

Advances in Geological CO₂ Sequestration and Co-Sequestration with O₂

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Synopsis: The injection of CO₂ 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 CO₂- and CO₂-O₂-saturated brine and supercritical CO₂ 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 CO₂ 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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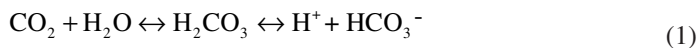
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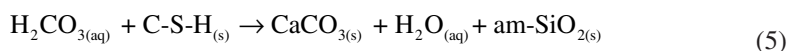
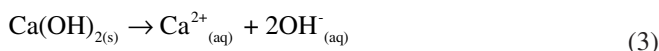
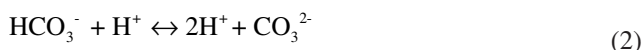
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INTRODUCTION

The Intergovernmental Panel on Climate Change recommended that mitigation of anthropogenic CO₂ 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 CO₂ 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 CO₂ 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 CO₂-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:





The precipitation of salts is encouraged as suggested by Pruess and Müller,¹⁴ as injection of CO₂ into the brine increases aqueous phase salinity. Downhole conditions are assumed to be static due to low formation permeability and porosity, so the CO₂ 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 ≤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 SO₂ models^{17,18} and experimental work with CO₂-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 CO₂ 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 CO₂ and is therefore ready for sequestration without post-combustion separation. However, excess O₂ and oxidized acid gas species such as SO₂ 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 O₂ and SO₂ 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 CO₂-rich environment. The experimental conditions selected for this study apply to in-situ conditions at potential CO₂ 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-contaminant 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 headspace 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 [$\text{Ca}_{10}(\text{PO}_4)_6\text{Cl}_2$, MgO, SiO_2 , TiO_2 , CaSO_4 (anhydrite), Fe_3O_4 (magnetite), and $\text{Na}_3\text{KAl}_4\text{Si}_4\text{O}_{16}$ (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° 2 θ . 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 SO_4 , CO_2 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 SO_4 .

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 CaCO_3 and Ca^{2+} depletion, and stainless steel corrosion can be attributed primarily to the O_2 addition.

Pure CO_2 and CO_2 - O_2 Gas Injection: Microanalysis of Cement Specimens

Verba et al.¹⁶ found that exposure of Class H cement to pure CO_2 at 50°C and 28.9 MPa (4200 psi), in higher salinity brines of 1-2 M NaCl, MgCl_2 , and CaCl_2 , 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 $1254 \pm 441 \mu\text{m}$ (0.049 in) after an 84-day exposure period. Alteration included large hydration halos surrounding C_2S and C_3S grains as continuous hydration allowed for conversion into interstitial CH and C-S-H .

Table 1— Total alteration depth of CO₂ and CO₂-O₂ exposure at 50/85°C. Alteration depth of CO₂ from Verba, 2011.

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

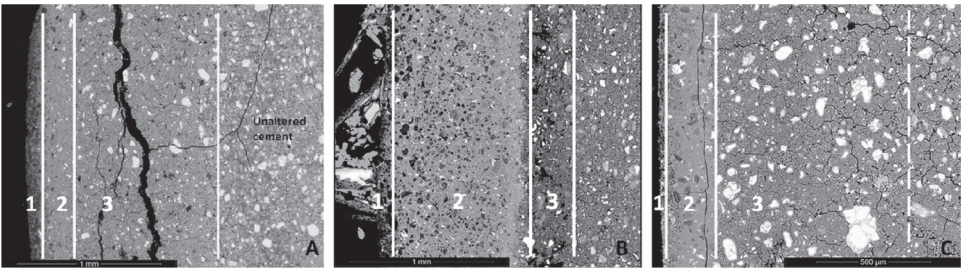


Fig. 1— Carbonation and alteration depth of portland cement cylinders exposed to A) 84 days and pure-CO₂ at 50°C, B) 53 days CO₂-O₂: 85°C, and C) 66 days CO₂-O₂ 50°C. Zone 1 is the porous-Si, zone 2 is CaCO₃, and zone 3 is the Ca²⁺ leading into unaltered cement. Dashed line indicates diffuse Ca²⁺ leached 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 μm; 0.047 in) CH crystals on the exterior of the cement cylinder. Small cubic halite grains (1-15 μm) 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.

CO₂-O₂ (96% CO₂ + 4% O₂) exposures led to more rapid cement degradation and ionic migration behavior compared to the pure CO₂ studies (Fig. 1b,c). The cement cylinders displayed a banded Si-porous zone of remnant silicates, a CaCO₃ band with thickness

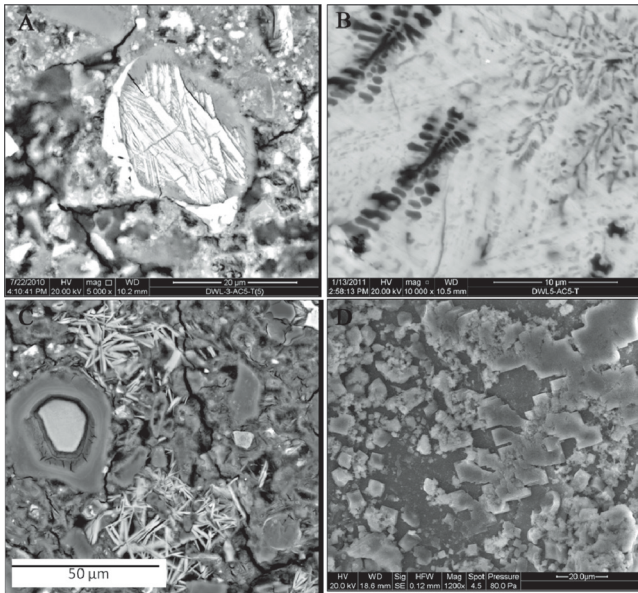


Fig. 2— Minerals and polymorphs in $\text{CO}_2\text{-O}_2$ injected samples. A) Calcium silicate polymorph, B) Hydrotalcite forming on ferrite grains, C) Ettringite needles in the Ca^{2+} depleted zone, and D) Cubic halite grains within the carbonated zone.

dependent on temperature, and a Ca^{2+} depleted zone. EMPA analyses found that the C-S-H structure contained roughly 1.5 wt% Fe^{2+} and had 20-30% water bound unaltered C-S-H. Significant differences from the pure CO_2 studies included: 1) the transformation of calcium silicates (C_2S) with bordering ferrite grains into polymorphs with significant twinning and 5-10% less Ca^{2+} ; 2) precipitation of dendritic hydrotalcite $[\text{Mg}_6\text{Al}_2(\text{CO}_3)(\text{OH})_{16}\cdot 4\text{H}_2\text{O}]$ on C_4AF grains; and 3) the precipitation of 10-50 μm long ettringite $[\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12}\cdot 26\text{H}_2\text{O}]$ needles within pores specifically in Ca^{2+} 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 Ca^{2+} and Al^{3+} , as well as S previously bound in C-S-H.

Ettringite formation occurred after the primary curing stage and during the $\text{CO}_2\text{-O}_2$ 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

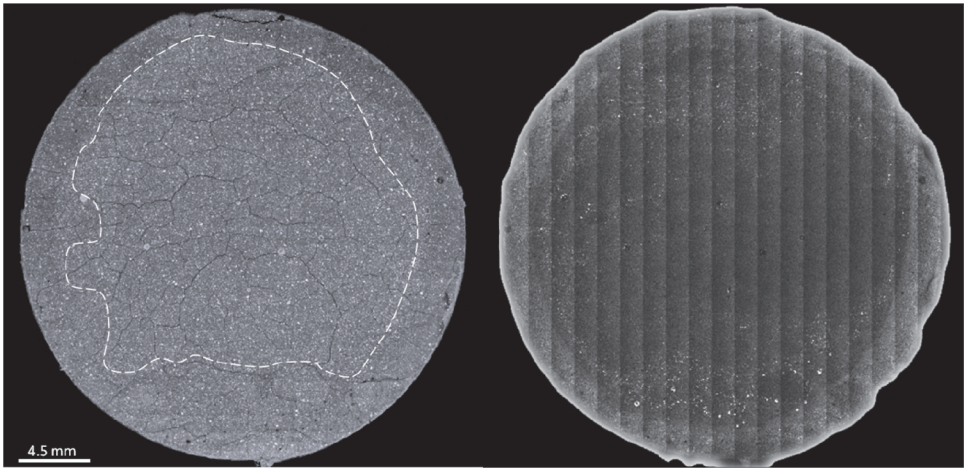


Fig. 3— Montage backscatter (BSE) image (left) and Ca^{2+} EDS map (right) of $\text{CO}_2\text{-O}_2$ exposure sample with diffuse alteration boundary (white outline) extending into the cylinder. Scale 4.5 mm (0.18 in).

sample prep often cut across mineral grains and stem into larger fractures. Etched and pitted features were also observed on the silicates and C_4AF , evidence of acid attack. EMPA data suggests $<2\%$ of the carbonate band contained FeCO_3 , which could not be confirmed via other instrument analyses in such trace amounts.

Total alteration depth versus time of the $\text{CO}_2\text{-O}_2$ 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 CaCO_3 band compared to pure CO_2 exposure. At 28 days of exposure, the alteration depth was minimal, up to $253 \pm 59 \mu\text{m}$ (0.01 in). After 53 days, the alteration zone extended to a depth of $916 \pm 94 \mu\text{m}$ (0.036 in), and the Ca^{2+} depleted zone ranged from $\sim 0.5\text{--}1 \text{ mm}$ (0.02-0.04 in), with large pores up to $160 \mu\text{m}$ (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 $514 \pm 109 \mu\text{m}$ (0.02 in) after 28 days, exceeded $680 \pm 132 \mu\text{m}$ (0.027 in) 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- CO_2 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-CO₂ and CO₂-O₂ exposure (wt%). Unit conversion: 100 µm = 0.003937 in

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
C	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 ₂ O 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 µm 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

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

(mg/L)	Surrogate CO ₂ 50°C				Surrogate CO ₂ -O ₂ 50°C				Surrogate CO ₂ -O ₂ 85°C		
	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	<DL	1.4	5.8	3.3	28	0.7	8.5	0.5 ¹
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

¹concentration at or below detection limit

*no measurement

and C-S-H had become depleted and replaced by CaCO₃, whereby CO₃²⁻ 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 CO₂-O₂ 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 CO₂ tests, and are thus likely indicative of equilibrium concentrations at the experimental parameters utilized. Aqueous Ca²⁺ 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 CO₂-O₂ exposure samples was 7-8 wt % greater than that in the pure-CO₂ samples. However, chemically-bound water content, calculated as the difference between the LOI and other volatiles (CO₂, free moisture, and sulfate) in these same

Table 4— XRD analyses of CO₂ and CO₂-O₂ exposure comparing the semi-quantified concentrations of minerals present due to gas and temperature differences in weight percent.

