SP-289.01

Advances in Geological CO₂ Sequestration and Co-Sequestration with O₂

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Synopsis: The injection of CO_2 for Enhanced Oil Recovery (EOR) and sequestration in brine-bearing formations for long term storage has been in practice or under investigation in many locations globally. This study focused on the assessment of cement wellbore seal integrity in CO_2 - and CO_2 - O_2 -saturated brine and supercritical CO_2 environments. Brine chemistries (NaCl, MgCl₂, CaCl₂) at various saline concentrations were investigated at a pressure of 28.9 MPa (4200 psi) at both 50°C and 85°C. These parameters were selected to simulate downhole conditions at several potential CO_2 injection sites in the United States. Class H portland cement is not thermodynamically stable under these conditions and the formation of carbonic acid degrades the cement. Dissociation occurs and leaches cations, forming a CaCO₃ buffered zone, amorphous silica, and other secondary minerals. Increased temperature affected the structure of C-S-H and the hydration of the cement leading to higher degradation rates.

Keywords: Carbon sequestration, oil-well cement, oxy-fuel combustion, secondary ettringite formation

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INTRODUCTION

The Intergovernmental Panel on Climate Change recommended that mitigation of anthropogenic CO_2 derived from the use of fossil fuels for energy production is necessary.¹ To this end, brine-bearing formations with large potential storage capacity for geologic sequestration of CO_2 have been identified.²⁻⁴ Candidate formations include enhanced oil recovery reservoirs and pilot tests sites in saline formations under the National Energy Technology Laboratory (NETL) Phase III Regional Partnership programs.^{5,6} Proposed wellbores use oil-well type portland cements to plug the well and bond the host rock to the steel casing, and are subjected to specific bore depths, high temperature, and high pressure environments.^{7,8} In addition, injection of CO_2 into a brine-bearing formation results in the formation of carbonic acid. Portland cement is not thermodynamically stable under these conditions and is subject to dissolution and ionic migration in a CO_2 -rich environment. Thus the integrity of the wellbore seal may be compromised, providing a potential leakage pathway up the wellbore into the atmosphere and/or surrounding substrates.⁹

CO₂ exists both as a supercritical fluid (SCCO₂) and dissolved in CO₂-saturated brines at sequestration injection depth.¹⁰ The production of carbonic acid (H₂CO₃) from dissolution of CO₂ into water, heavily alters cement as the portlandite (CH) is dissolved and replaced by CaCO_{3 (s)}, which fills pore spaces.¹¹ Compressive strength increases initially and CaCO₃ provides a pH buffer.¹² Ongoing diffusion of carbonic acid leaches Ca²⁺ from the cement, creating a zoned alteration rind of amorphous silica. CaCO₃ solubility is significantly lower than that of CH so CaCO₃ becomes unstable, causing bicarbonate to reach aqueous saturation and local dissolution of calcium species.^{11,13} The diffusion of calcium species out of the cement is driven by the fluctuating pH and propagates further degradation. The following equations show the degradation process:

$$CO_2 + H_2O \leftrightarrow H_2CO_3 \leftrightarrow H^+ + HCO_3^-$$
(1)

$$HCO_{3}^{-} + H^{+} \leftrightarrow 2H^{+} + CO_{3}^{-2}$$
⁽²⁾

$$\operatorname{Ca(OH)}_{2(s)} \to \operatorname{Ca}^{2+}_{(aq)} + 2\operatorname{OH}^{-}_{(aq)}$$
(3)

$$\operatorname{Ca}^{2+}_{(aq)} + \operatorname{HCO}_{3}_{(aq)} + \operatorname{OH}_{(aq)} \to \operatorname{CaCO}_{3(s)} + \operatorname{H}_{2}\operatorname{O}$$
(4)

$$H_2CO_{3(aq)} + C-S-H_{(s)} \rightarrow CaCO_{3(s)} + H_2O_{(aq)} + am-SiO_{2(s)}$$
(5)

$$H_2CO_{3(aq)} + CaCO_{3(s)} \rightarrow Ca(HCO3)_{2(aq)}$$
(6)

The precipitation of salts is encouraged as suggested by Pruess and Müller,¹⁴ as injection of CO_2 into the brine increases aqueous phase salinity. Downhole conditions are assumed to be static due to low formation permeability and porosity, so the CO_2 system and cement reaction can be considered homogeneous.¹⁵

