The impact of carbonation on the microstructure and solubility of major constituents in microconcrete materials with varying alkalinities due to fly ash replacement of ordinary Portland cement

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Abstract

The impact of alkalinity on the carbonation reaction in microconcrete mortars was assessed by evaluating the changes in the microstructure, solubility, and migration of major constituents (i.e., calcium, aluminum, and silicon), for cases of partial replacement of the Portland cement with different fly ashes having varying alkalinity. Several experimental techniques (i.e., SEM-EDS, U.S. EPA Method 1313, TIC, and TGA) were used and compared as tools to characterize changes due to the carbonation reaction. The rate and extent of carbonation was inversely related to the alkalinity of the material as evident by the increase in carbonation depth, reduction of the natural pH of the material, extent of the changes in the microstructure, and extent of reaction. Calcium migrated to the carbonated region while conversely silicon migrated from the carbonated region in response to relative solubility and therefore different diffusivity in the carbonated and uncarbonated regions for each constituent.

Keywords: alkalinity; carbonation; fly ash; microstructure

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1. Introduction

The service life of cement-based materials is a critical parameter for management of virgin and secondary materials in the cement and concrete applications. Structural degradation is especially important for cementitious materials in nuclear waste applications due to the potential for release of radioactive constituents which could adversely affect human health and the environment.

Cementitious materials for nuclear waste management include binding matrices for low-activity waste forms and physical barriers such as grouts for waste tank capping, concrete vaults for waste containment, and mass pours for reactor entombments [1]. Often these materials contain supplemental cementitious materials (SCMs) designed to modify material performance. In these applications, it is desirable that cementitious materials maintain structural, hydraulic and chemical performance to the extent possible for lifetimes up to thousands of years. Although many of the mix designs for nuclear waste applications rely on coarse aggregate, the study of chemical performance and degradation often focus on the reactions and structure of the cement paste or of cement mortars. With regard to leaching and degradation of commercial concretes, microconcretes (i.e., mortars with high levels of fine aggregate that mimic concrete rheology) have been shown effective as surrogates for concretes containing coarse aggregate[2, 3].

Much of the physical and chemical durability of cementitious materials has been attributed to the formation of a highly-buffered alkaline matrix consisting mainly of calcium-silicate-hydrates (C-S-H) and portlandite $[\text{Ca}(\text{OH})_2]$. However, a key mechanism for degradation of cementitious matrices is reaction of the alkaline matrix with atmospheric or soil-gas carbon dioxide (CO_2), also known as carbonation. Over the extended material performance intervals for nuclear waste applications, degradation due to carbonation can potentially lead to the release of radionuclides [4]. Atmospheric or soil-gas CO_2 reacts with dissolved minerals in the cement pore water

resulting in (i) depletion of matrix alkalinity which neutralizes pore water and affects the solubility of pH-dependent constituents and (ii) precipitation of relative insoluble carbonate phases which alters the pore structure of the matrix. In extreme cases, carbonation may lead to depassivation of reinforcing steel, physical degradation of the cementitious material, and loss of strength due to cracking in both nuclear and non-nuclear applications. Therefore, considerable effort has been placed on characterizing the primary degradation mechanisms of cementitious materials including the penetration of CO_2 and reaction rate of carbonation [5-8].

Microstructural analysis is key to understanding the overall behavior of the material, especially under conditions where changes in the microstructure and porosity occur due to the formation of carbonated products [9]. Analysis of the microstructure can identify the composition, morphology and spatial distribution of phases present in the system providing useful information on the mechanisms of hydration or degradation [10]. Characterization of the cement microstructure and redistribution of elements as a result of carbonation may lead to a better understanding of the macroscopic deterioration that occurs in concrete over extended periods.

This study evaluates the impact of material alkalinity on the carbonation process for three microconcrete materials with different alkalinities by assessing the changes in solubility of the major constituents (i.e., calcium, aluminum, and silicon), microstructure, distribution of elemental constituents across a reacted carbonated front, extent of reaction, and reaction capacity. The results of this study are intended as input to a framework to predict material durability in commercial and nuclear applications and the migration/release of heavy metals and radionuclides from cementitious materials used in nuclear waste applications.

2. Carbonation in cementitious media

The penetration CO₂ gas from air or soil media into a porous cement material results in subsequent reaction of aqueous CO₂ with hydration minerals including portlandite, C-S-H, and ettringite [Ca₆Al₂(SO₄)₃(OH)₁₂·26H₂O] to form carbonated products [11, 12]. In particular, the reaction of CO₂ with portlandite is of interest because of its abundance in the material and its responsibility for decreasing the pH of the material. Padadakis et al. [7] represented the overall reaction between portlandite and CO₂ as two steps: the dissolution of the portlandite (Eq.1) and the overall carbonation reaction (Eq.2), which is comprised of other elementary steps.

These steps are cyclic in that the consumption of free hydroxide ions in the pore solution (Eq. 2) results in further dissolution of portlandite leading to depletion and reduced pH in carbonated materials. Localized depletion of portlandite results in subsequent decalcification of C-S-H[7, 13] according to Eq. 3:

Since portlandite is more soluble ($K_{\text{sp}} = 5.5 \times 10^{-6}$ at 25° C) than CaCO₃ ($K_{\text{sp}} = 4.7 \times 10^{-9}$ at 25° C)[14] and there is a shift in the pH of the material, the concentration of constituent ions in the pore solution is expected to be different in the carbonated region of the material compared to the uncarbonated region. Studies of the changes in the leaching behavior upon carbonation of cementitious materials indicate that the differences in the pore solution concentrations of the major constituent ions (i.e., calcium, aluminum, and silicon) will significantly impact the time-

dependent leaching of these constituents from concrete materials[2, 15-17]. Therefore, leaching tests intended to characterize the liquid-solid partitioning of calcium, aluminum, and silicon in solid materials can be used to identify changes in constituent solubility and concentration of constituents in the pore water solution due to the phase changes associated with the carbonation reactions.

The carbonation of cementitious materials is a complex process that is further complicated by the addition of SCMs which may be used as replacement for a portion of the Portland cement component in blended cementitious materials. Replacement of a fraction of the Portland cement with SCMs often improves the mechanical performance of these systems and reduces the need for virgin cement. For example, the addition of coal combustion fly ash promotes the conversion of portlandite to C-S-H during hydration and, hence, refines the microstructure of the concrete which ultimately affects the transport properties of the matrix which controls the diffusivity of CO_2 [18, 19]. Previous studies suggest that the presence of fly ash increases the rate of carbonation because of a change in material alkalinity and the availability of portlandite [18, 20-22]. Models have been designed to predict the penetration depth of the carbonation reaction front in concrete materials with fly ash replacement [23, 24], yet more effort is needed to characterize the evolution of the microstructure coupled with the elemental distribution for these materials. However, since the amount of alkalinity provided by fly ash can vary significantly based on coal source and combustion configurations [25], the uncertainty about prediction of the carbonation rate and extent of microstructural effects increased.