	Pure CO ₂ 50°C	96% CO ₂ -4% O ₂ 85°C		96% CO ₂ -4% O ₂ 50°C	
	84 days	28 days	53 days	28 days	56 days
Portlandite Ca(OH) ₂	24.2 ± 4.2	10.5 ± 1.8	11.2 ± 2.1	19.5 ± 1.2	12 ± 2.1
Brownmillerite Ca ₂ FeAlO ₅	8.8 ± 1.5	8.3 ± 1.2	8.3 ± 1.8	12.4 ± 1.8	5.3 ± 0.9
Hatruite Calcium Silicate Ca ₃ SiO ₅	17 ± 2.1	6.3 ± 1.2	13.8 ± 3.9	12.1 ± 2.1	10 ± 2.4
Larnite Ca ₂ (SiO ₄)	16.6 ± 4.8	13.4 ± 3.9	13.5 ± 3.9	9.5 ± 0.3	2.7 ± 1.5
Ettringite Ca ₆ (Al(OH) ₆) ₂ (SO ₄) ₃ (H ₂ O) _{25.7}	0	3.9 ± 0.9	7.5 ± 2.1	9.6 ± 2.1	12 ± 2.4
Hydrotalcite Mg ₆ Al ₂ (CO ₃) (OH) ₁₆ *4H ₂ O	Trace	2.3 ± 0.9	2.3 ± 1.2	4.2 ± 1.2	3.5 ± 0.9
Total CaCO ₃ (Calcite, Vaterite, Aragonite)	22.5 ± 3.9	54.6 ± 3.3	54.2 ± 1.9	26.7 ± 1.2	23.2 ± 2
Amorphous	1.9 ± 0.9	0.6 ± 0.3	2.2 ± 4.2	6 ± 0.3	30.7 ± 4.2

Error = reported error x3, Materials Data Inc., Jade

samples was virtually zero, while that in the pure CO₂ samples was 4-7 wt%. This could be interpreted as an indication of the advanced degradation of the cement paste, resulting from the CO₂-O₂ exposure tests, in which all of the hydration water bound in the CH (replaced by CaCO₃), ettringite, and C-S-H was freed due to advanced alteration of those phases. The loss of Fe from ferrite grains was not evident based on the solids analysis, as the Fe₂O₃ concentration in the cement pastes was either relatively constant or increased. The increase in Fe, Ni, and Cr concentrations in solution, specifically in the higher temperature sample, suggests that these cations were derived from corrosion of the stainless steel autoclave, which complicates the interpretation of the cement alteration.

Semi-Quantative XRD

Crystalline phase identification of dominant mineral species and precipitated phases post-CO₂ exposure were completed by XRD on the exterior ~2 mm (0.08 in) rim of the cylinders (Table 4). Phases identified in typical hydrated portland cement analysis included portlandite (CH: Ca(OH)₂), brownmillerite (C₄AF: 2*Ca₂AlFeO₅), alite (C₃S: Ca₃SiO₅), belite (C₂S: β-Ca₂SiO₄), a hydrated calcium silicate polymorph pattern (Ca₃SiO₅-type), and an amorphous background hump, indicative of C-S-H. The influence of CO₂ mixed gas exposures on the cements shows the formation of ettringite, hydrotalcite, and carbonates, including calcite, vaterite, aragonite, and trace dolomite.

Carbonation differences were identified between the different gas-exposure samples. The amount of total carbonate is higher in the CO₂-O₂ cement samples than the pure-CO₂ samples. As expected when CaCO₃ is a dominate precipitant, CH is low, and vice versa. At both temperatures, the concentration of CH in the CO₂-O₂ tests is significantly lower (50% less) than that in the CO₂ tests. Carbonate formed more rapidly in CO₂-O₂ than pure CO₂, with total CaCO₃ nearly double (54.6±3.3 wt%) at elevated temperature, an indication that

temperature has a significant influence on carbonation rates as well as C-S-H degradation. The lower temperature sample reflected an increased amorphous content with less carbonation than the higher temperature sample. The addition of oxygen may increase the solubility and efficiency of mineral dissolution in a ligand-type complex behavior. Although calcite was the dominant carbonate, both vaterite and aragonite appeared to have higher saturation with increasing temperature from 50 to 85°C.

Precipitation of a hydrotalcite-type (HT) phases is known to occur in hydrated cement, and while only trace amounts were found in pure-CO₂ samples, significant amounts were found throughout all the CO₂-O₂ samples after petrographic and SEM examination. The precipitation of HT is believed to result from hydration coupled either a) with Mg salt attack or b) as an alternative to brucite formation. With a constant supply of Mg-rich brine for hydration, the combination of a less permeable CaCO₃ zone and rapid penetration rate of O₂ allowed nucleation of this carbonate only on C₄AF grains, rather than within the C-S-H structure. This released Fe³⁺, which may have contributed to the cylinder's dark brownish-red, rusty color, more so than seen in the pure-CO₂ exposed samples. The source of Fe was assumed to primarily be the stainless steel autoclave, with only small concentrations derived from C-S-H and ferrite clinker. No siderite, goethite or Fe-oxide were identified by XRD within the cement itself. However, spalled solids collected from the bottom of the vessel did contain goethite and Fe-oxides, which corroborates the presumed source of Fe.

The ettringite increase is of interest because Class H cement has little or no C₃A content; therefore, the main source of Al is from the C₄AF. In the pure-CO₂ samples, sulfur was bound in the C-S-H structure and was fairly uniform in unaltered cement paste. The gypsum (~5 wt%) addition to the cement did not differ in either test as the same cement batch was used. Ettringite was absent in pure CO₂ samples, and increased over time in CO₂-O₂ studies at both exposure temperatures. The ettringite precipitation appeared to be dependent on the rate of CO₂ and O₂ migration into the cement, and occurred after hydrotalcite had formed. As with previous studies examining the Fe-replacement in aluminoferrite grains, the addition of O₂ must influence the Fe²⁺ present, resulting in ettringite precipitation. This increase, coupled with the formation of microfractures, suggests that detrimental DEF could be initiated at higher temperature exposure.

pH Estimate and Mineral Saturation

The measurement of pH at experimental conditions is difficult but of great interest because carbonic acid produced in a high-pressure CO₂ system is a primary component in the cement reaction sequence. Geochemical modeling of the influence of CO₂ and the CO₂-O₂ mixture was conducted using *CHIM-XPT* methods outlined by Reed and Spycher²⁴ and Reed²⁵ with multiple iterations to demonstrate kinetically-favored phases used to predict mineral saturation and pH at downhole conditions. At selected temperature and pressure conditions *CHIM-XPT* computed the distribution of thermodynamic components of aqueous species, gases, and minerals, using equilibrium constants derived from the database *SOLTherm*. These equilibrium constants are modifications of mineral thermodynamic data where log *K*'s (saturation index based on dissolution reactions) were computed for cement minerals. The aqueous activity coefficients are determined by using the modified extended Debye-Hückel equation and gas fugacity coefficients.

balance was applied to the brine solution chemistry measured at one atmosphere and 25°C to calculate pH under: 1) base pH at neutral waters after the curing process, with a result of 11.8; 2) under CO₂ conditions yielding a pH of 3.0; and 3) CO₂-O₂ mixture conditions with a predicted pH of 3.95. The pH prediction for the solution enhanced the understanding of the pH gradients diffusing into the cement and identified specific conditions for mineral dissolution and precipitation.

The mineral saturation indices were calculated using the post-reacted brine chemical analysis. In both gas exposure experiments, the post-curing interval pH of 11.8 was reflected experimentally by the presence of the CH crystals on the cement cylinder surface, which produced a pH buffer during CaCO₃ precipitation. The pure CO₂ solutions were under-saturated in minerals, except for quartz, which was not observed. Modeling of the CO₂-O₂ mixture predicted precipitation of quartz and goethite, which was confirmed experimentally by XRD results of spalled material.

Corrosion of Stainless Steel Autoclaves

The experimental apparatus for the subject tests consisted of stainless steel (316 CrNiMo) autoclave vessels and fittings. Although CO₂ can be corrosive when dissolved in water, carbonic acid has no corrosive impact on stainless steel as confirmed in the pure-CO₂ experiments.²⁷ However, the addition of O₂ led to corrosion due to chloride attack (pitting and/or crevice corrosion), particularly at higher temperature, and termination of the tests after ~ 2 months duration (Fig. 4). The mechanism is too complex for detailed discussion here, but the presence of hydrated iron oxides and lack of FeCO₃ in the corrosion products, as identified by XRD, confirms the deleterious role of Cl⁻ and oxygen in the degradation of stainless steel, which can be explained by the autocatalytic mechanism of pit growth.²⁸

The CO₂-O₂ gas exposure tests were repeated using Teflon liners placed in the autoclave bodies to prevent further corrosion of the vessel. However, corrosion of the thermocouple thermowell, which extends down into the brine from the autoclave head, led to termination of the repeated tests after 73 days. Lessons learned from the corrosion experienced during these O₂-bearing gas exposure tests include 1) the use of protective liners and/or coatings (Teflon) on all stainless steel parts exposed to the high chloride brine during O₂-bearing gas exposure intervals, 2) curing of the cement cylinder specimens at pressure under argon as a substitute for hydraulic curing, to eliminate the exposure of all fittings in the head to the high chloride brine, and 3) minimization of local static environments created by improper alignment of parts and specimens in the autoclave, which can exacerbate corrosion issues. The corrosion experience and analysis garnered from these tests, while not part of the original test plan, provided valuable insight into the impact of O₂ addition to the gas injection stream. These results suggest that co-sequestration of O₂ may present a significant challenge to the integrity of both the well cement and well casing when injecting the gas mixture into high salinity and higher temperature saline formations.

FURTHER RESEARCH

The effects of co-sequestration using a mixture of ~4% O₂, 1.5% SO₂, and balance CO₂, will also be investigated and compared with the subject tests. The results of these experiments are intended to contribute to the evaluation of co-sequestration as a valid sequestration methodology. Flue gases containing SO_x or sour hydrocarbon gas (H₂S) could

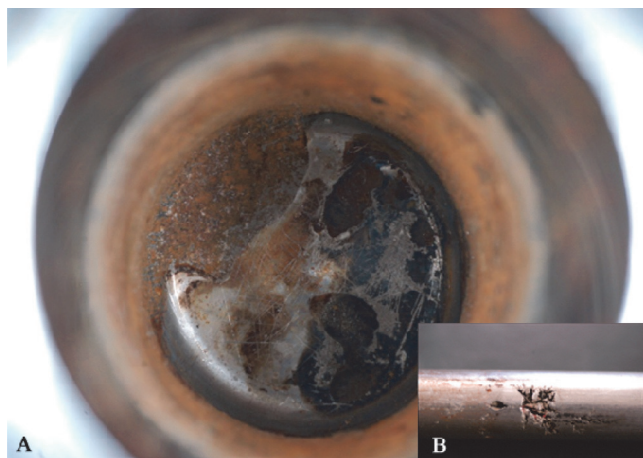


Fig. 4— A) Chloride attack on stainless steel autoclave and B) thermocouple thermowell corrosion result of CO₂-O₂ exposure tests.

potentially produce pyrite or other sulfur-bearing species in the cement via mineralization trapping. Additional research on the potential for DEF under these conditions is necessary, as ettringite is a possible precipitate in sulfur gas exposure studies.

CONCLUSIONS

The addition of 4% O₂ to the CO₂ gas injection stream during Class H portland cement exposure tests resulted in rapid formation of CaCO₃, enhanced cation diffusion, and mineralogical differences in the cement, compared to pure CO₂ exposure tests. In addition, secondary ettringite formation (possibly DEF), dicalcium silicate (C₂S) polymorphs, and hydrotalcite-like phase were observed in the CO₂-O₂ exposed cements. Modeling of this system suggests that the observed mineralogical changes were made possible by pH changes from the brine into the cement during exposure and extended hydration periods. The formation of delayed ettringite could potentially result in expansion and fracture formation; however, it is difficult to quantify any direct damage after the duration of subject tests. These observations suggest that the integrity of the wellbore is a concern with O₂ addition to the injected gas stream. Higher salinity and temperature affected the structure of C-S-H and hydration of the cement, which led to higher degradation rate and advanced degradation. Poor cement consolidation, poor bonding to the wellbore casing, or fracture development could lead to corrosion of the casing and degradation of the cement which could provide a leakage pathway along the well bore for the injected gas (CO₂). The potential for corrosion of the steel casing in formations with high chloride brine concentrations was demonstrated, as corrosion of the experimental stainless steel autoclaves was observed in the subject tests.