Previous findings suggest that the rates of alteration are low (1 mm to 1 cm [0.04 to 0.4 in] over 30 years) in simple brines.^{5,9,12} It is therefore suggested that CO₂ sequestration is a probable means of carbon storage at those conditions. However, formation brines range in salt species and in salinity, which impact the degree of cement alteration. In the subject study, where salinity was $\leq 1 M$, higher CO₂ solubility led to a depth of cement degradation exceeding 1 mm (0.04 in). Where salinity was >1.2M, depth of degradation was ~0.5 mm (0.02 in) after CO₂ exposure of the same duration.¹⁶

Carbon dioxide co-sequestration studies have been limited to $SO_2 \text{ models}^{17,18}$ and experimental work with CO_2 -H₂S, where Fe²⁺ in the C-S-H and iron substitution in ferrite clinker precipitated ettringite and pyrite.^{19,20} The interest in co-sequestration is driven by the high cost of CO_2 capture from conventional combustion flue gas, thus novel types of fossil fuel energy conversion systems, such as oxy-fueled combustion, chemical looping combustion, and coal gasification are under investigation. The flue gas from these technologies consists mostly of CO_2 and is therefore ready for sequestration without post-combustion separation. However, excess O_2 and oxidized acid gas species such as SO_2 remain at low concentrations (1-4%) in the untreated combustion flue gas, requiring separation or a co-sequestration methodology. The latter could provide an economic advantage by eliminating the need to remove the O_2 and SO_2 prior to injection. However, these gas species would likely produce

a more aggressive environment and potential degradation to cement well seal integrity that is not currently well understood.

RESEARCH SIGNIFICANCE

This research addresses a critical issue in carbon sequestration evaluation and the basic understanding of wellbore cement stability in a CO_2 -rich environment. The experimental conditions selected for this study apply to in-situ conditions at potential CO_2 injection sites in the United States. The multiple chloride species and variable concentrations comprising the synthetic brines in this study mark a departure from prior studies. The addition of flue gas co-contaminate gases could provide an economic advantage due to reduced separation costs and potential storage enhancement (physical or mineral trapping). However, the impact of co-sequestration on cement integrity is not clearly understood.

EXPERIMENTAL PROCEDURE

Class H portland (Lafarge, North America) well cement was prepared based on the American Petroleum Institute (API) practices 10B with a w/c of 0.38.²¹ The cement powder (weight percent) comprised of approximately 64.5% tricalcium silicate (C₃S); 11.77% dicalcium silicate (C₂S); 13.24% calcium aluminosulfate (C₄AF); no tricalcium aluminate (C₃A); 2.94% MgO; 2.8% SO₄²⁻; 0.16% total alkali content (Na₂O); 0.62% free lime, and a loss on ignition (LOI) of 0.73. The cement paste was cast into 25 mm diameter x 152 mm (1x6 in) long PVC-pipe forms, cured at temperatures of 50°C and 85°C under a hydraulic pressure of 28.9 MPa (4200 psi), in 1.2 L stainless steel (316 CrNiMo) static autoclave vessels filled with 600 mL of the synthetic brine. After 24 hours, the forms were removed and the cement paste cylinders held at temperature and pressure for the remainder of the 28 day curing period prior to injection.

The cement paste cylinders were in contact with several CO₂-saturated brines to simulate formation brines and depths at three NETL Phase III Regional Partnership injection sites. Discussion of results using the various brines will be presented in a subsequent publication. This paper focuses on the synthetic "control" brine adjusted to a 1 *M* concentration (0.82 *M* NaCl, 0.02 *M* MgCl₂, & 0.16 *M* CaCl₂) modeled after several NETL sandstone formation brine chemistries.²²

The CO₂ mixed gas exposure tests were performed using two gas mixtures, 1) pure CO₂ and 2) a mixture of 96% CO₂ + 4% O₂. The tests were conducted at geothermal gradients designed to simulate the sequestration environment, including a supercritical CO₂ head-space and CO₂-saturated brine. The two temperatures were investigated to determine the effect of temperature on the cement paste and specifically on C-S-H structure. Following the curing interval, the autoclaves were purged with the CO₂-gas mixture and then maintained at temperature and pressure for exposure intervals up to 84 days (after the initial 28-day cure). Corrosion of the stainless steel autoclaves was observed during conduct of CO₂-O₂ exposure tests, and is discussed later.

