ERDC TR-20-2

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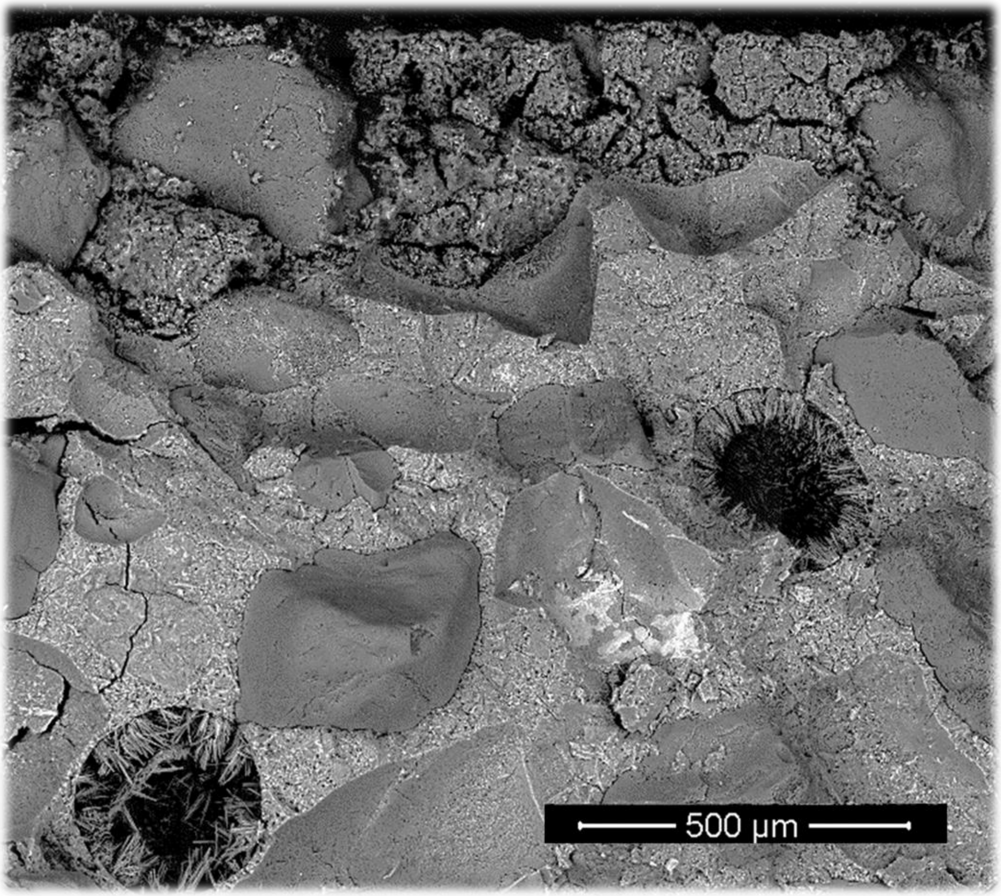

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Final report

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Under MIPR CLCC 2D0E28

Abstract

This study focused on examining the susceptibility of three concrete materials to carbonation-induced deterioration in a simulated CO_2 chemical fish barrier system. The concrete materials tested were modeled after concretes and aggregate mineralogies used in civil works structures. The exposure conditions consisted of 74 mg/L and 225 mg/L concentrations of CO_2 in an aqueous solution maintained at both 21°C and 40°C. Visual examination and pH indicator solutions were used to monitor the progression of any deterioration in specimens during the experiment. Surface deterioration was not observed until 90- and 180-day measurements. Characterization performed on affected materials and surface deterioration products indicated that the damage was induced by carbonation mechanisms with Ca^{2+} leaching from the concrete microstructure reacting with CO_2 in solution. These processes were limited to the top 1 mm of the concrete, even at 180 days with any severe microstructural alteration and changes in pH limited to 100-200 μm of depth. The primary conclusion from this Phase 1 study is that carbonation-induced deterioration can occur in the simulated fish barrier environment, but the rates of carbonation are not of concern and are similar to those that would be expected for concrete exposed to normal atmospheric conditions and CO_2 concentrations.

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Preface

This study was conducted for the U.S. Army Engineer Research and Development Center, Environmental Laboratory (EL), and the U.S. Army Corps of Engineers Chicago District under MIPR CLCC 2DOE28. The technical monitor was Dr. David L. Smith, EL.

The work was performed by the Concrete and Materials Branch (GMC) of the Engineering Systems and Materials Division (GM), U.S. Army Engineer Research and Development Center, Geotechnical and Structures Laboratory (ERDC-GSL). The technical monitor was Dr. Robert D. Moser.

At the time of publication, Mr. Christopher M. Moore was Chief, GMC; Mr. Justin Strickler was Chief, GM; and Ms. Pamela Kinnebrew, GTZ, was the Technical Director for Military Engineering. The Deputy Director of ERDC-GSL was Mr. Charles W. Ertle, and the Director was Mr. Bartley P. Durst.

COL Teresa A. Schlosser was the Commander of ERDC, and Dr. David W. Pittman was the Director.

1 Introduction

The Concrete and Materials Branch (CMB) of the Geotechnical and Structures Laboratory, U.S. Army Engineer Research and Development Center (ERDC), was asked to perform an analysis on the chemical effect of carbon dioxide exposure to underwater concrete structures by the ERDC Environmental Laboratory (EL) and the Corps of Engineers Chicago District (LRC). Many of the structures of concern were built from the 1920s through the early 1960s on the Mississippi River and its tributaries. The U.S. Army Corps of Engineers (USACE) is currently investigating suitable physical, behavioral, and chemical barrier systems to mitigate northern migration of Asian Carp through the Mississippi River and its tributaries into the Great Lakes Ecosystem. In particular, use of a chemical CO_2 barrier has been shown to effectively deter unwanted migration by this aquatic nuisance species in small-scale laboratory studies. However, it remains unclear how underwater concrete infrastructures along the Mississippi River would be affected by this constant, long-term exposure to elevated CO_2 concentrations. In this ongoing study, submerged concrete samples were designed to emulate the at-risk concrete in an underwater exposure tank infused with CO_2 at a concentration comparable to that of the proposed CO_2 fish barrier.

Of primary concern is the potential for accelerated carbonation of concrete materials and the impact of reductions in pH associated with concentrated CO_2 injections into the aqueous environment. Cementitious materials such as concrete are rich in calcium due to the use of calcined limestone and other minerals for the production of conventional portland cements. When combined with water, hydration reactions result in a microstructure that contains various forms of hydrated calcium silicates, calcium sulfoaluminates, calcium hydroxide, and a high ionic strength in solution (pore solution that is rich in Ca^{2+}, K^+, Na^+, and $SO4^{2-}$ among other species). Over time, hardened concrete will bind with CO_2 in the reverse process of calcination called carbonation. This process is generally attributed to the reaction between CO_2 and the calcium hydroxide/portlandite [$Ca(OH)_2$] phase present in portland cement paste to form calcium carbonate. In atmospheric conditions, carbonate occurs at a rate of approximately 1 mm/yr. in typical concrete. In submerged conditions with elevated CO_2 concentrations, i.e., above 200-400 ppm, the potential carbonation rates are unknown.

The structural consequences associated with carbonation are primarily related to the shift in pore solution pH that occurs following the corrosion process. As calcium hydroxide (a solid phase that buffers the pore solution to a pH >12.5) is consumed and calcium carbonate forms, the pH of the pore solution is reduced from 13-13.5 to 9-10. High pHs in the range of 12.5 to 13 will passivate the reinforcing steel and prevent corrosion. Lowering the pH makes the reinforcing steel susceptible to corrosion. While it is generally simple to predict service lives associated with carbonation-induced corrosion in structures with an atmospheric exposure, i.e., common knowledge of anticipated carbonation rates, it is unknown how rapid carbonation will occur in submerged concrete structures that are exposed to high concentrations of CO_2.

Another potential deterioration mechanism associated with the CO_2 barrier is related to the type of aggregate used to produce the concrete and the existing aggregate at Brandon Road Lock and Dam, the study site. Siliceous aggregates, e.g., granite, chert, and basalt, are highly resistant to deterioration when exposed to high concentrations of CO_2 in aqueous environments. However, limestone aggregates that are commonly used in many USACE concrete structures are vulnerable to rapid dissolution when exposed to high concentrations of CO_2 through the production of carbonic acid. This susceptibility to dissolution will largely depend on the carbonate alkalinity of the local water and the effect of the selected CO_2 concentration on water alkalinity.

There is little to no information in the literature regarding underwater carbonation of concrete and other potential deterioration mechanisms. Thus, the study presented herein was commissioned in order to address this lack of understanding and to identify potential deterioration concerns should such a CO_2 chemical fish barrier system be incorporated into a USACE structure.

2 Research Scope

The following tasks were performed to determine the effect of reduced pH and elevated CO_2 levels in concrete samples cast to emulate the structures of concern. These tasks were developed in coordination with project stakeholders and executed over the course of the project:

- Task 1: Conduct a review of Brandon Road Lock and Dam design documents and quality assurance reports and use the gathered information to simulate specimens of similar mix design for carbonation exposure. Study other concrete formulations, aggregate types, and cementitious materials used in the repair of these structures. Develop a plan of different concrete mixture proportions and conduct trial batching using various aggregates and supplementary cementitious materials to simulate anticipated ranges of concretes that may be used in various Corps of Engineers structures across the United States.
- Task 2: Batch and cast a sufficient quantity of 3-in. by 6-in. concrete cylinders for multiple analyses at different chemical CO_2 concentrations and temperatures. The specimens represent the various mixture proportions and materials identified in Task 1. Record mechanical properties and information on mixture proportion from each batch of cylinders to assess the integrity of the concrete.
- Task 3: Design and construct an experimental system to simulate the exposure induced in the concrete specimen by the CO_2 chemical fish barrier. Provide an experimental set up with exposure concentrations targeted by the Environmental Laboratory studies and recommendations of project collaborators from LRC and the U.S. Geologic Survey and allow for the data collection of carbonation rates, pH, and solution temperatures.
- Task 4: Provide data from periodic sampling of the concrete specimen in the experimental set up. Collect data for pH of reverse osmosis (RO) water and river water simulant, periodic pH indicator measurements, thermogravimetric analysis (TGA), optical microscopy, and scanning electron microscopy (SEM).
- In addition, place samples of limestone, quartzite, and granite aggregate material in the exposure system. See Appendix A for photographs, mass data, and associated changes.

3 Materials and Methods

3.1 Materials

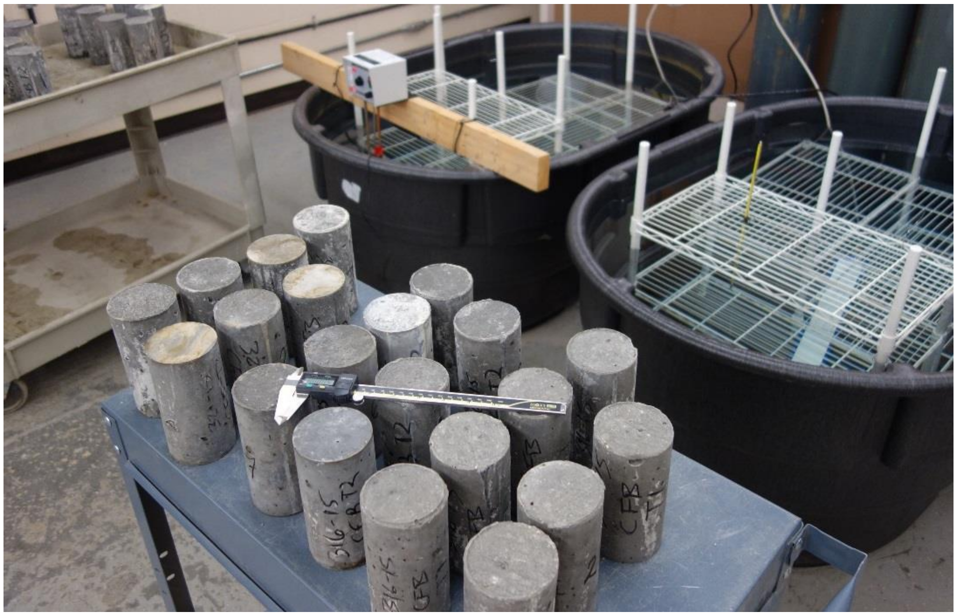
The Concrete and Materials Branch cast a total of 21 3- by 6-in. cylinders composed of three different mix designs, designated T1, T2, and T3; each were placed in a tank. Specimen T1 consisted of 75% Type I/II Portland Cement (PC) and 25% Fly Ash (FA) Class F, and a chert aggregate with a maximum nominal size of 3/8 in.; Specimen T2 consisted of 100% Type I/II Portland Cement with a chert aggregate with a maximum nominal size of 3/8 in.; and Specimen T3 consisted of 100% Type I/II Portland Cement with a #89 limestone aggregate (see Figures 1a and 1b). Companion paste samples were also produced without any aggregate primarily for use in mineralogical analysis to simplify complications introduced by the presence and needed removal of aggregates prior to analysis. In addition, samples of limestone, quartzite, and granite aggregates were placed in the exposure system. A photograph of the concrete cylinders used for testing is shown in Figure 1.

3.2 Simulated fish barrier exposure setup and operation

Two 150-gal tanks were used to simulate the CO_2 chemical fish barrier system such that one targeted CO_2 concentration was studied at two different temperature levels for 365 days. The tanks were filled with (RO) water and marked to indicate a standard volume of 150 gal. This volume was adjusted twice a week, as needed, throughout the duration of the experiment. During the first phase, one tank was kept at 21±2°C, and the other was heated to 40±2°C. Both tanks were induced with CO_2 gas (74 mg/L) bubbled in via micro bubble ceramic (36 in. x 4 in.) diffusers. Twenty-one cylinders were placed in each tank, 7 of each mix design, and sampling was performed on days 7, 28, 56, 90, 180, and 365. After 365 days, the analysis was terminated and transitioned to a second phase of testing. During phase two, both tanks were kept at 21±2°C. Each tank was induced with differing CO_2 concentration levels, 74 mg/L and 225 mg/L. Sampling was performed on days 545 and 730 for specimens exposed to 74mg/L CO_2 and after 180 and 365 days of exposure to 225 mg/L CO_2. Since the concrete contains pore solution and soluble minerals that buffer the pH solution in the tank, the system required routine acidification to maintain desired pH levels. More details on the experimental setup, operation of the tanks, conditioning to standard pH and CO_2 concentrations, and measurement methods are provided in subsequent sections. A photograph of the overall experimental setup is shown in Figure 2.

Figure 1. Photograph of concrete cylinder specimens T1, T2, and T3 near experimental setup.

(a) Photographs of specimens T1, T2, and T3.



(b) Photographs of experimental setup.

Figure 2. Carbonation exposure system consisting of two tanks with CO_2 injection systems and heater to control tank two temperature.

Overlying water quality parameters were measured within each tank every weekday during the course of the experiment. Measurements were collected using a digital pH probe (model SDL100 Extech Instruments, Boston, MA) that was calibrated prior to use with NIST (National Institute of Standards and Technology) Traceable pH 4, 7, and 10 Buffer calibration solutions (Figure 3).

Figure 3. Carbonation Extech digital meters (pH, temperature, carbon dioxide, and relative humidity).

Both tanks 1 and 2 recorded pH levels of approximately 7.0 prior to the dispersion of carbon dioxide in the water. Each tank holds 150 gal (±5 gal) of fluid. This analysis used (RO) water, and measurements for the baseline were recorded in triplicate and averaged. It was established that the most accurate and reliable method to perform the measurements was by use of titration using a Hach Carbon Dioxide titration kit. Our measurements collected for addition of CO_2 using this equipment are given in Figure 5a and 5b. This measurement method is explained in detail in section 4.3.

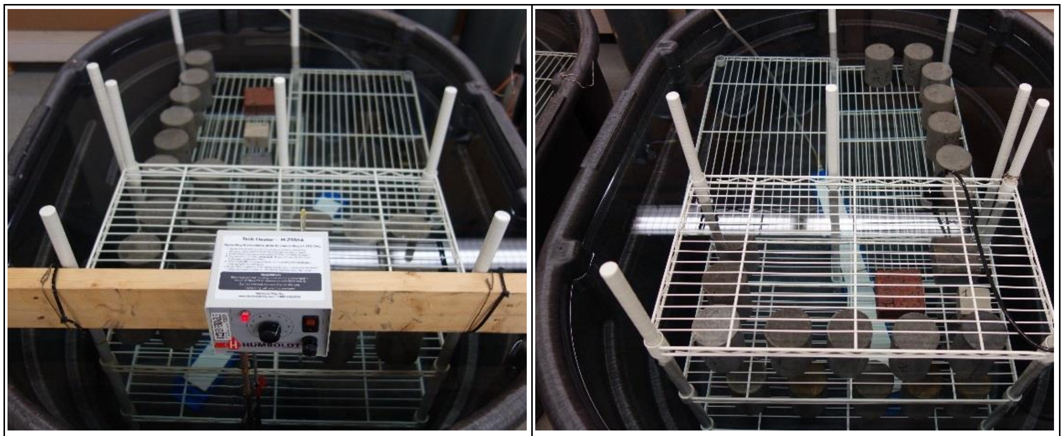
Due to the complexity of the chemistry taking place within the systems of tanks 1 and 2 and as a result of the concrete specimens leaching alkalis, it was found the Oxyguard CO_2 meter was not a reliable source for measuring dissolved carbon dioxide concentrations within the system. It has been established that the most accurate and reliable method to perform the measurements is by use of titration with a Hach Carbon Dioxide titration test kit.

To begin the titration process, the initial dissolved carbon dioxide level, pH, and temperature for each tank were recorded; the tanks are referenced as tank one (T1) and tank two (T2). Tank one (T1) was maintained at 21±2°C, and tank two (T2) was maintained at 40±2°C for the first 365 days of the analysis. During phase two, both tanks were kept at 21±2°C. Tank one (T1) was kept at a CO_2 concentration of 225 mg/L, and tank two (T2) was kept at a CO_2 concentration of 74 mg/L. Once the system reached constant levels of pH, dissolved CO_2, and temperature, the titration process was initiated. The titration process was as follows: carbon dioxide was pumped into the tanks at a rate of 15 cubic ft per hr (CFH) for a time of 15 sec during the initial readings, 30 sec at mid-concentration readings, and 45 sec for the final readings.

After each dosage of carbon dioxide, a titration procedure was performed to record the concentration of dissolved CO_2 in the system. This process was performed at the baseline with zero (CFH) of CO_2 pumped in the system, up to the final dosage of 165 mg/L. We used these data points to record a best fit line in a linear regression analysis and used the parameters to define the amount of time required to reach a dissolved carbon dioxide level of 74 mg/L or 225 mg/L set by the Environmental Laboratory (EL).

Once the carbonation levels were established in the tanks, daily maintanance occurred to ensure CO_2 levels were constant. Tanks were checked each morning during the week days, pH levels were balanced, and temperature readings were logged. The RO water level was maintained prior to any final diffusion of CO_2 in the sytem. On average, tank one (T1) required the addition of 7 gal RO water once a week, and tank two (T2) required the addition of 13 gal twice a week. The tank levels were maintained on Mondays and Thursdays; if a holiday fell on these days, prior planning took place to ensure accuracy. Tank two (T2) had a higher system temperature equal to 40°C (+/- 2°C), causing a higher evaporation rate. An established diffusion rate of 1 sec of CO_2 at 15 (CFH) was added per each gallon of RO water added to the system during the process. This rate was determined by use of the CO_2 loss titration curves and the linear regression equation (see Figure 4a through 4d, Figure 5a through 5d, and Figure 6a through 6b).

Figure 4. Tank adjustment images (a-d).



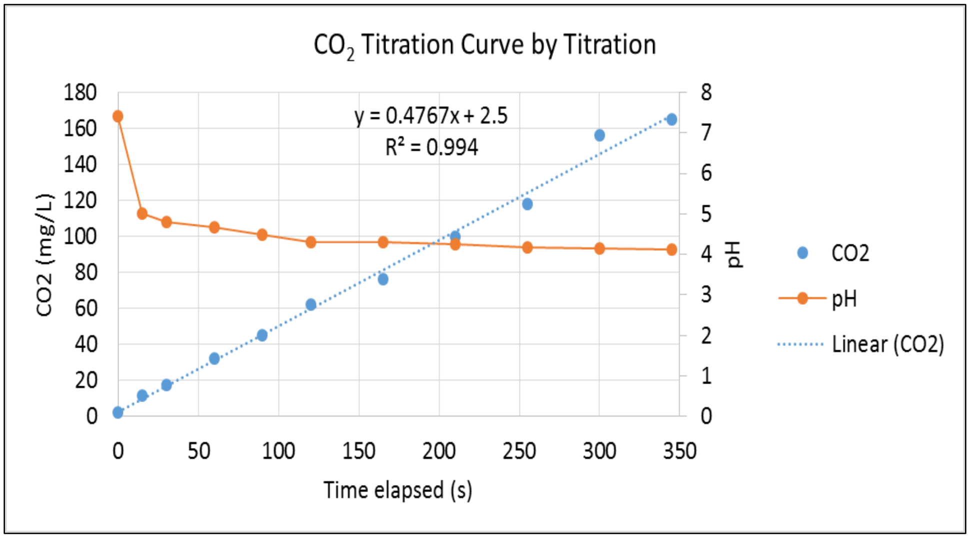
(a) Tank One (T1, 21±2°C).

(b) Tank Two (T2, 40±2°C).

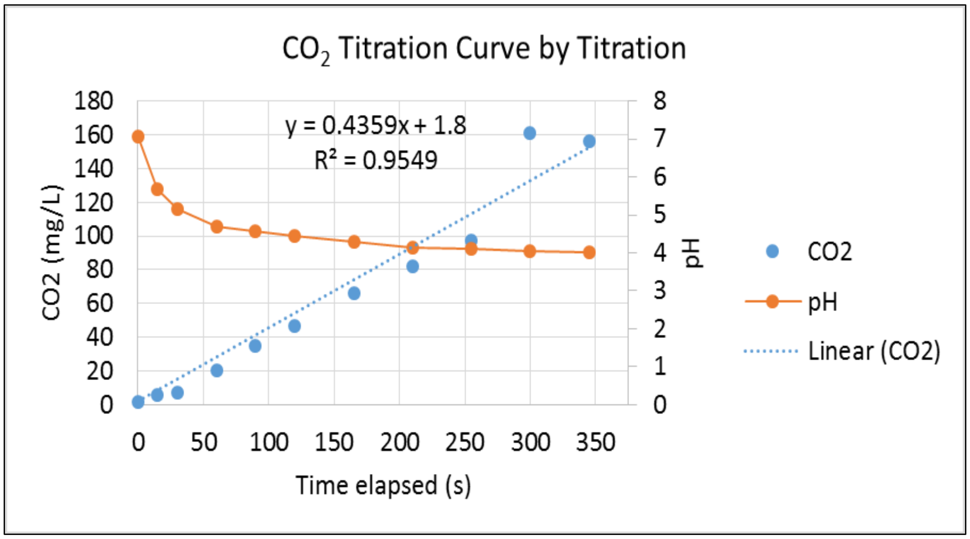
(c) Carbon dioxide manifold and volume control (CFH).

(d) Hach titration system.

Figure 5. pH calibration for tank one and tank two (a-b).

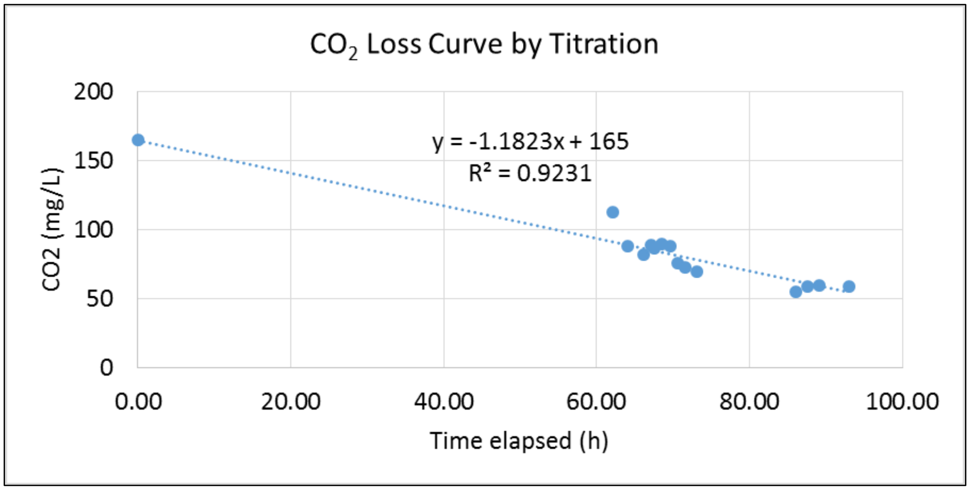


(a) Tank one [21±2°C] titration/pH curve.

