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## The role of seawater in interaction of slag and silica fume with cement in low water-to-binder ratio pastes at the early age of hydration

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### HIGHLIGHTS

- Seawater changed the interaction of SF and slag with cement in favor the autogenous shrinkage.
- Seawater increased the role of cement and slag in the strength development.
- Seawater increased the role of slag in the hydration of the cement.
- The reactivity of the SF particles was decreased in seawater blended paste.

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### ABSTRACT

Very low water-to-binder ratio of ultra-high performance concrete (UHPC) may facilitate using seawater as the mixing water, as there may not be sufficient moisture and air in its dense matrix to initiate the corrosion of steel reinforcements. However, extensive research is needed to investigate the effects of intermixed chloride from seawater on fresh and hardened properties UHPC. This study investigated the role of seawater in the interaction of slag and silica fume with cement in very low water-to-binder paste of UHPC at early ages of hydration. The results showed that seawater increased the reactivity of slag and enhanced its interaction with cement due to triggered reactions between seawater components and rich Al-phases in cement and slag. On the contrary, seawater decreased the interaction of silica fume with cement. The overall influence of seawater in the low water-to-binder paste enhanced the hydration kinetics of binary and ternary binders and restrained the autogenous shrinkage. Furthermore, the early age compressive strength was increased. The findings of the study showed that using seawater was in favor of early age properties of paste with very low water-to-binder ratio.

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### 1. Introduction

The needs for concrete infrastructure expend abundant amount of natural resources like aggregates and freshwater, which is more evident in fast developing countries like China. In coastal areas, where the quantity of fresh water is very limited, its usage as mixing water will be extremely costly and the work efficiency during the construction will be very low. Hence, incorporation of seawater as mixing water can facilitate construction of marine structures more efficiently and at lower costs, while cuts down on the excessive usage of fresh water resources. However, there is a debate on applicability of the seawater usage as it contains aggressive compounds [1].

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Some scholars reported that employing seawater as mixing water in concrete changes the strength development of the matrix. For example, it attributes to the early age strength gain and reduces the setting time [2–4]. Furthermore, the concrete microstructure is improved due to the acceleration of the hydration process by chloride ions input, the induced chemical reactions; and formation of precipitations in the pore structure [4,5]. The inclusion of seawater in concrete with supplementary cementitious materials (SCMs) can further refine the pore structure. Shi et al. [5] found that the combined effect of Metakaolin (MK) as an alumina rich SCM and seawater was beneficial to the microstructure of conventional concrete, due to formation of precipitations and filler compounds through chemical reactions of salt ions in seawater and alumina phases of MK. They also showed that the hybrid system of MK and seawater improved the chloride resistance of concrete by increasing the amount of chemically bound chloride through the formation of Friedel's salt. Also, Li et al. [6]

reported that the compressive strength of concrete mixed with seawater exhibited the highest value in MKA containing concrete specimens as compared with plain ones.

Although some research affirms the advantages of using seawater as mixing or curing water in concrete [5,6], many studies reported its deteriorating effect due to the formation of expansive compounds in reaction with hydration products [7–12]. More importantly, the use of seawater as mixing water will escalate corrosion risk of the embedded steel in reinforced concrete [1]. Reportedly, the corrosion of conventional concrete exposed to seawater resulted in serious problems with millions of dollars spent for maintenance, repair or replacement of damaged structures [13,14]. Mohammed et al. [15] showed that the seawater mixed concrete exhibited higher re-bar corrosion in tidal environments when compared with fresh water mixed concrete. Some other studies also confirmed that the usage of seawater as mixing water accelerated the corrosion of reinforcement in concrete and caused the spalling and cracking of structural members [16–18]. Therefore, the high risk of corrosion in seawater mixed reinforced concrete has led to its prohibition by various international standard regulations. However, it has been allowed in plain concrete manufacture under the proviso that it complies with the given standards criteria of the pertinent regulation [19,20].

Unlike the conventional concretes, the incorporation of seawater as the mixing water in concretes with high density and low permeability such as ultra-high performance concrete (UHPC) can be of less harm. UHPC is a cement-based composite with a compressive strength typically higher than 150 MPa and tensile strength greater than 20 MPa. The raw materials of UHPC include cement, supplementary cementitious materials, quartz sand, superplasticizer, and fibers. The use of low water-to-binder ratio ( $\sim 0.18$ ) and SCMs in the UHPC decreases the porosity and refines the pore structure to denser and less interconnected voids [21]. Alkaysi et al. [22] reported that the porosity and the charge pass in UHPC were as low as 5.9% and 89 C, respectively. In another study by Tafraoui et al. [23], the gas permeability of UHPC and chloride diffusion coefficient were reported to be lower than  $1.5 \times 10^{-19} \text{ m}^2$  and  $1.7 \times 10^{-14} \text{ (m}^2/\text{s)}$ , respectively. Therefore, it is assumed that the dense microstructure of UHPC along with the high chloride binding capacity due to incorporation of SCMs can immobilize the corrosive components available in seawater. Furthermore, there is not sufficient moisture and air in the dense matrix of low water-to-binder ratio bulk paste to initiate the corrosion of steel reinforcements in UHPC. However, few issues need to be carefully addressed in the usage of seawater as mixing water in the production of UHPC. Firstly, the role of seawater in interaction of slag and silica fume with cement and its effect on the hydration kinetics needs to be studied. In the low water-to-paste, the hydration process can directly affect the autogenous shrinkage, which is a critical issue in UHPC [24,25]. The interaction of slag and silica fume with cement in fresh water mixed systems and its effect on autogenous shrinkage of UHPC is well documented [26–29]. However, the relatively higher pH and the existence of salts in the seawater can change the interaction and the consequent early age properties. There is little information on the hydration kinetics of the binary and ternary cementitious systems mixed with seawater. Secondly, the possibility of corrosion of reinforcement in the seawater mixed UHPC needs further attention.

