Degradation of Well Cement by CO_2 under Geologic Sequestration Conditions

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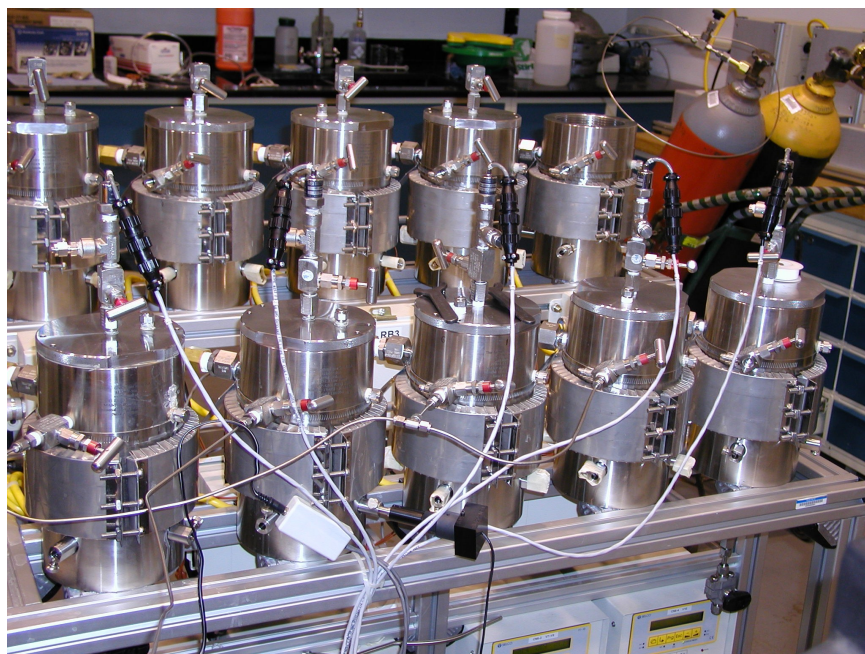 phone: 412-386-5988; fax: 412-386-4806; email: brian.strazisar@netl.doe.gov

Figure S1. Cement sequestration experiments were carried out in 1.3 liter (17-4PH-1150 stainless steel) high-pressure vessels (101.5 mm diameter x 165 mm depth) manufactured by Thar Technologies, Inc. specifically for NETL's Geologic Sequestration Core Flow Laboratory.   The vessels have a maximum operating pressure of 41.4 MPa (6000 psi) and maximum operating temperature of 150°C.

