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Research Article

Retardation of Portland Cement Hydration with Photosynthetic Algal Biomass

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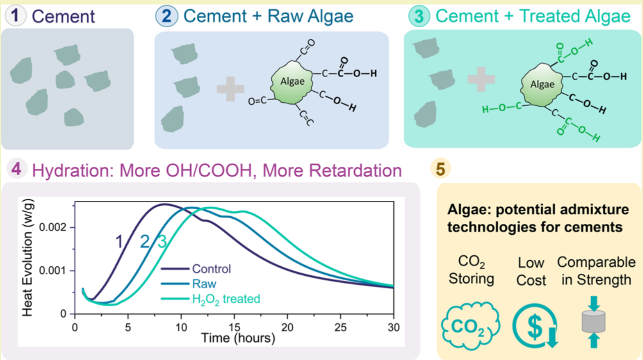
ABSTRACT: In this work, the effects of raw algal biomass on the hydration kinetics of portland cement are reported. Specifically, direct addition of 0.3%, 0.5%, 1.0%, and 3.0% photosynthetic *Chlorella* algal biomass to cement paste substantially delayed cement hydration, as indicated by 16.5%, 29.4%, 82.4%, and 812% delays in the main peak of heat evolution measured by isothermal calorimetry. Retardation was confirmed via FTIR to be mechanistically caused by the existence of −COOH and −OH functional groups in raw algae. We substantiated the observation that elimination of −COOH and −OH functional groups in the algae through heat treatment coincided with the disappearance in the retardation effect, while enhancement of these functional groups through H_2O_2 treatment induced further retardation. In addition, the effects of untreated and treated algae on the morphology, mineralogy, and compressive strength of cement pastes containing 0.5% *Chlorella* were found to be negligible. An addition of 0.5% algal biomass is estimated to cost approximately USD \$1.6−2.6/m^3 of concrete, suggesting that raw algae could be used as a renewable, cost-competitive, CO_2-storing set-retarding admixture for portland cement-based materials.



KEYWORDS: *algae, Chlorella, cement, admixture, retardation*

1. INTRODUCTION

Algae, a class of photosynthetic organisms, can be divided into two primary categories: microalgae and macroalgae.[1] Macroalgae are multicellular plants (e.g., seaweed) that can grow up to 60 m in length. Microalgae are photosynthetic unicellular microorganisms on the order of ∼1 μm in size.[2] Algal biomass is regarded as a sustainable feedstock for many emergent applications due to its rapid growth rate and high capacity for CO_2 fixation in comparison to biomass from plants.[3,4] Algae can exhibit biomass doubling times on the order of hours.[5] Photosynthetic algae are highly efficient at converting CO_2 into fixed carbon-based molecules, like sugars and other organic molecules. In fact, 1 g of dry algal biomass takes ∼1.8 g of CO_2 to produce.[5] Such algae-based CO_2 sequestration is efficient, especially when compared to that of plants (i.e., a most important photosynthetic system), which usually take years to reach their peak of CO_2 sequestration and require large areas of land.[4]

Over the past two decades, substantial research and development have led to the commercialization of many algae-based products for the pharmaceutical, cosmetic, food, agricultural, and biofuel industries.[6,7] Algae systems have also been integrated into some wastewater infrastructure applications for the express purpose of decontamination by leveraging their natural bioadsorption processes.[2,8,9] Such adsorption capability is primarily attributable to the presence of functional groups, including −COOH, −OH, $-RCOO^-$, $-HPO_4^{2-}$, and $-NH_2$, from polysaccharides and lipids in the algal biomass.[10]

The use of algae in cement and concrete research has been limited. One barrier could be that some evidence exists regarding algae-induced biodeterioration on cement and geopolymer substrates.[11,12] However, the deterioration is mainly caused by the organism's physical activity (e.g., growth) on the surface,[13] which should be of little concern for nonliving biomass incorporated as an additive into cement paste or concrete. In one related study, the extract from brown marine algae was used as a viscosity-enhancing admixture for cements by forming a transient, gel-like network of alginate chains and cement particles.[14] Algae-derived biopolymers have been used to produce hydrogels that mitigate autogenous shrinkage in cement pastes.[15] Concrete samples containing brown algae

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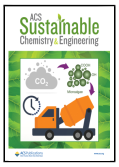

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extract exhibited comparable strength and enhanced durability in terms of chloride diffusion.[16] Additionally, researchers have shown that incorporation of thermally treated algal biochar can exhibit an ability to tailor the physical properties of cement paste and concrete, including strength and water absorption,[17] and promote carbonate formation under CO_2 curing to enhance CO_2 sequestration.[18,19]

To the authors' knowledge, no studies have yet explored the potential for untreated algae to accelerate or retard the hydration of portland cement. Algae possess functional groups such as −COOH that exhibit potential for retarding the kinetics of cement hydration,[20,21] unlike other types of biomass, including cellulosics and lignins, that exhibit fewer −COOH groups.[22] While some alginate-based biopolymers have exhibited retardation effects on portland cement hydration,[16] the biopolymers also accelerated the hydration of calcium alumina cements, because the −COOH groups adsorb calcium ions and serve as nucleation sites for the formation of calcium aluminate hydrate phases.[23] Therefore, our hypothesis was that the presence of −COOH groups in raw algal biomass could be mechanistically leveraged to delay the hydration of portland cement.

