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Letter

Feasibility of Using Calcium Silicate Carbonation to Synthesize High-Performance and Low-Carbon Cements

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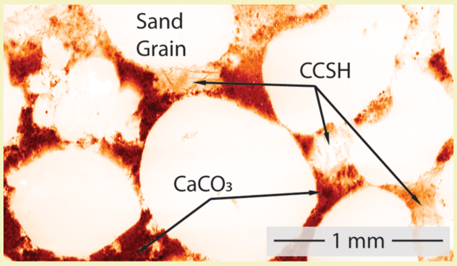

ABSTRACT: Cement is the world's most widely consumed man-made material and it contributes between 5% and 10% of the total annual anthropogenic CO_2 emissions. Here, we report on a new method for producing crystalline calcium silicate hydrate (CCSH) phases with low lifecycle carbon emissions. The materials were made by curing silicate feedstocks, principally pseudowollastonite ($CaSiO_3$), under elevated partial pressures of CO_2 in buffered aqueous solutions. CCSH mortars cured for 7 days achieved compressive strength of 13.9 MPa, which is comparable to the 28-day strength of Type-S ordinary Portland cement mortars. Bromine diffusivity tests, used as an indicator of durability of the materials, show that CCSH mortars have significantly lower diffusivity than ordinary Portland cement. The resistance to dissolution at low pH of the materials was measured using acid exposure tests and found that CCSH mortar lost only 3.1% of its mass compared to 12.1% in OPC. Total carbon measurements showed that these materials can sequester between 169 and 338 g of CO_2 per kg of cement, as opposed to ordinary Portland cement, which emits nearly 1000 g of CO_2 per kg, indicating this calcium silicate carbonation process could be enabling chemistry for all-new low-carbon and high-performance infrastructure materials.

KEYWORDS: *Alternative cementitious materials, Pseudowollastonite, Calcium silicate hydrate, Carbonation, Precast*

■ INTRODUCTION

Cement is the most important building material in modern infrastructure. However, its production is carbon intensive, and its performance is limited in many applications.[1−4] Ordinary Portland cement (OPC), the most common form of cement used worldwide, is produced by calcinating limestone, producing CO_2 as a byproduct, at high temperatures, which requires fossil fuel combustion. The chemistry of OPC is complex and varied but is generally related to its calcium:silicon ratio and the structure of calcium silicate hydrate (CSH) gels that emerge when the material is hydrated.[5] Cements often degrade when cations (e.g., sulfate, carbonate) attack calcium hydroxide and CSH gels.[6] The precipitates from these reactions (e.g., ettringite, brucite, aragonite) often adsorb water, causing swelling and cracking.[7] In reinforced structures, water, often containing high salt concentrations, reaches metal reinforcements leading to corrosion, allowing the feedback loop to continue.

Efforts to develop cements with improved durability have generally focused on additives that reduce the permeability of the material since corrosion typically occurs via solute penetration and attack.[8] Efforts to reduce the environmental impact of cements have generally sought to blend pozzolanic industrial waste materials rich in silica (e.g., fly ash, slag) with virgin cement to partially offset the energy and emissions required to manufacture OPC. Ongoing work seeks to create nonhydraulic calcium silicates that react with CO_2 to produce $CaCO_3$ and SiO_2via[9]

$$CaSiO_{3(s)} + 2CO_{2(aq)} + H_2O \rightarrow Ca^{2+} + 2HCO_3^- + SiO_{2(am)} \qquad (1)$$

These ions can then precipitate out of solution to form carbonate species via

$$Ca^{2+} + 2HCO_3^- \rightleftharpoons CaCO_{3(s)} + CO_{2(aqq)} + H_2O \qquad (2)$$

These cements sequester a significant amount of CO_2 during curing but may not perform well in some environments, such as under mildly acidic conditions, where the calcium carbonate will dissolve.

