Effect of seawater on early age hydration, microstructure and mechanical properties of cement paste

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Abstract: Using seawater for concrete manufacturing promisingly provides significant economical and environmental benefits. In this study, ordinary Portland cement (OPC) hydration in distilled water and seawater and compares the evolution of solid phases was investigated by heat evolution, hydrated phase, hydration kinetics, and microstructure characterization. The results show that seawater can promote the early hydration of tricalcium silicate (C\textsubscript{3}S) during the hydration acceleration period. The hydrated phase assemblage was influenced by the dissolved ions in seawater. Friedel’s salt was detected as a specific hydration phase in seawater, which was formed by chemical combination between the aluminate ferrite monosulfate (AFm) phase and chloride ions. In addition, the monocarboaluminate can be converted into a stable phase as Friedel’s salt in the seawater, due to the reaction with chloride ions. Furthermore, the ettringite becomes more stable when coexists with Friedel’s salt than that with monocarboaluminate, and thus ettringite formed in seawater remains 67\% higher than that formed in distilled water at the later curing age. Moreover, additional unhydrated cement and less amorphous calcium silicate hydrate (C-S-H) were formed in seawater, which might be responsible for the slightly lower compressive strength of cement mortar prepared by seawater. Generally, a modeled evolution of the solid phase and pore solution have been established.

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which agrees well with the characteristics of the dissolution of mineral phase, precipitation of hydration products and changes of pore solution. The related results can provide an insight into the applications of seawater and sea sand concrete for infrastructures.

**Keywords:** Seawater; Cement hydration; Chloride ion; Mechanical strength; Microstructure

1. Introduction

The rapid development in urbanization and industrialization causes a heavy demand for new concrete infrastructures such as buildings, bridges, pavements, and ports, etc. [1]. Due to low cost and high durability requirements, concrete has become the most commonly used material of about 30 billion tons used annually [2]. However, concrete manufacturing is always accompanied by huge carbon emissions and results in harmful effects on the environment [3, 4]. In addition, large concrete demands lead to considerable consumption of the sand, clay, rock, and water, which severely threaten the ecology of the land, water resources, and air quality. In other words, concrete manufacturing inevitably causes a significant impact on the environment, such as contamination of groundwater and soil, riverbed erosion and biodiversity deterioration. Thus, it is essential to develop sustainable concrete with both economic and ecological benefits [5-13].

Applications of seawater and sea sand in concrete is a promising option for easing resources crisis and construction cost, especially in the coastal and island regions. However, due to the excess chloride in seawater and sea sand, issues should be firstly solved on the aspect of physico-mechanical performance, durability reduction and rebar corrosion [14]. Investigations found that concrete using seawater can cause a 20% reduction in initial slump flow and a nearly 30% loss in initial setting time, compared with the freshwater-made concrete at the same water to bind ratio [15, 16]. In addition, using
Seawater increases the early concrete strength by about 10 to 25% within 14 days, and makes limited influences on the later age strength [15-19]; the drying shrinkage of concrete made by seawater is approximately 15% lower than that of concrete with fresh water [20]. These property changes are mainly attributed to the introduced ions, such as sodium, magnesium and sulfate, etc, and the high concentration of chloride would significantly affect the cement hydration. It has been proposed that two main reasons are responsible for the stimulated hydration by chloride. Firstly, calcium hydroxide (CH) would react with calcium chloride (CaCl₂) to form insoluble solid phase calcium oxychloride (CAOXY) when seawater is used as mixing water mixed with cement [21], as illustrated in Eq. (1). During the reaction process, chloride reduces the concentration of alkalinity and calcium in solution, which promotes the dissolution of cement particles for improving the hydration rate. Secondly, chloride can react with aluminates and ferrites [22, 23], forming insoluble phase as 3CaO·Al₂O₃·CaCl₂·10H₂O, (or if iron presents, 3CaO·Al₂O₃·Fe₂O₃·CaCl₂·10H₂O), as described in Eq. (2). The phase has been named as Friedel’s salt [24], which belongs to the family of hydrated calcium aluminate phase (AFm phase) [25]. This group of compounds is formed as a lamellar structure related to M(OH)₆ octahedral ions based on brucite-like layers, and become charged by one-third of divalent cations replaced by trivalent cation (e.g. aluminum and iron). As a result, the charged AFm phase attracts positive ions such as sulfate, carbonate, and chloride. The general formula of these compounds can be described as [Ca₂(Al, Fe)(OH)₆]-X·xH₂O, where X represents the attracted monovalent anion or half of divalent anion bound [26-29]. Friedel’s salt is beneficial to densify the cement matrix [30], and can convert mutually with monosulfate by changing the concentration of sulfate and chloride ions [31]. Most studies have found that using seawater seems
not to introduce serious defects in concrete structure, but can improve physical and mechanical properties such as density, compressive strength and elastic modulus \([15,17,32-34]\). The contradictories are basically the strength developments at later curing age in concrete with seawater, such as an one-year superiority of compressive strength in concrete with seawater \([16]\), a 13\% lower 28-day compressive strength \([35]\) or the comparable strength \([15,36]\). Furthermore, concerns still remain due to the issue of rebar corrosion and undetermined durability by chloride ions.