Figure S2. Looking inside one of the high-pressure vessels following a CO_2 sequestration experiment with hardened cement samples in place.
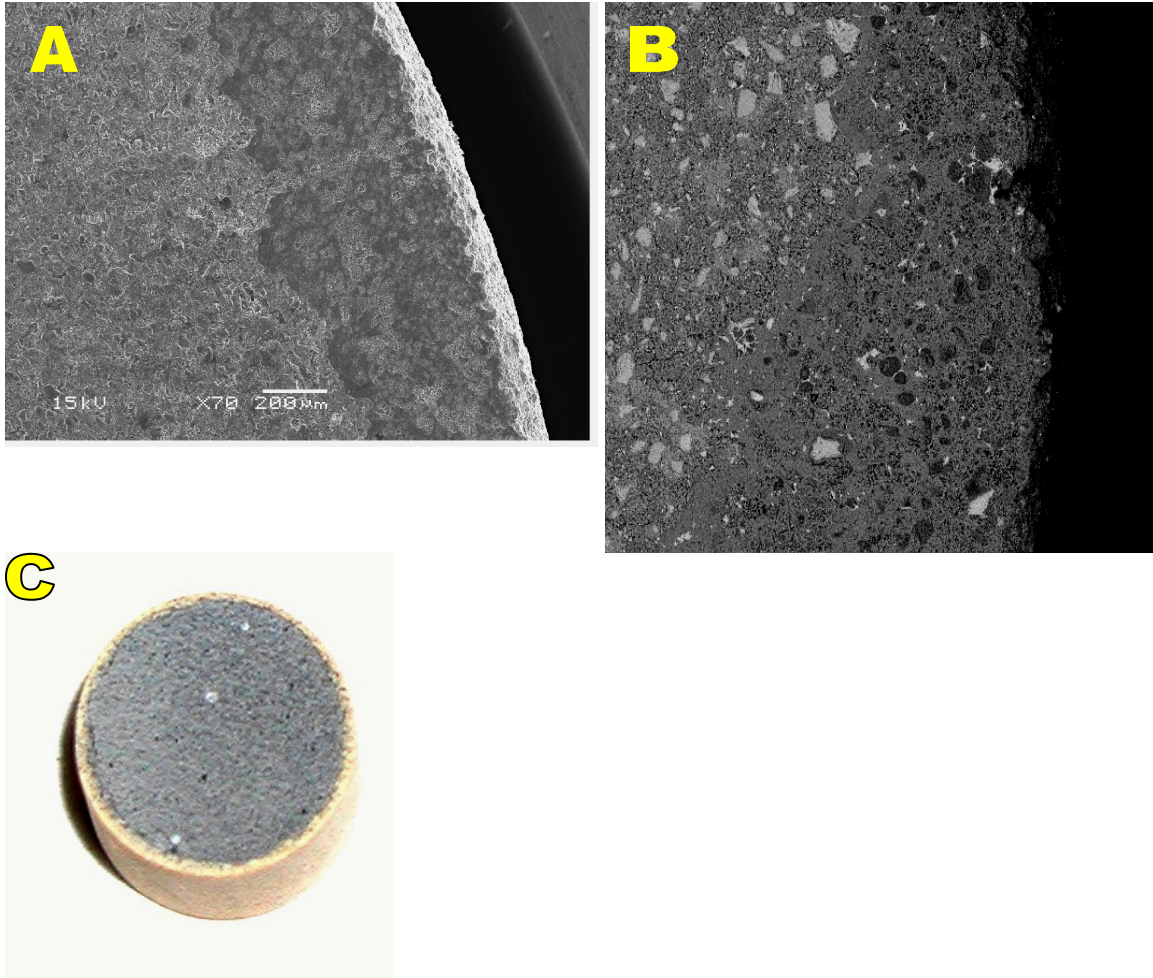
Figure S3. Images showing altered region of cement cured under ambient conditions and exposed to CO_2 sequestration conditions for 9 days. Secondary electron (SE) scanning microscopy image (A); backscattered electron (BSE) image (B); macroscopic image (C)
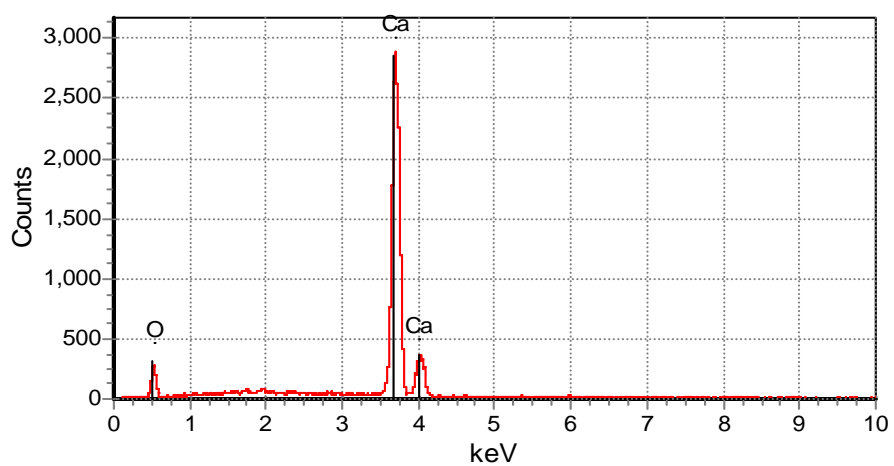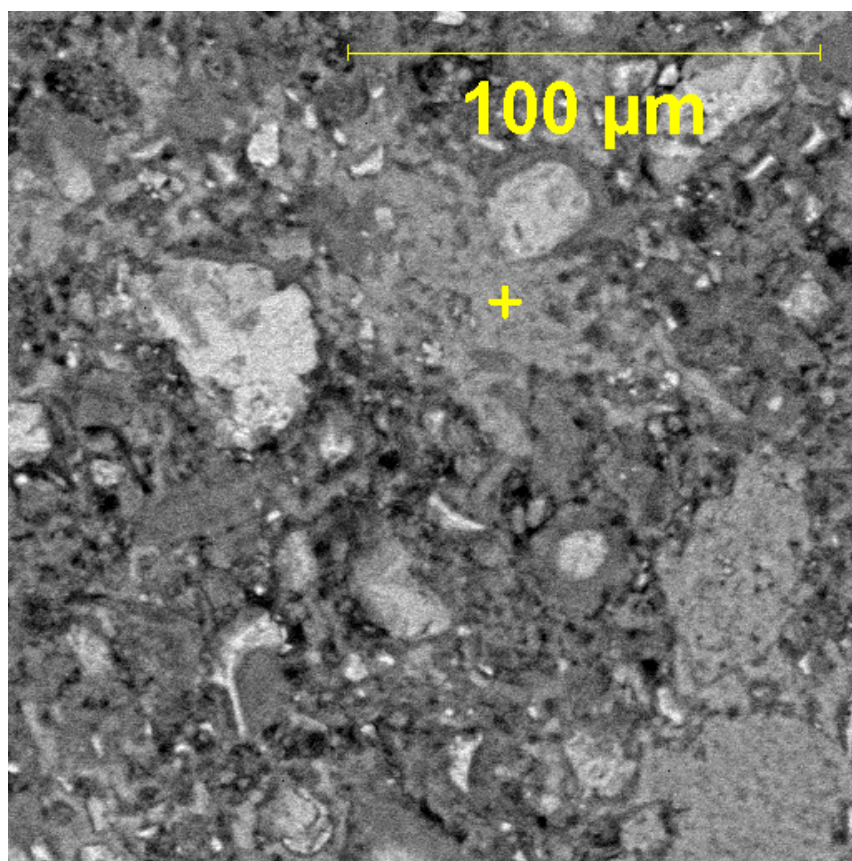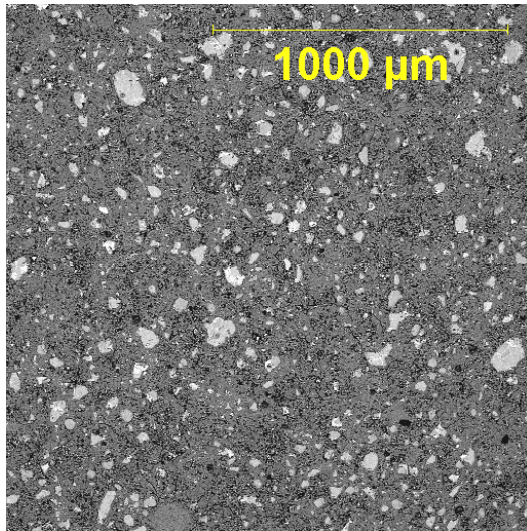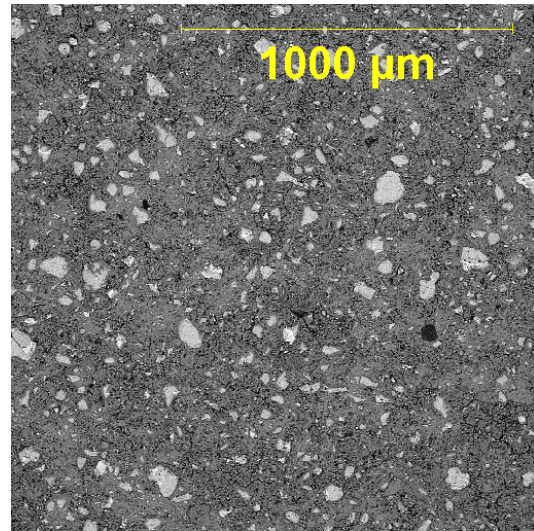
Figure S4. BSE image with elemental spectrum showing typical Ca(OH)$_2$ phase in ambient cured cement.
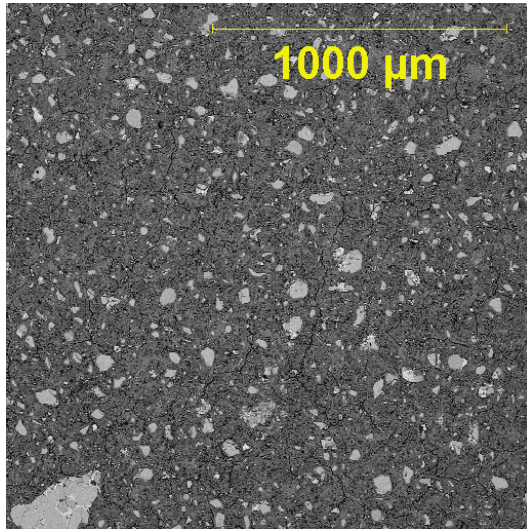
Sample A: 22°C, 1 atm

Sample B: 22°C, 30.3 MPa

Sample C: 50°C, 1 atm

Sample D: 50°C, 30.3 MPa
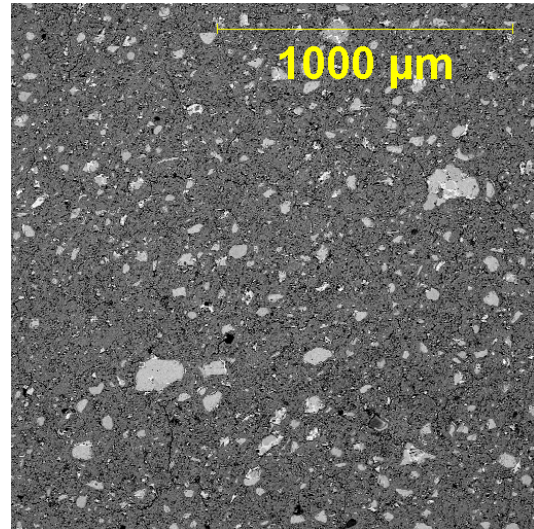
Figure S5. BSE images of the unexposed cement cured under four conditions. These images illustrate the regions of $Ca(OH)_2$ in the samples cured at ambient temperatures. In BSE images, intensity decreases in the order of unhydrated cement grains > calcium hydroxide > C-S-H > pores.

