Effect of Phaeodactylum Tricornutum in Seawater on the Hydration of Blended Cement Pastes

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Abstract: Seawater can be used as mixing water for concrete with no steel reinforcement in some areas with difficult access to fresh water. Diatoms such as Phaeodactylum tricornutum are among the most abundant micro-organisms living in seawater, and they could be unavoidable when collecting seawater. In fact, diatoms can provide bio-SiO$_2$ and bio-CaCO$_3$ sources, namely amorphous nano-SiO$_2$ and crystallised nano-CaCO$_3$, which could be beneficial to cement hydration. Thus, the effects of different Phaeodactylum tricornutum concentrations (0%, 2.5% and 5% by weight of suspension of seawater and diatoms) in seawater on cement hydration in ordinary Portland cement (OPC) mixes (100% OPC) and ground granulated blast-furnace slag (GGBS) mixes (70% OPC + 30% GGBS) were investigated through tests of compressive strength, XRD, DTG–DTA and SEM. The results show that diatoms accelerated cement hydration by providing the nucleus for C-S-H structure and contributed pozzolanic reactions by amorphous nano-SiO$_2$ and nano-CaCO$_3$. The accelerated cement hydration was also confirmed by the fact that more Ca(OH)$_2$ was formed in cement pastes with diatoms. However, it has also been found that diatoms decreased the compressive strength of cement pastes by leaving more weak bonds between the C-S-H structure, which was considered to be caused by the organic parts and the micron gap formed in diatoms. When comparing an OPC paste mix with 5% diatoms to a blank OPC paste, the reduction in compressive strength at 28 days can reach a maximum of 50.1%. The ability to provide bridging effects between C-S-H particles in GGBS paste was discovered to depend on the development of additional ettringite. This resulted in a 7.6% loss in compressive strength after 28 days in a GGBS paste with 5% diatoms.

Keywords: diatom; cement hydration; amorphous nano-SiO$_2$; strength; microstructure

1. Introduction

In some areas, such as the UAE in the Middle East, with large areas of desert but adjacent to the sea, the use of seawater in plain concrete is unavoidable [1–11]. Recent studies [1,2] have reported that the application of seawater as mixing water in cementitious materials was beneficial for concrete strength development because of the accelerated hydration of cement caused by the salts in seawater [12], and an increase at even above 50% on the compressive strength of ordinary Portland cement (OPC) paste was reported by Wang et al. [1,2]. However, some previous studies showed a reduction in compressive strength when seawater was used as mixing water [12,13]. These conflicts could be caused by the different seawaters used, such as seawater that was filtered through 5 µm by Wang et al. [1,2], but some researchers [12,14] may use unfiltered seawater because filtration steps
take more time and thus increase costs. Impurities such as micro-organisms in seawater could decrease the strength of cementitious materials.

Many micro-organisms, such as diatoms, exist abundantly in seawater and cannot be avoided when pumping water from the sea directly. Locally accumulated diatoms in seawater could exceed 5% by weight of seawater. Thus, the effects of impurities such as micro-organisms on the physical properties of cementitious materials need to be investigated. For simplicity, one of the most abundant micro-organisms in seawater, the diatom, was considered in this study. It is known that diatoms are rich in amorphous nano-SiO$_2$ [15–20], which could contribute to the hydration of cement. Nano-SiO$_2$ particles [21–27] could increase the compressive strength of concrete by increasing compactness and providing the nucleus for C-S-H. However, the use of diatoms in seawater also has drawbacks, such as high water demand [28] and a sudden decrease in compressive strength with an increase in dosages [29]. Thus, the substitution quantities of diatoms are generally limited to 10% without compromising strength [28,30]. To the best of the authors’ knowledge, no research has ever been conducted on how diatoms affect the hydration of blended cement paste. Thus, the effect of different concentrations of diatoms in seawater (0%, 2.5% and 5% by weight of suspension with seawater and diatoms) on the compressive strength, hydration products and microstructure of OPC and blended cement pastes was investigated. Two types of cement (100% OPC, 70% OPC + 30% GGBS) were considered, to obtain the effect of diatoms in different types of cementitious materials. In this study, the high concentrations of diatoms (2.5% and 5% by weight of seawater and diatoms) were used in order to obtain an obvious effect of the diatoms. Mechanisms of diatoms on cement hydration were analysed through XRD, DTG-DTA and SEM results.