3. Materials and methods

3.1. Microconcretes

Microconcrete mortars with different levels of total alkalinity were prepared by mixing Type I/II ordinary Portland cement (OPC), fly ash (FA02 or FA39), river sand (fine aggregate), and water according to the mix designs shown in Table 1 [26]. FA02 is a low calcium (1.9% by mass) Class F fly ash from the combustion of bituminous coal and FA39 is a high calcium (17.1% by mass) Class C fly ash from the combustion of sub-bituminous coal. The microconcretes include a control material with no fly ash (M-00), a blended microconcrete with 45% of the OPC fraction replaced by FA02 (M-02), and a blended microconcrete with 45% replacement of OPC with FA39 (M-39). A sieve analysis was performed on the fine aggregate (Table S1). The material source details and characteristic leaching data for these materials have been reported elsewhere [3]; however, the naming scheme for the microconcretes has been simplified to improve the presentation clarity of this study.

Table 1.
Microconcrete formulations

	Control	Blend	Control	Blend
Nominal Mix (lb./cy)	866	866		
Fly ash replacement (%)	-	45		
	Composition (wt%)		Composition (kg/m ³)	
Portland Cement	22.2	12.2	301	165
Fly ash	-	10	-	136
Water	9.9	10.1	135	136
Fine Aggregate	67.9	67.7	940	920

For each microconcrete, ten cylindrical monoliths (6.5 cm diameter x 9.0 cm height) were cast and cured for 6 months at 100% relative humidity (RH) in a sealed 5-gallon bucket maintained at

ambient temperature ($21 \pm 2^\circ\text{C}$). After the 6-month cure, three of the monoliths for each microconcrete were carbonated for an additional 6 months in a Thermo Scientific 3531 environmental chamber (Thermo Fisher Scientific, Inc., Waltham, MA) maintained at 5% CO_2 , 65% RH, and ambient temperature. These carbonated materials are denoted as samples MC-00, MC-02, and MC-39. In parallel, three monoliths for each microconcrete, labeled M-00, M-02 and M-39, remained in the sealed buckets for an additional 6 months of curing without exposure to CO_2 . Four monoliths for each microconcrete were collected after the initial 6-month cure and crushed using a parallel plate grinder until at least 85 percent by mass (wt%) of the material was less than 2 mm in diameter. Half of this granular material was placed in the same carbonation chamber with the monolith samples for 6 months and the remaining half was returned to the sealed bucket for additional 6 months of curing. For the purposes of these experiments, particle size reduction was intended to maximize the extent of carbonation over 6 months by increasing the surface area exposed to CO_2 . In addition, United States Environmental Protection Agency (U.S. EPA) Method 1313, thermogravimetric analysis (TGA), and total inorganic carbon (TIC) used to characterize the carbonation reaction require a size reduced material and therefore the crushed microconcretes were used in these test methods. A summary of the microconcretes curing, crushing, carbonation conditions, and test method for each material is summarized in Table 2.

Table 2.
Microconcrete coding scheme

Material Code	Cured	Crushed	Carbonated	Test Method
M-00, M-02, M-39	12 months	No	No	Phenolphthalein, SEM-EDS
MC-00, MC-02, MC-39	6 months	No	6 months	Phenolphthalein, SEM-EDS
M-00, M-02, M-39	12 months	Yes	No	Method 1313, TGA, TIC
MC-00, MC-02, MC-39	6 months	Yes	6 months	Method 1313, TGA, TIC

3.2. Major Constituent Solubility as a Function of pH

The liquid-solid partitioning of calcium, aluminum, and silicon between the solid material and a contacting aqueous phase as a function of pH was determined using U.S EPA Method 1313 [28]. This method also provides the acid-base titration curve used to estimate total and carbonate alkalinities. Method 1313 is a standard, pH-dependence leaching method consisting of parallel batch extractions of a solid material under various pH conditions and at a liquid-to-solid ratio (L/S) of 10 mL/g-dry. Details on the procedure and application of this method can be found elsewhere [27-29]. For each carbonated and non-carbonated microconcrete and their components (i.e., OPC, FA02, and FA39), the test was conducted in duplicate. For each microconcrete, the calcium, aluminum, and silicon concentrations in the eluate were determined by inductively couple plasma-optical emission spectrometry (ICP-OES) following U.S. EPA Method 6010C [30]. The titration curve for each material was derived based on the amount of acid added ($\text{mol}_{\text{H}^+}/\text{kg-dry}$) and the resulting end-point pH for each extraction using a best fit fourth degree polynomial from the two replications from the material's natural pH¹ to the pH of 4.5. This data was used to calculate the total, hydroxide, and carbonate alkalinities according to this titration curve for each microconcrete and component. This alkalinity calculations parallel Standard 2320 described in the Standard Methods for the Examination of Water and Wastewater to determine alkalinity [31]. The distribution of the different alkalinity contributions was modified from the Standard Method 2320 because significant bicarbonate alkalinity is not expected in cementitious materials and because of the variation in the inflection point pH near the phenolphthalein alkalinity point (pH 8.3) in the titration curve of each material. Therefore, the hydroxide alkalinity contribution was estimated as the acid addition from the material's natural

¹ The natural pH, or "own pH," is the end point pH when extracted with only deionized water at liquid-solid ratio of 10 mL/g dry weight

pH to the inflection point near pH of 8.3 for each material. The carbonate alkalinity contribution was estimated as the acid addition from the inflection point near pH of 8.3 in each material to a pH of 4.5. The total amount of inorganic carbon present in the carbonate form according to the carbonate alkalinity was then calculated for each material. Two representative titration curves and the regions associated with hydroxide and carbonate alkalinities are shown in Figure 1. The uncertainty associated with determining the hydroxide, carbonate, and total alkalinity, the inorganic carbon, and solubilities was estimated according to the mean coefficient of variation (CV) across all samples and replicates for each measurement type.