The objectives of this study were (1) to examine if untreated *Chlorella*, a common microalgae species[24] cultured at-scale and commercially available in dry powder form, would affect the hydration of portland cement and, if so, (2) to understand the mechanisms associated with such effects. *Chlorella* and its genera are among the most ubiquitous algae and are found in a multitude of aquatic, terrestrial, and aerophytic environments around the world.[25] First, untreated *Chlorella* algal biomass was found to substantially retard the hydration of portland cement. Second, a hydrogen peroxide (H_2O_2) or heat treatment was used to selectively enhance or remove the −COOH and −OH groups from the algal biomass, respectively, to explicitly elucidate the role the functional groups played in delaying cement hydration. Then, the effects of both treated and untreated *Chlorella* biomass on the microstructure, mineralogy, and strength of resultant cement pastes were measured and reported herein. Finally, the impact on the embodied carbon of typical concrete mixtures is estimated and discussed, given the CO_2 fixation of photosynthetic algae and its potential use as a set-retarding admixture in portland cement concrete.

2. MATERIALS AND EXPERIMENTAL METHODS

2.1. Materials. Commercially available Type I/II portland cement (Quikrete) that complies with ASTM C150[26] was used in this study. The chemical composition of the portland cement is shown in Table 1. *Chlorella* algae pellets from Earth Circle Organics (Las Vegas, NV) were ground with a mortar and pestle to pass through a sieve of 125 μm opening before adding into the cement pastes. Hydrogen peroxide (H_2O_2, 30%, Fisher Scientific, Waltham, MA) was also obtained and diluted for treating the *Chlorella* algae before adding it into select cement paste samples.

2.2. Sample Preparation. *2.2.1. Treatment of Algae.* One set of cement paste samples contained algae in its raw, untreated form. The second set of cement paste samples contained algae that had been exposed to a physical heat pretreatment. The ground *Chlorella* powders were heated using a Carbolite tube furnace under a 50 mL/min flow of N_2 gas. The temperature was increased from room temperature (20 °C) to 300 °C at a rate of 10 °C/min; 300 °C was chosen to ensure thermal decomposition of *Chlorella*, as was previously reported in 27. After being held at 300 °C for 1 h, the samples were then cooled at 20 °C/min to room temperature (20 °C). The third set of cement paste samples contained algae that had been exposed to chemical treatment. Ten grams of ground *Chlorella* were soaked in 200 mL of 10% H_2O_2 solution; this reaction mixture was diluted from a 30 wt % stock solution with deionized water and was stirred for 24 h. The mixture was then centrifuged with a Thermo Scientific Sorvall Legend X1R at 5000 rpm for 30 min. Once the liquid was poured out, the solid residue was mixed homogeneously with 200 mL of deionized water, and the mixture was centrifuged for 30 min. This washing process was repeated a total of three times.

Table 1. Oxide Content (wt%) of Type I/II Portland Cement Used in This Study

SiO_2	Al_2O_3	CaO	Fe_2O_3	K_2O	Na_2O	MgO	SO_3	LOI
19.7	4.38	62.0	3.33	0.76	0.19	1.38	3.32	2.96

2.2.2. Preparation of Cement Pastes. Each cement paste sample was prepared at a constant water-to-cement (w/c) ratio of 0.4. Untreated algae were added to cement paste in dosages of 0.3%, 0.5%, 1.0%, and 3.0% by weight of cement. H_2O_2-treated or heat-treated algae were added at 0.5% by weight of cement. All algae samples (raw and treated) were vacuum-dried and dosed in solid form into the cement pastes. The algae were first intermixed with cement particles before mixing with water. Cement, algae, and water were then mixed with a Caframo Ultra Speed BDC6015 overhead stirrer at 140 rpm for 30 s and subsequently mixed at 285 rpm for 2.5 min: the same mixing protocol that was adopted and reported in an earlier study.[28] In between the two speeds of the mixing procedure, materials on the edges of the mixing cup were scraped. Immediately following mixing, the cement pastes were cured at ambient conditions (approximately 30% humidity and 20 °C temperature) for 2 days and then in a sealed condition at ∼20 °C until further testing/processing at 28 days of curing. To stop the hydration for XRD tests, 1.0 g of the paste samples, upon being ground to pass through a 125-μm sieve, was soaked in 50 mL of isopropanol for 15 min.[29,30]

2.3. Hydration Kinetics of Algae-Modified Cement Pastes. Reaction kinetics of the cement pastes without and with algae were monitored at 21 °C. Freshly mixed paste (∼14 g) was placed in a glass ampule and subsequently placed into a chamber of a Thermometric TAM Air 8-Channel Isothermal Conduction Calorimeter (TA Instruments). Siliceous sand (∼14 g) was used as the reference material. The heat generated from the hydration was monitored, and the heat evolution and total cumulative heat were normalized by weight of the cement paste.

