Interdependence between Structural Engineering and Construction Management
Edited by Ozevin, D., Ataei, H., Modares, M., Gurgun, A., Yazdani, S., and Singh, A.

ISBN: 978-0-9960437-6-2

MICROSTRUCTURE INVESTIGATION OF SEAWATER VS. FRESHWATER CEMENT PASTES

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Recently, seawater has emerged as viable mixing water for concrete, especially in the case of non-reinforced concrete applications or with the use of non-corrosive reinforcement. Previous studies concerning seawater-mixed concrete mostly revealed an initial slight increase in its strength performance (i.e., till Day 14 following mixing), followed by a strength reduction of 7–15% (i.e., after 28 days or longer) as compared to the conventional freshwater-mixed concrete. With an attempt to explain such observations, this paper aims at comparing the microstructure of freshwater- and seawater-mixed cement pastes. Scanning electron microscopy was utilized to observe the microstructure of freshwater and seawater pastes at Days 3 and 28 following mixing. At Day 3, seawater paste was observed to have more densified microstructure as compared to that of the freshwater counterpart, resulting in relatively higher strength performance. At Day 28, the microstructure was almost similar for the two cement pastes. However, seawater paste was observed to have salt impurities as a result of seawater ions, which possibly cause a slightly lower strength performance as compared to the freshwater paste.

Keywords: Sustainability, Seawater-mixed concrete, Scanning electron microscopy, Secondary electrons, Back-scattered electrons, Energy dispersive X-ray.

1 INTRODUCTION

More often than not, there has been a growing interest in using alternative resources of raw materials in concrete to achieve sustainability goals (Saeed *et al.* 2012, Suraneni *et al.* 2018, Xiao *et al.* 2017), given the significant environmental impacts of producing concrete using the current practices (Miller *et al.* 2016). With the increase of global concern of freshwater scarcity (Mekonnen and Hoekstra 2016), seawater is being increasingly proposed as an alternative mixing water for concrete, especially after the development of non-corrosive reinforcement such as fiber-reinforced polymer (FRP) to counter possible corrosion (Aly *et al.* 2006, Benmokrane *et al.* 2006). In principle, using seawater concrete in association with FRP reinforcement seems to be viable from both technical and economic standpoints (Younis *et al.* 2017, 2018a).

Significant research efforts were devoted in the past few decades to grasp, as possible, the effects of seawater mixing on the strength performance of the resulted concrete (Kaushik and Islam 1995, Nishida *et al.* 2013, Wegian 2010, Xiao *et al.* 2017, Younis *et al.* 2018b). In summary, an initial slight increase was observed in the strength performance of seawater concrete as compared to the freshwater-mixed counterpart (until 7–14 days following mixing), followed by a slight reduction of 7–15% after 28 days. The current paper aims at providing some explanations for such observations through the lens of microstructure investigation. Scanning electron microscopy was used to study the microstructure of both seawater and freshwater pastes at Days 3 and 28 following mixing. At first, materials and test methods adopted in this study will be explained. After that, test results will be presented and discussed, from which the conclusions of this comparison will be drawn.

2 METHODOLOGY

2.1 Materials

A comparison was established between freshwater and seawater cement pastes of the same water-to-cement ratio (0.34). The difference between the two mixtures was only in the mixing water. Chemical characteristics were obtained for both types of mixing water and stipulated in Table 1. The pH and alkalinity measurements were within the acceptable limits for both water types. However, the sulfates, chlorides, and dissolved solids in seawater were (as expected) significantly higher than those of the freshwater or even the allowable limits. Table 2 presents the chemical composition of the ordinary Portland cement used in this study, obtained by BS EN 196-2 (2013). The fineness obtained using Blaine air permeability test (by BS EN 196-6 2010) was measured as 3350 cm^2/g.

Table 1. Chemical characterization of the two mixing water types.

Measure (unit)	**Method**	**Max. limit**	**Freshwater results**	**Seawater results**
Chloride (mg/L)	BS 1377-3 (1990)	1000	14.1	18600
Sulfate (mg/L)	BS 1377-3 (1990)	2000	20.9	2359
Alkalinity (mg/L)	BS 6068-2.51 (1996)	500	69.5	149
Total dissolved solids (mg/L)	BS 1377-2 (1990)	2000	62.0	30300
pH at 25 ºC (-)	BS 6068-2.5 (1995)	6.5–9.0	8.1	8.2

Table 2. The chemical composition of the cement used.

Chemical	**Composition (% wt.)**
SiO_2	19.90
Al_2O_3	4.30
Fe_2O_3	3.21
CaO	61.84
MgO	4.49
$Na_2O + K_2O$	0.51
S	2.70
Cl	0.051
Loss on Ignition	2.34
$C_2S + C_3S$	69.98
C_3A	5.96
C_4AF	9.76

2.2 Observation Methods

Scanning electron microscopy was performed, in accordance with ASTM C1723 (2016), for seawater and freshwater pastes at Days 3 and 28 following mixing. Three analysis techniques were utilized (Winter 2012):

- Secondary electron (SE) imaging: in which the secondary electrons (generated as a result of the collision with the passing electron beam) were detected. This provides information about the morphology of the specimen's surface, and therefore, the specimens used in this technique were surface-fractured.