\[
\text{CaCl}_2 + 3\text{Ca(OH)}_2 + 12\text{H}_2\text{O} \Rightarrow 3\text{Ca(OH)}_2 \cdot \text{CaCl}_2 \cdot 12\text{H}_2\text{O} \tag{1}
\]

\[
\text{C}_3\text{A} + 2\text{NaCl} + \text{Ca(OH)}_2 + 10\text{H}_2\text{O} \Rightarrow \text{C}_3\text{A} \cdot \text{CaCl}_2 \cdot 10\text{H}_2\text{O} + 2\text{Na}^+ + 2(\text{OH})^- \tag{2}
\]

Therefore, further studies are imperative to fundamentally investigate the properties of cement composites with seawater as mixing water including hydration mechanism, mechanical properties and durability. The aim of this study is to investigate the effect of seawater on the cement hydration and microstructure development, and to establish a correlation with the mechanical properties for Portland cement. This study applied the modern characterization methods to investigate the heat evolution of hydration, phase assemblages, kinetics, morphology, microstructure development and compressive and flexural strengths of cement paste with seawater, and compared the results with the ones mixed with distilled water. The measured and calculated changes of phase compositions are compared for the evolution of the effect of seawater on cement hydration and delivered an extensive experimental investigations on the effect of seawater in cement martor. The related results will provide an insight into the prospect of seawater concrete design and application for concrete infrastructures with special consideration of mitigating the chloride induced steel reinforcement corrosion.
2. Experimental program

2.1 Raw materials

The cement used in the study was the OPC conforming to Australian standard AS 3972 (General purpose and blended cements). The oxide compositions of the cement measured by X-ray fluorescence (XRF) were summarized in Table 1. The contents of limestone and gypsum were provided by the cement supplier. After the XRF data was corrected by deducing the chemical composition of the two given minerals, the approximate mineral composition in OPC was obtained through Bogue calculation [38]. The minieral composition and physical properties are shown in Table 2. Two types of mixing water: (1) distilled water (D-water); and (2) natural seawater (S-water), were applied. The natural seawater was obtained from the Congwong Beach of Sydney coast in Australia. Table 3 shows the chemical composition of D-water determined by inductively coupled plasma mass spectrometry (ICP-MS), which is close to the world average concentrations of ions in surface seawater [39]. Natural river sand (R-sand) and washed sea sand (S-sand) are used in cement mortars, which contains few impurities such as clay and sea salt. The particle sizes distribution of the used R-sand and S-sand are shown in Fig. 1.

2.2 Experimental methods

2.2.1 Heat of hydration

To investigate the effect of seawater on the hydration of OPC, an isothermal heat conduction calorimeter (TAM Air) was applied to measure the heat of hydration during the first 60 hrs. D-water and S-water were used as mixing water in samples. The water to binder (w/b) ratios of the samples are 0.5 and 0.7. Firstly, 30.00 g cement was weighed and mixed with weighted D-water or S-water
for 60 sec, followed by being injected into ampoules through a syringe. Afterward, the ampoules loaded with samples and those with references were capped and lowered into the calorimeter simultaneously. Due to the external premixing procedure, very early cement hydration cannot be measured from calorimeter, and the signal of heat flow became stable after approximately 60 mins. In order to reduce the experimental error, the references applied dry sand (quartz) and distilled water to respectively simulate the OPC and the certain water used in samples, with the same total heat capacity. The composition of the samples with S-water and D-water were summarized in Table 4. The samples were denoted by their “water type + w/b ratio”. For example, the “D-0.5” represented OPC with D-water at a w/b ratio of 0.5. The final exotherms were corrected by subtracting the baseline obtained before and after the measuring process.

2.2.2 Phase and micromorphology

Semi-quantitative X-ray diffraction (XRD), Thermogravimetry/Differential scanning calorimetry (TG/DSC) and Scanning electron microscope-Energy dispersive X-ray spectroscopy (SEM-EDS) were adopted to analyze the phase evolution during cement hydration in D-water and S-water. The samples were OPC pastes with D-water or S-water at w/b ratio of 0.5. The pastes were prepared in a Hobart mixer and cast in seated plastic molds at the size of 50 mm × 50 mm × 50 mm, then cured in a standard curing chamber with a temperature of 20 °C and 95% relative humidity. After 1 day of hydration, the samples were demolded and further cured at the previous condition. Afterward, the samples with different hydration ages were dried by two different treatments. For those hydrated less than 1 day, the samples were transferred into a vacuum freeze dryer to remove free water after reaching the specified ages; the drying process lasted for 2 days at -55 °C in vacuumed condition.
For those hydrated longer than 1 day, the hardened cement pastes were crushed into small pieces and the debris from the inside part of paste were collected, followed by being immersed into isopropanol for the hydration stoppage. In this way, the ongoing hydration process can be terminated. After immersed for 7 days, the debris was transferred and stored in a desiccator over silica gel for 3 days. Furthermore, some debris was ground to pass through a sieve with a screen aperture of 75 μm, as the powder samples applied to TG and XRD measurement.