ACKNOWLEDGMENTS

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Self-Compacting High-Performance Concretes

by Mario Collepardi, Roberto Troli, and
Stefano Maringoni

Synopsis: Self-compacting high-performance concretes have been manufactured by mixing natural aggregates, portland cement and ground limestone filler in the presence of a poly-carboxylate superplasticizer.

In some concrete mixtures a shrinkage-reducing admixture (SRA) was used to decrease the drying shrinkage by 30% with respect to the control mix without SRA when the specimens were kept at room temperature with a relative humidity (RH) permanently kept as low as 55%.

A special SCC was manufactured combining a CaO-based expansive agent with SRA and the restrained expansion was measured in the absence of any wet curing in very dry environment (RH = 50%). After 2-3 months the restrained expansion was lost but no crack was recorded although the RH was very low.

Similar results were obtained by using a combination of PVA macrofibres with SRA: no reduction in drying shrinkage was recorded in the PVA-SRA concrete with respect to the SRA concrete. However, in the presence of PVA both the number and the thickness of the cracks were significantly reduced. The combined uses of SRA with the expansive agent or the macrofibres make more reliable concretes from the durability point of view because of the absence of cracks.

Keywords: Crack-freedom. Drying shrinkage. Expansive agent. Self-compacting concrete. Shrinkage-reducing admixture. Superplasticizer.

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INTRODUCTION

Self compacting concretes were manufactured with special requirements in terms of high compressive strength, low water/cementitious material ratio and low drying shrinkage, even in dry environments.

MATERIALS AND EXPERIMENTAL

A combination of about 400 kg/m^3 (676 lb/yd^3) of portland cement – type CEM I 52.5 R according to the European norm EN 197¹- and about 95 kg/m^3 (160 lb/yd^3) of ground limestone filler with a Blaine fineness of $450 \text{ m}^2/\text{kg}$ (245.5 lb/yd^2) were used to manufacture cohesive self-compacting concretes (SCCs) with a slump-flow of at least 700 mm (27 in) without bleeding and segregation.

A shrinkage-reducing admixture (SRA) was used at a dosage of 1% by cement weight to keep as low as possible the drying shrinkage.

In one of these SCCs, 30 kg/m^3 (50 lb/yd^3) of the filler was replaced by a CaO-based expansive agent to manufacture a shrinkage-compensating concrete.²

In one of the SCCs, 15-mm (0.6-in) long and 0.5-mm (0.02-in) thick synthetic macrofibres PVA (poly-vinyl-alcohol) were used in order to study whether or not they can reduce the number and/or the thickness of cracks, if any.

A poly-carboxylate superplasticizer (PCS) at a dosage of 12 kg/m^3 (20 lb/yd^3) was used to keep the water-cementitious material ratio (w/cm) as low as 0.42 in all the concrete mixtures.

Table 1 shows the composition of the *control mix* (SCC without SRA, CaO, and fibers) and that of the other three SCCs containing SRA with or without the CaO-based expansive agent or the PVA fibers which will be respectively called: *SRA mix*; *SRA/CaO mix*; *SRA/PVA mix*.

The following measurements were carried out to characterize the SCCs:

- slump flow, bleeding and specific weight of fresh mixes after 5 min of mixing;
- compressive strength (1-180 days) at room temperature (20°C) and RH of 95% ;

Table 1—Composition of the SCC mixtures with a w/ cm of 0.42 and a slump-flow of 720 mm (28.1 in)

SCC Type	CEM I 52.5 R kg/m ³ (lb/ yd ³)	Filler kg/ m ³ (lb/ yd ³)	Expansive Agent kg/ m ³ (lb/ yd ³)	Aggregate* kg/m ³ (lb/ yd ³)	Water kg/m ³ (lb/yd ³)	PCS kg/m ³ (lb/yd ³)	SRA kg/ m ³ (lb/ yd ³)	PVA Fibers kg/m ³ (lb/yd ³)
Control Mix	396 (669.24)	94 (158.56)	—	1740 (2940.6)	166 (208.54)	12 (20.28)	—	—
SRA Mix	398 (672.62)	95 (160.55)	—	1741 (2942.29)	167 (282.23)	12 (20.28)	4 (6.76)	—
SRA/CaO Mix	398 (672.62)	65 (109.85)	30 (50.7)	1741 (2942.29)	167 (282.23)	12 (20.28)	4 (6.76)	—
SRA/PVA Mix	396 (669.24)	94 (158.56)	—	1740 (2940.6)	166 (208.54)	12 (20.28)	4 (6.76)	4 (6.76)

*Sand 0–4 mm (0–0.16 in) = 60%; gravel 4–16 mm (0.16–0.62 in) = 40%

- free shrinkage according the Italian norm UNI 11307³ of the unreinforced specimens demolded at 1 day and then kept at a RH of 55%;
- restrained expansion of reinforced specimens demoulded at 6 hours, protected by a plastic coating for 2 days and then exposed to air with a RH of 55%, according to the Italian norm UNI 8148- B method.⁴
- modulus of elasticity at longer ages (180 days);
- visual measurements at 180 days of cracks and their size opening by using a hand-held equipment with magnifying lens in field tests to monitor 8 m-long, 400 mm-wide and 60 mm-thick (8.75-yd long, 16-in wide and 2.3-in thick) concrete slabs exposed to open air and restrained to the end in order to induce tensile stresses caused by drying shrinkage (Fig. 1); one slab per concrete mixture was used to determine cracks and their size opening.

RESULTS

Figure 2 shows the compressive strength as a function of the curing time. Because of the presence of SRA there is a strength reduction in all the SCCs with respect to the control mix. The effect is smaller in the *SRA/CaO Mix* -where the strength loss is about 5-10%-than in the *SRA Mix* or in the *SRA/PVA Mix*. These results agree with those of the modulus of elasticity at 180 days: 45 GPa for the *Control Mix*, 44 GPa for the *SRA/CaO Mix* and 43 GPa for the other two mixtures containing SRA.

Figure 3 shows the free length change of the unreinforced concrete specimens (except those containing the expansive agent) caused by drying shrinkage. There is a significantly lower drying shrinkage (about 25-30%) in all the SCCs containing SRA with respect the *Control Mix*. The addition of PVA to the *SRA Mix* does not reduce the drying shrinkage.

Figure 4 shows the length change of the restrained reinforced specimens of the *SRA/CaO Mix*. There is an expansion during the first 5 days, when the specimen was protected from drying by an envelopment made by a thin plastic coating, and then there is a slow decrease up to 6 months of permanent exposure to a dry environment with a RH of 55%.

Table 2 shows the number of the cracks and the crack-width determined on the restrained concrete slabs exposed to open air: no cracking occurred in the *SRA/CaO Mix* as well as in



Fig.1 – Field tests on restrained drying shrinkage of concrete slabs 8 m long, 400 mm wide and 60 mm thick (8.75-yd long, 16-in wide and 2.3-in thick).

the *SRA/PVA Mix* although in the latter mixture the drying shrinkage was the same as that of the *SRA Mix* (Fig. 2). This behavior indicates the influence of the PVA macrofibers in removing the crack appearance provided that the drying shrinkage is lower than the *Control Mix* because of the presence of the SRA (Fig. 3).

CONCLUSIONS

Some special self-compacting high-performance concretes were studied. The combined use of a shrinkage-reducing admixture (SRA) with PVA macrofibers or a CaO-based expansive agent in superplasticized SCCs produced crack-free concrete slabs even in the

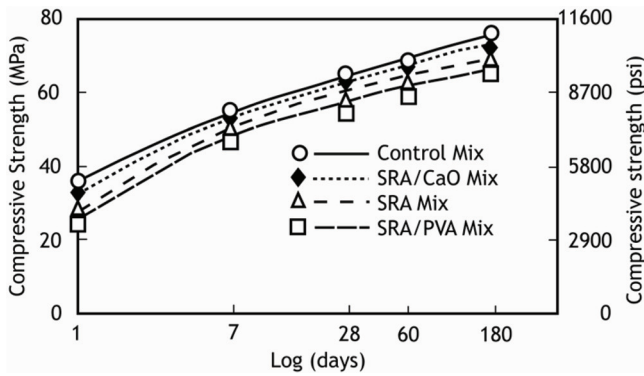


Fig. 2 – Compressive strength at different ages for the SCCs.

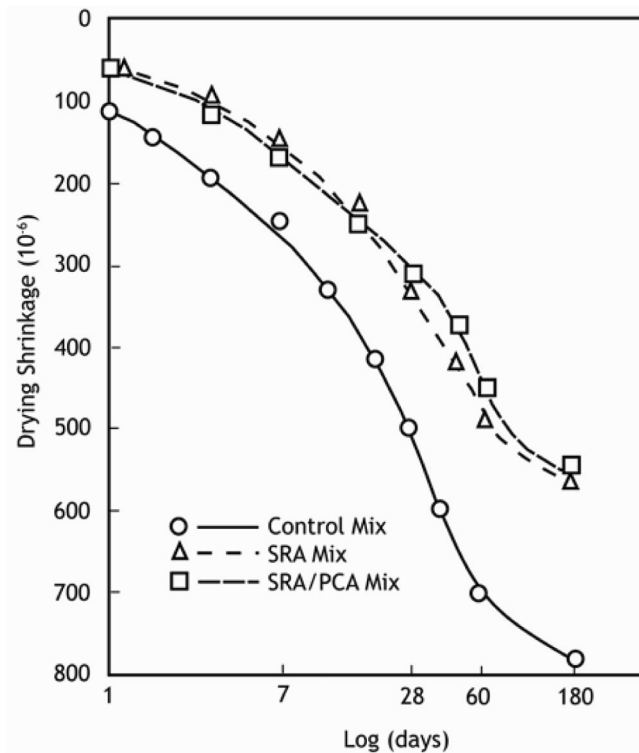


Fig. 3 – Drying shrinkage at different ages of the concretes after demoulded at 1 day.

absence of wet curing. Consequently, more durable and reliable structures without cracks can be made by using this technique in self-compacting concretes.

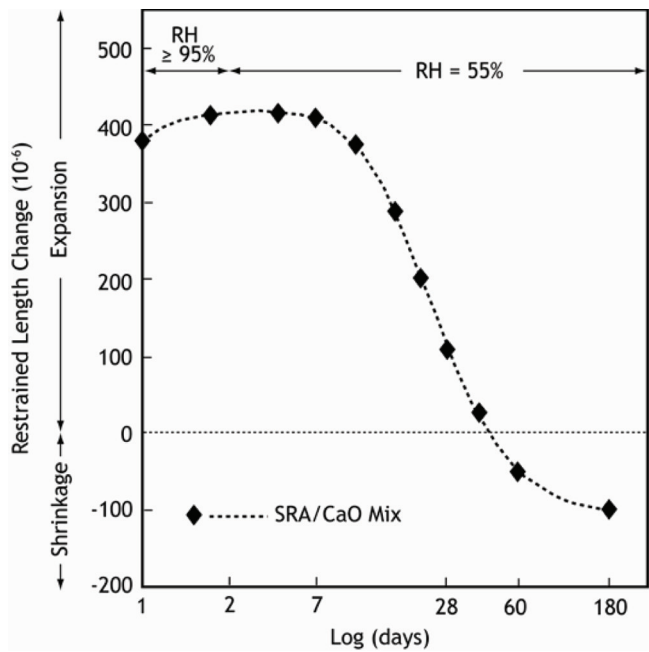


Fig. 4 – Restrained length change in the SRA/CaO Mix at different ages of the concrete demolded at 6 hours.

