A Review of Recent Advances in the Science and Technology of Seawater-Mixed Concrete

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Abstract

A review of the last 16 years of research (2005 – 2021) on seawater-mixed concrete is presented. A very significant amount of research, both fundamental and applied, has been performed on this topic, and there is worldwide interest in the use of seawater-mixed concrete to reduce concrete freshwater consumption. Seawater-mixed concrete should be used either for unreinforced concrete or for concrete using non-corrosive reinforcement (fiber reinforced polymer or stainless steel). The complex effects of seawater on hydration processes, concrete microstructure, and interactions with supplementary cementitious materials are relatively well understood. On the other hand, only limited information is available on the long-term durability of seawater-mixed concrete. Modeling of seawater-mixed concrete at a variety of scales appears to be nascent. A primary challenge with the large-scale adoption of seawater-mixed concrete remains the absence of codes and specifications that address the use of such material. As an increasing number of structures are constructed using seawater-mixed concrete and a greater understanding of long-term behavior is obtained, it is hoped that greater adoption for the right applications will eventually follow.

Keywords: Seawater; concrete technology; supplementary cementitious materials; hydration; durability

1. Introduction and Historical Perspective

Seawater-mixed concrete is concrete in which freshwater used for mixing concrete is replaced with seawater. The justification for using seawater instead of freshwater is simple: the construction industry uses a massive amount of freshwater – 16.6 x 10^9 m^3 of water is consumed annually for concrete production worldwide, which is ~18% of global annual industrial water consumption, and roughly equal to the annual domestic usage of 150 million residents of the US [1]. Miller et al. state that in 2050, 75% of the water demand for concrete is likely to occur in regions that may experience water stress [1]. Considering the vast availability of seawater and increasing shortfalls in freshwater as a natural resource, the potential for the use of seawater in concrete must not be ignored.

The use of seawater-mixed concrete is likely to be most beneficial in desert locations (for example, the Middle East, which relies extensively on expensive desalination processes to produce freshwater), isolated islands, and in regions after the occurrence of natural disasters which lead to simultaneous reconstruction needs and freshwater shortfalls [2,3]. The use of seawater-mixed concrete could be a solution for marine/offshore structures, where conventional concrete performs poorly; indeed some research shows that for marine conditions, seawater-mixed concrete outperforms the freshwater-alternative in terms of strength gain [2]. Other wastewaters, and desalination brines in regions which rely heavily on desalination, could also be considered as freshwater replacements. A limited amount of research has been performed on cementitious materials mixed with desalination brines and results appear to show performance similar to seawater-mixed and freshwater alternatives [4,5]. Desalination brines are out of the scope of this work and are not discussed further in the text.

The idea of using seawater for concrete mixing (and curing) is certainly not new. It could be argued that the ancient Romans innovated seawater-mixed concrete, as the composition of Roman (marine) concrete is lime, pumiceous volcanic ash, and zeolitic tuff, mixed with seawater [6,7]. Conventional modern concrete is cement-based and not lime-based, so the reactions that occur in conventional concrete are different from those in Roman concrete. The hydration products in Roman concrete were identified as poorly crystalline C-A-S-H and Al-tobermorite, which could form a matrix with greater long-term stability than conventional concrete matrices [6]. However, these phases could be different from originally formed phases due to thermodynamically driven phase transformations over time. Al-tobermorite may have formed due to alkali cations from the ash and seawater and elevated temperatures during reaction; this phase is not commonly seen in modern concretes cured at room temperature [6,8]. Mixture designs with low/no cement content, high content of high-alumina natural pozzolans, and seawater could potentially function as sustainable and durable modern day equivalents of Roman concretes [9]. Use of high-alumina alternative cementitious materials or alkali-activated materials mixed with seawater could be other interesting options [10]. Such mixtures may be a worthwhile endeavor to pursue as certain Roman concrete structures have survived over 2000 years in seawater without significant damage (although survivorship bias, cost, labor, and a variety of other factors must be considered when comparing ancient Roman concrete and modern concrete structures). In principle, understanding the science and technology of seawater-mixed concrete and Roman concretes is required to recreate Roman concretes and could help create more durable modern concretes.

When comparing ancient and modern concretes, apart from the use of cement, another major difference is the use of steel reinforcement. Naturally, a major concern with the use of chloride-rich seawater in modern concrete is the potential for steel corrosion. The concentration of Cl^- in seawater is approximately 20,000 ppm (0.5 mol/L) [11]. A simple back of the envelope calculation suggests that mixing with seawater will immediately lead to chloride concentrations 0.5 – 1.5% by mass of cement, depending on mixture design. The free chloride amount will likely reduce over time due to chloride binding, leaching, and other phenomena [11]. However, considering that water-soluble allowable admixed chloride limits are typically lower than 0.5% by mass of cement (a detailed discussion of the complexity of chloride limits, the *admixed chloride conundrum*, is given in [12] for interested readers), mixing with seawater is not typically suggested when conventional steel reinforcement is being used. While the concerns regarding corrosion of conventional steel reinforcement are fully justified, there does not appear to be an obvious reason why seawater should not be used in unreinforced concrete elements. In addition, the use of non-corrosive reinforcement, specifically fiber reinforced polymers (FRP), has seen tremendous advances in the last few decades, and a large amount of research indicates the feasibility of using seawater-mixed concrete reinforced with FRP [13].

1.1. Scope and Research Significance

A significant amount of research has been performed on seawater-mixed concrete, with searches of indices revealing hundreds of papers on the topic published yearly. Other anecdotal evidence of the significant research on this topic includes a) large, funded proposals to investigate seawater-mixed concrete in Europe, Qatar, and Hong Kong, including the authors of this publication as investigators (SEACON, NPRP 9–110–2–052, etc.), and b) a special issue of the journal Advances in Civil Engineering Materials on *Concrete Using Seawater and Salt-*

Contaminated Aggregates which was Guest Edited by the corresponding author of this publication, and c) five review papers published on seawater and sea sand concrete between 2017 and 2021 [13-17].

In spite of five existing review papers on this topic, this current publication is novel because three review papers focus on seawater and sea sand concrete [13,14,16], one focuses on FRP [15], and only one focuses on seawater-mixed concrete [17]. Xiao et al. [13] present a comprehensive discussion of the more engineering aspects of seawater-mixed concrete, and topics such as hydration, microstructure, etc. are not discussed in detail. On the other hand, Li et al. [17] present a fundamental but narrow discussion of the hydration, microstructure, and mechanical strength of seawater-mixed concrete but not other aspects of concrete technology. Therefore, while there is some overlap of this paper with [13,17], it is minimized as we make a conscious attempt to link the science and technology of seawater-mixed concrete, with the ultimate aim of increasing adoption of this technology. An additional attempt to reduce overlap is made by reviewing only papers from 2005 – 2021 in this paper, unless older publications present information that is unique or not replicated in later publications. We do not discuss sea sand in this review because replacing sand and replacing water in concrete will cause fundamentally different changes to the concrete. The objective of linking the science and technology of seawater-mixed concrete is more applied than in most other research that appears in this journal. However, this work is being published as part of a journal Special Issue on *Advances in Concrete Technology and Sustainability*, justifying the more applied approach.

The scope of this work covers topics ranging from hydration to later-age durability to case studies of structures constructed with seawater-mixed concrete.

2. Effects of Seawater on Hydration and Microstructure

2.1. Impacts of seawater on cement hydration

Multiple studies have shown that seawater accelerates the early-age hydration of cement [11,16-26]. Some studies show that the induction period is unaffected, while others show a shortening in the duration of the induction period. These differences are due to the complexity/accuracy of early-age hydration measurements, and presence of SCMs and chemical admixtures [11,16-21]. Isothermal calorimetry results show acceleration in terms of time of peak, peak height, and cumulative heat release [11,17,18]. Seawater-mixed cement pastes showed a 35-40% greater silicate peak height, 15-30% earlier silicate peak time, 5-10% higher 3-day heat release, and comparable 7-day heat release when compared to freshwater-mixed cement paste [11,17,18]. A schematic showing effects of seawater on the heat flow is shown in Figure 1.