In terms of TG/DSC analysis, the equipment STA449 F5 JUPITER was used to determine caloric effects and mass changes in the temperature-rise period. About 30 mg of dried powder sample was loaded into an alumina crucible, purged with nitrogen and heated from 25 °C to 1000 °C with the temperature increasing rate of 10 °C/min. With the increase of temperature, the decomposition of hydration products can be determined by mass loss from chemically bound water and carbonate, and thus the content of the corresponding hydrate phase can be determined. In addition, the endothermic peaks exhibited in DSC curves illustrated the enthalpies of transitions from decompositions of phase. As a result, the area of the endothermic peak can be converted into the value of enthalpy of transition, which helps determine the certain reaction, molar content of involved substance, and solid composition. Furthermore, some moist samples as contrast groups were also measured which were not terminated hydration, ground and dried before, to determine the content of pore solution.

X-ray diffraction analysis was conducted by Bruker D8 Discover with the diffraction angle (2θ) ranged from 5° to 70° and the scan step size of 0.02°. Cu K(α) radiation (k = 1.54056 Å) was used as the X-ray source. Before measurement, the powder samples were blended with 10% titanium oxide as the special ingredients of the internal standard method. Semiquantitative analysis of mineral
solid phases was conducted through the peak heights and peak areas of the intensity of corresponding phases. Micromorphology analysis was conducted by applying the scanning electron microscope (SEM) Zeiss Supra 55vp combining with energy dispersive X-ray spectrometry (SEM-EDS).

2.2.3 Mechanical strength

Cement mortars were prepared for compressive strength measurements according to ASTM C109 (Standard Test Method for Compressive Strength of Hydraulic Cement Mortars). For each group, three cubic specimens (50 mm × 50 mm × 50 mm) were prepared. The mix design of cement mortar was listed in Table 5. All specimens were cured for 1 day in the chamber before demolded and further cured in standard curing chamber (temperature of 25 °C and relative humidity of 95%). The cement mortars were tested at different curing ages of 7, 14 and 28 days for compression test. The compression machine of UH500 was applied with a loading rate of 0.1 mm/min in stroke. Cement mortars were prepared for flexural strength measurements. For each group, three prismatic specimens (40 mm × 40 mm × 160 mm) were prepared. The curing condition and tested ages are as same as those for compressive strength. The flexural strength test in accordance with ASTM C348-18 (Standard Test Method for Flexural Strength of Hydraulic-Cement Mortars). The cement mortars were tested at different curing ages of 7, 14 and 28 days.

3. Results and discussions

3.1 Heat evolution of hydration

Hydration heat evolution of OPC was measured with w/b ratios of 0.5 and 0.7 hydrated in D-water and S-water, respectively. The exotherm of OPC in 60 hrs was shown in Fig. 2(a). The ordinates of the figure, normalized heat/heat flow, are the quantifiable exothermic units released per gram of
cement. At the early age of the hydration process, the period exhibiting insignificant heat flow was
the induction period, which was caused by the restricted precipitation and the extremely slow rate of
dissolution of cement [40-43]. It was observed that the duration of the induction period of hydration
in D-0.5 and S-0.5 ranged from 1.54 to 1.56 hrs. Furthermore, increasing the w/b ratios from 0.5 to
0.7 had a limited impact on the period of induction. It reveals that the dissolved ions in S-water do
not have a great influence on the initial dissolution and precipitation process, although there might be
a new solid phase formed. The initial hydration still subjected to the limited surface with low
interfacial energy, which is consistent with the dissolution theory based on a geochemical approach
to crystal dissolution [44, 45].

In the acceleration period, it was observed that the duration to reach the hydration peak (Peak I)
was greatly reduced by 36% for the OPC paste with S-water, in comparison to the OPC with D-water.
Furthermore, the exotherm peak of paste in S-water exhibited 44% higher than that with D-water.
Hence, it demonstrates that the dissolved ions in S-water can significantly promote cement hydration.
According to the previous studies [21, 22], chloride was the dominator that can chemically bind with
calcium, aluminate, and ferrite ions to form insoluble phases such as calcium oxychloride and
Friedel’s salt. The involved chloride ions contribute to promoting the precipitation of the dissolved
mineral ions in solution. Thus, according to the chemical equilibrium, the dissolution rate of
unhydrated clinkers is promoted. The stimulating effect is a particular significance to the main mineral
tricalcium silicate (C₃S) [46].

