Influence of Hydration Time Prior to Carbonation in Portland Cement Admixed with CaO Expansive Additive

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Portland cement slurries have undergone degradation due to carbonation-induced corrosion in contact with a CO2-rich environment. Many studies have observed degradation such as a decrease in the mechanical strength and an increase of permeability and porosity. When utilized in wells as a zonal isolation material in the CO2-rich environment, such degradation can be worsened by hydration shrinkage of Portland cement, in which micro-annuli are formed and, thus, effective permeability is increased. In this work, CaO was employed as an expansive additive admixed with Portland cement. The samples were hydrated for 1 and 7 days prior to carbonation for 14 days in an autoclave to simulate shorter and longer hydration times before contacted with a CO2-rich environment. Before carbonated in the autoclave, the samples were analyzed by X-ray diffraction. The expansion of the hydrated slurries was also observed for the first 24 h of hydration. After carbonation, the percentage of the corroded area was calculated, and a three-point bending test was conducted. The result shows that the CaO additive below 15% by weight of cement in the Portland cement slurry can enhance the slurry resistance against corrosion encroachment induced by the carbonation process. The presence of the CaO additive in the Portland cement slurry can mitigate the severe detrimental effect induced by carbonation.

Keywords Portland cement; Carbonation; CaO; Expansive; Hydration time

I. INTRODUCTION

Class G Portland cement is extensively applied in the well construction because of its availability and affordability. As a basic well cement according to the American Petroleum Institute (API) Specification 10A [1], class G Portland cement must perform over a wide range of pressures and temperatures and ensure predictable performance when various cement additives are admixed [2].

Carbonation is a process that can not be avoided for Portland cement which is utilized as a zonal isolation material in the wells surrounded by a CO2-rich water, i.e., in CO2 geologic sequestration. The carbonation process might start when the cement is placed into the well for a few days, weeks, and even months after the cement is placed into the well. Several investigations relating to this matter have been carried out through either field sampling [3–6], laboratory testing [7–11], or modeling [12–15]. These investigations showed degradation in the carbonated cement, such as increased permeability, increased porosity, and a decreased mechanical strength. This degradation can thwart the cementing function to provide comprehensive and effective zone isolation in the well.

In the water medium, CO2 dissociates as

$$\text{CO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{CO}_3 \rightleftharpoons \text{H}^+ + \text{HCO}_3^- \rightleftharpoons 2\text{H}^+ + \text{CO}_3^{2-}. $$

The carbonic acid formed in the above reaction reacts with cement hydration products, namely, Ca(OH)2 and calcium...
silicate hydrates (C-S-H):

\[
\begin{align*}
\text{Ca(OH)}_2(aq) & \rightarrow \text{Ca}^{2+}(aq) + 2\text{OH}^- \\
\text{Ca(OH)}_2(aq) + 2\text{H}^+ + \text{CO}_3^{2-} & \rightarrow \text{CaCO}_3(s) + 2\text{H}_2\text{O} \\
\text{Ca(OH)}_2(aq) + 2\text{H}^+ + \text{HCO}_3^- & \rightarrow \text{CaCO}_3(s) + 2\text{H}_2\text{O} \\
\text{C-S-H}_x(s) + 2\text{H}^+ + \text{CO}_3^{2-} & \rightarrow \text{CaCO}_3(s) + \text{SiO}_4\text{OH}_x(s) \\
\text{C-S-H}_x(s) + 2\text{H}^+ + \text{HCO}_3^- & \rightarrow \text{CaCO}_3(s) + \text{SiO}_4\text{OH}_x(s)
\end{align*}
\]

Here, the subscripts (aq) and (s) describe the physical states of the substances, i.e., a soluble state in water and a solid state, respectively. CaCO_3(s), which is relatively more difficult to dissolve than Ca(OH)_2, precipitates in the pore structure of the cement so that its diffusivity is reduced. The carbonation process becomes obstructed or even stopped. However, in the zone where Ca(OH)_2 is depleted, the pH drops below 11.0 because there is no more Ca(OH)_2 to buffer the pH. The H^+ ion begins to react with CaCO_3(s) to form bicarbonate, which easily diffuses out of the cement matrix, and the carbonation process continues as follows [16, 17]:

\[
\text{H}^+(aq) + \text{CaCO}_3(s) \rightarrow \text{Ca}^{2+}(aq) + \text{HCO}_3^-
\]