ANALYTICAL PROCEDURE

Petrographic analyses were performed with an optical microscope, and an FEI Inspect F Scanning Electron Microscope (SEM) was used to obtain backscattered electron (BSE) images and energy dispersive spectroscopy (EDS) data on polished epoxy-impregnated

mounts. SEM elemental intensities were optimized using a Cu-K α standard for quantification and measurement of alteration depth, determined by EDS and spot analysis. Alteration in the cement paste was mapped by measuring the distribution of calcium, silicon, and chlorine in 14 samples over a total of 84 sites. Electron microprobe analysis (EMPA) using wavelength-dispersive spectrometry (WDS) with standard errors, and a correction matrix for cement [oxide weight percent concentrations] was utilized for quantification. X-rays diffracted by specific analyzing crystals (TAP: Na, Al, Mg; LPET: Si, Ca, S, Cl; and LIF: Fe, Ti) determine composition by comparison with intensities of known standards [Ca₁₀(PO₄)₆Cl₂, MgO, SiO₂, TiO₂, CaSO₄ (anhydrite), Fe₃O₄ (magnetite), and Na₃KAl₄Si₄O₁₆ (nepheline)] to the unknown materials in the cement paste. Analysis of cements is very difficult due to the composition of hydrated phases and its intrinsic heterogeneity. Atomic number, adsorption, and fluorescence (ZAF), time dependent intensity (TDI), background continuum, and oxide corrections provide a summation of concentrations representative to the stoichiometric analysis of calcium silicate grains, hydration products, and within alteration zones.

The cementitious phases were identified using X-ray diffraction (XRD) collected by a Rigaku Ultima III with a 40KV/40mA Cu k- α source and a step speed of 1°/min over a scan angle, 5°-90° 20. The qualitative analysis of XRD data was performed using the International Center for Diffraction Data (ICDD) pattern databases and Jade Plus software v9.1.4.²³

Solid chemistry on hydrated paste (ground into powder and vacuum sealed) was determined by several methodologies, including a LECO gas analyzer for sulfur and carbon, lithium meta-borate fusion with X-ray fluorescence (XRF) for metal oxides, carbonate leach and gravimetric analysis for SO₄, CO₂ by coulometer, and acid digestion and titration for FeO. Solution alkalinity was determined by titration, using sodium carbonate and hydrochloric acid. Nitric acid digestion with inductively coupled argon plasma spectroscopy (ICP-AES) methods were used for metals analysis, while ion chromatography was used for Br, Cl, and SO₄.

EXPERIMENTAL RESULTS AND DISCUSSION

Results from pure CO_2 exposure tests¹⁶ were compared to the CO_2 - O_2 experimental results, each using the same raw cement batch composition, brine chemistries, and experimental conditions. This methodology isolated the change in conditions to the addition of 4% O_2 to the gas mixture, thus any change in mineralogy, alteration depth as indicated by CaCO₃ and Ca²⁺ depletion, and stainless steel corrosion can be attributed primarily to the O_2 addition.

Pure CO₂ and CO₂-O₂ Gas Injection: Microanalysis of Cement Specimens

Verba et al.¹⁶ found that exposure of Class H cement to pure CO₂ at 50°C and 28.9 MPa (4200 psi), in higher salinity brines of 1-2 *M* NaCl, MgCl₂, and CaCl₂, resulted in alteration zones in the cement that increase in depth and become more defined with time. The carbonation depths versus time are provided in Table 1, while the alteration zones are depicted in Fig. 1a. Total alteration depth extended into the core up to $1254\pm441 \,\mu\text{m}$ (0.049 in) after an 84-day exposure period. Alteration included large hydration halos surrounding C₂S and C₃S grains as continuous hydration allowed for conversion into interstitial CH and C-S-H.

