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Investigation on the Effects of Different Concentration of CO_2 Gas Injected into Fresh Cement Paste Along with the Addition of Superplasticizer on the Mechanical Properties of Cement

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ABSTRACT This paper focused on examining the impact of injecting varying concentrations of carbon dioxide (CO_2) gas on the mechanical characteristics of both the fresh and hardened states of cement paste. This study also considered the influence of the presence or absence of polycarboxylate superplasticizer in cement mixture on these properties. Many researchers discovered the benefit of CO_2 gas utilization in cement mixture to accelerate the early strength of cement or concrete hydration by its carbonation that form calcium carbonate ($CaCO_3$). The application method is to directly inject CO_2 gas in a curing chamber for air-curing of precast concrete. Alternatively, carbonated water is mixed with cement during concrete mixing. However, the use of CO_2 gas does not significantly improve the 28-day strength of concrete. This study explores how to improve the carbonation impact on mechanical properties of cement paste and apply it to ground improvement. In this study, the method adopted is direct injection of CO_2 gas during cement slurry mixing with different injection duration. The influence of CO_2 in the presence of superplasticizer (SP) in cement slurry was also studied as SP is generally used for grouting. The results showed that the carbonation of cement paste with additional of superplasticizer significantly affect its flow, viscosity and bleeding properties. Unlike samples with SP addition, the samples without SP addition showed higher compressive strength after 28 days of curing up to certain CO_2 injection time. For all CO_2 gas injection time, smaller porosity rates were observed for 7-day cured samples with SP addition compared to those without SP addition. This is due to accelerated carbonation due to SP presence in cement mixture. From the results, the optimum of CO_2 gas injection time for one liter mixture of cement paste to improve its compressive strength (up to 123% increase) have been discovered. It can be inferred that the addition of superplasticizer in cement slurry reduces the amount of CO_3^{2-} ions and Ca^{2+} ions during carbonation process of cement hydration products, which are strongly related to the pH level in pore solution. These ions play a significant roles in determining the mechanical properties of cement slurry.

KEYWORDS CO_2 Gas Injection, Carbonation, Cement Paste, Superplasticizer, Polycarboxylate, Compressive Strength, Porosity, Grout Injection, CO_2 concentration

1 INTRODUCTION

In ground improvement methods such as ground anchor and jet grouting, it is important to carefully consider mechanical properties and quality of the injected cement slurry in order to control the grout strength (Gullu, 2017). Cement slurry is prepared by mixing cement with water in mixer prior to being pumped underground. Maintaining desirable cement slurry flowability plays an important role to prevent pipe blockages and ensuring it can penetrate underground cracks before setting (Sun et al., 2022). Setting time is also an important factor which indicates when cement slurry starts hardening as a measure of hydration process (Yin et al., 2022).

Admixture such as superplasticizer (SP) is commonly applied in cement mixture to enhance workability, pumpability and fluidity of grout. Admixture also increases the setting time through deflocculating of cement particles, making them repeal each other (Celestine and Ebuka, 2021; Puertas et al., 2005). One of the most widely used SP is Polycarboxylate (PCE) superplasticizer which contains polycarboxylic acid in polyoxyalkylene groups. It consists of one main chain and two side chains (EO polymer and carboxyl). The repulsion force of cement particles was associated with the adsorption of these long lateral ether chains (Puertas et al., 2005). SP can make cement paste denser and provides better dispersibility of cement particles that influence the motion of entrapped water (Tao et al., 2020) thereby producing slurry with higher fluidity (Park and Tia, 1986). However, while SP enhances the workability of cement slurry, it reduces on the initial setting time of cement slurry (Zhang et al., 2010). If the setting time is either too fast or too slow, it will affect the process of cement hydration, potentially hindering the achievable compressive strength after 28 days of curing (Yin et al., 2022).

Comprehensive understanding of cement slurry behavior is required to ensure consistent and desirable mechanical properties. The initial stages of cement hydration start immediately after the cement comes into contact with water. The reactions that occur are shown in Equations (1) to (5) (Kashef-Haghighi et al., 2015; Abid et al., 2015; Bullrad et al., 2011):

$$3\ CaO.SiO_2 + H_2O \rightarrow C\text{-}S\text{-}H + Ca(OH)_2 \quad (1)$$

$$2\ CaO.SiO_2 + H_2O \rightarrow C\text{-}S\text{-}H + Ca(OH)_2 \quad (2)$$

$$3\ CaO.Al_2O_3 + H_2O\text{-} \rightarrow 3\ CaO.Al_2O_3.6H_2O \quad (3)$$

$$3\ CaO.Al_2O_3 + H_2O + CaSO_4 \rightarrow 3\ CaO.Al_2O_3.CaSO_4.12H_2O \quad (4)$$

$$4\ CaO.Al_2O_3.Fe_2O_3 + H_2O\text{-} \rightarrow 3\ CaO.Al_2O_3.6H_2O + CaO.Fe_2O_3.H_2O \quad (5)$$

As these reactions progress, the fluidity of the cement slurry gradually decreases and eventually hardens over time.

Carbon dioxide (CO_2) can react with the cement hydration products (Equations 8-12) to accelerate the hardening of cement (Kashef-Haghighi et al., 2015; Abid et al., 2015). Since CO_2 emission is one of the major contributors to greenhouse emission, by utilizing CO_2 gas in concrete production, CO_2 can be trapped in the concrete. Extensive research efforts have been devoted to understanding the mechanism for cement carbonation when CO_2 gas is used to cure cement-based materials or precast concrete under various conditions. CO_2 curing on cement paste with high concentration of CO_2 gas under different temperature conditions have been shown to accelerate its early compressive strength by more than 20 MPa after only 2 hours of CO_2 curing (Lu et al., 2002). The usage of carbonated water as mixing water to produce cement-based materials also gave benefit to increase their compressive strength at the ages of 3 and 7 days by 18% and 12.5%, respectively (Suescum-Morales et al., 2022).