Besides experiencing degradation due to carbonation, one of properties of Portland cement is a shrinkage when it is hydrated [2]. This shrinkage results in the emergence of micro-annulus gaps. The gap can occur between the cement body and the outer surface of the casting or between the cement body and the surface of the formation rock. Since the micro-annulus is a gap for fluid migration from one rock layer to another, the micro-annulus formation means that the cement material may fail to function as a zonal isolation material. If this shrinkage can be compensated without significantly reducing the mechanical strength, the risk of the insolation failure between the rock layer zones can be significantly reduced [18]. Examples of the shrinkage-induced reduction of the cement bulk volume in the range of 0.5–5% have been reported [2]. According to the calculations [2, 19, 20], the shrinkage of the cement used as an annulus seal causes the formation of the micro-annulus gaps, which increase the effective permeability because permeability is proportional to the cube of the gap width. Effective permeability recommended by the API is under 200 microdarcy [21]. This shrinkage occurs due to chemical and physical processes in the hydration process. Chemically, hydration of cement produces a gel-water consisting of a solid phase and the water whose total volume at the end of hydration is smaller than that of the components involved in the hydration process. Regarding physics, the gel-water attaches four to five layers of water dipoles to the newly formed negatively charged surface or the hydrate phase of the gel. The volume of the formed gel-water occupies only 75% of its initial volume [22]. Based on the principles underlying cement shrinkage mentioned above, the shrinkage can occur in two extreme ways: (1) external dimensions do not change, but vacuum chambers are formed in all parts of the cement structure, and (2) the vacuum spaces are not formed in the cement structures, but the external dimensions are shrinking (Figure 1).

Case A: In the hydration period where the slurry is still liquid, no structure supports the Ca(OH)_2 crystals formed by hydration of CaO, and thus the external size increase is very little or even none at all.

Case B: In the hydration period where the slurry is plastic, the cement structure can support the grown crystal. If the crystal size is large enough, the crystal will attain the pore wall of cement, where the crystal is located, and the external size of the cement structure increases. Suppose that cracks arise in the cement structure due to a crystal growth pressure during this period. In that case, it is possible that, in the vicinity of the cracks, there is still enough cement to hydrate to cover the cracks.

Case C: In the hydration period where the slurry hardens, the crystal growth continues to press the cement pore walls, which have hardened so that the external size increase of the cement structure is minimal. If the pressure exceeds the triaxial strength of the cement structure, the cement structure will crack. The crack can no longer be covered because hydration from the remaining cement around the crack is inadequate.

The damaged cement structure due to the Ca(OH)_2 crystal growth might occur. Therefore, the hydration rates and structure-forming phase of the swelling additives must be mutually harmonized with respect to the time [22].

In CO₂ geologic sequestration where the formation water contains CO₂, Portland cement, which is placed into a water well as a zonal isolation material, will instantly come into contact with CO₂, and the carbonation process will be also
instantly commenced. Another case could happen in CO₂ geologic sequestration if the formation water does not contain CO₂; thus, carbonation of the zonal isolation material (in this case, Portland cement) of the well begins when CO₂ is injected.

This study was conducted to provide insight into the effect of the hydration time of cement with the CaO additive before contacting the CO₂-rich water, i.e., before commencement of carbonation. The results of this study can provide insight into the differences in the impact caused by the carbonation process in cement with the CaO additive if carbonation starts immediately after the cement suspension is placed in a well (in this case, the formation water contains CO₂) or if carbonation starts when CO₂ starts to be injected for several days after the cement suspension is placed. The percentage of the corroded area and the modulus of rupture (MOR) of carbonated samples are used to assess the magnitude of the effect of carbonation. Before carbonation, the samples were hydrated in the storage water (wet-curing) for 1 and 7 days with a temperature treatment of 50 ± 1°C.

II. MATERIALS AND METHODS

A. Materials

According to API Specification 10 A [1], class G Portland cement was used as a base cement. CaO used was the Merck product in the chunks, which were then grounded using a ring mill to have a mean diameter of 5.59 μm with a specific surface of 7270.9 cm² g⁻¹, which were measured by a laser particle size analyzer. For sample preparation, demineralized water was used as a make-up water.