2. Materials and Methods
2.1. Materials
2.1.1. Diatoms

Figure 1a shows the common diatoms contained in seawater (used as mixing water) for the cementitious materials in this study. The name of the diatom is Phaeodactylum tricornutum (strain CCAP 1055/1) (CCAP: the culture collection of algae and protozoa). It can be seen that there are two shapes of this diatom, which is because of the different Si contents in their bodies [15,16]. Diatoms were ground into powder using a pestle and mortar. The powder was then passed through a sieve of 75 µm. XRD patterns of diatoms were collected using a Bruker D8 powder diffractometer (Bruker, Karlsruhe, Germany) with scanning angles (2θ) ranging from 5° to 95° at a rate of 0.3 s/step and 0.02°/step using a CuKα radiation source (λ = 1.5418 Å) at 40 kV and 40 mA. Figure 1b shows the XRD patterns of a diatom powder sample, and it can be seen that there are a large number of amorphous nano-SiO$_2$ particles at about 20–25 degrees and obvious peaks of well-crystallised nano-CaCO$_3$ and nano-Mg(OH)$_2$. Figure 1c shows the micromorphology of a raw diatom under SEM, which exhibited a rougher and more irregular structure. The diatom powder was gold-coated and then observed under high-vacuum condition using a JSM7401 field emission scanning electron microscope (JEOL, Eching b., München, Germany).
Figure 1. Characterisation of diatoms: (a) Observation of raw diatoms (P. tricornutum) under optical microscopy; XRD result (b) and SEM image (c) of diatom powder.

2.1.2. OPC and GGBS

The chemical compositions of OPC (type 1, conforming to ASTM C150M) and GGBS from XRF are shown in Table 1. The results show that GGBS has a much higher content of aluminium phases (Al$_2$O$_3$) than OPC and a lower content of CaO.
Table 1. Chemical composition of OPC and GGBS (%).

| Composition | CaO | SiO₂ | Al₂O₃ | Fe₂O₃ | SO₃ | MgO | K₂O | Na₂O | LOI |
|-------------|-----|------|-------|-------|-----|-----|-----|------|-----|
| OPC         | 63.02 | 18.97 | 5.32  | 4.26  | 3.01 | 1.56 | 0.54 | 0.29  | 3.03 |
| GGBS        | 34.65 | 34.33 | 16.68 | 1.73  | 1.79 | 7.27 | 0.33 | 0.25  | 2.97 |

2.1.3. Seawater

Seawater from a local beach was collected and used as mixing water for the cementitious materials in this study. Table 2 shows the ion concentration of seawater by ICP-MS after filtration through 5 µm apertures.

Table 2. Ion concentration of seawater.

| Ion       | Cl⁻ | Na⁺ | Mg²⁺ | SO₄²⁻ | K⁺ | Ca²⁺ |
|-----------|-----|-----|------|-------|----|------|
| Concentration (g/L) | 19.67 | 11.98 | 2.13 | 2.06 | 0.45 | 0.40 |

2.2. Mix Proportions and Preparation of Test Samples

The mix design of the samples is shown in Table 3. The effect of diatoms on the hydration of cement paste was considered from three levels of diatoms (0%, 2.5% and 5.0%) and two types of cementitious materials (OPC and GGBS mixes). OPC mixes contained 100% OPC only, and GGBS mixes contained 70% OPC + 30% GGBS. The wt.% of diatoms in seawater is the dry weight of diatoms under 60 °C for 24 h to the weight of the mixed suspension of seawater and diatoms. The different concentrations of diatoms were adjusted by adding different amounts of the filtered seawater.