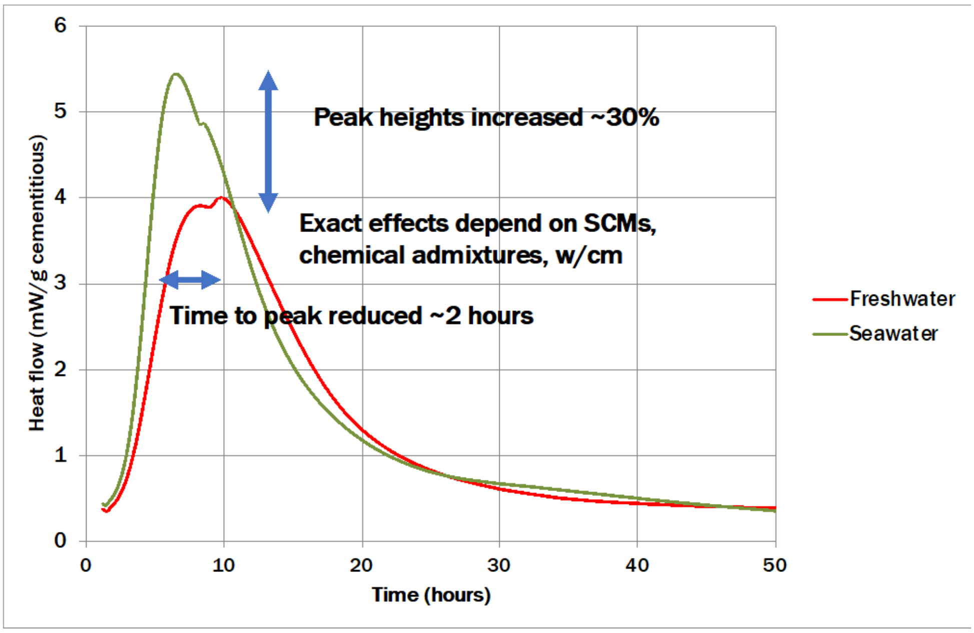

Figure 1. Schematic of effects of seawater on heat flow of cementitious pastes (recreated using data published in [11]).

The largest differences in the hydration behavior are typically seen within the first day, after which the freshwater mixture *catches up* with the seawater mixture in terms of hydration rate. The acceleration in hydration has been attributed to the presence of various ions in seawater, which supposedly accelerate the hydration of tricalcium silicate (C_3S). Direct studies of C_3S hydration in the presence of seawater confirm the acceleration both in terms of time and peak heights that is seen in cements with results broadly similar to those shown in Figure 1 [19,25]. The mechanism of hydration acceleration in in C_3S pastes is suggested to be as follows [19]: calcium hydroxide reacts with the soluble ions in seawater, which leads to greater pH, and increased formation of greater amounts of gypsum (Eq. 1). This step is followed by reaction of the sodium hydroxide with salts in seawater such as calcium chloride, leading to the formation of additional calcium hydroxides (Eq. 2).

$$3Ca(OH)_2 + 3Na_2SO_4 \rightarrow 3CaSO_4 + 6NaOH \qquad \text{Eq. 1}$$

$$CaCl_2 + 2NaOH \rightarrow Ca(OH)_2 + 2NaCl \qquad \text{Eq. 2}$$

Increased formation of calcium hydroxide and greater pH have been observed in seawater cement paste and seawater-C_3S systems, providing support for the hypothesis above [11,19]. Additionally, the accelerating effects of calcium chloride and chloride ions on cement and alite are well known (calcium chloride was commonly used as a concrete accelerator in the past) [19]. Considering the composition of seawater, it can be considered to some extent to behave similarly to a mixture of chloride solutions, although effects specific to magnesium and sulfate cannot be ignored.

To further simplify the effects of seawater on hydration processes, hydration of alite in the presence of three salts (sodium chloride NaCl, magnesium chloride $MgCl_2$, and sodium sulfate Na_2SO_4) was studied [25]. Unlike in cement pastes, all salts reduced the induction period considerably. Increases in peak heights in depended on the salt used and ranged from 50-80%. The authors used thermodynamic modeling and solution concentration data to show increasing dissolution rate of alite and increase in concentration of calcium species with the salts; however, it should be noted that thermodynamic modeling may not be completely accurate at very early ages [25]. Gypsum was found in the Na_2SO_4 system, as suggested by Eq.

1. Apart from changes in dissolution behavior, changes in the morphology of the C-S-H were also suggested that could potentially accelerate hydration; microstructural changes are discussed in Section 2.3.

The effects of seawater on aluminate phases are less clear. Acceleration in aluminate reactions due to additional reactions leading to the formation of Friedel's salt and similar phases and the greater pH have been suggested [17,18,20]. A study which directly studied the effect of seawater on tricalcium aluminate (C_3A) hydration showed that seawater retarded C_3A hydration and reduced its reaction degree due to the poisoning of reactive C_3A sites caused by adsorption of calcium and sulfate [26]. However, in this study, hydration of C_3A was compared in DI water and seawater, which likely led to a magnification of the effects of sulfates in retardation of hydration. Ideally, studies should be carried out using pore solutions or using C_3S-C_3A-sulfate systems to obtain further fundamental information about hydration processes.

Acceleration mechanisms involving oxychloride phases have also been suggested, though evidence for such claims is limited [17,20]. Such phases typically form only at high concentrations of $CaCl_2$, which are unlikely in seawater pastes [27]. Direct evidence for oxychloride phase formation in seawater systems is unavailable. Impacts of seawater on hydration of ferrite phases have not been studied in detail except in one study [17,18,20,28] where the hydration of high ferrite portland cement was studied. In this system, early-age acceleration and strength increase due to the seawater was greater than in OPC systems, suggesting that seawater could significantly impact the hydration of ferrite phases.

The enhanced hydration is responsible for the greater early-age strength of seawater-mixed concretes when compared to freshwater-mixed concrete, although most evidence suggests that the strength difference is relatively minimal after 7 days of curing [2].

2.2. Impacts of seawater on pore solution composition

There is limited work that has studied the detailed impacts of seawater on the pore solution [11]. Figure 2 shows that the use of seawater significantly increases Na^+ (~10 times) and Cl^- (~1000 times) in seawater-mixed pastes when compared to freshwater-mixed pastes. K^+ concentrations are unaffected and OH^- concentrations are slightly increased due to the use of seawater. When considering the composition of seawater and the composition of a typical cement paste pore solution, the composition of a seawater-mixed cement paste solution is not particularly surprising. However, some important nuances exist. As hydration progresses, Na^+ and OH^- concentrations increase, and Cl^- concentrations decrease. The Na^+ concentration in seawater-mixed pastes is higher than in seawater due to pore solution concentration as water is consumed [11]. On the other hand, Cl^- concentrations decrease, especially from 12 hours to 3 days due to chloride binding (due to C-S-H and Friedel's salt formation) and possible participation of chloride in hydration reactions [25]. While the decrease in the pore solution (free) chloride concentrations could be considered in the use of steel reinforcement in seawater-mixed concretes, at 28 days values of chloride contents are ~0.67% by mass of cement [18], on the higher side for safe use of steel reinforcement. Based on several assumptions, the pore solution concentrations were used to estimate chloride and alkali uptakes of ~5 mg Cl^-/g C-S-H and ~2 mg Na^+/g C-S-H. Ionic concentrations in alite-salt solution at high water-binder ratio show similar results and trends, including notably a 20% reduction in the Cl^- concentration from 6 hours to 28 days, however, in this case, unlike with cement, the reduction was largely in the first day [25].

Seawater increased the pore solution pH by about 0.15 units, with effects increasing at later ages. Seawater also caused a large increase in the pore solution ionic strength, with the ionic strength increasing four times in seawater-mixed pastes due to increased Na^+ and Cl^- concentrations. Finally, pore solution electrical resistivity was reduced by ~50% due to the use of seawater [11]. The high concentrations of various ions in the pore solution may lead to potential leaching when exposed to ground water or rain. When exposed to seawater, they may also result in lower seawater ingress and leaching due to reduced concentration gradients leading to potentially improved long-term strength [2,11]. The higher pH is anticipated to increase alkali silica reaction in seawater-mixed concrete.