3.3. Thermogravimetric analysis

A TA Instruments Q600 SDT analyzer (New Castle, Delaware, USA) was used to estimate the mass fraction of C-S-H, portlandite and their respective carbonation products in granular subsamples of the carbonated and non-carbonated microconcretes and the mass fraction of carbonate present in the fly ashes and OPC. TGA is an accepted method that has been used in many studies to quantify the mass fraction of these mineral phases in cement materials, especially portlandite, because there is little or no interference with other phases in cementitious materials in the portlandite decomposition temperature range [32-34]. For each material, TGA was conducted on duplicate subsamples of approximately 40 mg to determine the mean mass fractions of C-S-H, portlandite, calcite [CaCO_3], and vaterite (also CaCO_3 but of a less stable form). The uncertainty associated with the reported mass fractions was estimated according to the mean CV across all the materials for each phase. Each TGA run was initially equilibrated at a temperature of 50° C prior to heating to 900° C at a rate of 10.0° C/min. The chamber was continuously flushed with nitrogen throughout the heating process with a flow rate of 100 mLmin⁻¹.

Literature values for the specific temperature ranges associated with mass loss from minerals phase vary slightly. For example, the temperature for decomposition of portlandite to lime and water is reported between 400° and 550° C [9, 34-36]; however, the peaks associated with mass loss from portlandite decomposition were observed in the temperature range of 400° to 500° C. For the decomposition of C-S-H, the approach of Jain and Neithalath [37] was adopted where the C-S-H fraction measured by mass loss in the temperature range from 150° to 400° C was adjusted by dividing the measured mass loss by 2.1 to account for hydrated water loss from C-S-H occurring below 150° C. Decalcification during carbonation alters the stoichiometry of C-S-H. However, since the exact stoichiometry is not well agreed upon and the amount of decalcified C-S-H in the materials relative to the amount of C-S-H is not known, the same stoichiometry to estimate C-S-H in the carbonated and non-carbonated materials was used. Therefore, C-S-H in the carbonated materials is only an estimate of the C-S-H.

CaCO_3 is identified by the mass loss in the temperature range between 500° and 1000° C according to the varying lower and upper temperature boundaries identified by many different literature sources which is compared and discussed in Haselbach [38]. CaCO_3 decomposition over this temperature range is from three different polymorphs that form during carbonation: aragonite, vaterite, and calcite [39]. Calcite forms directly during carbonation, but vaterite and aragonite form during the carbonization of C-S-H and eventually transform into calcite under extended periods of time [35] or when heating at approximately 450° C, as what occurs during TGA [40]. The calcite originating from aragonite and vaterite decomposes at a slightly lower temperature range compared to the calcite formed during carbonation [41]. Based on work done by Villain et al. and the peaks observed in this study, the temperature range of 520° to 650° C was used to identify the amount of calcite originating from vaterite [35]. Vaterite is expected to

dominate in well-hydrated cements and therefore aragonite composition was not considered further in this study [42]. The temperature range of 650° to 750° C was used to determine the amount of calcite formed directly during carbonation. Higher temperature ranges associated with the decomposition of calcite originating from aggregates [34] were not evaluated.

The amount of calcium carbonate in fly ash components and OPC sample were determined from the mass loss between 520° and 750° C. This temperature range was based on observations of mass loss peaks for the FA02 and FA39 materials and is consistent with the temperature ranges for determination of vaterite and calcite in the microconcretes as well as the calcium carbonate content in other studies on fly ash materials [43, 44].

In addition, results from TGA were used to assess extent of reaction in each material by evaluating the ratio of calcium that reacted during carbonation compared to the theoretical amount of available calcium that could react (i.e., reaction capacity). Ca (g/g-material) was derived from the stoichiometry of each phase. The relationship used to determine the extent of reaction is shown in Eq. 4.

$$\text{Extent of reaction} = [\Delta(\text{Ca}_{\text{vaterite}} + \text{Ca}_{\text{calcite}})_{\text{carb,non-carb}}] / [(\text{Ca}_{\text{C-S-H}} + \text{Ca}_{\text{portlandite}})_{\text{non-carb}}] \times 100\% \quad \text{Eq. 4}$$

Where $\Delta(\text{Ca}_{\text{vaterite}} + \text{Ca}_{\text{calcite}})_{\text{carb,non-carb}}$ is the difference in the total amount of calcium in the vaterite phase ($\text{Ca}_{\text{vaterite}}$) and total amount of calcium in the calcite phase ($\text{Ca}_{\text{calcite}}$) between the carbonated and non-carbonated material, $\text{Ca}_{\text{C-S-H}}$ is the total amount of calcium contained in the C-S-H phase of the non-carbonated material, and $\text{Ca}_{\text{portlandite}}$ is the total amount of calcium contained in the portlandite phase of the non-carbonated material.

3.4.Total inorganic carbon

A Shimadzu model TOC-V CPH/CPN combined with a SSM-5000A unit (Shimadzu Scientific Instruments, Columbia, MA, USA) for solid samples was used to estimate the TIC in each microconcrete and component on a mass of approximately 25 mg per material. A volume of 500 μL of concentrated phosphoric acid (85% assay) was added to each standard and sample to release CO_2 . The furnace was set to 200°C and zero air at 150 mL/min was used as the carrier gas. Four-point calibration curves using a sodium bicarbonate standard for TIC were generated for an analytical mass range between 10 mg and 75 mg and were accepted with a correlation coefficient of at least 0.995. The uncertainty associated with this method was estimated according to the mean CV across all the materials.

3.5. Scanning electron microscopy-energy dispersive x-ray spectrometry

Scanning electron microscopy (SEM) is a common microstructural and elemental analysis tool for concrete and cement research [10, 45]. The microstructure of microconcrete materials was characterized by a combination of backscattered SEM and energy dispersive spectroscopy (EDS) to assess changes in the microstructure and redistribution of species within the material as a result of carbonation. Two interior sections from the top exposed surface of the monolith (2 cm exposed surface x 1 cm depth) were cut for each material to minimize edge effect while retaining the exposed surface. One section was sprayed with 1% solution of phenolphthalein in ethanol for an initial screening assessment to locate the approximate depth of that carbonation front to compare to the SEM analysis. The other section was exchanged with ethanol to remove any remaining pore water, embedded in epoxy, and polished until smooth and flat using a series of specialized polishing cloths with an alcohol-based lubricant (Table S2).