Table 3. Mix proportions.

| Mix ID | w/b | OPC (wt.%) | GGBS (wt.%) | Diatom (wt.%) |
|--------|-----|------------|-------------|---------------|
| OPC    | 0.4 | 100        | 0           | 0             |
| OPC + 2.5% Diatom | 0.4 | 100        | 0           | 2.5           |
| OPC + 5% Diatom | 0.4 | 100        | 0           | 5.0           |
| GGBS   | 0.4 | 70         | 30          | 0             |
| GGBS + 2.5% Diatom | 0.4 | 70         | 30          | 2.5           |
| GGBS + 5% Diatom | 0.4 | 70         | 30          | 5.0           |

The mixing procedure was: the OPC powder with or without GGBS was firstly mixed evenly in the mixer, and then, the seawater with different concentrations of diatoms was added with a mixing speed of 133 rpm for 4 min. The fresh pastes were then transferred into 50 mm cube moulds. The moulds with pastes inside were vibrated for 10 s and then transferred into a standard curing chamber (20 °C, R.H. 97%). All samples were demoulded after 24 h and returned to the standard curing chamber until further tests.

2.3. Test Methods

2.3.1. Compressive Strength

After curing for 1, 7 and 28 days in the standard curing chamber, the cubic samples were taken out for compressive strength tests. The tests were conducted in a displacement-controlled mode at a speed of 0.02 mm/s with an MTS machine (MTS Criterion 43, Mechanical Testing & Simulation, Eden Prairie, MN, USA). Three samples were tested for each group.

2.3.2. XRD

The grinding steps of hardened pastes were consistent with those of diatoms. One gram of powder was used for XRD measurement each time. A Rigaku SmartLab XRD machine (Rigaku, Tokyo, Japan) was used. The working voltage was 40 kV, and the current was 150 mA. The scanning was from 5° to 70°, and the scanning rate was 10°/min.
2.3.3. DTG/DTA

The powder samples prepared using the method above were also used for DTG/DTA measurements (HCT-3, Henven Scientific Instrument Factory, Beijing, China). The samples were heated from 25 to 960 °C at a rate of 10 °C/min in a N₂ environment. Samples were stabilised for 20 min in the chamber before the measurements started.

2.3.4. SEM

Selected representative cement paste samples from the inside part of specimens were firstly gold-coated and then observed under high-vacuum condition using a Merlin Compact Field Emission SEM machine (Merlin Compact, Carl Zeiss NTS GmbH, Jena, Germany). The analyses of various morphologies were conducted at 20 kV with a 10 mm working distance.

3. Results and Discussions

3.1. Compressive Strength

Figure 2 shows the results on compressive strength of all mixes after standard curing for 1, 7 and 28 days. It can be seen that the effect of diatoms on cement hydration is different in the different mixes, and it is affected by different concentrations of diatoms in seawater and different cementitious materials. At 1 day, the effect of diatom concentration on the change of compressive strength is not obvious in both OPC and GGBS mixes, and there is only a slight decrease in compressive strength with increasing diatom concentration. However, at 7 and 28 days, the effect of diatom concentration on compressive strength became significant, especially in OPC mixes. In OPC mixes, with the increasing diatom concentrations from 0% to 2.5% and 5%, the decrease in compressive strength was 24.5% and 49.1% at 7 days, and 21.0% and 50.1% at 28 days. In GGBS mixes, with the same increasing diatom concentrations from 0% to 2.5% and 5%, the decrease in compressive strength was 5.2% and 8.6% at 7 days, and only 2.2% and 7.6% at 28 days. It is interesting to see the deleterious effect of diatom on strength development was not as significant in GGBS mixes as in OPC mixes. GGBS mixes can more effectively resist the adverse effects of diatoms on the compressive strength of paste than OPC mixes. From the chemical compositions shown in Table 3, the aluminium phases in GGBS are much higher than in OPC, so the existence of amorphous nano-SiO₂ in the diatoms [17–20] could facilitate additional reaction with the aluminium phases by forming more ettringite in GGBS mixes [31–35] compared to that in OPC mixes, by accelerating the hydration process and providing nucleus sites. The related mechanisms are discussed through the XRD, DTG/DTA and SEM results.

