

Strength Development and Carbonation Characteristics of Slag Cement/Class C Fly Ash blended CO₂ Injection Well Sealant

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ABSTRACT

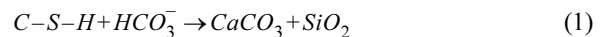
CO₂ injection well sealant is vulnerable to supercritical CO₂ (scCO₂) exposure. To develop an alternative to the conventional sealant system (class G cement/class F fly ash), the performance of slag cement (SPC) systems containing class F fly ash (FFA) or class C fly ash (CFA) was evaluated and compared with the conventional sealant under scCO₂ conditions. All sealant systems showed an immediate increase in compressive strength upon scCO₂ exposure and, at 37.6 MPa, SPC/CFA showed the highest compressive strength after 14 days, which was much higher than the 29.8 MPa of the conventional sealant system. Substantial decreases in porosity were observed in all sealant systems, which were partly responsible for the increase in strength. Carbonation reactions led to pH decreases in the tested sealants from 12.5 to 10~11.6. In particular, the greatest decrease in pH in slag cement/class C fly ash probably supported relatively sustainable alkali activation reactions and the integrity of cement hydrates in this system. XRD revealed the presence of CaCO₃ and a decrease in the content of cement hydrates in the tested sealants upon scCO₂ exposure. TGA demonstrated a greater increase of CaCO₃ and calcium-silicate-hydrate phases in SPC/CFA than in the conventional sealant upon scCO₂ exposure.

Key words : CO₂ storage, Oil well cement, Slag cement, Fly ash, Carbonation

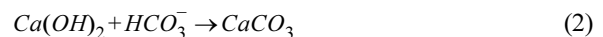
1. Introduction

Sealing CO₂ injection wells is necessary to secure well-bore integrity and prevent CO₂ leakage in the long term. When CO₂ gas is injected into the ground at a depth of more than 800m, it assumes a supercritical state. However, scCO₂ tends to rise to the surface as result of its buoyancy and leaks into the groundwater and atmosphere. There are many potential leakage pathways around an injection well, such as via sealant and casing, sealant and caprock, and casing and caprock. Within these pathways, leakage through the cracks generated by the degradation of sealant exposed to scCO₂ is a major pathway (Gasda et al., 2004; Celia et al., 2004). Class G or H Portland cement is the conventional well sealant and was originally designed to close wells in oil fields. However, it has been reported that long-term scCO₂ exposure compromises the integrity of the cementitious CO₂ injection well sealant by destroying cal-

cium-silicate-hydrate (C-S-H) structures, as shown in Eq. (1) (Onan, 1984; Barlet-Goudard et al., 2008; Fabri et al., 2009). This degradation reaction greatly impairs the mechanical properties of the sealant as a consequence of increases in the permeability and porosity of the sealant.



Other studies reported that the conversion of Ca(OH)₂ into CaCO₃, as depicted in Eq. (2), leads to a decrease in porosity and permeability as a result of the larger molar volume of CaCO₃ relative to Ca(OH)₂ (Carey et al., 2007; Rimmelet al., 2008; Liteanu and Spiers, 2011).



These pore-sealing effects caused by reactions between sealant and CO₂ are considered not persistent but limited (Kutchko et al., 2007, 2008). Not only long-term integrity, but also early strength development is important in main-

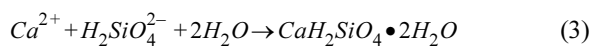
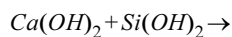
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taining the mechanical properties of a sealant. However, early strength development during the hydration process under scCO₂ exposure conditions has not been intensively studied.

Fly ash is widely used as a pozzolanic additive for reducing cement density and increasing workability during construction. A mixture of oil well cement and class F fly ash (65:35 weight ratio) has been recommended as a conventional sealant system. This conventional sealant system exhibited a greater decrease in porosity and permeability than neat oil well cement when exposed to scCO₂ conditions (Kutchko et al., 2009). Under CO₂ storage conditions, a reduction of the proportion of cement in the sealant system was found to suppress C-S-H degradation upon scCO₂ attack (Gaurina-Medjimurec and Pasic, 2013). When pozzolanic additives are used in a sealant, three major elements (Ca, Si, Al) undergo hydration reactions to form C-S-H or calcium-aluminum-silicate-hydrate (C-A-S-H), which add strength to the sealant. Especially the proportion of Ca in the sealant is an important factor in determining sealant integrity under CO₂ storage conditions because carbonation is a major reaction that transforms Ca-containing phases into CaCO₃. Therefore, strength development by pozzolanic sealants is closely related to the carbonation of Ca-based hydration products such as C-S-H and of Ca(OH)₂ into CaCO₃. As depicted in the pozzolanic reaction of a conventional sealant system (Eq. (3)), silica contained in fly ash may form additional C-S-H, thus maintaining the integrity of sealant. However, in the long term, the amount of Ca which can form C-S-H is likely to be limited in the conventional system owing to its carbonation as shown in Eq. (4).