B. Methods

1. Slurry preparation

The cement suspension was made with the composition and identification as Table 1. Cement and CaO were mixed evenly before adding 40% by weight of cement (BWOC) make-up water and stirred using an electric stirrer.

Table 1: Sample composition and identification.

| Sample | CaO content (% BWOC) | Hydration time (days) |
|--------|----------------------|-----------------------|
| C0-1d  | 0                    | 1                     |
| C0-7d  |                      | 7                     |
| C5-1d  | 5                    | 1                     |
| C5-7d  |                      | 7                     |
| C10-1d | 10                   | 1                     |
| C10-7d |                      | 7                     |
| C15-1d | 15                   | 1                     |
| C15-7d |                      | 7                     |
| C20-1d | 20                   | 1                     |
| C20-7d |                      | 7                     |

2. Expansion measurement

The uniaxial expansion of the cement slurry was measured using an atmospheric expansion cell fitted with a dial gauge as a displacement indicator (Figure 2). The expansion cell, which was filled with the slurry, was submerged in a thermostatic bath set at 50 ± 1°C. Designation of displacement indicators was recorded every 5 min within 24 h. After 24 h of the measurements, the hardened slurry was removed from the expansion cell to measure its final length. The sample’s initial length was obtained by subtracting the final length by the final increasing length, as indicated by the displacement indicator.

3. X-ray diffraction and Rietveld analysis

An approximately 5 mL of the slurry was poured into a sealed plastic mold to avoid leaching and contamination of CO₂ dissolved in the storage water. The samples were then hydrated in a thermostatic bath for 1 and 7 days, with the temperature set at 50 ± 1°C. When the slurry reaches the specified hydration time, the hardened slurry was removed from the sealed plastic mold, and X-ray diffraction (XRD) measurements were immediately performed. The measurements were carried out in an angle range between 5° and 90° (with a 0.02° step) using an instrument from Rigaku with a Cu Kα radiation X-ray tube. The XRD data were then analyzed by the Rietveld method to determine a relative percentage of the crystalline phases. The software used for the Rietveld analysis was Highscore Plus (ver. 3.0.5) [25]. The Rietveld analysis results were used to compare the content of the crystalline phases found in the slurries that were hydrated for 1 day with those that were hydrated for 7 days.

4. Carbonation experiment

Samples for the carbonation experiments were made by pouring the cement slurry into cylindrical silicon rubber molds with a size of φ20 mm × 12 mm (depth) and beamed
shape with a size of 30 mm (length) × 11 mm (width) × 3 mm (height). The cement slurry-filled molds were then immersed in the atmospheric pressure storage water, with the temperature maintained at 50 ± 1°C for 3 h. After 3 h, the samples were demolded and were put back into the storage water to continue hydration until 1 day, and the 7-day hydration time was achieved. Six samples were made for each slurry composition (Table 1), and of the six samples, three were hydrated for 1 day, and the remaining three were hydrated for 7 days. After achieving the hydration time as previously determined, the samples were put into the autoclave to be carbonated for 14 days at a pressure of 300 psi and a temperature of 50 ± 1°C (Figure 3).

5. Carbonation depth and image analyses for area calculation

After carbonation in the autoclave, the samples were broken transversely to obtain a circular fractured surface. The fracture profile surface was then sprayed with a phenolphthalein solution (1 wt%) to provide a pink contrast to the non-carbonated area. The fracture profile surface was then photographed using a digital camera with a macro-lens. The images were processed using a free image analyzer software (ImageJ) to calculate the corroded area. The calculated area was then divided by the total area of the fracture profile surface and was multiplied by 100 to obtain the corroded area percentage. The higher the percentage of the corroded area of a sample was, the more susceptible it was to corrosion.

6. Three-point bending test

The beam-shaped samples from the carbonation experiment described above were used for a three-point bending test. The samples were put into a universal testing machine (the HT-9501 series). A custom-made sample stage was built with a 22.0-mm distance between the two supporting points. The loading rod was pushed down at a speed of 0.5 mm min⁻¹, and the displacement point was recorded along with the loading force applied to the sample.