Table 2– Number of visible cracks and their width

SCC Type	Number of cracks	Width
Control Mix	5	1.1 mm (0.04 in)
SRA Mix	2	0.3 mm (0.01 in)
SRA/CaO Mix	0	—
SRA/PVA mix	0	—

Therefore these SCCs are more reliable and less dependent on the quality of the workmanship on the job site for both placing and curing with respect to the ordinary concrete mixtures.

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Dynamic Performance of Eco-Friendly Prestressed Concrete Sleeper

by Tae-Hoon Koh, Young-Hoon Bae, Seon-Keun Hwang, and Myung Sagong

Synopsis: In Korea, high-early-strength Portland cement has been used for railway PC (Prestressed Concrete) sleeper to provide high strength and rapid hardening satisfactorily at early period. However, it is fact that carbon dioxide (CO₂) emission from the cement production has been recently one of the main social issues. In this study, eco-friendly PC sleeper, which was developed in order to reduce the usage of cement and natural resources (fine aggregate) as main ingredients of concrete, was tested using UTM (Universal Testing Machine) test facility in order to estimate its dynamic performance optionally required by the European Standard. Based on a series of dynamic performance tests, it was found that eco-friendly PC sleeper can be an environmental as well as mechanical alternative to the ordinary PC sleeper.

Keywords: CO₂ emissions, Dynamic performance, Electric arc furnace oxidizing slag, Ground granulated blast furnace slag, Prestressed concrete sleeper

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INTRODUCTION

Cement and natural aggregates are main concrete ingredients. On the other hand, carbon dioxide (CO₂) emissions from the cement production have been recently one of the main social issues. Recently the important social impacts of recycled materials as concrete ingredients are widely recognized. From this point of view, in this study, eco-friendly PC sleeper, which was developed in order to reduce the usage of cement and natural resources (fine aggregate) as main ingredients of the concrete, was tested using UTM (Universal Testing Machine) test facility in order to estimate its dynamic performance optionally required by the European Standard.¹ Based on a series of laboratory tests, it was found that eco-friendly PC sleeper can be an environmental as well as mechanical alternative to traditional PC sleeper.

RESEARCH SIGNIFICANCE

The PC sleeper is one of the railway infrastructures directly subject to dynamic wheel loading. Its required tests prior to the field application include the static test at rail seat and center sections, vertical load test for cast-in fastening components and electrical resistance test.² In this study, even though previous studies on dynamic performance of previous studies on dynamic performance of PC sleeper are very limited due to the large time-consumption and high cost, authors performed the dynamic and fatigue tests for the recently developed eco-friendly PC sleeper, even optional performance test, in accordance with European Standard for its commercialization.

Table 1 – Requirements for mixing design of PC sleeper³

Items	Unit	Requirements
$G_{\max}^a$	mm (in.)	19 (0.75)
Air	%	3.5 ± 1.5
Slump	mm (in.)	80 ± 20 (3.15 ± 0.98)
Amount of cement (High-early-strength Portland cement)	Kg/m ³ (lb/ft ³)	Max. 440 (27.5)
W/C	%	Less than 35
Initial compressive strength ^b	MPa (ksi)	Above 35 (above 5.08)
28-day compressive strength	MPa (ksi)	Above 50 (above 7.25)

^a Maximum size of coarse aggregate

^b Concrete compressive strength at transfer of prestress force

Table 2 – Chemical compositions and physical properties of binders

Binders	CaO (%)	SiO ₂ (%)	Al ₂ O ₃ (%)	MgO (%)	SO ₃ (%)	Fe ₂ O ₃ (%)	Ig. loss (%)	Density g/cm ³ (lb/ft ³)
High-early-strength Portland cement	62.1	19.7	5.9	3.53	3.25	3.0	1.0	3.14 (196.0)
GGBFS	41.9	34.1	14.8	3.7	1.8	0.98	0.7	2.88 (179.8)

Table 3 – Chemical compositions and EAF oxidizing slag fine aggregate

Fe ₂ O ₃ (%)	CaO (%)	SiO ₂ (%)	Al ₂ O ₃ (%)	MgO (%)
31.8	27.7	15.3	7.39	6.61

MATERIAL PROPERTIES AND MIX DESIGN

PC sleeper developed in this study is for ballasted track on the conventional line, which was manufactured by pretensioning method. Requirements for its concrete mixing design in accordance with Korean Railway Standard³ are listed in Table 1.

Materials

GGBFS, an admixture for use in concrete,⁴ was used as another binder for eco-friendly PC sleeper in addition to high-early-strength Portland cement. It has been reported that concrete manufactured with Portland cement and GGBFS shows the improved performances: long-term strength and freeze-thaw resistance etc.⁵ Table 2 shows chemical compositions and physical properties of binders used for PC sleepers in this study.

While EAF oxidizing slag, a byproduct of steel making recovered after the oxidizing process, is an acceptable fine aggregate for concrete,⁶ its application has been very limited in the construction industry. Table 3 presents chemical compositions of EAF oxidizing slag used as a fine aggregate for eco-friendly PC sleeper, and Table 4 shows physical properties of aggregates used for PC sleepers in this study.

Table 4 – Physical properties of aggregates

Aggregates	Absorption (%)	Density, g/cm ³ (lb/ft ³)
Natural fine aggregate	1.4	2.60 (162.3)
EAF oxidizing slag fine aggregate	1.81	3.40 (212.2)
Coarse aggregate	0.8	2.67 (166.7)

Table 5 – Properties of AE water reducer

Main composition	Specific gravity	Type	Color
Polycarbonic acid	1.05	Liquid	Dark brown

Table 6 – Compressive strength of specimens mixed for PC sleepers

Duration of curing	Compressive strength, MPa (ksi)		Acceptance criteria MPa (ksi)
	Ordinary PC sleeper	Eco-friendly PC sleeper	
Initial (13hr) curing	36.7 (5.32)	44.7 – 51.2 (6.48 – 7.42)	Above 35 (above 5.08)
28-day curing	58.5 (8.48)	63.7 – 72.8 (9.24 – 10.56)	Above 50 (above 7.25)

The polycarbonic acid-based water reducer shown in Table 5 was added as an admixture for PC sleepers in this study.

Mix Design and Prototype Manufacture

A series of laboratory trial mix approach was carried out in order to determine appropriate mix proportions for eco-friendly PC sleeper, which satisfied requirements of mixing design of PC sleeper. Based on the mixing design results, reduction of cement usage for eco-friendly PC sleeper induce the reduction of carbon dioxide emissions of about 10 kg when compared to the ordinary PC sleeper. As shown in Table 6, specimen mixed for eco-friendly has higher compressive strength than one for ordinary PC sleeper as well as its required strength at initial curing and 28-day curing conditions, respectively.

Several prototypes of eco-friendly PC sleeper as well as ordinary ones were manufactured in order to estimate optional performances of PC sleeper. Figure 1 shows the prototype of eco-friendly PC sleeper with the same profile of the ordinary one.

An alternative to natural fine aggregate used for eco-friendly PC sleeper, EAF oxidizing slag leads to the weight gain of about 10% comparing with ordinary PC sleeper because of its heavier density than natural fine aggregate, that can contribute the track safety.⁷

TEST METHODS FOR ESTIMATION OF DYNAMIC PERFORMANCE

The optional performance tests are in accordance with European Standard which are defined as dynamic test and fatigue test in this study. Test arrangement and procedure for each test are shown Figure 2 and Figure 3, respectively. Tests were performed using UTM (Universal Testing Machine) test facility (Figure 4).



Figure 1 – Prototype of eco-friendly PC sleeper (Modified after ²)

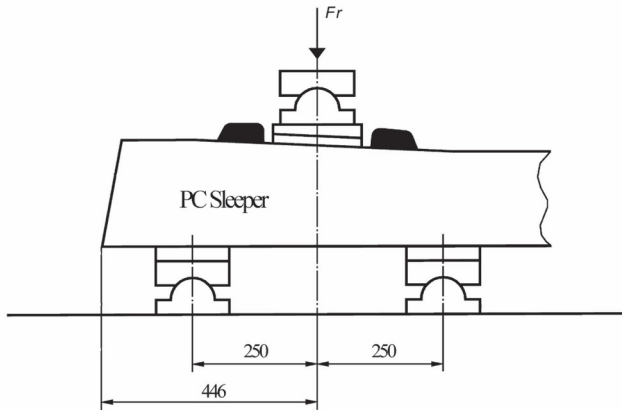


Figure 2 – Test arrangement at the rail seat section for the dynamic and fatigue test (dimensions in mm, 1 mm = 0.0394 in.) (Modified after ¹)

The dynamic test at rail seat section of PC sleepers (12 eco-friendly PC sleeper specimens and 3 ordinary PC sleeper specimens) was performed in accordance with EN 13230-2. Positive initial reference test load ($Fr_0 = 154 \text{ kN}$ (34.6 kips)) was calculated according to EN 13230-1⁸ and UIC 713 R.⁹ In each load step, 5,000 load cycles and 5Hz frequency were applied to the PC sleeper specimens. Loads ($Fr_{0.05}$ and $Fr_{0.50}$) were checked at crack width of 0.05 mm (0.002 in.) and 0.50 mm (0.02 in.) developed while the cyclic load was applied to the rail seat section.

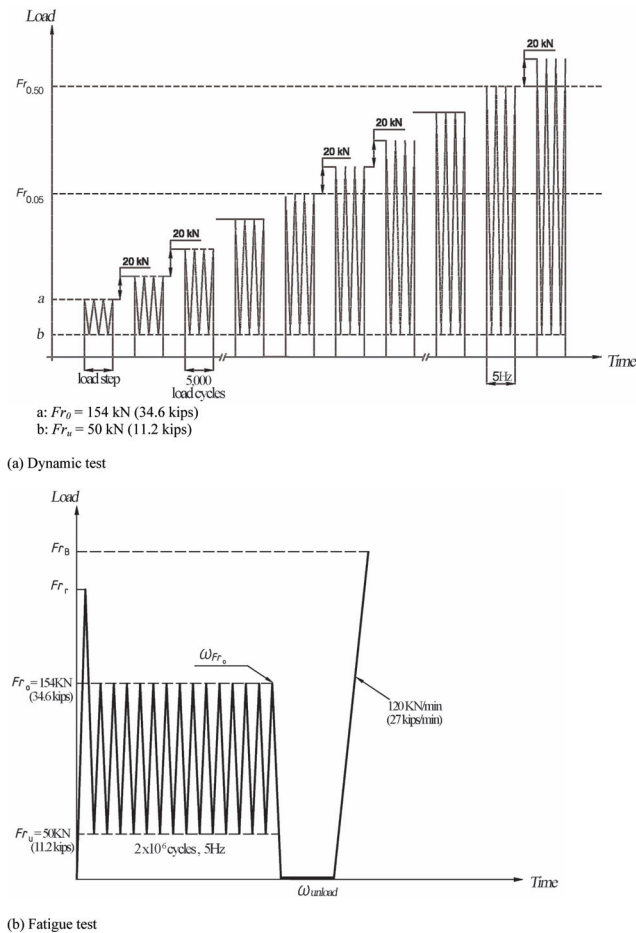


Figure 3 – Test procedures at the rail seat section (Modified after ¹)

The fatigue test at rail seat section of the PC sleepers (2 eco-friendly PC sleeper specimens and 1 ordinary PC sleeper specimen) was performed in accordance with EN 13230-2. Loading of first cycle in the fatigue test was continued to first crack formation to determine Fr_r , and then dynamic loading from a minimum load of 50 kN (11.2 kips) to a maximum load of 154 kN (34.6 kips) was applied at a frequency of 5 Hz. Crack width was monitored when loaded at Fr_0 after 2×10^6 cycles and when unloaded condition. Finally, maximum positive test load was checked at fracture.