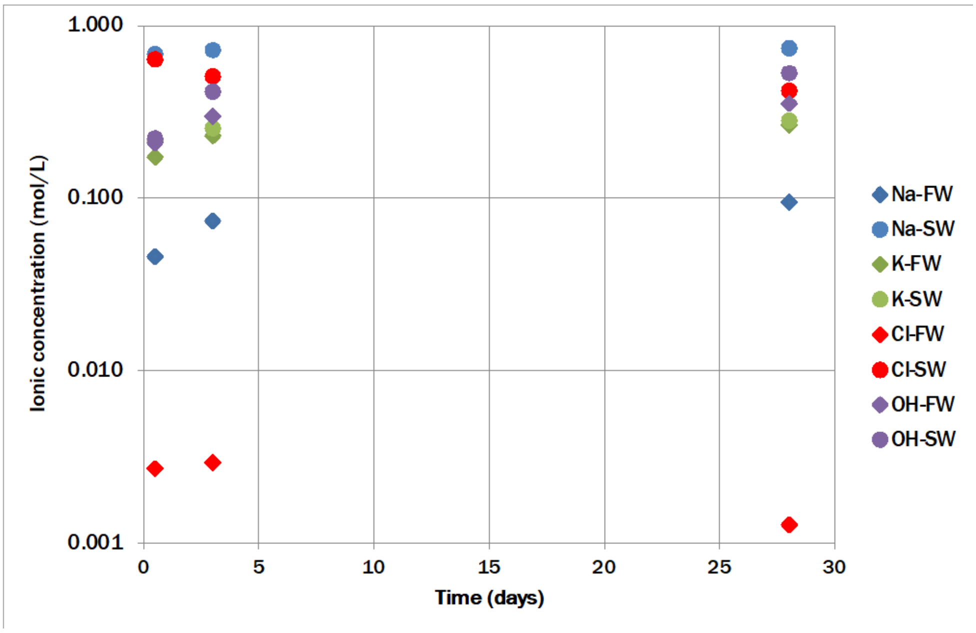

Figure 2. Evolution of pore solution ions in freshwater (FW) and seawater (SW) plain cementitious pastes (recreated using data published in [11]). Results for cementitious pastes containing 20% fly ash by mass were similar.

2.3. Impacts of seawater on microstructure

Pore size distributions in seawater-mixed cement pastes have been studied using quantitative several techniques (mercury intrusion porosimetry, dynamic vapor sorption, specific surface area using nitrogen adsorption and Brunauer, Emmett and Teller (BET) theory) [11,17,18,21-24,29]. Seawater reduces the porosity and causes a refinement of the pore sizes (lesser capillary pores, especially large capillary pores) [11,16,18,21,23]. As with compressive strength, the impact on the pore sizes is significant at early ages (less than 3 days) and relatively minor at later ages [2,11,17], likely because the differences in pore structure between the freshwater and seawater mixes are largely driven by differences in the degree of hydration. These findings hold true in both neat cement pastes and cement pastes with SCMs [11,19,21].

In addition to changing the pore sizes and porosity due to differences in hydration degree, seawater also impacts pore characteristics through a change in the morphology of the hydrates. It has been suggested that seawater encourages the formation of “high surface area C-S-H matrix phases” due to the formation of nanocrystals finely intermixed with the C-S-H using results from scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Reported BET surface areas for cement pastes mixed with seawater were 27 m^2/g, double that with freshwater [16-18]. Alternatively, formation of high Ca/Si C-S-H as well as formation of Friedel's salt have also been postulated as reasons for the microstructure densification [22].

Early age (12-hour) SEM images show anhydrous grains in freshwater mixtures remain smooth and show limited amount of C-S-H growth, whereas intensive precipitation of C-S-H was observed in seawater mixtures [20], confirming early-age hydration acceleration reported using isothermal calorimetry. A “denser” and less porous microstructure on the basis of fracture surface SEM imaging in seawater mixtures at earlier ages is suggested by multiple authors [17]. This microstructure has been attributed to intermixing of nanocrystals and higher surface area hydrates, although one must keep in mind that fracture surfaces are quite variable, which makes such assessments subjective [17,18,20]. Nevertheless, the reduced porosity and pore structure refinement observed by several authors [11,18,21,23] confirms microstructural densification. Clear evidence of Friedel's salt formation is seen from SEM and from energy-dispersive X-ray spectroscopy (EDX) [18,20]; thermogravimetric analysis (TGA) also confirms the formation of Friedel's salt at 1 day, which increases in amount at 3 days [11].

EDX also confirms the greatly enhanced contents of Na^+ and Cl^- in seawater-mixed concrete and chloride sorption in the C-S-H phase [3,20]. Depending on the curing conditions and the usage of SCMs, the amount of Friedel's salt may reduce or increase at later ages [11,18,20]. In seawater-mixed C_3S pastes, the seawater appeared to promote calcium hydroxide crystal growth with a hexagonal platelet morphology [19]. The C-S-H gel appeared as a "dense-cluster morphology" that grew outward from the grain surface and was connected with needle-like gypsum crystals. TEM images of alite hydrated in the presence of NaCl, $MgCl_2$, and Na_2SO_4 show increase in the average early-age C-S-H fiber length, attributed to a faster hydration rate [25]. Nuclear magnetic resonance (NMR) results showed an increase in the early-age silicate mean chain length and polymerization degree, which could explain the longer fibers. Neither technique showed significant differences in the C-S-H morphologies in seawater and freshwater-mixed pastes at later ages [25].

X-ray diffraction, TGA, and Fourier transform infrared spectroscopy have also been performed on seawater-mixed cement pastes [11,18-27]. The results from these tests largely confirm acceleration (increased contents of hydrate phases) due to various ions in the seawater, the formation of Friedel's salt, and changes in the nature of the hydration products at early-ages. None of the techniques showed major effects of the seawater at later-ages.

3. Interactions with Supplementary Cementitious Materials and Chemical Admixtures

3.1. Interactions with supplementary cementitious materials

SCMs and chemical admixtures have long been used to improve concrete properties and to increase concrete sustainability and durability. A large amount of research on seawater-mixed concrete has included mixture designs with SCMs and various types of chemical admixtures. Depending on the required concrete properties, the use of certain chemical admixtures, such as retarders to slow down rapid setting, might be essential [3]. Studies performed on seawater-mixed concrete (or cement paste or mortar) have generally found that incorporation of SCMs resulted in performance improvements when compared to the seawater-mixed concrete without SCMs [2,18-24]. Research on the effects of SCMs and seawater on fresh and hardened properties is discussed in other sections, here, we largely focus on interactions between SCMs and seawater.

A comparison of hydration of cement pastes with seawater and cement pastes with slag, silica fume, and seawater revealed that the acceleratory effects of seawater were higher in the latter mixture [22]. Compressive strength measurements confirm that effects of seawater are greater in mixtures incorporating slag than in plain cement mixtures. Studies have shown similar results for other SCMs, including metakaolin and fly ash [29-33]. Explanations proposed include the greater pore solution pH [11] accelerating reaction of SCMs, formation of hydration products such as hydrocalumite, and pore size refinement [22,30,31]. In the case of metakaolin and seawater, the synergy is explained due to early-age impacts of seawater which alters hydration, hydration products, and porosity, combined by later-age impacts of metakaolin, which alters hydration products and the pore size distribution [30,31]. The synergy between seawater and SCMs can in principle allow for the use of higher SCM replacement levels (such as for fly ash) [34], as the seawater can somewhat compensate for the early-age strength reduction which often limits SCM replacement levels in practice. While these studies show clear evidence of seawater-SCM synergy, it is not completely clear if the seawater *directly* affects the reaction of the SCMs. Studies using model systems, such as the R^3 type of tests, which directly evaluate SCM reactivity [35,36], with seawater replacing freshwater could provide the answer to this question. These tests could also be run using pore solutions expected using seawater [11] or by varying pore solution pH and Cl^-. Doing so will allow to compare the effects of seawater for different SCMs, explain how SCM physicochemical properties influence seawater interactions, and estimate effects of seawater on SCM reaction kinetics.

Nanosilica and rice husk ash have also been investigated in seawater systems. Both materials result in promising properties, potential synergies with seawater, and improved compressive and flexural strength, due to enhanced hydration and microstructure refinement [24,37]. In seawater-mixed concrete with SCMs, mixtures with lower water-to-cementitious ratios (w/cm) demonstrate better synergies and increasing seawater ionic concentration also improved the strength behavior [38]. More involved mixtures, where combinations of slag and metakaolin, in addition to lightweight aggregate (for internal curing) have also been evaluated; again, the combination of SCMs and seawater resulted in improved strength behavior [39]. Another study [22] investigated cement-silica fume-slag binder systems for ultra-high performance concrete cement paste and somewhat different levels of interactions/synergies of seawater with slag and silica fume were observed. Specifically, a greater level of synergy with slag was suggested as compared to silica fume (the authors state that "seawater increased the reactivity of slag " and "seawater decreased the interaction of silica fume with cement"), however, the reason why is unclear. The accelerating effect of seawater on hydration and strength allows to use low reactive (coarse or low amorphous content) SCMs [40] and possibly inert materials in concrete mixtures without compromising early-age strength.

3.2. Interactions with chemical admixtures

An analysis of mixture designs incorporating seawater reveals extensive usage of chemical admixtures such as superplasticizers, retarders, and air entraining agents [2,3,41-43]. Calcium nitrate has been used as accelerator in seawater-mixed concrete, resulting in acceleration of later-age strength [16], however, other accelerators have not been studied. Shrinkage reducing admixtures appear to have not been researched, which is a missing area of research because of the high shrinkage associated with these mixtures [17,23].