However, there are limited studies about the carbonation effects in the fresh state of concrete, especially related to grouting materials. Moreover, there was also a research gap to understand how much CO_2 gas could actually be injected into cement slurry without giving negative effects to its mechanical strength. Therefore, the objective of this study is to compare the effects of direct injection of CO_2 gas in cement grout material, with and without superplasticizer, on their mechanical properties. We also aim to formulate the optimum CO_2 gas injection time to reach the maximum compressive strength and yet maintain the other properties of the cement slurry for ground improvement materials.

2 EXPERIMENT DETAILS

2.1 Materials

Ordinary Portland cement was used in this study with chemical composition shown in Table 1. The cement was obtained from the cement supplier, Taiheiyo Cement. The density and specific surface area of the cement were 3.16 g/cm^3 and 3340 cm^2/g, respectively.

Table 1. Chemical compositions of Ordinary Portland Cement from supplier

Chemical Compositions, % by weight *	
Ignition loss	2.26
MgO	1.41
SO_3	2.10
Cl^-	0.015
Na_2O	0.50
Alite (C_3S)	56
Belite (C_2S)	18
Celite (C_3A)	9
Felite (C_4AF)	9

* Comply with JIS R 5210.

Polycarboxylate (PCE) type superplasticizer was supplied by Masters Builders (Master Glenium SP8SV type) that complies with JIS A 6204 was used in this study. The density of superplasticizer was 1.1 g/cm^3. The amount of SP used in this study was 0.5% of the cement's dry weight. In addition, tap water was used to create the samples.

2.2 Sample Preparation

In this study, the cement pastes were prepared with fixed water-to-cement ratio (W+SP)/C of 50% for all cases. Table 2 shows the combination of superplasticizer amount and CO_2 gas injection duration for the samples investigated. The total volume of mixture for every test is 1000 mL throughout the cases so that the distribution of CO_2 gas amount injected into cement paste will be as consistent as possible for all samples.

Table 2. Case studies of mixtures (W/C = 50%)

Case	SP amount (C x SP %)	Mixing step 1	Mixing step 2 *
		C+(W+SP) mixing time	CO_2 gas injection duration
	(%)	(min.)	(min.)
N50SP0	0	3	0
N50SP0.5	0.5	3	0
C50SP0+CO_2(2.5)	0	3	2.5
C50SP0+CO_2(5)	0	3	5.0
C50SP0+CO_2(10)	0	3	10.0
C50SP0+CO_2(15)	0	3	15.0
C50SP0.5+CO_2(2.5)	0.5	3	2.5
C50SP0.5+CO_2(5)	0.5	3	5.0
C50SP0.5+CO_2(10)	0.5	3	10.0
C50SP0.5+CO_2(15)	0.5	3	15.0

Figure 1 shows the schematic of CO_2 gas injection into cement paste. A Hobart mixer N50 type was used to mix the materials with the following sequence:

① For the mixture with addition of SP, stir water with SP in mixer manually by hand for 30 seconds.

② Then add cement into the mixer and start the mixer and mix them at low speed (speed no.1 of the mixer) for 3 minutes.

③ After 3-minutes mixing have been passed, CO_2 gas is immediately injected into cement paste by using a tube placed at the bottom of the mixer. The pressure of CO_2 gas injection is controlled at 0.1 MPa to obtain a constant flow rate of 1 L/minute. During CO_2 gas injection process, the mixer was covered by plastic sheet with lid and sealed by tape at the bottom of mixer. The sealed plastic cover is to facilitate the containment of the released CO_2 gas from cement paste, ensuring that it remains in close proximity to the sample surface as much as possible, with the intentions for having additional reaction with cement paste at surface area and for human safety during CO_2 gas injection. Note that the system should allow released CO_2 gas to seep out from the plastic cover to outside so that CO_2 gas input able to be injected continuously.

④ Samples used for compressive strength test were casted in molds with diameter of 50 mm and height of 100 mm. The top surfaces of molds were sealed by plastic, then they were cured under constant temperature of 20°C for 7 and 28 days.

* Mixing step 2 begins after mixing step 1 is finished.

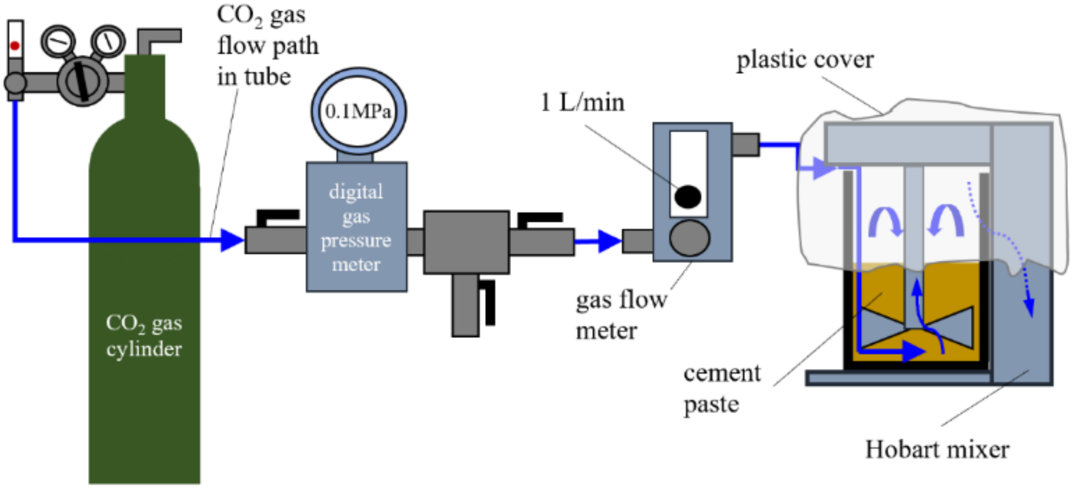

Figure 1. Schematic of CO_2 gas injection into cement paste.