Sample D: 50°C, 30.3 MPa
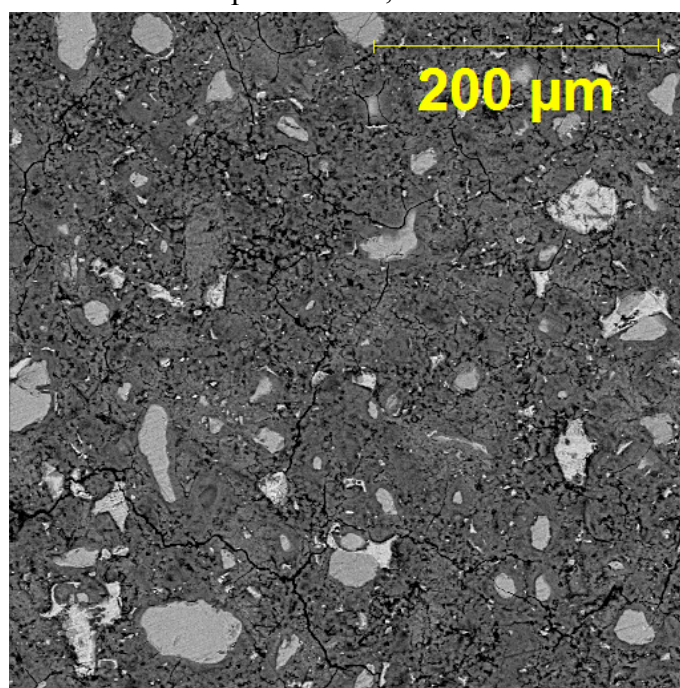
Sample A: 22°C, 1 atm
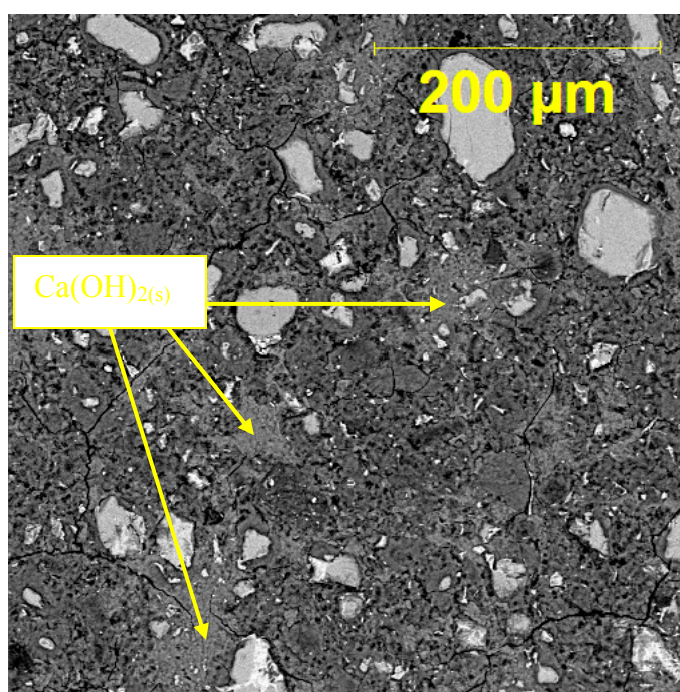
Figure S6. BSE images of Sample A and Sample D showing the difference in Ca(OH)$_2$ distribution.
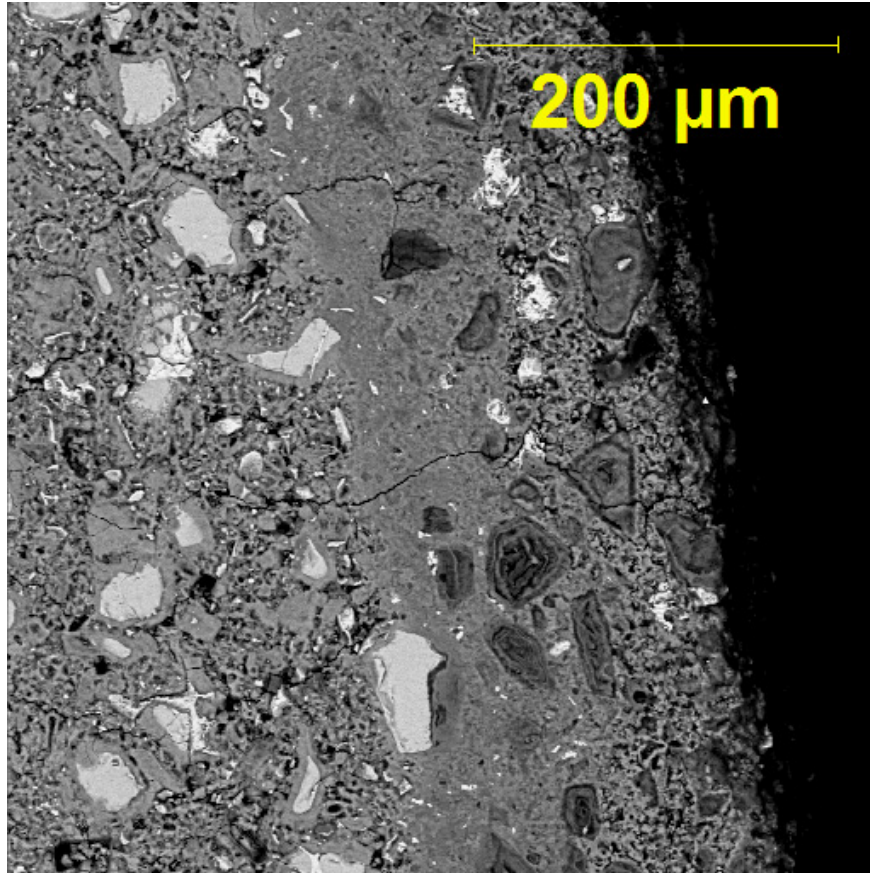
Figure S7. BSE image illustrating the carbonated zone (zone 2) in a cement sample cured under high temperature and pressure and exposed to CO_2 under sequestration conditions.
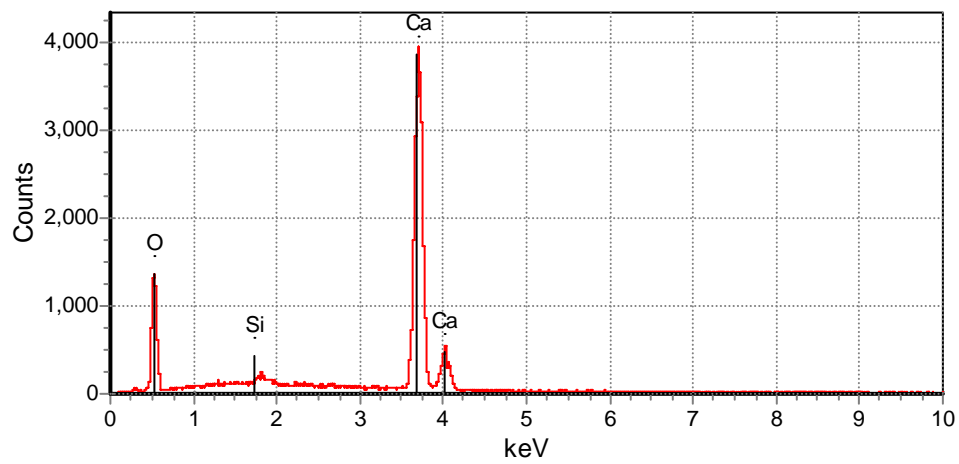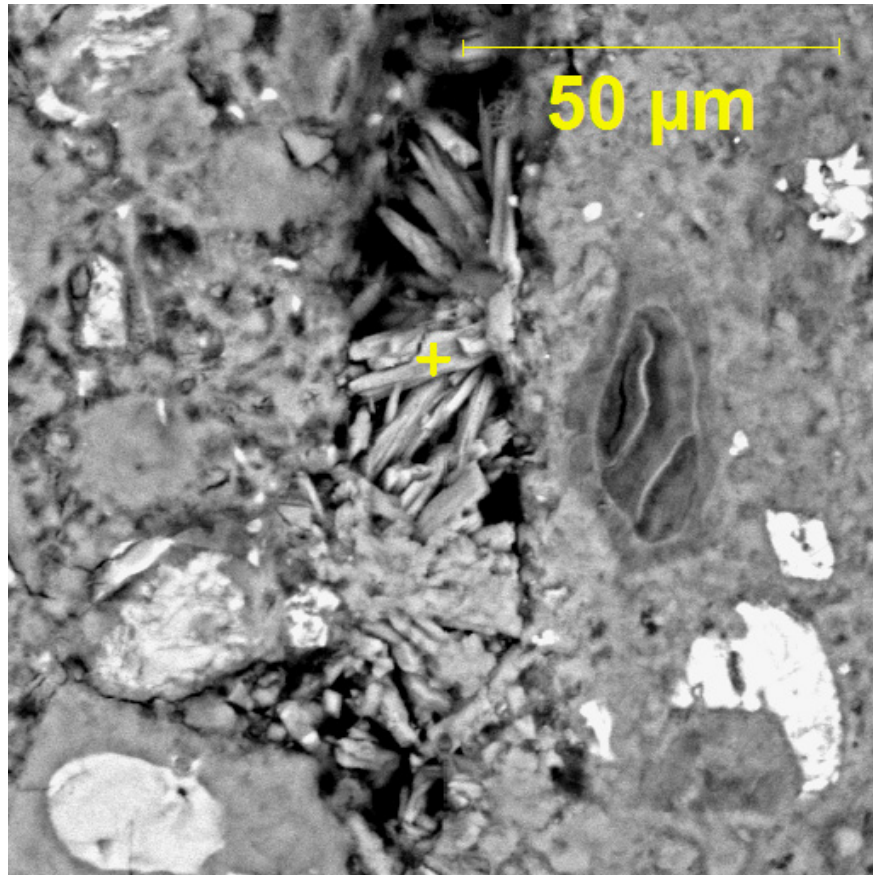