Several recent studies have reported that the carbonation of a model calcium silicate at elevated temperatures results in the formation of carbonate in addition to crystalline calcium silicate hydrate (CCSH) phases.[10,11] These CCSH phases are mixed, consisting of a mineral species such as tobermorites via

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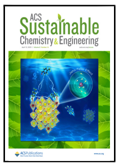

$$3CaSiO_{3(s)} + OH^- + H_2O \xrightarrow{heat} Ca_2Si_3O_9(OH)\cdot H_2O + Ca^{2+} \quad (3)$$

pectolite via

$$2CaSiO_{3(s)} + OH^- + Na^+ \rightarrow \text{CSH gel} \xrightarrow{heat} Ca_2NaSi_3O_8(OH) + 0.5O_2 \quad (4)$$

and a number of other mineral phases (e.g., plombierite and rankinite). Centuries ago, Roman engineers generated famously durable hydraulic cements, which yielded plate-like crystalline calcium silicate hydrate mineral phases such as tobermorite and phillipsite, among others.[12] Roman cements relied on raw materials that are unavailable outside of volcanically active regions and are therefore difficult to scale.[13]

Here, we report on a new method to synthesize crystalline calcium silicate hydrate (CCSH) phases, similar to those in Roman cements, while also utilizing and permanently storing CO_2. The reactions that lead to these phases are sensitive to the Ca:Si ratio in the dissolved aqueous phase as well as pH and partial pressure of CO_2. This work seeks to test the hypothesis that these materials have mechanical properties that are comparable or superior to conventional OPC because of the cementitious behavior of the transecting crystalline precipitates. In addition, the cement formulated here may be of particular interest from an environmental perspective because it requires a lower calcium content (resulting in less CO_2 production from calcination) and because carbon is sequestered during the curing phase.

METHODS

Pseudowollastonite Synthesis. A 1:1 calcium:silicon mixture was produced on the kilogram-scale by ball milling HuberCrete G Extra Fine Limestone (Huber Engineered Materials) with Elkem Microsilica 965U (Elkem Materials, Inc.). The milled powder was moistened with water and NaOH (5%) to act as a binder and flux during annealing at 1225 °C.[14] The resulting pseudowollastonite was milled to diameters less than 75 um. X-ray diffraction was conducted via a Panalytical X'pert Pro diffractometer with a copper source ($K\alpha$ = 1.5406 Å) from 15°−65° 2θ. Analysis with the PDF-4+ 2019 database confirmed high-purity pseudowollastonite.

Mortar Cube Tests. Two inch mortar cubes were cast and tested in compression in accordance with ASTM specification C109. On the basis of our prior work, we established a general method for curing the mortar specimens, which includes elevating the pH of the mix water, curing the specimens at 90 °C, and elevated pressure of CO_2 gas for 72 h until the specimens are hardened, then demolding and submerging them in an alkaline solution again at elevated temperature with $CO_{2(aq)}$ for 96 h, for a total of 7 days of curing. Specifically, this work sought to characterize curing conditions in which the initial mix water pH (equilibrated with CO_2 in the headspace of the pressure vessel) was 6.5, and the pressure of CO_2 was 0.55 MPa. Also, the pH of the 4-day curing water (equilibrated with headspace CO_2) was 6.5 with 0.76 MPa CO_2 at 140 °C. The water−CO_2 equilibrium pH was calculated with the PHREEQC database. Compressive strength was measured with a Humboldt Master Loader Elite Series load frame.

Carbon Uptake. Crushed mortar specimens were collected, ground with a mortar and pestle, and analyzed via a Shimadzu SSM5000A total carbon analyzer. Because the samples include the sand from the mortar, the carbon content, a percent of the original sample mass, was adjusted to be expressed in terms of the mass of cement (pseudowollastonite) based on the mix proportions of cement to sand.

Synchrotron X-ray Fluorescence Mapping. A small cylindrical mortar sample (14 mm diameter by 30 mm length) was cast and cured in conditions identical to the curing conditions used for the 2 in. cubes, with the exception that it was set in dry CO_2 for 24 h and then set in the aqueous phase for 48 h. This curing duration was adequate for obtaining hardened samples on this smaller scale, while it was insufficient for the larger cube specimens due to the limitations of diffusion. SEM analyses indicated that similar phases precipitated in the mortar specimens as the smaller cylinders. For comparison, a cylindrical OPC mortar specimen (Type I/II) of the same size was cured for 1 day in the mold, then submerged, demolded in water, and allowed to cure for 6 more days. Subsequently, to analyze diffusivity, all cured samples were simultaneously submerged in a 0.1 M NaBr solution for 6 h at room temperature where the Br diffused from the solution into the samples. They were then removed and dried in an oven at 75 °C, epoxied, and sectioned lengthwise.