2.3 Testing Methods

Tests of samples for all cases were repeated for several times to ensure data consistency.

2.3.1 Table Flow Test and pH Measurement

Table flow test was the first test that was conducted immediately after material mixing (or after CO_2 gas injection) was completed, prior to conducting other tests or preparing samples in molds. Similar flow test values can be interpretated as good consistency between batches. The table flow test was conducted according to JIS R 5201 standard requirements, using a flow table apparatus and an acrylic glass cylinder with 80 mm diameter and 160 mm height. After filling the sample into the acrylic glass cylinder, lift the cylinder to let the sample flows freely for about 30 seconds prior to measuring the flow diameters (horizontal and 90-degree or perpendicular directions).

The pH of the samples was also measured by using pH indicator paper prior to viscosity test. The color that appeared on the pH indicator paper due to reaction with sample was interpreted visually into pH by using pH-color guidance from the indicator tool.

2.3.2 Viscosity Test

Viscosity test was performed in accordance with JIS Z8803 standard by using a digital rotational viscometer (Toki Sangyo TVB-15 type). The purpose of this test is to investigate the internal characteristic of the sample up to the designated time of 2 hours. Viscosity of samples were measured every 30-minutes in which at every interval the tests were done four times under different spindle speeds (6 rpm, 12 rpm, 30 rpm and 60 rpm) sequentially, for 1 minute. During the 30-minutes of test-waiting time, the samples were mixed at low speed to avoid hardening.

2.3.3 Bleeding Test

JSCE-F522 standard of “Bleeding Rate and Expansion Rate Test Method of grouting Mortar of Prepacked Concrete (Polyethylene Bag Method)” was used as the reference for bleeding test in this study. A 1000 mL mixture could prepare two bleeding sample plastic bags. The test was done at elapsed time of 1-hour, 3-hour and 24-hour after the mixing. Initial volume (V_1) and bleeding water volume (V_{bleed}) were measured by inserting the sample bag into 1000 mL graduated cylinder filled with water at dedicated volume scale as the measurement basis. The bleeding measurement is performed by inserting the bleeding sample bag into graduated cylinder filled with water, then matching the water level of sample inside the bag with water level inside the graduated cylinder (see Figure 2). The bleeding data reading was recorded when the surface line of cement paste inside bleeding sample bag meet with the surface line of water of the graduated cylinder. Then, the bleeding rate is calculated by using the following Equation (6):

$$Br\ (\%) = \frac{V_{bleed}}{V_1} \times\ 100\ \% \tag{6}$$

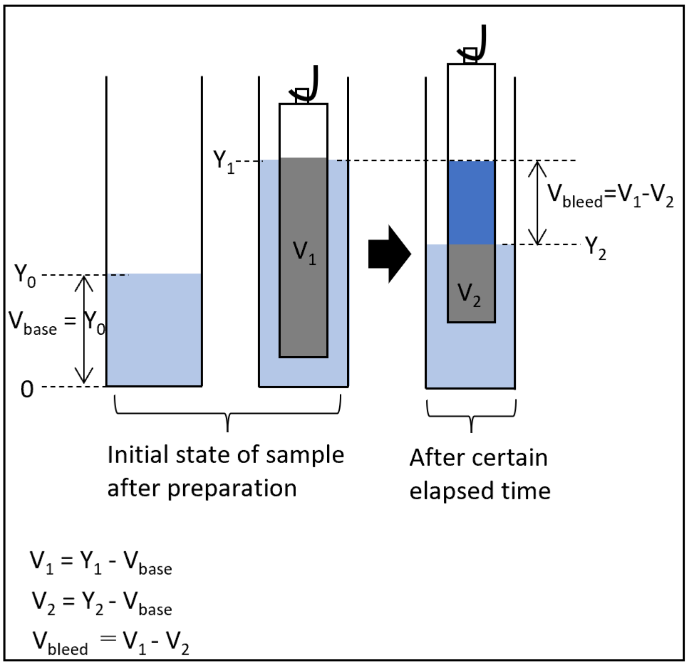

Figure 2. Concept of bleeding test method.

2.3.4 Compressive Strength Test

The compressive strength test was performed at 7-days and 28-days curing periods, in accordance with JIS A 1108 standard requirements. A compression test machine with constant stress increment rate of 0.6 MPa/s was used in this study. The preparation of the samples prior to the test includes cutting the top surface, mold demolding and wet grinding process. After curing, the samples were air-dried in room temperature of 20°C for a few hours, then samples sizes were measured and weighed just before the test.

2.3.5 Porosity Test

The samples for porosity tests were prepared by prolonging the mixing time of samples to 5 hours after the 3-minutes cement mixing plus CO_2 gas injection time were achieved. This extended mixing duration is implemented in order to guarantee the reaction of CO_2 gas with cement product throughout the entire sample, addressing the issue of excessive free water in the pores of cement paste that can hinder the entry of CO_2 gas into the sample interior. After a few attempts, it has been decided to select 5-hour extended mixing to best suit our concern. After the extended mixing, the samples were then casted in molds, sealed and cured in constant 20°C air temperature room. On the testing day, the 100 mm samples were cut to roughly 10 mm thick discs (i.e., 10 discs per samples). Their volumes (V_t) were calculated from the measured diameters and thickness. Their saturated weights (W_{sat}) and dry weights (W_{dry}) were also measured after 24-hour water immersion and after 24-hour drying process in an oven at 105°C, respectively. The open porosity was calculated using Equation (7):

$$n\ (\%) = \{\frac{(W_{sat}-W_{dry})}{\rho_w}\}\ /\ V_t\ x\ 100\ \% \tag{7}$$

ρ_w is density of water (1g/cm^3)

Note that only the open porosity of samples could be measured by using this technique, while the closed porosity cannot be measured in this study. Closed pores are formed when air is trapped during sample preparation or as the reaction products between cement product and CO_2. The closed porosity was assumed to be in tiny amount thus was ignored.