Figure S8. BSE image and elemental spectrum showing growth of calcite in the carbonated zone (zone 2) of sample shown in Figure S7. Presence of calcite was confirmed using XRD.
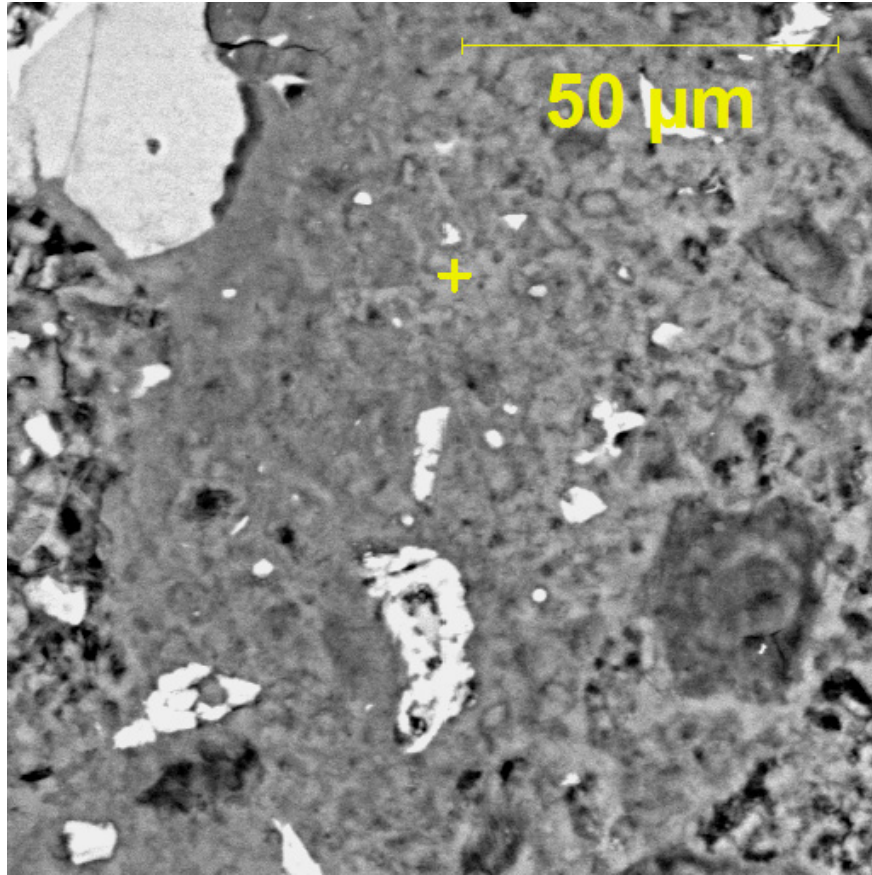
Figure S9. BSE image illustrating the carbonated zone (zone 2) of sample shown in Figure S7.
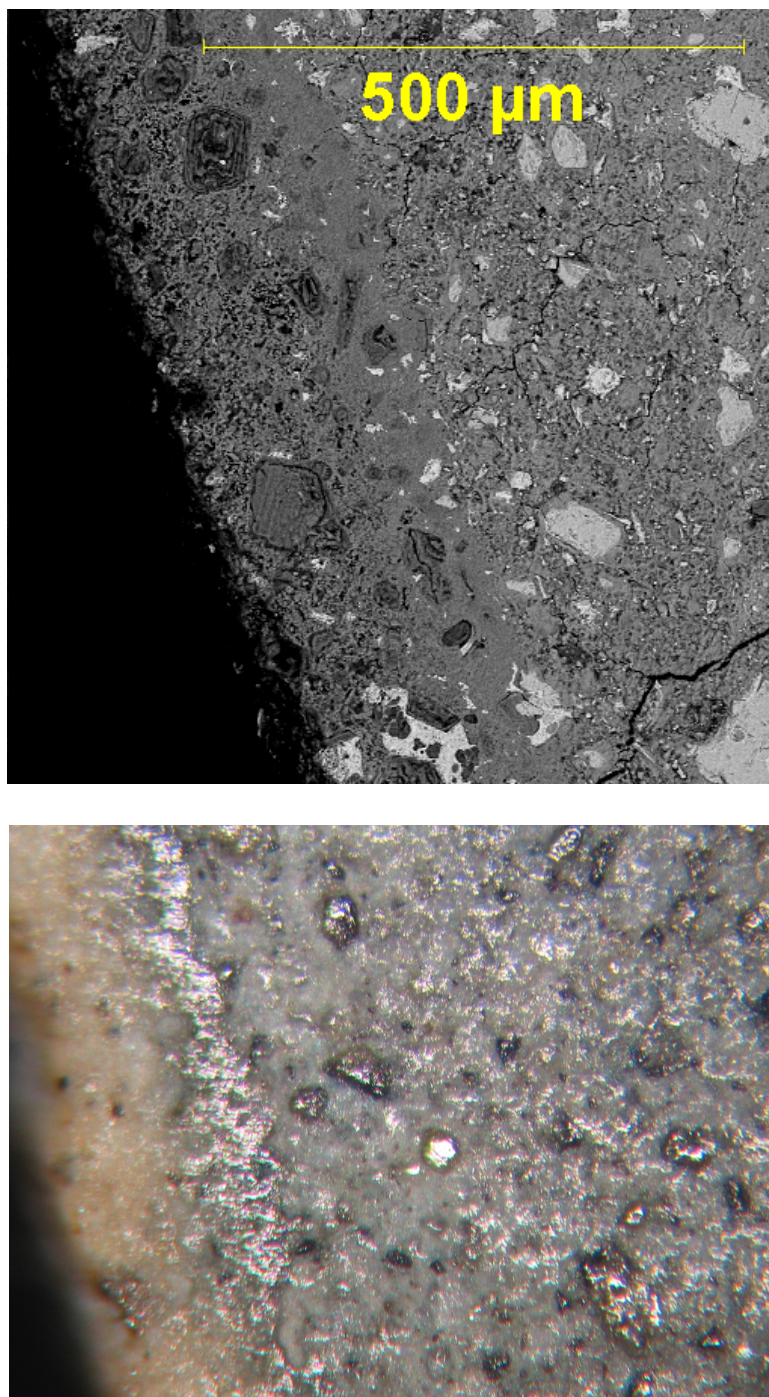
Figure S10. BSE image (top) and stereo-optical microscope image (bottom) illustrating the altered region in a cement sample cured under high temperature and pressure and exposed to CO_2 under sequestration conditions for 9 days.
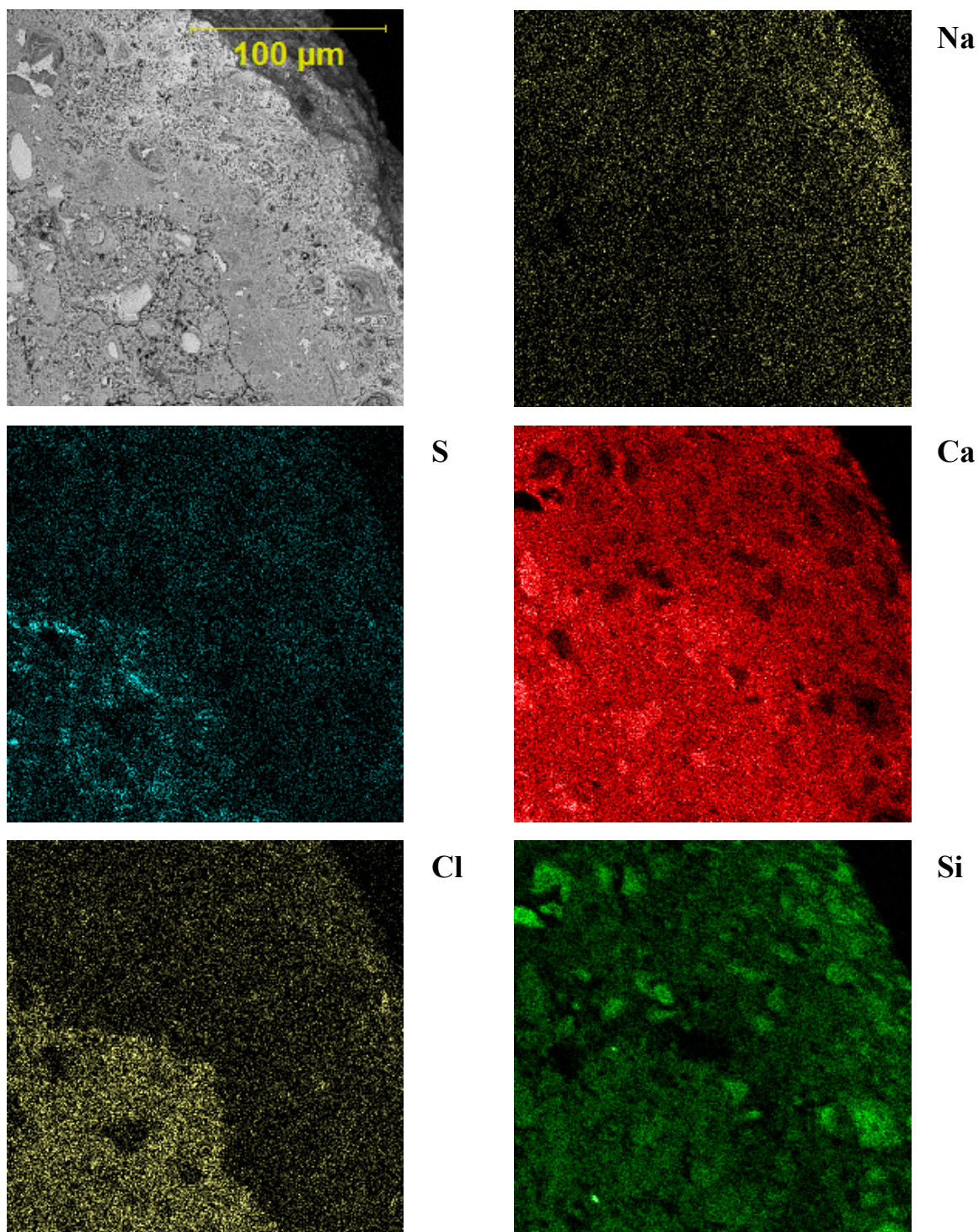