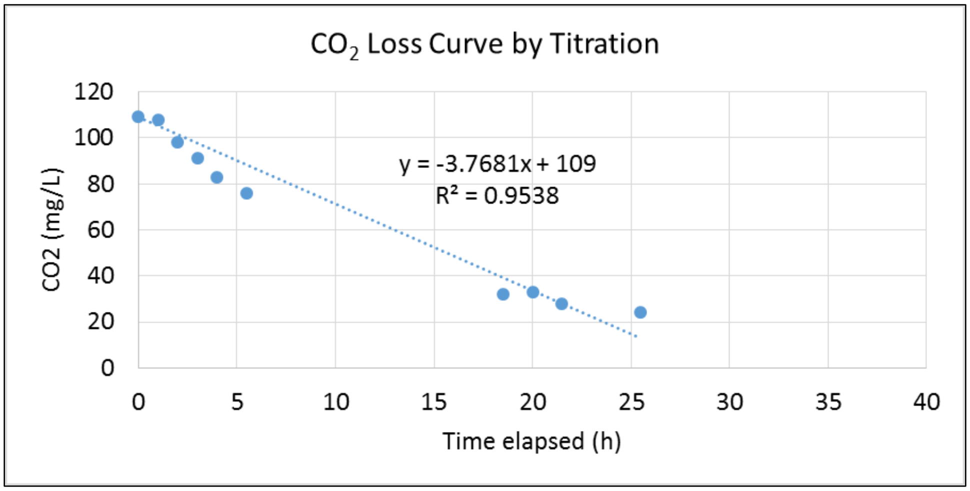


(b) Tank two [40±2°C] titration/pH curve.

Figure 6. Tank carbonation adjustment (a-b).



(a) Tank one (T1) CO_2 evaporation curve [21±2°C]



(b) Tank two (T2) CO_2 evaporation curve [40±2°C].

3.3 Analysis methods

3.3.1 Visual observations

Visual inspection of the concrete cores consisted of a qualitative assessment of the overall condition of the concrete, and a surface saturated dry (SSD) mass was obtained. At 7, 28, 56, 90, 180, and 365 days of phase one testing, cylinders and paste cubes were removed. For phase 2, cylinders and paste cubes were removed at 180 and 365 days. Specimens were surface dried, re-weighed, photographed, and then cut in half at the mid-height. At this point, pH indicator solution was applied to the freshly exposed surface; all specimens with pH indicator applied were photographed with a reference scale.

3.3.2 Compressive strength of concrete cylinders

Unconfined compressive strengths were obtained for each concrete mixture (T1, T2, and T3) for the 3-in. x 6-in. concrete cylinders (2:1 aspect ratio) according to the provisions outlined in ASTM C39 - Standard Test Method for Cylindrical Concrete Specimens. The strengths were obtained prior to placement in the CO_2 system. Strength data were also collected for the portland cement and fly ash paste cube specimens used for mineralogical analyses, ASTM C109.

Results of the unconfined compressive strength (UCS) measured in triplicates for each batch of specimens (T1, T2, and T3) are shown in Table 1. All of the concrete tested from specimens T1, T2, and T3 exhibited strengths in excess of 6,900 psi, which indicated that the concrete structurally and visually met the target mixture proportion specifications (see Table 1). Results of compressive strength tests for specimens T1, T2, and T3 and for portland cement and fly ash cubes are given in Tables 1 and 2, respectively. The strengths were measured prior to placement in the CO_2 system. From this point forward, team research focused on reaction of CO_2 as a function of time with the samples; as such, no further strength measurements were taken on the samples.

Table 1. Results of compressive strength tests for specimens T1, T2, and T3.

Sample ID	Diameter to Height (in.) (2:1 Ratio)	Compressive Strength at 28 days (psi)
T1	3x6	6,920
T2	3x6	8,450
T3	3x6	8,960

Table 2. Results of compressive strength tests for portland cement and fly ash cubes.

Sample ID	Diameter to Height (in.) (1:1 Ratio)	Compressive Strength at 28 days (psi)
Portland Cement	2x2	10,610
Fly Ash	2x2	8,080

3.3.3 Phenolphthalein indicator analysis (visual carbonation)

The phenolphthalein (pH) indicator analysis test is a method of visual analysis that provides a quick, reliable assessment of the extent to which the concrete has carbonated. The indicator turns pink when pH is higher than approximately 10 and remains clear at lower levels of pH. This indicator is a quick measurement of the depth and rate of carbonation taking place. The assessment was performed for each specimen (T1, T2, and T3) of the 3-in. x 6-in. concrete cylinders and the paste cubes at each test age 7, 28, 56, 90, 180, 365, 545, and 730 days of exposure. The pH indicator solution was applied to the freshly exposed surface; specimens with pH indicator applied were photographed with a reference scale.

3.3.4 Thermogravimetric analysis (TGA)

TGA was used to determine $Ca(OH)_2$ and $CaCO_3$ contents in the center of the paste samples to serve as an uncarbonated baseline measurement. TGA was also used to analyze powders collected from the surface of paste samples at different intervals of testing to identify shifts in mineralogy due to carbonation processes. Materials were ground with a mortar and pestle and passed through a No. 325 sieve such that the maximum particle size was 44 µm. Then, approximately 20 mg of the resulting powder was transferred to an aluminum oxide crucible and entered into the machine for testing. TGA was performed using a Netzsch STA 449 F1 Jupiter Thermal Analyzer on triplicate samples from each core from 35°C to 1000°C at a rate of 10°C/ minute in an N_2 atmosphere.

3.3.5 Optical microscopy

Optical microscopy was performed on all samples designated for petrographic analysis, and at least three samples were analyzed from each of the three test specimens (T1, T2, and T3). Specimens were freshly fractured prior to imaging to expose internal structures. Images were obtained by using a Carl Zeiss stereo microscope. Observations focused on the appearance of the carbonation of the outer surface of the specimen after pH indicator sprays at the macro and micro scales; any additional observations were recorded, including potential for paste deterioration and other types of distress.

3.3.6 Scanning electron microscopy (SEM)

Scanning electron microscopy (SEM) was performed on freshly fractured surfaces of the specimens collected following pH indicator analysis to determine whether the addition of CO_2 substantially influenced the microstructure of the specimens (T1, T2, T3). SEM imaging was performed using an FEI Nova NanoSEM 630 field emission SEM. Due to the low conductivity of the particles, all imaging was performed in low-vacuum mode. Operating parameters of 15 kV, spot size 5.0 µm, and vacuum levels of 0.1- to 1 mbar were used. Images were captured from several different areas of the specimen at multiple magnifications.

3.3.7 Mineralogical analysis

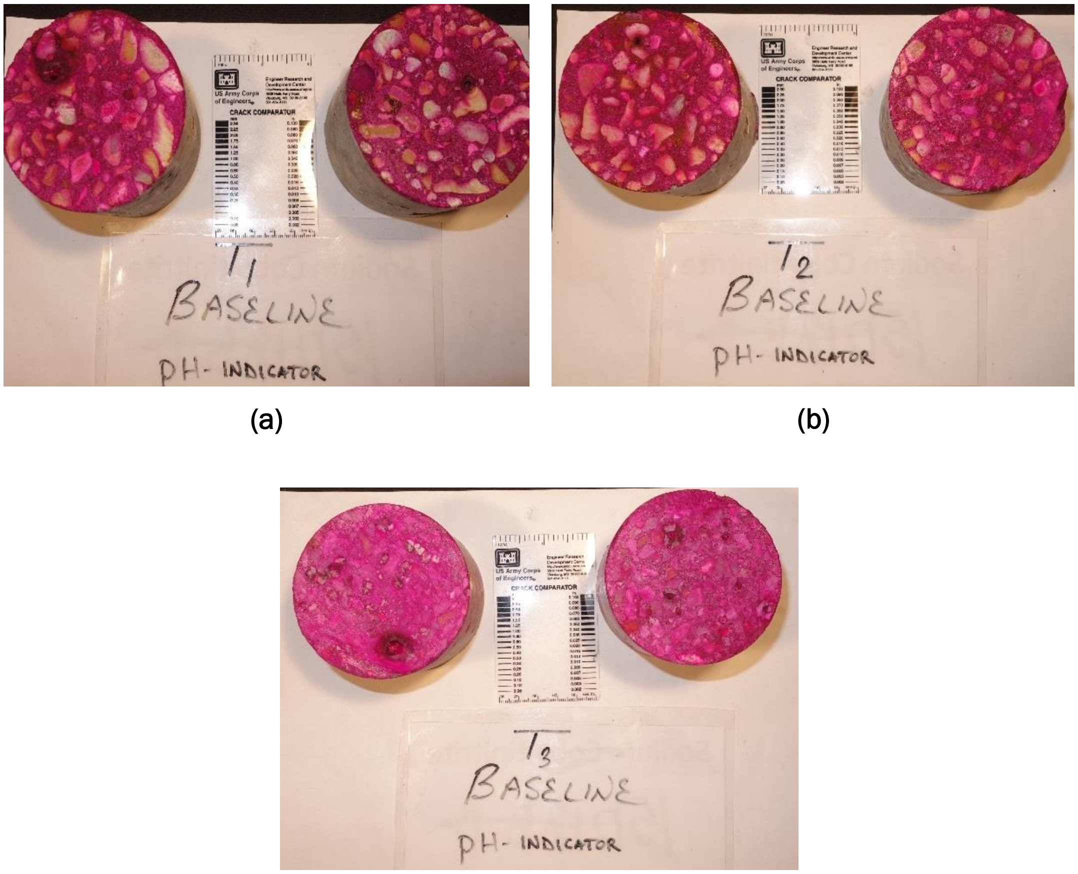
A representative sample from each of the test mixes for specimen (T1, T2, and T3) and paste cubes that represent the cement and fly ash were analyzed to determine the mineralogy of the concrete batched for the CO_2 analysis. In the case of non-paste samples, the coarse and fine fractions were separated to provide an accurate understanding of the mineralogy from each component. A baseline analysis was conducted on the uncarbonated samples. As the testing progressed, powders were collected directly off the exposed surface to identify mineralogical changes associated with carbonation processes. This analysis was performed using X-ray diffraction on a reverse pack loose-powder sample. The samples were manually crushed and pulverized to separate the aggregate and mortar fractions; these fractions were then ground using a pulverizing ball mill and passed through a 44-µm sieve to ensure a uniform grain size throughout the loose-powder samples.

XRD patterns were collected from a Panalytical Inc. X-Pert Pro Multipurpose Powder Diffractometer (MPD) system that used standard techniques for phase identification. The run conditions included Co-Kα radiation, scanning from 2 to 70°2θ with a step size less than 0.02°2θ at a rate of approximately 0.5°2θ/min. Diffraction patterns were collected using the PC-based Windows version of X-Pert Pro Data Collector, and analysis of the patterns was performed using the Jade2010 program from Materials Data Inc. Whole-pattern fits of the sample provided semi-quantitative analysis of the material.

4 Specimen Monitoring Using pH Indicator Solution and Visual Observations

The phenolphthalein (pH) indicator analysis was run for each of the 3-in. x 6-in. concrete cylinder specimens (T1, T2, and T3) at test ages of 7, 28, 56, 90, 180, 365, 545, and 730 days of exposure to 74 mg/L CO_2 (see Figure 7 through Figure 15).The pH indicator spray was also applied to the cement and fly ash paste cubes at the same time intervals. The pH indicator spray was applied to concrete cylinder specimens and cement and fly ash paste cubes exposed to CO_2 concentrations of 225 mg/L at test ages of 180 and 365 days. The pH indicator solution was applied to the freshly exposed (cut) specimen surface. The specimens with newly applied pH indicator were photographed with a reference scale (Figure 7). Observations were recorded; in the event of notable carbonation penetrating the specimen surface, further analysis was conducted. Results of these tests are compared to the exposed day-one baseline samples to determine the inward movement of carbonation. At the test age of 90 days, the formation of a precipitate forming on the outer surface of the concrete and paste specimen was noted for the first time; this precipitate is explained in further detail in subsequent sections. The formation of precipitates and visually apparent changes in the surface of samples continued to progress beyond 90 days through the 730-day observations (see Figures 11 through Figure 13). From this point, further analysis such as microscopy, SEM, TGA, and XRD were performed in the event of visible changes due to carbonation within the specimen. These tests give a more comprehensive analysis of what reactions are occurring.

Figure 7. Baseline measurement specimens (T1, T2, and T3).



(a) (b)

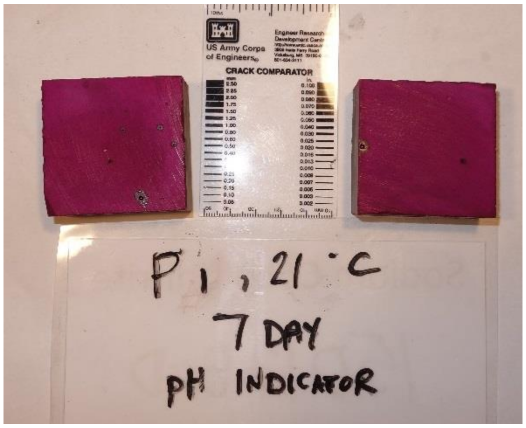
(c)

Figure 8. Seven-day measurement specimens, 74mg/L (T1, T2, and T3).

(a) (b)

(c) (d)

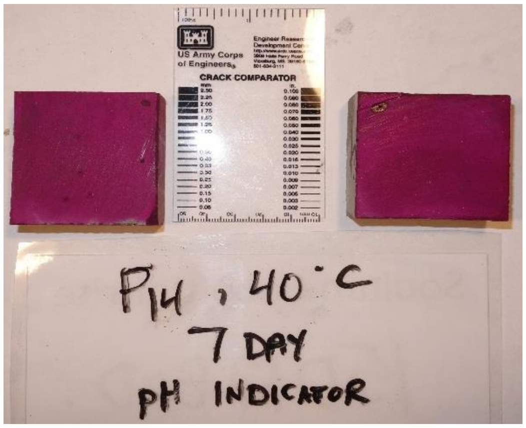
(e) (f)


US Army Corps of Engineers
CRACK COMPARATOR
P1, 21 °C
7 DAY
pH INDICATOR

(g)


US Army Corps of Engineers
F1, 20 °C
7 DAY
pH INDICATOR

(h)

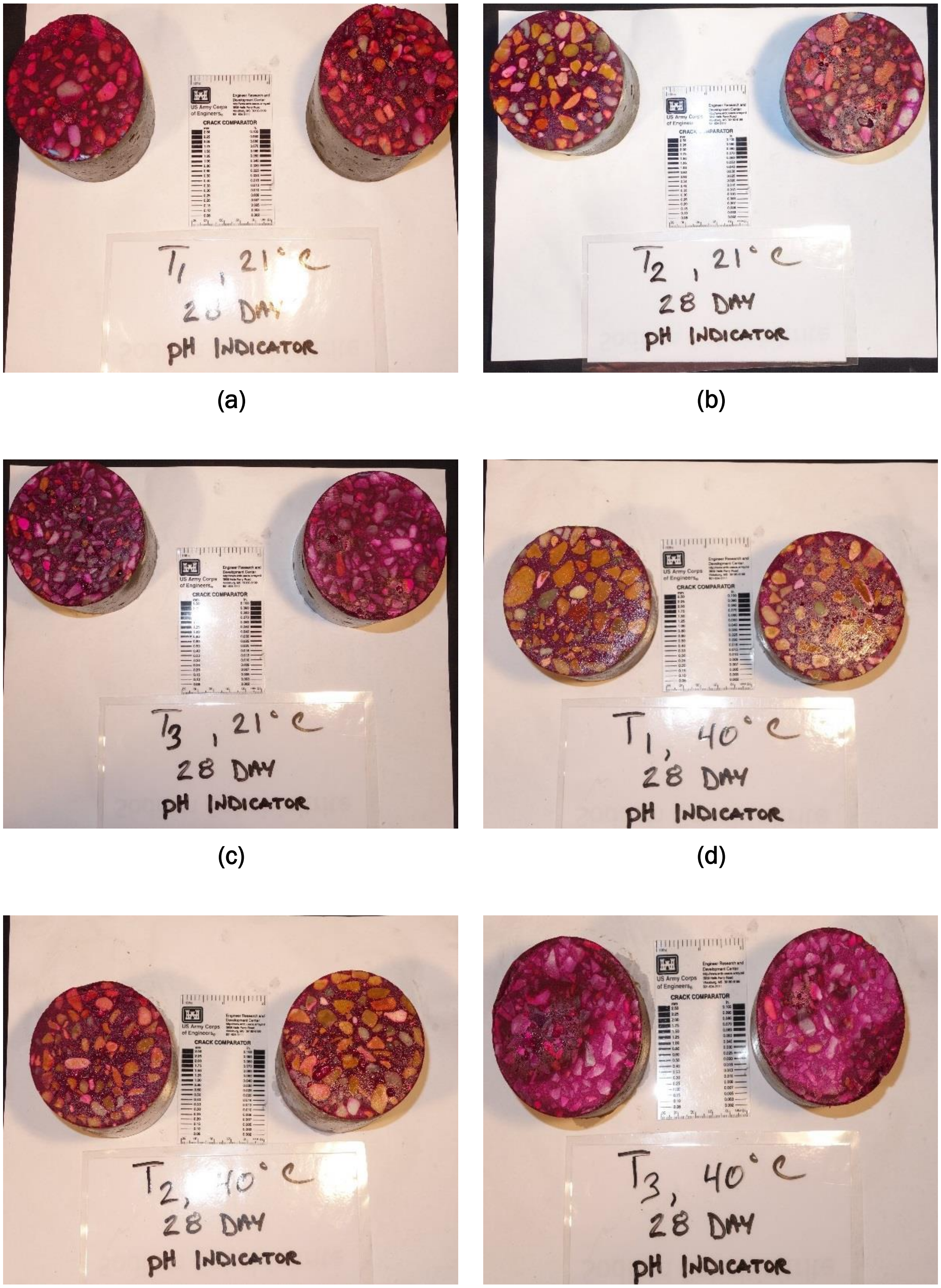

US Army Corps of Engineers
CRACK COMPARATOR
P14, 40 °C
7 DAY
pH INDICATOR

(i)


US Army Corps of Engineers
CRACK COMPARATOR
F14, 40 °C
7 DAY
pH INDICATOR

(j)

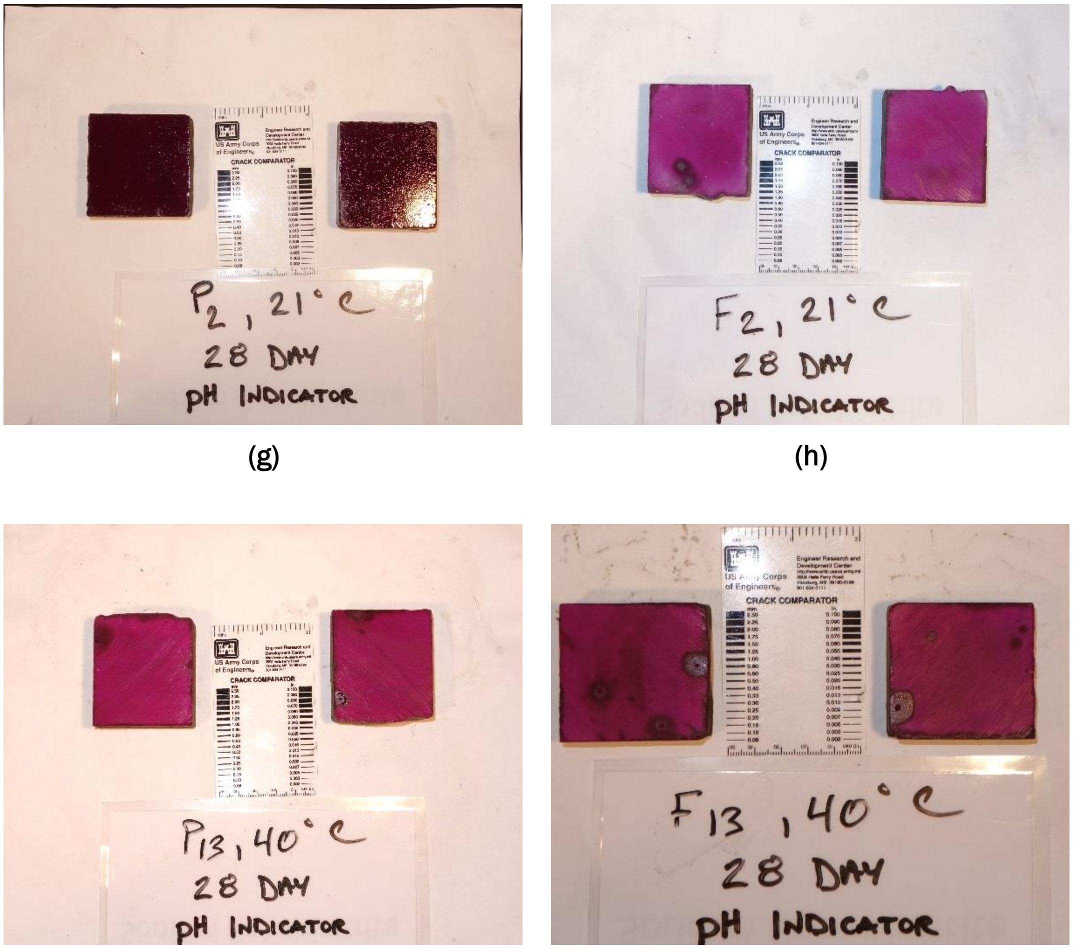
Figure 9. Twenty-eight-day measurement specimens, 74mg/L (T1, T2, and T3).