Backscattered electron SEM images (0.25 $\mu\text{m}/\text{pixel}$) and EDS data (1 $\mu\text{m}/\text{pixel}$, 500 frames per site) were collected for the carbonated and non-carbonated microconcretes in environmental SEM mode at 130 Pa, 10 keV accelerating voltage, a working distance of 10.0 mm, and a spot size of 3.0 using an FEI Quanta 650 field emission electron microscope (Hillsboro, Oregon) equipped with an Oxford Instruments 50 mm^2 silicon drift EDS detector (Abingdon, Oxfordshire, UK). A large area scan (approximately 0.9 mm along the expose carbonation edge by 2.5 mm into the matrix) was comprised of multiple smaller sites with a horizontal field width of 256 μm corresponding to a magnification of 496x. In addition, the microstructure was evaluated at a higher magnification of 1500x corresponding to an 86.6- μm horizontal field width for five randomly selected areas for each the carbonated and non-carbonated microconcrete.

The “non-cement” image components (e.g., fly ash particles, sand aggregates, and epoxy-filled pores) were segregated from the cement region in the large area EDS scans (Table S3) and the remaining cement region was homogenized to remove noise in the data due to the presence of different hydration products and to better represent the changes in the chemical speciation of the cement due to degradation. Homogenization using an elemental moving average value was calculated for each pixel of the EDS map using the mean value of all pixels in a 35 x 35 pixel box centered at the pixel. A heat map indicating the ratio of calcium to aluminum+silicon (C/AS) was produced for each large area. The ratio of these elements was evaluated to normalize the EDS data between different phases. The C/AS was plotted as a function of the distance from the exposed surface using a 10% locally weighted scatterplot smoothing factor to reduce the noise of the plot.

4. Results

4.1. Material properties

Analysis of total, hydroxide, and carbonate-based alkalinity data from the titration curves (Table 3) revealed differences in the alkalinity between the component materials and also between microconcretes. Of the component materials, OPC had a much greater total alkalinity than either of the fly ashes which is attributed to the large hydroxide alkalinity of the OPC. FA02 had very little hydroxide, carbonate, and total alkalinity. FA39 had an intermediate hydroxide and total alkalinity compared to OPC and FA39. However, the true inflection point could not be determined for FA39 and therefore its location was estimated according to the position of the complex root located near the phenolphthalein alkalinity in the 2nd derivative of the polynomial. Therefore, the distribution of hydroxide and carbonated in FA39 may not reflect the true distribution of these alkalinities. In the non-carbonated microconcretes, the material made without fly ash replacement (M-00) had the highest alkalinity mostly attributed to the hydroxide alkalinity and the material created with the lowest alkalinity fly ash (M-02) had the corresponding lowest hydroxide and total alkalinity. These results are consistent with the alkalinity measurements in the component materials and the calcium loading in the microconcrete based on the calcium in the OPC, FA39 and FA02. Upon carbonation, the hydroxide alkalinity in the microconcretes was significantly reduced and the carbonate alkalinity increased for all microconcretes. The carbonated microconcrete material made without fly ash replacement (MC-00) had the highest hydroxide and total alkalinity compared to the carbonated materials made with fly ash. Correspondingly, the carbonated microconcrete made with the lowest alkalinity fly ash (MC-02) had the smallest total alkalinity and hydroxide alkalinity was

completely eliminated. These results are consistent with the original alkalinity measurements in their respective non-carbonated microconcretes.

Table 3.

pH and hydroxide, carbonate, and total alkalinity of the components and microconcretes ($\pm$ mean CV) determined from titrating with 4 N HNO₃ from natural pH to a pH of 4.5. Alkalinity measurements are expressed as mg CaCO₃ per g-dry of solid material

	Natural pH ($\pm$ 1%)	Hydroxide ($\pm$ 6%)	Carbonate ($\pm$ 23%)	Total Alkalinity ($\pm$ 5%)
OPC	12.7	19.2	1.0	20.2
FA39*	12.1	7.7	3.0	10.6
FA02	10.1	0.1	0.1	0.3
M-00	12.7	3.2	0.6	3.8
M-39	12.9	2.4	0.7	3.1
M-02	12.8	2.1	0.3	2.3
MC-00	12.1	0.9	2.5	3.4
MC-39	11.4	0.1	2.7	2.8
MC-02	10.3	-	2.1	2.1

*No true inflection point determined from the FA39 titration curve

TGA (Figure 2) showed characteristic mass loss peaks in three general temperature regions corresponding to the temperature ranges described previously. The results in Figure 2 also include a peak at approximately 105° C associated with the loss of evaporable water. The first region of interest is the slow mass loss in the temperature range from 150° to 400° C and peaks near 400° C for M-00 and MC-00 which are attributed to the decomposition of C-S-H. A sharp peak in the temperature range of 400° to 500° C, associated with the decomposition of portlandite, is evident for all non-carbonated microconcretes (i.e., M-00, M-02, M-39) and also for the MC-00 carbonated material. However, no peak was observed in this temperature range for either of the carbonated materials containing fly ash (i.e., MC-02 and MC-39) and, therefore, portlandite content is not reported for either MC-02 or MC-39. The final region of interest contains the peaks associated with carbonated phases starting at a temperature of 520°

C, progressing to a sharp peak beginning around 650° C, and ending around 750° C. There was a slight variation in the beginning and ending temperatures of the carbonate peaks for the three carbonated microconcrete materials. The slow rise in the carbonate peak, which is indistinguishable itself as a separate peak in the carbonated materials, may be attributed to decomposition of calcite formed from the heating of vaterite, whereas the beginning of the sharp peak may be attributed to the loss of CO₂ from the dissociation of calcite formed directly during carbonation.

The mass % of each phase derived from the mass loss associated with the described temperature ranges is summarized in Table 4. In addition, the last column in the table compares the percentage of reacted calcium (% Ca Reacted) that was determined from the relative changes in each of these phases between the non-carbonated and carbonated material. The extent of reaction was inversely related to the alkalinity of the original material.

Table 4.