For each sample, synchrotron X-ray fluorescence mapping of Br was conducted on a 3 mm wide by 4.5 mm deep section that began at the outer edge of the specimen. The mapping was completed at the 13-IDE sector at the Advanced Photon Source with a four-element silicon drift diode detector at an incident energy of 18 keV with 20 μm steps and dwell times of 20 ms.[15,16] Map data were visualized in Python 3.6 with the viridis colormap. The colormap ranges were identical between both maps.

Acid Dissolution Tests. Two mortar cubes were cured to test their resistance to acid dissolution. Because the CCSH phases precipitate when pH is buffered (here, with NaOH), two additional cubes were created with the same mix but without any pH buffering from NaOH. These mortar specimens predominantly produce calcium carbonate upon curing, so acid resistance between CCSH-predominant specimens could be compared to carbonate-predominant specimens. Additionally, OPC cubes were cured for 28 days. All six cubes were dried, weighed, and submerged for 7 days in a 1 M sodium acetate and acetic acid solution at pH 5.[17] After 7 days, the specimens were removed and oven-dried. Loose materials were gently removed by hand, and they were then reweighed. Compressive strengths could not be determined because the surfaces of the specimens were rough and no longer planar in some cases.

RESULTS

Synthesis of Crystalline Calcium Silicate Hydrates.

Experimental results published recently by several independent research groups including ours suggests that the coprecipitation of crystalline calcium silicate hydrates (CCSH) phases and carbonates is possible using pseudowollastonite, a polymorph of $CaSiO_3$, which is more reactive than the alternate polymorph, wollastonite[10,11] The formation of CCSH phases, represented in eqs 3 and 4, may occur in parallel or sequence with the carbonation reactions that proceed via eq 2, but typically, one class of precipitate predominates, depending on reaction conditions. XRF maps, such as the one used in the abstract graphic, reveal that CCSHs tend to precipitate along solid interfaces such as sand grains, whereas carbonates tend to precipitate indiscriminately throughout pore bodies.[18] The relative abundance of $CaCO_3$ to CCSH phases appears to be influenced by at least three factors: (1) The reactivity of the parent silicate (eq 1) is important because pseudowollastonite dissolves congruently, whereas wollastonite dissolves incongruently.[19] Since many of the CCSH mineral phases have Ca:Si ratios of approximately 1, the dissolution of mineral species like wollastonite, that leach calcium selectively (resulting in a solid layer of unreactive silica), do not have the molar ratios needed to produce CCSHs. (2) CO_2 is important in driving the reactions, even though it is not necessarily incorporated into the CCSH phases. It accelerates the dissolution (eq 1), and formation of $CaCO_3$ may be a