(a) (b)

(c) (d)

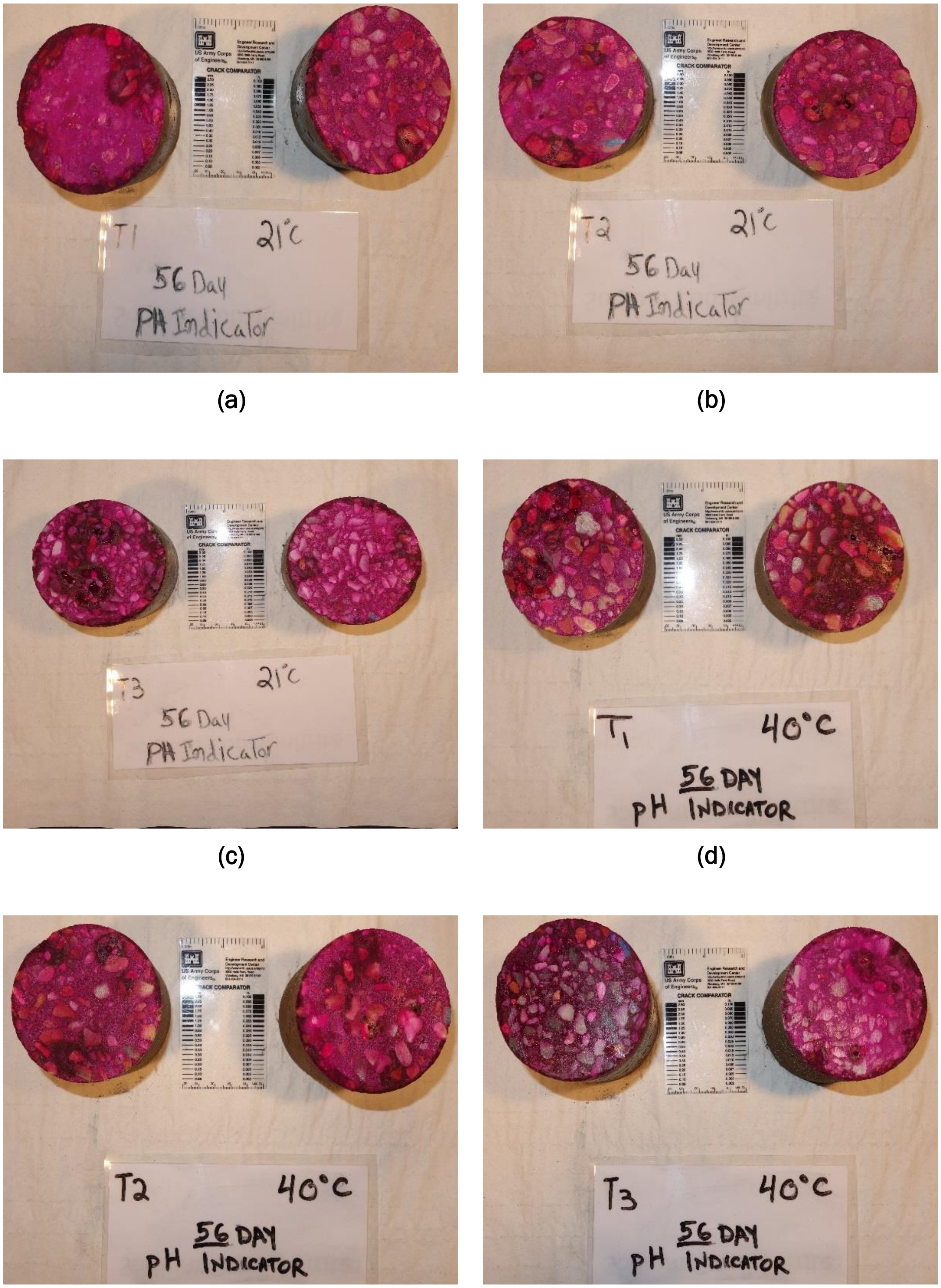
(e) (f)


P2, 21° C
28 DAY
pH INDICATOR
F2, 21° C
28 DAY
pH INDICATOR
P13, 40° C
28 DAY
pH INDICATOR
F13, 40° C
28 DAY
pH INDICATOR
US Army Corps of Engineers
CRACK COMPARATOR

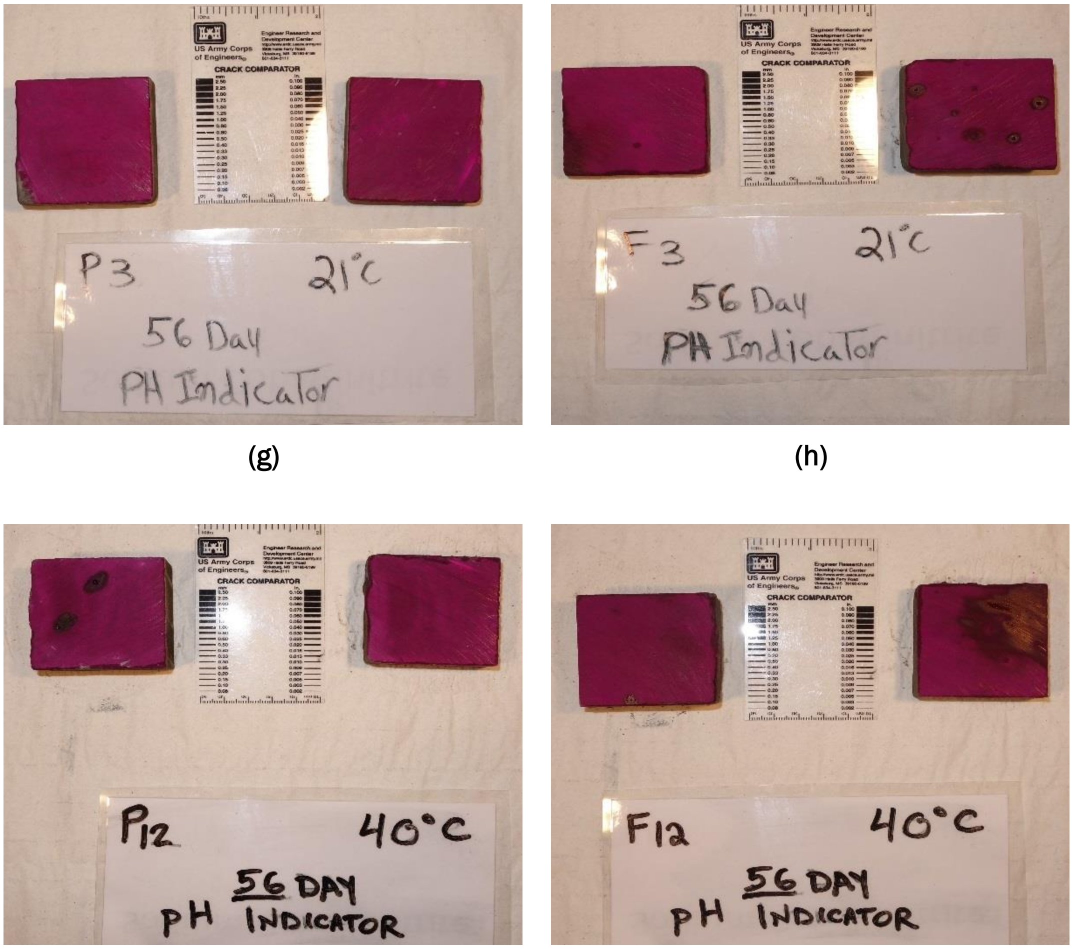
(g) (h)

(i) (j)

Figure 10. Fifty-six-day measurement specimens, 74mg/L (T1, T2, and T3).



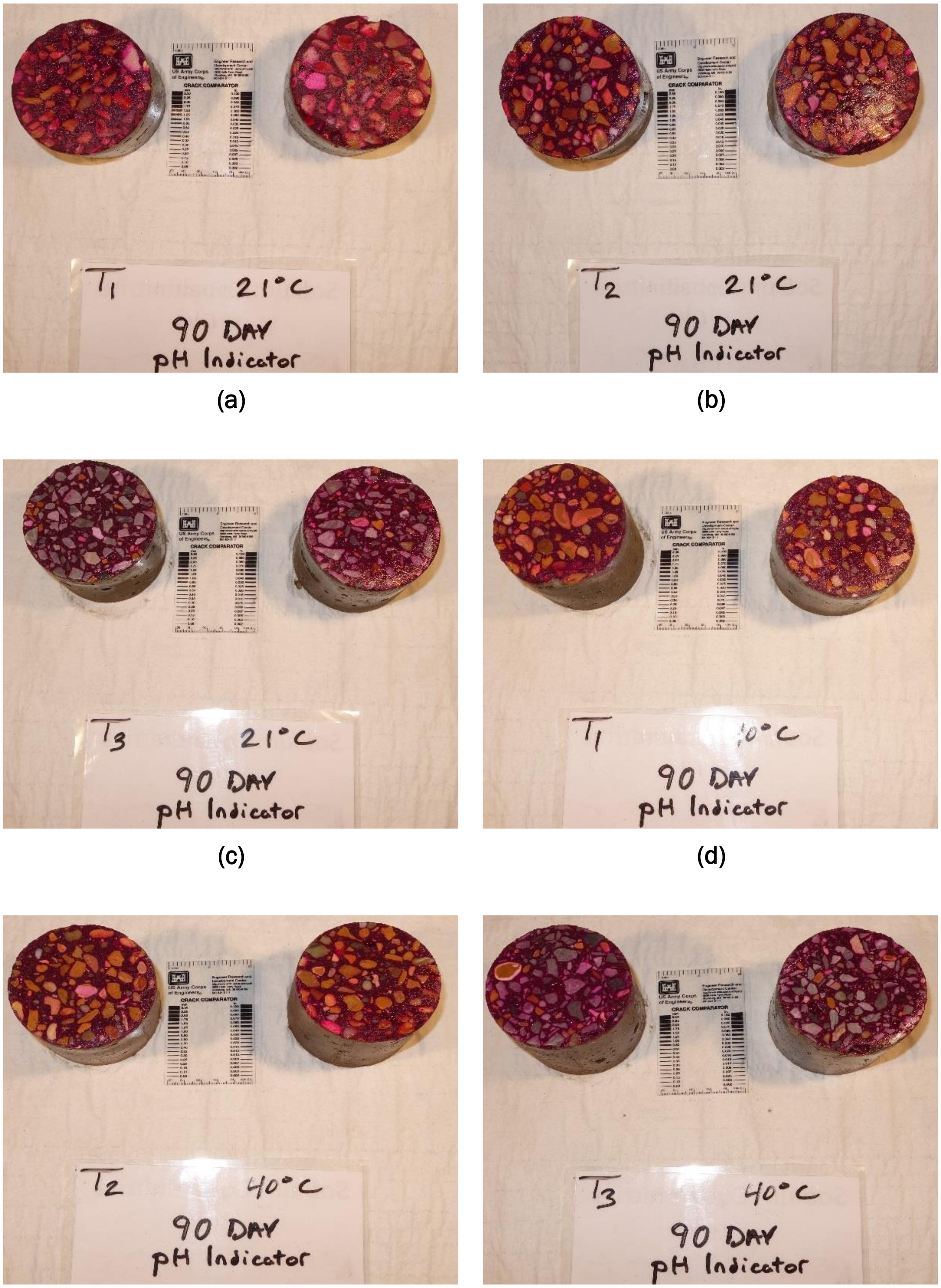
(a) (b) (c) (d) (e) (f)


P3
21°C
56 Day
PH Indicator
F3
21°C
56 Day
PH Indicator
P12
40°C
56 DAY
pH INDICATOR
F12
40°C
56 DAY
pH INDICATOR
US Army Corps of Engineers
CRACK COMPARATOR

(g) (h)

(i) (j)

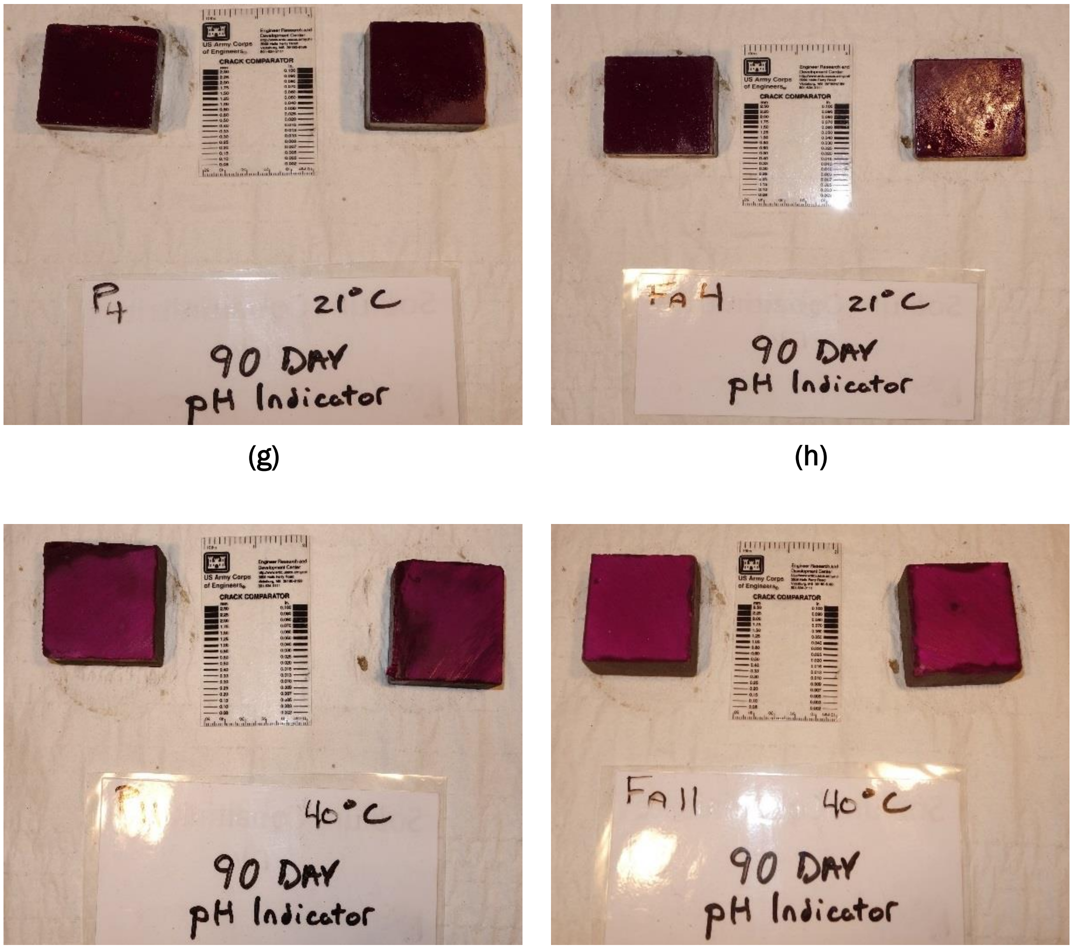
Figure 11. Ninety-day measurement specimens, 74mg/L (T1, T2, and T3).



(a) (b)

(c) (d)

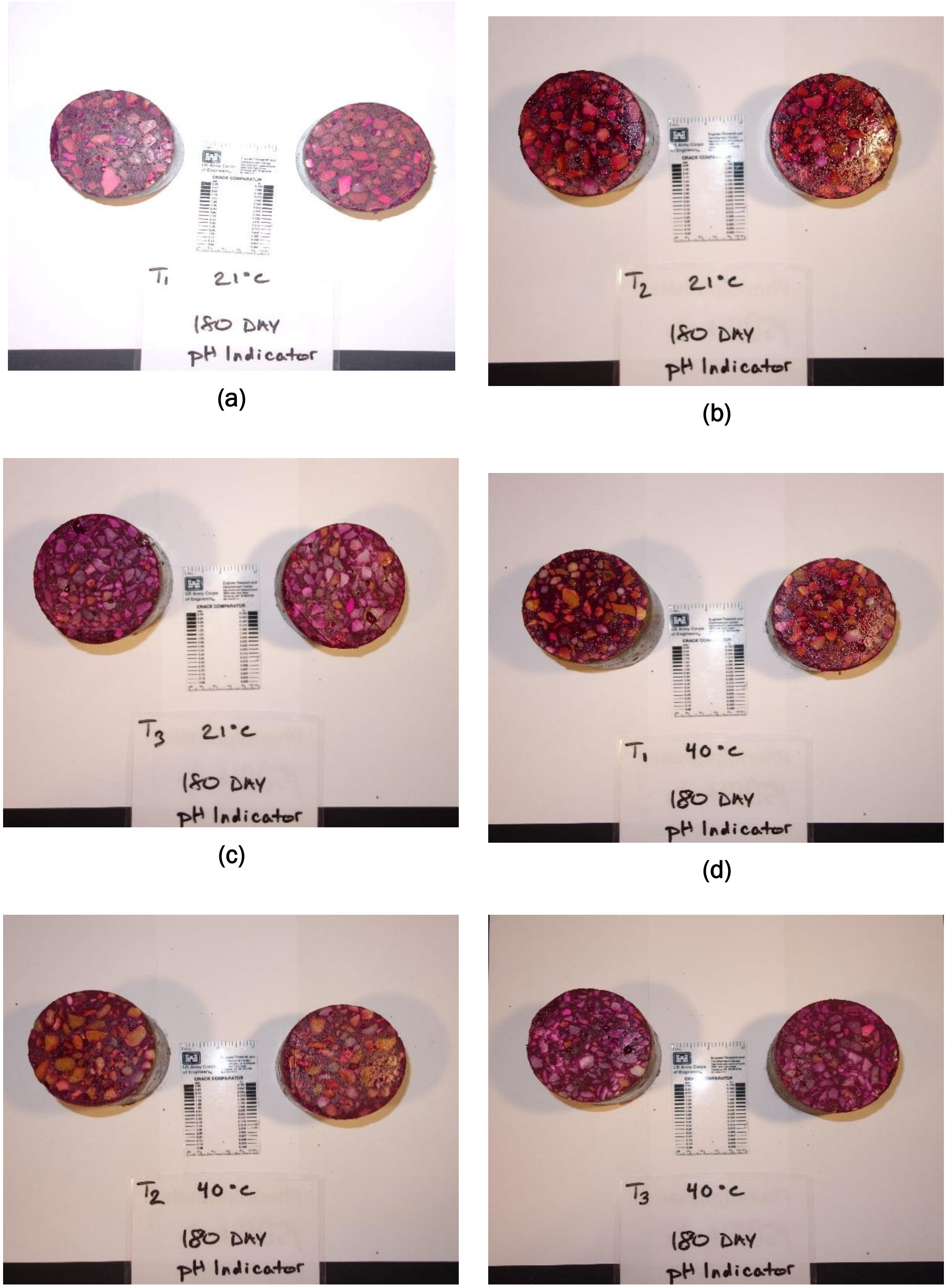
(e) (f)


P4
21°C
90 DAY
pH Indicator
FA 4
21°C
90 DAY
pH Indicator
P11
40°C
90 DAY
pH Indicator
FA 11
40°C
90 DAY
pH Indicator
CRACK COMPARATOR
US Army Corps of Engineers

(g) (h)

(i) (j)

Figure 12. One-hundred-eighty-day measurement specimens, 74mg/L (T1, T2, and T3).



(a) (b)

(c) (d)

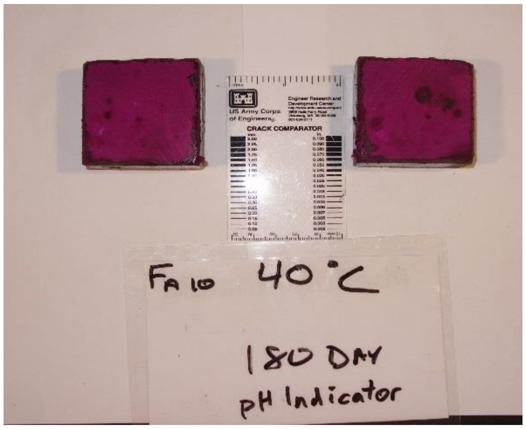
(e) (f)


P5 21°C
180 DAY
pH Indicator

(g)

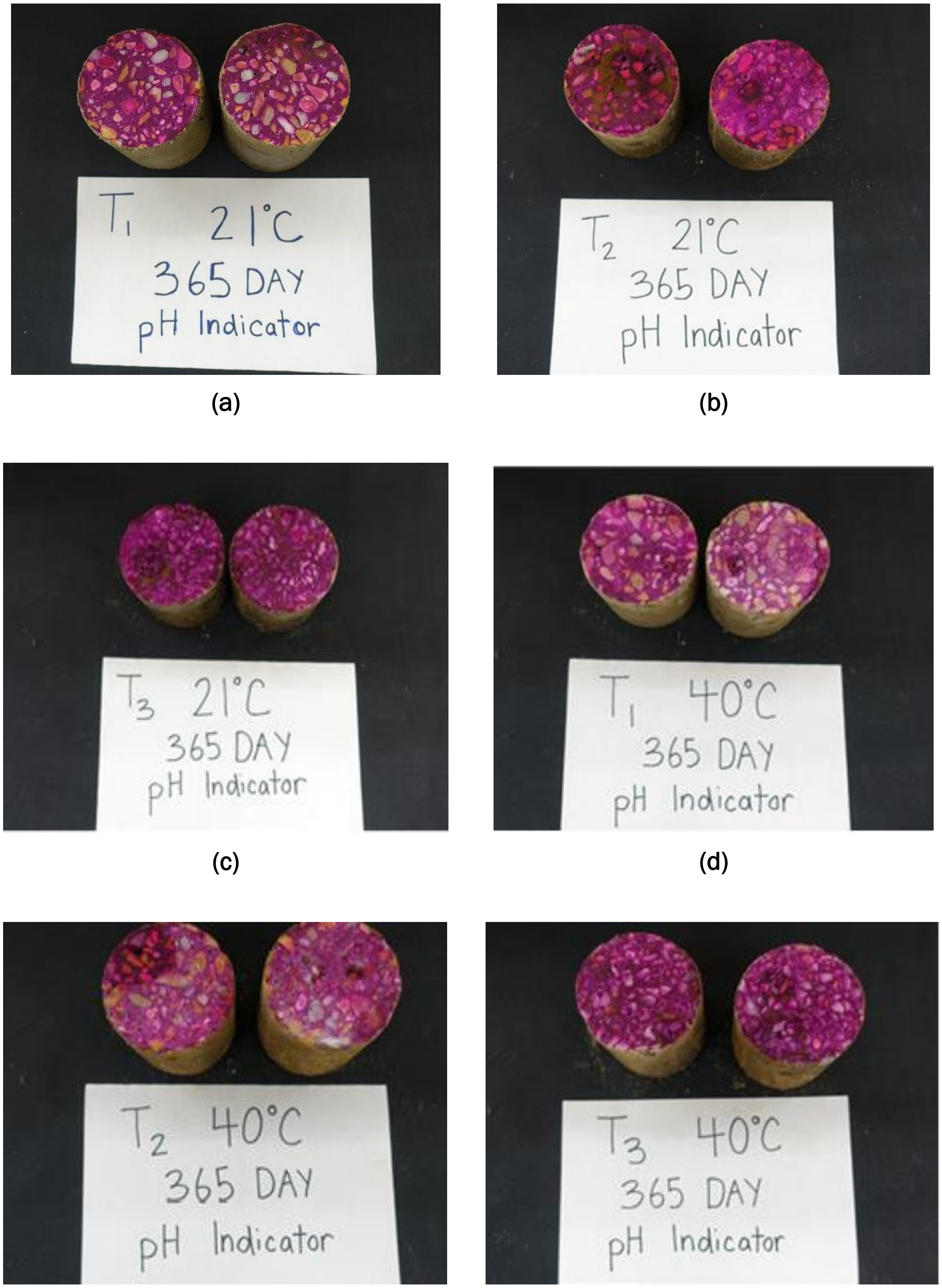

FA5 21°C
180 DAY
pH Indicator

(h)


FA10 40°C
180 DAY
pH Indicator

(i)

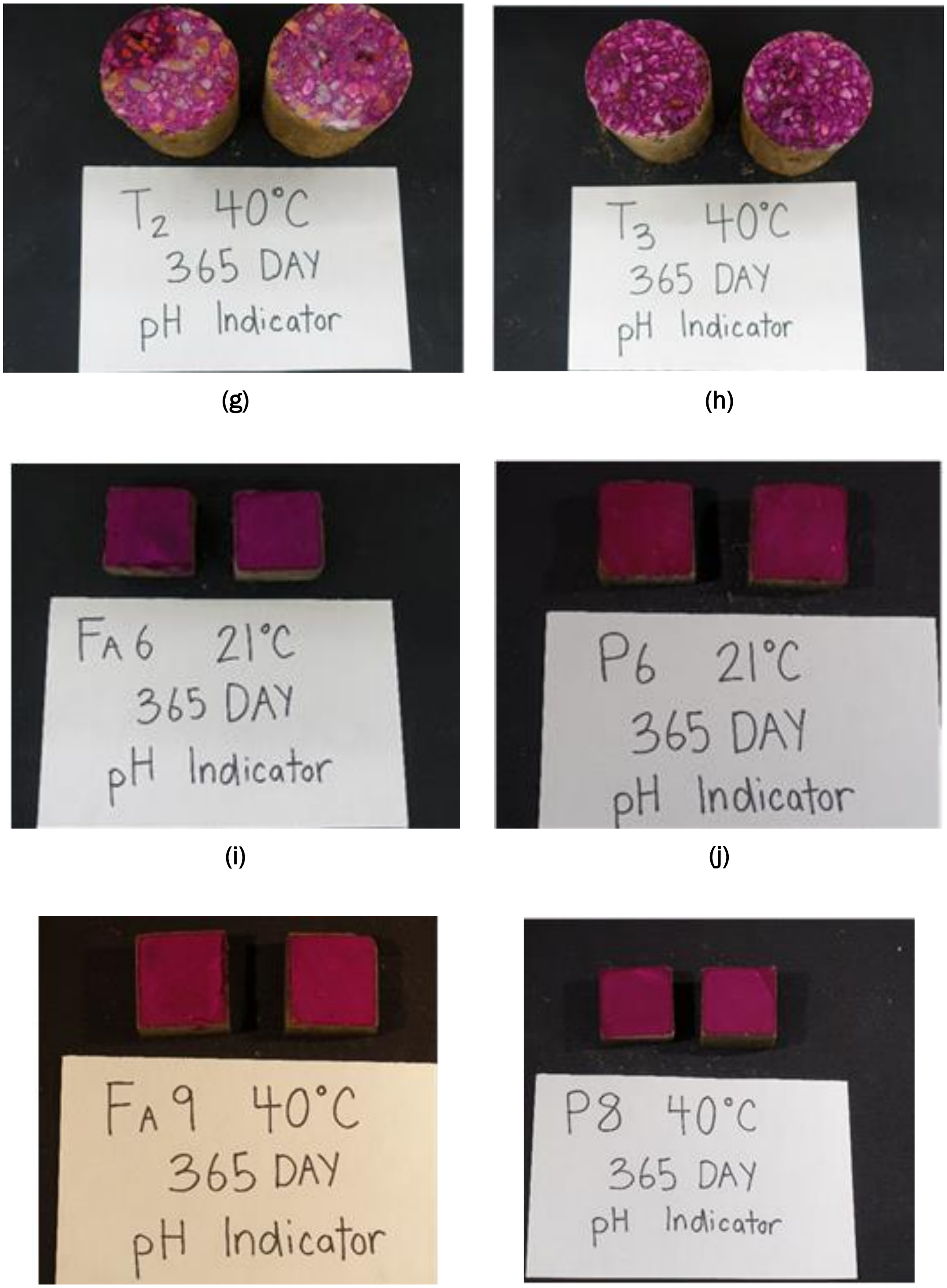
Figure 13. Three-hundred-sixty-five-day measurement specimens, 74mg/L (T1, T2, and T3).