Figure S11. X-Ray map of the altered region of a cement sample cured under high temperature and pressure and exposed to CO_2 under sequestration conditions for 9 days. Note that the sulfur, chloride and calcium decreases in the degraded area.
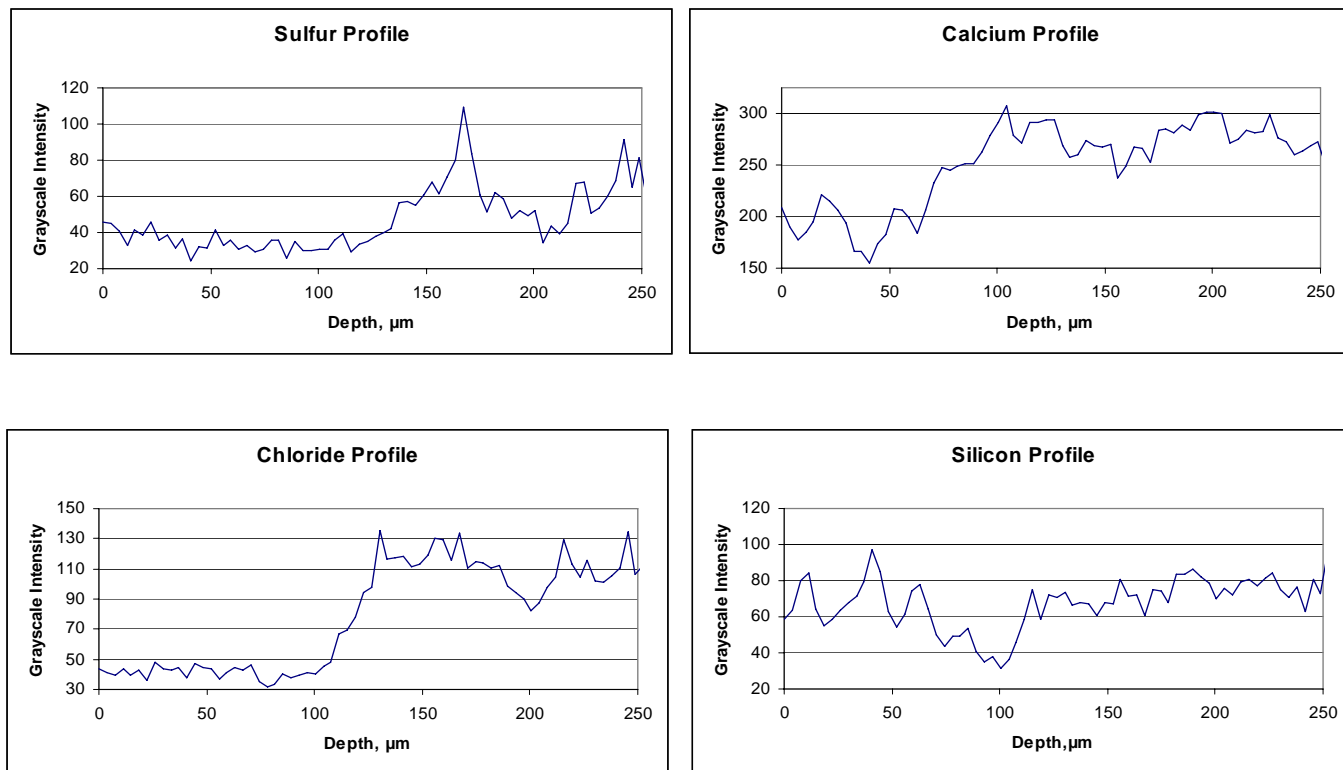
Figure S12. Elemental profiles generated from the X-Ray map (Fig. S11) of the altered region in a cement sample cured under high temperature and pressure and exposed to CO_2 under sequestration conditions for 9 days. The zero depth corresponds to the outer surface of the sample, moving inward toward the center of the sample. A higher grayscale intensity indicates a greater concentration of the element.