Gas Type	Temperature (°C)	Exposure Duration	Alteration Depth (µm)		
CO ₂	50	28	151 ± 20		
CO ₂	50	56	714 ± 61		
CO ₂	50	84	1254 ± 441		
CO ₂ -O ₂	85	28	253 ± 59		
CO ₂ -O ₂	85	53	737 ± 94		
CO ₂ -O ₂	85	73	1585 ± 422		
CO ₂ -O ₂	50	28	514 ± 109		
CO ₂ -O ₂	50	56	680 ± 132		
CO ₂ -O ₂	50	73	700 ± 100		

Table 1— Total alteration depth of CO_2 and CO_2 - O_2 exposure at 50/85°C. Alteration depth of CO_2 from Verba, 2011.



Fig. 1— Carbonation and alteration depth of portland cement cylinders exposed to A) 84 days and pure- CO_2 at 50°C, B) 53 days CO_2 - O_2 : 85°C, and C) 66 days CO_2 - O_2 50°C. Zone 1 is the porous-Si, zone 2 is CaCO₃, and zone 3 is the Ca²⁺ leading into unaltered cement. Dashed line indicates diffuse Ca²⁺ leached zone; no boundary. Scale bar 1 mm (0.04 in).

Remnant calcium silicates and hydration products were in the Ca²⁺ depletion zone whereas all calcium silicates in the carbonated zone turned into amorphous silica with a banded appearance from zoning loss of Ca²⁺. SEM-EDS and EMPA confirmed a Cl-enriched (~3 wt%) and S-enriched zone (1-3 wt%) in the Ca²⁺ depletion zone, presumably incorporated into the C-S-H structure. EMPA identified both Fe³⁺ (at <5%) and Fe²⁺ (<2%) in the C-S-H structure as well.

The higher salinity and multiple chloride species in the brine led to precipitation of large (50-1200 μ m; 0.047 in) CH crystals on the exterior of the cement cylinder. Small cubic halite grains (1-15 μ m) also crystallized in the cement while the cement maintained a lower pH (<6) and was dehydrated in the presence of early SCCO₂. The precipitation of the additional minerals, specifically exterior CH, reduced the maximum alteration depth and permeability after an exposure of 84 days.

 CO_2 - O_2 (96% CO_2 + 4% O_2) exposures led to more rapid cement degradation and ionic migration behavior compared to the pure CO_2 studies (Fig. 1b,c). The cement cylinders displayed a banded Si-porous zone of remnant silicates, a CaCO₃ band with thickness



Fig. 2— Minerals and polymorphs in CO_2 - O_2 injected samples. A) Calcium silicate polymorph, B) Hydrotalcite forming on ferrite grains, C) Ettringite needles in the Ca²⁺ depleted zone, and D) Cubic halite grains within the carbonated zone.

dependent on temperature, and a Ca²⁺ depleted zone. EMPA analyses found that the C-S-H structure contained roughly 1.5 wt% Fe²⁺ and had 20-30% water bound unaltered C-S-H. Significant differences from the pure CO₂ studies included: 1) the transformation of calcium silicates (C₂S) with bordering ferrite grains into polymorphs with significant twinning and 5-10% less Ca²⁺; 2) precipitation of dendritic hydrotalcite [Mg₆Al₂(CO₃)(OH)₁₆·4H₂O] on C₄AF grains; and 3) the precipitation of 10-50 µm long ettringite [Ca₆Al₂(SO₄)₃(OH)₁₂· 26H₂O] needles within pores specifically in Ca²⁺ depleted zones (Fig. 2). The authors suggest that change in pH between the solution and the cement within the Ca depletion zone allowed for ettringite formation, coupled with leaching of Ca²⁺ and Al³⁺, as well as S previously bound in C-S-H.

Ettringite formation occurred after the primary curing stage and during the CO_2 - O_2 gas exposure interval, after carbonation had occurred as determined by SEM and XRD analysis. This secondary [delayed] ettringite formation (DEF) can lead to loss of cement paste integrity, degradation, expansion, and fracturing.¹³ Expansion of the cement paste or the development of microfractures could serve as potential leakage pathways for the injected gases or liquids, either out of the wellbore or to the wellbore steel casing. Microfractures ranging from 0.5-3 µm wide extend from many of the pores containing ettringite, and propagated in the least resistant pathway around mineral grains. These are not interpreted as an artifact of sample prep, due to the small fracture sizes, where fractures induced during



Fig. 3— Montage backscatter (BSE) image (left) and Ca^{2+} EDS map (right) of CO_2 - O_2 exposure sample with diffuse alteration boundary (white outline) extending into the cylinder. Scale 4.5 mm (0.18 in).

sample prep often cut across mineral grains and stem into larger fractures. Etched and pitted features were also observed on the silicates and C₄AF, evidence of acid attack. EMPA data suggests <2% of the carbonate band contained FeCO₃, which could not be confirmed via other instrument analyses in such trace amounts.