3 RESULTS AND DISCUSSIONS

3.1 Effect of CO_2 Gas Injection Time to Physical Properties of Fresh Cement Paste

3.1.1 Workability

The test results are tabulated in Table 3. From the results, it can be seen that CO_2 gas injection has the effect of reducing flow values of fresh cement paste, as a result of carbonation process on cement hydration product. The flow reduction rate is increased accordingly as CO2 gas injection time is extended. Moreover, the flow reduction in cases without SP were lesser than that of cases with SP addition. This is because of the influence of SP that dispersed the cement particles, increasing the spacing between cement particles, thus increasing the specific surface of cement particles, hence accelerating the carbonation rate.

Some researchers (Kashef-Haghighi et al., 2015; Suescum-Morales et al., 2022; Peter et al., 2008) reported that the initial carbonation reactions occurs when CO_2 gas comes into contact with water, becoming carbonated water; H_2CO_3. Then, it comes into contact with cement paste so that the reactions happen between carbonic ion (CO_3^{2-}) from CO_2 solvation (Equation 8 and 9) and dissociated Ca^{2+} ions from both calcium hydroxide ($Ca(OH)_2$) (Equation 10) and calcium silicate hydrates (C-S-H) dissociation to precipitates calcium carbonate ($CaCO_3$) and silica gel (Equation 11 and 12), so that the samples became denser than the normal cement paste. Accordingly, the flowability was reduced, but the flow values were still within acceptable range (≤ 250mm) for the grouting material.

$$CO_2 + H_2O \rightarrow H_2CO_3 \rightarrow H^+ + HCO_3^- \rightarrow 2H^+ + CO_3^{2-} \tag{8}$$

$$CO_{2\ (aq)} + OH^- \rightarrow HCO_3^- \rightarrow H^+ + CO_3^{2-} \tag{9}$$

$$Ca(OH)_{2\ (s)} \rightarrow Ca^{2+}_{(aq)} + 2OH^-_{(aq)} \tag{10}$$

$$Ca^{2+} + 2OH^- + H^+ + CO_3^{2-} \rightarrow CaCO_3 + H_2O \tag{11}$$

$$C\text{-}S\text{-}H + CO_3^{2-} \rightarrow CaCO_3 + SiO_2 \bullet \mu H_2O \tag{12}$$

Table 3. Effect of CO_2 gas injection time to flow

Case	Average Flow (mm)	Flow Reduction (%)	pH Sample
N50SP0	295	100	13
C50SP0+CO_2(2.5)	280	94.67	13
C50SP0+CO_2(5)	273	92.34	13
C50SP0+CO_2(10)	261	88.27	11~12
C50SP0+CO_2(15)	254	86.07	11
N50SP0.5	433	100	13
C50SP0.5+CO_2(2.5)	383	88.31	12~13
C50SP0.5+CO_2(5)	373	86.05	12
C50SP0.5+CO_2(10)	339	78.09	11~12
C50SP0.5+CO_2(15)	320	73.71	11~12

3.1.2 Viscosity

The viscosity over time under four different spindle speeds shows similar trends: viscosity values were reduced within 30 minutes, but then gradually increased until end of our observation (2 hours). Figure 3 shows the example of viscosity values for 2-hours observation under 6 rpm, 12 rpm, 30 rpm and 60 rpm spindle speeds for all cases with and without SP addition. At immediate measurement (0-minute), due to CO_2 gas injection, the viscosity has been increased moderately.

Moreover, unlike normal cases (N50) of which their viscosities almost unchanged over time, the CO_2 injected samples (C50) showed increased but fluctuated viscosities, especially for cases without SP addition. The samples with SP addition showed lower viscosities than those without SP addition. These viscosities trends were supported by other studies done (Zhang et al., 2022) in which they stated that presence of PCE superplasticizer in cement mixture delays the initial C_3S hydration induction period significantly, resulted in reduced initial plastic viscosity. However, after 15 minutes the plastic viscosity start increasing rapidly over time. It happened because of the reduced concentration of OH^- ions and the increase amount of AlO_2^-, as the effects of SP presence in mixture.

Since the viscosity values of C50 cases did not increase significantly even after 2 hours, thus the cement slurry is usable for construction work without any issue even if the construction idle or waiting time is about 2 hours. Maximum construction idle time of 2 hours is considered as acceptable in this study.

Moreover, the fluctuated viscosity behaviour of samples appears to be influenced by the amount of available anhydrate C_3S and C_2S within 2 hours of hydration process, leading to their reaction with CO_2 (in a form of carbonated water), resulting in increased production of $CaCO_3$ and silica gel. Peter et al. (2008) reported that unhyrated constituents in cement paste such as C_3S and C_2S are susceptible to carbonation, with the following reactions Equation (13) and (14):

$$(3CaO.SiO_2) + 3CO_2 + nH_2O \rightarrow (SiO_2.nH_2O) + 3CaCO_3 \quad (13)$$

$$(2CaO.SiO_2) + 2CO_2 + nH_2O \rightarrow (SiO_2.nH_2O) + 2CaCO_3 \quad (14)$$

Liu Z. and Meng W. (2021) also reported that the carbonation on unhydrated C_3A and C_4AF occurred but with low reaction degree. Therefore, the more gradually increasing viscosities values of injected CO_2 samples, compared to normal samples, explains the carbonation process was still ongoing.