Class F fly ash contains less than 8% CaO, whereas high-calcium class C fly ash contains more than 20% Ca and has self-hardening properties when mixed with water (Thomas, 2007). The addition of class C fly ash to cement systems is expected to increase early strength development by giving rise to more C-S-H and to increase the proportion of CaO that can potentially be transformed into CaCO₃. These char-

acteristics are expected to both fill the pores and maintain the integrity of the sealant system.

Slag cement, whose performance is comparable to Portland cement, develops strength more slowly but achieves high strength in the long term when hydrated. In addition, the slag particles in this cement release CaO upon activation with alkali and this CaO can form additional C-S-H. Besides, CaO is expected to seal the pores in the sealant structure by forming CaCO₃ under CO₂ storage conditions. However, mixtures containing class C fly ash or slag cement have not been tested as injection well sealants. Further, there are only limited studies on conventional sealants utilizing oil well cement and oil well cement is not even produced in Korea. Therefore, it is essential to investigate sealant systems and to find alternatives to the conventional sealant system in developing technologies for geological carbon dioxide sequestration.

The objective of this study was to evaluate the performance of new sealant systems made with slag cement and fly ash (class C and F) and to compare these systems with the conventional sealant system. The performance of each sealant was assessed by measuring compressive strength, pH, porosity and mineralogy before and after exposure to scCO₂ conditions.

2. Materials and methods

2.1. Supercritical CO₂ exposure test

A high pressure cell was used to simulate geological CO₂ storage conditions. Specimens were placed in the cell and liquefied CO₂ was injected until specified scCO₂ conditions were reached. The cell was then separated from the CO₂ injection line and the temperature and pressure of the cell were maintained at 50°C and 100 bar, respectively, during the incubation of the specimens.

2.2. Sealant design and preparation of specimen

Various sealant systems consisting of cement (oil well cement (PC), slag cement) and fly ash (class C, class F) were tested (Table 1). Blending ratios were designed to obtain similar Si and Al contents as in the conventional sealant system. Materials used were: Portland cement (class G cement; Shandong Huayin, China), blast furnace slag

Table 1. Chemical composition of sealants used in this study

Sealant	Mixing ratio	Oxides (%)		
		CaO	SiO ₂	Al ₂ O ₃
PC/CFA	70:30	53.3	25.9	8.0
PC/FFA	70:30	46.4	31.1	10.3
SPC/CFA	80:20	53.1	30.0	8.8
SPC/FFA	80:20	48.4	31.5	10.4

*PC, Portland cement; SPC, slag cement; CFA, class C fly ash; FFA, class F fly ash

cement (POSCO, Korea), and fly ash (class C and F, F1-TECH, Korea). The water/solid ratio was 0.44 and bentonite was added at a weight ratio of 3%. A cylindrical specimen was cast in a mold with dimensions of 12.5 mm × 25 mm with 3-day curing.

2.3. Methodology

To measure compressive strength, specimens (12.5 × 25 mm) were loaded onto a Uniaxial Compression Tester (YEON. Co. Ltd) at a loading rate of 0.5 mm/min. Porosity was calculated from the weight difference between the water-saturated specimen and the dry specimen. To prepare a water-saturated specimen, the specimen was soaked in a water-filled vacuum desiccator, before the pressure was decreased to -0.7 bar by means of a vacuum pump. The specimen was then dried at 105°C in a drying oven for 24 hours. Carbonation depth was determined by spraying 2% phenolphthalein indicator onto the surface of the vertical section of a cylindrical specimen. The carbonated area was identified by observing changes in the color of the surface that had been sprayed from purple to colorless. The average depth of the colorless area on the vertical section was measured with a Digimatic Caliper (Mitutoyo, Japan). To measure pH, the crushed specimen and water were mixed at a weight ratio of 1:5 for 1 hour and the pH of the solution was determined with a pH meter (Orion 4-Star, Thermo, USA).

X-ray Diffractometry (XRD) analysis was conducted with a Shimadzu XRD-6000 (Japan) at the wavelength of Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$) and a step size of 0.02° and a count time of 4 s per step. The results of 2 θ values between 5° and 80° were matched with the help of PDF2 search software and the JCPDS (Joint Committee on Powder Diffraction Standards) database.