Mass % ($\pm$ mean CV) of C-S-H, portlandite, vaterite (associated with carbonation of C-S-H), and calcite according to the weight loss of the DTG curve in the respected temperature ranges

Material	C-S-H ($\pm$ 3%)	Portlandite ($\pm$ 6%)	Vaterite($\pm$ 10%)	Calcite ($\pm$ 9%)	% Ca Reacted ($\pm$ 14%)
M-00	15.2	6.3	1.7	2.3	N/A
M-39	14.6	2.1	1.8	1.1	N/A
M-02	12.8	1.9	1.6	1.4	N/A
MC-00	12.0	2.7	3.4	6.5	26
MC-39	13.0	-	4.0	7.9	54
MC-02	9.3	-	4.0	7.8	58

A comparison of the total wt% of inorganic carbon in carbonate form in each component and the materials as determined from the Method 1313 leaching test titration (i.e., extractions), TIC (i.e., digestion), and TGA (i.e., solid) methods was calculated for comparison purposes and to assess

the differences in these techniques to characterize the difference in the uptake of CO₂ during carbonation across materials with different alkalinities (Table 5). As expected, the wt% inorganic C determined from all three methods was higher in each carbonated microconcrete compared to their respective non-carbonated microconcrete. The inorganic C increased by approximately 1 wt% according to the alkalinity and TGA data and by approximately 2 wt% according to the TIC data from the non-carbonated to the carbonated materials. In general, the wt% inorganic C in the carbonated microconcretes increased as the alkalinity of the materials decreased according to TGA and TIC analysis. No trend between the alkalinity and the wt% inorganic C in the carbonated materials could be observed in the alkalinity data. In addition there was no trend in the wt% inorganic C in the components especially since the true inflection point could not be determined for FA39 in the titration curve. Therefore, the reported wt% inorganic C of FA39 may not reflect the actual amount of carbon contained in the material.

Table 5.

Comparison of measured inorganic carbon (wt% $\pm$ mean CV) determined from alkalinity, TIC, and TGA in the microconcretes and their components

Material	Alkalinity ($\pm$ 23%) (Titration)	TIC ($\pm$ 15%) (Digestion)	TGA ($\pm$ 12%) (Solid)
OPC	0.6	0.1	0.1
FA39	1.8*	0.1	<0.1
FA02	0.1	0.1	0.2
M-00	0.4	0.2	0.5
M-39	0.4	0.2	0.3
M-02	0.2	0.5	0.4
MC-00	1.5	2.1	1.2
MC-39	1.6	2.4	1.4
MC-02	1.3	2.9	1.4

*No true inflection point determined from the FA39 titration curve

4.2. Carbonation depth by pH using phenolphthalein indicator

The carbonation depth was initially estimated by determining the change in color of a 1% solution of phenolphthalein sprayed on a cross-section of each carbonated microconcrete. In each sample, the top exposed layer remained colorless, indicating a pH less than 10 due to carbonation while the interior portion of the sample turned bright pink, indicating the pH remained greater than 10 which corresponds to an uncarbonated region. The depth of the colorless layer varied across the surface for each microconcrete, especially near aggregates, with MC-02 showing the greatest mean depth of carbonation at 1.2 mm and MC-00 showing the smallest mean depth of carbonation at 0.4 mm. MC-39 had a mean carbonation depth at 0.7 mm which is intermediate of the indicated carbonation depths for MC-02 and MC-00.

4.3. Liquid-solid partitioning of major constituents as a function of pH

Comparison of the calcium, aluminum, and silicon solubility curves plotted as a function of pH from Method 1313 showed the shift in pH-dependent concentration between carbonated and non-carbonated samples (Figure 3). For all materials, the measured natural pH decreased in carbonated samples relative to non-carbonated samples (Table 6) and the order of decrease was inversely proportional to the alkalinity in each sample (i.e., MC-00 had the highest natural pH and MC-02 had the lowest natural pH). The result of the shift in pH-dependent behavior and the decrease in natural pH is that the solubility of calcium at the natural pH for each microconcrete also decreased for the carbonated materials compared to the non-carbonated materials.

Conversely, the solubility of silicon increased in the carbonated materials compared to the non-carbonated materials. There was no significant trend observed for the changes in the aluminum solubility curves between the carbonated and non-carbonated materials. Portions of the data relative to the calcium solubility in materials MC-00 and MC-02 has previously been reported [26].

Table 6.

Mean solubility (mg/L) of calcium, aluminum, and silicon ($\pm$ mean CV) and corresponding natural pH (± 1 pooled σ) for two replicates of each microconcrete material from EPA Method 1313

Material	Natural pH ($\pm 1\%$)	Ca Solubility ($\pm 5\%$)	Al Solubility ($\pm 16\%$)	Si Solubility ($\pm 10\%$)
M-00	12.7	902.6	0.2	0.2
M-39	12.9	426.7	1.5	0.7
M-02	12.8	1119.5	2.4	0.8
MC-00	12.1	156.2	1.5	8.1
MC-39	11.4	52.4	2.0	13.5
MC-02	10.3	117.3	0.1	22.6

4.4. Microstructural analysis

Backscattered electron images at 1500x and EDS maps for each microconcrete in the carbonated and non-carbonated materials revealed different elemental composition and microstructure between these two regions (representative images **Figure 4.A-C**). Additionally, the microstructure and composition was different between the three material types. A uniform carbonated phase was observed in MC-00. The bulk concentration of the carbonated region (excluding the aggregate located at the upper left hand region seen in **Figure 4.A**) was increased in calcium and decreased in aluminum and silicon content compared to the bulk of the non-carbonated material (Table 7). Other differences in composition for the remaining elements in Table 7 were observed between the carbonated and non-carbonated regions.

The heat maps of C/AS ratios for MC-02& MC-39 shown in **Figure 4.B & C** indicate two distinct phases in the carbonated region: a region where carbonated phases (e.g., calcium carbonate) dominate (**Region A, Figure 4.B & C**) and a region where decalcified C-S-H phase is present (**Region B, Figure 4.B & C**). The presence of minor and trace constituents (i.e., Na, Mg,

Al, P, S, and K) from EDS data in these regions indicate that other carbonated or calcium-silicate bearing phases exist to some degree in these two regions although the calcium carbonate and decalcified C-S-H dominate in their respective regions. These two regions are distinguished by the higher calcium and lower silicon in Region A containing carbonated phases relative to Region B containing decalcified C-S-H. In addition, the carbonate phases in Region A show decreases in the sodium, aluminum, and potassium (Table 7). Between the two microconcretes containing fly ash, the two separate phases were less pronounced in MC-39. The decalcification of C-S-H during carbonation conditions has been well-documented [9, 46] and observed in backscattered electron images [10] as a darker and more heterogeneous regions than the lighter more homogeneous carbonate phase. In the uncarbonated region, the backscattered electron images showed the presence of both portlandite and normal C-S-H phases.

Table 7.