(a) (b)

(c) (d)

(e) (f)

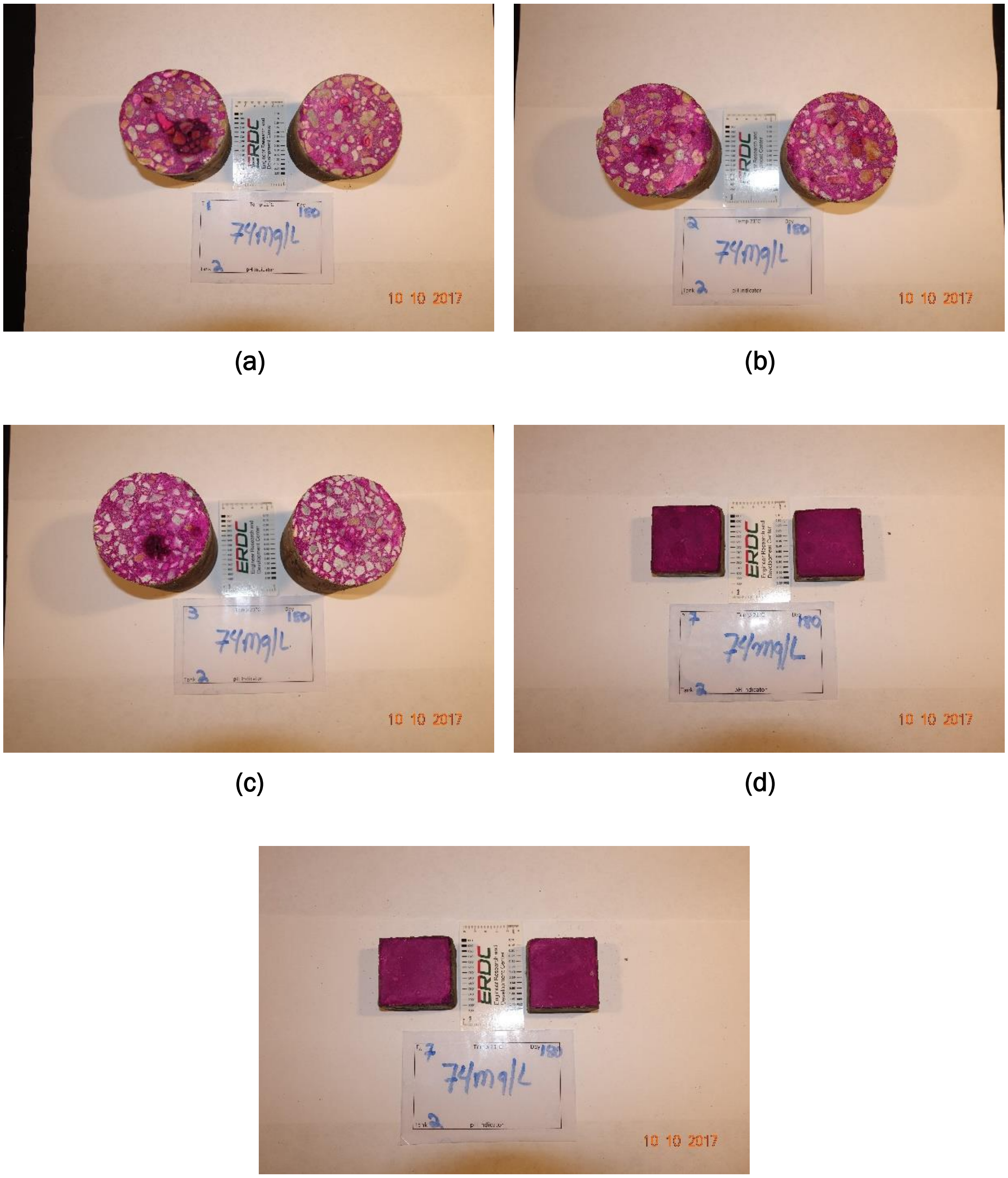

T_2 40°C
365 DAY
pH Indicator
T_3 40°C
365 DAY
pH Indicator
FA 6 21°C
365 DAY
pH Indicator
P6 21°C
365 DAY
pH Indicator
FA 9 40°C
365 DAY
pH Indicator
P8 40°C
365 DAY
pH Indicator

(g) (h)

(i) (j)

(k) (l)

Figure 14. Five-hundred-forty-five-day measurement specimens, 74mg/L (T1, T2, and T3).



(a)

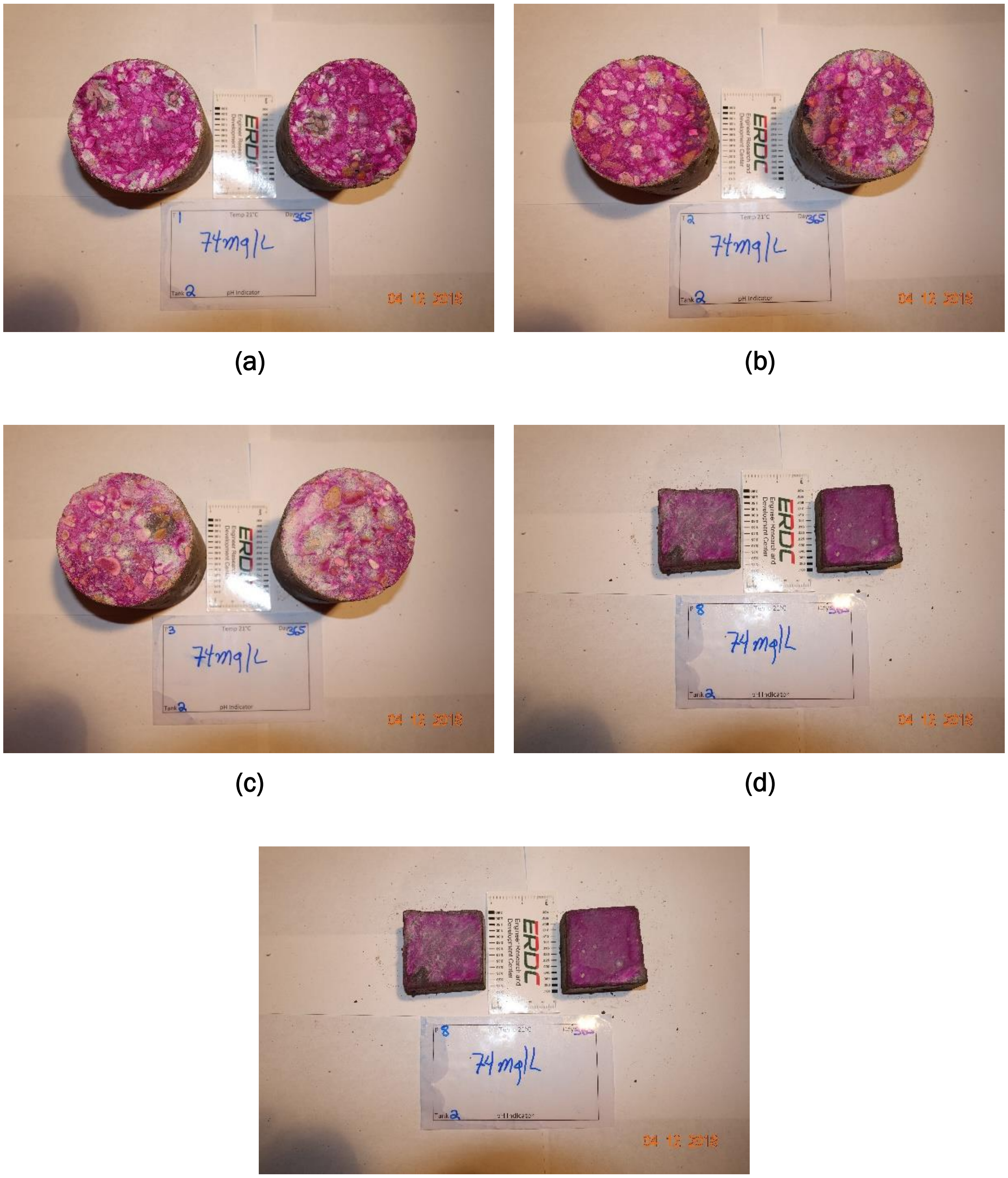
(b)

(c)

(d)

(e)

Figure 15. Seven-hundred-thirty-day measurement specimens, 74mg/L (T1, T2, T3).



(a) (b)

(c) (d)

(e)

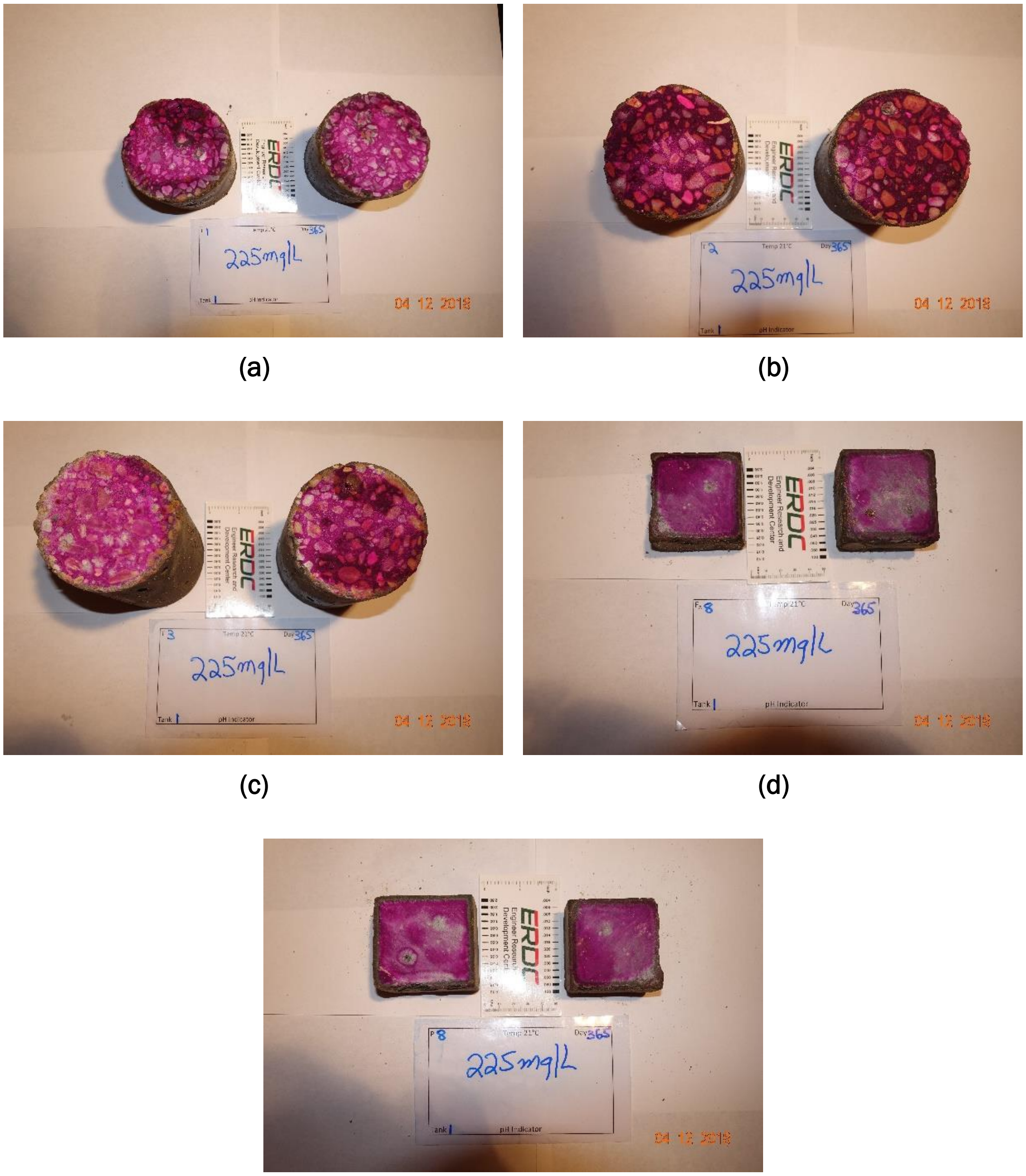
Figure 16. One-hundred-eighty-day measurement specimens, 225mg/L CO_2 (T1, T2, T3).

(a) (b)

(c) (d)

(e)

Figure 17. Three-hundred-sixty-five-day measurement specimens, 225mg/L CO_2 (T1, T2, T3).



(a) (b)

(c) (d)

(e)

5 Characterization of Carbonation-Induced Surface Deterioration

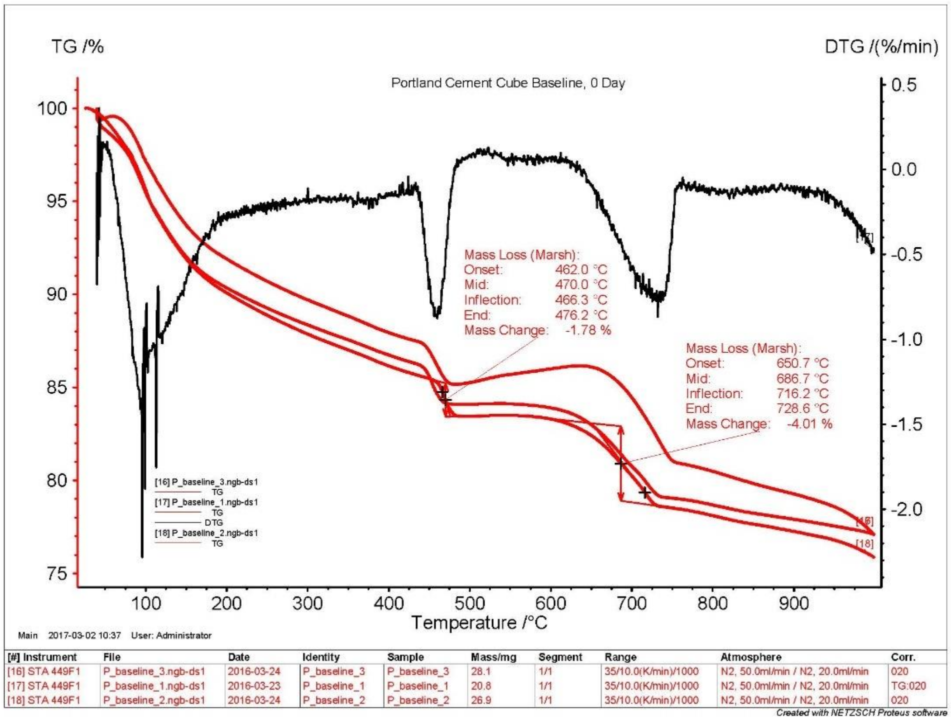
As visual observations and pH indicator solutions evidenced surface deterioration associated with carbonation processes, additional analyses were performed to understand how the internal microstructure of the specimens was being modified, the depth of damage, and what specific mechanisms were controlling the observed deterioration. The following sections describe the results of in-depth characterization studies of specimens exhibiting carbonation-induced surface deterioration.

5.1 Thermogravimetric analysis (TGA)

The results of the thermogravimetric Analysis (TGA) for the specimens are shown in Figure 14 for test days 0, 28, 90, and 180. From these results, it was concluded that the chemical fish barrier carbonation system did have an effect on the concrete and paste specimens. The TGA data found in Figure 14a indicates that a mass loss occurred between the temperatures of 450 and 500°C representing a loss of calcium hydroxide and a secondary mass loss occurring between 600 and 900°C of 14% representing a loss of calcium carbonate.

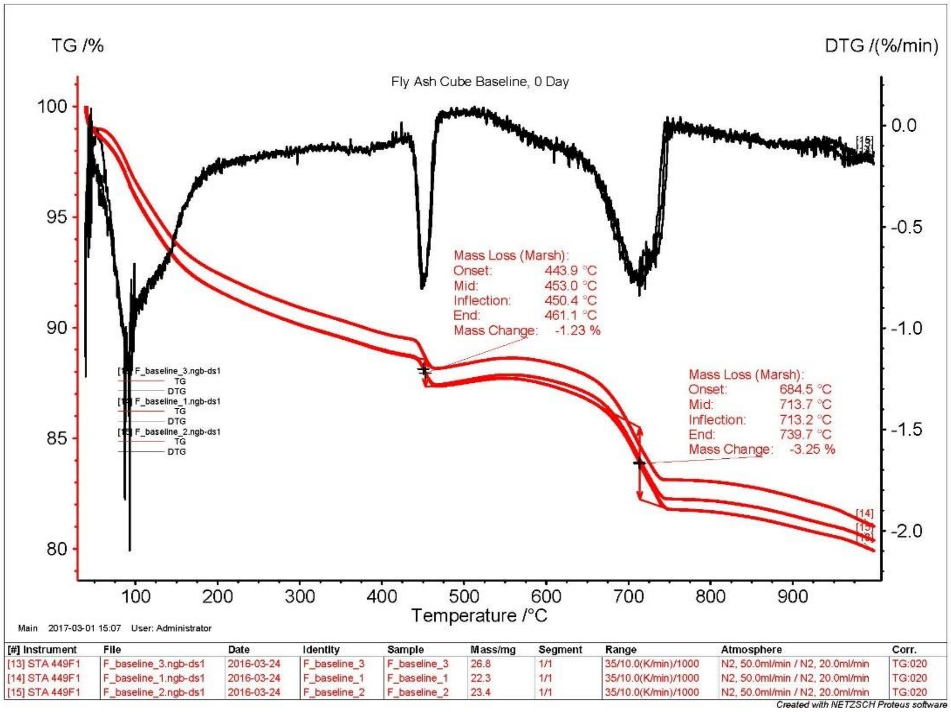
The TGA data shown in Figure 18d indicates carbonation is more defined within the specimen at later ages, i.e., test day 90. It was also noted during the pH indicator analysis that the formation of a precipitate began on the outer surface of the concrete and paste specimens at 90 days. However, there was no mass loss in the range that would typically see calcium hydroxide at approximately 450-550°C; however, a substantial mass loss was seen in the range that would typically see calcium carbonate, which is approximately 600-800°C. It appears that calcium ions are precipitating out and then reacting with carbonic acid and/or free CO_2 in solution to form calcium carbonate on the surface of the specimen. The rough surfaces on the specimen and concrete structures have the potential to be great nucleation sites. The data also suggest researchers are seeing carbonation occur internally in the cement paste.

Figure 18. TGA analysis results (a, b, c, d, and e).



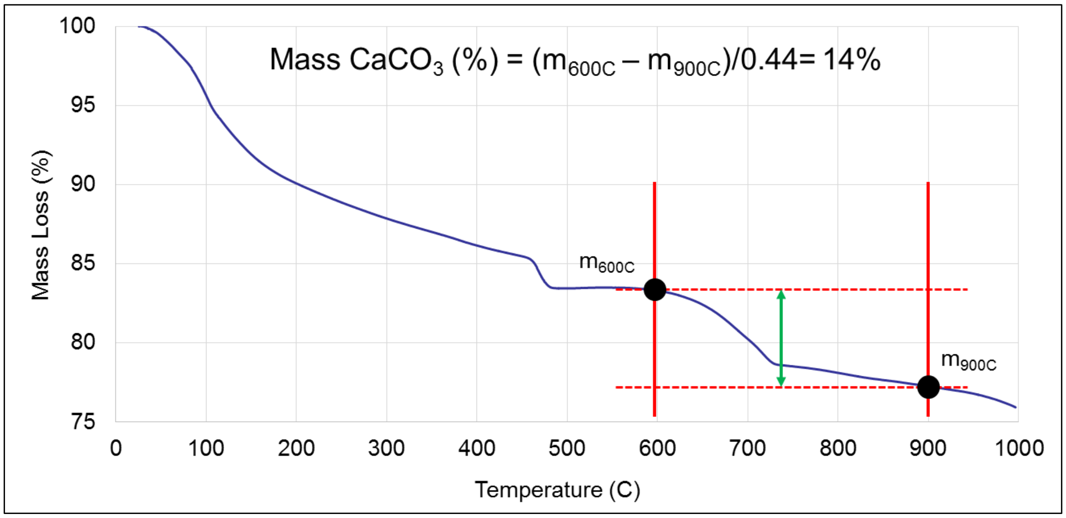
[#] Instrument	File	Date	Identity	Sample	Mass/mg	Segment	Range	Atmosphere	Corr.
[16] STA 449F1	P_baseline_3.ngb-ds1	2016-03-24	P_baseline_3	P_baseline_3	28.1	1/1	35/10.0(K/min)/1000	N2, 50.0ml/min / N2, 20.0ml/min	020
[17] STA 449F1	P_baseline_1.ngb-ds1	2016-03-23	P_baseline_1	P_baseline_1	20.8	1/1	35/10.0(K/min)/1000	N2, 50.0ml/min / N2, 20.0ml/min	TG:020
[18] STA 449F1	P_baseline_2.ngb-ds1	2016-03-24	P_baseline_2	P_baseline_2	26.9	1/1	35/10.0(K/min)/1000	N2, 50.0ml/min / N2, 20.0ml/min	020

(a) TGA analysis of cement paste cube (paste) baseline.

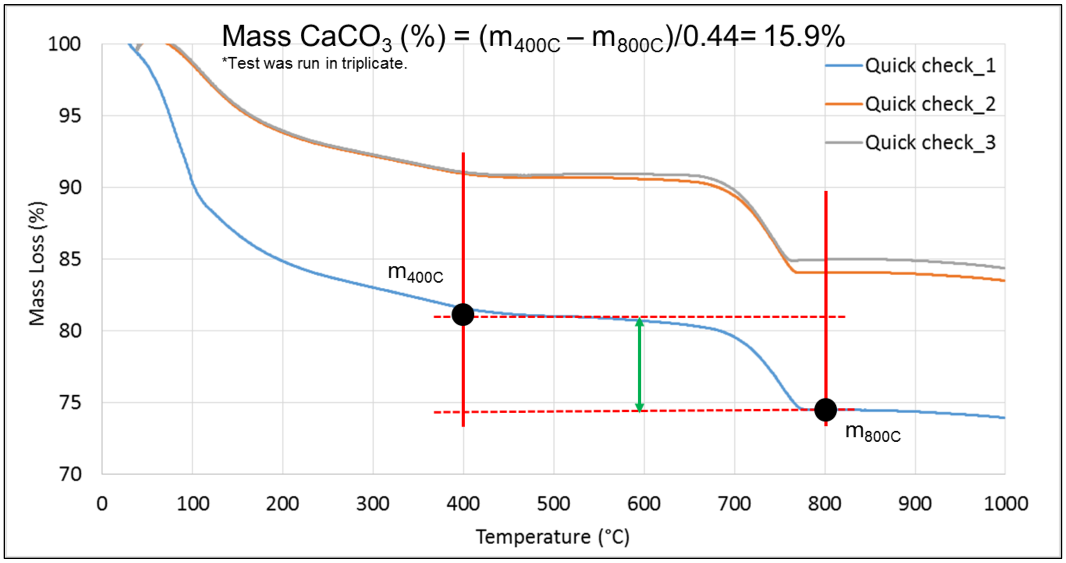


[#] Instrument	File	Date	Identity	Sample	Mass/mg	Segment	Range	Atmosphere	Corr.
[13] STA 449F1	F_baseline_3.ngb-ds1	2016-03-24	F_baseline_3	F_baseline_3	26.8	1/1	35/10.0(K/min)/1000	N2, 50.0ml/min / N2, 20.0ml/min	TG:020
[14] STA 449F1	F_baseline_1.ngb-ds1	2016-03-24	F_baseline_1	F_baseline_1	22.3	1/1	35/10.0(K/min)/1000	N2, 50.0ml/min / N2, 20.0ml/min	TG:020
[15] STA 449F1	F_baseline_2.ngb-ds1	2016-03-24	F_baseline_2	F_baseline_2	23.4	1/1	35/10.0(K/min)/1000	N2, 50.0ml/min / N2, 20.0ml/min	TG:020

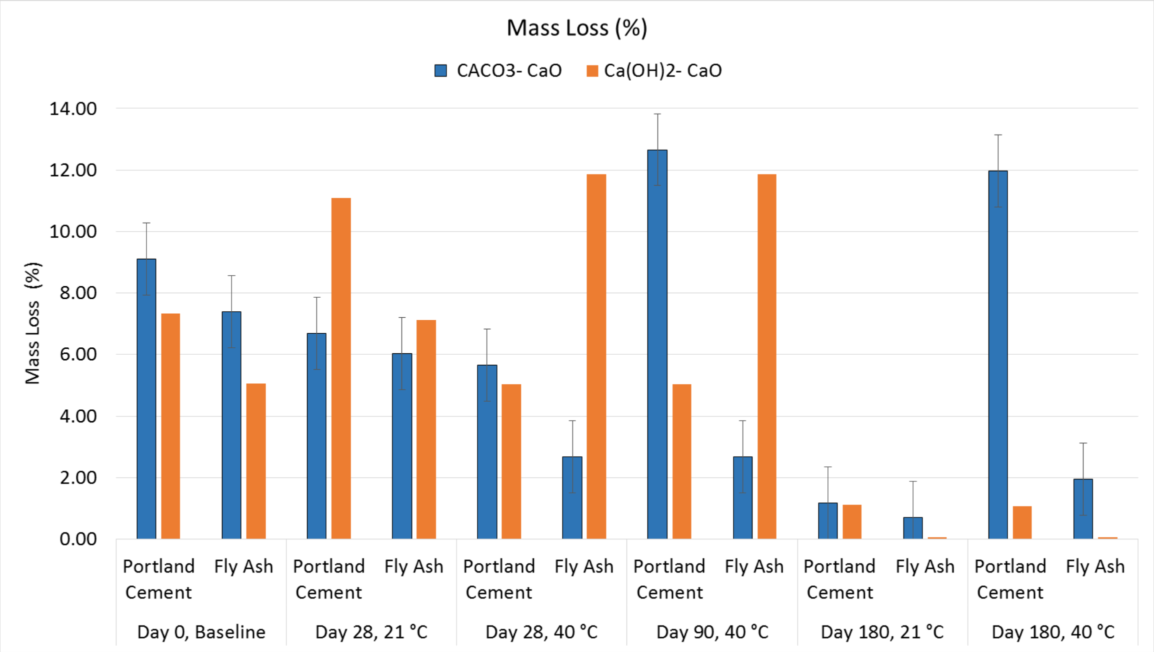
(b) TGA analysis of fly ash cube (paste) baseline.