When the heat flow started to decrease, an exotherm with acromion presented from around 10 to
15 hrs or later. The acromion was a part of another peak (Peak II), which was overlapped with Peak I.
The Peak II was formed from the heat of hydration of calcium aluminate (C₃A) and calcium aluminoferrite (C₄AF) [28]. During this hydration period, the concentration of sulfate in solution decreased over time since the gypsum has completely depleted before C₃A and C₄AF. Ettringite, therefore, became less stable with a lower sulfate solution and subsequently started to convert into the AFm phase [47]. In S-water, however, the hydration rate increased during this period, which was greatly affected by the various dissolved ions, especially under the condition with a high concentration of chloride. During the period, it was found from the following analysis of TG and XRD that Friedel’s salt was intensively formed after gypsum was completely consumed. Thus, the formation of Friedel’s salt promoted the hydration of aluminate and ferrite minerals. Furthermore, an extension of acromion appeared in samples at a high w/b ratio of 0.7, in which the mass diffusion and transformation were less restricted than the samples at a low w/b ratio. For the OPC with S-water at the w/b ratio of 0.7, more ions from seawater were involved in cement hydration, and thus the acceleration effect of hydration can be further improved, in comparison to the counterpart at w/b ratio of 0.5.

In Fig. 2(b), the accumulated heat evolution shows that the gap of hydration heat released from S-0.5 and S-0.7 started to widen after 5 hrs, and S-0.7 released nearly 20% additional heat after 60 hrs. As for D-0.5 and D-0.7, however, the two exotherms showed a limited difference, releasing less heat than those in S-water. It indicates that the dissolved ions in S-water can promote hydration, especially chloride which accounted for more than half of the ions in S-water. The following conclusions can be drawn through the comparison: the hydration rate of C₃S is greatly affected by the concentration of chloride in solution, which is correlated with the equilibrium concentration of
CAOXY. If the involved chloride is increased but the concentration of chloride in mixing water is not changed, such as of S-0.5 and S-0.7, the hydration rate of C₃S will not be obviously accelerated. Unlike C₃S, the hydration of aluminate and ferrite can be stimulated with the increasing content of chloride involved, which is due to the further formation of Friedel’s salt.

3.2 Thermogravimetric and X-ray diffraction analysis

The compositions of OPC paste with D-water and S-water were determined by TG/DSC and XRD analysis. Fig. 3 shows the TG and the derivative thermogravimetry (DTG) results of OPC paste in D-water at various hydration times. The peaks of mass loss displayed in DTG curves indicate that the precipitation of ettringite and dissolution of gypsum took place earlier even in 1 hr of hydration. The other hydrated phases, such as C-S-H and portlandite, had hardly formed yet during the initial hydration period, which resulted in the DTG curves exhibited closer to zero significantly. After 8 hrs of hydration, it was observed that portlandite and C-S-H had formed and constituted the main part of the hydrated phase, indicating the hydration reaction of C₃S happened rapidly during this period. The rapid reaction was consistent with the aforementioned characteristic of heat release in the acceleration period.

After 12 hrs hydration, gypsum was completely dissolved and depleted. Due to the decreasing concentration of sulfate in the pore solution, the preformed ettringite had become unstable and gradually converted to the AFm-formed phase at a slow rate [48]. In DTG curves, it was found that the sample with a 12 hrs hydration had the largest peak at around 100 °C, compared to the samples with other lengths of hydration time. The peak indicated a maximum mass loss, which attributed to the dehydration of ettringite, water desorption and water loss from C-S-H gel layers. As an
amorphous solid phase, the dehydration reaction of C-S-H occurred continuously from 105 °C to 1000 °C [49], and the amount of dehydrated water increased with the increasing temperature. In Fig. 3, it was observed that the mass loss increased with the increasing hydration age, especially from 200 to 400 °C, which illustrated an increasing content of C-S-H with ongoing hydration.

The decomposition of portlandite took place at approximately 420 °C, followed by the decomposition of the carbonate phase at the temperature over 600 °C. As the main production of OPC, the content of CH and C-S-H increased with the hydration degree, and their growth rates gradually decreased at the later age. After 28-day hydration, the content of CH and C-S-H was nearly constant and hardly increased. Monocarboaluminate (carbo-AFm), instead of monosulfooaluminate (sulfo-AFm), was detected as the final hydration product of the residual aluminate phase, due to the excess of carbonate ions provided from limestone [50, 51]. Calcite is the major mineral phase of limestone added in OPC cement, which was found slightly decreased during the ongoing hydration period. The other type of carbonate, magnesite, was found increased at the later age, which decomposed at around 600 °C [52].

