

Effect of Seawater on the Hydration of Tricalcium Silicate

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ABSTRACT

Coastal cities like Hong Kong rely heavily on their coastal and marine infrastructure for social-economic development. A major challenge for marine infrastructure is steel corrosion, which is the main cause for infrastructure deterioration. Also, fresh water is a scarce resource for some remote islands, and to meet the water requirement for concrete preparation in these regions, seawater is increasingly being considered as an alternative which would inevitable aggravate the deterioration problem due to steel corrosion. Up to now, a number of studies have focused on the effects of seawater on the workability, mechanical strength and durability (in particular corrosion of steel reinforcement) of cement pastes and reinforced concrete. However, the understanding on the influence of seawater on the composition and microstructure of cement hydration products is limited. This paper presents a preliminary study on the effects of individual salt components of seawater on the hydration process of C_3S . The microstructure changes of the hydration products were also studied. The mechanism of the acceleration effect is analyzed. Na^+ and Mg^{2+} can affect the dissolution of C_3S and the participation of the hydration products. For the later age, Mg^{2+} can substitute part of Ca^{2+} and change the composition of the final reaction products.

INTRODUCTION

Cement and concrete are most-used construction materials in the world, and about 4.1 billion tonnes of cement was produced worldwide in the year 2017[1]. IEA's report shows that cement consumption is expected to continually increase in foreseeable future[2]. Freshwater is still the key constituent for concrete mixing, and it is estimated that about 250 - 300 L mixing water is needed for the preparation of 1 m³ concrete, which means a large quantity of freshwater is required. However, in some places of the world, the shortage of freshwater has always been an important issue, such as in the Middle East, North Africa and some remote islands[3]. About 71% of the earth's surface is covered by water, but about 96.5% is seawater.[4, 5] So, it is of great interest to assess whether seawater can be used to substitute freshwater as an alternative mixing water for concrete.

In the past, the application of seawater in construction is prohibited due to its deleterious effect on the properties of steel bars embedded in concrete as the abundant chloride ions (Cl^-) contribute to the corrosion of steel bars[6-8]. However, with the development of fiber reinforced polymer (FRP) concrete, the adoption of seawater as a mixing water seems to be possible, since the Cl^- content at seawater level has limited effect on FRP composites[9-12]. Many past studies focused on the effects of seawater on the workability, mechanical strength and durability (in particular corrosion of steel reinforcement) of cement pastes and reinforced concrete. However, the understanding on the influence of seawater on the composition and microstructure of cement hydration products is limited.

MATERIALS AND METHODS

The elemental and crystalline phase compositions of C₃S used in this study are shown in Table 1. The prepared simulated seawater was based on the specifications of ASTM D1141-98. Also, NaCl (NC), MgCl₂ (MC), and Na₂SO₄ (NS) solutions with a concentration of 0.48 M, 0.055 M and 0.029 M respectively were prepared.

Table 1 Oxide and crystalline phase compositions of raw material

Composition	wt.%
MgO	0.0866
Al ₂ O ₃	0.912
SiO ₂	26.4
P ₂ O ₅	0.114
SO ₃	0.0234
K ₂ O	0.0473
CaO	72.4
Fe ₂ O ₃	0.0224
SrO	0.0142
ZrO ₂	0.0238
Alite-M	8.2
Alite-T	81.1
B-C ₂ S	10.7

C₃S was mixed evenly with different types of single salt solutions of the simulated seawater at W/C ratio of 10 [20]. Samples are sealed in plastic bottles and cured at 20 °C for 6 h, 12 h, 1 d, 3 d, 7 d, 14 d, and 28 d. At the desired curing age, the solid phase was separated from the solutions by 0.45 μm filter papers. The solid phase was immersed in 50 mL isopropanol and the solution phase was acidified after pH measurement for ICP tests [21, 22]. Isothermal calorimetry test was conducted to determine the heat evolution patterns of the different mixees. Powder samples were inter-ground with 20 wt.% internal standards (α -Al₂O₃) for characterization by X-ray diffraction (XRD).

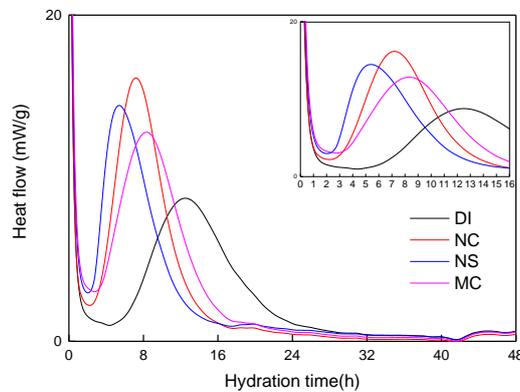


Fig. 1. Calorimetry tests results

The calorimetry test results (Fig. 1) show that the hydration process of C_3S was accelerated by the addition of NC, NS and MC solutions when compared with the reference samples prepared with deionized water (DI). The addition of single salt shortened the induction period and led to a higher rate of hydration in the acceleration period. NS induced the most significant acceleration effect followed by NC and MC.