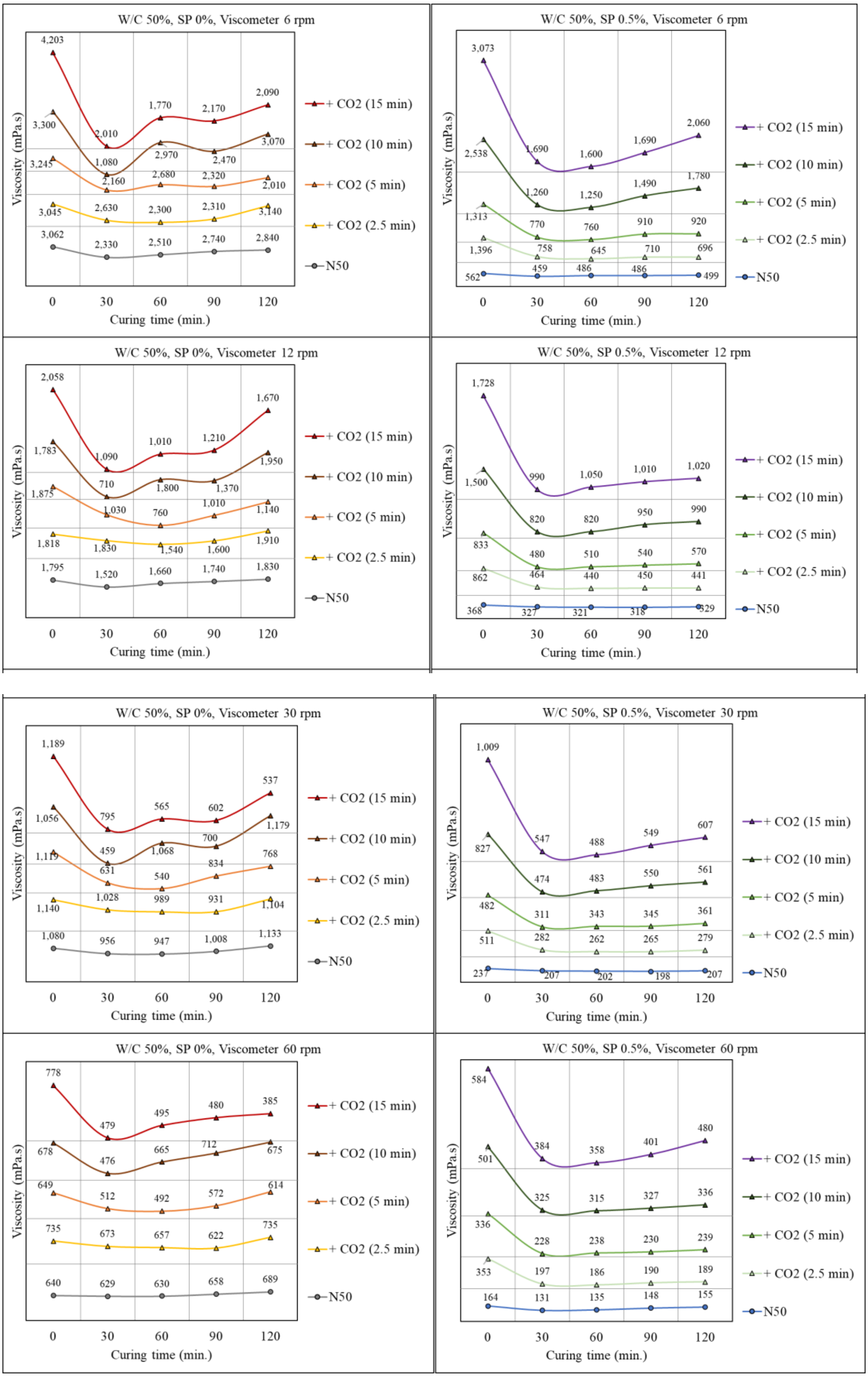

Figure 3. Stacked line charts of viscosity test results over curing time under spindle speed viscometer of 6 rpm, 12 rpm, 30 rpm and 60 rpm for group of cases without SP (left) and with SP 0.5% (right).

3.1.3 Bleeding Rate

As shown in Figure 4, when CO_2 gas concentration was low (i.e. 2.5 and 5 minutes), the pH of pore solution was still above 11, so it means that there was enough amount of dissolved Ca^{2+} from $Ca(OH)_2$ prior to reacting with CO_3^- ions to form $CaCO_3$ and filing the sample pores. This phenomenon has consequences of increasing bleeding rates up to 66.5% and 100.8% for both group case without SP and with SP addition, respectively. The similar results were also observed in other studies (Kashef-Haghighi et al., 2015; Monkman et al., 2018). As reported by Kashef-Haghighi et al. (2015) in their studies, at pH above 10 the abundance of OH^- ion in carbonated cement led to dominant formation of CO_3^{2-} ion. Then, the released Ca^{2+} ion from dissolution of C_3S and C_2S react with CO_3^{2-} and form $CaCO_3$ and additional H_2O as free water. It was suggested that the increase of bleeding water volume in the samples seems linked to the fact of additional free water also part of the carbonation product.

When the CO_2 gas concentration in cement paste was high (i.e. 10-minute and 15-minute injection), the carbonation occurred on both hydration products such as $Ca(OH)_2$ and C-S-H (Equation 8-12), and on unhydrated cement particles in the samples (Abid et al., 2015). Hence, the amount of carbonation products was bigger than that of lower CO_2 gas concentration. As a result, the bleeding rates of both group cases (samples without and with SP addition) in this particular CO_2 gas injection time range have reduced to the values similar to those samples without CO_2 gas injection.

Carbonation effect on bleeding rate is a complex reactions which is affected by hardening time, cement particles (such as agglomeration and dispersion) and other factors. Further investigation of the pH of pore water influence on bleeding rate during carbonation process is still ongoing.