For a rectangular sample under load in a three-point bending setup, the load force is converted to flexural stress ($\sigma_f$) by [26]

$$\sigma_f = \frac{3FL}{2wh^2},$$

where $F$ is an applied force (kgf), $L$ is a distance between supporting points (m), $w$ and $h$ are the width and height of the sample (m), respectively, and, thus, the flexural stress is given in Pa. The MOR can then be calculated using Eq. (1), where $F$ is the ultimate force applied to the sample before the sample was broken.

III. RESULTS AND DISCUSSION

A. XRD and Rietveld analysis

Figure 4 presents the XRD patterns of the samples immediately after they were hydrated. Each panel shows a comparison between the patterns of hydrated samples for 1 and 7 days. The Crystallography Open Database (COD) numbers (Table 2) were used to identify the phases. The relative quantification analysis of the crystalline phases by the Rietveld refinement method is shown in Table 3.

| Phase                                      | COD number   |
|--------------------------------------------|--------------|
| C3S (3CaO·SiO$_2$ or alite)                | 9016125      |
| C2S (2CaO·SiO$_2$ or belite)               | 9012789      |
| C3A (3CaO·Al$_2$O$_3$) or aluminite        | 9014359      |
| C4AF (4CaO·Al$_2$O$_3$·Fe$_2$O$_3$)        | 9016157      |
| CaO or lime                                | 1011095      |
| Portlandite (Ca(OH)$_2$)                   | 9000113      |
| Hillebrandite (C-S-H)                      | 9001689      |
In general, the diffraction patterns are not much different where the diffraction peaks occur at the same angle but only differ in intensity. The presence of convex patterns at intervals of 25° and 35° can also be seen on all XRD charts. The convex pattern is a manifestation of an amorphous phase, where C-S-H dominates [27, 28]. In the hydrated sample for 7 days, the convex pattern was more conspicuous than the hydrated sample for 1 day. This is because the hydration time is longer, the C-S-H as one of the hydration products becomes more numerous. Portlandite as a hydration product is also seen to increase its intensity with increasing the hydration time. As for the silicate phase, the intensity decreases as the hydration time increases. The apparent intensity of the silicate phase decreases at an interval of 40° to 42°. Ettringite is formed from alumina phase hydration [29] in the initial hydration period. With increasing the hydration time, ettringite was increasingly diminished.

The data in Table 3 shows that the composition of portlandite increases as the CaO additive composition increases for the same hydration time. This is because the hydration of CaO also produces portlandite by hydration of Portland cement with the same COD number (9000113). The data in Table 3 also shows that CaO has run out even at the end of the first day. This means that the addition of portlandite from the end of the first day to the seventh day came from hydration of Portland cement only (not from CaO hydration).

According to Costa et al. [30], the more hydration products can decrease porosity and permeability. The initial porosity and permeability of the cement before carbonation determine the corrosion rate caused by CO₂ [31]. Therefore, the composition of hydration products determines the corrosion rate of cement in an environment containing CO₂.

| CaO content (% BWCO) | Crystalline phase (%) |
|----------------------|-----------------------|
| Hydration time (days) | 0.0 | 5.0 | 10.0 | 15.0 | 20.0 |
| 1 | 7 | 1 | 7 | 1 | 7 | 1 | 7 | 1 | 7 |
| Etritngite | 0.4 | 4.3 | 6.7 | 3.6 | 4.1 | 5.4 | 6.2 | 4.0 | 4.7 | 5.7 |
| Portlandite | 11.2 | 29.3 | 22.9 | 41.0 | 25.5 | 33.5 | 24.9 | 43.8 | 35.0 | 42.7 |
| Hillebrandite (C-S-H type) | 15.9 | 20.8 | 14.1 | 10.0 | 12.8 | 20.7 | 12.0 | 20.1 | 12.5 | 12.8 |
| CaO (remaining) | N/A | N/A | 0.0 | 0.0 | 0.1 | 0.2 | 0.0 | 0.1 | 0.0 | 0.0 |
| Anhydrous (C3S, C2S, C3A, C4AF) | 72.5 | 45.8 | 56.3 | 45.4 | 57.4 | 40.2 | 55.8 | 32.0 | 47.9 | 33.8 |
B. Expansion measurement