Elemental distribution (mass wt%) showing species migration between the carbonated and uncarbonated regions and the decalcification of the C-S-H gel in carbonated region in the presence of carbonated portlandite and C-S-H. The remaining mass percentage is assumed to be hydrogen, due to the presence of hydrated phases

Material	Region	C	O	Na	Mg	Al	Si	S	K	Ca	Fe	C/AS
M-00	Uncarbonated	7.6	46.7	0.1	0.9	1.6	8.3	1.1	0.4	26.2	2.1	2.7
MC-00	Carbonated	9.1	46.3	0.2	1.0	1.4	5.6	0.9	0.8	26.4	1.8	3.8
MC-39	A	8.2	49.0	1.6	0.8	2.0	3.9	-	1.4	28.4	1.4	4.8
	B	7.6	48.8	2.6	1.0	4.3	11.7	0.2	3.2	14.4	2.8	0.9
MC-02	A	6.9	47.7	0.2	0.7	2.0	7.5	0.6	0.4	24.7	2.1	2.6
	B	8.8	47.8	0.4	0.7	3.1	15.4	0.9	2.0	12.2	2.4	0.7

Large area maps created using the 496x magnification scans revealed the formation of CaCO_3 either in the form of calcite or vaterite at the exposed surface of each material (Figure 5.A-C) and the formation of these phases was supported by TGA data (Table 4). In the large area maps, the carbonation depth was defined as the depth where the lighter grey carbonated products could no longer be observed in the backscattered electron image and is marked by a white line across the

backscattered and C/AS maps. The smallest depth of carbonation was observed for the OPC-based microconcrete (MC-00) while an increasing carbonation depths were noted for microconcretes containing fly ash (e.g., MC-39 and MC-02). The MC-02 sample had the largest carbonation depth. Measurements taken across the exposed surface (Table 8) showed that significant variation in the carbonation depth was observed in MC-02 and MC-39. Conversely, MC-00 had consistent depth of carbonation across the surface area; however, a smaller area of carbonation not connected to the bulk carbonation front was observed at a deeper level in the material and between two large aggregates. This remote carbonation zone may have been the result of a preferential diffusion pathway through the material pore structure during carbonation.

Table 8.

Carbonation depth (mm) according to backscattered electron imaging

	Mean	Min	Max
MC-00	0.5	0.5	0.5
MC-39	0.8	0.5	1.0
MC-02	1.8	1.5	2.2

For each material, the highest C/AS were observed in the carbonated regions and the lowest ratios were observed in the uncarbonated regions according to the C/AS as a function of distance from the exposed surface plots (Figure 5.A-C). In MC-00, the C/AS heat map revealed a significant decrease in the C/AS at the interface of where the calcium carbonate could no longer be observed. The C/AS below this interface was slightly higher, but less than that observed in the carbonated region. The large area maps corresponding to the C/AS showed a decrease in the C/AS as the distance from the exposed surface increased. For MC-39, ratios were not evaluated below a depth of 1.6 mm because an aggregate comprised the entire image area below that depth.

For each microconcrete, the approximate calcium, silicon, and aluminum wt% in the carbonated and uncarbonated regions (excluding the aggregate and large fly ash particles) revealed an

increase in the calcium content, a decrease in the silicon content, and a slight decrease in the aluminum content in the carbonated region compared to the uncarbonated region for each material (Table 9). This corresponds to the increase in the C/AS observed in the carbonated region. Higher C/AS in the MC-00 were observed in all regions of the sample compared to MC-02 and MC-39 because the material has a higher concentration of calcium in the mixture. A lower C/AS was observed in all regions of the MC-02 material compared to MC-39 because of the lower calcium content in the fly ash.

Table 9.
Mean composition (mass wt%) of cement paste excluding aggregates and fly ash

	Uncarbonated Region				Carbonated Region			
	Ca	Si	Al	C/AS	Ca	Si	Al	C/AS
MC-00	23.9	8.7	1.4	2.4	24.9	7.7	1.4	2.7
MC-39	18.0	7.9	3.3	1.6	21.2	7.6	2.9	2.0
MC-02	17.1	9.9	3.0	1.3	20.0	9.2	2.8	1.7

5. Discussion

This study presents that results of several different, but complimentary, evaluations of carbonation in cementitious material pastes. These results serve as lines of evidence that support improved knowledge of the carbonation process including the role of matrix alkalinity in resisting the carbonation reaction and the depth of carbonate penetration, the distribution of calcium between carbonated and uncarbonated phases, and the impact of fine aggregates on the penetration of a carbonation front.

5.1. The role of alkalinity in carbonation

Several observations in this study support that the carbonation reaction is strongly influenced by the alkalinity of the microconcrete. Specifically, the differences in the carbonation depth and

microstructure determined from SEM-EDS, measured pH determined from U.S. EPA Method 1313, and extent of reaction determined from alkalinity, TIC, and TGA measurements reveal variations between the materials and impact of material alkalinity on the carbonation reaction. The relationship between these observations and the material alkalinity is summarized in Table 10 and are discussed further in this section.

Table 10.
Relationship of alkalinity and carbonation

Property	Relationship	Note
Total Alkalinity	OPC > FA39 > FA02 M-00 > M-39 > M-02 MC-00 > MC-39 > MC-02	Component alkalinity is related to alkalinity of resultant material
Carbonation Depth	MC-02 > MC-39 > MC-00	Carbonation depth ↑ as alkalinity ↓
Microstructural Changes	MC-02 > MC-39 > MC-00	Extent of microstructural changes ↑ as alkalinity ↓
Extent of Reaction	MC-02 > MC-39 > MC-00	Extent of reaction ↑ as alkalinity ↓
Reaction Capacity	M-00 > M-39 > M-02	Reaction capacity ↑ as alkalinity ↑
Natural pH	OPC > FA39 > FA02 M-00 ≈ M-39 ≈ M-02 MC-00 > MC-39 > MC-02	Natural pH ↑ as alkalinity ↑

5.1.1. Carbonation depth

Estimates of depth of the carbonation reaction front from backscattered electron imaging revealed that the depth of carbonation is inversely related to the alkalinity of the microconcrete. The mix design with the highest initial alkalinity (M-00) resulted in a carbonated material with the smallest depth of carbonation (MC-00). Conversely, the greatest penetration depth (MC-02) was observed for the mix design that provides the least initial alkalinity (M-02).

The differences in the hydroxide alkalinity in the non-carbonated microconcretes support that different reactive capacities exist across the different materials to react with calcium and CO₂ as in Equation 2. The hydroxide alkalinity was significantly reduced in the carbonated

microconcretes because of the consumption of hydroxide in this reaction. It is evident based on the increased carbonation depth and smaller hydroxide alkalinity of MC-02 and MC-39 that there is less capacity to react with diffused CO_2 and therefore unreacted CO_2 can proceed to the interior of the sample to consume hydroxide in deeper portions of the sample. In contrast, the large hydroxide alkalinity of MC-00 suggests that larger amounts of CO_2 can be consumed by the carbonation reaction in the material resulting in a smaller carbonation depth.