A SDT Q600 (TA Instruments, USA) was used for thermogravimetric analysis (TGA). This was operated at a flow rate of 50 ml-air/min and the temperature was increased from 50°C to 800°C at a rate of 10°C/min. Weights of relevant hydrated and carbonated phases were calculated by measuring weight changes between intervals in TGA curves that were indicated by the peaks in differential scanning calorimetry (DSC) curves (Villain et al., 2007).

3. Results and discussions

3.1. Compressive strength and porosity

Fig. 1 shows changes in the compressive strength of sealants consisting of blends of Portland cement (PC), slag cement (SPC), class C fly ash (CFA), and class F fly ash (FFA) exposed to scCO₂ conditions and ambient conditions, respectively. The strength of all sealant systems before exposure to scCO₂ was under 10 MPa. However, the strength approximately doubled after a 3-day exposure to scCO₂. In particular, the strength increase of fly ash-containing sealants was substantially greater than that of PC after the same period.

SPC/CFA showed the greatest strength among the sealants exposed to scCO₂, measuring 37.6 MPa on the 14th day, which was two times greater than that of PC at 18.5 MPa. SPC/FFA exhibited a similar strength development as SPC/CFA up to the 7th day. However, its strength on the 14th day was 22.1 MPa, which was significantly lower than that of SPC/CFA, at 37.6 MPa (Fig 1(b)). It was not possible to measure the strength of PC/CFA on the 14th day because of sample expansion during drying. PC/FFA showed the second highest strength, at 29.8 MPa, on the 14th day, and this was five times greater than before exposure to scCO₂. In particular, its strength on the 3rd day was the highest among

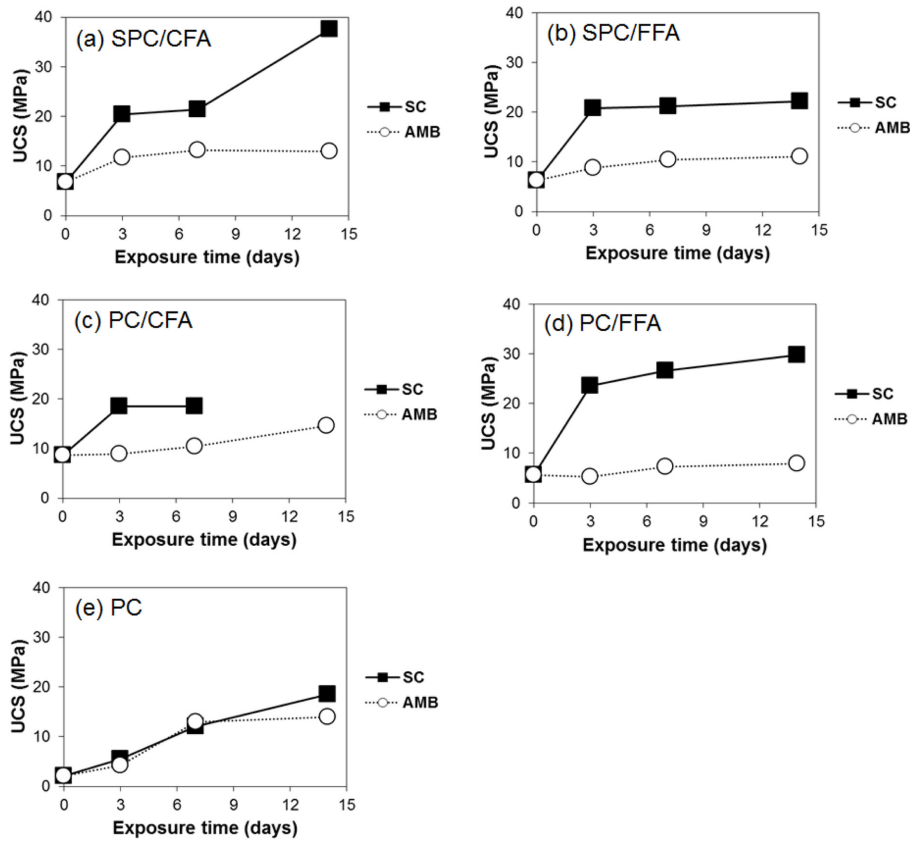


Fig. 1. Compressive strength of sealants exposed to supercritical CO₂ conditions (SC) and ambient conditions (AMB). PC: Portland cement; SPC: slag cement; CFA: class C fly ash; FFA: class F fly ash.

the sealants. The strength development of PC under scCO₂ conditions was very similar to that observed under ambient condition until the 7th day. On the 14th day, PC exhibited a strength of 18.5 MPa, lower than those of the fly ash-containing sealants.