In this study, the role of seawater in the interaction of slag and silica fume with cement in the binding matrix of UHPC will be studied. The overarching purpose of this study is to investigate the effect of seawater as the mixing water on the binary and ternary binder of slag, silica fume and cement with a very low water-to-binder ratio. Accordingly, heat evolution, autogenous shrinkage and compressive strength tests were used to show the synergic effect of seawater and cementitious materials in the paste at the

macro-level. A factorial design system based on Wadsworth's study [30], was applied to quantify the effect of each component on the examined properties at the early age of hydration. To elaborate the underlying mechanisms, Thermogravimetric Analysis (TGA), Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD) and Nitrogen adsorption and desorption (NAD) were applied to assess the role of seawater in the interaction of slag and silica fume with cement in very low water-to-binder ratio pastes.

## 2. Raw materials and experimental methods

### 2.1. Raw materials

Portland cement P.I 42.5 complying with the Chinese Standards GB175-2007 and silica fume (SF) with 63% particle of 0.1–0.5  $\mu\text{m}$  and specific surface area of 18500  $\text{m}^2/\text{kg}$ , and slag with specific surface area of 446  $\text{m}^2/\text{kg}$  were used. Table 1 presents the chemical compositions of the cement, SF and slag. A polycarboxylates based superplasticizer (SP) with solid content of 49% was used to guarantee a good flowability of the paste.

The seawater used in this study was prepared by synthetic method as complied with ASTM D-14. The chemical composition of seawater is presented in Table 2. The pH of seawater was 8.4.

### 2.2. Mixture proportion and specimen preparation

To characterize and quantify the interaction of SF, slag and cement with the presence of seawater, the seven-batch factorial design method was used in this study. Two series of specimens were cast; with fresh water or seawater. Mixture proportion of cement paste with w/b ratio of 0.2 was used in this study and the SP dosage was kept at 2% by the mass of binder. The detailed proportions are shown in Table 3. Initially, the binary and ternary mixtures were mixed in a mixer for 1 min at high speed; water and SP were added into the mixer and mixed for 3 min under low speed and high-speed conditions, respectively. When pastes were ready, they were cast into  $40 \times 40 \times 160 \text{ mm}$  molds and vibrated for 1 min. After the vibration, all the specimens were moved to a curing chamber under temperature of 20 °C and RH of 95%  $\pm 5$  for 24 h. Then, the specimens were demolded and kept in curing conditions to testing ages. The sample preparation and curing regime complied with Chinese standard GB/T50081-2002.

**Table 1**  
Chemical compositions of cementitious materials (%).

Chemical Composition	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO	MgO
Cement	25.26	6.38	4.05	64.67	2.68
SF	90.82	1.03	1.50	0.45	0.83
Slag	33	13.91	0.82	39.11	10.04

**Table 2**  
The artificial seawater specified by ASTM D-14 (g/L).

Types	NaCl	MgCl <sub>2</sub> ·6H <sub>2</sub> O	Na <sub>2</sub> SO <sub>4</sub>	CaCl <sub>2</sub>	KCl
Content	24.5	2.54	4.1	1.2	0.1

**Table 3**  
Mixture design of pastes.

Number	Cement (%)	SF (%)	Slag (%)	SP (%)	W/B ratio	Water type
SW1	100	0	0	2	0.20	Seawater
SW2	85	15	0	2	0.20	Seawater
SW3	75	0	25	2	0.20	Seawater
SW4	72.2	11.1	16.7	2	0.20	Seawater
SW5	70	30	0	2	0.20	Seawater
SW6	58.3	16.7	25	2	0.20	Seawater
SW7	50	0	50	2	0.20	Seawater
FW1	100	0	0	2	0.20	Freshwater
FW2	85	15	0	2	0.20	Freshwater
FW3	75	0	25	2	0.20	Freshwater
FW4	72.2	11.1	16.7	2	0.20	Freshwater
FW5	70	30	0	2	0.20	Freshwater
FW6	58.3	16.7	25	2	0.20	Freshwater
FW7	50	0	50	2	0.20	Freshwater

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