2.4. Algae Characterization. The morphology of the algae particles was examined using a Hitachi SU3500 SEM instrument. The microscope was operated between 10 and 15 kV in secondary electron imaging mode. Prior to imaging, samples were coated with a gold film of ∼10 nm under a vacuum (<0.15 mb).

Untreated and treated algae were examined through an attenuated total reflectance (ATR) Fourier-transform infrared (FTIR) instrument (ThermoScientific Nicolet iS20 FTIR). Each spectrum was an average of 32 measurements scanned from 2000 to 600 cm^{-1} at a resolution of 4 cm^{-1}.

2.5. Microstructure and Compressive Strength of Algae-Modified Cement pastes. After having understood the effects of algae on the hydration kinetics of cement pastes, the effects of algae on the morphology, mineralogy, and compressive strength of cement paste were examined.

The fracture surfaces of the hardened cement pastes without and with the addition of algae after 28 days of curing were coated with gold film and examined under SEM in the same condition for algae as described above (see Section 2.4).

A Bruker D8 Advance XRD instrument was used to characterize the mineralogy of the cement pastes after 28 days of curing. Following soaking in isopropanol to halt hydration, the ground cement paste powders were resuspended in ethanol, and this suspension was dropped onto a Si crystal zero-background plate and dried under ambient conditions. Each sample was scanned using Cu Kα X-ray radiation (wavelength 1.5406 Å) from 5 to 60° 2θ with a step size of 0.02° and a dwell time of 2 s per step. Crystalline phases were identified using Bruker DIFFRAC.EVA software and the International Center for Diffraction Data (ICDD) PDF-4 AXIOM 2019 database.[31]

Compressive strength was measured for the cement pastes without and with algae after 7 and 28 days of curing. Five cylindrical samples per test group were used in accordance with ASTM C39/C39 M,[32] a standard designed for concrete cylinder samples. For the current cement paste samples, a smaller sample size was adopted, specifically 12.5 mm in diameter and 25 mm in length. Samples were tested using an Instron Universal Testing Machine with 48.9 kN capacity at a loading rate of 0.25 ± 0.05 MPa/s.

3. RESULTS AND DISCUSSION

3.1. Algae Retards Cement Hydration.

3.1.1. Isothermal Calorimetry. Figure 1 shows the heat evolution and total cumulative heat of the cement pastes without and with untreated *Chlorella*, up to 3.0% by weight of cement. While the heat evolution for the 3.0% mixture remains low throughout the first 45 h, the curves of all other mixtures exhibit a dormant period followed by a main reaction peak characterized by an acceleration and deceleration period typical of portland cement hydration.

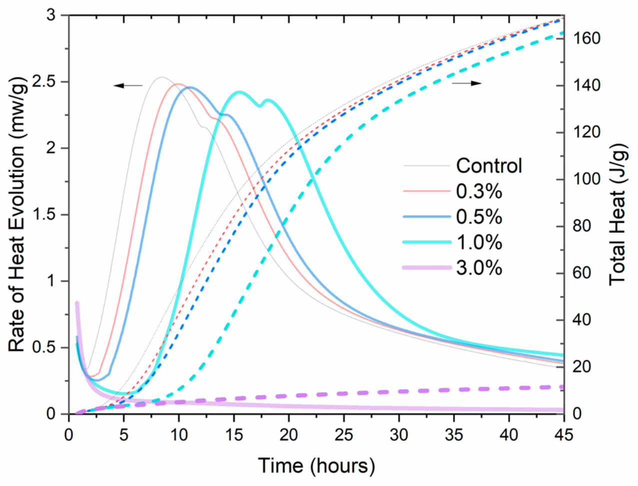

Figure 1. Rate of heat evolution and total cumulative heat for cement pastes with *Chlorella* at 0.0% (control), 0.3%, 0.5%, 1.0% and 3.0% by weight of cement. Data were normalized by total weight of cement paste.

Table 2. Peak Time of Heat Evolution and Total Heat at 40 h for Cement Pastes without and with Addition of Algae

Cement paste	Chlorella (wt % of cement)	Peak time		Cumulative heat at 40 h(J/g)
		hours	% compared to control	
No additive	0.0 (control)	8.5	NA	163
Raw algae	0.3	9.9	+16.5	162
	0.5	11.0	+29.4	161
	1.0	15.5	+82.4	155
	3.0	77.5	+811.8	1.7
H_2O_2-treated algae	0.5	12.8	+50.6	162
Heat-treated algae	0.5	8.5	0	162