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BSE Image Profile

Figure S13. Plot profile showing the grayscale intensity change of the above BSE image of altered region shown in yellow illustrating the altered region in a cement sample cured under ambient temperature and pressure and exposed to CO_2 under sequestration conditions for 9 days.
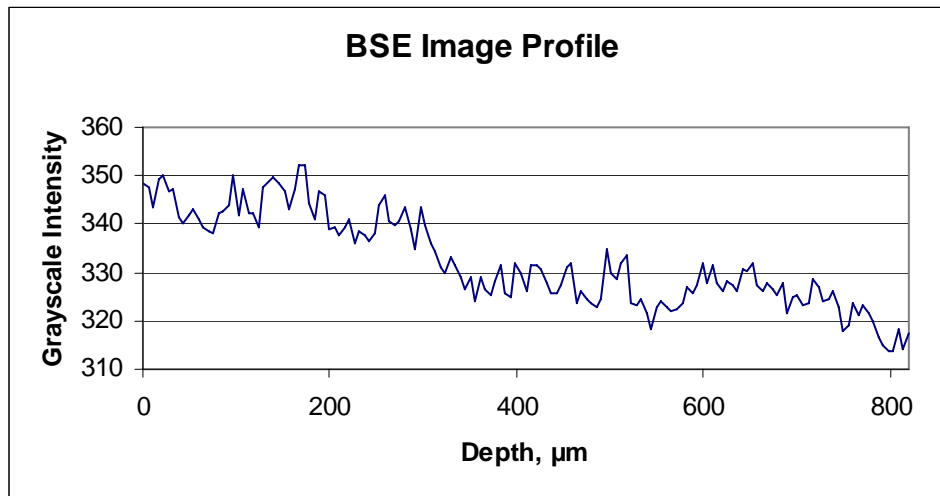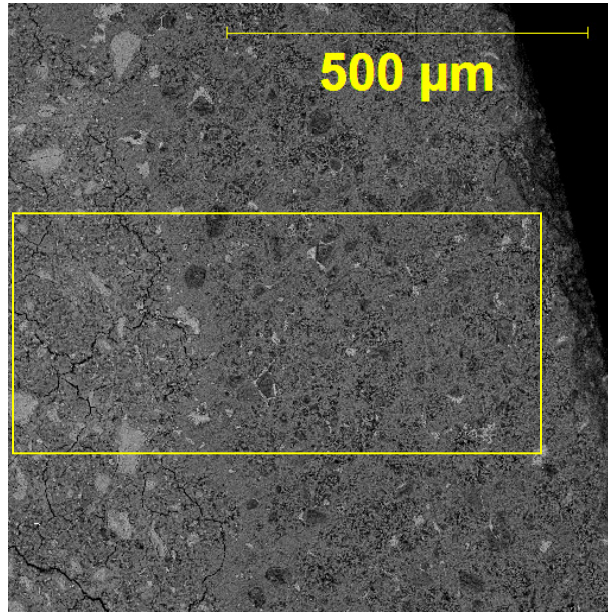
Additional experimental details:

Scanning Electron Microscopy (SEM)

The cement samples were analyzed at the National Energy Technology Laboratory
(NETL) using the Personal SEM (Aspex Instruments) equipped with backscattered and
secondary electron detectors coupled with EDS.   The parameters used for SEM analysis
consisted of 20 KeV accelerating voltage and a working distance of 15 mm.

DTA/TGA

Differential thermal analysis combined with thermogravimetric analysis (DTA/TGA) was
performed using TA Instruments; model SDT Q600 at RJ Lee Group. Between 10 and
15 mg of crushed sample was placed in a Pt cup and heated in a nitrogen atmosphere at a
temperature range from ambient to 1000°C at a heating rate of 5°C/min. DTA locates the
ranges corresponding to thermal decompositions of different cement phases and TGA
measures the weight loss due to those decompositions. The weight loss of water is
attributed to the dehydroxylation of $Ca(OH)_{2(s)}$:

$$Ca(OH)_{2(s)} \rightarrow H_2O + CaO$$
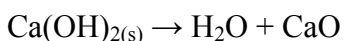
Relative $Ca(OH)_{2(s)}$ amounts were calculated from DTA/TGA curves showing the mass
loss from $Ca(OH)_{2(s)}$ dehydroxylation (*S1,S2*).