![Figure 2. Compressive strength results of different samples at ages of 1, 7 and 28 days.](image-url)
3.2. XRD Results

Figure 3 shows the diffractograms of the crystals identified by XRD in different samples after curing for 1 and 28 days. The relative peak heights can be related to the Y-axis values. It can be seen that the results in OPC mixes and GGBS mixes are different. The peak heights of Ca(OH)$_2$ in OPC mixes are generally higher than those in GGBS mixes at both 1 and 28 days, which is due to the consumption of Ca(OH)$_2$ produced by OPC hydration as an alkali activator of GGBS.

It is noted that there are obvious peaks of Friedel’s salt in all OPC and GGBS mixes with or without diatoms. The existence of high amounts of chlorides provided the reaction to form Friedel’s salt in cement pastes [1,2,7,8]. At 1 day (Figure 3a), the effect of different diatom concentrations on the peak heights and peak areas of Ca(OH)$_2$ was not obvious. At 28 days (Figure 3b), in both GGBS and OPC mixes, the peak heights and peak areas of Ca(OH)$_2$ increased gradually with increasing diatom concentrations from 0% to 2.5% and 5%. This could indicate accelerated hydration of C$_3$S by the existence of amorphous nao-SiO$_2$ in the diatoms, to some extent. Figure 3 also shows that the peak heights and peak areas of ettringite in GGBS mixes are higher than in OPC mixes, indicating there could be more ettringite in GGBS mixes. This is caused by the higher amounts of aluminium phases in GGBS than OPC, as shown in Table 1.
Figure 3. XRD results of different mixes: (a) 1 day, (b) 28 days.

3.3. DTG/DTA Results

Figure 4 shows the effect of different diatom concentrations on the DTG results of the OPC and GGBS mixes after curing for 1 and 28 days. It can be seen that the main peaks correspond to ettringite (80–100 °C [36,37]), Friedel’s salt (120, 160 and 360 °C [1,2]), Ca(OH)₂ (450 °C [38,39]) and CaCO₃ (680–720 °C [21,38]), which agrees well with the crystals identified in XRD results (Figure 3). At 1 day, the peaks of ettringite and Ca(OH)₂ in OPC mixes are higher than those in GGBS mixes in Figure 3 because the GGBS has a lower content of CaO and SO₃ than OPC (from Table 1). At 28 days, it is interesting to see that the peak of ettringite in mix OPC + 5% diatom is much lower than that in mix OPC + 2.5% diatom—this could indicate that the amorphous nano-SiO₂ in diatoms may facilitate the transformation of some ettringite to Friedel’s salt, which could be evidenced by the higher DTA peak (Figure 5) in the mix OPC + 5% diatom than that in the mix OPC + 2.5% diatom. The fluctuations in Figure 4 at the local range could be caused by the minimal
impurities from the reaction between the trace amounts of other salts (except NaCl) and the OPC minerals or the organic parts in diatoms.

Figure 5 shows the DTA results caused by different diatom concentrations in OPC and GGBS mixes. The corresponding changes in each peak have been marked in the figure, and the differences in each peak can be related to the changes illustrated in Figure 4. The results show that the most obvious energy change occurs at the temperature range of Ca(OH)$_2$. This agrees well with the DTG results. The difference of DTA results between OPC and GGBS mixes is found to be higher than the difference caused by different diatom concentrations. The DTA peaks of CaCO$_3$ are not obvious in all mixes, indicating the energy change caused by the decomposition of CaCO$_3$ in cement pastes is not significant at this stage. Compared to the DTG results, the DTA results could not provide accurate information on the existence of CaCO$_3$ in cement pastes. Additionally, it was discovered that peaks in the DTA at the sites for ettringite and Ca(OH)$_2$ could not accurately compare the percentages of these phases.