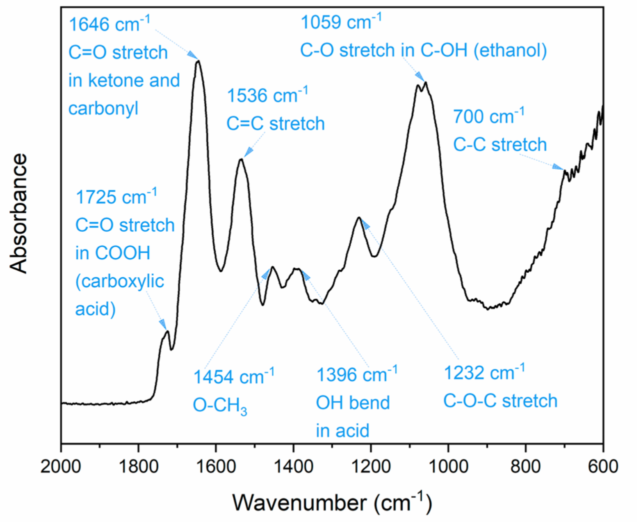

Figure 2. FTIR spectrum of the raw Chlorella showing the presence of various functional groups.

The right shift of the main reaction peak reveals substantial retardation of cement hydration via the addition of raw *Chlorella*. As summarized in Table 2, the peak time increases from 8.5 h (control cement paste) to 11.0 h (0.5% *Chlorella*) and 15.5 h (1.0% *Chlorella*), respectively. A much further delay to 77.5 h was observed for the 3.0% raw *Chlorella* paste. Correspondingly, total cumulative heat was concomitantly delayed. The 40-h heat of the control samples was 163 J/g, whereas 3.0% *Chlorella* reduced the 40-h heat to 1.7 J/g, which subsequently accelerated to 200 J/g at 160 h (data not shown).

3.1.2. Retardation Mechanism. To understand the retardation mechanisms of raw *Chlorella*, its chemical structure was examined via FTIR. Algae are well-known to possess only trace (<5%) inorganic components (e.g., Na, Ca, K).[24] Thus, our analysis focused exclusively on elucidating the role of the organic functional groups on retardation. As labeled in Figure 2, various functional groups were observed, including C=O in −COOH (1725 cm^{-1}), C=O stretch in ketone and carbonyl acid (1646 cm^{-1}), O−CH_3 (1454 cm^{-1}), OH in acid (1396 cm^{-1}), C−OH (1059 cm^{-1}), and C−C (700 cm^{-1}), the assignments of which were based on an earlier study.[33]

Of the identified functional groups, the carboxyl (−COOH) and hydroxyl (−OH) groups have been commonly found to retard cement hydration.[20,21] The addition of glycolic acid that possesses carboxyl and hydroxyl groups has been shown to substantially retard the hydration of cement. For instance, addition of 0.2% glycolic acid extended the induction period of cement paste from 1.5 to 8 h (w/c = 0.35).[20]

Mechanistically, the carboxyl and hydroxyl groups retard cement hydration via adsorption onto minerals found in cement, especially hydroxylated C_3S.[20] For instance, these functional groups from glycolic acid or calcium glycolate are hypothesized to interact with surrounding water molecules and form hydrogen bonds, which form a stable hydrogen bond network covering the surfaces of cement particles. This hypothesis is supported by experimental observations and computational simulations in other studies that showed that hydroxyl groups of calcium glycolate form a strong hydrogen bond with the surfaces of calcium hydroxide and C_3S.[20] On the basis of a series of comprehensive 2D $^{13}C-^{1}H$ and $^{29}Si-^{1}H$ NMR tests, the −OH functional groups from sucrose molecules were found to adsorb onto silanol and silicate hydration products via hydrogen bonding,[34] and the carboxylic acid was found to nonselectively adsorb onto hydrated silicates and aluminates (i.e., the hydration products of cement phases).[35] These observations reject other possible alternative mechanisms, such as the potential for hydroxycarboxylic acids to chelate calcium.[36,37]

3.2. Further Validation. To further validate if the retardation effects of *Chorella* demonstrated above were due to the presence of the −OH and −COOH functional groups, the *Chlorella* was treated to either increase or reduce the number of these groups prior to mixing with the cement pastes.

3.2.1. Treatment of Algae. One algae treatment was to heat the *Chlorella* under N_2 gas, a common process for producing biochar.[38,39] The other algae treatment was to soak it in H_2O_2 solution. To examine any changes of the −OH and −COOH groups in the algae, the chemical and physical reactions that potentially occur during treatments are reviewed, followed by the experimental characterization of the associated structural changes.

3.2.1.1. Chemical Reactions. During heat treatment, algae go through a series of chemical and physical reactions. Up to 150 °C, the primary physical reaction is the evaporation of free water. As temperature further increases, the biopolymers, namely, the proteins, lipids, and carbohydrates, in algae begin to decompose.[27] Pyrolysis between 300 and 400 °C generates CO_2, a reaction that has been attributed to the breaking and reforming of C=O and −COOH functional groups in the biopolymers,[33] as schematically depicted in Figure 3. More specifically, for algae, the emission of CO_2 above 150 °C has been attributed to the decomposition of carbohydrates between 180 and 270 °C and protein from 320 to 450 °C.[40]

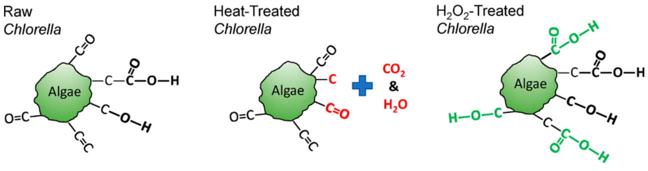

Figure 3. Schematic showing changes in the −COOH and −OH functional groups caused by the H_2O_2-treatment and heat-treatment of algae.