The aforementioned TG analysis can be further confirmed by XRD analysis. Fig. 4 gives the representative diffraction patterns for the OPC paste with D-water. It was observed that the amounts of the four main OPC minerals decreased at different rates. Due to the high solubility, C₃A and gypsum reacted rapidly to form ettringite which can be detected after 2 hrs of hydration. The hydration properties of C₄AF was similar to that of C₃A, but the rate was much slower. When gypsum was completely depleted after 12 hrs of hydration, the XRD showed no sulfo-AFm phase (characteristic peak 2-Theta at 9.895°) during the following hydration period. Instead, the content of
carbo-AFm (characteristic peak 2-Theta at 11.670°) was found increasing along with hydration. In terms of silicate minerals, a great amount of C$_3$S was found dissolved in the first 2 days of hydration, and the further hydration rate gradually decreased with the hydration time. After 63 days, the extent of hydration of C$_3$S was observed nearly unchanged in hardened OPC paste. For another OPC mineral, the C$_2$S hydrated much slower, attributed to the less solubility than that of C$_3$S. It could be found that some of the C$_2$S remained unhydrated after 63 days of hydration.

In Fig. 5, the cement paste with S-water shows a higher weight loss within 7 days than that of paste with D-water, which reveals the enhanced early hydration of OPC paste in S-water, due to the influences by salt ions such as sodium, sulfate, and especially chloride ions. As mentioned above, the presence of chloride could accelerate the precipitation of calcium ions, which was beneficial to the dissolution of minerals. In terms of the sulfate ions involved in hydration, 0.034 molar of sulfate could be supplied from the 5.84 wt.% of gypsum in 100 g of OPC, and 0.0014 molar of sulfate was introduced from S-water, which accounts for only 4% of that from gypsum. However, despite the small variation of sulfate content, Fig. 5 reveals a similar or less amount of ettringite formed in the S-water after 1 hr and 2 hrs of cement hydration. This is probably due to the formation of calcium oxychloride [21], which occupies the limited surface of cement particles and restricts the formation of ettringite [40]. As a result, the generation of ettringite was slightly retarded at the initial stage of cement hydration.

The formation of Friedel’s salt was the most significant difference between pastes with D-water and S-water. The Friedel’s salt could be dehydrated at 120 °C [53], and thus cannot be distinguished with carbo-AFm from TG analysis. In the X-ray patterns of cement paste with S-water, the
characteristic peak (2-Theta at 11.192°) confirmed the presence of Friedel’s salt as shown in Fig. 6.

In particular, the hydration products carbo-AFm was never formed in cement paste with S-water, which was quite different from cement paste with D-water. The results suggest that carbo-AFm was instable with chloride ions and could be converted into Friedel’s salt in seawater. Also, it was feasible to bind chloride ions by increasing the content of the AFm phase in OPC. Furthermore, it should be noted that more carbonate was observed decomposed over 600 °C in cement paste with S-water, which was due to the formed magnesite from the excess carbonate from the decomposition of carbo-AFm and the additional magnesium introduced from S-water.

### 3.3 Modeling of hydration

The evolution of the solid phase and pore solution was investigated by applying the quantitative analysis of TG/DSC results and semiquantitative analysis of XRD patterns. The peak areas in the DSC curve represented the enthalpy change, which reflected the energy transfer from a certain reaction of decomposition [54], to support the quantitative analysis from mass loss. Taking samples of cement paste with D-water in 2 hrs and cement paste with S-water in 12 hrs, as shown in Fig 7, the corresponding hydration phase could be quantified through methods combining TG and DSC. Based on these data, a linear regression was used to investigate the correlation between the TG and DSC. Fig. 8 demonstrates a reasonable agreement and close values to the linear relation for evaluating gypsum, portlandite, and calcite. Therefore, the data from DSC confirmed the TG results, which could be the supplementation and correction in the estimation of the solid phase. The extent of OPC hydration was evaluated based on the changes in the peak intensity of the crystalline phase in XRD patterns. The peak intensity was corrected by the intensity of TiO₂, which was the calibration
According to the result, a modeled evolution was set up regarding the various phases from OPC hydration in D-water and S-water as a function to the hydration time as shown in Figs. 9 and 10. It was observed that a small amount of gypsum dissolved in the first 1.5 hrs, along with the hydration of C₃A minerals, and a small amount of ettringite was found precipitated. After 8 hrs of hydration, it was noted that 35% of C₃S dissolved in S-water, which was 16% more than that in D-water, conformed to the aforementioned greater heat released from the hydration in S-water during this period. After 7 days of hydration, the total amount of hydrated C₃S in D-water was nearly catch up with that of paste in S-water. At the later age of 63 days, the C₃S minerals were almost completely hydrated in D-water. However, 8% C₃S was detected remaining unhydrated in S-water, showing that S-water might decrease the later-age hydration rate of OPC. Furthermore, the total content of C-S-H in S-water was lower, although it was beneficial to form C-S-H rapidly in the early 7 to 15 days of hydration. Overall, the results showed that the amount of C-S-H decreased by nearly 10 wt.% in S-water after 63 days of hydration. The decreases might be due to the increasing proportion of other hydration products such as ettringite and Friedel’s salt, which led to a less negative effect on the later age strength of OPC.