With the uniaxial expansion cell, a sample length was measured every 5 min. The percentage of expansion over time is then plotted on the graphic, as shown in Figure 5. In the 24-h observation range, the expansion of the sample containing the CaO additives did not start from the beginning but was preceded by a period in which there was no expansion. At the beginning of the observation, the slurry was still liquid, so no structure supports the grown crystals [22]. When slurry hydration enters the plastic period, the grown crystals can already be supported by a cement structure and the external size is increased as detected by a uniaxial expansion cell. The expansion rate in the samples containing the CaO additives was initially slow but progressively faster, then constant, and finally slowed to a complete standstill. The samples without the CaO additives did not experience expansion or shrinkage during 24 h of observation. This shows the chemical and physical shrinkage in the sample without the CaO additive, which did not change the external size of the cement structure but did form scattered pore spaces in the interior (Figure 1a). The pore space becomes more significant as the cement hydration process continues.

In Figure 5, it can be seen that, with the increase in the CaO composition, the percentage of the final expansion is higher, except for the slurries with the composition of the CaO additives of 15 and 20% BWOC, whose expansion curves coincide. The samples with the 5% BWOC CaO additive follows the Case A expansion pattern. Most of CaO is hydrated in the liquid period. Only a small amount of CaO is hydrated in the plastic period, and thus only a slight expansion of the external dimensions is observed. Expansion of the samples with an additive composition of CaO 10% BWOC follows Case B. Most of the CaO hydrates in the plastic period, and there may not be any CaO left when hydration enters the hardened period. Expansion of the samples with CaO additive of 15 and 20% BWOC may continue until the hardening period (Case C), where there is still CaO remaining to hydrate in the hardened cement period. The magnitude of sample expansion with the 20% BWOC CaO additive can only equal to that with an additive of 15% BWOC. Although there is still CaO that is hydrated in the cement hardening period because the cement is hardened and its strength is sufficient to offset the pressure from the growth of the Ca(OH)₂ crystals, it does not produce changes in the external size of the cement body.

Also shown in Figure 5 is the tendency that the higher CaO additive composition results in the faster expansion onset. This indicates faster hydration of the cement suspension entering the plastic period (i.e., a short liquid period). In the process of cementing the well, a suspension of cement with a short liquid period runs the risk of thwarting the cementing process. The cement has become unable to be pumped when the cementing process has not been completed.

C. Image analysis and the percentage of the corroded area (corrosion resistance)

In this study, the percentage of the area affected by the carbonation process (hereinafter referred to as the percentage of corroded areas) is used to measure the vulnerability of the cement structure to carbonation as in other studies [30, 32]. The more significant the percentage of the corroded area is, the more susceptible the sample is to carbonation.

Figure 6a shows an image captured from the surface of a fractured sample. Furthermore, the image was processed using ImageJ software to separate the corroded areas from the intact areas. The result is as shown in Figure 6b. The calculation of the percentage of the corroded area and the
reduction of the percentage of the corroded area due to the presence of the CaO additive are presented in Table 4. Figure 7 presents the bar chart to compare the corroded area between the 1-day and 7-day hydration samples. Figure 8 presents the chart of the percentage reduction of the corroded area due to the presence of the CaO additive.

The chart in Figure 7 shows that increasing the hydration time from 1 to 7 days results in the cement suspension becoming more susceptible to corrosion for all samples. The increasing percentage of the corroded area is indicated by increasing the hydration time from 1 to 7 days. However, compared with control samples (the samples without the CaO additive), for the same hydration time, the graph in Figure 7 shows that the presence of the CaO additives with a specific composition could reduce the percentage of the corroded area, i.e., increase in corrosion resistance. To quantify the amount of reduction in the percentage of the corroded area due to the presence of the CaO additives, the difference between the percentage of the corroded area of the sample containing CaO and the percentage of the corroded area of the control sample compared to the percentage of the corroded area of the control sample and expressed as a percentage [column (2) in Table 4]. The percentage of reduction in the corroded area, which is positive, indicates increased corrosion resistance. Conversely, the percentage of reduction in the corroded area, which is negative, indicates an increase in corrosion resistance.