No study reported incompatibilities or poor behavior caused by admixtures. The use of a retarder in seawater-mixed concrete is relatively common if it is desired to control the acceleration caused by the seawater [2,3,44,45], for example in hot regions or instances of long-transit. The use of superplasticizers and other water reducing admixtures is common in seawater-mixed concrete, especially because seawater somewhat reduces the workability of concrete [2,3]. Use of high-surface area SCMs such as rice husk and metakaolin can result in further reductions of workability, which would make the usage of superplasticizer essential [30,31,37]. Superplasticizer requirements may be higher in seawater-mixed cement pastes due to the lower workability and increased yield stress in seawater systems [16,17,40]. Li et al. carried out a detailed investigation on superplasticized seawater cement pastes where 25 seawater pastes and 10 freshwater pastes were evaluated for a variety of rheological properties [43]. The found that addition of superplasticizer (or increased dosage) improved workability, strength, packing density, but reduced the adhesiveness of both seawater and freshwater pastes. The superplasticizer performed "equally well" for the seawater and freshwater pastes. Properties such as slump, flow rate, and adhesion in seawater pastes were strongly correlated to the water film thickness (WFT) and superplasticizer dosage, which controlled the rheological behavior of seawater pastes [43].

Compatibility or admixture interactions have not been evaluated in detail, except for Li et al. [43] and studies using pure phases and lab-synthesized admixtures are warranted. Studies generally focused more on cement paste/concrete performance, rather than specific interactions with admixtures. Therefore, it is unclear if certain classes of retarders will not work in seawater due to the high ionic concentrations, or whether air void characteristics in seawater-mixed concrete are similar to those in freshwater concrete. Further study on seawater-chemical admixture interactions, accompanied by research on other admixture types (such as shrinkage reducing admixtures) is needed for widespread adoption of seawater-mixed concrete.

4. Fresh and Hardened Properties

4.1. Fresh properties

Much research has been performed on the fresh properties of seawater-mixed concrete (or cement pastes) and similar results were demonstrated, regardless of mixture composition. The use of seawater increases the concrete density, but the effect is rather minimal, because the densities of seawater and fresh water differ by only 2-3% [3]. The minimal effect of seawater on the density has been confirmed in conventional concretes, concrete with SCMs, concretes with recycled aggregates, and concrete with lightweight or other unconventional aggregates [2,3,39-42,45]. Seawater somewhat reduces the workability of concrete, although exact effects depend on SCM and chemical admixture amounts [2,3,43]. Using seawater with high-surface area SCMs such as metakaolin or silica fume will result in poor workability; but the same would be true when using freshwater [30,31,37]. Reductions in workability are commonly accompanied by a reduction in the slump retention [3]. Impacts on workability and workability retention can be more negative when recycled aggregates are used instead of conventional aggregates [45]. The reduction in workability is an expected consequence of the acceleration of the cement hydration due to the ions in the seawater [22]. While the reduction in workability is a potential concern, strategic use of superplasticizers, which have widely been demonstrated to work in seawater-mixed concrete [43], is a relatively simple solution, although their use can result in an increase in the mixture cost.

Two studies studied the rheology of seawater-mixed cement pastes in significant detail (beyond simple measurements of slump or slump flow that were done in other studies) [38,42]. Li et al. measured workability, adhesiveness, and WFT in several seawater cement pastes and found that the use of seawater leads to lower workability, higher adhesiveness, lower packing density, smaller WFT, and slightly higher strength. These differences were attributed to faster hydration, but also to higher viscosity of the seawater and the presence of suspended solids in seawater. The authors suggested that further studies are needed to better understand some of the observed phenomena [38]. Wang et al. studied the effects of w/cm, SCMs, and salt concentration on properties of seawater-mixed cement pastes; correlations between the rheological properties and hardened properties were also explored [42]. Their findings are broadly similar to those of Li et al. [38] – the plastic viscosity, dynamic yield stress, thixotropic area, and compressive strength increased in seawater mixtures compared to deionized water mixtures. Interestingly, the increase in strength was more significant in pastes with lower w/cm values. Increase in seawater ionic concentration had a non-monotonic effect on the compressive strength, possibly because of non-monotonic effects on hydration rates and microstructure development. Other studies also confirmed that seawater increases the plastic viscosity and yield stress in cement pastes [40].

Due to the acceleration provided by seawater, initial and final setting times are reduced in seawater-mixed concretes [11,18,22,31,44-46]. Values vary considerably depending on mixture design, but reductions in set times (or peak times) are about 30% [3,20]. When used in hot regions or together with fine SCMs, which may cause acceleration on their own, undesirably rapid setting may ensue. Controlling this setting using retarders appears to be a simple and effective solution [2,3], which may be accompanied by increasing costs (similar to the case with the superplasticizer discussed above). Nominal contents of air entrainer have been used in seawater-mixed concretes and no significant difference in air content was observed [2,3,45], but the effect of seawater on air entrainment in cold-region concrete mixtures (air content in the vicinity of 6%) is unknown.

4.2. Hardened properties

The vast majority of "older" research on seawater-mixed concrete focused on strength and issues related to corrosion. A wealth of evidence confirms that early-age compressive strength is increased when using seawater, while later-age strength is affected only slightly [2,3,13,14,20-22,24-34,37-51]. The increased strength is attributed to enhanced hydration, pore size refinement, and generation of hydrates with different microstructure [11,18-24]. Early-age strength compressive strength is increased between 4 – 23%. Long-term studies show variable results, with some showing comparable strengths, some showing slight reductions, and others showing slight increases [2]. Long-term impacts on mechanical properties are relatively insignificant, which is because the hydration acceleration induced by the seawater does not persist beyond the first three days. Considering variable curing conditions, differences in mixture designs, and differences in testing procedures, the differences in later-age strength are unsurprising [2,13,44]. However, there is some evidence which suggests that the long-term performance of seawater-mixed concrete is better in marine conditions (when exposed to seawater), due to lower seawater ingress and leaching [2]. When exposed to "conventional" curing conditions, such as a fog room, seawater-mixed concrete can show slightly lower long-term strength than conventional concrete, due to leaching of hydrates [2,3]. A schematic of strength development of seawater-mixed concrete is shown in Figure 3.

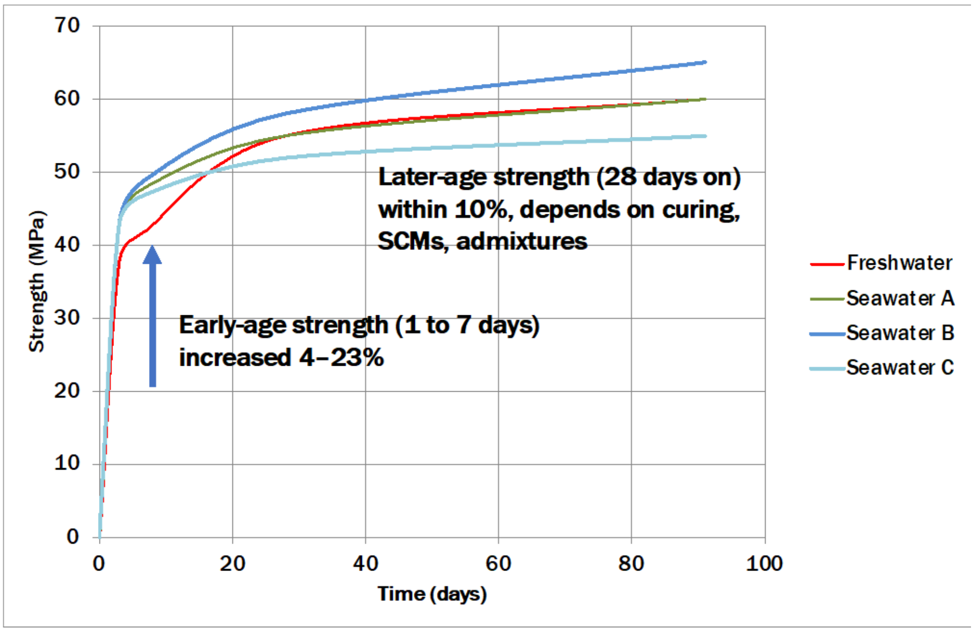

Figure 3. Schematic of effects of seawater on concrete early-age and later-age compressive strength (adapted from [2]).

Comparisons of strength between seawater-mixed concrete and freshwater concrete are affected by the use of SCMs, chemical admixtures, and unconventional aggregates [2,3,13,16,20-22,24-34,37-51]. As a specific case, when relatively low-quality aggregate such as recycled concrete aggregate is used, substantially lower strengths were observed (although this is also true for conventional concrete) due to poor interfacial properties, and reductions in the w/cm may be needed to reach targeted strength [41,45]. At any rate, the majority of available evidence indicates that strength is not a limiting factor in the use of seawater-mixed concrete, including in field conditions [41,42]. Using seawater together with SCMs may be especially advantageous due to the apparent synergies, which leads to higher strengths in both the short- and long-term [2,22,30,34]. Flexural strength has not been studied by as many authors, but results are similar to compressive strength – significant early-age enhancement and minimal later-age effects [21,24,42].