The strength of CFA-containing sealants was generally higher than that of FFA-containing sealants. This is thought to be due to the fact that the Ca content of SPC/CFA (53.1%) is 6.7% higher than that of PC/FFA (46.4%). In other words, CFA in SPC/CFA induces the formation of more C-S-H and/or CaCO₃ than FFA in PC/FFA owing to its higher Ca content.

Before exposure to scCO₂ conditions, PC/CFA showed the highest strength at 8.6 MPa and SPC/CFA the second highest strength, at 6.8 MPa. During hydration, fly ash reacts with portlandite (Ca(OH)₂) and forms compact C-S-H structures (Thomas, 2007). C-S-H formed by the pozzolanic reaction is more easily degraded to form CaCO₃ upon expo-

sure to scCO₂. These reactions appeared to be more active in fly ash-containing sealant systems than in PC systems. Thus, greater amounts of CaCO₃ were available for filling vacancies (pores) in the solidified structures of CFA-containing systems.

The porosity of all sealants was significantly lower after exposure to scCO₂ for 3 days (Fig. 2). This is likely to at least partially account for the development of compressive strength, as shown in Fig. 1. CFA-containing sealants showed a decrease in porosity by about 46% (0.38 to 0.21), which was slightly more than the decrease of 41% (0.33 to 0.20) observed for FFA-containing sealants. Porosity stayed at about 0.2 after 12 days of scCO₂ exposure, and variation among tested sealants was small. Sealants at ambient conditions showed almost no porosity changes. Porosity changes during the exposure time under both conditions (scCO₂ and ambient) were not significant. Therefore, the reduction in porosity under scCO₂ conditions appears to be caused by

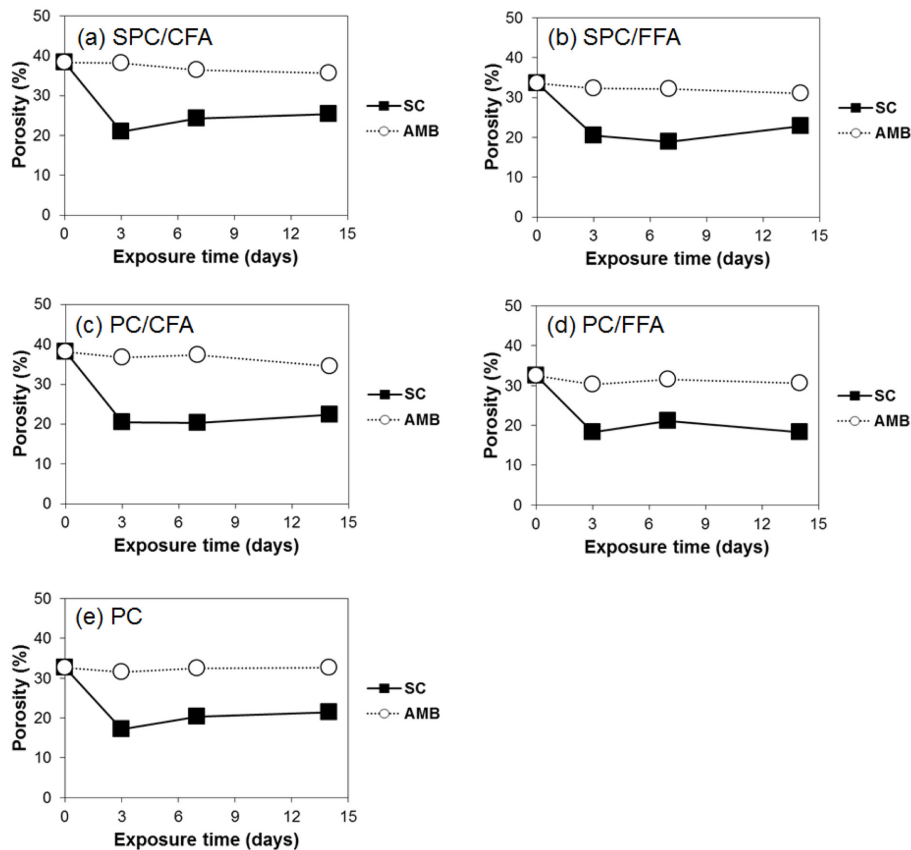


Fig. 2. Porosity of sealants exposed to supercritical CO₂ conditions (SC) and ambient conditions (AMB).

materials generated by reactions between sealants and scCO₂ during the earlier stage, rather than due to the products of prolonged hydration processes.