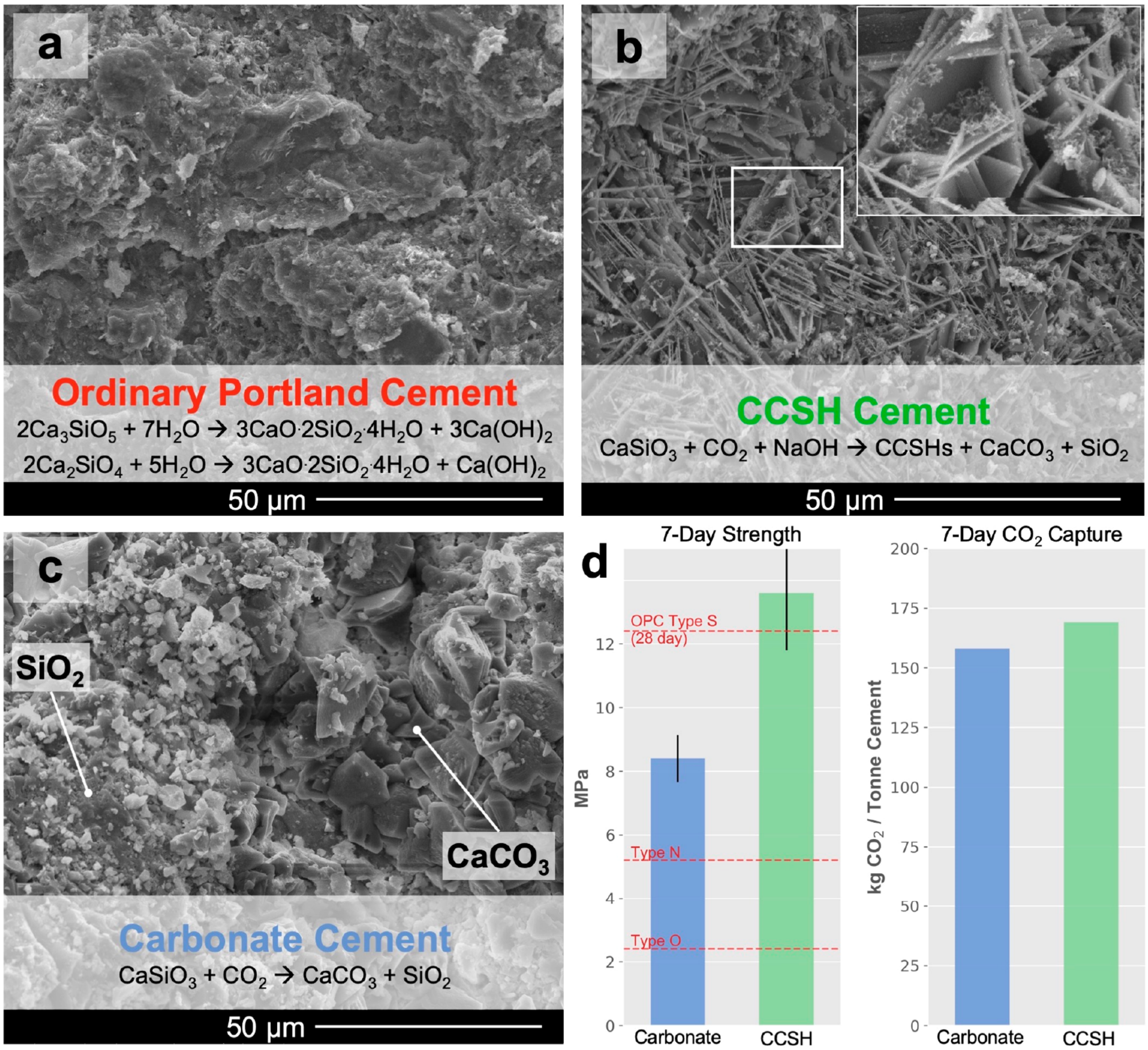

Figure 1. Structural, mechanical, and CO_2 uptake capacity. Macro- and microscale differences between (a) ordinary Portland cement mortar, (b) CCSH cement mortar, and (c) carbonate cement mortar. Panel (d) shows the compressive strength of 28-day OPC formulations (based on ASTM C270) relative to 7-day compressive strengths of the alternative cements, along with 7-day CO_2 uptake measurements.

necessary intermediate in the formation of some CCSHs. That hypothesis is still under investigation. (3) The presence of NaOH is important because OH^- buffers the pH of the solution, and Na^+ may play an important role in nucleating the CCSH phases. Na^+ can also be incorporated directly in some of the CCSH mineral phases (e.g., eq 4).[18,19]

Compressive Strength and Carbon Utilization of Various Cement Types. OPC derives its strength from the hydration of tricalcium and dicalcium silicates (alite and belite) that form amorphous calcium silicate hydrate (CSH) gels, shown in Figure 1a.[20] The CSH gels form around aggregate, binding the materials together and increasing in strength over the course of weeks. Figure 1b shows how distinct the morphology of CCSH phases synthesized in this work are from the CSH phases in OPC. In our experiments, the CCSH phases tend to precipitate on solid−fluid interfaces (i.e., on sand grains) and form a lattice-like structure that is dissimilar in morphology to calcium carbonate precipitation, which occurs under the same conditions when pH is not buffered (shown in Figure 1c).[18]

Mortar specimens were tested in triplicate and generally followed the ASTM C109[21] procedure for mixing and compressive testing procedures with standard mix ratios for unit masonry from ASTM C270.[22] Because we foresee unit masonry being a useful application for CCSH cements, given the curing requirements, we compared compressive strength with OPC standard strengths of unit masonry presented as red lines in Figure 1d. Our experiments concluded that CCSH mortar achieved compressive strengths as high as 13.6 MPa in 7 days of curing. To test the strength of carbonate mortar, similar specimens without any pH adjustment were tested in parallel and were found to have a compressive strength of 8.4 MPa, indicated in Figure 1d.