The intermediate penetration depth observed in MC-39 is an important finding because this case eliminates the possibility that the differences in the carbonation depth were due solely to the fly ash altering to pore structure of the material and therefore changing the diffusion properties. Although, the addition of fly ash most certainly can reduce the diffusion of CO_2 into the matrix by refining the pore structure and can change the rate of ingress of carbonation as observed in prior studies [18, 19, 47, 48], the relationship between carbonation depth and alkalinity of the three microconcretes and their components supports the conclusion that alkalinity plays an important role in controlling the depth of the carbonation front.

Thus, hydroxide alkalinity can be considered to provide a reactive capacity to the material that resists penetration of the carbonation front into the matrix. On a local level, the reactive capacity limits the transport of unreacted CO_2 until the alkalinity is consumed. The microconcretes with fly ash replacement had less initial hydroxide alkalinity (i.e., portlandite); therefore, the carbonation front penetrated further into the material than in the case of carbonation of the OPC microconcrete. This observation is consistent with the suggestions at that SCMs may lead to an increase in the carbonation ingress rate [22].

The depth measured by backscattered imaging were slightly larger in each microconcrete than the depths measured by phenolphthalein indicating that carbonation occurring near the boundary of the carbonated and uncarbonated region had not yet consumed enough free hydroxide to lower the pH below the threshold required for the color change in phenolphthalein. This suggests that backscattered imaging is a more robust and powerful tool to evaluate the depth of carbonation.

5.1.2. Microstructure

The alkalinity affects the extent of the microstructural changes observed in the carbonated materials predominantly due to the decalcification of the C-S-H gel and formation of CaCO_3 in the form of calcite and vaterite according to TGA results. The lower alkalinity non-carbonated materials (M-02 and M-39) showed the formation of the decalcified C-S-H phase and a CaCO_3 in their respective carbonated materials (MC-02 and MC-39). Because there was less hydroxide to react with CO_2 , a higher extent of reaction occurred in the MC-02 compared to the MC-39. In addition, these two materials also had a higher extent of reaction compared to MC-00. MC-00 only showed the formation of CaCO_3 and there was no observable decalcification C-S-H because much more hydroxide from the portlandite is available to dissolve and react with diffused CO_2 . MC-39 has an intermediate hydroxide alkalinity so there was less decalcification and reaction of the C-S-H phase compared to MC-02, but this decalcification and reaction was still observed to some extent. This observation is consistent with a study completed by Borges et al. [41] which concluded that smaller initial amounts of portlandite (and, therefore, less alkalinity) in cement materials due to the addition of blast furnace slag increased the extent of carbonation of the C-S-H phase. In addition, regions located near the surface of MC-02 and MC-39 had a much higher extent of carbonation because the carbonation front had passed those regions and was continuing to react at further distances in the sample. Therefore, the formation of the two distinct phases of

the decalcified C-S-H and the carbonated phase could be attributed to a greater extent of reaction in those regions.

5.1.3. Extent of Reaction

The differences in the alkalinities correlated to the extent of reaction and reaction capacity of hydroxide determined from TGA (Table 4). M-00 had a significantly larger amount of portlandite and a slightly larger amount of C-S-H due to its larger calcium concentration compared to the M-02 and M-39, indicating a higher capacity of hydroxide and calcium to react with diffused CO₂. This observation confirms the material's higher alkalinity since alkalinity is directly related to the calcium concentration. C-S-H and portlandite decreased and vaterite and calcite increased in all of the carbonated materials compared to the non-carbonated materials. Portlandite was completely eliminated in the MC-02 and MC-39 materials, whereas some portlandite remained in the MC-00. Therefore, the extent of reaction according to Eq. 4 was highest for the MC-02 and lowest for the MC-00. This supports that the extent of reaction in the microconcrete materials is a function of the original alkalinity of the material.

Differences in the wt% inorganic C values derived from alkalinity, TIC, and TGA measurements for each component and microconcrete are a result of the different limitations associated with each method to determine the exact wt% inorganic C. In the titration curve, silicates and phosphates provide additional buffering capacity which is captured as carbonate alkalinity by this method. Therefore, the measured amount of carbonate determined from the titration curve may be larger than what is in the system. In addition, titration data represents the buffering capacity of the soluble phases in the material and therefore may not reflect the composition of entire material. A limitation of TGA to determine wt% inorganic C is that only vaterite and

calcite were calculated based on the stoichiometry of their decomposition over the specified temperature. Other minor carbonated phases such as magnesium carbonate are not captured by this method because 1) these phases may decompose over a different temperature range than the vaterite and calcite 2) the wt% inorganic C was derived based on the stoichiometry of the vaterite and calcite which may not capture other phases decomposing over the same temperature range. Conversely, TIC captures the inorganic carbon from all carbonated species digested during the procedure. This is reflected by the slightly larger wt% inorganic C values measured by TIC compared to TGA for the carbonated materials. Despite these limitations, the wt% inorganic C reported was relatively consistent for all three of the methods. The only major variability between the three methods occurs in the wt% inorganic C determined from titration of FA39. This may be due to the lack of a true inflection point in the titration curve.

5.1.4. pH

The alkalinity of the material affected the reduction of the natural pH under carbonating conditions. MC-02 and MC-39, had further reduction in the natural pH for the carbonated microconcretes compared to the respective non-carbonated microconcretes (M-02 and M-39) as determined by Method 1313 than what was observed for the high alkalinity control microconcrete, MC-00. The mean carbonation depth of 1.2 mm determined by the phenolphthalein test for MC-02 indicates a 2 mm granular material would be fully carbonated assuming CO₂ diffused radially inward from all exposed surfaces of the granular material. A mean carbonation depth of 0.7 mm for MC-39 would not fully penetrate the material, therefore only a portion of the sample was carbonated and the natural pH indicated by Method 1313 does not represent the entire carbonated region. A mean carbonation depth of 0.4 mm for MC-00 indicates the majority of the material was not carbonated, therefore only a very slight reduction

in pH was observed. Therefore, in addition to the influence of the alkalinity, these penetration depths may also be responsible for the differences in the decrease of the natural pH in the crushed carbonated microconcrete materials.