The porosity of CFA-containing sealant was about 5% higher than that of FFA-containing sealant. This difference may be due to the difference in particle sizes between CFA (37.3 μm) and FFA (35.6 μm) or the effect of different hydration processes in the two sealant systems. PC/FFA showed the lowest porosity, at 0.18, on the 14th day, and the decrease from the initial porosity (0th day) was likewise 44%, which was the highest relative reduction (Fig. 2(d)). The decrease in porosity in PC/FFA is thought to be caused by carbonation and subsequent filling of pore spaces by CaCO₃ (Kutchko et al., 2009).

3.2. Carbonation depth and pH

Fig. 3 shows carbonation depth changes and pH changes in the specimens under scCO₂ and ambient conditions respectively. Carbonation fronts in the blended sealant spec-

imens reached the center of the specimens (6.25 mm) within 3 days of scCO₂ exposure. In contrast, in the case of PC, the carbonation depth was 4 mm on the 3rd day and gradually increased to reach 5.04 mm on the 14th day. The large amount of portlandite (Ca(OH)₂) in PC appears to prevent the extensive carbonation of the specimen.

The pH of sealants containing fly ash decreased to below 12 after 3 days. Further, on the 14th day the pH decrement was much greater than in PC, in which the pH stayed above 12. Generally, sealants containing FFA showed greater pH decreases than sealants containing CFA. SPC/FFA showed a noticeable decrease in pH from 12.5 to 10 in 14 days (Fig. 3(b)). In contrast, SPC/CFA showed a marginal pH decrease from 12.6 to 11.6. This implies that the extent of carbonation in SPC/CFA was lower than that in SPC/FFA or that the hydration products in SPC/CFA was greater than in SPC/FFA. The higher pH of the SPC/CFA system is attributed to the higher Ca content of CFA, which allowed for the formation of more Ca(OH)₂ and/or C-S-H. In particular, the