While H_2O_2 treatment has only previously been reported to oxidize biochar samples,[41,42] it was hypothesized that H_2O_2 would react with the raw algae biomass in a similar manner, considering that both contain the same relevant functional groups. In a biochar sample, H_2O_2 solutions (up to 30 wt %) increased the FTIR peak of −COOH (1700 cm^{-1}) but decreased that of C=C (1585 cm^{-1}), a change that occurs more substantially as H_2O_2 is more concentrated.[41] This is consistent with an increase of −COOH groups in a peanut hull-based biochar upon H_2O_2 treatment.[42] Additionally, such treatment increased the C−H peak (775 cm^{-1}), likely caused by the conversion of the C=C ring structure.[43] The hypothesized reaction was confirmed herein via FTIR, as discussed in the following section.

3.2.1.2. Structural Characterization after Treatment. In Figure 4, the FTIR spectra of both heat-treated and H_2O_2-treated *Chlorella*, together with the raw *Chlorella*, are presented. The two most substantial changes upon the treatments occur at peaks of 1729 and 1062 cm^{-1}, which are attributed to the −COOH and −OH groups, respectively. Specifically, while the H_2O_2 treatment enhanced both these peaks, the heat treatment decreased or even eliminated both of them. Such changes indicated that the −COOH and −OH groups were increased with the H_2O_2 treatment but substantially decreased with the heat treatment, an observation that aligns with the potential reactions discussed in Section 3.2.1.1.

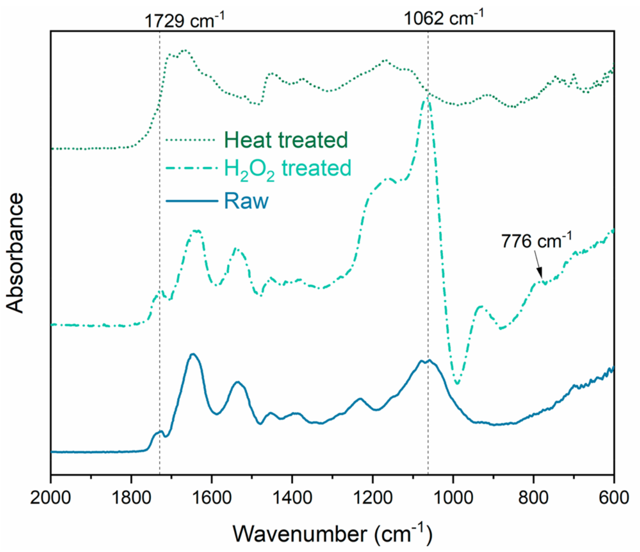

Figure 4. FTIR spectra of the raw and treated *Chlorella*.

The morphological changes of the treated versus the raw algae were further examined under SEM. As shown in Figure 5a,c, both the raw and H_2O_2-treated *Chlorella* exhibited rugged surfaces that are composed of small-sized particles/plates (roughly under 5 μm in diameter). The surface becomes smooth upon the heat treatment, as shown in Figure 5b. Such different morphology upon heat treatment (i.e., lack of small-sized particles/plates) could relate to the disappearance of the −OH and −COOH functional groups as schematically and experimentally seen in Figure 3 and Figure 4. As an additional minor point, the clean and smooth morphology of the heat-treated sample suggests the treatment is gentle, consistent with an earlier examination that a 300 °C treatment did not cause a porous and fragmented morphology as seen under higher temperatures.[44]

3.2.2. Effects of Treated Algae on Cement Hydration. The calorimetry curves of cement pastes without and with 0.5% of the *Chlorella* additives (i.e., raw, H_2O_2-treated, and heat-treated) are presented in Figure 6. The "Control" and "Raw" curves in Figure 6 are the same as curves of cement pastes with 0.0% (i.e., control) and 0.5% raw *Chlorella* presented in Figure 1. Compared to the sample with raw *Chlorella*, the H_2O_2-treated *Chlorella* further delayed the main reaction peak, specifically from 11.0 to 12.8 h, as summarized in Table 2. To the contrary, the heat-treated *Chlorella* accelerated the peak position to 8.5 h, which overlaps with the peak for the control paste. However, the total heat for all these samples remained approximately the same, for example, around 162 J/g at 40 h (as summarized in Table 2). This same total heat at a relatively later age indicated that the algae-induced retardation occurs only to delay hydration without compromising the total degree of hydration, a characteristic preferred for retarders of cementitious materials.