(c) TGA analysis of cement paste cube (paste)-28 days.



(d) TGA analysis of cement paste cube (surface powder)-90 days.

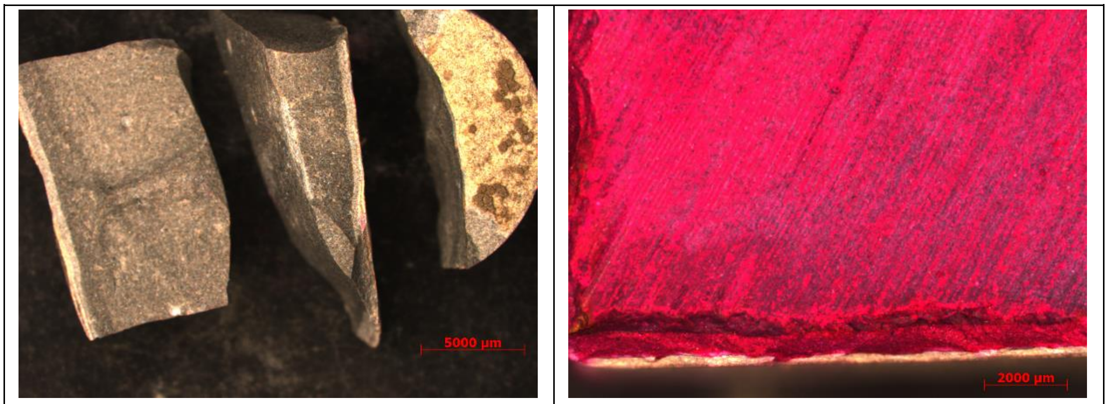


(e) Cement paste cube (surface powder) 0- to 180-day TGA mass loss.

5.2 Optical microscopy

Optical microscopy was performed on specimens that displayed physical changes, such as evidence of carbonation, during pH indicator analyses after 90, 180, and 365 days of exposure. Samples were analyzed from each of the three test specimens (T1, T2, and T3), and the portland cement and fly ash (FA) paste cubes were included. Concrete samples were cored from the specimen with a drill press, taking care to minimize sample deterioration. Optical images of the most notable changes in the paste cube specimens are shown in Figure 19. These optical images give a better understanding of the formation of the precipitate. Observations focused on the appearance of the carbonation of the outer surface of the specimen at the macro- and micro-scale; any additional observations were recorded. A whitish deposition was observed at the surface of the sample. Spraying the fracture surface indicated that only the very near surface concrete was fully carbonated as the depth of discoloration was not directly associated with the shift in pH from alkaline to near neutral conditions caused by carbonation. This result provides evidence of what type of mechanism may be controlling the observed surface deterioration. It is likely that the white discoloration in the near surface of the concrete that extends to depths of approximately 1 mm is caused by calcium leaching in the submerged condition. This zone may still exhibit a higher pH even with leaching occurring. As CaO leaches and reacts with CO_2 present in the water, it precipitates calcium carbonate with near neutral pH, which is associated with the white layer on the surface of the specimens that extends to a depth of approximately 100 µm.

Figure 19. Optical micrographs obtained at 180 days (a, b).



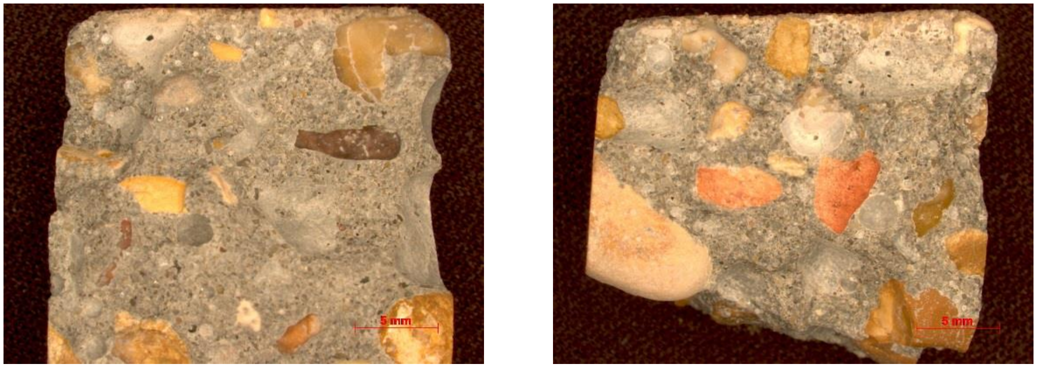
(a) Optical micrographs of fractured specimens showing white discoloration on surface.

(b) pH indicator solution showing evidence of pH changes only in first approximately 100-µm depth rather than to full depth of discoloration.

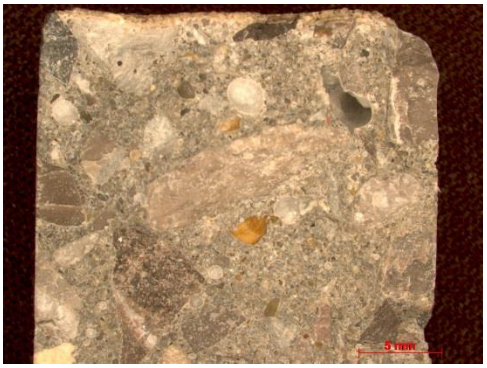
Additional optical micrographs of samples from concrete mixtures T1, T2, and T3 at 180 days exposed to 21°C temperatures are provided in Figure 20. Similar trends were observed in the concrete specimens with depths of discoloration of approximately 1 mm observed. This depth appeared not to depend on the mixture proportion used (i.e., with or without fly ash) or the aggregate composition. Air voids were partially infilled with calcium carbonate depositions, which are anticipated in this submerged environment. No other distresses were observed. The increased temperature of 40°C was not observed to have any measurable impact on the depth of discoloration of carbonation/pH shift.

The small carbonation depths observed using optical microscopy were not a concern from a durability perspective. Discoloration associate with leaching was observed to depths of approximately 1 mm. However, this discoloration was not directly associated with pH reductions, which were observed only in the top approximately 100 µm of material. This rate of carbonation is less than what is expected for normal-strength concrete under normal atmospheric exposure and, thus, does not introduce any new durability concerns.

Figure 20. Optical micrographs obtained at 180 days for samples T1, T2, and T3 at 21°C (a, b, c). Similar depths of discoloration were observed in concrete specimens as those observed in paste cubes. Increased temperature did not appear to cause any marked increase in depth of discoloration and carbonation.



(a) T1 (b) T2

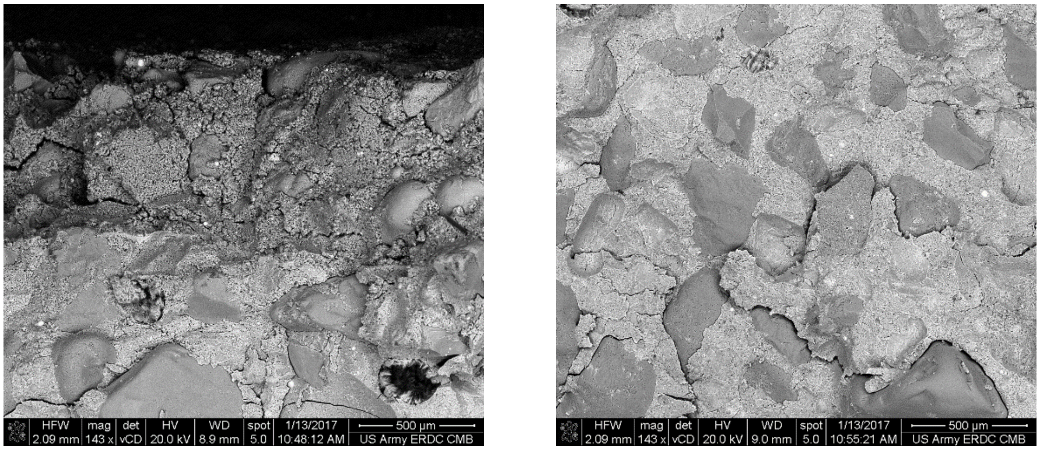


(c) T3

5.3 Scanning electron microscopy (SEM)

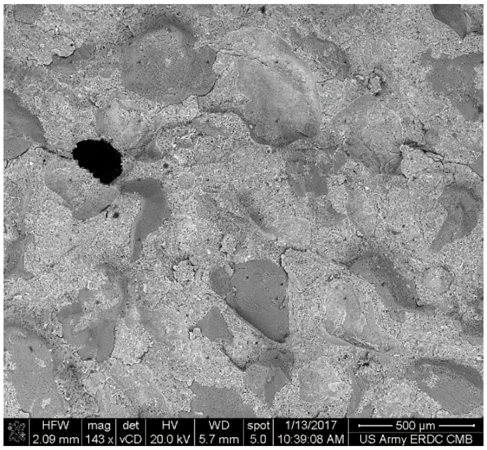
SEM imaging of freshly cut, cored, and fractured surfaces was performed to better characterize surface deterioration processes and internal microstructural alternations occurring in specimens T1, T2, and T3 than could be obtained using optical microscopy. SEM micrographs of the top surface, near surface (top 1 mm of material), and internal microstructure of mortar samples T1, T2, and T3 are shown in Figures 21, 22, and 23, respectively.

Figure 21. SEM micrographs of microstructure in top surface (a), near surface (b), and internal (c) microstructure of samples T1 at 21°C at 180 days, and top surface (d), near surface (e), and internal (f) for T1 at 21°C at 365 days. Similar trends were observed at 40°C.

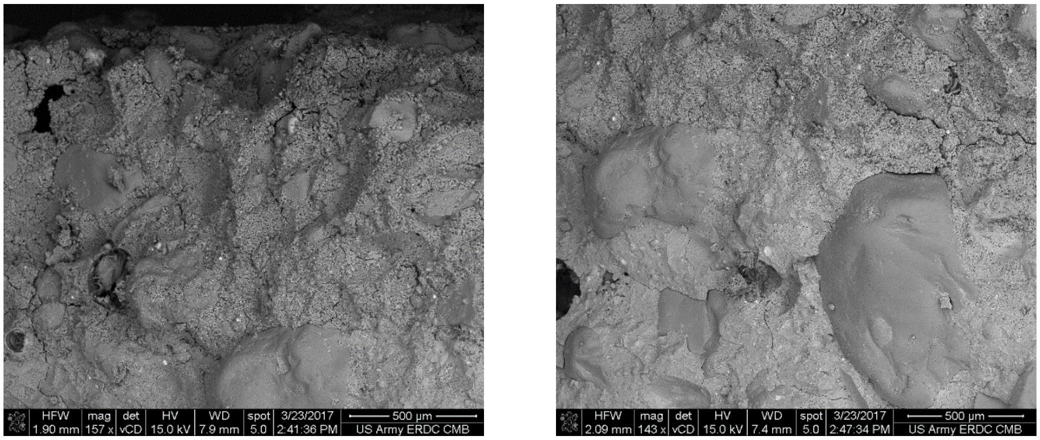


(a) Top surface.

(b) Near surface.

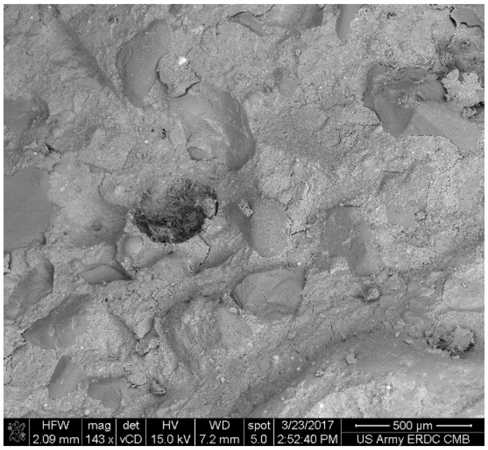


(c) Internal.



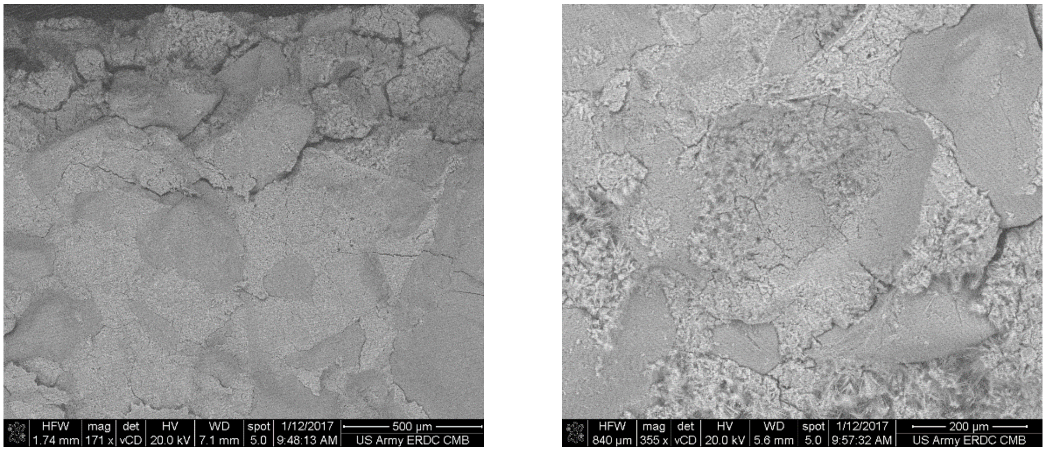
(d) Top surface.

(e) Near surface.



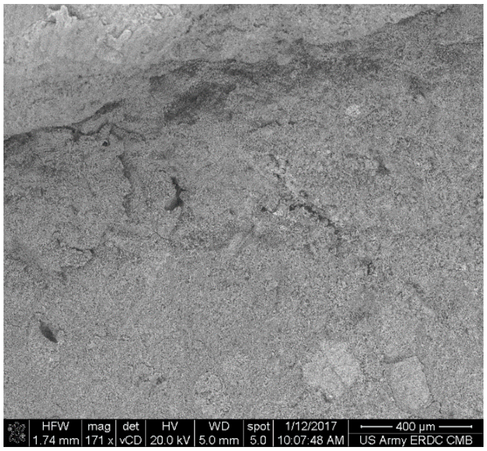
(f) Internal.

Figure 22. SEM micrographs of microstructure in top surface (a), near surface (b), and internal (c) microstructure of samples T2 at 21°C at 180 days, and top surface (d), near surface (e), and internal (f) for T2 at 21°C at 365 days. Similar trends were observed at 40°C.

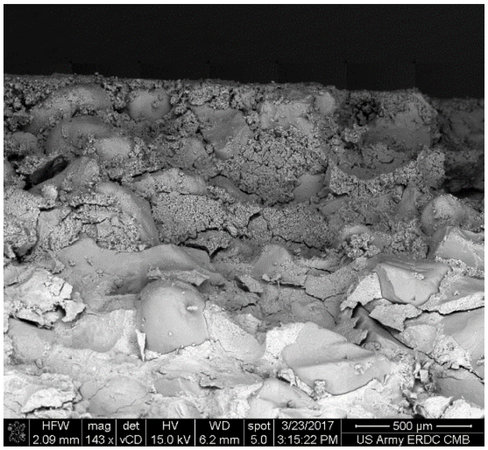


(a) Top surface.

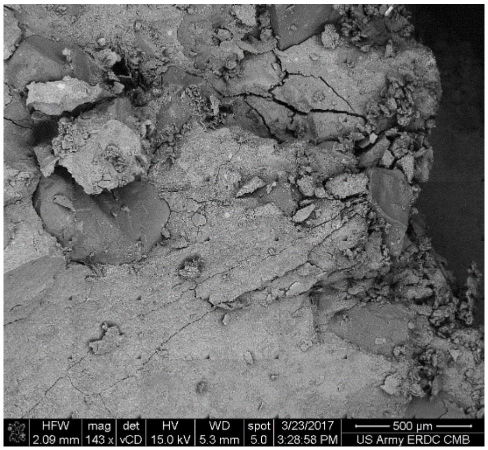
(b) Near surface.



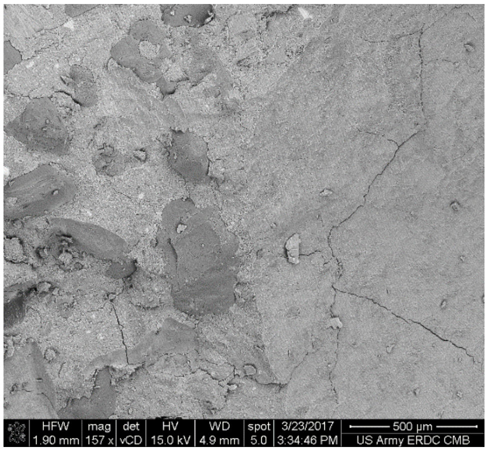
(c) Internal.



(d) Top surface.

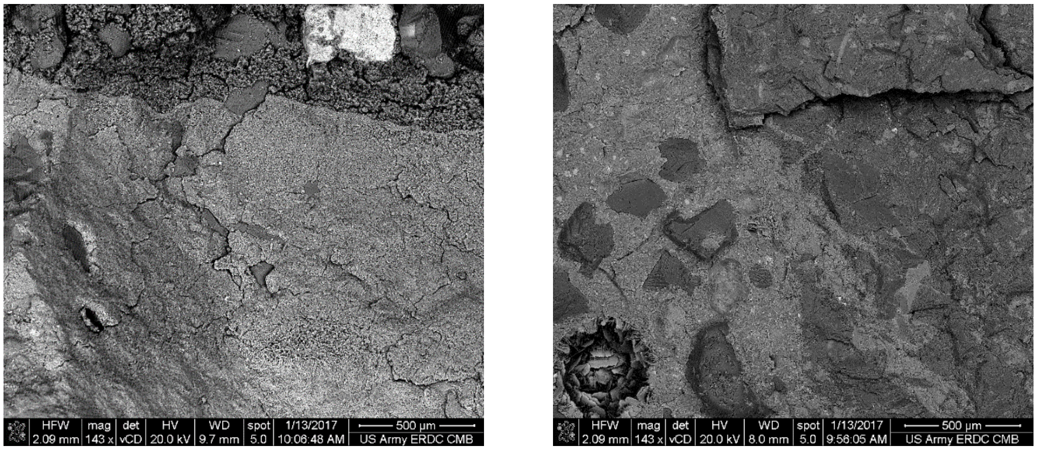


(e) Near surface.

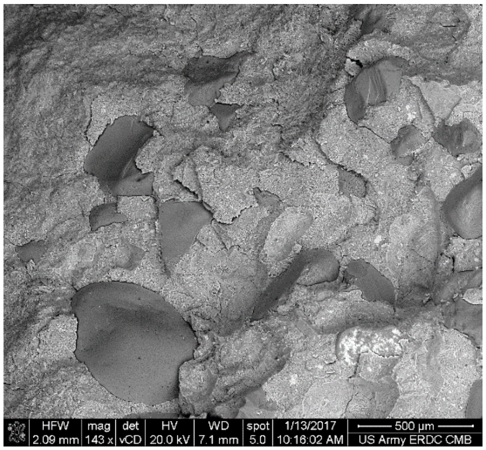


(f) Internal.

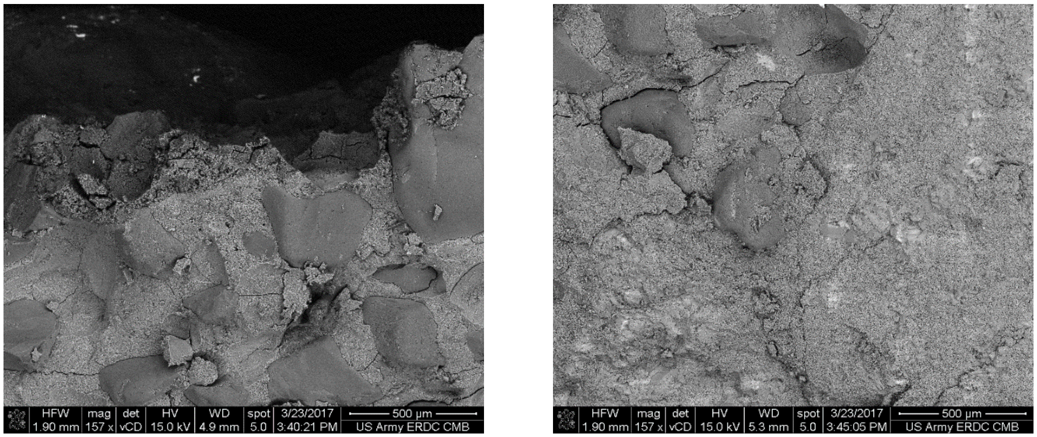
Figure 23. SEM micrographs of microstructure in top surface (a), near surface (b), and internal (c) microstructure of samples T3 at 21°C at 180 days, and top surface (e), near surface (f), and internal (g) for T3 at 21°C at 365 days. Similar trends were observed at 40°C.



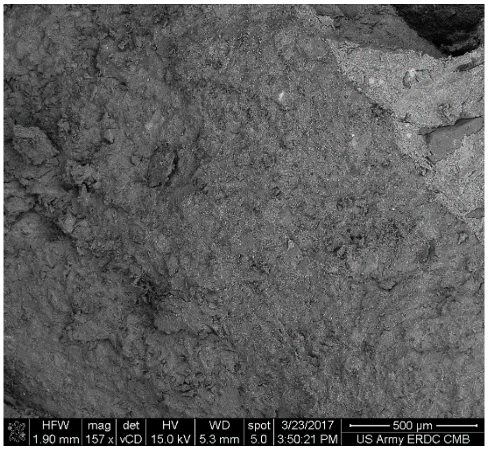
(a) Top surface. (b) Near surface.



(c) Internal.



(d) Top surface. (e) Near surface.



(f) Internal.

Surface deterioration consisting of severe leaching of Ca and deposition of calcium carbonate was observed in all samples. An example of this is illustrated in Figure 24, where a surface layer of highly porous calcium carbonate is observed. This layer extends a few hundred micrometers into the specimen but well less than 1 mm in all samples. A minor increase in porosity is observed in the near-surface concrete to depths up to 1 mm, which is likely associated with the discoloration observed in optical micrographs and caused by leaching of Ca in the submerged condition.

Additional precipitation of ettringite and calcium carbonate (in the form of calcite rhombs) was observed in near-surface air voids. Examples of these precipitated mineral structures are shown in Figures 25 and 26. The presence of ettringite is anticipated in the submerged conditions, and its concomitance with calcite is also anticipated due to the presence of CO_2 in the exposure solution, which would promote the deposition of calcite as well. Nonetheless, the presence of these minerals do not indicate any potentially deleterious deterioration mechanisms present due to the high CO_2 aqueous exposure condition.

Figure 24. Low-magnification SEM micrograph of fracture surface showing surface modification and deposition of calcium carbonate to depth of 100-200 µm (green arrow). Internal air voids are also noted to be partially infilled with mineral deposits (blue arrows, likely ettringite and portlandite).