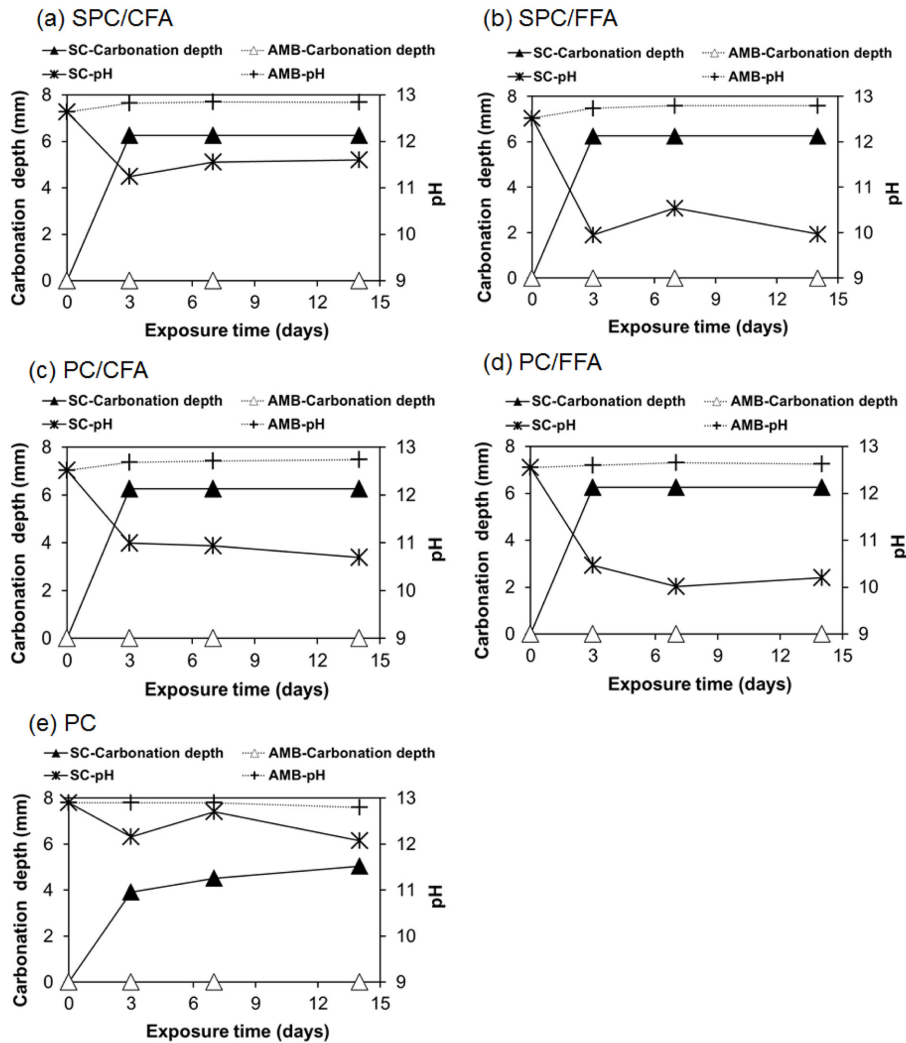


Fig. 3. Carbonation depth and pH of sealants exposed to supercritical CO₂ conditions (SC) and ambient conditions (AMB).

pH of SPC/CFA was higher than that of PC/CFA, by 0.5 pH units. This indicates that the amount of Ca(OH)₂ in SPC/CFA was higher than in PC/CFA.

3.3. Mineralogical/Carbonation Characteristics

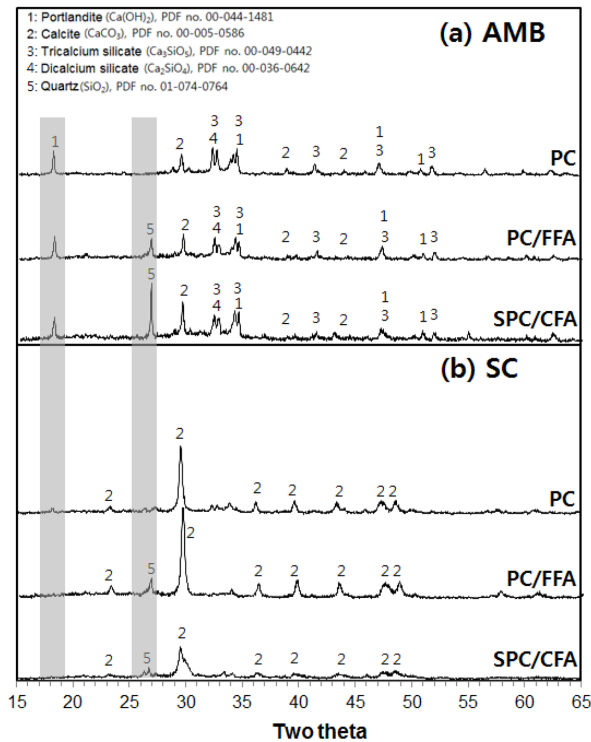
The mineralogical characteristics of SPC/CFA and PC/FFA, which performed well in terms of compressive strength, were investigated and compared. Mineralogical changes in sealants that were exposed to both scCO₂ and ambient conditions for 3 days were analyzed by means of X-ray diffraction (Fig. 4). After exposure to ambient conditions, Ca(OH)₂ and dehydrated tricalcium silicate (C₃S) and dicalcium silicate (C₂S) were found in specimens. Quartz (SiO₂) was also found in SPC/CFA in addition to these phases. The

intensity of the calcite (CaCO₃) peak was much greater for the specimens exposed to scCO₂, indicating that extensive carbonation reactions had taken place (Fig. 4(b)).

Thermogravimetric analysis (TGA) was performed in the temperature range from 0 to 800°C to quantify carbonation and hydration phases in the specimens exposed to ambient and scCO₂ conditions (Fig. 5). The hydrated and carbonated phases detected by TGA were the same as those found by XRD analysis. Table 2 shows weight changes due to the breakdown of hydrated and carbonated phases. The CaCO₃ content generally increased by more than 7% after exposure to scCO₂. SPC/CFA showed the greatest increase, of up to 8.85%. While SPC/CFA contained 53.1% Ca, which was lower than PC (64.3%), the increment in CaCO₃ con-

Table 2. Weight changes of compounds derived from TGA-DSC

		Ambient condition		
Temperature (°C)	Compound	Weight loss (%)		
		PC	PC/FFA	SPC/CFA
0-100	H ₂ O	2.11	0.86	0.91
100-210	CSH	2.00	1.59	1.65
413.35-442.21	Ca(OH) ₂	1.50	1.19	1.17
645.10-674.32	CaCO ₃	0.53	0.98	0.82
		scCO ₂ condition		
Temperature	Compound	Weight loss (%)		
		PC	PC/FFA	SPC/CFA
0-100	H ₂ O	1.63	1.77	1.65
100-210	CSH	2.21	1.74	2.38
435.01-445.06	Ca(OH) ₂	0.21	0.18	0.23
697.81-757.05	CaCO ₃	8.77	8.53	9.67
		scCO ₂ condition - ambient condition		
Compound	Weight changes (%)			
	PC	PC/FFA	SPC/CFA	
H ₂ O	-0.48	0.91	0.74	
CSH	0.21	0.15	0.73	
Ca(OH) ₂	-1.29	-1.01	-0.94	
CaCO ₃	8.24	7.55	8.85	