The percentage of reduction in the corroded area is presented in a chart as shown in Figure 8. The maximum percentage of the reduction in the corroded area was achieved at the 10% BWOC CaO additive for both hydration times (1 and 7 days). The addition of more than 10% of CaO further reduces the corrosion resistance and, to a certain extent, reaches a negative value as shown in the composition of the CaO additive with 20% BWOC. For the slurries with the 10 and 15% BWOC CaO additives, prolonged hydration time before carbonation from 1 to 7 days lowers the effectiveness of the CaO additive to increase the corrosion resistance. Conversely, for the slurries with the 5 and 20% BWOC CaO additives, extending the hydration time before carbonation from 1 to 7 days increases the CaO additive to increase the corrosion resistance. Thus, care must be taken when admixing the CaO additive between 5 and 10% BWOC with Portland cement. The reversal effect of the hydration time to the corrosion resistance occurs within the range of 5 and 10% BWOC of the CaO additive.

Incremental corrosion resistance by admixing Portland cement with the CaO expansive additive can be achieved by adding the CaO expansive additive of no more than 15% BWOC. The CaO additives above 15% BWOC leads to the corrosion resistance which is lower than that of the control sample. The presence of excessive CaO might lead the expansion to emerge as “Case C”, where the crack that occurred due to the expansion could no longer be covered. Thus, corrosive CO$_3^{2-}$ can easily penetrate the sample.

The yellow points in Figure 8 show the cross points where the hydration time prior to carbonation does not affect the corrosion resistance. Each yellow point corresponds to a specific value of the composition of the CaO additives. One of the values lies between 5 and 10% BWOC (approximately 7% BWOC), and another value lies between 15 and 20% BWOC.

### Table 4: Percentage of the corroded area of all samples and the reduction of percentage of the corroded area due to the presence of the CaO additive.

| Sample | 1 day cures | 7 day cures |
|--------|-------------|-------------|
|        | (1) | (2) | (1) | (2) |
| C0     | 21.99 | -   | 27.07 | -   |
| C5     | 18.66 | 15.17 | 20.19 | 25.42 |
| C10    | 10.35 | 52.93 | 17.53 | 35.24 |
| C15    | 16.03 | 27.12 | 22.72 | 16.07 |
| C20    | 25.37 | -15.33 | 27.55 | -1.76 |

(1) Percentage of the corroded area (%).
(2) Reduction of percentage of the corroded area due to the presence of the CaO additive (%).

Figure 7: Percentage of the corroded area of the carbonated samples in the autoclave.

Figure 8: Reduction of corroded area due to presence of CaO. The negative reduction indicates the increment of corroded area. The yellow circles correspond to the points where the hydration time prior to carbonation does not affect the corrosion resistance.
20% BWOC (approximately 17.5% BWOC) of the CaO additives. The corrosion resistance of slurry with one of those compositions can not be influenced by the prolonged hydration time before carbonation from 1 to 7 days.

D. Modulus of rupture

In Figure 9, it can be seen that, for the hydration time of 1 day before carbonation, all MORs from the CaO-added samples are lower than those of the samples without the CaO additive. However, suppose the hydration time before carbonation is extended to 7 days, the reverse effect occurs where the MORs of the CaO-added samples are higher than the sample without the CaO additive. The control sample experienced a remarkable reduction of the MOR from 16.59 to 8.88 MPa due to the prolonged hydration time from 1 to 7 days. The samples with CaO additive also experienced a reduction of MOR due to prolonged hydration time from 1 to 7 days but not as much as that of the control sample. The C20 sample even experienced an increase in the MOR with the prolonged hydration time from 1 to 7 days. From the above description, it can be concluded that the CaO additives can mitigate the detrimental effect of carbonation on the mechanical strength due to the prolonged hydration time from 1 to 7 days.

The cement slurry with the CaO additive also experienced a reduction of the MOR due to the prolonged hydration time before carbonation from 1 to 7 days, but the reduction is much lower than that of the control sample. Somehow, the presence of the CaO additive in the cement slurry can mitigate the detrimental effect of carbonation on the mechanical strength.

