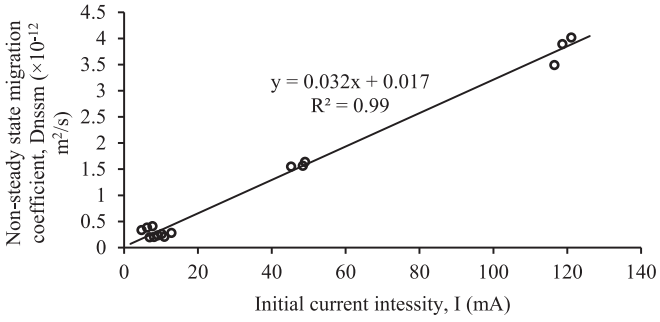


**Fig. 7.** Correlation between chloride migration coefficient and initial current intensity.

- Replacement of cement by industrial by-products as SCMs produces reasonably higher compressive strength (up to 10.8%) due to the formation of rigid hydration products, homogeneous ITZ, and improved particle packing density. Overall, seawater, when used in curing, has a negative effect on strength, however, the strength loss is more prominent in control mix compared to SCM based UHP-SWSSC.
- The 50% SCM incorporated ternary mix reduces water absorption, VPV, and sorptivity coefficients by 51.9%, 52.6%, and 75%, respectively, due to the filler and pozzolanic effects of silica fume. The addition of only slag does not notably improve the transport properties.
- Resistance against chloride penetration is significantly enhanced (reduction of migration coefficient by up to 95%) as silica fume is added due to its ability to refine and disconnect the pores. Despite the high voltage to drive chloride into the dense microstructure of UHP-SWSSC, the Joule heating effect does not affect the mobility of chloride ions.
- Initial current intensity during chloride migration tests can be considered as an indicator of resistance against chloride transport. However, an extensive study is deemed necessary to establish the suitability of such parameters to evaluate the quality of UHPCs.
- The optimum water-to-binder ratio to achieve the maximum mechanical and durability performance was found to be 0.2, below which the voids present in the microstructure inhibit further improvement.

## CRediT authorship contribution statement

**Shameer Saleh:** Conceptualization, Methodology, Validation, Investigation, Formal analysis, Data curation, Writing – original draft, Writing – review & editing. **Aziz Hasan Mahmood:** Methodology, Investigation, Writing – review & editing. **Xiao-Ling Zhao:** Supervision, Resources, Funding acquisition, Conceptualization, Writing – review & editing. **Ehab Hamed:** Supervision, Conceptualization, Writing – review & editing.

## Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

## Data availability

Data will be made available on request.

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