TEST RESULTS

The dynamic and fatigue performances of the PC sleepers satisfied the acceptance criteria of EN 13230-2 as shown in Table 7. In other words, dynamic loads developed at crack width of 0.05 mm (0.002 in.) and 0.50 mm (0.02 in.) were higher than the standard loads

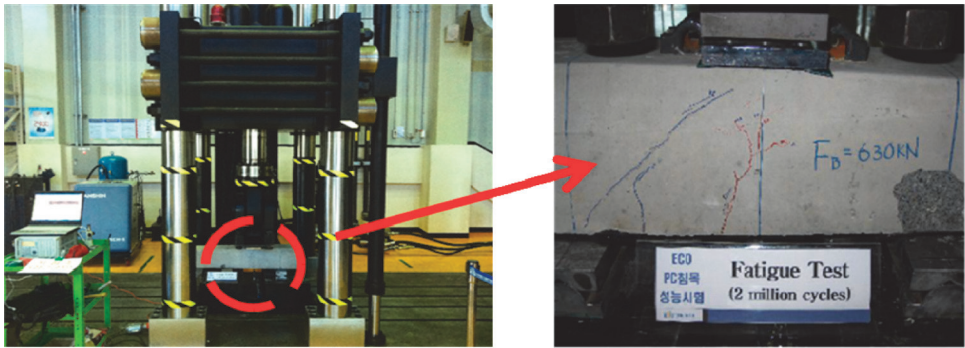


Figure 4 – UTM test facility

Table 7 – Test results

Test items		Ordinary PC sleeper	Eco-friendly PC sleeper	Acceptance criteria
Dynamic Test	$Fr_{0.05}^a$, kN (kips)	277.3 (62.3)	397.3 – 412.3 (89.3 – 92.7)	Above 231 ^f (above 51.9)
	$Fr_{0.50}^b$, kN (kips)	370.0 (83.2)	480.7 – 522.3 (108.1 – 117.4)	Above 339 ^g (above 76.2)
Fatigue Test	$w_{Fr_0}^c$, mm (in.)	Less than 0.01 (0.0004)	Less than 0.01 (0.0004)	Below 0.10 (below 0.004)
	w_{unload}^d , mm (in.)	Less than 0.01 (0.0004)	Less than 0.01 (0.0004)	Below 0.05 (below 0.002)
	Fr_B^e , kN (kips)	480.0 (107.9)	630.0 – 700.0 (141.6 – 157.4)	Above 385 ^h (above 86.6)

^a Maximum test load for which a crack width of 0.05 mm (0.002 in.) at the bottom of the rail section persists after removal of the load

^b Maximum test load for which a crack width of 0.50 mm (0.020 in.) at the bottom of the rail section persists after removal of the load

^c Crack width at Fr_0 after fatigue test

^d Crack width at unloaded condition after fatigue test

^e Maximum positive test load at the rail seat section which cannot be increased

^f $k_{1d}Fr_0 = 1.5154 = 231$ kN

^g $k_{2d}Fr_0 = 2.2154 = 339$ kN

^h $k_3Fr_0 = 2.5154 = 385$ kN

specified from EN 13230-2. Little cracks less than 0.1 mm (0.004 in.) and 0.05 mm (0.002 in.) were monitored at Fr_0 after cyclic test and unloaded condition after fatigue test, and fracture load was higher than the standard load specified from EN 13230-2. Besides, the developed eco-friendly PC sleeper has superior performances to the ordinary PC sleeper.

SUMMARY AND CONCLUSIONS

In order to manufacture the eco-friendly PC sleeper, high-early-strength Portland cement was partially replaced by GGBFS, and EAF oxidizing slag was used as an alternative to fine aggregate. In mixing design, mix proportions for the eco-friendly PC sleeper were determined in accordance with the mixing design criteria for PC sleeper. From the dynamic

and fatigue tests defined by the European Standard (EN 13230-2), it was found that eco-friendly PC sleeper has superior performances to the ordinary PC sleeper.

Based on the research findings, it can be concluded that GGBFS and EAF oxidizing slag are suitable alternative concrete ingredients to cement and natural resources for concrete infrastructure applications. Moreover, the eco-friendly PC sleeper is able to contribute the reduction of CO₂ emissions as well as preservation of natural resources and recycling of byproducts in railway concrete infrastructure.

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Parameters Influencing the Performance of Shrinkage-Compensating Concrete

by Cataldo Matteo Corcella, Cristiano Cereda,
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Daniela Gastaldi

Synopsis: The performance of shrinkage-compensating concrete, in terms of reducing the risk of cracking, mainly depends on correct synchronisation between two different processes inside the concrete: the evolution of its early age mechanical strength which is controlled by cement hydration, and the expansion rate which is controlled by expansive agent hydration. Recently, the use of shrinkage reducing admixtures (SRA) has been recommended for the production of shrinkage-compensating concrete. Thanks to the synergy achieved by combining SRA and expansive agents there is an improvement in the performance of this kind of concrete even in the absence of prolonged wet curing. Some studies state that this positive combination is caused by retardation in the hydration rate of the expansive agent, which is able to induce a more efficient reinforcement tension. In this paper, the influence of the type of superplasticizer, SRA and temperature (10°-20°-30°C) on the hydration processes of the cement and the expansive agent have been tested in concrete and analysed with thermogravimetric analysis in cement paste. Compressive strength, workability loss, setting time and restrained expansion tests were carried out on concrete mixes. The results indicate that the type of superplasticizer used and/or the temperature have different effects on the hydration rate of the cement and the expansive agent. Some indications about the correct way to design a shrinkage-compensating concrete in different curing conditions are presented.

Keywords: Expansive agent, Shrinkage compensating concrete, SRA, Superplasticizer

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INTRODUCTION

Cracking is one of the main problems of reinforced concrete as it not only influences the aesthetic value, but it can also cause durability issues in the structures. Shrinkage-compensating concrete was created as a solution to eliminate or reduce cracking induced by medium to long term restrained drying shrinkage. The main aim of shrinkage-compensating concrete,¹ is to reduce delayed tensile stress produced by restrained drying shrinkage. This is generally obtained by chemically pre-compressing the concrete by using a powder expansive agent. If this component is introduced in adequately steel reinforced concrete, it is able to produce an initial expansion in the hardened concrete that generates a tensile stress in the steel reinforcement and a compressive stress in the concrete. The expansive agents most commonly used for this type of concrete are calcium oxide (CaO) or alternatively a mixture of calcium and magnesium oxides (CaO, MgO). It is very important to point out that the initial expansion, and therefore the efficiency of shrinkage compensation,

Table 1 – Chemical and mineralogical composition of cement as determined by XRD and XRF analysis

Phase	wt. %	Oxide content	wt. %
C ₃ S	64,8	CaO	63,4
C ₂ S	8,9	SiO ₂	19,0
C ₄ AF	10,8	Al ₂ O ₃	4,7
C ₃ A cubic	0,9	SO ₃	2,6
C ₃ A Na orthorhombic	5,2	Fe ₂ O ₃	3,3
Calcite	3,1	MgO	2,1
Portlandite	1,7	K ₂ O	1,0
Quartz	0,2	Na ₂ O	0,4
Gypsum	0,6	S ⁻	0,1
Hemihydrate	2,9	Cl ⁻	0,04
Dolomite	0,9	loss on ignition	2,6

closely depends on the correct synergy of two different processes inside the concrete²: (a) the evolution of the bonds between the cement paste and the steel reinforcement (resulting from the initial cement hydration); (b) the rate of concrete expansion (controlled by the degree of hydration of the expansive agent). It is clear that if the hydration of the expansive agent is too fast with respect to that of the cement, the tensile stress obtained in the steel reinforcement is reduced. This is due to the fact that the majority of the concrete expansion will occur while the system is in the plastic state. Recently some authors³ have reported that in this case a possible solution consists in using a combination of (CaO, MgO) based expansive agent and a suitable shrinkage reducer admixtures (SRA), which probably delays the expansive agent hydration. The aim of this paper is to verify this hypothesis and clarify the part which other parameters play, for example temperature and the type of superplasticizer.

RESEARCH SIGNIFICANCE

The aim of this work was the study of the real concrete systems. In particular the concrete tests were carried out at different temperatures and using different types of superplasticizers. The samples for the detection of the expansion were prepared one hour after the initial mixing of the concrete in order to simulate a long transportation time, as typically happens in industrial application. Most of literature reports data from tests performed on simplified system such as mortars or cement pastes under standard conditions (T= 20°C).

EXPERIMENTAL INVESTIGATION

Materials

A normal portland cement CEM I 42.5 R (according to EN 197-1) was used as the main binder, the composition of which is reported in Table 1. The natural aggregate is made up of one fine sand and two gravels, distributed according to a Bolomey reference curve. The

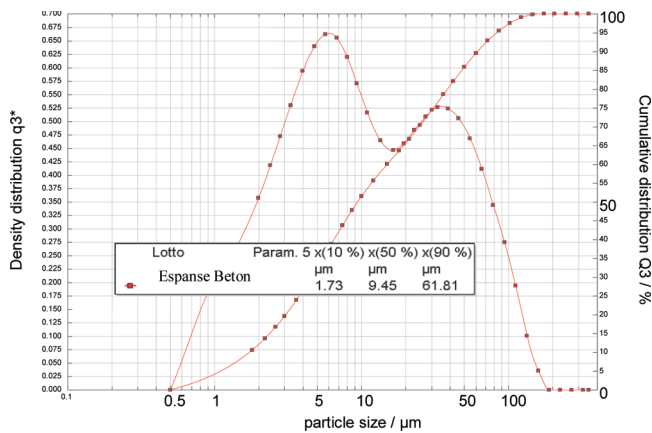


Fig. 1 – Particle size distribution of expansive agent

expansive agent (EA) used is sintered calcium oxide characterized by an average diameter of 10 microns (0.0004 in.). To make up for the lack of fines in the sand and to compensate for the presence of fines introduced as expansive agent, a limestone filler characterized by a particle size 100% less than 0.1 mm (0.004 in.) and a density of 2.7 kg/l (168.5 lb/ft³) was used. The particle-size distributions of the expansive agent and the limestone filler are shown in Figs. 1 and 2. The shrinkage reducing admixture (SRA) is a liquid admixture made up of synthetic glycols which reduces the surface tension of the water in the capillary pores of cement systems, increasing their stability. Three different types of polycarboxylate ether high-range water reducing admixtures (HRWRA) were used, characterized by different behaviors in terms of the concrete workability retention and accelerating effect:

- **SP1:** high performance superplasticizer admixture characterized by a retarding side effect related to the setting times;
- **SP2:** high performance superplasticizer admixture characterized a neutral behavior related to the setting times;
- **SP3:** high performance superplasticizer characterized by an accelerating side effect related to the setting times.

Systems

Table 2 shows the concrete mixture proportions investigated.