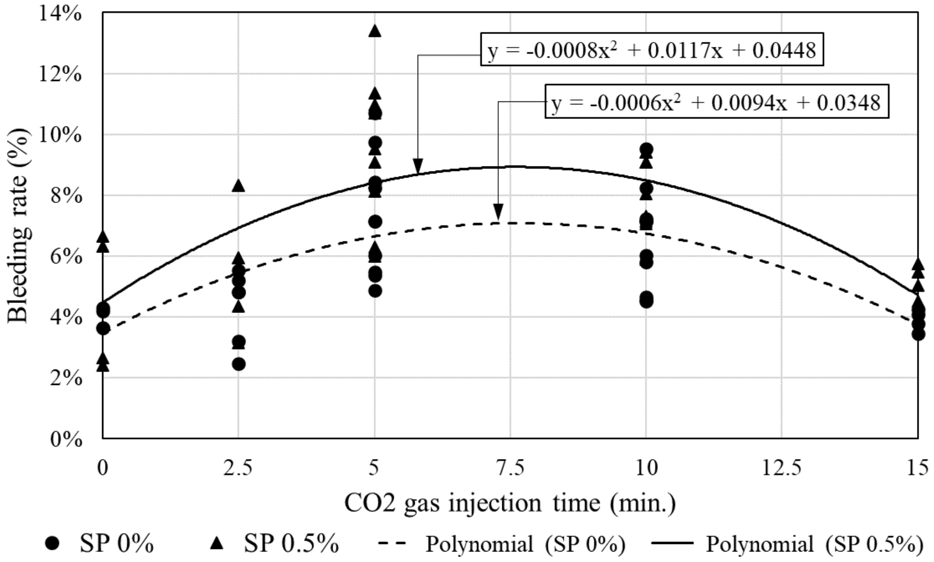

Figure 4. Relationship between CO2 gas injection time and bleeding rates at 24-hour of samples with and without SP.

3.2 Effect of CO_2 Gas Injection Time to Properties of Hardened Cement Paste

3.2.1 Compressive Strength and Density

Figure 5 shows the relationship between CO_2 gas injection time and compressive strength and density of each cases. Based on the test results, regardless of the presence or absence of SP addition, the compressive strength reached its maximum (up to 123% increase) after an injection time of 5 minutes. As the CO_2 gas injection time was prolonged, the compressive strength decreased instead. This phenomenon is consistent by other studies done by Abid et al. (2015). The decrease in compressive strength is due to release of weak amorphous silica gel from the reaction between excessive amount of H_2CO_3 and depleted amount of C-S-H from cement matrix.

The increase of compressive strength for samples with SP addition was not that significant compared to that of samples without SP addition. It seems that SP in mixture have effect that inhibits the early stage of cement hydration, as supported by other findings from Zhang et al. (2022). The delayed of cement hydration product such as Ca(OH)2, C-S-H, ettringite (Aft) and others means also delay the carbonation process. It can be speculated that at that time most carbonation process has taken place mainly on unhyrated constituents (such as C_3S, C_2S, etc.) of the sample, while some carbonation on $Ca(OH)_2$ is delayed. However, this hypothesis consider the small amount of PCE superplasticizer used in this study (0.5%). As reported by Zhang et al. (2022), the inhibit process of early stage of cement hydration should depends on the amount of PCE SP in mixture.

In the event of low pH, the abundance of HCO_3^- ions in sample leads to formation of calcium bicarbonate; $Ca(HCO_3)_2$. This could impede the cement hydration so that having more amount of anhydrate cement in the sample. This was consistent with other findings from Kashef-Haghighi et al.(2015) and Abid et al.(2015) in which H_2CO_3 is unstable and can leach out of the cement matrix. This behaviour is known as bi-carbonation and expressed using the following reaction Equation (15) and (16):

$$Ca^{2+} + HCO_{3\,(aq)}^{-} + CO_2 \rightarrow Ca(HCO_3)_2 \qquad (15)$$

$$H^{+}_{(aq)} + CaCO_{3(s)} + OH^{-} \rightarrow Ca^{2+}_{(aq)} + HCO_{3\,(aq)}^{-} \qquad (16)$$