The carbon content of the CCSH mortars and the carbonate mortar were measured by sampling fractured pieces from the compression tests. We found that for the CCSH mortar, an average of 1.23% (mass) was carbon, which indicates that 169 kg of CO_2 per tonne of pseudowollastonite cement could be captured and utilized during the (7-day) curing phase. For two specimens that were cured for 28 days, that percent increased

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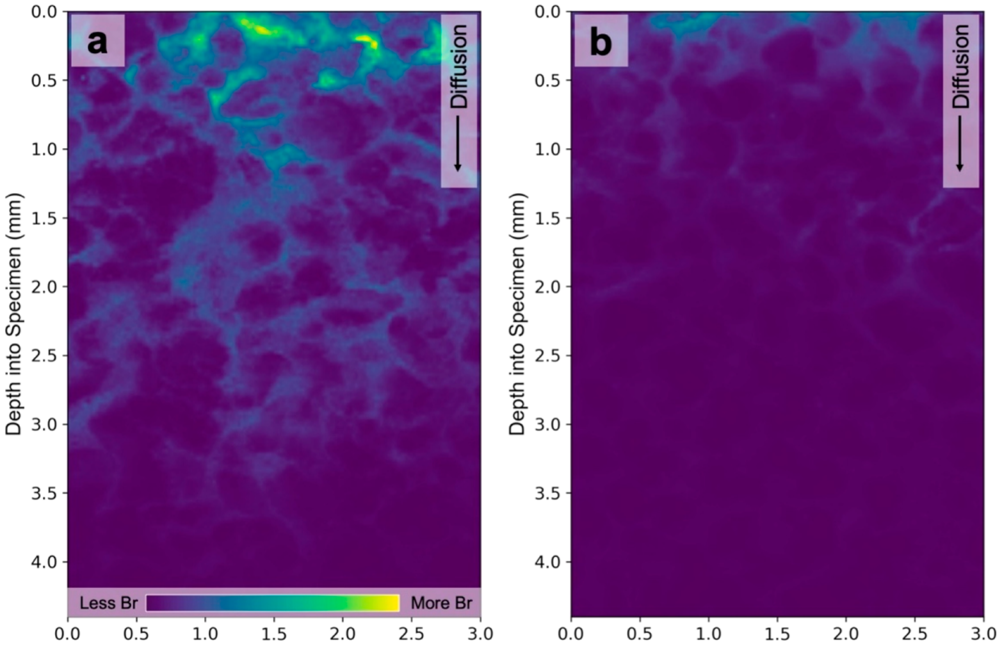

Figure 2. Assessment of durability via ion diffusivity. Diffusion of a Br tracer into (a) a 7-day OPC mortar specimen and (b) a 72-h CCSH cement mortar specimen measured by synchrotron-based X-ray fluorescence. The top of both maps align with the outer edge of the specimens, and a color map is shared, allowing a comparison of relative Br concentrations.

to 2.46%, or 338 kg CO_2 per tonne of cement. The carbon uptake in 7-day carbonate mortar was 1.15%, indicating utilization of 158 kg CO_2 per tonne of cement, and the percent increased to 1.93% (265 kg CO_2 per tonne) in 28 days. While there is some calcium carbonate present in the CCSH mortar, the fact that its carbon uptake was greater than that of the carbonate mortar could be indicative of the CCSH phases incorporating carbon as phases such as scawtite [$Ca_7(Si_3O_9)_2CO_3{\cdot}2H_2O$)] or spurrite [$Ca_5(SiO_4)_2(CO_3)$], in addition to noncarbon-containing phases similar to tobermorite. In previous work, we demonstrate that the CCSH phases that formed under similar conditions were of mixed composition, with a range of calcium-to-silicon ratios (median of approximately 1) and a variety of crystal lattice parameters.[18]

Comparisons of Durability. Chlorine is often used to determine diffusivity in cement samples but in order to visualize the ion diffusion using synchrotron-based fluorescence at 13-IDE, we used bromine, which has comparable size, electronegativity, and diffusivity in clays.[23] The results shown in Figure 2 show that over a 6-h exposure to the NaBr solution the bromine penetrated significantly further into the OPC sample (Figure 2a) than it did into the CCSH sample (Figure 2b).