The dosage of the different HRWRAs was fixed to obtain similar initial consistency at the same w/c. In order to evaluate the influence of temperature, concrete tests were carried out at 10°C, 20°C and 30°C, as reported in Table 3. The tests at 10°C with SP1 and 30°C with SP3, were not carried out due to practical difficulties in executing the tests (excessive retardation and excessive stiffening behavior respectively).

Methods and procedures

A common drum-type concrete mixer (capacity 30 litre) (1.1 ft³) was used for concrete preparation. For systems A.3 with SP1 and SP2, extra tests were carried out at 50 °C while

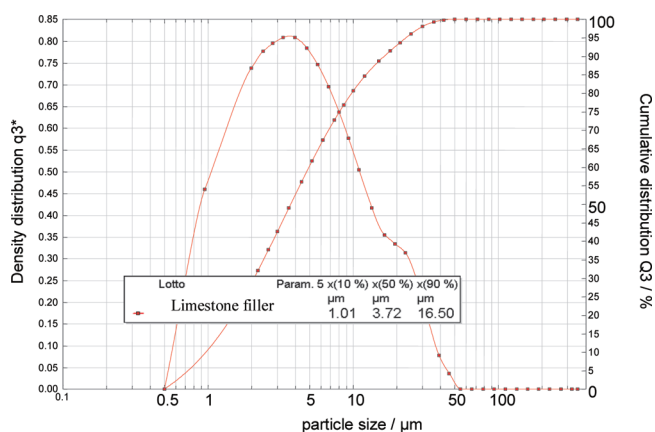


Fig. 2 – Particle size distribution of limestone filler

Table 2 – Concrete mixture proportions

Components	A.1	A.2	A.3
Cem I 42,5 R, kg/m ³ (lb/ft ³)	310 (19.3)	310 (19.3)	310 (19.3)
Filler CaCO ₃ , kg/m ³ (lb/ft ³)	155 (9.7)	125 (9.7)	125 (9.7)
Espansive agent, kg/m ³ (lb/ft ³)	-	30 (1.9)	30 (1.9)
SRA, kg/m ³ (lb/ft ³)	-	-	5.5 (0.34)
HRWRA, kg/m ³ (lb/ft ³)	**	**	**
w/c	0.51	0.51	0.51
Aggregate, kg/m ³ (lb/ft ³)	1815 (113.4)	1815 (113.4)	1815 (113.4)

**Dosages of HRWRA, kg/m³ (lb/ft³): SP1 3.0 (0.19), SP2 2.0 (0.125), SP3 2.0 (0.125)

Table 3 – Systems

Concrete	10°	20°	30°
SP1	-	X	X
SP2	X	X	X
SP3	X	X	-

"-" = not carried out caused by an excessive retardation effect (SP1 at 10°C) or excessive stiffening behavior (SP3 at 30°C)

the expansive agent was added after 60 min at the end of the workability retention test and before casting the samples. The flow table test (UNI EN 12350-5) was carried out at 0, 30, 45 and 60 min, in order to determine the workability retention, then the following steps were carried out:

- measurement of the bulk density and air content according to UNI EN 12350-6 and UNI EN 12350-7;

- preparation of 80x80x240 mm (3,15x3,15x9,45 in) samples for measuring the restrained expansion up to 60 days, according with UNI 8148 method B.
- determination of setting times according to the UNI 7123.
- preparation of 100x100x100 mm (3.9x3.9x3.9 in) samples for determining the compressive strength at 1, 2, 7 and 28 days, using metal moulds according to the UNI EN 12390-3. The concrete samples prepared at 10°C and 30°C were cured at 10°C and 30°C respectively after removal from the mould.

The hydration kinetics of the expansive agent was determined using thermogravimetry analysis (TG) with a TGA/DSC 1/1600 Mettler Toledo on cement paste prepared with $w/c=0.4$ and cured at 10°C, 20°C and 30°C for 24h. The sample was measured with TG analysis and the percentage of calcium hydroxide content was determined after 24 hours using alumina crucibles in an air flow (80 ml/min (4,8 in³/min)). A second series of tests were carried out using limestone filler instead of cement with a $w/f=0.4$ in order to differentiate the contribution of Ca(OH)_2 formed respectively from cement and from CaO hydration. The estimated content of Ca(OH)_2 in the sample was worked out by evaluating the percentage weight loss after total calcium hydroxide dehydration, which takes place between 400 and 450°C.

The tests were carried out on cement paste mixtures composed of 90% cement and 10% CaO. For each of the 3 HRWRA tests at 10°C, 20°C and 30°C with and without SRA were carried out.

In the case of SP1 at 20°C two extra tests using limestone filler instead of cement, with and without SRA were carried out.

EXPERIMENTAL RESULTS

Workability

In Figs. 3, 4 and 5 the workability retentions for all concrete mixtures at 10°, 20° C and 30°C are shown.

The addition of the expansive agent negatively influences both the initial fluidity and the workability retention at all temperatures, in particular with SP3 at 20°C and SP2 at 30°C. On the other hand, the addition of the SRA shows no significant influence on the rheology of the concrete.

Setting times

The data presented in Table 4 indicates that:

- the setting times of the concrete mixtures without expansive agent and SRA are consistent with the expected performances of HRWRAs at all temperatures ;
- the use of the expansive agent accelerates the concrete setting times at all temperatures, especially when a retarding HRWRA (SP1) is used.
- SRA induces a general slowing down of hydration kinetics, which causes a longer setting time, in particular for the system containing the SP2 at 10°C.

Compressive Strengths

In Table 5, the compressive strengths measured at different temperature and on concrete prepared with different types of admixture are reported. The results indicate that the expansive

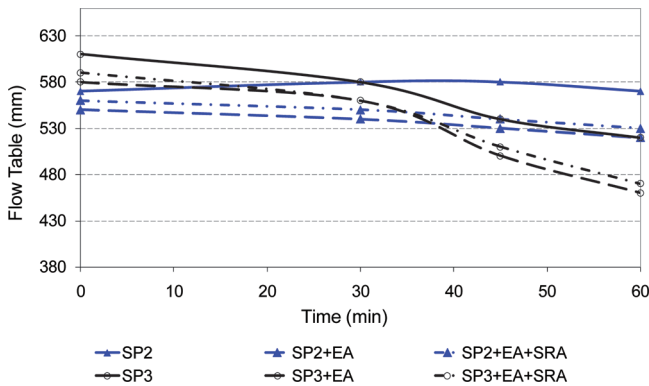


Fig. 3 – Workability retention at 10°C evaluated by flow table test (1 mm→0.04 in.)

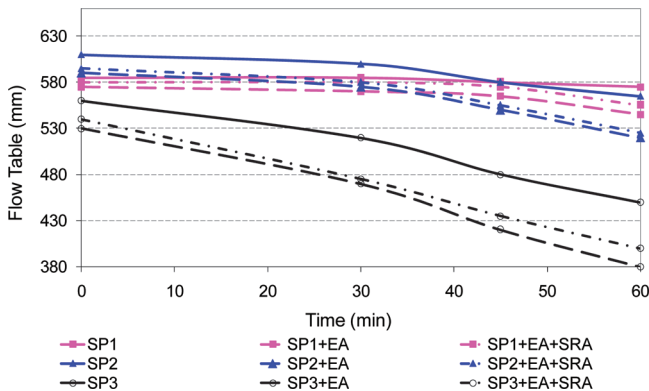


Fig. 4 – Workability retention at 20°C evaluated by flow table test (1 mm→0.04 in.)

sive agent (EA) acts as a hardening accelerator at an early age: in fact its presence increases the compressive strength at earlier ages, in particular at 10°C and 20°C, and decreases the compressive strength at 28 days at high temperature.

The addition of the SRA, as reported by other authors,⁴ produces a drop in the compressive strengths in particular at early ages especially in delayed systems (low temperature of curing and presence of HRWRA with retarding effect). The compressive strength decrease becomes irrelevant at 30°C.

Restrained expansion and relative shrinkage

Tables 6 and 7, and Figs. 6-10 show the restrained expansion tests results according to method B of the standard UNI 8148 at 10°C, 20°C and 30°C. As indicated by this standard, the samples are wrapped in a cellophane sheet for two days and afterwards cured in a controlled humidity environment. This procedure is much more realistic than curing in

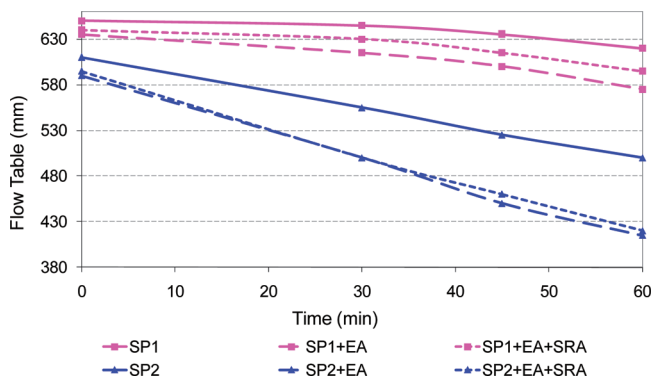


Fig. 5 – Workability retention at 30°C evaluated by flow table test (1 mm→0.04 in.)

Table 4 – Setting times for concretes at 10°C, 20°C and 30°C

Time (h)	10°C	20°C	30°C
SP1	-	12,3	10,5
SP1+EA	-	9	6,3
SP1+EA+SRA	-	9,8	7,8
Time (h)	10°C	20°C	30°C
SP2	11	7,3	5,7
SP2+EA	10,3	6	4
SP2+EA+SRA	13,5	6,4	4,8
Time (h)	10°C	20°C	30°C
SP3	8,7	5,5	-
SP3+EA	7,9	4,0	-
SP3+EA+SRA	9,1	4,7	-

“-” = not carried out due to an excessive retardation effect (SP1 at 10°C) or excessive stiffening behavior (SP3 at 30°C).

water once the specimens have been removed from the mould, and allows the quantification of the synergistic effect produced by the combined use of expansive agent and SRA.

The performance of a shrinkage compensating concrete is the result of the combination of three main effects:

- a) the value of initial expansion;
- b) the synergistic effect of the combined use of expansive agent and SRA;
- c) the absolute value of the drying shrinkage.

Based on the results of restrained expansion tests performed on concrete, the following considerations on the latter effects can be made:

- a) apart from the temperature, the initial expansion is higher when the retarding effect of the HRWRA is lower (SP3>SP2>SP1); moreover comparing different temperatures, the

Table 5 – Compressive strength (MPa) for concretes at 10°C, 20°C and 30°C.