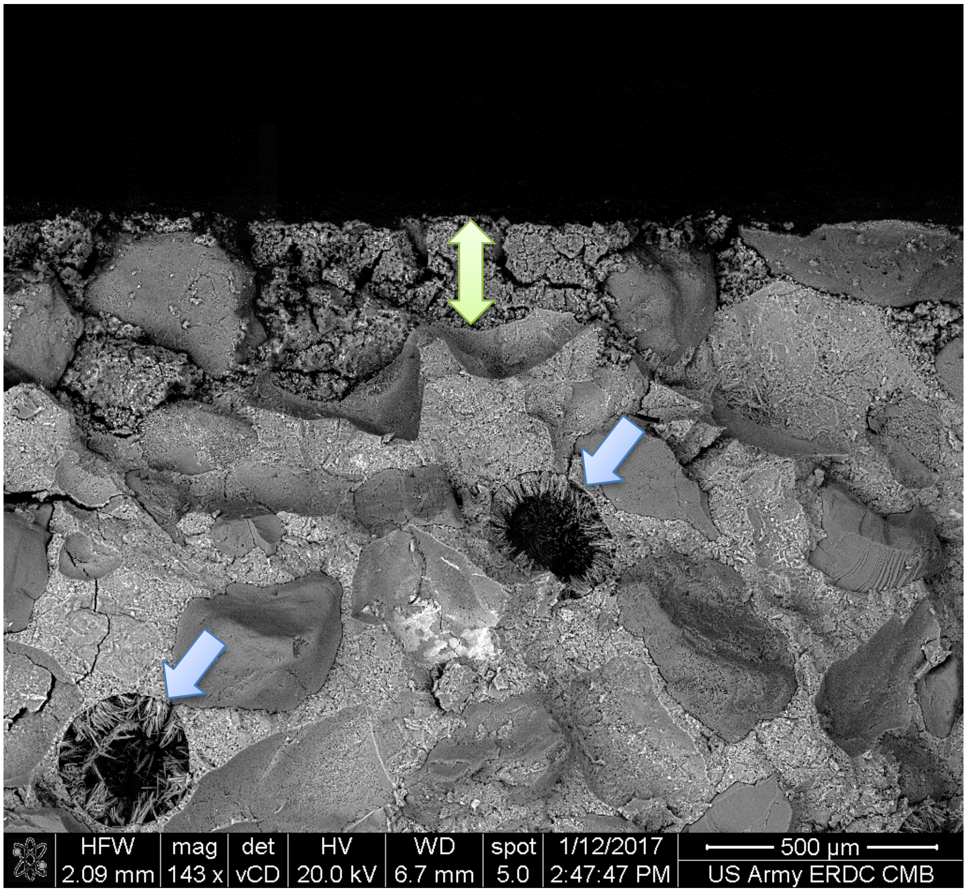


Figure 25. Acicular ettringite crystals precipitated at perimeter of a near-surface air void.

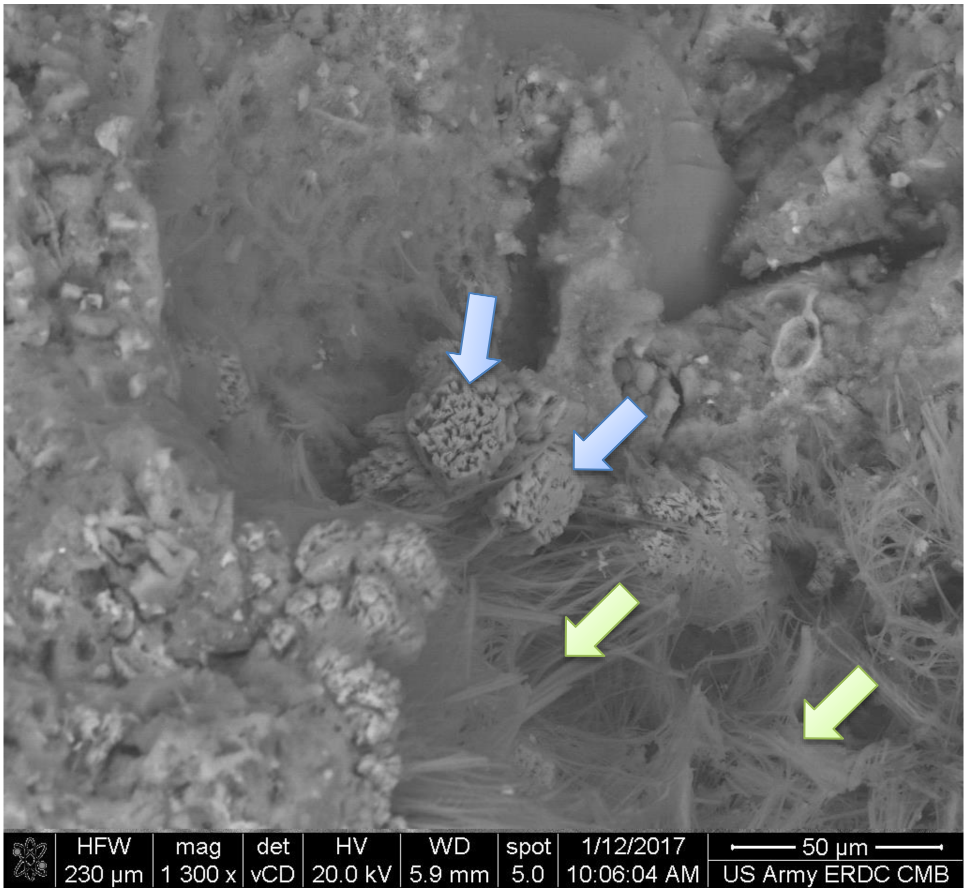
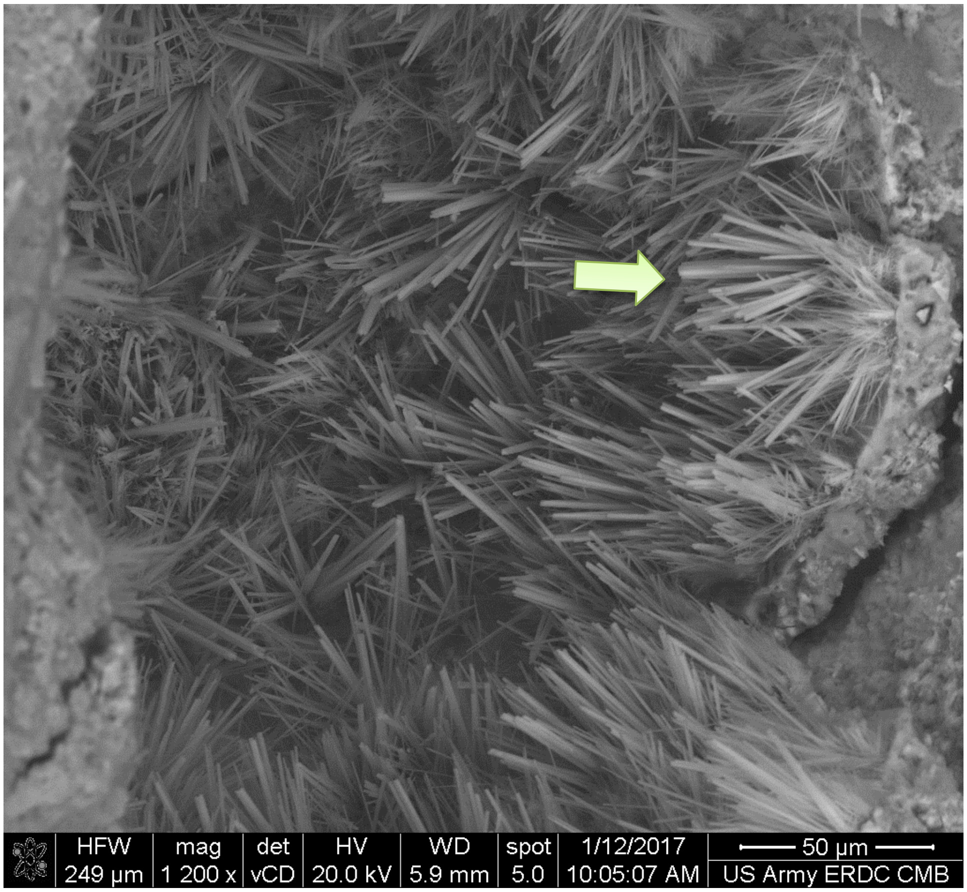
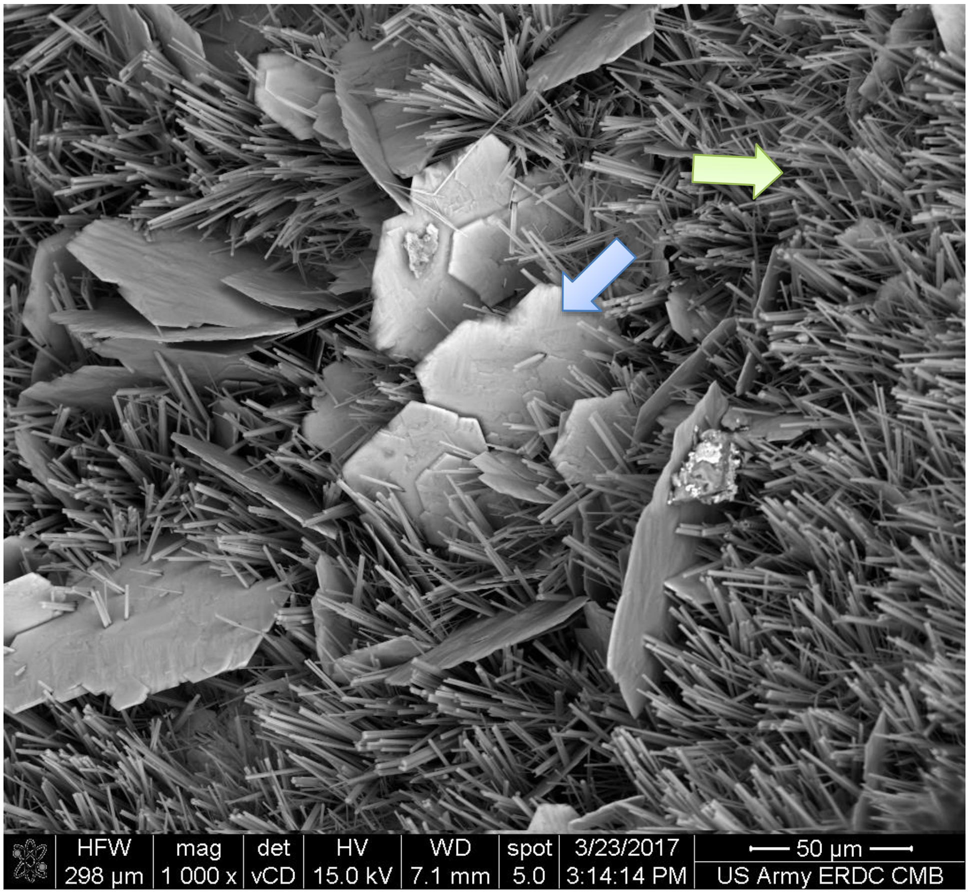


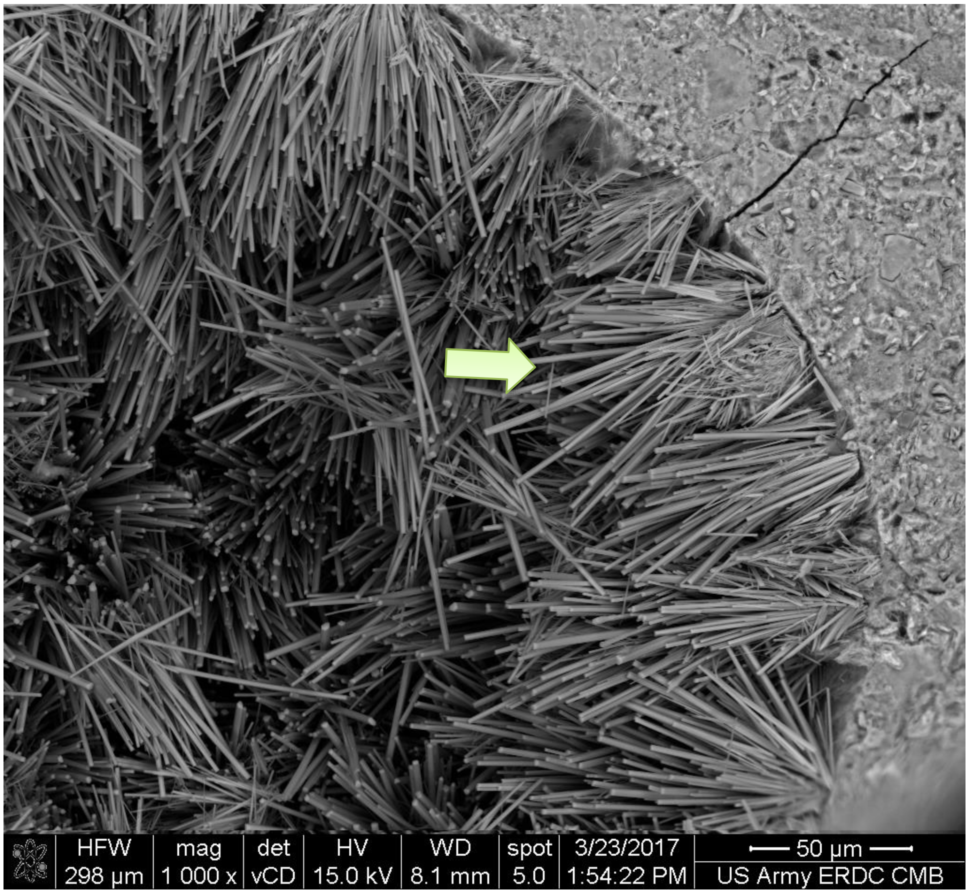
Figure 26. Ettringite crystals (green arrow) along with portlandite (blue arrow), precipitated in a near-surface air void (a), (b), and (c).



(a)


HFW
298 µm
mag
1 000 x
det
vCD
HV
15.0 kV
WD
7.1 mm
spot
5.0
3/23/2017
3:14:14 PM
50 µm
US Army ERDC CMB

(b)



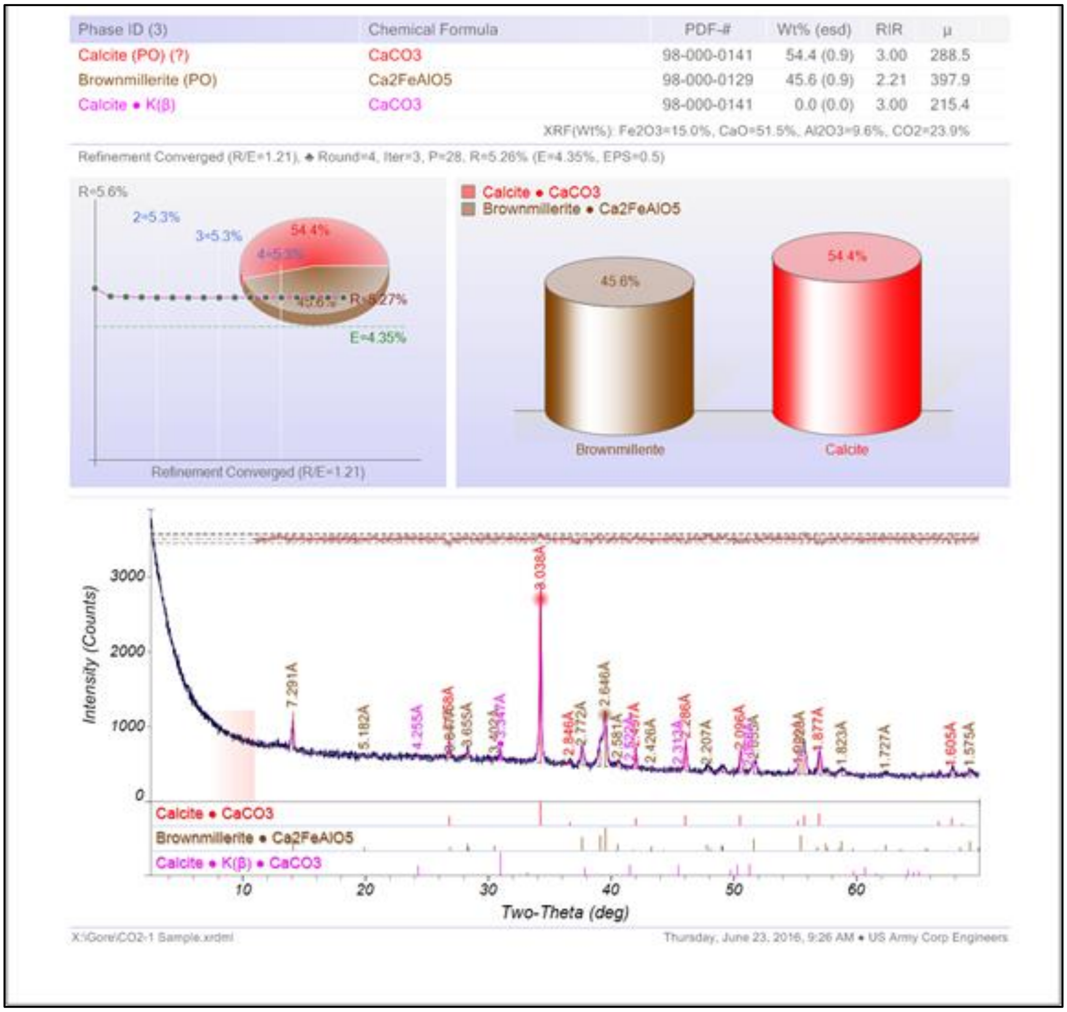
(c)

5.4 Mineralogical analysis

XRD was used to analyze the composition of whitish precipitates observed on the surface of the specimens. The surface of the cement paste cube specimens was scraped to remove the outer material. In preparation for XRD analysis, a portion of the sample was passed through a 45-µm (No. 325) sieve. Random orientation powder (back loaded) mounts of bulk samples were analyzed using XRD to determine the mineral constituents present in each sample. Results obtained for this material are shown in Figure 27. Similar compositions were observed in all samples analyzed.

Phase identification of the material indicated the presence of calcite ($CaCO_3$) and brownmillerite (Ca_2FeAlO_5). The formation of calcite is surmised to occur at the surface of the cement paste sample as a result of dissolution of portlandite ($Ca[OH]_2$) reacting with dissolved CO_2 in the water. The brownmillerite is a recalcitrant reactant phase found in the portland cement and is a residual cement phase subsequent to cement hydration. The presence of both phases corroborates the findings of other characterization methods and supports that this surface distress is not aggressive nor would lead to any worse deterioration than what may occur under typical atmospheric exposure conditions.

Figure 27. XRD results including phase identification and semi-quantitative analysis.



Phase ID (3)	Chemical Formula	PDF-#	Wt% (esd)	RIR	µ
Calcite (PO) (?)	CaCO3	98-000-0141	54.4 (0.9)	3.00	288.5
Brownmillerite (PO)	Ca2FeAlO5	98-000-0129	45.6 (0.9)	2.21	397.9
Calcite • K(β)	CaCO3	98-000-0141	0.0 (0.0)	3.00	215.4

XRF(Wt%): Fe2O3=15.0%, CaO=51.5%, Al2O3=9.6%, CO2=23.9%

Refinement Converged (R/E=1.21), ♣ Round=4, Iter=3, P=28, R=5.26% (E=4.35%, EPS=0.5)

X:\Gore\CO2-1 Sample.xrdml

Thursday, June 23, 2016, 9:26 AM • US Army Corp Engineers

6 Conclusions

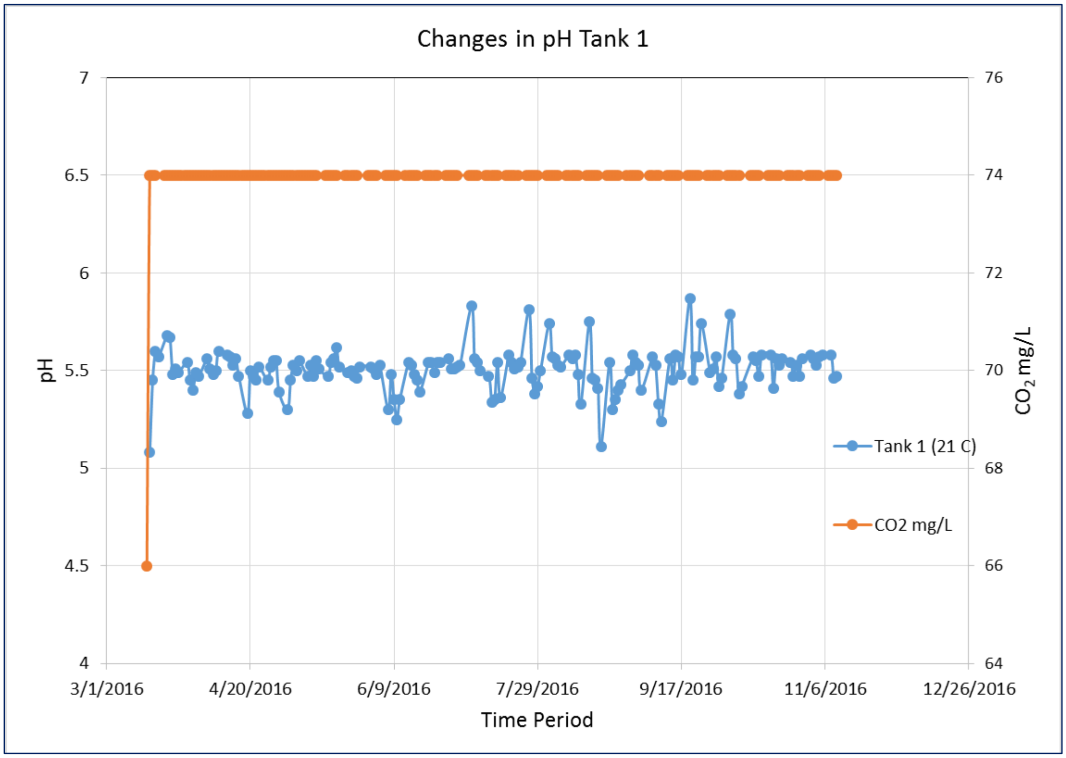
This study examined the effect of induced chemical carbonation on a total of 42 3-in. x 6-in. concrete cylinders composed of three different mixture proportions designated T1, T2, and T3. These specimens were placed in tanks (T1 and T2). One tank was kept at 21±2°C, and the other was heated to 40±2°C during phase 1. During phase two, both tanks were kept at 21±2°C. Both tanks were induced with CO_2 gas (74 mg/L or 225mg/L) bubbled in via micro bubble ceramic (36 in. x 4 in.) diffusers. Twenty-one cylinders were placed in each tank, seven of each mix design, and sampling was conducted on 0, 7, 28, 56, 90, 180, 365, 545, and 730 days of exposure to 74 mg/L CO_2 and on 180 and 365 additional days of exposure to 225 mg/L CO_2. In addition, samples of limestone, quartzite, and granite were placed in the system. Mass changes can be observed in Appendix A. A variety of techniques including visual inspection, pH Indicator analysis, TGA, optical microscopy, SEM, and mineralogical analysis were used to determine the effects and rate of chemical-induced carbonation.

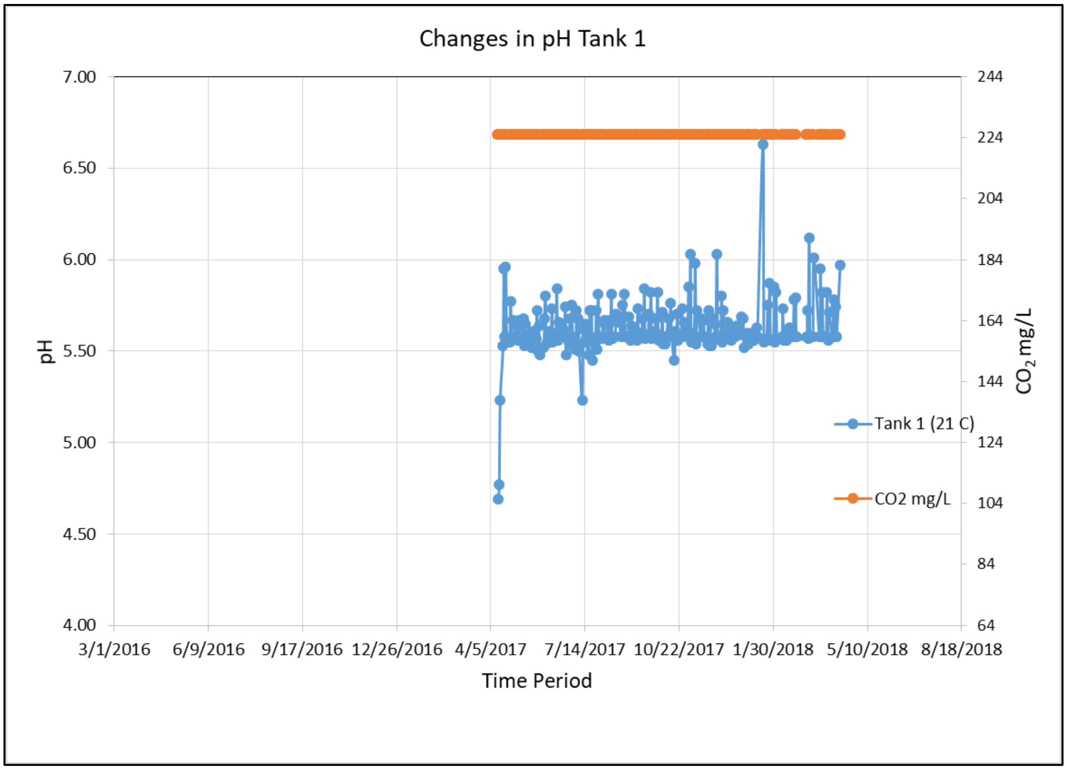
Overall, the results of the investigation concluded that the concrete has suffered from long-term exposure to elevated CO_2 concentrations. This conclusion is based on formation of carbonate minerals on the surface of the concrete. This deterioration was observed after 90, 180, and 365 days of exposure of all samples. The different mixture proportions, constituent materials, CO_2 concentrations, and temperatures studied did not appear to have a measureable impact on rates of carbonation. Characterization of results indicated that, for specimens exposed to 74mg/L CO_2 concentrations, Ca had leached to depths of approximately 1 mm at the 180- and 365-day exposure durations and to depths of approximately 1.5 mm at the 730-day exposure durations. For specimens exposed to 225 mg/L CO_2 concentrations, Ca had leached to depths of approximately 1.5-2.0 mm after 365 additional days of exposure and reacted with CO_2 present in solution, resulting in a deposition of carbonate minerals in the top surface of the concrete to a depth of 100-200 µm. This behavior was supported by optical microscopy, TGA, SEM, and XRD measurements.