As mentioned in an earlier section, seawater reduces the porosity and results in a refinement of the porosity, especially at early ages [11,18,21,23]. Some authors have shown minimal changes in permeability or chloride resistance measured using rapid chloride permeability, water absorption and chloride migration tests when comparing seawater-mixed concrete with the freshwater alternative [3,45]. Others have shown some reductions in sorptivity and water absorption in the seawater-mixed concretes [23,24,41,42]. Similar to strength, other later-age properties do not show consistent trends, and differences may be caused by different amounts of SCMs, chemical admixtures, and curing conditions. However, most differences at later ages due to the use of seawater are relatively minimal (< 10%). Electrical resistivity measurements on seawater mixed concrete are limited. One study showed increased concrete electrical resistivity when using seawater, however, the curing conditions were unusual (high temperature curing) [2]. Interpretation of electrical resistivity in seawater-mixed concretes is complex because the seawater decreases the pore solution resistivity [11].

5. *Special* Concretes using Seawater

Considering that seawater does not induce strong negative effects on concrete properties, behaves promisingly with SCMs, and is compatible with chemical admixtures, production of high-performance concrete using seawater is feasible. using seawater is feasible. Seawater has recently been used to make ultrahigh-performance concrete (UHPC), engineered cementitious composites (ECC), and self-compacting concrete (SCC). Compared to the extensive work on fresh and hardened properties and interactions with SCMs, work on *special* concretes using seawater is somewhat limited. Interestingly, all of the works cited in this section are from 2014 or later.

5.1. Ultrahigh-performance concrete (UHPC)

Li et al. [22] appears to be the first study on UHPC paste mixed with seawater. Teng et al. [52] report the first study on the development of UHPC with seawater and sea sand, in which they successfully produced UHPC without steel fibers with a compressive strength of over 180 MPa. Findings from [22] are already discussed in Section 3.1, and 3-day strengths were between 80 – 100 MPa. Similar to ordinary UHPC, UHPC mixed with seawater generally has a low w/cm (around 0.2), and has cement, silica fume, other SCMs (such as slag and fly ash), and sand [22,52]. As commonly observed in conventional concrete, the ions in seawater generally lead to a slight increase in the early-age strength but a slight decrease in the workability and the later-age strength in UHPC. As the salinity of natural seawater varies depending on the seawater source, Teng et al. [52] studied the effects of seawater salinity on the properties of UHPC and demonstrated that workability decreased with the salinity of mixing water, and an optimum salinity may exist for the compressive strength of UHPC. Similar conclusions have been made for conventional cement pastes mixed with seawater, although the optimum salinity for strength also seemed to depend on the age of testing [38]. Others have shown using sodium chloride that the strength of UHPC slightly decreased with the content of sodium chloride [53]. Teng et al. [52] showed the possibility of varying mixture constituents and using white cement and Class F fly ash in seawater-mixed UHPC. Li et al. [54] recently prepared a seawater sea sand high performance concrete with strengths of about 150 MPa; other studies have shown UHPC with strength of about 140 MPa [55].

It is considered that steel fibers cannot be used in seawater-mixed concrete due to the risk of corrosion. However, UHPC has a dense microstructure, which impedes the diffusion of oxygen, water and chloride into the concrete. Two studies have been conducted on steel fiber-UHPC mixed using seawater [54] and sodium chloride [53]. Both studies suggested that corrosion may not be a major problem for the steel fibers inside UHPC due to its low permeability, although corrosion did occur on a thin layer of steel fibers close to the surface of the specimens. The durability of seawater-mixed UHPC was investigated in some detail in [54] using lab testing and exposure in a real marine environment. Lab testing showed essentially no carbonation or damage after 1000 freeze-thaw cycles in the lab. Minimal reductions in compressive strength, carbonation and corrosion were observed after one year exposure to the marine environment. Long-term durability testing of seawater-mixed UHPC is missing.

5.2. Engineered Cementitious Composites (ECC)

Some researchers have investigated the use of seawater to produce ECC and demonstrated its feasibility [56-59]. The tensile strength of polyethylene fibers does not change significantly after being soaked in seawater for two years, and the mechanical properties of normal-strength seawater-mixed ECC with polyethylene fibers are almost the same as those of the corresponding freshwater-mixed ECC [56]. Polyvinyl alcohol has also been used as a fiber to produce normal-strength ECC with seawater and sea sand, and the compressive strength was slightly higher, although its tensile strength was slightly lower than corresponding freshwater ECC [57].The use of seawater and sea sand may change the crack width and crack pattern of ECC. Huang et al. [58] performed comprehensive studies on high-strength seawater-mixed

ECC. Seawater-mixed ECC with a compressive strength of over 130 MPa, a tensile strength of over 8 MPa, and an ultimate tensile strain of over 5% was produced. The effects of a number of key parameters (i.e., the volume ratio and length of polyethylene fibers, and the size of sea sand) on the crack characteristics and mechanical properties of seawater ECC have been examined and probabilistic models for the stochastic evolution of crack widths of seawater ECC have been proposed [56-59]. The existing studies on seawater ECC (and other high performance concretes) have been limited and it is currently unclear how the use of seawater affects the long-term behavior, including the fiber-to-matrix bond behavior.

5.3 Self-compacting concrete (SCC)

Researchers in Indonesia [60-64] conducted extensive studies on seawater-mixed SCC using Portland cement (OPC), fly ash, and other materials. Zhou et al. [65] developed *high-volume fly ash-self compacting concrete with seawater*, using large amounts (> 50%) of fly ash replacing cement. These studies demonstrate the feasibility of producing seawater-mixed SCC which satisfies the existing guidelines for SCC, although the seawater slightly decreases the workability of fresh SCC, similar to the case for conventional concrete [61]. The compressive and tensile strengths of seawater-mixed SCC were found to be generally higher than those of the corresponding freshwater-mixed SCC even at later ages, especially when a large amount of fly ash is used in the mixture [61,62,65]. As suggested by the other studies, this enhancement could be due to the synergistic effects between seawater and SCMs. Microstructural investigations of seawater-mixed SCC have also been performed [62-64] and effects of curing methods on strength development in SCC have been explored [61]. Raidyarto et al. (2020) demonstrated the feasibility of producing seawater SCC with steel fibers; although corrosion was not explored in this study [66]. While producing UHPC with steel fibers resulted in limited corrosion issues, the same may not to be the case with SCC.

6. Concrete Durability

The use of seawater as mixing water might affect the durability of plain concrete as well as that of reinforced concrete. For plain concrete, investigations on sulfate attack and alkali-silica reaction are likely to be critical, whilst, for (steel) reinforced concrete, in addition, chloride penetration and carbonation are of major concern. Shrinkage, although not a degradation phenomenon, is also discussed in this section (restrained shrinkage causes cracking, which leads to an increase in the ingress of deleterious species into concrete, leading to a reduction of the durability). While research has considered the durability of seawater-mixed concrete, it seems to have been very limited in extent and work is needed to shed further light on the durability behavior of seawater-mixed concretes. Understanding the durability of seawater-mixed concrete is a major factor limiting their widespread adoption.

Studies on the sulfate attack resistance of seawater-mixed concrete are limited. Ting et al. [49] studied the sulfate resistance of OPC concrete with a w/cm 0.32 exposed up to 90 days to a 5% sodium sulfate solution. A significant loss of compressive strength was noted after 90 days. Replacing freshwater with seawater slightly reduced damage caused by sulfate attack. While not directly studying seawater-mixed concrete, Zhao et al. [67] conducted a study on concrete with w/cm 0.485 made with OPC and freshwater with admixed chlorides (3% NaCl). After exposure up to 1 year to sodium sulfate solutions with concentrations of 3%, 5% and 10%, concretes with admixed chlorides showed a higher volume expansion and mass loss and a lower compressive strength in comparison to concretes without chlorides. The damage was more severe as the solution concentration and the time of exposure increased. These two studies seem to contradict, and the different behavior might be caused by the different chloride concentrations, w/cm, among other reasons. While later-age hydration products and microstructure are not substantially different in seawater-mixed concrete, the system does have greater free and bound alkali chloride and sulfate (high Na+ and Cl- in the pore solution and

C-S-H, and formation of Friedel's salt). Understanding how ingressing sulfate is influenced by the already existing chloride and sulfate is key to explaining sulfate attack behavior in seawater-mixed concrete.