XRD

Cement samples were analyzed by XRD at the Pittsburgh NETL lab. All samples were
ground using an agate mortar and pestle and placed on glass holders, which were

mounted in a PANalytical X'Pert PRO model XRD equipped with a copper anode tube, and a high speed detector.   All samples were scanned at 0.02° continuous step size for 400 seconds from 5° to 65° 2θ.

Calculation of Effect of High Temperature and Pressure on Initial pH in Aqueous Solution:

This section provides the calculations determining the initial pH of the 1% NaCl solution used in the cement sequestration experiments. The first part provides the calculations used to determine the effect of temperature on the thermodynamic constants as given by the van't Hoff equation. Next, the temperature-adjusted constants were used to calculate the effect of pressure. This is followed by calculations for the salinity of the solution using the Davies Equation. The initial pH solution is ultimately determined using equilibrium constant values calculated by combining corrections for temperature, pressure and salinity.

Conditions: 50°C (323 K)
             4400 psi (299 atm)
                      1% NaCl solution = 1 g NaCl/100 ml of solution = 0.1709 mol/L

Formulas

Effect of temperature on thermodynamic constants given by van't Hoff equation (*S3*):
$\ln k_{t2} = (\Delta H°/R) (1/T_1 - 1/T_2) + \ln (k_{t1})$
- where $\Delta H°$ represents the enthalpy change of the reaction and remains constant over the temperature range.

Effect of pressure on thermodynamic constants given by (*S3*):
$\ln k_{p2} = (-\Delta V°/RT) (P - P_o) + \ln (k_{Po})$
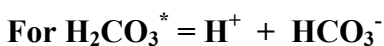- where $\Delta V°$ represents the change in volume of the system

To calculate activity coeffecients (Davies Equation) (*S4*):
$\log \gamma = Az_i^2 [I^{0.5}/(1 + I^{0.5})] - bI$

- Ionic Strength given by $I = \frac{1}{2} \Sigma C_i z_i^2$
- where NaCl is a 1:1 electrolyte
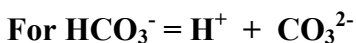- $I = 0.1709$ mol/L, $A = 0.51$, and $b = 0.2$

Calculate effect of temperature (T=50°C) on equilibrium constants
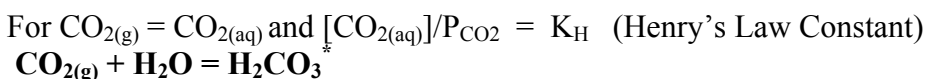- Enthalpy data and equilibrium constants from (*S5*).

For $H_2CO_3^* = H^+ + HCO_3^-$

where $\Delta H = 7.7$ kJ/mol for 25°C $\qquad$ $T_1 = 25°C$ (298 K)
$\qquad$ $R = 8.31$ x 10-3 kJ/mol $\qquad\qquad$ $T_2 = 50°C$ (323 K)
$\qquad$ $k_{T1} = 10^{-6.3}$

$k_{T50} = 10^{-6.21}$ *(Calculated value for T = 50°C)*

For $HCO_3^- = H^+ + CO_3^{2-}$

where $\Delta H = 14.9$ kJ/mol $\qquad\qquad$ $T_1 = 25°C$ (298 K)
$\qquad$ $R = 8.31$ x 10-3 kJ/mol $\qquad\qquad$ $T_2 = 50°C$ (323 K)
$\qquad$ $k_{T1} = 10^{-10.33}$

$k_{T50} = 10^{-10.13}$ *(Calculated value for T = 50°C)*

For $CO_{2(g)} = CO_{2(aq)}$ and $[CO_{2(aq)}]/P_{CO2} = K_H$ (Henry's Law Constant)
$CO_{2(g)} + H_2O = H_2CO_3^*$

where $\Delta H = -20.37$ kJ/mol $\qquad\qquad$ $T_1 = 25°C$ (298 K)
$\qquad$ $R = 8.31$ x 10^{-3} kJ/mol $\qquad\qquad$ $T_2 = 50°C$ (323 K)
$\qquad$ $k_H = 10^{-1.46}$

$k_{HT50} = 10^{-1.736}$

Calculate effect of pressure (P = 299 atm) on equilibrium constants

The following expressions were used to calculate the molar volume change (cm^3/mol) for each reaction, where t is the temperature in °C and S is the salinity of the solution where $S = 0$ for pure water (6).

For $H_2CO_3^* = H^+ + HCO_3^-$
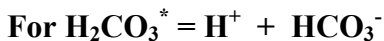
$-\Delta V°_{HCO3^-} = 25.5 + 0.151(S - 34.8) - 0.127t$

$-\Delta V^\circ_{HCO3^-}$ = $25.5 + 0.151(10 - 34.8) - 0.127(50°C)$

$= 25.5 - 3.7448 - 6.35$

$-\Delta V^\circ_{HCO3^-}$ = 15.4052 cm^3/mol

and $R = 8.31 \times 10^{-3}$ kJ/mol $t = 50°C$ (323 K) $S = 10$ ppt
$k_{T50} = 10^{-6.21}$ calculated value for $T = 50°C$

$\ln kp =$ $\dfrac{15.4052 \text{ cm}^3/\text{mol}}{(8.314\text{J/mol}\cdot\text{k})(323\text{K})}$ x $(P - P_o) + \ln k_{po}$

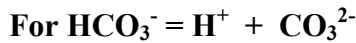$\ln kp =$ $(5.734 \times 10^{-3}$ cm^3/J$)(P - P_o) + \ln k_{po}$

Convert 5.734×10^{-3} cm^3/J to atm:
$(5.734 \times 10^{-3}$ cm^3/J$)(1$J/1N·m$)(1$m/100cm$)^3 = 5.734 \times 10^{-9}$ m^2/N
$= (5.734 \times 10^{-9}$ Pa$^{-1})(1.01 \times 10^5$ Pa/1 atm$) = 5.79 \times 10^{-4}$ atm^{-1}

Solve for ln kp:
$\ln kp =$ $(5.79 \times 10^{-4}$ atm$^{-1})(299$ atm $- 1$ atm$) + \ln 10^{-6.21}$
$= 0.1725 + (-14.299) = -14.12655$

$kp_{HCO3^-} = 10^{-6.135}$

For $HCO_3^- = H^+ + CO_3^{2-}$

$-\Delta V^\circ_{CO3}{}^{2-}$ = $15.82 + 0.321(S - 34.8) - 0.0219t$

$-\Delta V^\circ_{CO3}{}^{2-}$ = $15.82 + 0.321(10$ ppt $- 34.8) - 0.0219(50°C)$
$= 15.82 + 7.9608 + 1.095$

$-\Delta V^\circ_{CO3}{}^{2-} = 24.875$ cm^3/mol

and $R = 8.31 \times 10^{-3}$ kJ/mol $t = 50°C$ (323 K) $S = 10$ ppt
$k_{T50} = 10^{-10.13}$ calculated value for $T = 50°C$