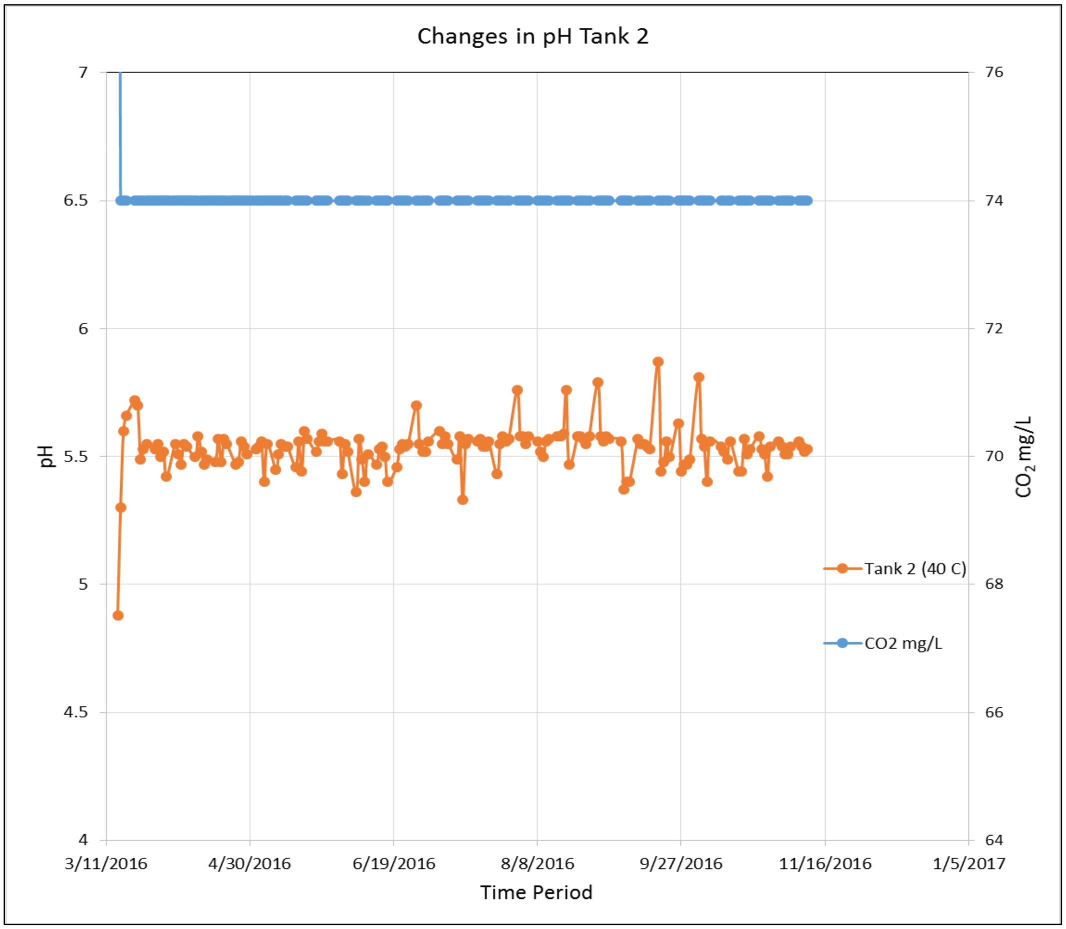
The results of the study indicated that carbon dioxide, even at low concentrations, can have an effect on the surface of the concrete. However, even at 730 days of exposure, depths of deterioration were minimal as noted above with microstructural alterations observed at depths up to 1 mm but with changes in mineralogy and pH limited to the top 100-200 µm of material. Due to the limited time of this study, it is unclear what the long-term effect of carbon dioxide will be on the concrete or what the definitive carbonation rates are. Although this study was performed in a limited time duration, given the slow rate of carbonation observed, it can be concluded that the rates of carbonation observed in this system are no more concerning than the carbonation of concrete that would occur under normal atmospheric exposure conditions, which are on the order of 1 mm/yr. for normal strength concrete. Additional research into the rate of reaction with an eye towards kinetics may be warranted as well as studying higher CO_2 concentrations than those recommended for this study from fish barrier developers. However, it is doubtful that reasonable increases in CO_2 concentration over that studied, e.g., doubling the concentration, would yield significant non-linear acceleration in carbonation rates.

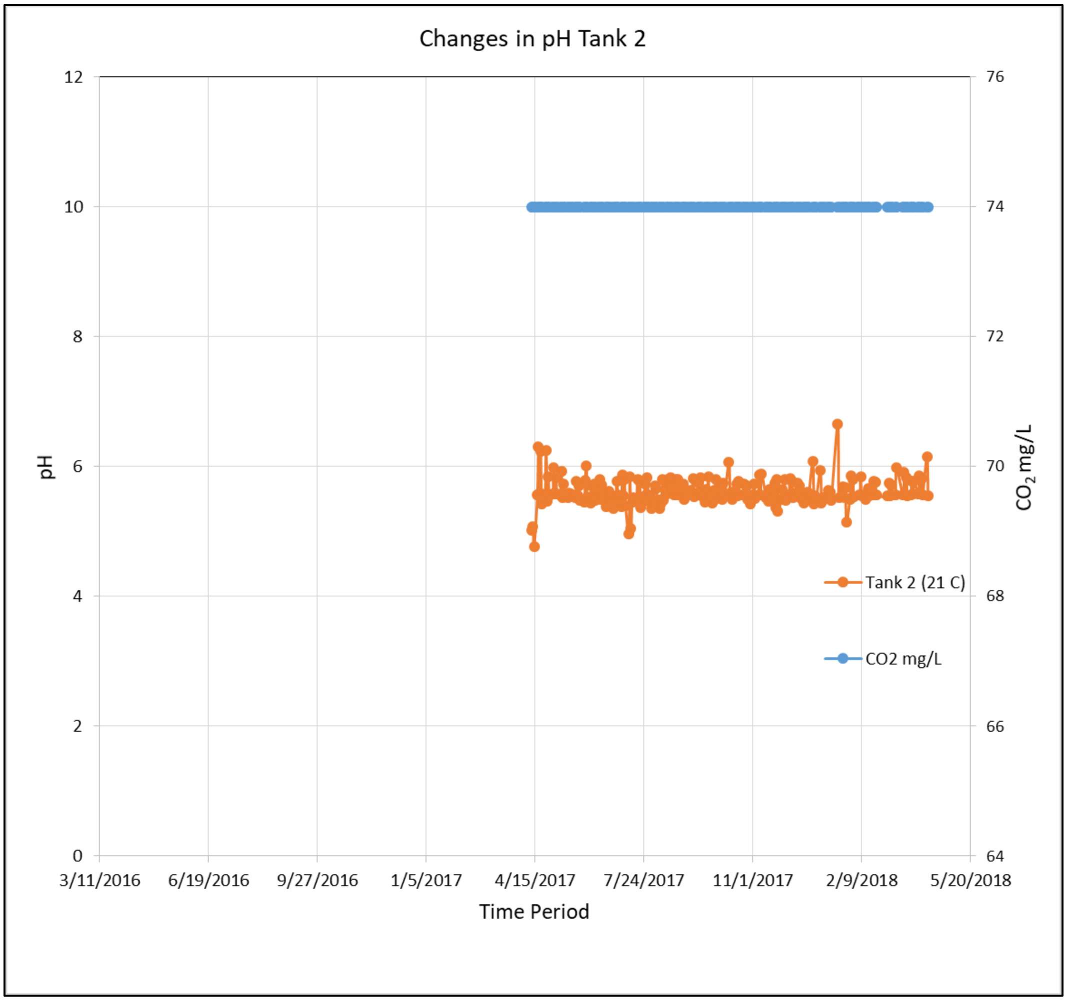
Appendix A: Carbonation (CO_2), pH, Temperature Readings, and mass change

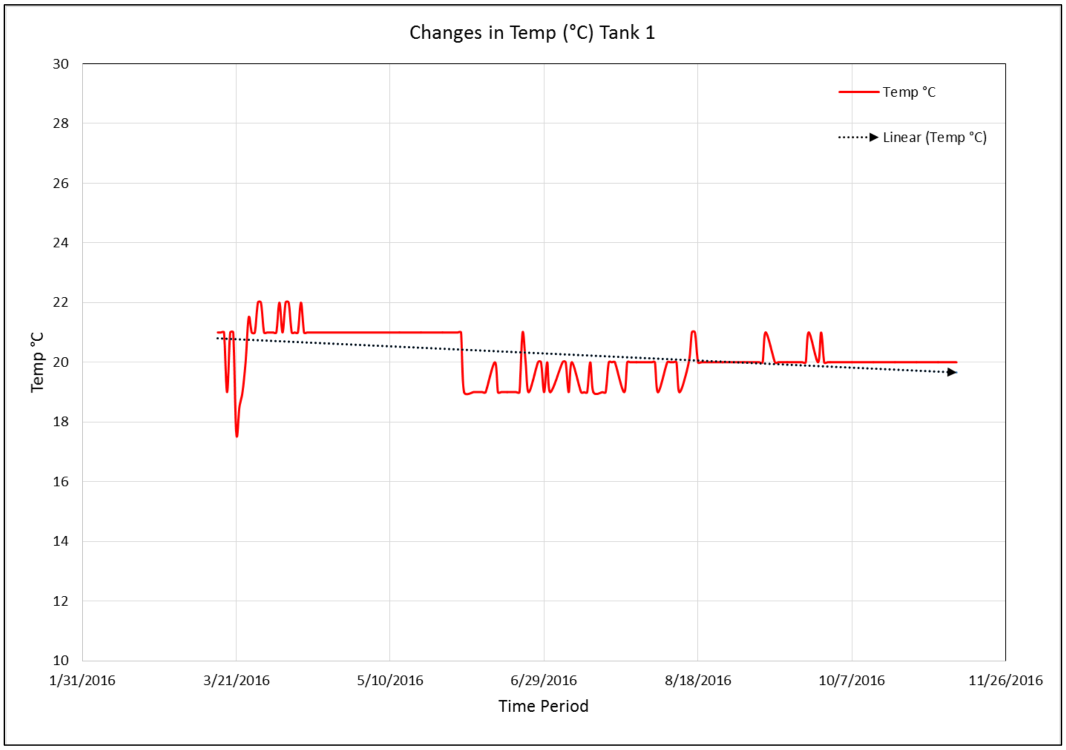
Figure A1. Logs of the daily recordings prior to and after system adjustments.

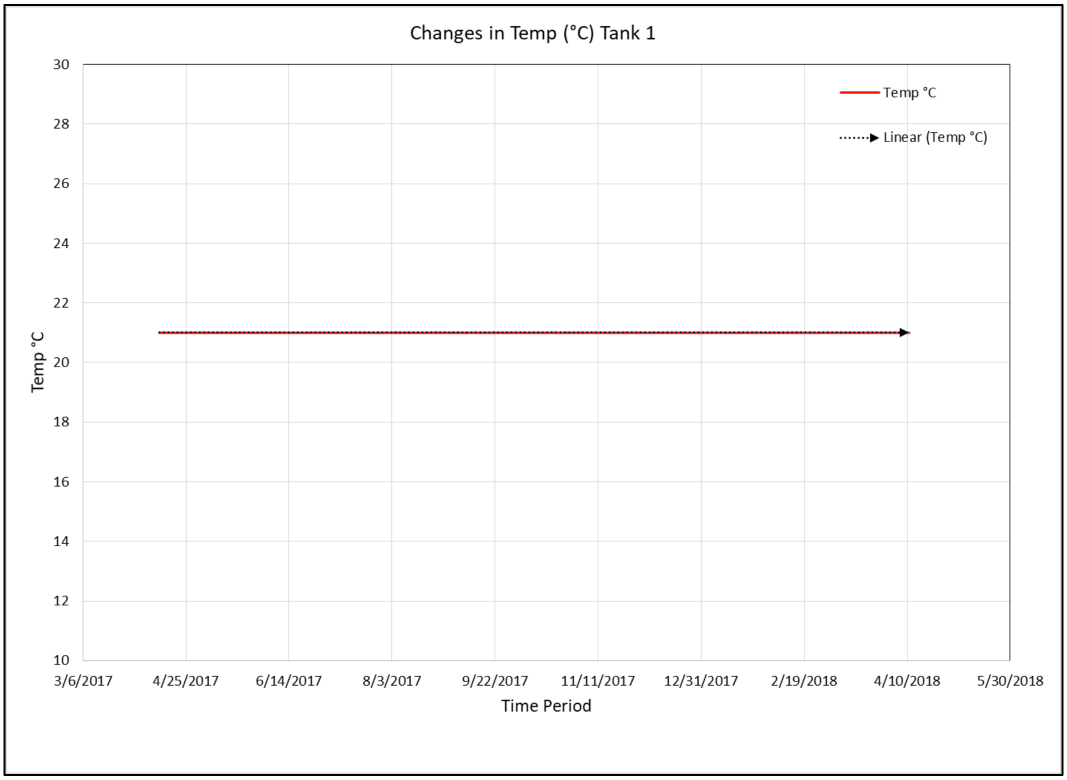


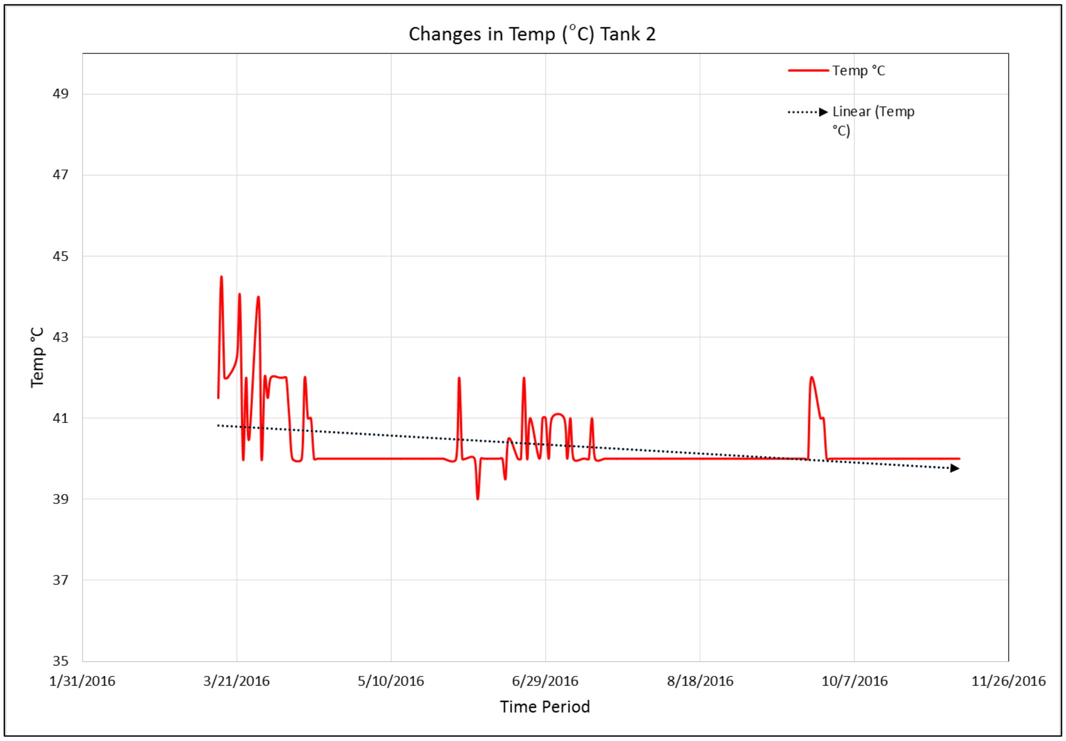

Changes in pH Tank 1
pH
7.00
6.50
6.00
5.50
5.00
4.50
4.00
CO$_2$ mg/L
244
224
204
184
164
144
124
104
84
64
3/1/2016
6/9/2016
9/17/2016
12/26/2016
4/5/2017
7/14/2017
10/22/2017
1/30/2018
5/10/2018
8/18/2018
Time Period
Tank 1 (21 C)
CO2 mg/L


Changes in pH Tank 2
pH
7
6.5
6
5.5
5
4.5
4
76
74
72
70
68
66
64
CO_2 mg/L
3/11/2016
4/30/2016
6/19/2016
8/8/2016
9/27/2016
11/16/2016
1/5/2017
Time Period
Tank 2 (40 C)
CO2 mg/L


Changes in pH Tank 2
pH
12
10
8
6
4
2
0
CO_2 mg/L
76
74
72
70
68
66
64
3/11/2016
6/19/2016
9/27/2016
1/5/2017
4/15/2017
7/24/2017
11/1/2017
2/9/2018
5/20/2018
Time Period
Tank 2 (21 C)
CO2 mg/L


Changes in Temp (°C) Tank 1
Temp °C
Linear (Temp °C)
Temp °C
30
28
26
24
22
20
18
16
14
12
10
1/31/2016
3/21/2016
5/10/2016
6/29/2016
8/18/2016
10/7/2016
11/26/2016
Time Period


Changes in Temp (°C) Tank 1
Temp °C
Linear (Temp °C)
Temp °C
30
28
26
24
22
20
18
16
14
12
10
3/6/2017
4/25/2017
6/14/2017
8/3/2017
9/22/2017
11/11/2017
12/31/2017
2/19/2018
4/10/2018
5/30/2018
Time Period


Changes in Temp (°C) Tank 2
Temp °C
Linear (Temp °C)
49
47
45
43
41
39
37
35
Temp °C
1/31/2016
3/21/2016
5/10/2016
6/29/2016
8/18/2016
10/7/2016
11/26/2016
Time Period

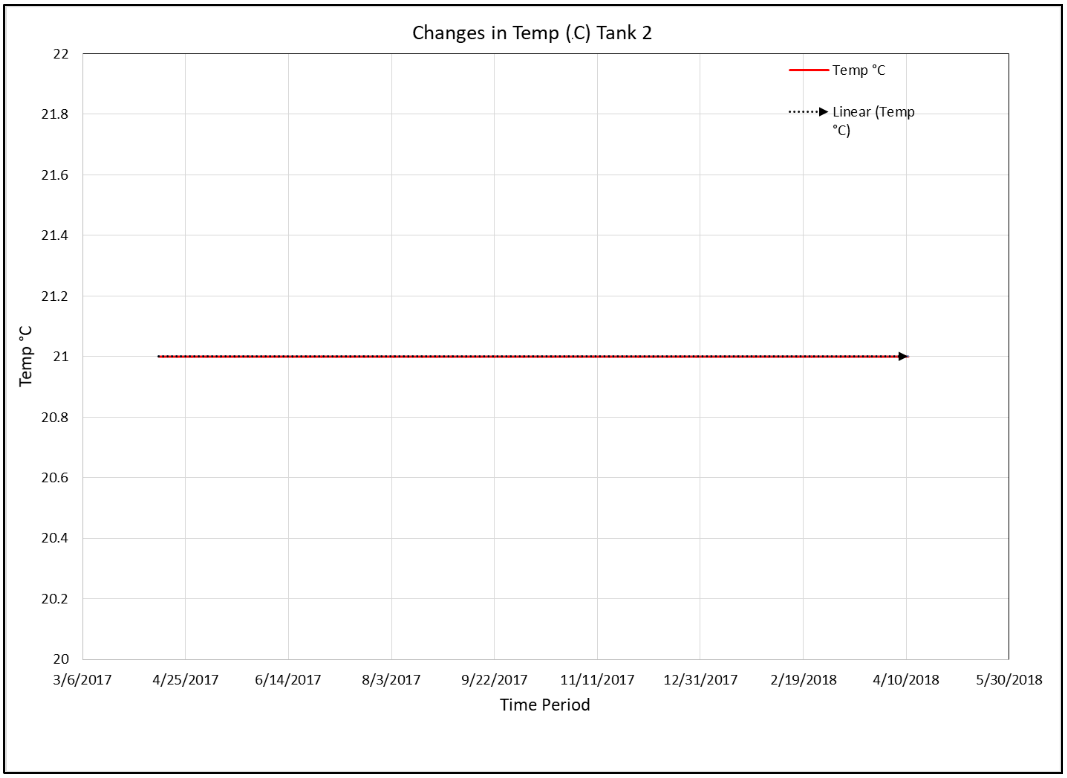

Changes in Temp (.C) Tank 2
Temp °C
Linear (Temp °C)
22
21.8
21.6
21.4
21.2
21
20.8
20.6
20.4
20.2
20
Temp °C
3/6/2017
4/25/2017
6/14/2017
8/3/2017
9/22/2017
11/11/2017
12/31/2017
2/19/2018
4/10/2018
5/30/2018
Time Period

Figure A2. Mass change as a function of time for gray limestone.

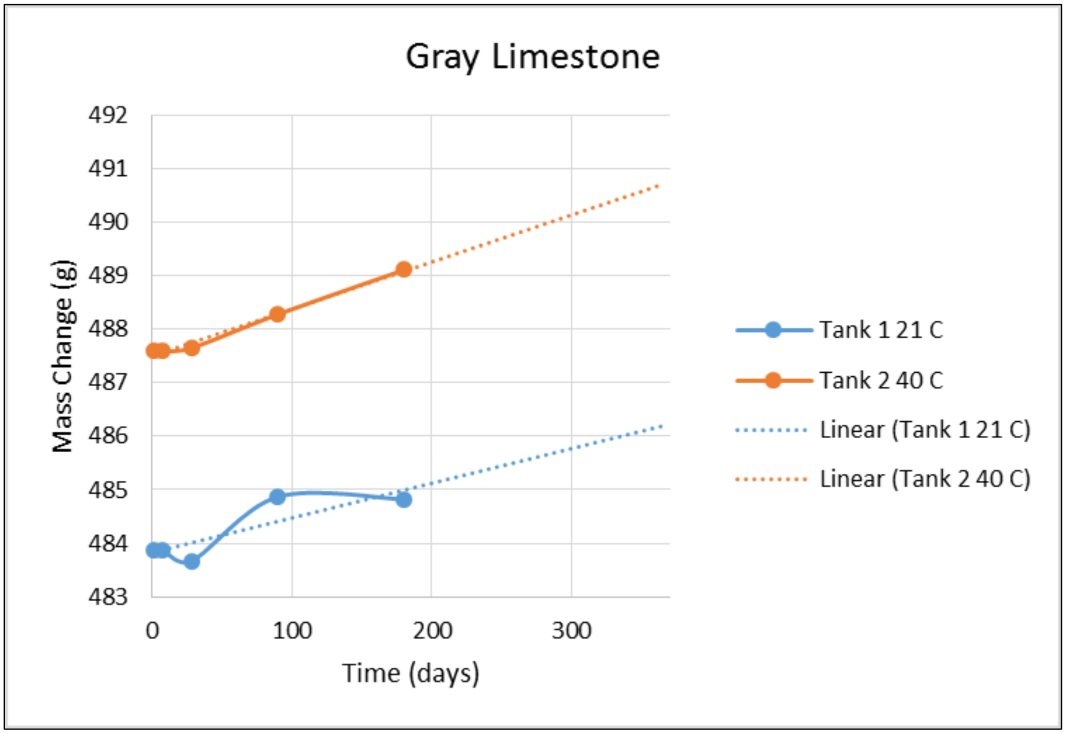


Figure A3. Mass change as a function of time for red granite.