Little attention has been paid in the literature to alkali-silica reaction degradation in seawater-mixed concrete. Adiwijaya et al. [68,69] investigated the expansion characteristics of seawater and freshwater concretes when reactive coarse aggregates were used. After 28-days of curing (water curing, seawater curing and moisture curing), specimens were exposed in a chamber at 40 °C and 100% RH, and the expansion was measured for 1 year. Concretes made with seawater and cured in all three curing regimes showed an expansion, due to the presence of a high amount of alkali in the mixtures. Concrete made with fresh water did not expand, even when cured for 28 days in seawater, suggesting that alkali-silica reaction did not occur if the intrinsic amount of alkali in concrete was low. The use of SCMs such as fly ash and slag limited the expansion in seawater concrete. Considering that the use of seawater increases cement hydration and later-age pore solution pH by about 0.15 units, the increased ASR expansion is expected. While further research is needed, when using reactive aggregates, increased SCM replacements are suggested for seawater-mixed concrete when compared to freshwater-mixed concrete.

Shrinkage of seawater concrete or mortar, due autogenous and drying, has been investigated in depth in one study. Khatibmasjedi et al. [23] studied the drying shrinkage of mortars, with w/cm 0.36 and 0.45 made with OPC and OPC with 20% fly ash replacement. Drying shrinkage was only slightly affected at w/cm 0.36, but a higher shrinkage was observed at w/cm 0.45 with the seawater mixtures. Specifically, the mortar with seawater and fly ash showed the highest drying shrinkage, likely due to a finer pore size distribution [11,18,21,23] and changes in mass loss behaviour. Increased pore solution pH and viscosity could also contribute to the increased drying shrinkage. A slight increase of drying shrinkage when seawater was used was observed by Younis et al. [3] at w/cm 0.34, whilst Olutoge and Modupeola [70] highlighted that the drying shrinkage of concrete with w/cm ratio of 0.6 was increased when seawater was used as mixing water. In lightweight concretes, the use of seawater led to a reduction of drying shrinkage [39]. These studies seem to suggest that seawater increases the drying shrinkage for high w/cm mixtures, whilst for low w/cm mixtures its effect is negligible. A higher autogenous shrinkage was observed when seawater was used as mixing water both by Khatibmasjedi et al. [23] and by Li et al. [22], attributed to the seawater enhancing cement hydration and (possibly) SCM reaction. While the increased shrinkages are concerning, seawater-mixed concretes are likely to be used in high-humidity or saturated environments, where shrinkage may not be a major issue. However, if shrinkage concerns are significant, then the use of shrinkage reducing admixtures or internal curing should be considered.

As with other durability studies, research on the carbonation of seawater-mixed concretes is limited. According to Carsana et al. [71], who performed tests in both accelerated condition (T = 20 °C, RH = 50%, CO_2 = 4%) and in natural exposure conditions (indoor) and Otsuki et al. [72], who carried out tests in accelerated conditions (CO_2 = 5 and 10%), seawater did not considerably affect the carbonation process. Conversely, according to Adiwijaya et al. [69], seawater improved the concrete resistance to both accelerated and natural carbonation, with and without SCMs (fly ash and slag), especially when concretes were air cured. As it is not common to use seawater-mixed concrete with conventional steel reinforcement, carbonation is unlikely to be a major issue in practice.

The resistance to chloride penetration was studied by several authors using the Rapid Chloride Penetration Test (RCPT), ASTM C1202, that measures the charge that passes through the specimen. In these studies, concretes were obtained with different types of cement, OPC [39,49], OPC with 65% slag replacement [3] and OPC with metakaolin replacements up to 6%

[47] and different w/cm, equal to 0.3 [39], 0.32 [49], 0.34 [3], and 0.45 [47]. Lightweight aggregate was used in [39]. From these tests, seawater had a negligible effect on chloride permeability of concrete at 28-days, since the ratio of chloride passed in the seawater-mixed concrete and freshwater-mixed concrete was between about 95% and 110% for most mixtures. Mixtures with metakaolin appeared to show some synergy as the seawater in this case increased the chloride resistance [47].

A chloride migration test was performed in [3] and, again, a negligible effect of seawater as mixing water was observed. Chloride penetration has been evaluated by other authors by means of immersion tests in a sodium chloride solution for a variety of mixture designs [71,73]. In both studies, the chloride penetration of concrete mixed with seawater (artificial in the study by [73]) was lower than that of reference concretes made with fresh water, leading to a lower diffusion coefficient.

It appears that the different behavior in terms of resistance to chloride penetration observed in the studies presented above depends on the type of test used to evaluate this property. This is not a finding specific for seawater-mixed concrete. In the RCPT and migration tests, chlorides are forced to penetrate into concrete through an electrical potential gradient, and the resistance to chloride penetration mainly depends on the pore structure of concrete. Conversely, in immersion tests, where diffusion is the main transport mechanism, chlorides penetrate due to a concentration gradient. Hence, the presence of an initial chloride content in seawater concretes, results in the decrease of chloride concentration difference between concrete and the sodium chloride solution where specimens are exposed and affects the resistance to chloride penetration together with the concrete microstructure. Since seawater-mixed concretes are typically not expected to be reinforced with steel reinforcement, the chloride penetration in these concretes may not be as critical to durability as with conventional concrete. However, they can be used as a general indicator of the quality of the concrete, and according to most results, the use of seawater does not negatively influence the concrete quality at later-ages.

Due to the limited available data and, in some case, due to contradictory results, the effect of seawater on concrete durability cannot be properly ascertained and further studies on this topic are sorely needed. Attention should be focused on how the mixture proportions of concrete affect the concrete durability when seawater is used instead of freshwater in addition to studying and understanding durability behavior from a fundamental perspective.

Figure 4 shows a schematic of the major effects that seawater induces in fresh and hardened concrete and on concrete durability. Changes in microstructure which could explain the reasons behind the observed differences at the macroscale are also listed, though a mapping of effects is not done as this information is unavailable in literature.

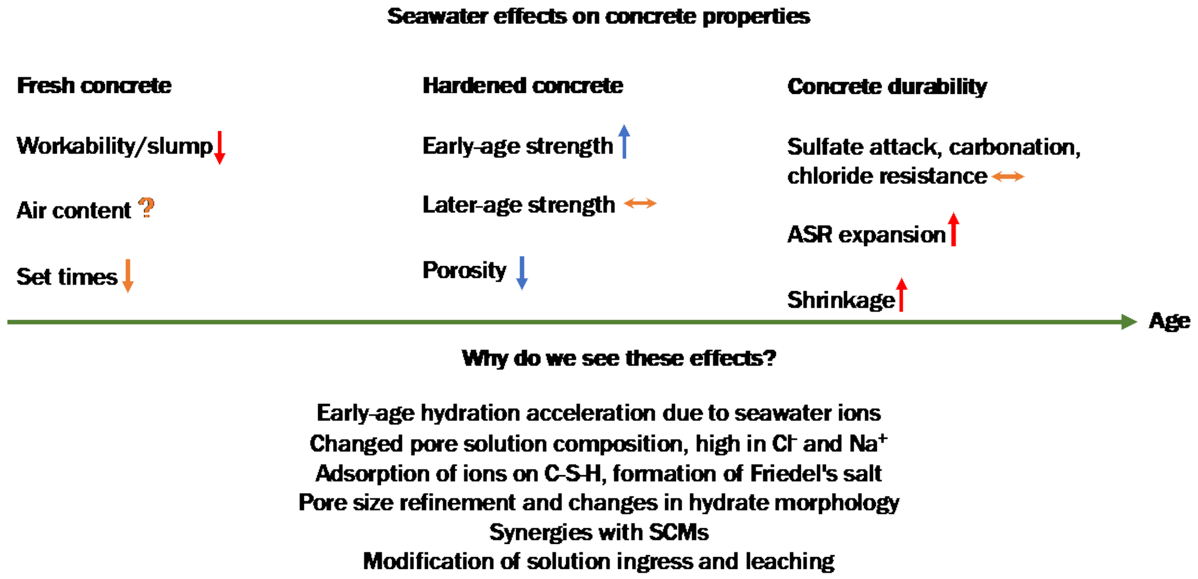

Figure 4. Micro- and macro-scale effects of seawater on concrete properties at various ages. Note that the number of studies on durability are limited.