The performance of cements is also evaluated in terms of its reactivity under acidic conditions, which are common in the environment and which can lead to deterioration and structural failure. Samples exposed to pH 5 acid (see Methods) exhibited clear visual differences as shown in Figure 3. Both the OPC specimens and the carbonate mortar specimens (Figures 3a and b, respectively) exhibited significant deterioration. The OPC specimens also experienced discoloration that was clearly visible in cross sections (Figure 3a, inset). The CCSH specimens (Figure 3c) remained largely intact under identical conditions. The OPC and carbonate specimens lost 12.1% and 14.7% of their mass, respectively, after drying. In contrast, the CCSH specimens lost only 3.1%. This difference in reactivity suggests that CCSH-based cements could be well suited for relatively aggressive applications and/or would provide a more permanent form of CO_2 storage than other cement types that might dissociate even under modestly low pH conditions.

■ CONCLUSIONS

The aqueous carbonation of pseudowollastonite is complex, but it may offer insight into underlying chemical reaction pathways that could lead to the synthesis of low-carbon cements. For example, the dissolution rate of pseudowollastonite (assumed to be the rate-limiting step) will increase with temperature (and indeed, higher strength cements were synthesized at higher temperatures), but the concentration of CO_2 (and diffusivity) will decrease with increasing temperature. We suggest that the conditions analyzed here may not necessarily include the optimal conditions for pseudowollastonite dissolution and subsequent carbonation but instead provide insight into the parameters of greatest importance. Clearly, buffered pH and elevated temperature play a critical role in CCSH formation, and those phases are capable of yielding high strength and durability in concrete applications. Previous work,[24] which found similar carbonation extents of wollastonite under comparable conditions but after only 30 min of reaction, highlighted that the particle size, stirring rate of the aqueous phase (or the presence of stirring), and the diffusion of CO_2, among other factors, can greatly impact the rate of carbonation, and each of these factors must be further investigated in the context of the curing rate in this work. The need to cure these materials suggests that they would be ideal substitutes for OPC in the rapidly growing precast cement market. The results presented here provide the first connection between formulations, curing methods, mechanical properties, and potential environmental impacts of CCSH phases in the context of infrastructure materials.

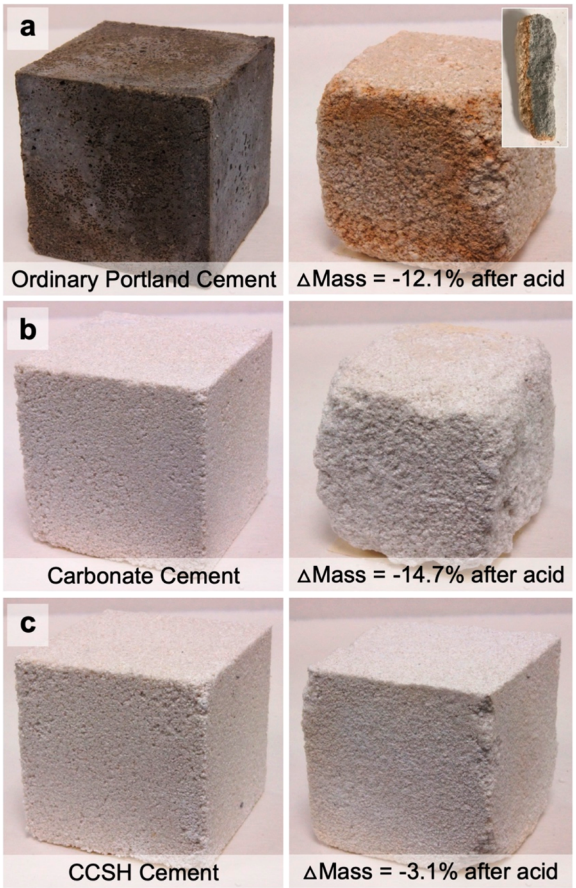

Figure 3. Comparison of acid resistance. The 2-in. mortar cubes made with (a) ordinary Portland cement, (b) carbonate-based cement, and (c) CCSH-based cement were aged for 7 days in an acidic solution (pH 5). The visible corrosion and change in mass reveal the extent to which CCSH phases are resistant to acid attack when compared to the alternatives presented in this work.

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Notes

The authors declare no competing financial interest.

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