The gypsum in D-water and S-water was completely disappeared after 12 hrs hydration. At this moment, the content of ettringite was no longer increased but started to convert to the AFm phase. For the cement paste with D-water, the content of ettringite accounted for 12.7% of the total mass and then decreased to 6.6% after 63 days. With the presence of limestone in OPC, nearly 48% ettringite was converted to the carbo-AFm phase instead of sulfo-AFm after 63 days, since carbonate
could replace sulfate ions from AFm to form the stable phase [50, 51]. In comparison, ettringite in S-water increased by 7% compared to that in D-water after 18 hrs. However, only 22% of ettringite had decomposed after 63 days, indicating that the ettringite exhibited more stable in S-water. The reason is that the introduced chloride ions in S-water are more stable to combine the AFm phase than carbonate from limestone. Therefore, the formation of sulfo-AFm became more difficult, which resulted in more uncombined sulfate ions presented in pore solution to hinder the decomposition of ettringite.

The hydration ratio of C₃A and C₄AF shows no significant discrepancy in D-water and S-water. Fig. 9 shows that C₃A and C₄AF were hydrated completely in 4 and 7 days, respectively. As for C₂S, only a similar 53% of this mineral phase was hydrated after 63 days in both D-water and S-water, although S-water can accelerate the hydration of C₂S by 5% in the first 3 days. The formation of Friedel’s salt can be detected after 1 day of hydration in cement paste with S-water, which gradually increased to nearly 7% of the total mass after 7 days and then kept unchanged in the further 56 days.

Friedel’s is formed mainly from the residual unhydrated aluminate phase and chloride after ettringite. The result showed that ettringite formed early than Friedel’s salt, which can be due to the higher stability and insolubility of ettringite than Friedel’s salt [31, 53,55]. In other words, Friedel’s salt cannot be formed when gypsum exists because only ettringite precipitates during this period, which was confirmed by the evolution of the solid phase from experimental results, as shown in Fig. 9. It means that ettringite does not have the chloride-binding capacity in the concentration of seawater. The point can also be drawn that if aluminate or ferrite minerals were used for binding chloride to reduce chloride concentration in cement, adding gypsum would weaken the binding effect.
Compare to the solid phase from hydration in D-water, it was observed that no carbo-AFm formed in S-water. The significant differences revealed that the chloride in S-water can convert carbo-AFm to Friedel’s salt by replacing carbonate ions, to form Friedel’s salt which was more stable than carbo-AFm. Furthermore, the study found no carbo-AFm formed throughout the hydration of 63 days, which illustrated that the involved chloride became beyond the binding capacity of aluminate and ferrite phase in OPC. Due to the replacement effect of carbonate in AFm, the S-water paste remained 1.5% more calcite and 2.3% more magnesite than those of D-water paste. The consumption volume of pore solution can represent the extent of hydration [56], from the reaction of free water converting into chemically combined water and hydroxyl. Throughout the entire hydration process, the amount of pore solution in S-water was always lower than that of D-water, particularly from 2 hrs to 15 days of hydration. The rapid consumption in S-water can inevitably influence the early strength and workability and may affect construction efficiency [15].

3.4 Microstructural characterization

The scanning electron microscopy (SEM) was conducted to morphologically describe the microstructure of the cement pastes with D-water and S-water in Fig. 11. After 12 hrs hydration, it could be observed that the C₃S particles in D-water remained very smooth, with only a small number of C-S-H nucleus attached in the surface of C₃S particles, as shown in Fig. 11(a). For the cement paste with S-water, however, the finer C-S-H nucleus precipitated intensively on the surface of C₃S particles in Fig. 11(b), conformed to the accelerating effect in S-water on early hydration. After 2 days of hydration, the hydration product of C-S-H, portlandite, and ettringite could be observed in OPC paste. The solid phase in D-water paste distributed randomly at the initial age of hydration, and
mutually overlapped and connected the nearby solid particles, as shown in Fig. 11(c). Due to the rapid hydration in S-water paste, a denser microstructure formed can be observed in Fig. 11(d), revealing the previous scattered phase has connected and converted to the plate-like forms. The rapid formation of the denser microstructure indicated S-water is beneficial to early strength.