Fig. 4. XRD patterns of sealants, (a) ambient conditions, exposure for 3 days (b) supercritical CO₂ conditions, exposure for 3 days.

tent was higher for SPC/CFA than PC (8.24%). Ca in SPC/CFA was more amenable to carbonation than Ca in PC, which mainly existed in phases such as C₃S and C₂S (Litvan and Meyer, 1986).

After scCO₂ exposure, the Ca(OH)₂ content decreased from about 1.2~1.5% by weight to about 0.2%. This indicates that most Ca(OH)₂ was transformed into CaCO₃. It is also notable that the C-S-H and Ca(OH)₂ contents of PC/FFA after scCO₂ exposure were 1.74% and 0.18%, respectively, lower than those of SPC/CFA and PC. This suggests that the strength development in PC/FFA was due to CaCO₃ formation reactions rather than hydration reactions. The C-S-H content increased slightly after exposure to scCO₂. The increment was 0.73% for SPC/CFA, which was greater than that of 0.15% for PC/FFA. This supports relatively active alkaline activation reactions in SPC/CFA systems. A series of instrumental analyses revealed that hydration reactions forming C-S-H or calcium aluminate silicate hydrate (C-A-S-H) and carbonation reactions were relatively more active in the SPC/CFA system, which resulted in higher strength. In conclusion, SPC/CFA performed better than the conven-

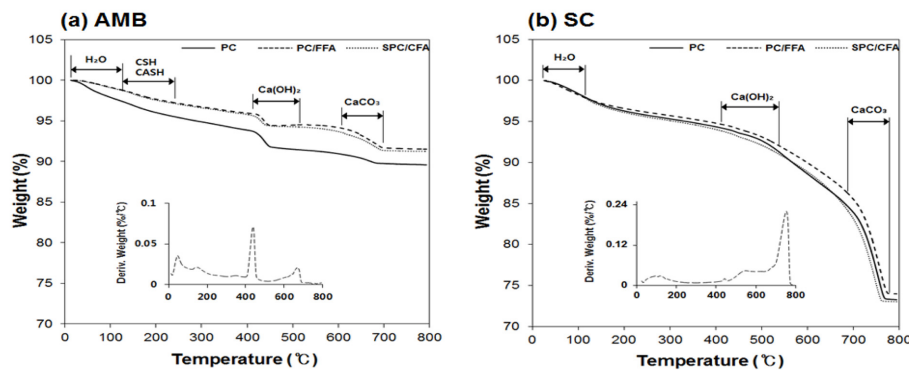


Fig. 5. TGA curves of sealants, (a) ambient conditions, exposure for 3 days (b) supercritical CO₂ conditions, exposure for 3 days.

tional sealant system (PC/FFA) because Ca activated by alkali in SPC/CFA formed CaCO₃, which can fill pores, as well as C-S-H or C-A-S-H, which leads to an increase in strength.

4. Conclusions

This study evaluated the feasibility of using slag cement (SPC) and fly ash (class C fly ash (CFA) and class F fly ash (FFA)) systems as an alternative to the conventional sealant system of Portland cement/class F fly ash (PC/FFA) by comparing their strength development and carbonation/hydration characteristics.

All sealant systems showed substantial increases in compressive strength after exposure to scCO₂ and strength increased over time. SPC/CFA had the highest compressive strength, at 37.6 MPa, which was much higher than that of PC/FFA, at 29.8 MPa. Porosity decreased significantly after 3 days of exposure to scCO₂ and reached values of approximately 0.2 on the 14th day. This contributed to the strength increases observed for the specimens.

Following scCO₂ exposure, the carbonation front reached a maximum depth in specimens within 3 days in all sealant systems. This implies that the carbonation reactions were very rapid and that carbonation contributed to strength development. Carbonation brought about pH decreases from 12.5 to 10–11.6 in the specimens. SPC/CFA showed the greatest decrease in pH, which is thought to have sustained alkaline activation reactions and the integrity of the hydrated phases in the SPC/CFA system.