The discrepancy in such retardation versus acceleration is likely caused by the different structural changes induced by

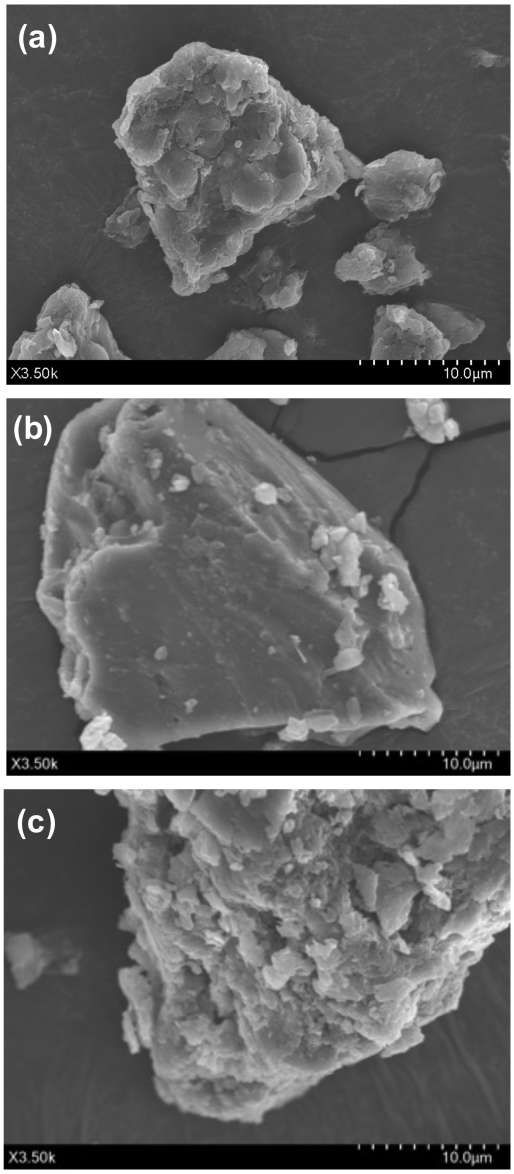

Figure 5. Morphology of the (a) raw, and (b) heat-treated, and (c) H_2O_2-treated *Chlorella*.

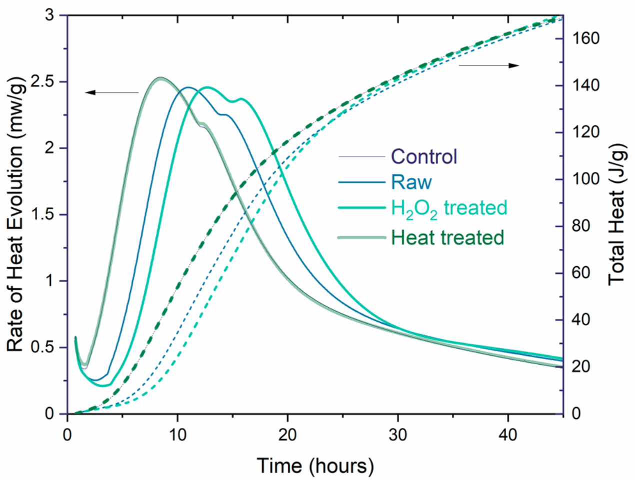

Figure 6. Rate of heat evolution and total heat for the control cement paste (i.e., without addition of algae) and those with addition of the *Chlorella* (raw, and H_2O_2-treated and heat-treated). Data were normalized by total weight of cement paste.

these treatments. The H_2O_2 treatment increased the −COOH and −OH functional groups, while the heat treatment has removed these two functional groups. Considering the capability of these groups to substantially retard the cement hydration as mechanistically discussed in Section 3.1.2, the further retardation with H_2O_2 treatment but acceleration with heat treatment provided further direct evidence that −COOH and −OH groups mechanistically govern the retardation effect of raw algae.

3.3. Microstructure and Compressive Strength of Algae-Modified Cement Paste. Considering that algae are cultivated at-scale and widely available, their strong retardation effects could potentially be exploited in engineering practice to supplant conventional set retarders. However, their addition could have detrimental effects on other microstructural and performance characteristics (e.g., mineralogy, compressive strength).

The microstructure and compressive strengths of the algae-modified cement pastes are discussed in this section. In relevance to the objective of this study (i.e., to elucidate the mechanisms of algae-induced retardation), the microstructural characteristics were qualitatively examined, which could be closely related to the chemical interaction during the retardation process. Since the heat-treated algae exhibited no retardation effects (Figure 6), only the raw and H_2O_2-treated algae-modified samples were analyzed.

Figure 7 shows the morphology of cement pastes without and with algae addition. Overall, the addition of the raw- and H_2O_2-treated *Chlorella* does not appear to alter the microstructure of the cement pastes. The control paste and pastes with raw and H_2O_2-treated algae all exhibit dense microstructures, though with some particle-like morphology (solid oval).