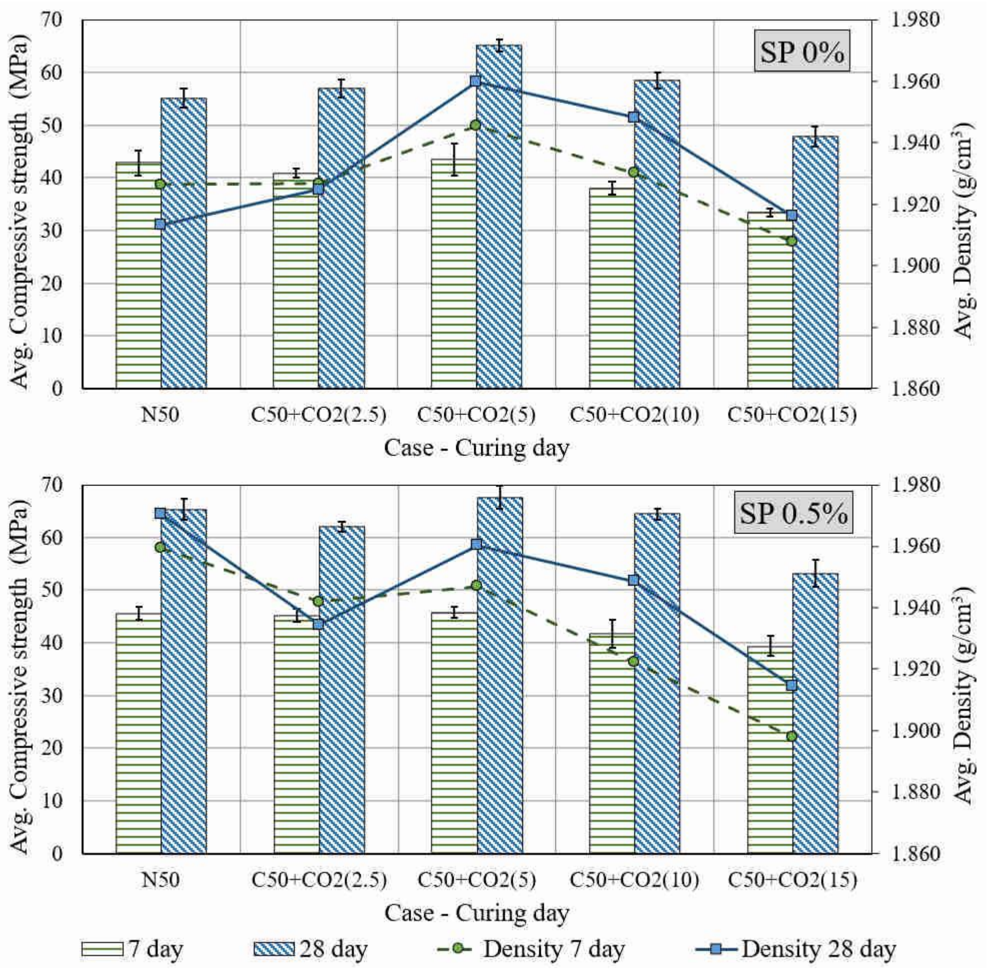

Figure 5. Relationship Between CO2 Gas Injection Time, Average Compressive Strength and Density of Samples without SP (above) and with SP 0.5% (below).

The cement paste degradation due to calcium silicate hydration depletion in the excessive carbonation process result in increasing porosity and permeability and thus reducing strength. However, it seems the formed $CaCO_3$ and silica gel from the early carbonation quickly filled the cement pores, so it inhibited the ingress of other CO_3^- ions and entrapped water to way out from pores, of which they eventually became closed pores.

Normally, for the samples with SP addition, the number of closed pores should be lesser than that of samples without SP due to PCE type superplasticizer effect on cement particles dispersibility. In normal hydration process, the addition of SP in cement paste will have less porosity of hardened samples because the bleeding water have seeped out the samples during early hydration, so that they became denser than samples without SP addition (Abadassi et al., 2023). However, in CO_2 gas injection case, the behavior trend is slightly different. For samples that injected with CO_2 gas up to 5 minutes, in early curing age (7-day), samples with SP addition generally have heavier densities to those samples without SP addition. But then, in extended curing age (28-day), apparently both cases have very similar densities (see Figure 6 and 7). This has strong correlation with porosity of samples, which will be discussed in the next sub chapter.

From the trendline of compressive strength test results (see Figure 6), one can predict the optimum of CO_2 gas injection time on 1000 mL cement slurry. For the case of cement paste without SP addition, the maximum compressive strength of about 63 MPa could be achieved when CO_2 gas is injected into it for 6 minutes and 16 seconds. While for the case of cement paste with SP addition, the maximum compressive strength that could be achieved is 67 MPa when injected with CO_2 gas for 4 minutes and 31 seconds, shorter duration than that without SP case. This is because on samples with SP addition, there was accelerated carbonation reactions due to wider cement particles area. Unfortunately, the quick carbonation also leads to unbalance reaction where excessive presence of carbonic ion CO_3^{2-}, cannot be balanced with presence of Ca^{2+} ions from cement hydration products. At this condition, prolonged CO_2 gas injection will only lead to decrease compressive strength.

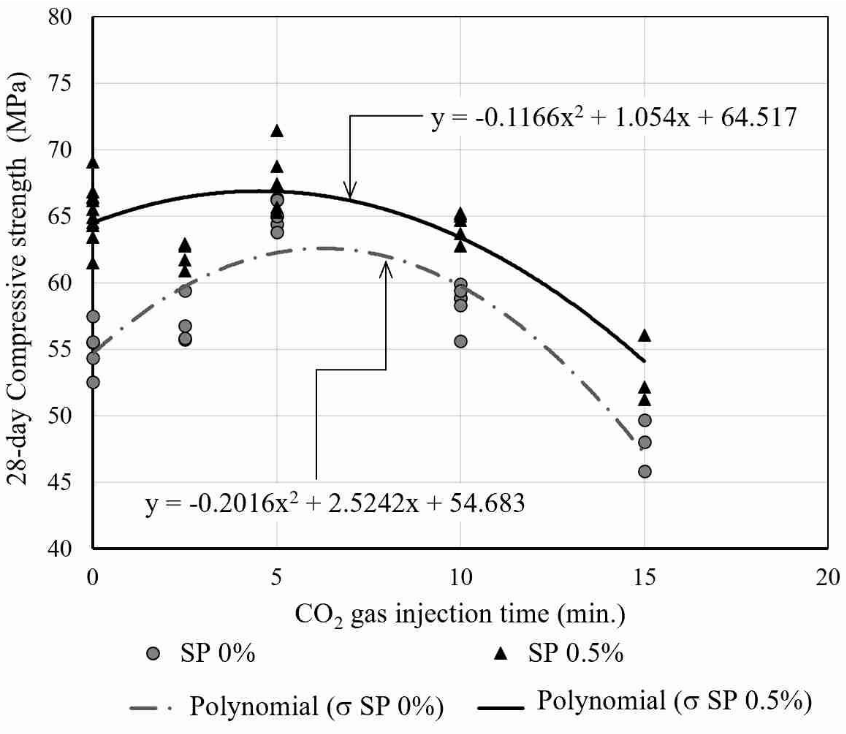

Figure 6. Relationship between CO_2 gas injection time and 28-day compressive strength.