3.4. Microstructure Analysis

Figures 6 and 7 show the microstructure under SEM observations of different OPC and GGBS mixes with 2.5% and 5% diatoms after standard curing for 1 and 28 days. The
existence of ettringite (AFT), Ca(OH)$_2$ and Friedel’s salt can be seen in different mixes. It is found that ettringite is more common than Friedel’s salt in the four cement pastes, indicating a higher amount of ettringite was formed than Friedel’s salt. This agrees well with the XRD results. It can be clearly seen that, in both OPC and GGBS mixes with 5% diatoms, there are two types of C-S-H [1,40,41], namely low-density C-S-H (LD C-S-H) and high-density C-S-H (HD C-S-H).

By comparing the mixes with 2.5% and 5% diatoms at 1 day in Figure 6, it can be found that, in both OPC and GGBS mixes, the paste with a higher concentration of diatoms (5%) had more clustered nuclear-shaped HD C-S-H. This indicates that the existence of amorphous nano-SiO$_2$ in diatoms [15–18] and nano-CaCO$_3$ [37,38] increased the nuclear sites for the formation of the HD C-S-H during the hydration process in cement paste within the early age (1 day). However, the higher amounts of diatoms contain a large amount of amorphous silica, which has high pozzolanic activity and will reduce the compressive strength [42–44] and could also introduce more weak parts in cement pastes. They are mainly caused by two factors, one of which is the organic carbon and moisture present in diatoms, which is evidenced by the disconnection between different piles of clustered nuclear-shaped HD C-S-H in both OPC and GGBS mixes [45–47]. The other is the micron gap formed by the diatoms themselves, which can be obtained by observing the microstructure visually. These agree well with the previously reported results on compressive strength which showed that diatoms in seawater caused a reduction in the compressive strength of cement paste in both OPC and GGBS mixes, especially after 1 day. In GGBS mixes, there is more ettringite formed [48–50], which could provide more bridging effects between disconnected C-S-H particles [51,52] and thus could partly compensate for the strength loss caused by organic parts in diatoms and the micron gap formed by the diatoms. This explains why the GGBS mixes had a lower rate of strength loss with increasing diatom concentration than the OPC mixes, as in Figure 2.

Figure 6. Microstructure observations of different paste samples under SEM at 1D: (a) OPC + 2.5% diatom, (b) OPC + 5% diatom, (c) GGBS + 2.5% diatom, (d) GGBS + 5% diatom.
4. Conclusions

The effect of diatom concentrations (0%, 2.5% and 5% by weight of suspension of seawater and diatoms) on the compressive strength, hydration products and microstructure of OPC and GGBS cement pastes was investigated, and the following conclusions can be drawn:

Diatoms in seawater can accelerate the hydration of cement and produce more Ca(OH)$_2$ and C-S-H. The microstructure revealed by SEM indicates that the amorphous nano-SiO$_2$ and nano-CaCO$_3$ in diatoms could provide the nucleus for C-S-H, and the amorphous nano-SiO$_2$ also contributes to the pozzolanic reaction in OPC and blended cement paste and thus promotes the hydration of OPC and blended cement.

Although diatoms can accelerate cement hydration, diatoms in seawater are not beneficial for strength development of cement paste, especially after 1 day. This is caused by the organic parts in diatoms and the micron gap formed by the diatoms, which provide weak bonds between C-S-H particles accumulated around the nano-SiO$_2$, as evidenced by the SEM results.

The reduction in compressive strength of cement paste with 5% diatoms can be up to 50.1% in OPC mixes, and this reduction is much lower in GGBS mixes, with only up to 8.6%. This difference was thought to be due to the fact that more ettringites formed in GGBS mixes than in OPC mixes, and the ettringites in the early ages provide bridging effects between separated C-S-H particles, thus partly compensating for the detrimental effects of the weak bonds between C-S-H particles in GGBS mixes.

Future research is suggested to investigate the long-term performance of concrete mixed with seawater and diatoms, especially on the GGBS mixes. Further, the allowable maximum concentration of diatoms in seawater should be investigated and quantified. The effect of low-concentrated diatoms in seawater on concrete performance needs to be carried out.

Figure 7. Microstructure observations of different paste samples under SEM at 28D: (a) OPC + 2.5% diatom, (b) OPC + 5% diatom, (c) GGBS + 2.5% diatom, (d) GGBS + 5% diatom.
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