7. Corrosion and Alternative Reinforcement

The major issue related to the use of seawater for mixing reinforced concrete is the high concentration of chlorides present in seawater, that will likely lead to the corrosion of conventional steel reinforcement. Considering the negative consequences of corrosion, seawater-mixed concrete should generally not be used together with conventional steel reinforcement. Several studies have been carried out to evaluate the corrosion behavior of carbon steel in seawater-mixed concrete, both natural and artificial, exposed in an environment with or without further chloride penetration. Almost all studies agree that carbon steel in specimens made with seawater as mixing water were prone to corrosion when exposed to further chloride penetration (for instance, a sprayed environment of 3.0% NaCl solution at 50 °C [74], alternate wetting–drying cycles with seawater [13], accelerated sprayed chamber with 50 °C of 3% NaCl solution [47] or ponding with a 3.5% NaCl solution [75]), when the concrete cover thickness was low [34,44,73,75,76]. The use of SCMs can affect the penetration of chlorides and the corrosion initiation time, although it will not prevent corrosion. Nishida et al. [44] observed that the initiation time was longer when slag was used to replace OPC. Similar results were obtained in the study by Otsuki et al. [73], whilst Daser et al. [76] did not observe any significant improvement using slag. According to Lollini et al. [75,77] the use of fly ash in seawater-mixed concrete led to a slight increase of the initiation time, while according to Lim et al. [34], fly ash did not significantly change the risk of corrosion. The monitoring of the corrosion conditions of carbon steel rebar in a demonstration project led to somewhat surprising results [78,79]. In seawater-mixed concrete, subjected to wetting and drying cycles and a water flow contaminated by chlorides resulting from the use of deicing salts for about one year, the corrosion rate of carbon steel rebar was negligible, even if corrosion initiation seemed incipient.

The use of seawater when further chloride penetration is not expected, i.e., for structures far from the sea, has not been investigated in detail. A study showed that carbon steel rebar corroded when exposed to high temperature and humidity, and a high corrosion rate was detected for carbonated concrete, even in mild climatic conditions, due to the presence of chlorides [80].

Various strategies have been proposed for overcoming the problem of steel reinforcement corrosion in seawater-mixed concrete. For example, the use of cathodic prevention [81], as well as the use of corrosion inhibitors [82-84] were explored to enhance the durability of seawater concrete. Epoxy coated rebars have been also proposed in combination with seawater-mixed concrete [76], however the presence of defects or scratches might drastically impair their reliability.

The well-known higher corrosion resistance makes stainless steel rebar an attractive solution that has been explored by some authors. As the corrosion resistance is a bulk property of stainless steel, their corrosion behavior is unaffected if their surface is cut or damaged during handling, unlike epoxy coated rebars. Although several grades of stainless steel have been proposed as reinforcement, 304L grade has been the most studied in combination with seawater concrete. Although relatively short-term testing has been carried out to evaluate the suitability of 304L stainless steel rebar embedded in seawater-mixed concrete, the initiation of corrosion did not occur in spite of further chloride penetration [75,76,85]. Other grades of stainless steel, including duplex 22-05 and 23-04, and the austenitic XM-28, were studied in the experimental work carried out by Lollini et al. [75,77]. Wet and dry cycles with a 3.5 % NaCl solution carried out after two years of ponding in the same solution, led to the initiation of corrosion on the austenitic XM-28 rebars but not the other rebars. This finding suggests that XM-28 was not suitable for use in structures built with seawater-mixed concrete and subject to the further chloride penetration (for example, in the splash zone). The other grades of stainless steel did not experience initiation of corrosion. No corrosion was also detected on 304L and 23-04 stainless steel embedded in seawater-mixed concrete of a culvert prototype, subjected to wetting and drying and deicing salts for about one year [78,79]. The feasibility of the 23-04 grade in seawater-mixed concrete was also assessed through tests in simulated pore solution, which however, might not be adequate to predict corrosion behaviour in concrete [86]. Nevertheless, results were comparable to those obtained through the modelling of the service life through a performance-based approach [87]. The corrosion behaviour of stainless steel rebar was not affected by the use of seawater as mixing water when concrete was not exposed to the further chloride penetration, even when the concrete was carbonated [80].

The use of FRP has increasingly been explored for seawater-mixed concrete. Despite the vast amount of research on FRP rebar durability, the FRP rebar behavior when embedded in seawater-mixed concrete has received somewhat limited attention. FRP durability in seawater-mixed concrete is covered only shortly here, and interested readers are directed to a review paper on this topic which is far more comprehensive [15]. The most important conclusions regarding the use of FRP in seawater-mixed concrete are:

1. Tensile, bond, and shear performance of GFRP rebars in seawater-mixed concrete is generally similar to that of rebars in concrete made with fresh water [15,88,89].
2. Increasing solution pH, temperature, and sustained loading in simulated conditions or in seawater-mixed concrete all lead to greater FRP degradation [15,89-95].
3. Better durability performance was determined for carbon FRP rebar, followed by the glass FRP and basalt FRP [15,92].

As the initial higher costs of FRP are a concern, life-cycle assessment (LCA) and life-cycle costing (LCC), similar to work that some authors have performed, is of interest [96,97].

8. Advances in Modeling and Modeling Opportunities

Modeling approaches for seawater-mixed concrete appear to be in their infancy. The major modeling approaches that have been studied in literature are briefly summarized below.

At the nano-scale, no study using molecular dynamics (MD) simulations or similar techniques were found on seawater-mixed concrete. One possibly relevant study is by Deng et al. [98] which evaluates interactions between sodium chloride solutions and C-S-H. The authors show alkali sorption, consistent with what is known for seawater-mixed pastes, and suggest that Na^+ ions can replace free Ca^{+2} ions on C-S-H surfaces. Another possibly relevant study is Yaphary et al. [99] who use MD to show that NaCl solutions can weaken the adhesion energy between epoxy and silica by approximately 60%. Other studies have studied degradation of FRP in aggressive environments using various MD approaches [100].

Multi-scale modeling provides a bridge between macroscale and the nano-scale, and is important to link atomistic modeling to experimental results. No multi-scale modeling studies have been performed on seawater-mixed concrete; similar to MD, studies exist on organic-inorganic interfaces, such as the epoxy-silica interface [101,102], which could in principle be applied to FRP in seawater-mixed concrete.

At the paste level, Li et al. [103] performed thermodynamic modeling using GEMS and a series of experimental tests to determine the role of role of Mg^{+2} in reactions in seawater-mixed cement pastes. Pastes were made with solutions with Mg^{+2} concentrations of 0% to 3.0%; seawater itself was not used in the study. Thermodynamic modeling was used to determine the amounts of various hydrate phases. Kinetics was incorporated into the modeling to determine the changes in phase amounts over time. Using both thermodynamic modeling and experiments, the authors demonstrated that Mg^{+2} prolongs the induction period and delays the acceleration period as it reduces the dissolution of the clinker and precipitation of the hydration products. It should be noted that when seawater itself is used, hydration is not retarded, but accelerated, as discussed in Section 2.1. Thermodynamic modeling was used in another study [20] to evaluate the evolution of hydrous and anhydrous phases over time in seawater and freshwater-mixed pastes. The authors showed that the hydration of C_3S was accelerated by seawater at early ages. Significant effects of seawater in accelerating the hydration of other phases were not detected, although the formation of different hydrates, such as Friedel's salt, in the seawater-mixed pastes was reported. Thermodynamic and early-age kinetic modeling were used to evaluate and compare the effects of NaCl, $CaCl_2$, Na_2SO_4, and $CaSO_4$ on hydration kinetics and hydrate assemblage in cement pastes [104]. It should be noted that thermodynamic modeling at early-ages and low degree of hydration may be inaccurate due to far from equilibrium conditions.

Paste hydration kinetics was also modelled using the Krstulovic-Dabic model [105] to compare the effects of seawater, NaCl, and Na_2SO_4 on cement paste hydration kinetics. The authors showed acceleration of hydration in the presence of these salts/seawater, formation of Friedel's salt in the presence of chloride, and increased early-age strength. Findings from modeling are consistent with the experimental results from other studies [2-4,11,18-22].

Modeling at the concrete scale has included structural-scale modeling of cracking and probabilistic modeling [58,59] and modeling of FRP behavior/degradation over the long-term using various prediction approaches such as the Arrhenius approach [93,106]. Some of these approaches are oversimplifications, because FRP degradation is a complex physicochemical process that cannot be modelled by a chemical Arrhenius approach. As further understanding of FRP degradation mechanisms and long-term data is obtained, more sophisticated modeling approaches can be employed. A detailed discussion of concrete-scale modeling is out of the scope of this work. Machine learning and similar approaches seem not to have been considered for seawater-mixed concrete, possibly because existing data is inadequate in volume for such approaches. However, one study used artificial neural networks to predict the corrosion current density of steel in seawater-mixed mortar [107].

Much is missing in terms of modeling for seawater-mixed concretes, mortars, and cement pastes. It is hoped that further work using various modeling approaches [108,109] will propel forward the understanding of seawater-mixed paste/mortar/concrete.