3.2.2 Effect of Carbonation to Porosity of Cement Paste

Figure 7 shows the porosity test results of all study cases. For samples without SP addition, the porosity rate was higher than those with SP addition. Consequently, less porosity rate resulted in heavier density, and vice versa. Both figures have the similar trends of which the carbonation of hardened cement paste on samples at 2.5 minutes and 5 minutes decreased the sample porosity percentages, and then increased for longer CO_2 gas injection time. This was, as explained previously, because of the formation of $CaCO_3$ from the carbonation has closed the sample pores. However, too much CO_2 concentration in cement paste inhibits the $CaCO_3$ formations because of lack of CO_3^- ions and lower pH condition. This analysis is in line with the other studies (Kunal et al., 2018; Burkan et al., 2004) which investigate the relationship between carbonation and porosity of concrete. They found that a greater number of initial pores in a sample increases the chances of getting carbonated. Then, since the carbonation process takes place on sample pores, the porosity will be reduced accordingly. This is consistent with the other findings (Pham and Prince, 2014) that suggest carbonation leads to a decrease in total pore volume, with the formation of new mesopores. The size of the pores seems to also plays an important role to determine how deep the carbonation process can be penetrated into cement paste.

For samples after 28 days curing age, the density and porosity rates were not so much different between the CO_2 gas injection time cases. It was suggested that the continuous cement hydration and carbonation have filled and closed the remaining open pores on samples.

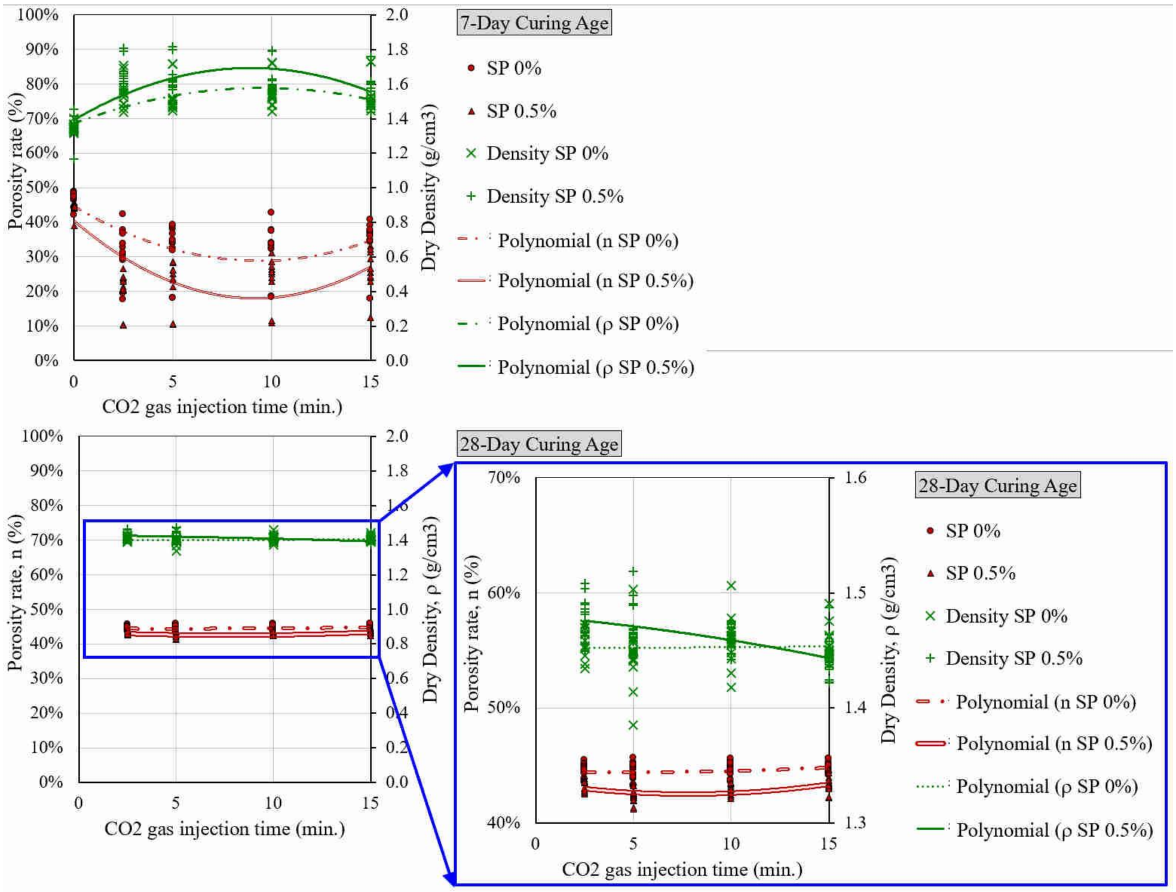

Figure 7. Relationship between CO_2 gas injection time, dry density and porosity of samples at 7-day and 28-day curing age.

4 CONCLUSION

It is possible to apply the carbonation process in cement slurry for ground improvement, such as grout injection, materials by directly injecting CO_2 gas into fresh state of cement paste. There were consequences of carbonation on 1000 mL cement slurry such as workability reduction, accelerated viscosity increase with time, higher bleeding rates until certain CO_2 gas injection time then reduced and compressive strength which depends on the CO_2 gas injection time. However, the results were still within the acceptable range of construction material requirements. The presence of polycarboxylate superplasticizer (PCE-SP) in a mixture have significant effects on carbonation process on cement hydration products, so it inflicts on different cement behaviour to a mixture without PCE-SP addition. In addition, the study confirms that the optimum CO_2 gas injection time which results in the maximum compressive strength of cement paste at 28-day age without SP and SP addition are estimated at 6-minutes 16-seconds and 4-minutes 31-seconds, respectively.

DISCLAIMER

The authors declare no conflict of interest.

AVAILABILITY OF DATA AND MATERIALS

All data are available from the author.

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