$\ln kp =$ $\dfrac{24.875 \text{ cm}^3/\text{mol}}{(8.314\text{J/mol}\cdot\text{k})(323\text{K})}$ x $(P - P_o) + \ln k_{po}$

$\ln kp =$ $(9.259 \times 10^{-3}$ cm^3/J$)(P - P_o) + \ln k_{po}$

convert 9.259×10^{-3} cm^3/J to atm:
$(9.259 \times 10^{-3}$ cm^3/J$)(1$J/1N·m$)(1$m/100cm$)^3 = 9.259 \times 10^{-9}$ m^2/N
$= (9.259 \times 10^{-9}$ Pa$^{-1})(1.01 \times 10^5$ Pa/1 atm$) = 9.352 \times 10^{-4}$ atm^{-1}

Solve for ln kp:

ln kp = $(9.352 \times 10^{-4} \, \text{atm}^{-1})(299 \, \text{atm} - 1 \, \text{atm}) + \ln 10^{-10.13}$
          = $0.2787 + (-23.325) = -23.046$

$kp_{CO_3}{}^{2-} = 10^{-10.01}$

Calculate activity coefficients (γ) for 1% NaCl solution using Davies Equation

$\gamma_{H2CO3}{}^{*} = 1$

$\log \gamma_i = -(0.51)z_i{}^2 \, ([I^{0.5}/(1+I^{0.5})] - 0.2I)$

$\log \gamma_H{}^{+} = -(0.51)(+1)^2 \, (0.1709^{0.5}/1+0.1709^{0.5} - 0.2(0.1709)$
$\log \gamma_H{}^{+} = -(0.51)(0.2583)$

$\log \gamma_H{}^{+} = -0.1317$ $\gamma_H{}^{+} = 0.738$

$\log \gamma_{CO_3}{}^{2-} = -(0.51)(-2)^2 \, (0.1709^{0.5}/1+0.1709^{0.5} - 0.2(0.1709)$
$\log \gamma_{CO_3}{}^{2-} = -(0.51)(-2)^2(0.2583)$

$\log \gamma_{CO_3}{}^{2-} = -0.5269$ $\gamma_{CO_3}{}^{2-} = 0.297$

$\log \gamma_{HCO_3}{}^{-} = -(0.51)(-1)^2 \, (0.1709^{0.5}/1+0.1709^{0.5} - 0.2(0.1709)$
$\log \gamma_{HCO_3}{}^{-} = -(0.51)(-1)^2(0.2583)$

$\log \gamma_{HCO_3}{}^{-} = -0.1317$ $\gamma_{HCO_3}{}^{-} = 0.738$

Calculate equilibrium constant values with combined corrections for I, T, and P

For $H_2CO_3{}^{*} = H^{+} + HCO_3{}^{-}$

$k_1 = \dfrac{\gamma_H{}^{+} [H^{+}] \, \gamma_{HCO_3}{}^{2-}[HCO_3{}^{2-}]}{\gamma_{H2CO3}{}^{*} \, [H_2CO_3{}^{*}]}$ *$k_1 = 10^{-6.135}$ calculated for T = 50°C & P = 299 atm*

$k_I = \dfrac{(10^{-6.135})(\gamma_{H2CO3}{}^{*})}{(\gamma_H{}^{+})(\gamma_{HCO3}{}^{-})}$ = $\dfrac{(10^{-6.135})(1)}{(0.738)(0.738)}$

$k_I = 1.346 \times 10^{-6} = 10^{-5.87}$

For $HCO_3{}^{-} = H^{+} + CO_3{}^{2-}$

$$K_2 = \frac{\gamma_{H^+} [H^+] \gamma_{CO_3^{2-}}[CO_3^{2-}]}{\gamma_{HCO3^-} [HCO_3^-]} \qquad k_2 = 10^{-10.01} \text{ calculated for } T = 50°C \ \& \ P = 299 \text{ atm}$$

$$k_I = \frac{(10^{-10.01})(\gamma_{HCO3^-})}{(\gamma_{H^+})(\gamma_{CO3^{2-}})} = \frac{(10^{-10.01})(0.738)}{(0.738)(0.297)}$$

$$k_I = 3.29 \times 10^{-10} = 10^{-9.48}$$

Calculate pH of solution for I = 0.17 M, T = 50 C, P = 299 atm

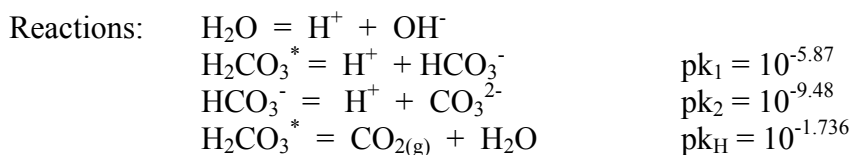Species:　　　H_2O, H^+, OH^-, $CO_{2(g)}$, $H_2CO_3^*$, HCO_3^-, CO_3^{2-}

Reactions:　　$H_2O = H^+ + OH^-$
　　　　　　　$H_2CO_3^* = H^+ + HCO_3^-$　　　　$pk_1 = 10^{-5.87}$
　　　　　　　$HCO_3^- = H^+ + CO_3^{2-}$　　　　$pk_2 = 10^{-9.48}$
　　　　　　　$H_2CO_3^* = CO_{2(g)} + H_2O$　　　$pk_H = 10^{-1.736}$

Tableau:

	H^+	$CO_{2(g)}$	H_2O
H^+	1		
OH^-	-1		1
$H_2CO_3^*$		1	1
HCO_3^-	-1	1	1
CO_3^{2-}	-2	1	1
$CO_{2(g)}$		1	
H_2O			1
$[CO_2]_T$		1	
$[H_2O]_T$			1

$$TOTH = [H^+] - [OH^-] - [HCO_3^-] - 2[CO_3^{2-}] = 0$$

Since we are adding CO_2 (weak acid) to water, assume pH < 7:
therefore,
　　　　$[H^+]$, $[HCO_3^-] \gg [OH^-]$, $[CO_3^{2-}]$

$$TOTH = [H^+] - [HCO_3^-] = 0$$

$$[H^+] = [HCO_3^-]$$

$[HCO_3^-] = (k_1) [H_2CO_3^*] [H^+]^{-1}$

$[H_2CO_3^*]$ calculated from Henry's Law Constant (for 50°C) and the fugacity of CO_2 (S7):

$[H_2CO_3^*] = (k_H)(f_{CO2}) = (10^{-1.736})(98) = 1.7998$ M (Total concentration of dissolved carbonic aced in the brine)

$[H^+] = [HCO_3^-] = (10^{-5.87})(1.7998M) [H^+]^{-1}$

$[H^+]^2 = 2.428 \times 10^{-6}$ $\qquad$ $[H^+] = 10^{-2.807}$ M $\;\to\; \{H^+\} = \gamma_H^+ [H^+] = (0.738)(10^{-2.807})$

$\{H^+\} = 10^{-2.939}$

pH = 2.94

Literature Cited

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(S7) Duan, Z., Moller, N., and Weare, J.H. An equation of state for the CH_4-CO_2-H_2O system: I. Pure systems for 0 to 1000°C and 0 to 8000 bar. *Geochim. Cosmochim.* **1992**, 56, 2605-2617.