Total alteration depth versus time of the CO_2-O_2 exposure samples is listed in Table 1. At both temperatures, the alteration depth exceeded initial depths (28-days) in comparison to pure- CO_2 exposure, but displayed diffuse and nonuniform alteration as shown in Fig. 3. The 85°C sample showed the highest rate of degradation with a large, thicker initial CaCO₃ band compared to pure CO_2 exposure. At 28 days of exposure, the alteration depth was minimal, up to $253\pm59 \ \mu m \ (0.01 \ in)$. After 53 days, the alteration zone extended to a depth of $916\pm94 \ \mu m \ (0.036 \ in)$, and the Ca²⁺ depleted zone ranged from ~0.5- 1 mm (0.02-0.04 in), with large pores up to 160 $\ \mu m \ (0.0063 \ in)$ in diameter. After 73 days, pieces of the cement shed off from the cylinder exterior, and alteration exceeded 1-2 mm (0.04-0.08 in). Thus, degradation increased in the higher temperature static conditions from 53-73 days of exposure. The 50°C sample, on the other hand, displayed an alteration depth at 514±109 $\ \mu m \ (0.02 \ in)$ after 28 days, exceeded 680±132 $\ \mu m \ (0.027in)$ after 56 days, but remained fairly constant over the duration of the test exposure.

Solid and Solution Chemistry

Solid chemistry of the unhydrated portland Class H cement, hydrated cement paste and post-gas exposure cement samples are included in Table 2. Brine solution chemistry for the post-curing interval and post gas-exposure intervals is included in Table 3.

The product solids from the pure-CO₂ tests showed a slight decrease in SiO_2 concentration between the post-cure and post-gas exposure samples, and leaching of Si from the cement was clearly evident from the Si concentration in the product solution over time,

Table 2— Solid chemical compositions of the unhydrated cement, the cured
hydrated cement paste, and cement paste post-CO ₂ and CO ₂ -O ₂ exposure
(wt%). Unit conversion: 100 μm = 0.003937 in

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Oxide wt%	Cement Powder	Cured Paste	CO ₂ 50°C	CO ₂ -O ₂ 50°C	CO ₂ -O ₂ 85°C	
SiO ₂	21.07	17.95	17.02	18.39	17.99	
Al ₂ O ₃	2.78	2.4	2.26	2.3	2.33	
Fe ₂ O ₃	4.37	3.64	3.54	5.64	3.77	
CaO	64.02	54.55	49.82	52.25	52.45	
MgO	2.94	2.49	2.27	2.39	2.29	
Na ₂ O	0.05	0.09	<0.01	<0.01	0.01	
K ₂ O	0.11	0.1	0.01	0.01	0.02	
Cr ₂ O ₃	0.01	0.01	0.02	0.02	<0.01	
TiO ₂	0.2	0.17	0.18	0.15	0.16	
MnO	0.06	0.05	0.05	0.07	0.07	
P ₂ O ₅	0.131	0.113	0.105	0.107	0.116	
SrO	0.1	0.08	0.06	0.08	0.08	
BaO	0.07	0.05	0.04	0.05	0.06	
LOI^1	0.73	16.85	22.9	17.05	18.9	
Total	96.64	98.55	98.27	98.5	98.25	
С	0.07	1.65	2.35	1.14	0.9	
CO ₂	0.3	6.1	8.6	3.5	3.2	
FeO	0.19	0.19	0.13	0.26	0.19	
H_2O^2	<0.01	5.55	4.93	11.9	13.7	
S	0.17	0.06	0.17	0.11	0.17	
SO ₃ ³	2.48	2	1.8	1.93	1.68	

¹LOI: Loss on Ignition, measured as the weight loss after 1 hour at 1000°C, in air.