Figure 8 shows XRD patterns for control, raw *Chlorella*, and H_2O_2-treated *Chlorella* cement pastes after 28 days of curing. While the addition of algae delays hydration kinetics, it does not appear to alter the crystal structures of the hydration products. Lack of evident changes in peak position and intensity indicates the same types of hydrated cement phases were formed in the control, raw *Chlorella*, and H_2O_2-treated *Chlorella* cement pastes. Furthermore, no evident peak broadening or narrowing indicates no evident changes in the crystallinity of each product phase. The presence of similar hydrated phases between pastes is consistent with SEM results which show no significant change in morphology with the addition of raw or treated *Chlorella*.

The compressive strength results of the control cement paste and those with the addition of raw- and H_2O_2-treated *Chlorella* are shown in Figure 9. All pastes exhibited an increase in strength from 7 to 28 days, as expected. Algae-modified pastes exhibited comparable compressive strengths as the control paste at both 7 and 28 days. The high variability in the 7-day algae-modified samples may be attributed to early age algae-water interaction effects that are subsequently resolved at later ages, as evidenced by the more consistent 28-day data. More specifically, dry algae may rehydrate and absorb water at very early ages, thereby limiting the availability of water for cement hydration. This water could be released at later ages to support continued hydration. Such behavior is akin to internal curing

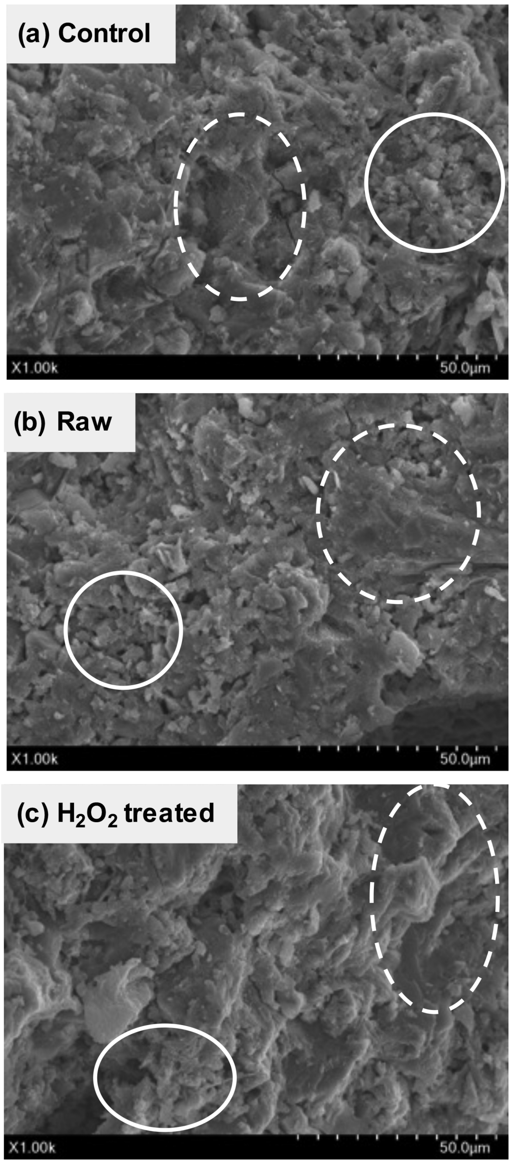

Figure 7. SEM images of (a) control cement paste and pastes with (b) raw and (c) H_2O_2-treated *Chlorella* at 0.5% by weight of cement when cured for 28 days.

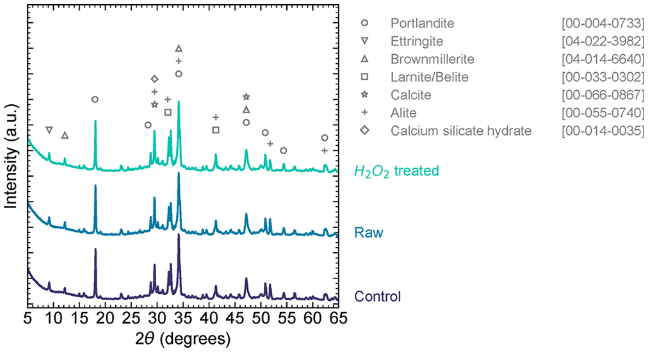

Figure 8. XRD patterns of control cement paste and pastes with raw and H_2O_2-treated *Chlorella* at 0.5% by weight of cement when cured for 28 days. PDF number is shown next to each corresponding phase.

agents, like saturated lightweight aggregates and super-absorbent polymers.[45]

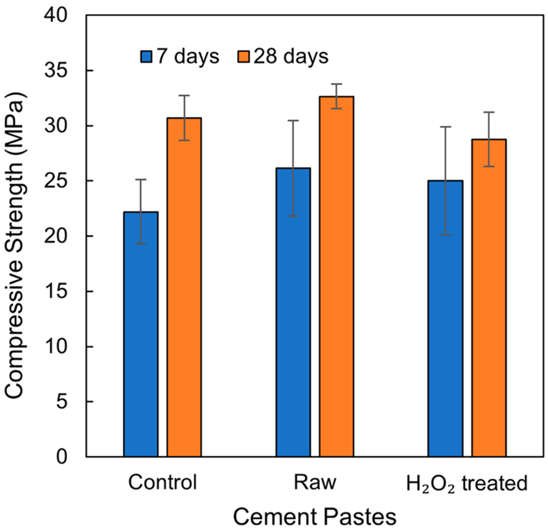

Figure 9. Compressive strength of control cement paste, and pastes with raw and H_2O_2-treated *Chlorella* at 0.5% by weight of cement when cured for 28 days.