To evaluate the effect of the presence of CaO to the MOR, the ratio of incremental of the MOR due to the addition of CaO to that of the control sample (i.e., the sample without the CaO additive) is presented as a percentage in column (2) in Table 5 and plotted in a line chart in Figure 10.

For the hydration time of 1 day before carbonation, every sample with the CaO additive shows a negative value of the MOR, i.e., the lower MOR than the MOR of the control sample. The presence of CaO 5% BWOC emerges expansion according to Case A where most of the CaO additive swells (i.e., expands) during the liquid period of the slurry. So, a structural damage is unlikely to occur due to expansion. Hence, the reduction of the MOR was merely due to the reduction of the cement (binder) content in the slurry mixture by the CaO additive presence. Following the reduction of the cement content in the slurry mixture, the presence of CaO 10% BWOC should lower the MOR more than CaO 5% BWOC. But the result in Figure 10 shows the opposite. This phenomenon can be elucidated as follows. With CaO 10% BWOC, some CaO swells in the liquid period of the cement slurry, but most CaO swells when the slurry was plastic (Case B). The grown Ca(OH)₂ crystals impinge the plastic cement structure and force it to deform but do not destroy the structure. The deformed structure permits the production of thin and solid articles or structures, as in mechanical prestressing [29]. This mechanical pre-stressing compensates for reducing the MOR due to the reduction of the cement content in the slurry mixture. Thus, the reduction of the MOR due to CaO 10% BWOC (17.34%) is lower than that of CaO 5% BWOC (21.57%). Incrementing the percentage of CaO above 10% BWOC leads to a higher reduction of the MOR. Above 10% BWOC, CaO is available with sufficient quantities so that there is still plenty of CaO left for further hydration in a hardened cement matrix.

![Figure 9: MOR of slurries with and without the CaO additive.](image)

![Figure 10: Incremental of the MOR due to the presence of the CaO additive.](image)

| Sample | 1 day cures | 7 day cures |
|--------|-------------|-------------|
|        | (1) | (2) | (1) | (2) |
| C0     | 16.59 | - | 8.00 | - |
| C5     | 13.01 | -21.57 | 11.72 | 31.99 |
| C10    | 13.71 | -17.34 | 11.23 | 26.45 |
| C15    | 11.69 | -29.52 | 11.02 | 24.06 |
| C20    | 8.88  | -46.47 | 10.76 | 21.15 |

(1) MOR (MPa).
(2) Incremental of the MOR due to the presence of the CaO additive (%).
period of the cement slurry (Case C). If the pressure exceeds the triaxial strength of the cement structure, the cement structure will crack. The crack can no longer be covered because hydration from the remaining cement around the crack is inadequate [22].

For the hydration time of 7 days before carbonation, every sample with the CaO additive shows a positive value of the MOR, i.e., the higher MOR than the control sample (a red line in Figure 10). As discussed above, prolonging the hydration time before carbonation from 1 to 7 days reduces the MOR of each sample except the C20 samples (Figure 9). However, the reduction of the MOR of the CaO-admixed samples (C5, C10, and C15) due to the prolonged hydration time is conspicuously much smaller than that of the control sample. Thus, for a longer hydration time before carbonation, the CaO-admixed cement slurry can endure the detrimental effect of carbonation to the mechanical strength better than the plain Portland cement slurry.

IV. CONCLUSION

Measurements of the percentage of the corroded areas and the MOR of the Portland cement suspension containing CaO as much as 0, 5, 10, 15, and 20% after being carbonated for 1 and 7 days have been carried out. A quantitative analysis of the composition of the crystalline phases of the sample 1 and 7 days have been carried out. Based on the results obtained, it can be concluded as follows:

1. The CaO additive below 15% BWOC in the Portland cement slurry can enhance the resistance of the cement slurry against corrosion encroachment induced by the carbonation process. The maximum corrosion resistance enhancement was achieved in the slurry with 10% BWOC of the CaO additive. Prolonging the hydration time from 1 to 7 days reduces the enhancement of the corrosion resistance for the slurry with the composition of the CaO additive between 7 and 17.5% BWOC.

2. The Portland cement slurry is vulnerable to severe structural detrimental effect of carbonation if hydrated for a long time before carbonation. The presence of the CaO additive in the Portland cement slurry can mitigate the detrimental effect of carbonation.

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