The elemental mapping of S-water paste after 4 days of hydration was displayed in Fig. 12, which was conducted by energy-dispersive X-ray spectrometry. By comparing the morphology of certain hydration products and the elemental composition, the formed hydration phases can be identified. It was found brucite or brucite-like layers hydrotalcite (Mg(Al, Fe) xH2O) in S-water paste from the hydration phase of magnesium [57]. Along with the interface between the hydrated phase of calcium and aluminate, Friedel’s salt can be identified with a higher content of chloride. The Friedel’s salt previously crystallized as flat hexagonal platelets [53] and subsequently stacked as a thicker form. In addition to the chloride binding capacity of the AFm phase, it showed that the chloride could be physically absorbed by C-S-H gels [58], which resulted in a wide distribution of chloride in cement paste.

3.5 Mechanical strength

The compressive strength of mortars prepared by D-water and S-water was investigated as illustrated in Fig. 13. It was found that S-water increased the early compressive strength of cement mortar at 7 days by nearly 15% in both specimens with river sand and sea sand, compared with those with D-water. As for the later curing age, however, the compressive strength of the cement mortar with D-water increased considerably than those with S-water. Although the specimens with S-water had higher compressive strength at 14 days, they were subsequently exceeded by their counterparts with
D-water after 28 days. It conformed to the promoted early hydration and the slightly retarded hydration of C₃S in S-water, which is the primary mineral phase in OPC contributing to compressive strength. In addition, river sand was better than sea sand regarding the growth of compressive strength, as a better grading distribution in river sand can obtain a denser structure. By contrast, the particle size distribution in sea sand is relatively concentrated, reducing the filling effect. Its smooth surface, furthermore, weakens the bound properties between cement and aggregates, thus gaining a relatively lower compressive strength. The difference between specimens with seawater and distilled water is less than 8% in flexural strength, as shown in Fig. 14. However, using sea sand reduces the flexural strength by nearly 25% from 7 days to 28 days, indicating that the ions in seawater present less impact but the flexural strength is greatly decreased by the poor particle size distribution of the aggregate.

4. Conclusions

In this study, the hydration properties of OPC in D-water and S-water have been investigated by analyzing the heat evolution, hydrated phase, hydration kinetics, and microstructures. The main conclusions can be drawn up as follows:

(1) The hydration of OPC can be accelerated by S-water, which is mainly due to the chloride promoting the precipitation of calcium, aluminate, and ferrite. The accelerated hydration rate indicates the positive effect of S-water, especially in the stage of 2 to 48 hrs. The formation of Friedel’s salt led to the accelerated hydration of C₃A and C₄AF, and therefore the hydration rates of the two minerals were increased at high w/b ratios, with additional chloride involved in hydration.
(2) The hydration rate of C₃S is greatly promoted in seawater especially at the early age of 1 day due to the involved chloride in hydration. At the same ion concentrations, the hydration rate of C₃S is not significantly increased by mixing with more seawater. However, the hydration of aluminate and ferrite can be stimulated with the increasing amount of seawater involved, which may be due to the formation of Friedel’s salt.

(3) Affected by the rapid hydration in S-water, the early compressive strength of OPC mortar increased rapidly. For the cement mortar with S-water at the w/b ratio of 0.4, the compressive strength of 7 days and 14 days increased by 15% and 5%, respectively compared to those of counterparts with D-water. However, the compressive strength of 28 days is nearly the same as that of specimens with D-water. Seawater can influence the flexural strength of less than 8% from 7 days to 28 days while using sea sand instead of river sand can decrease flexural strength by 25% due to the poor particle size distribution.

(4) The chloride in S-water promoted the early hydration reaction and influenced the hydrate assemblage of the hydrating cement paste. In the presence of chloride, Friedel’s salt was more stable than carbo-AFm in OPC paste. Due to chemical equilibrium, the decomposition rate of ettringite at 63 days was reduced from 51% to 22%, and more carbonate was formed, such as magnesite from 2.3% to 4.6% of the total mass. As a result, the chloride binding capacity of OPC could be weakened by sulfate from gypsum, for that gypsum can react with aluminate to form stable phase ettringite, which has no chloride-binding capacity.

(5) It was found that in the later age of 28 days, 8% C₃S remains unhydrated in OPC paste with S-water, and the mass of C-S-H is 10% lower than that of OPC paste with D-water. The decrease
in mass might be due to the increasing proportion of other hydration products, such as ettringite and Friedel’s salt, and thus had a less negative effect on the later strength of OPC.

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.