The comparable strength is consistent with the calorimetry, SEM, and XRD results. Despite a delay of reaction at the early age, the addition of the algae exhibited similar accumulated heat at around 40 h and later (see Figure 6). The addition of algae does not induce any morphological or mineralogical changes in the cement pastes from the results of SEM (see Figure 7) and XRD (see Figure 8). Such minimum effects on strength and microstructures indicate a great potential of *Chlorella*, as a typical type of algae, to be promoted as a sustainable biobased retarder for cementitious materials.

3.4. Significance. We have demonstrated and elucidated that *Chlorella*, a typical class of algae, retards cement hydration. The addition of 1.0 wt % of algae delayed the main peak of the heat evolution by 82.4%, a degree of retardation slightly higher than that seen with 0.15 wt % of sucrose, a well-known strong retarder for cements,[46] albeit at a much higher dosage. Considering the availability and sustainability (i.e., CO_2 fixation potential) of algae, *Chlorella* and other types of algae could be used as an effective hydration retarder. Furthermore, the addition of algae was found not to affect the microstructures or the compressive strength of the cement pastes, further suggesting the potential of algae to be used as a sustainable retarder in engineering practice.

Besides serving as a retarder or a viscosity-modifying agent in the fresh state,[14] algae exhibit great potential for developing functional cementitious materials. As reviewed in our recent paper,[47] the introduction of algae, among other microorganisms, potentially equips cementitious materials with the functionality of removing heavy metals in wastewater and cleaning pollutants from the air. Additionally, the chemical functional groups in algal lipids, proteins, and carbohydrates (e.g., $-COOH$, $-OH$, $-RCOO^-$, $-HPO_4^{2-}$, $-NH_2$)[10] exhibit great potential to be functionalized with other organic/inorganic or metallic components, as reported in the fields of cementitious materials[48,49] and other functional materials and biotechnologies,[50−52] implicating a promising area of algae-based functional portland and geopolymer cements.[53]

In terms of potential large-scale applications, the advantage of algae-based admixtures lies in their cost-effectiveness and environmental sustainability. Considering that algae cost between USD \$472-\$1137 per ton[54,55] and 1 m^3 of concrete typically consumes ~450 kg cement, an addition of 0.5 wt % algae (i.e., 2.25 kg) would cost approximately USD \$1.6−2.6 for 1 m^3 of concrete, a rate that lies at the lower end for typical chemical admixtures.[56] The cost-effectiveness could further improve if cost reductions of algal production can be achieved.[57] In terms of environmental sustainability, the embodied carbon of raw algal biomass equates to approximately −1.8 $kgCO_2e/kg$,[5] a figure that neglects any additional emissions associated with processing and purification. Considering that the embodied carbon of a Type I portland cement is 0.95 kg CO_2e/kg,[58] a 0.5 wt % of algae addition would account for a ~ 1% reduction in embodied carbon of cement. This fraction is a nontrivial sum of CO_2 reduction from the perspective of chemical admixtures, among many other efficiencies achieved by innovations in the cement production process (e.g., energy efficiency).[59] On the contrary, common types of set retarders (i.e., polycarboxylate ethers and naphthalenesulfonates) either contain toxic formalin or require complicated synthesis, including raw chemicals and controlled conditions.[60,61] Though a more precise life cycle analysis is required, these initial findings highlight the potential of using algae to develop a suite of nontoxic, economically competitive, carbon-storing admixture technologies.

4. CONCLUSIONS

The mechanism by which *Chlorella* algae retards the hydration of portland cement was elucidated in this work. The retardation effects of algae were confirmed via calorimetry. The heat-evolution peak for cement hydration was substantially delayed, specifically by 29.4%, 82.4%, and 811.8%, with the addition of 0.5%, 1.0%, and 3.0% of algae, respectively. Such retardation is caused by the −COOH and −OH functional groups of the algae. While −COOH and −OH are well-known retarding functional groups for cementitious materials, their presence in the algae was confirmed via FTIR. Furthermore, we also demonstrated (1) enhanced retardation by algae with enhanced −COOH and −OH groups and (2) reduced retardation by eliminating these groups in the algae through H_2O_2 and heat treatment, respectively.

To ultimately promote algae as a retarder for cement and concrete in engineering practice, it was further demonstrated that the addition of algae exhibited negligible effects on the morphology, crystal structure, and compressive strength of algae-modified cement pastes. It is estimated that an algae dosage of 0.5% would cost USD \$1.6−2.6 per 1 m^3 concrete and could reduce the embodied carbon of the concrete by ~1%. Considering the retardation capacity and negligible effects on compressive strength, the competitive economic cost and environmental benefits highlight the potential for large-scale application of algae in cementitious materials.

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Notes

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