	10°C				20°C				30°C			
Curing time	Cs1	Cs2	Cs7	Cs28	Cs1	Cs2	Cs7	Cs28	Cs1	Cs2	Cs7	Cs28
SP1	-	-	-	-	22	38	51	56	35	44	55	62
SP1+EA	-	-	-	-	29	40	53	55	36	42	57	58
SP1+EA+SRA	-	-	-	-	18	33	48	51	31	42	50	57
SRA Retarding effect%	-	-	-	-	-38	-17	-9	-8	-14	-12	-12	-3
	10°C				20°C				30°C			
SP2	6	24	46	57	26	38	50	53	34	41	49	55
SP2+EA	7,5	26	47	57	30	40	48	55	36	43	52	52
SP2+EA+SRA	3,5	18	40	54	22	35	44	49	32	38	46	52
SRA Retarding effect%	-55	-30	-14	-4	-26	-13	-11	-11	-12	-11	-12	0
	10°C				20°C				30°C			
SP3	7,5	25	44	56	28	39	49	51	-	-	-	-
SP3+EA	9,5	26	45	56	32	41	48	53	-	-	-	-
SP3+EA+SRA	4,5	19	39	50	24	34	45	50	-	-	-	-
SRA Retarding effect%	-54	-28	-14	-10	-27	-17	-6	-6	-	-	-	-

(1 MPa→145 psi).

initial expansion is higher at 20°C. Under this condition the highest value is reached after 2 days when SP3 is used;

b) the combined use of EA and SRA produces a synergistic effect which is higher at a low temperature and reaches the highest value at 10°C. In this condition the lower initial expansion is fully compensated by the introduction of SRA. On the other hand, this effect is almost irrelevant at 30°C;

c) the shrinkage evolution in the absence of the expansive agent and SRA is independent of the temperature and of the type of superplasticizer used;

d) the mixture containing the expansive agent shows a lower relative shrinkage [D60d-Dxd] (defined as the difference between the highest value of expansion and final shrinkage value) at low temperatures, in particular if SRA is present (Table 7);

e) the long term role of SRA in decreasing the drying shrinkage is independent of temperature and admixtures used (Table 7).

It is important to point out that the lower the temperature, the later the system reaches the highest expansion (Table 6). In particular at 10°C when SRA is present, the expansion peak can occur even after 7 days.

All this data shows that there is an interaction between the presence of SRA, the retarding effect of the superplasticizer admixtures and the concrete temperature. Referring to the production of shrinkage compensated concrete, it is interesting to note that the value of final expansion is similar at 10°C and 20°C. On the contrary, it is more difficult to predict the values of the final expansion at 30°C and therefore more difficult to design the concrete.

In order to define the reasons of such behaviour, some of the tests at 30°C were repeated,

Table 6 – Expansion tests result values (micron/meter) at 10°C, 20°C and 30°C.

	10°C					20°C					30°C				
Curing time	1d	2d	3d	7d	60d	1d	2d	3d	7d	60d	1d	2d	3d	7d	60d
SP1+EA	-	-	-	-	-	236	247	207	137	-142	202	197	162	77	-170
SP1+EA+SRA	-	-	-	-	-	286	301	282	258	82	210	202	168	105	11
Synergistic effect	-					+54					+8				
SP1	-	-	-	-	-	4	-30	-	-133	-370	-25	-43	-	-142	-354
SP2+EA	128	304	310	279	16	307	367	346	282	13	309	323	273	175	-54
SP2+EA+SRA	104	386	410	444	280	444	455	453	444	249	354	334	274	191	137
Synergistic effect	+134					+88					+31				
SP2	6	15	-	-87	-360	12	-1	-	-141	-385	-14	-55	-	-149	-364
SP3+EA	158	303	312	286	34	408	463	412	332	102	-	-	-	-	-
SP3+EA+SRA	183	468	508	568	400	589	643	626	567	428	-	-	-	-	-
Synergistic effect	+256					+180					-				
SP3	10	20	-	-100	-370	26	18	-	-131	-379	-	-	-	-	-

(1 micron/meter → 10⁻⁶)

adding the expansive agent after 60 minutes at the end of the workability retention test (Figs. 9-10). The results of these tests indicate that the delayed introduction of the expansive agent that allow the hydration of expansive agent during the concrete setting, notably increases the initial expansion regardless of the type of superplasticizer used.

Thermogravimetric analysis

Table 8 shows the amount of Ca(OH)₂ measured in the cement paste with TG analysis after 24 h of curing at different temperatures. Ca(OH)₂ is the most relevant parameter that can be used for assessing the degree of hydration of the cement paste and expansive agent. It is possible to notice that the development of Ca(OH)₂ is strongly influenced by the temperature and the presence of SRA: in particular low temperature and the presence of SRA in all mixtures causes a delay in the development of Ca(OH)₂.

On the other hand the type of HRWRA used does not significantly affect the Ca(OH)₂ development.

As it is impossible to differentiate with TG analysis the contribution from Ca(OH)₂ forming from cement hydration and from CaO, a second series of tests was carried out using limestone filler instead of cement. Table 9 reports the amount of Ca(OH)₂ calculated as the differences between the Ca(OH)₂ developed when adding CaO to the cement sample and to the limestone filler for systems with SP2 and SRA. Six hours after initial mixing

Table 7 – Relative Shrinkage [D60d-Dxd] (micron/meter) at 10°C, 20°C and 30°C.

	10°C			20°C			30°C		
Curing time	xd	60d	D60d-Dxd	xd	60d	D60d-Dxd	xd	60d	D60d-Dxd
SP1+EA	-	-	-	247(2d)	-142	389	202(1d)	-170	372
SP1+EA+SRA	-	-	-	301(2d)	82	219	210(1d)	11	199
SRA long term efficiency	-			43%			46%		
SP1	-	-	-	4(1d)	370	374	0(0d)	-354	354
SP2+EA	310(3d)	16	294	367(2d)	13	354	323(2d)	-54	377
SP2+EA+SRA	444(7d)	280	164	455(2d)	249	206	354(1d)	137	217
SRA long term efficiency	44%			42%			42%		
SP2	15(2d)	-360	375	12(1d)	-385	397	0	-364	364
SP3+EA	312(3d)	34	278	463(2d)	102	361	-	-	-
SP3+EA+SRA	568(7d)	400	168	643(2d)	428	215	-	-	-
SRA long term efficiency	40%			40%			-		
SP3	20(2d)	-370	390	26(1d)	-379	405	-	-	-

(1 micron/meter → 10⁻⁶)

(Table 9), the predominant contribution to Ca(OH)₂ formation is provided by hydration of the expansive agent, whereas the two contributions are quantitatively similar after 24 hours.

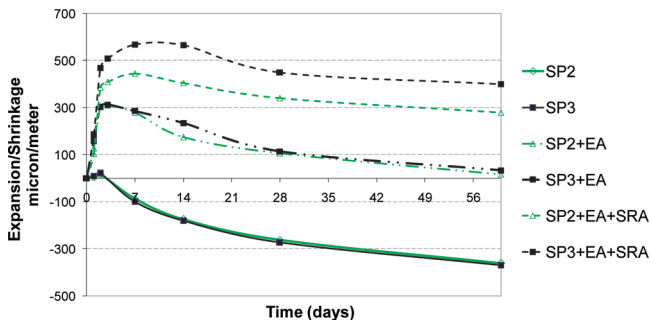


Fig. 6 – Restrained Expansion Test results at T=10°C

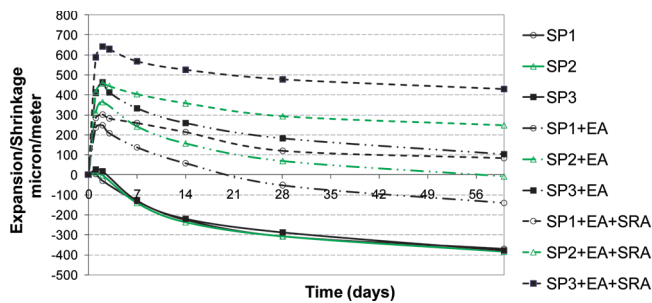


Fig. 7 – Restrained Expansion Test results at T=20°C

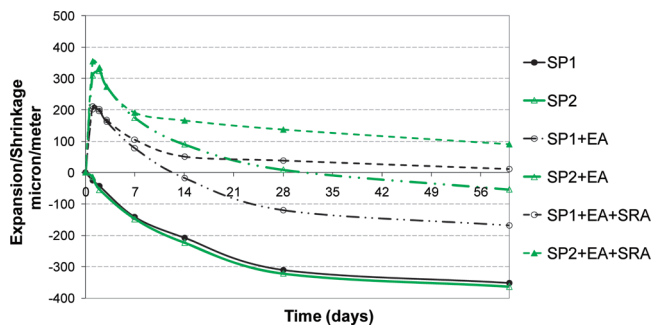


Fig. 8 – Restrained Expansion Test results at T=30°C

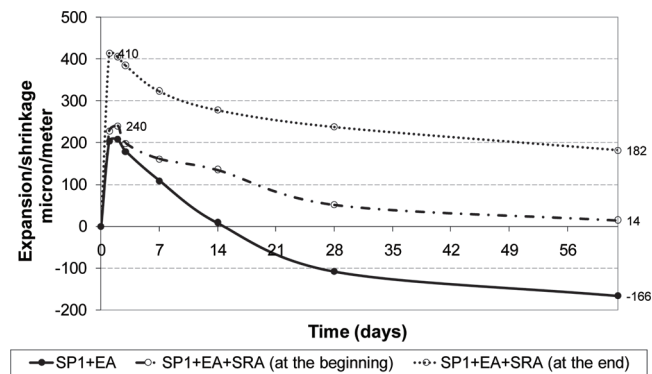


Fig. 9–Values of restrained expansion at 30°C, SP1, delayed introduction of the expansive agent.

Addition of the SRA reduces the expansive agent hydration after both 6 hours and 24 hours, while the effect on the development of the $\text{Ca}(\text{OH})_2$ originating from the cement is significantly lower. This clearly indicates that a delaying effect is caused by the presence of SRA on the expansive agent hydration as reported in literature.⁴

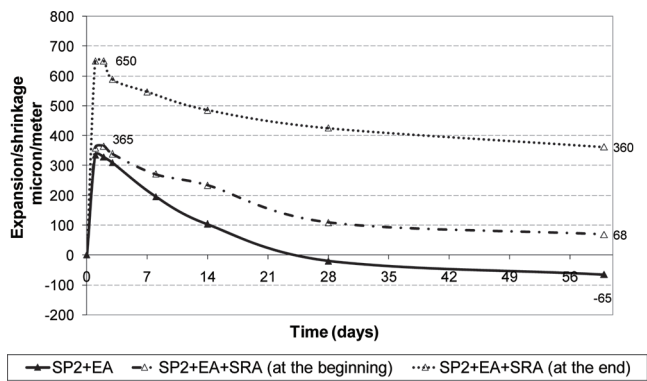


Fig. 10–Values of restrained expansion at 30°C, SP2, delayed introduction of the expansive agent.

Table 8 – Thermogravimetric analysis results at different temperatures at 24h

%Ca(OH) ₂	10°C	20°C	30°C
SP1+EA	-	17,1	18,1
SP1+EA+SRA	-	14,1	15,8
%Ca(OH) ₂	10°C	20°C	30°C
SP2+EA	10,1	16,8	18,9
SP2+EA+SRA	8,7	13,9	16,8
%Ca(OH) ₂	10°C	20°C	30°C
SP3+EA	11,3	17,8	-
SP3+EA+SRA	8,6	13,9	-

DISCUSSION

The extent of the initial expansive process is maximised when the reactions of the cement hydration are kinetically favoured compared to the expansive agent hydration. In the competition between these hydration processes, factors such as, concrete temperature, SRA addition and type of HRWRA used play a key role.

The system that showed the maximum value of initial expansion was the concrete prepared and cured at 20°C, formulated with the SP3 (the least retarding HRWRA) in the presence of SRA. On the contrary, the system which showed the lowest initial expansion was the concrete prepared and cured at T=30°C with the SP1 (with the most retarding HRWRA) and without SRA.