²Free moisture, measured as the weight loss after 1 hour at 105°C, in air.

³Sulfate sulfur-carbonate leach

which increased from <10 to >50 mg/L. These results are reflected in the 57-205 μ m deep amorphous silica zone identified in the cement cylinders by microanalysis, which is indicative of dissolution of the CH and C-S-H in that zone, mobilization of the Ca²⁺ cations, followed by re-precipitation of most of the free silica. The CaO content in the pure CO₂ exposure cement decreased nearly 5 wt% after 84 days, apparently due to leaching of Ca²⁺ cations from the cement, as described previously. However, the Ca²⁺ trend in the product solution decreased dramatically over time, from >8000 to <2000 mg/L, once CO₂ was injected. This apparent contradiction is best explained by calcium carbonate precipitation during the CO₂ exposure interval which exceeded the Ca²⁺ dissolution rates. Locally, CH

	Surrogate CO ₂ 50°C			Surrogate CO ₂ -O ₂ 50°C			Surrogate CO ₂ -O ₂ 85°C				
(mg/L)	Cured	Exposure			Cured	Exposure		Cured	Exposure		
Dura- tion (days)	28	28	56	84	28	28	56	66	28	28	53
HCO ₃	*	*	*	*	665	945	335	287	335	451	402
Cl-	40700	37300	38100	39700	28000	31000	33000	17000	28000	31000	28000
SO4 2-	<1	8	7	8	480	50	100	100	1200	100 ¹	100 ¹
Ca	8450	1869	1770	1694	3400	4400	3800	3600	4100	2000	2100
Cr	0.0226	0.033	<dl< td=""><td><dl< td=""><td>1.4</td><td>5.8</td><td>3.3</td><td>28</td><td>0.7</td><td>8.5</td><td>0.51</td></dl<></td></dl<>	<dl< td=""><td>1.4</td><td>5.8</td><td>3.3</td><td>28</td><td>0.7</td><td>8.5</td><td>0.51</td></dl<>	1.4	5.8	3.3	28	0.7	8.5	0.51
Fe	0.0196	0.167	0.549	0.263	5	36	20	200	5	66	5 ¹
K	6.13	59.8	56.6	57	750	79	120	110	600	50 ¹	62
Mg	626	1395	948	784	79	360	430	660	50	360	350
Na	24160	25530	18200	19700	14000	16000	17000	21000	13000	17000	14000
Ni	1^{1}	12.58	15.85	22.94	1	61	180	380	1^{1}	750	260
Si	7.644	47.6	53.68	52.01	5.1	51	51	46	2.5 ¹	78	9
Free CO ₂	*	*	*	*	5.10E-05	1300	62	46	1.0E-04	950	17

Table 3— Brine solution chemical compositions of the post-cured solution and the post-gas exposure solutions taken at several exposure intervals (mg/L).

¹concentration at or below detection limit

*no measurement

and C-S-H had become depleted and replaced by $CaCO_3$, whereby CO_3^{2-} decreased as bicarbonate became the dominant aqueous species in the system.

Solids analysis for the cured hydrated cement and post-gas exposure cement samples for the CO_2 - O_2 gas mixture tests indicated little to no change in SiO₂ and CaO concentration at both temperatures (85°C and 50 °C). This was reflected by the thinner silica-porous band observed in the cement cylinders during microanalysis. While Si concentration in solution increased in both the 50°C and 85°C tests, these concentrations compare favorably with those observed in the pure CO_2 tests, and are thus likely indicative of equilibrium concentrations at the experimental parameters utilized. Aqueous Ca^{2+} concentration initially increased after 28 days of exposure, from 3400 mg/L to 4400 mg/L in the 50°C sample, as cations diffused into solution, but then decreased in concentration after longer exposure time, likely due to CaCO₃ precipitation. In contrast, the higher temperature solution displayed a 50% decrease in Ca²⁺ concentration after both 28 and 53 days of exposure. These trends suggest that calcium carbonate mineral precipitation was favored kinetically at the higher temperature.

The free water content in the CO_2 - O_2 exposure samples was 7-8 wt % greater than that in the pure- CO_2 samples. However, chemically-bound water content, calculated as the difference between the LOI and other volatiles (CO_2 , free moisture, and sulfate) in those same