Acknowledgments

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Table 1 Chemical composition of the OPC (oxide composites)

<table>
<thead>
<tr>
<th>Chemical Component (wt.%)</th>
<th>CaO</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>Fe₂O₃</th>
<th>MgO</th>
<th>SO₃</th>
<th>Na₂O</th>
<th>K₂O</th>
<th>CO₂</th>
<th>MnO</th>
<th>P₂O₅</th>
<th>LOI*</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>62.9</td>
<td>20.3</td>
<td>4.5</td>
<td>4.6</td>
<td>1.2</td>
<td>2.6</td>
<td>0.3</td>
<td>0.3</td>
<td>2.0</td>
<td>—</td>
<td>—</td>
<td>4.0</td>
</tr>
</tbody>
</table>

Note: LOI* presents loss on ignition
Table 2 Mineral composition of Portland cement and its physical properties

<table>
<thead>
<tr>
<th>Minerals</th>
<th>C₃S</th>
<th>C₂S</th>
<th>C₃A</th>
<th>C₄AF</th>
<th>Limestone</th>
<th>Gypsum</th>
</tr>
</thead>
<tbody>
<tr>
<td>Content (wt.%)</td>
<td>47.16</td>
<td>22.72</td>
<td>4.14</td>
<td>14.00</td>
<td>4.54</td>
<td>5.59</td>
</tr>
</tbody>
</table>

Note: Specific gravity is 2800-3200; bulk density is 1200-1600kg/m³ and average particle size (d₅₀) is 8 μm.
### Table 3 Major chemical composition of seawater from Sydney Congwong Beach

<table>
<thead>
<tr>
<th>Dissolved ions</th>
<th>Na$^+$</th>
<th>K$^+$</th>
<th>Ca$^{2+}$</th>
<th>Mg$^{2+}$</th>
<th>Cl$^-$</th>
<th>SO$_4^{2-}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentration (mol/l)</td>
<td>0.47</td>
<td>0.01</td>
<td>0.01</td>
<td>0.05</td>
<td>0.54</td>
<td>0.03</td>
</tr>
</tbody>
</table>
Table 4 Mix design of cement paste for hydration heat analysis

<table>
<thead>
<tr>
<th>Index</th>
<th>W/b ratio</th>
<th>OPC</th>
<th>D-water</th>
<th>S-water</th>
<th>Sand (Quartz)</th>
<th>D-water</th>
<th>S-water</th>
<th>Total heat capacity (J/K·g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>D-0.5</td>
<td>0.5</td>
<td>9.40</td>
<td>4.70</td>
<td>—</td>
<td>9.40</td>
<td>4.70</td>
<td>—</td>
<td>26.70</td>
</tr>
<tr>
<td>S-0.5</td>
<td>0.5</td>
<td>9.40</td>
<td>—</td>
<td>4.70</td>
<td>9.40</td>
<td>—</td>
<td>4.70</td>
<td>26.70</td>
</tr>
<tr>
<td>D-0.7</td>
<td>0.7</td>
<td>7.40</td>
<td>5.17</td>
<td>—</td>
<td>7.40</td>
<td>5.17</td>
<td>—</td>
<td>27.17</td>
</tr>
<tr>
<td>S-0.7</td>
<td>0.7</td>
<td>7.40</td>
<td>—</td>
<td>5.17</td>
<td>7.40</td>
<td>—</td>
<td>5.17</td>
<td>27.17</td>
</tr>
</tbody>
</table>
Table 5 Mix design of cement mortar

<table>
<thead>
<tr>
<th>Mix</th>
<th>Cement (kg/m³)</th>
<th>D-water (kg/m³)</th>
<th>S-water (kg/m³)</th>
<th>R-sand (kg/m³)</th>
<th>S-sand (kg/m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DR*</td>
<td>800</td>
<td>320</td>
<td>—</td>
<td>1600</td>
<td>—</td>
</tr>
<tr>
<td>DS*</td>
<td>800</td>
<td>320</td>
<td>—</td>
<td>—</td>
<td>1600</td>
</tr>
<tr>
<td>SR*</td>
<td>800</td>
<td>—</td>
<td>320</td>
<td>1600</td>
<td>—</td>
</tr>
<tr>
<td>SS*</td>
<td>800</td>
<td>—</td>
<td>320</td>
<td>—</td>
<td>1600</td>
</tr>
</tbody>
</table>

Note: DR* presents the mortars prepared by D-water and R-sand; DS* represents the mortars prepared by D-water and S-sand; SR* is the mortars prepared by S-water and R-sand; SS* means the mortars prepared by S-water and S-sand.
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Fig. 6. XRD pattern of OPC in S-water after 2, 8 hr, and 2, 28, 63 days of hydration at w/b ratio of 0.5 (A –C₃S, B –C₂S, C –calcite, E –ettringite, F –Friedel’s salt, G –gypsum, P –portlandite, M –magnesite, C₆ –C₃A, C₄ –C₄AF, Ti –titanium oxide for calibration reference)

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Formation: Friedel’s salt

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(b) Cumulative heat of hydration at w/b ratios of 0.5 and 0.7

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