The variation of different ions in solution are shown in Fig. 2 and Fig.3. Initially, the concentration of Ca^{2+} in NC and NS solutions increased and were higher than that of the reference group. Then the concentration decreased to a stable level similar to the reference group. The concentration of Ca^{2+} increased in the MC sample continually before 1 d, and the final concentration was higher than that of the reference group. Na^+ concentrations in NC and NS solutions showed the reverse trend. These results are consistent with the calorimetry test results in which Na^+ and Mg^{2+} tended to react with the silicate ions released by the congruent dissolution of C_3S [27], lowering the concentration of silicate ions and accelerating the dissolution of C_3S . That caused the increase of Ca^{2+} and the decrease of Na^+ and Mg^{2+} concentrations. When the concentration of Ca^{2+} reached a limiting value, C-S-H and CH began to nucleate and grow, and the concentration of Ca^{2+} decreased. Since C-S-H is more insoluble than sodium silicate, Na^+ was replaced by Ca^{2+} and the concentration of Na^+ increased. Mg^{2+} was precipitated with the silicate ions initially [6], and there was no big difference at the later age.

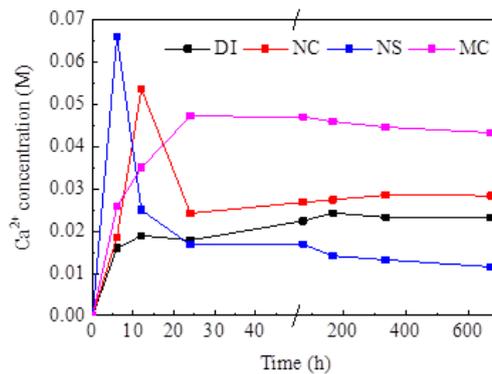


Fig. 2 Concentration of Ca^{2+} in solution

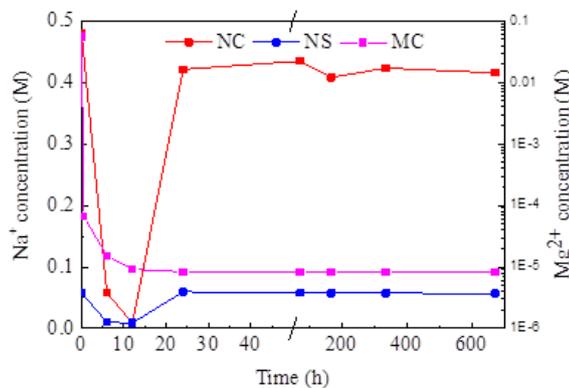


Fig. 3. Concentrations of Na^+ and Mg^{2+} in solution

The evolution of the crystalline phases of C_3S hydration in different single salt solutions was studied over a period of one month. The phases were primarily identified and analyzed by X-ray diffraction and quantified by the Rietveld method (Fig. 4). The XRD results of the 28 d samples show besides the conventional portlandite that there was no new crystalline phase produced except for the MC group, where part of Mg^{2+} precipitated with OH^- to form brucite. In general, the hydration rate of C_3S was enhanced with the addition of the single salt solutions compared with the reference group within one day, and this was no big difference at 28 d. At 28 d, over 95 wt.% C_3S was consumed. Within 1 d, NC and MC had more significant effects on the hydration rate than that of NS. After the first 6 h, over 70 wt.% of C_3S was hydrated for the NC group, and that for NS and MC and the reference groups were 47 wt.%, 49 wt.% and 29 wt.% respectively. This was consistent with the calorimetry test results.

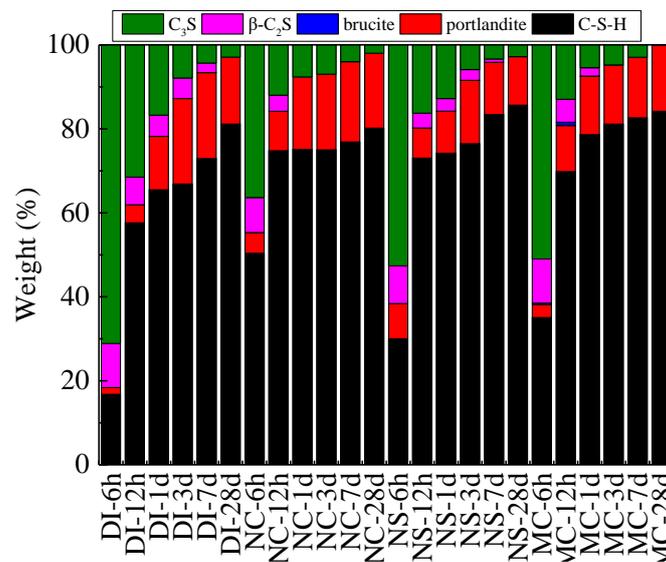


Fig. 4. Phase compositions determined by XRD-Rietveld method

CONCLUSION

C_3S was hydrated in four single salts solutions (DI, NC, NS, MC) of the simulated seawater to reveal the hydration mechanisms. Based on the results of this study, the following conclusions can be drawn: the incorporation of the single salts of the simulated seawater accelerates the hydration of C_3S . The induction period is shortened and more C_3S is dissolved in solution in a short time period due to the presence of Na^+ and Mg^{2+} , which tend to combine with silicate ions released from the C_3S . That can contribute to the enhancement of the dissolution of C_3S , and more Ca^{2+} would be produced in a short time period and the oversaturation of $Ca(OH)_2$ and C-S-H is reached at an early age.

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