9. Case Studies and Data from Field

Etxeberria et al. [40,41] report the results of lab and field work for concrete dyke blocks produced using seawater and coarse recycled aggregates. The blocks were 2.8 m cubes and manufactured in-situ in the Port of Barcelona and then used for dyke production. The blocks were exposed to the sea for one year, and cores were extracted at one year. The use of seawater had a negligible impact on the strength, however, it had a positive impact on the capillary sorption and the permeability. Results from the lab and field phases of the project were remarkably consistent in terms of the impacts of the seawater used for mixing.

As part of the funded projects described in Section 1.1, field demonstration projects using seawater-mixed concrete were carried out. These included a reinforced concrete culvert and a bridge in two locations with different environmental conditions [13,15]. Other demonstration projects that have used seawater-mixed concrete include parking garages, water-treatment plants, and concrete pavements [13,15,110]. Several of these structures have been instrumented and will provide valuable field data in the years to come.

Three publications describe the design, construction, and monitoring results of the demonstration projects from [13,15] in detail [78,111,112]. Redaelli et al. [78] describe the materials characterization and corrosion monitoring of a concrete culvert built along the A1 motorway, close to Piacenza, Italy. The authors suggest that appropriate use of dosage of superplasticizers and retarders is critical to allow for the use of seawater-mixed concretes which develop the required strength properties. As mentioned in Section 7, a somewhat surprising result was that the corrosion rate of carbon steel rebars was negligible, even if corrosion initiation seemed incipient, although the exposure conditions were quite harsh. The performance of stainless steel in such conditions was outstanding, and service life of over 100 years was predicted. LCA and LCC analyses showed that the use of stainless steel and GFRP was promising; however, GFRP had an advantage in terms of cost. Cadenazzi et al. [111] perform detailed LCA and LCC analyses on an FRP bridge with reinforced concrete and prestressed concrete in Florida with some of the concrete being seawater-mixed concrete. The authors show that the FRP alternative outperforms the carbon steel alternative in both costs and environmental impacts over the lifetime. The "iDock" reconstruction project is discussed in [112], a replacement of a hurricane-damaged dock, using several seawater-mixed concrete elements reinforced with GFRP and BFRP and constructed using accelerated bridge construction (ABC) methods and prefabricated bridge elements and systems (PBES). The entire design and construction process is described, including potential problems and creative solutions. Studies on the seawater-concrete were limited to mechanical studies, where comparable performance to the freshwater alternative was found.

10. Challenges and the Future

Table S1 in the Supplementary Material summarizes the main findings, limitations, and areas in which future work is needed.

Much research has focused on hydration, interactions with SCMs, fresh and hardened properties, and corrosion and alternative reinforcement; however, research has been rather applied, and fundamental understanding through study of model systems is missing. Research is needed on *special* concretes, FRP, durability, and using modeling approaches. The field studies that have been carried out have all shown promising data for seawater-mixed concrete. However, changing codes or specifications to allow for the use of seawater-mixed concrete is likely to be a challenging and complex task. For many agencies, the thought of corrosion might be enough to deter them from a serious consideration of seawater-mixed concrete. In addition, practically, preventing the corrosion of steel and other metals that may be exposed to seawater during mixing and construction operations is also a major concern. However, at least for certain regions and/or selected projects, seawater-mixed concrete could be an attractive alternative to conventional concrete. Obtaining long-term field data demonstrating the feasibility of seawater-mixed concrete and durability over several years will certainly influence changes in codes and specifications. As freshwater shortfalls increase, it is anticipated that seawater-mixed concrete will become a more common option in many regions across the world, especially for certain niche applications.

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Supplementary Material

Review Methodology

The following topics are in the scope of this review: historical perspective, effects of seawater on hydration and microstructure, interactions with supplementary cementitious materials (SCMs) and chemical admixtures, fresh and hardened properties of seawater-mixed concrete, *special* concretes using seawater, durability of seawater-mixed concrete, corrosion and alternative reinforcement, modeling advances, and case studies. Considering the scope of the journal and other published reviews, structural engineering or large-scale testing are not discussed. As an example, mechanical behavior at the concrete cube/cylinder scale for different types of concrete is relevant and is discussed, but the performance of large-scale concrete slabs is not covered here. Alternative binders mixed with seawater are not discussed because the amount of research existing on them is extremely limited.

This review was performed in a systematic manner by searching 21+ terms relevant to the aforementioned scope (for example *seawater mixed concrete historical perspective, seawater mixed concrete hydration, etc.*) in Google Scholar using the 2005 – 2021 search filter in January 2021. Further searches were also made using by making minor modifications to the search terms: by removing *mixed*; by replacing *concrete* with *cement*, *cement paste*, *mortar*; and by replacing *seawater* with *sea water*, *salt water*, etc. The first 30 papers that were returned for each search term were quickly scanned and if the title was not relevant, the paper was ignored. If the title was relevant, then the abstract was read. If the abstract was relevant, the paper was downloaded, read in detail, its findings are summarized here, and the paper is cited. References in the relevant papers were also scanned and the same process was followed with the references if they were missed by the Google search. Google Scholar was chosen instead of other databases due to its generally greater coverage, however, it also returned papers from low-impact and obscure journals or conference publications with inadequately detailed descriptions of experimental methods and results. All publications were dealt in the same manner cited here if relevant. While extensive searching was performed and returned numerous valuable publications, a few relevant publications known to the authors were not returned. These publications are also cited in this manuscript, as relevant.

Summary of major findings, limitations, and areas for further work

Table S1 summarizes the main findings in terms of the various research topics covered in this study. Limitations and areas in which future work is needed are also shown in Table 1.

Table S1. Summary of main findings from literature, limitations, and thoughts for future work. The approximate number of studies that have studied on each topic for seawater-mixed cement paste, mortar, and concrete, is shown in parentheses in the first column.

Topic	*Major findings*	*Limitations and future work*
Hydration (15) Pore solution (2) Porosity (6) Microstructure (15+)	1. Acceleration of early age hydration. 2. Increased Na^+ and Cl^- in pore solution. 3. Reduction of porosity and pore size refinement. 4. Friedel's salt formation and changes in hydrate morphology.	1. Many studies, topic well understood. 2. Work on pore solution limited. 3. Work on pure phases limited.
Interactions with SCMs (15+) Interactions with chemical admixtures (3)	1. Synergies with multiple SCMs. 2. Extensively used with superplasticizers, retarders, and air entraining agents. 3. Incompatibilities with chemical admixtures not reported.	1. Unclear if seawater directly increases SCM reactivity. 2. Specific and fundamental interactions with admixtures not understood. 3. Performance of shrinkage reducing admixtures and accelerators unknown.

Fresh properties (20+) Hardened properties (50+)	1. Slight reduction in workability, reduction in set times. 2. Early-age strength increased; later-age strength impacts variable but generally minor. Other hardened properties similar to strength. 3. Later-age impacts depend on SCMs, curing conditions, etc.	1. Many studies, topic well understood.
UHPC (5) ECC (4) SCC (5)	1. Seawater-mixed UHPC, ECC, and SCC produced with satisfactory properties. 2. Impacts of seawater on property development limited; properties comparable to freshwater mixtures.	1. Studies on *special* concretes generally limited. 2. Further work with wide range of raw materials needed. 3. Long-term effects of seawater on fibers and bond not understood.
Sulfate attack (2) Carbonation (3) Chloride (20+) Alkali-silica reaction (2) Drying shrinkage (5) Autogenous shrinkage (2)	1. Contradictory results with sulfate attack, carbonation, and chloride diffusion/penetration. 2. Alkali-silica reaction expansion increased. 3. Increase in drying and autogenous shrinkage, dependent on mixture design.	1. Number of durability studies extremely limited. 2. No durability mechanism has been examined in adequate detail. 3. Fundamental impacts of seawater on durability need to be understood.
Corrosion (20+) Alternative reinforcement (100+)	1. In principle, carbon steel in seawater-mixed concrete will corrode. 2. In practice, corrosion behavior more complex. 3. Stainless steel and FRP generally perform well.	1. Many studies, topic well understood, however, some inconsistencies in results. 2. Long-term data on behavior of carbon steel, stainless steel, and FRP missing.
Modeling (<10)	1. Paste kinetic and thermodynamic modeling has been performed. 2. Concrete structural modeling and FRP long-term modeling has been performed. 3. MD and other models evaluated for FRP but not for seawater-mixed concrete.	1. Number of modeling studies very limited. 2. Modeling approaches, including MD, multi-scale modeling, machine learning, and others need to be evaluated for seawater-mixed concrete.
Case studies and field data (10)	1. Multiple field studies show feasibility of using seawater-mixed concrete. 2. Lab and field data are similar.	1. Long-term monitoring data is missing.