Comparing the data obtained from compressive strengths, restrained expansion, TG analysis, and setting times (the latter can be used as indicators of the hardening process resulting from the hydration of the cement components) the following considerations can be made:

Table 9 – Analysis of cement and expansive agent contribution to the total content of $\text{Ca}(\text{OH})_2$ at 20°C.

system	% $\text{Ca}(\text{OH})_2$	at 6h	at24h	system	% $\text{Ca}(\text{OH})_2$	at 6h	at24h
SP2	from Cement	2,3	9,4	SP2+SRA	from Cement	1,9	9,5
	from EA	6,5	7,4		from EA	5,2	5,6

- SRA retards both cement and expansive agent hydration, but the latter to a greater extent;
- the types of HRWRA used affect mainly the cement hydration. When a retarding HRWRA is used, a large part of the expansive action is wasted as it occurs in plastic concrete, and thus in a system that cannot produce any deformation of the steel inside the specimen;
- the concrete temperature affects both cement and expansive agent hydration: at 10°C the hydration of cement is slowed much more by temperature than by the expansive agent hydration. The opposite happens at 30°C.

The TG test results confirm that the main effect of SRA is the delaying of the calcium oxide hydration, in accordance with other authors³ which causes an increase of the initial expansive process.

It is interesting to note that at 30°C, the delaying action of SRA on the expansive agent is insufficient to overcome the accelerating effect caused by the temperature, at least at the analysed dosage.

CONCLUSIONS

Taking into account all these results, some practical considerations must be pointed out when ready-mix shrinkage compensating concretes are designed, in order to have the maximum efficiency:

1. Regardless of the temperature, any over-performance of the HRWRA in terms of workability retention, must be avoided because it implies a reduction of the initial expansion of the concrete and thus a reduction in the efficiency of shrinkage compensation, due to the slowdown of the cement hydration rate. The choice of the correct type of HRWRA is therefore crucial to achieve the maximum performance in any temperature conditions.
2. At low and moderate temperatures (10-20°C) the evolution of the shrinkage/expansion is different however, using the same HRWRA, the final values are quite similar. In fact at 10°C even though the initial expansion process is lower and delayed in comparison to that at 20°C, good effectiveness of the compensating process is guaranteed by a lower relative shrinkage value and a higher synergistic effect of the SRA. These are the ideal conditions to produce and deliver this kind of concrete.
3. At a high temperature (30°C) the performance of shrinkage compensating concrete depends on the transportation time required. If HRWRA characterized by a setting time retarding effect (or a retarding admixture) is used to extend the workability time of the concrete, as at this temperature the hydration rate of the expansive agent is accelerated more than the hydration of cement, a large part of the expansive agent is wasted in the plastic state. As a consequence, the initial expansion is reduced. In this condition the introduction of SRA only partially compensates for the lack of performance as the synergistic

effect is lower. The test results indicate that a possible solution is to delay the introduction of the expansive agent (for example: addition of the expansive agent at the job-site) in order to synchronize the hydration of the expansive agent with the hydration of the cement. This will lower the amount of expansive agent hydrated during transport without any positive contribution to the expansion of the hardened concrete.

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Bond Behavior between NSM FRP Rods and Concrete: Experimental and Numerical Investigation

by Aniello Palmieri, Stijn Matthys, and Luc Taerwe

Synopsis: The use of near surface mounted (NSM) fibers reinforced polymers (FRP) is being increasingly recognized as a valid technique for repairing and strengthening of concrete members. As this technology emerges, the structural behavior of NSM FRP strengthened elements needs to be characterized, and bond between NSM FRP bars and concrete is the first issue to be addressed. This paper presents the results of a series of 18 double shear tests on NSM FRP strengthened concrete. Aim of the project is to investigate the feasibility of the adopted test method and to investigate the mechanism of bond between NSM reinforcement and substrate material. Experimental results confirm the efficiency and reliability of the test method and the bond effectiveness of the NSM technique. Moreover, a local bond stress-slip relationship is determined based on experimental results and the outcome of a numerical investigation obtained from the DIANA TNO finite element analysis.

Keywords: NSM, concrete, bond, FRP, FEM

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INTRODUCTION

The fiber reinforced polymer (FRP) has become increasingly popular as a strengthening material given the increasing number of FRP strengthening applications worldwide. One of the most common ways to strengthen structures is to externally bond (EB) FRP textile or laminates on the surface of the structures. During last decade a relatively recent development in the strengthening industry is the use of near surface mounted NSM FRP bars, which consist of placing the FRP (round, square or rectangular bars) into grooves pre-cut into the concrete cover member and inserted along with a high strength adhesive (epoxy or mortar). The NSM FRP application offers several advantages over the external bonding of the FRP such as a better anchoring capacity into the adjacent members, better bond capacity, more ductile behavior, possibility to strength the members in their negative moment regions, less surface preparation (e.g. the members do not require the grinding of the surface) and better protection from the environment, vandalism and fire (mainly due to the protection provided by the partial embedment in the concrete).

The main concern governing the design of a FRP strengthening application is the debonding of the FRP, which is generally initiated before the tensile strength of the FRP reinforcement can be reached. Although various test methods to examine the local bond behavior of NSM FRP strengthening systems to concrete have been proposed thus far¹⁻⁶ their implementation can lead to a wide range of results and a standard methodology has yet to be generally accepted.

RESEARCH SIGNIFICANCE

Despite the amount of research that has been carried out so far, there are still some research needs in the field of the NSM FRP strengthening technique. The structural behavior of NSM FRP strengthened elements needs to be characterized and bond between NSM FRP bars and concrete is the first issue to be addressed. This paper presents the results of a series of 18 double shear tests on NSM FRP strengthened concrete. Aim of the project is to investigate the feasibility of the adopted test method and to investigate the mechanism of bond between NSM reinforcement and substrate material.

EXPERIMENTAL INVESTIGATION

Test specimens and parameters

The experimental program comprises 18 double face shear bond tests. The specimen (nominal dimension 150 x 150 x 800 mm [6 x 6 x 31.5 in.]) is composed of two concrete blocks (150 x 150 x 400 mm [6 x 6 x 15.7 in.]) with a square groove in the middle on both sides for embedment of the NSM rod/strip. A thin metal plate separates the two concrete blocks; the height of this plate is 135 mm [0.59 in.] (15 mm [0.6 in.] less than the height of the prisms) so that both prisms are connected and remain aligned during hardening of the resin, specimen manipulation and FRP application. Two steel re-bars, with a diameter of 16 mm [0.6 in.], are embedded in each prism. These internal steel bars do not connect the two concrete parts, which means that the two blocks are only joined through the NSM FRP bars. The FRP reinforcement is left un-bonded over a central zone of 100 mm [4.0 in.] (where the two concrete blocks connect each other). Only one block is the test region, with a bond length of 300 mm [12.0 in.] for all the test specimens. To prevent bond failure in the second concrete block a bond length of 350 mm [13.7 in.] and extra clamp anchorage are used. The double face shear bond test is schematically represented in Fig. 1 (all dimensions are in mm). The FRP NSM rods/strips were applied according to the procedures specified by the manufacturers. After hardening of the concrete, the grooves were saw-cut and then air-blasted to remove the powdered concrete produced by the cutting. The grooves were filled half way with epoxy resin and the bars were then positioned and lightly pressed. More material was applied if needed and the surface was leveled. Curing of the FRP NSM was allowed for at least 7 days under laboratory environment. No pressing devices were applied during curing.

The influence of FRP reinforcement shape (rods versus strips), the type of fibers, as well as the type of surface treatment (sand coated, smooth and ribbed bars) were evaluated. An overview of the different test specimen and the main test parameters is given in Table 1. The NSM FRP reinforcement used comprised CFRP (Carbon Fiber Reinforced polymer) BFRP (Basalt Fiber Reinforced Polymer) and GFRP (Glass Fiber Reinforced Polymer). The specimens are listed using the following designation: the first letter C, B or G indicates carbon, basalt or glass fibers, respectively; the second notation, SC, RB, SM and STR indicates the type of reinforcement: sand coated rods, ribbed rods, smooth rods and smooth strips. For each parameter three specimens have been tested.

Materials

Three concrete batches with the same concrete composition were used. The mean cylinder compressive strength (f_c) at 28 days equals 37.4 N/mm² [5.42 ksi], 36.2 N/mm² [5.25 ksi], and 35.0 N/mm² [5.07 ksi] respectively. Five types of FRP reinforcement were used in this study: CFRP rods and strips (type Aslan 200 and Aslan 500, supplied by Hughes Brothers/Fortius and type Sika Carbodur, supplied by Sika), BFRP rods (type Rockbar, supplied by Magmatech) and GFRP rods (type Aslan 100, supplied by Hughes Brothers/Fortius). The tensile properties of the NSM FRP reinforcement, as provided by the manufacturers, in terms of bar type, tensile strength, f_t , modulus of elasticity, E_t , ultimate failure strain ϵ_f and axial stiffness, $E_t A_f$, are given in Table 2. All the NSM FRP reinforcement, were embedded into the grooves by means of epoxy resin as suggested by the manufacturers. The CFRP

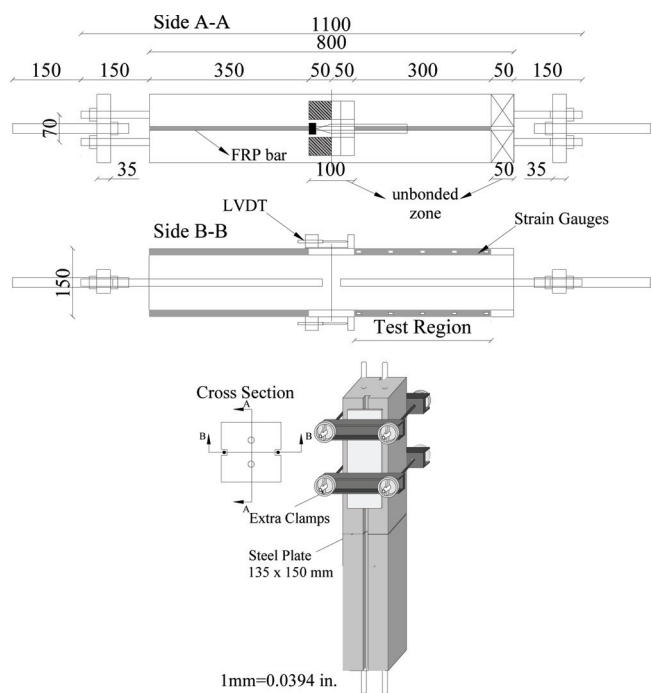


Fig. 1 – Double face shear bond test set-up

Table 1–Test matrix

Specimens	Fiber	Surface	Dimension mm (in.)	Groove dim. mm (in.)	Batch No.
C_SC_9	Carbon	Sand coated	9.5 (0.37)	15x15(0.59x0.59)	1
B_SC_6	Basalt	Sand coated	6 (0.23)	12x12(0.47x0.47)	1
B_SC_8	Basalt	Sand coated	8 (0.31)	15x15(0.59x0.59)	2
G_RB_10	Glass	Ribbed	10 (0.39)	15x15(0.59x0.59)	2
C_STR_2x16	Carbon	Smooth	2x16 (0.08x0.63)	8x25(0.31x0.98)	3
C_SM_8	Carbon	Smooth	8 (0.31)	15x15(0.59x0.59)	3

rods and strips were embedded with an epoxy resin (type Fortresin CFL, supplied by forties) with a tensile strength of 50 MPa [7.25 ksi], while the GFRP and BFRP rods with an epoxy resin (type Sikadur-30, supplied by Sika) with a tensile strength of 30 MPa [4.35 ksi] and an elastic modulus of 12.8 GPa [1.85 psi10⁶].

Test set-up and procedure

A schematic view of the test set-up is given in Fig. 1. The specimens are aligned in a universal testing machine. Testing was conducted in displacement control mode with a