- Backscattered electron (BSE) imaging: in which the backscattered electrons were detected. BSE imaging provides a general indication of the atomic distribution using the discrepancy in the surface brightness. In accordance with ASTM C1723 (2016), the specimens analyzed by BSE imaging had a polished surface.
- Energy-dispersive X-ray microanalysis (EDX): in which the X-rays (produced as a result of the collision with the projected electron beam) were detected. Analyzing the resulting X-ray spectra is regarded as a useful tool to identify the chemical composition.

3 RESULTS AND DISCUSSION

3.1 Early-Age Microstructure

Figure 1 shows the difference in BSE images between freshwater and seawater pastes at Day 3 following mixing. From a qualitative viewpoint, seawater paste generally showed a more densified microstructure as compared to that of the freshwater counterpart. In the case of freshwater paste, it was observed that pores (black-colored) and anhydrous cement (white-colored) occupy a larger area as compared to that of the seawater-mixed counterpart. Likewise, the higher early-age strength of seawater paste can be evidenced by comparing the SE images of both 3-day-aged pastes (Figure 2). By observing the morphological behavior, it can be realized that the C-S-H needles (Franus *et al.* 2015) were less densified and more distributed in the freshwater paste (Figure 2-a); whereas a more solid microstructure can be observed in case of seawater paste (Figure 2-b). Such observations may explain the relatively higher early-strength performance of seawater concrete as reported in previous studies (Kaushik and Islam 1995, Nishida *et al.* 2013, Wegian 2010, Xiao *et al.* 2017). The higher early-age strength of seawater concrete can be attributed to the lower porosity due to the acceleration of cement hydration (Kaushik and Islam 1995). It is also suggested that ettringite and gypsum crystals fill in the voids in the seawater paste and thus further densify the microstructure (Katano *et al.* 2012).

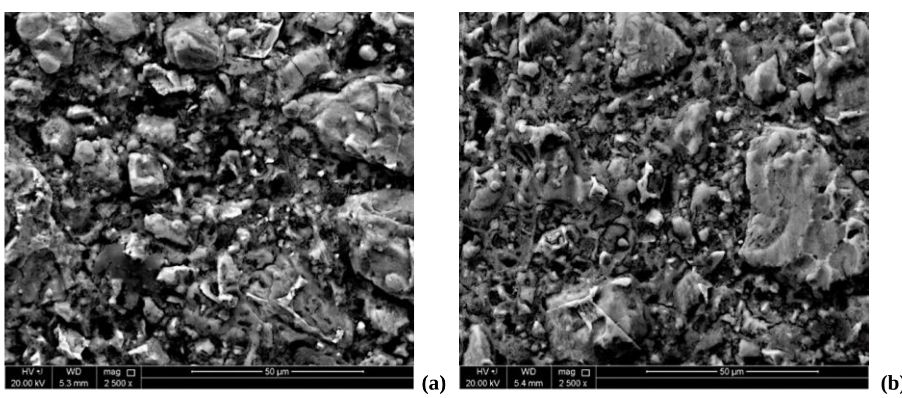

Figure 1. BSE images for (a) freshwater paste and (b) seawater paste at Day 3.

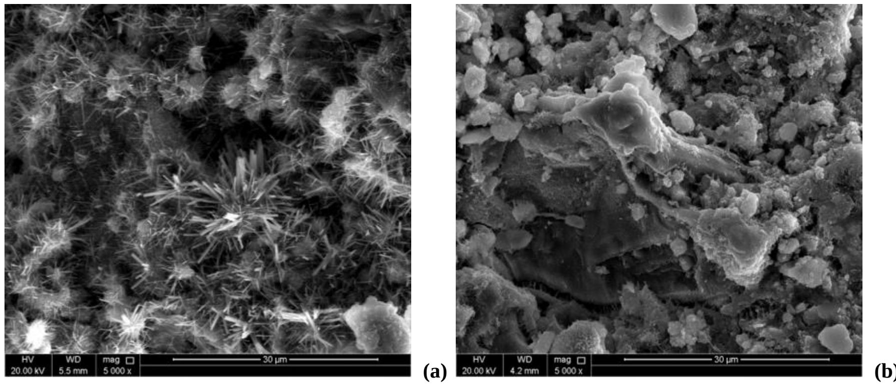

Figure 2. SE images for (a) freshwater paste and (b) seawater paste at Day 3.

3.2 Later-Age Microstructure

Figure 3 shows the BSE images for both pastes at Day 28 following mixing. As intuitively expected, the microstructure of the freshwater and seawater pastes at later ages was more densified than that of the early-age pastes (in Figure 1). The microstructure solidness of seawater and freshwater pastes, however, appeared to be the same when observed through the lens of Figure 3. With a more in-depth insight (i.e., SE imaging accompanied by EDX microanalysis), one can observe the formation of salt impurities in seawater paste (see Figure 4), that are most likely to be gypsum as shown from the EDX and also suggested by Weerdt and Justnes (2015). It is suggested that part of the calcium in the pore solution reacted with the sulfate ions (that are abundant in seawater) to form such phases. In this mechanism, magnesium sulfates ($MgSO_4$) in seawater react with calcium hydroxide ($Ca(OH)_2$) in the pore solution to form soluble magnesium hydroxide ($Mg(OH)_2$) and gypsum ($CaSO_4.2H_2O$), yielding an expansive crystallization pressure that decreases concrete strength (Wegian 2010). This can be regarded as a possible explanation for the slight reduction in the strength performance of seawater mature concrete as compared to that of freshwater-mixed counterpart (Nishida *et al.* 2013, Xiao *et al.* 2017).