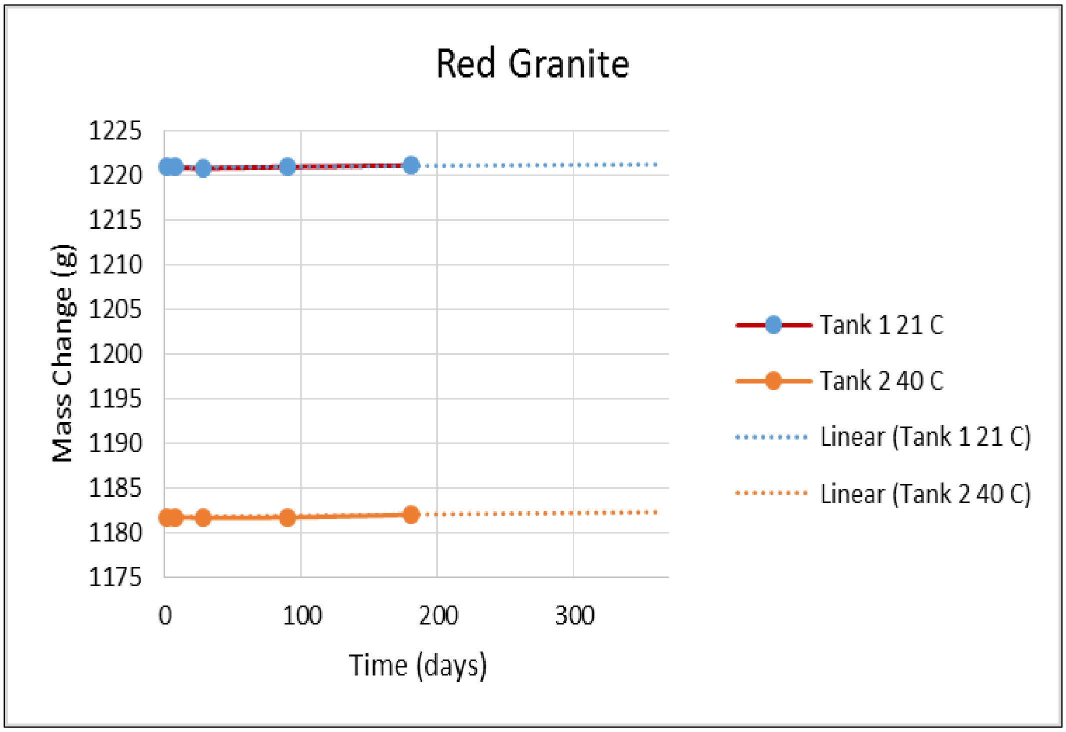


Figure A4. Mass change as a function of time for gray quartzite.

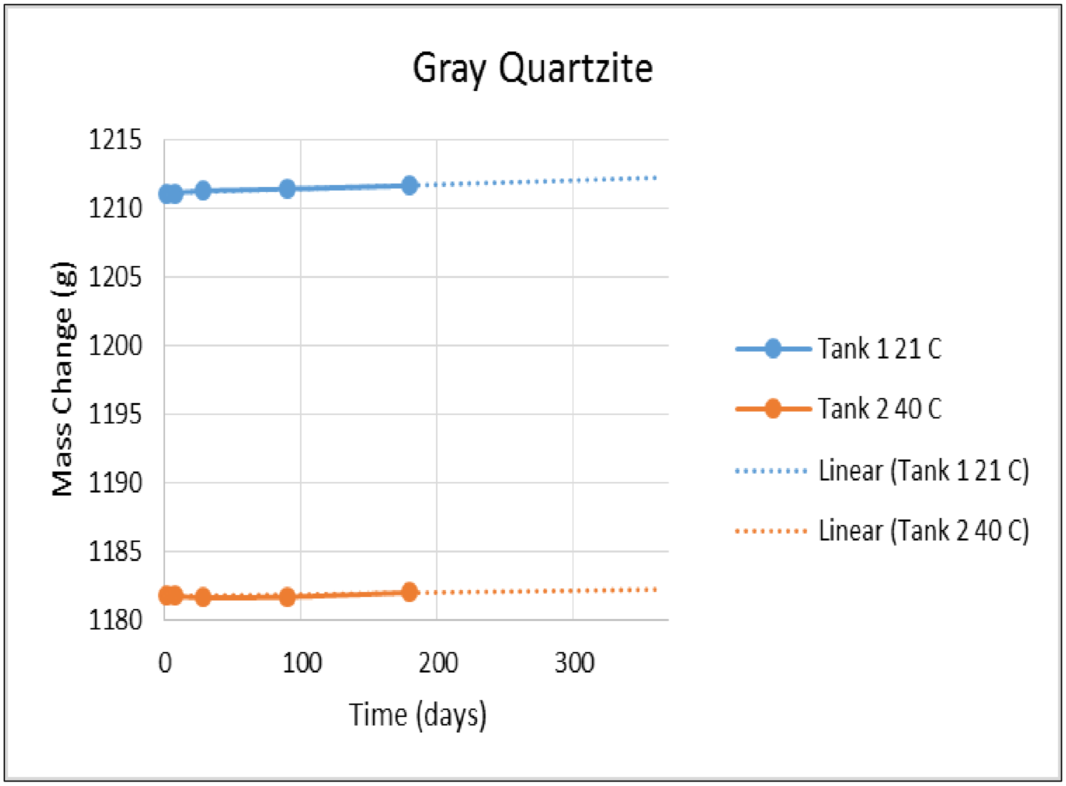
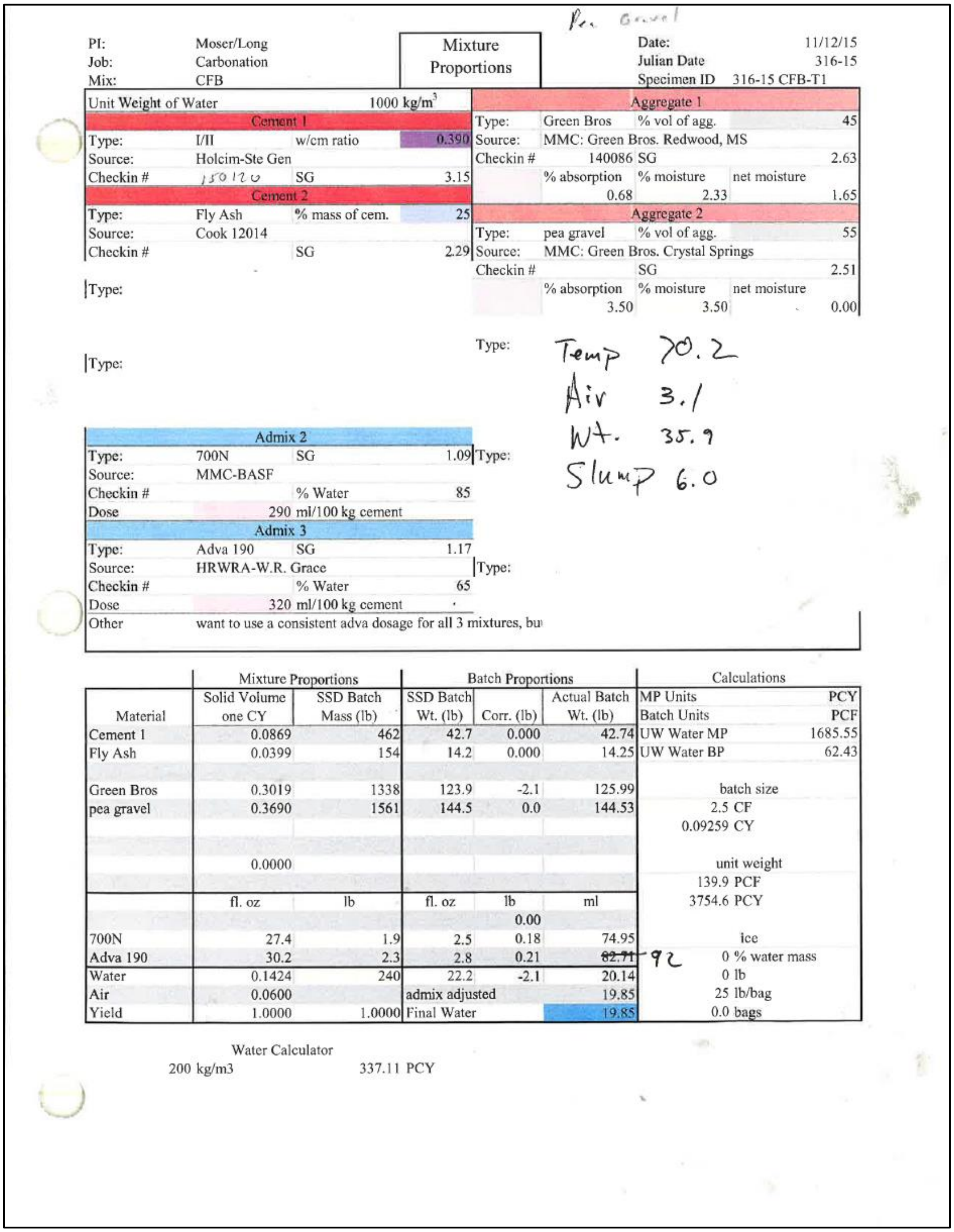


Figure A5. Specimens in tanks one and two.

Figure A6. Gray limestone, red granite, and gray quartzite specimens.

Appendix B: Concrete Mixture Proportioning Worksheets

Figure B1. Mixture proportion for material T1.



Pea Gravel

PI: Moser/Long
Job: Carbonation
Mix: CFB

Mixture Proportions

Date: 11/12/15
Julian Date 316-15
Specimen ID 316-15 CFB-T1

Unit Weight of Water 1000 kg/m³

Cement 1

Type:	I/II	w/cm ratio	0.390
Source:	Holcim-Ste Gen		
Checkin #	150120	SG	3.15

Cement 2

Type:	Fly Ash	% mass of cem.	25
Source:	Cook 12014		
Checkin #		SG	2.29

Type:

Type:

Aggregate 1

Type:	Green Bros	% vol of agg.	45
Source:	MMC: Green Bros. Redwood, MS		
Checkin #	140086	SG	2.63
	% absorption	% moisture	net moisture
	0.68	2.33	1.65

Aggregate 2

Type:	pea gravel	% vol of agg.	55
Source:	MMC: Green Bros. Crystal Springs		
Checkin #		SG	2.51
	% absorption	% moisture	net moisture
	3.50	3.50	0.00

Type:

Temp 70.2
Air 3.1
Wt. 35.9
Slump 6.0

Admix 2

Type:	700N	SG	1.09
Source:	MMC-BASF		
Checkin #		% Water	85
Dose	290	ml/100 kg cement	

Type:

Admix 3

Type:	Adva 190	SG	1.17
Source:	HRWRA-W.R. Grace		
Checkin #		% Water	65
Dose	320	ml/100 kg cement	

Type:

Other want to use a consistent adva dosage for all 3 mixtures, bu

	Mixture Proportions		Batch Proportions		
Material	Solid Volume one CY	SSD Batch Mass (lb)	SSD Batch Wt. (lb)	Corr. (lb)	Actual Batch Wt. (lb)
Cement 1	0.0869	462	42.7	0.000	42.74
Fly Ash	0.0399	154	14.2	0.000	14.25
Green Bros	0.3019	1338	123.9	-2.1	125.99
pea gravel	0.3690	1561	144.5	0.0	144.53
	0.0000				
	fl. oz	lb	fl. oz	lb	ml
				0.00	
700N	27.4	1.9	2.5	0.18	74.95
Adva 190	30.2	2.3	2.8	0.21	~~82.71~~ 92
Water	0.1424	240	22.2	-2.1	20.14
Air	0.0600		admix adjusted		19.85
Yield	1.0000	1.0000	Final Water		19.85

Calculations

MP Units	PCY
Batch Units	PCF
UW Water MP	1685.55
UW Water BP	62.43

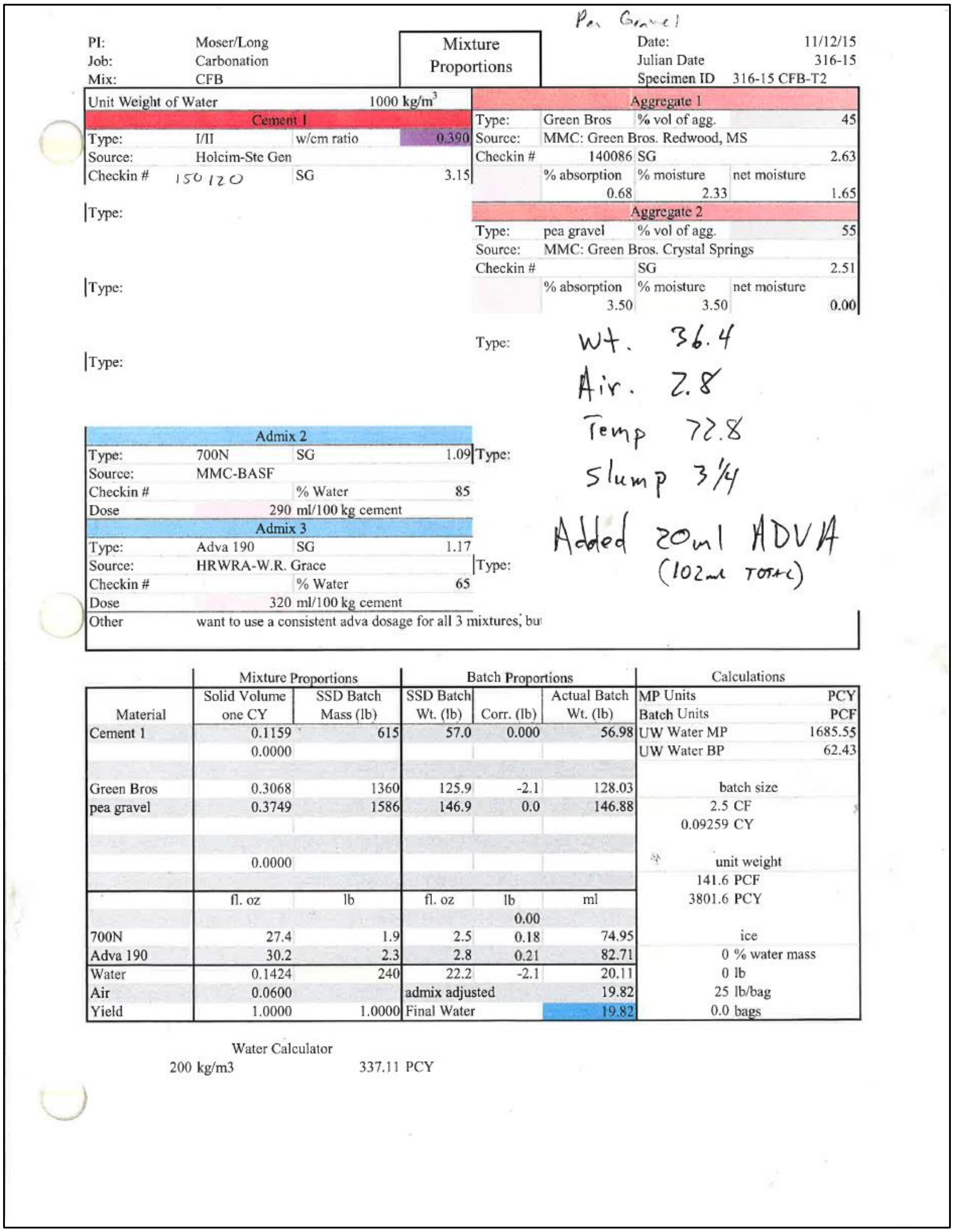
batch size
2.5 CF
0.09259 CY

unit weight
139.9 PCF
3754.6 PCY

ice
0 % water mass
0 lb
25 lb/bag
0.0 bags

Water Calculator
200 kg/m3 337.11 PCY

Figure B2. Mixture proportion for material T2.



Pea Gravel

Mixture Proportions

PI: Moser/Long
Job: Carbonation
Mix: CFB

Date: 11/12/15
Julian Date 316-15
Specimen ID 316-15 CFB-T2

Unit Weight of Water 1000 kg/m^3

Cement 1			
Type:	I/II	w/cm ratio	0.390
Source:	Holcim-Ste Gen		
Checkin #	150120	SG	3.15

Type:

Type:

Type:

Aggregate 1			
Type:	Green Bros	% vol of agg.	45
Source:	MMC: Green Bros. Redwood, MS		
Checkin #	140086	SG	2.63
	% absorption	% moisture	net moisture
	0.68	2.33	1.65

Aggregate 2			
Type:	pea gravel	% vol of agg.	55
Source:	MMC: Green Bros. Crystal Springs		
Checkin #		SG	2.51
	% absorption	% moisture	net moisture
	3.50	3.50	0.00

Type:

Wt. 36.4
Air. 2.8
Temp 72.8
slump 3 1/4

Admix 2			
Type:	700N	SG	1.09
Source:	MMC-BASF		
Checkin #		% Water	85
Dose	290	ml/100 kg cement	

Type:

Admix 3			
Type:	Adva 190	SG	1.17
Source:	HRWRA-W.R. Grace		
Checkin #		% Water	65
Dose	320	ml/100 kg cement	

Type:

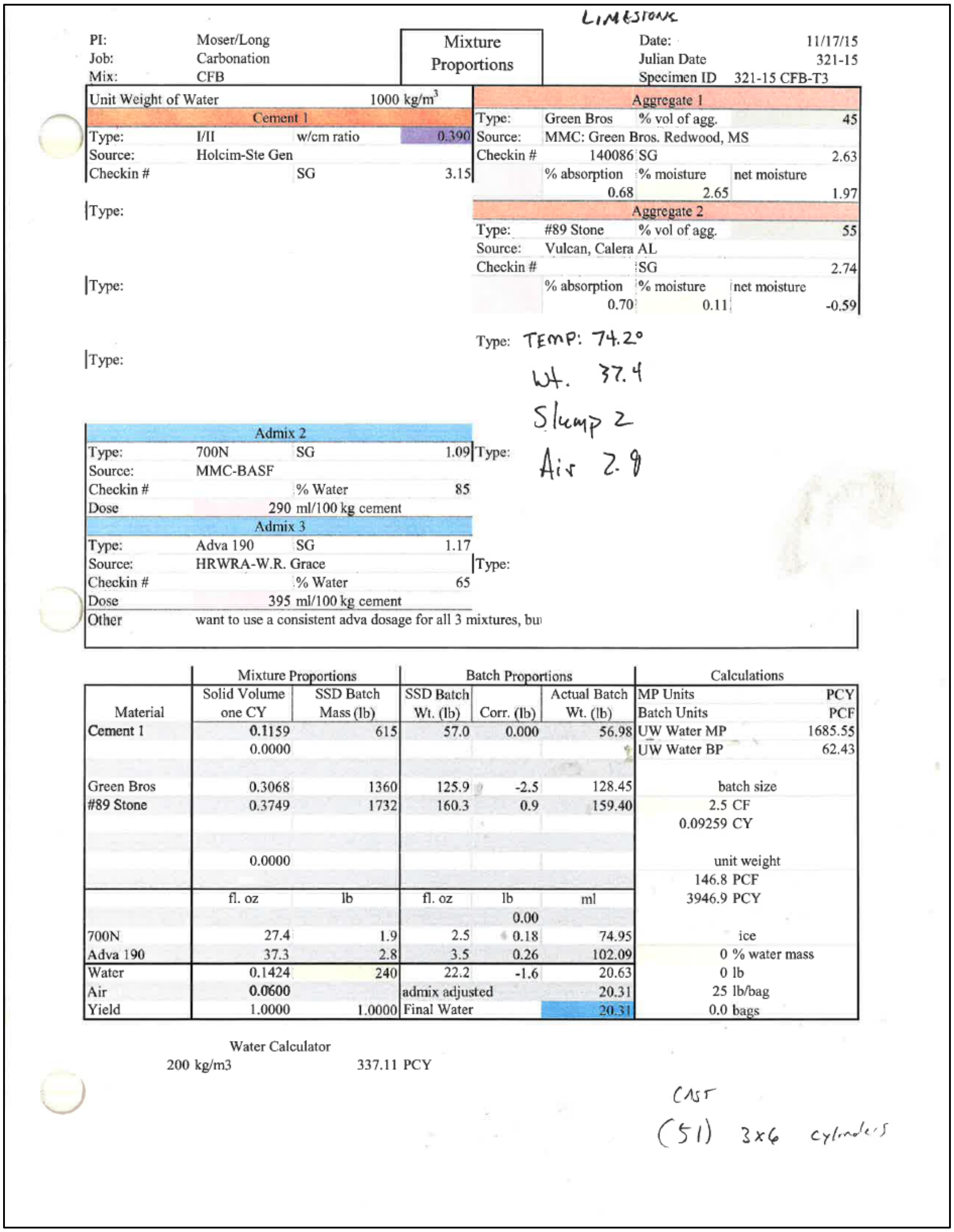
Added 20ml ADVA
(102ml TOTAL)

Other want to use a consistent adva dosage for all 3 mixtures, bu

	Mixture Proportions		Batch Proportions			Calculations	
Material	Solid Volume one CY	SSD Batch Mass (lb)	SSD Batch Wt. (lb)	Corr. (lb)	Actual Batch Wt. (lb)	MP Units	PCY
						Batch Units	PCF
Cement 1	0.1159	615	57.0	0.000	56.98	UW Water MP	1685.55
	0.0000					UW Water BP	62.43
Green Bros	0.3068	1360	125.9	-2.1	128.03	batch size	
pea gravel	0.3749	1586	146.9	0.0	146.88	2.5 CF	
						0.09259 CY	
	0.0000					unit weight	
						141.6 PCF	
	fl. oz	lb	fl. oz	lb	ml	3801.6 PCY	
				0.00			
700N	27.4	1.9	2.5	0.18	74.95	ice	
Adva 190	30.2	2.3	2.8	0.21	82.71	0 % water mass	
Water	0.1424	240	22.2	-2.1	20.11	0 lb	
Air	0.0600		admix adjusted		19.82	25 lb/bag	
Yield	1.0000	1.0000	Final Water		19.82	0.0 bags	

Water Calculator
200 kg/m3 337.11 PCY

Figure B3. Mixture proportion for material T3.



LIMESTONE

PI: Moser/Long
Job: Carbonation
Mix: CFB

Mixture Proportions

Date: 11/17/15
Julian Date 321-15
Specimen ID 321-15 CFB-T3

Unit Weight of Water 1000 kg/m^3

Cement 1			
Type:	I/II	w/cm ratio	0.390
Source:	Holcim-Ste Gen		
Checkin #		SG	3.15

Type:

Type:

Type:

Aggregate 1			
Type:	Green Bros	% vol of agg.	45
Source:	MMC: Green Bros. Redwood, MS		
Checkin #	140086	SG	2.63
	% absorption	% moisture	net moisture
	0.68	2.65	1.97

Aggregate 2			
Type:	#89 Stone	% vol of agg.	55
Source:	Vulcan, Calera AL		
Checkin #		SG	2.74
	% absorption	% moisture	net moisture
	0.70	0.11	-0.59

Type: TEMP: 74.2°
Wt. 37.4
Slump 2
Air 2.9

Admix 2			
Type:	700N	SG	1.09
Source:	MMC-BASF		
Checkin #		% Water	85
Dose	290 ml/100 kg cement		

Type:

Admix 3			
Type:	Adva 190	SG	1.17
Source:	HRWRA-W.R. Grace		
Checkin #		% Water	65
Dose	395 ml/100 kg cement		

Type:

Other want to use a consistent adva dosage for all 3 mixtures, bu

	Mixture Proportions		Batch Proportions			Calculations	
Material	Solid Volume one CY	SSD Batch Mass (lb)	SSD Batch Wt. (lb)	Corr. (lb)	Actual Batch Wt. (lb)	MP Units Batch Units	PCY PCF
Cement 1	0.1159	615	57.0	0.000	56.98	UW Water MP	1685.55
	0.0000					UW Water BP	62.43
Green Bros	0.3068	1360	125.9	-2.5	128.45	batch size	
#89 Stone	0.3749	1732	160.3	0.9	159.40	2.5 CF	
						0.09259 CY	
	0.0000					unit weight	
						146.8 PCF	
	fl. oz	lb	fl. oz	lb	ml	3946.9 PCY	
				0.00			
700N	27.4	1.9	2.5	0.18	74.95	ice	
Adva 190	37.3	2.8	3.5	0.26	102.09	0 % water mass	
Water	0.1424	240	22.2	-1.6	20.63	0 lb	
Air	0.0600		admix adjusted		20.31	25 lb/bag	
Yield	1.0000	1.0000	Final Water		20.31	0.0 bags	

Water Calculator
200 kg/m3 337.11 PCY

CAST
(51) 3x6 cylinders

REPORT DOCUMENTATION PAGE

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14. ABSTRACT

This study focused on examining the susceptibility of three concrete materials to carbonation-induced deterioration in a simulated CO_2 chemical fish barrier system. The concrete materials tested were modeled after concretes and aggregate mineralogies used in civil works structures. The exposure conditions consisted of 74 mg/L and 225 mg/L concentrations of CO_2 in an aqueous solution maintained at both 21°C and 40°C. Visual examination and pH indicator solutions were used to monitor the progression of any deterioration in specimens during the experiment. Surface deterioration was not observed until 90- and 180-day measurements. Characterization performed on affected materials and surface deterioration products indicated that the damage was induced by carbonation mechanisms with Ca^{2+} leaching from the concrete microstructure reacting with CO_2 in solution. These processes were limited to the top 1 mm of the concrete, even at 180 days with any severe microstructural alteration and changes in pH limited to 100-200 µm of depth. The primary conclusion from this Phase 1 study is that carbonation-induced deterioration can occur in the simulated fish barrier environment, but the rates of carbonation are not of concern and are similar to those that would be expected for concrete exposed to normal atmospheric conditions and CO_2 concentrations.

15. SUBJECT TERMS
Concrete
Carbonation
Hydrogen-ion concentration
Carbon Dioxide
Fish Barrier
Concrete—Corrosion
Concrete--Deterioration
Lock
Deterioration
Concrete hydraulic structures
Carbon dioxide

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