XRD analysis showed that the peaks associated with

hydrates weakened and that CaCO₃ was formed following scCO₂ exposure. TGA revealed that the increase of C-S-H and CaCO₃ was substantially greater in SPC/CFA than in PC/FFA after scCO₂ exposure. This demonstrated the development of a resilient structure and the decrease in porosity of the SPC/CFA system can be attributed to C-S-H and CaCO₃.

This study shows that the ultimate strength of well sealant can be manipulated by changing the Ca content of the sealant and that SPC/CFA has the potential to be developed into a new sealant system.

Acknowledgements

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References

- Barlet-Gouédard, V., Ayache, B., and Rimmelé, G., 2008, Cementitious Material Behaviour under CO₂ environment. A laboratory comparison, *Proceedings of the 4th Meeting of the Well Bore Integrity Network*, Paris, France, p. 18-19.
- Carey, J.W., Wigand, M., Chipera, S.J., WoldeGabriel, G., Pawar, R., Lichtner, P.C., Wehner, S.C., Raines, M.a., and Guthrie, G.D., 2007, Analysis and performance of oil well cement with 30 years of CO₂ exposure from the SACROC Unit, West Texas, USA, *Int. J. Greenh. Gas. Con.*, 1(1), 75-85.
- Celia, M.A., Bachu, S., Nordbotten, J.M., Gasda, S.E., and Dahle, H.K., 2004, Quantitative estimation of CO₂ leakage from geological storage: Analytical models, numerical models and data needs, *Proceedings of the 7th International Conference on*

Greenhouse Gas Control Technologies(GHGT-7), p. 663-672.

Fabbri, A., Corvisier, J., Schubnel, A., Brunet, F., Goffé, B., Rimmelé, G., and Barlet-Gouédard, V., 2009, Effect of carbonation on the hydro-mechanical properties of Portland cements, *Cement. Concrete. Res.*, **39**(12), 1156-1163.

Gasda, S.E., Bachu, S., and Celia, M.A., 2004, Spatial characterization of the location of potentially leaky wells penetrating a deep saline aquifer in a mature sedimentary basin, *Environ. Geol.*, **46**(6-7), 707-720.

Gaurina-Medjimurec, N. and Pasic, B., 2013, CO₂ Underground Storage and Wellbore Integrity, Risk Analysis for Prevention of Hazardous Situations in Petroleum and Natural Gas Engineering, Engineering Science Reference, Hershey, PA, USA, 322 p.

Kutchko, B.G., Strazisar, B.R., Dzombak, D.A., Lowry, G.V., and Thaulow, N., 2007, Degradation of well cement by CO₂ under geologic sequestration conditions, *Environ. Sci. Technol.*, **41**(13), 4787-4792.

Kutchko, B.G., Strazisar, B.R., Lowry, G.V., Dzombak, D.A., and Thaulow, N., 2008, Rate of CO₂ attack on hydrated Class H well cement under geologic sequestration conditions, *Environ. Sci. Technol.*, **42**(16), 6237-6242.

Kutchko, B.G., Strazisar, B.R., Huerta, N., Lowry, G.V., Dzombak, D.A., and Thaulow, N., 2009, CO₂ reaction with hydrated

class H well cement under geologic sequestration conditions: effects of flyash admixtures, *Environ. Sci. Technol.*, **43**(10), 3947-3952.

Liteanu, E. and Spiers, C.J., 2011, Fracture healing and transport properties of wellbore cement in the presence of supercritical CO₂, *Chem. Geol.*, **281**(3), 195-210.

Litvan, G.G. and Meyer, A., 1986, Carbonation of granulated blast furnace slag cement concrete during twenty years of field exposure, *Proceedings of Second International Conference*, Madrid, Spain, **91**(2), p1445-1462.

Onan, D.D., 1984, Effects of supercritical carbon dioxide on well cements, *Proceedings of Permian Basin Oil and Gas Recovery Conference*, Society of Petroleum Engineers, p161.

Rimmelé, G., Barlet-Gouédard, V., Porcherie, O., Goffé, B., and Brunet, F., 2008, Heterogeneous porosity distribution in Portland cement exposed to CO₂-rich fluids, *Cement. Concrete. Res.*, **38**(8), 1038-1048.

Thomas, M.D.A., 2007, Optimizing the Use of Fly Ash in Concrete (Vol. 5420), Portland Cement Association, Skokie, IL, USA, 24 p.

Villain, G., Thiery, M., and Platret, G., 2007, Measurement methods of carbonation profiles in concrete: thermogravimetry, chemical analysis and gammadensimetry, *Cement. Concrete. Res.*, **37**(8), 1182-1192.