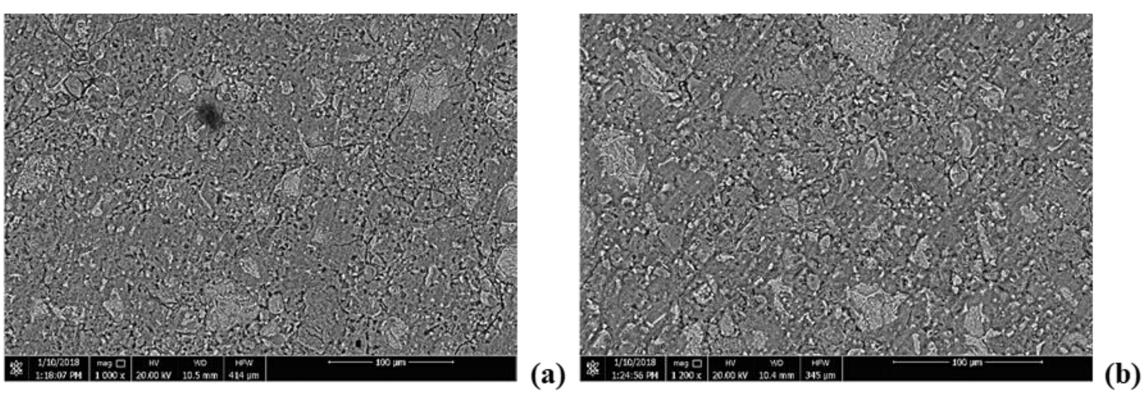

Figure 3. BSE images for (a) freshwater paste and (b) seawater paste at Day 28.

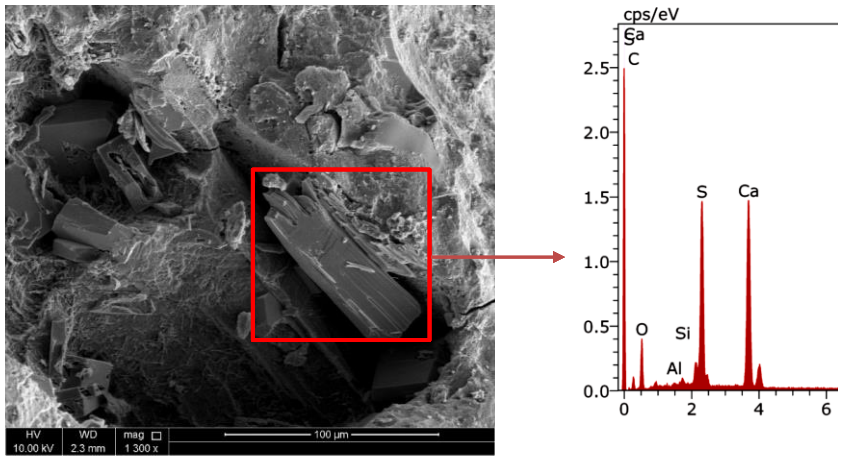

Figure 4. Crystallization of salt impurities in seawater paste.

4 CONCLUSION

This paper aimed at investigating the difference in the microstructure between seawater and freshwater cement pastes. To achieve this, scanning electron microscopy was utilized as an analytical technique to study the microstructure of both pastes using secondary electron imaging, back-scattered electron imaging, and energy dispersive X-ray microanalysis. Each paste was observed at Day 3 and Day 28 following mixing. Based on the study results, the following conclusions have been drawn:

- The more densified microstructure was observed in seawater paste at early ages as compared to that of the freshwater counterpart. This explains the relatively higher early-strength performance of seawater concrete (i.e., within 5% higher as of 14 days following mixing) as reported in the literature.
- At later ages, the microstructure was almost similar for the two cement pastes. However, salt impurities were observed in seawater paste as a result of seawater ions. Such phases can be regarded as a possible explanation to the slightly inferior strength performance of seawater concrete at later ages (i.e., within 7–15% lower after 28 days or later) as reported in the literature.

Finally, it should be emphasized that, given its high contents of chloride, the use of seawater in concrete mixtures is deemed most practical in concrete structures with non-reinforced applications or with the use of non-corrosive reinforcement (e.g., FRP).

Acknowledgments

This paper was made possible by the NPRP grant # NPRP 9-110-2-052 from the Qatar National Research Fund (a member of Qatar Foundation). The findings achieved herein solely the responsibility of the authors. Special thanks are due to Readymix Qatar (as a part of LafargeHolcim) for providing the expertise that greatly assists the authors in their research.

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