The differences that alkalinities and the influence of alkalinity in these microconcrete materials on the carbonation reaction suggest that the total alkalinity of the material could be used to determine the relative rates of carbonation depth and extent of reaction between different materials. The alkalinities of the components used in the mixtures were related to the alkalinities of the microconcretes and therefore predicting the carbonation reaction between different materials could be determined based on alkalinities of the components. Moreover, the alkalinities measurements approximated the amount of portlandite and carbonate in each system. However, characterizing the carbonation reaction as a function of alkalinity may only apply for materials with similar porosities, densities, tortuosities, relative saturations, and external CO₂ concentrations. These are additional factors that may need to be considered when estimating the overall impact of carbonation in materials with varying alkalinities.

5.2. Solubility of major constituents in carbonated matrices

Coupling the results of the liquid-solid portioning test as a function of pH (Figure 3) with the increase in concentration of calcium in the carbonated regions observed in EDS measurements (Table 9) suggest that calcium ions in the pore solution from the dissolution of the more soluble portlandite phase in the uncarbonated region diffuse to the carbonated region of the material where the less soluble CaCO₃ phase has formed. This results in a slight decalcification of the uncarbonated region and a deposition of calcium in the carbonated region as observed in the EDS heat maps for each material.

The corresponding increase in the solubility of silicon in carbonated materials and the decrease in silicon in the carbonated region also adds further evidence that the dissolution of C-S-H occurs, as discussed in terms of the influence of the alkalinity on the carbonation reaction. While calcium ions are consumed in the carbonation reaction, silicon remains in the pore solution and re-establishes equilibrium by diffusing to the less soluble uncarbonated region where it can react with calcium ions that are in greater concentration in the pore solution to potentially reform C-S-H. The formation of calcite and vaterite in these regions is supported by TGA which indicates a reduction of portlandite and C-S-H and an increase of the vaterite (from carbonation of C-S-H) and calcite phases in the carbonated samples compared to the non-carbonated samples.

Since no significant trends in the aluminum solubility were observed it is unclear whether or not the differences in the aluminum content were a result of differences in the aluminum solubility of carbonated and non-carbonated materials. However, the presence of other calcium-silicate bearing phases such as calcium aluminosilicate hydrate that are expected in cementitious materials [49] indicate that similar migration patterns could be observed if solubility is a contributing factor. Evaluation of this phase and additional calcium-silicate phases was outside the scope of this work.

5.3. Aggregates

The amount and orientation of aggregates may be responsible for significant variation in the observed carbonation depth across the same microconcrete. The interfacial transition zone (ITZ) may create a preferential diffusion pathway for CO₂ compared to the bulk paste as shown by the variation of the carbonation depth around the aggregates and the localized pocket in the ITZ between aggregates in Figure 5.A. This could be explained by the increase in porosity that is

expected in the ITZ [50]. However, aggregates may also inhibit CO_2 diffusion in localized regions because the aggregates themselves are less permeable to gas diffusion compared to the cement paste. Therefore, the aggregates reduce the effective cross-sectional area for CO_2 diffusion and may inhibit the penetration of a carbonation front into the matrix. For example, the heat map for MC-00 (Figure 5.A) shows bottleneck region formed between two aggregates where significant decalcification of C-S-H was observed which suggests a localized reaction and limited transport of CO_2 . Furthermore, aggregates composed of CaCO_3 , such as limestone, could significantly alter the localized equilibrium conditions of the pore solution and influence the availability of calcium to react with CO_2 .

Although the microconcretes studied here are composed of solely of fine aggregate and not a combination of fine and coarse aggregates, these observation are likely transferrable to concretes because the fraction of aggregates is designed to approximate the same interfacial area of concrete materials [51]. Therefore, robust efforts to model carbonation in concrete matrices should consider the amount, morphology and composition of aggregates to account for the effects of preferential pathways and effective diffusive areas. These ideas necessitate further experimental verification and complex modeling techniques which could account for the variability seen in the carbonation depth.

6. Conclusions

The purpose of this study was to characterize the impact of alkalinity derived from the titration curve of the material on the carbonation reaction in microconcrete materials with varying alkalinities due to the partial replacement of the Portland cement with fly ash utilizing a variety

of experimental techniques to better understand and predict the long-term performance of cementitious materials containing SCMs. The main conclusions from this study are:

1. Material alkalinity derived from the titration curve of microconcrete is inversely related to the rate of carbonation and the chemical and microstructural alteration in the matrix as shown by multiple experimental characterizations. Therefore, alkalinity derived from the acid-base titration curve of the solid material and their components may provide an estimate of the potential extent of the carbonation reaction and the potential chemical and microstructural changes for other cementitious materials.

2. A powerful and robust characterization of the chemical and microstructural changes in cementitious materials due to carbonation is the result of a combination of different, but complementary analysis. SEM-EDS provides additional detailed information regarding the spatial distribution of elements and microstructural changes, and variability of the carbonation depth.

3. Differences in the solubility of phases formed during carbonation cause the migration and re-precipitation of solubility-sensitive species including calcium and silicon.

4. The quantity and orientation of aggregates can create preferential diffusion pathways for CO₂ gas in some regions of the material or inhibit CO₂ gas diffusion in others because of increased CO₂ diffusion at the aggregate-paste interface which is a consideration for complex carbonation modeling. Work to further characterize the impact of aggregates on the preferential diffusion of CO₂ is ongoing.

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List of Figures

Figure 1: Fourth degree polynomial fit of the titration curves generated for M-00 and MC-00.

Figure 2: TGA results plotted as the derivative of the mass and temperature versus the temperature for one replication of the A) non-carbonated microconcretes and the B) carbonated microconcretes

Figure 3: EPA Method 1313 for M-00, MC-00, M-02, MC-39, MC-39, M-02, and MC-02 with circles around data point indicating a test position at the material's natural pH.

Figure 4.A-C: 1500x backscattered electron images and C/AS heat maps of the uncarbonated and carbonated regions of A) MC-00, B) MC-39, and C) MC-02

Figure 5.A-C: Backscattered electron image and C/AS heat map with the corresponding C/AS as a function of distance from the exposed surface for A) MC-00, B) MC-39, and C) MC-02. Dark blue areas indicate aggregates that were excluded from the heat map calculations. *The darker red region and C/AS peak highlighted is due to a small carbonated region not connected to the bulk carbonation front.

Figure 1

Figure 2

Figure 3

Figure 4

A) MC-00

uncarbonated

carbonated

C/AS

86 μm

B) MC-39

uncarbonated

carbonated

A
B

86 μm

C) MC-02

uncarbonated

carbonated

A
B

86 μm

Figure 5a

A) MC-00

Figure 5b

B) MC-39

Figure 5c

C) MC-02