CO₂ attack on API Class-G cement and the role of CaO swelling cements admixtures

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Abstract. API Class-G cement is Portland cement that commonly applied as zonal isolation material in oil and/or gas well. Corrosion against the zonal isolation could lead to potential leakage of formation fluid such as oil, gas, or water. It is well known that ordinary Portland cement is thermodynamically unstable in the CO₂ rich environment, which can be found in the CO₂ geological sequestration. The CO₂ attack on API Class-G cement had been observed through experiments that simulate the downhole condition of Geological Sequestration of CO₂. Some of the experiment revealed the detrimental effect of CO₂ such as increase of porosity and permeability of the cement sheath corroded by the CO₂ attack. The degradation of API Class-G cement by CO₂ involves formation and crystallization of CaCO₃ from Ca(OH)₂ which is formed during hydration of cement. In this experiment, we examine the role of the addition of CaO swelling cement by weight fraction to mitigate the corrosion caused by CO₂ against downhole hardened API Class-G cement thus inhibits the occurrence of leakage path of CO₂. The characterization and analysis by XRD, optical microscope and cement paste uniaxial volumetric expansion were presented in this paper. The conclusion will provide insights into the design of carbonation resistant cement slurries using swelling cement admixtures.

1. Introduction

API Class-G cement is one of Portland cement specification defined by American Petroleum Institute (API) specification 10A and is the most common material applied for downhole zonal isolation in oil/gas well. The presence of CO₂ under downhole condition is inevitable in some geological formation especially in CO₂ geological sequestration. The corrosion potential to CO₂ have been known through experiments [1-8]. When Portland cement was exposed to CO₂, portlandite (Ca(OH)₂) or C-S-H phase in the Portland cement is carbonated to form calcium carbonate (CaCO₃) at the cement surface by following chemical reactions:

\[
\text{Ca(OH)}_2 + \text{H}_2\text{CO}_3 \rightarrow \text{CaCO}_3 + 2\text{H}_2\text{O} \quad (1)
\]

\[
\text{C-S-H} (\text{CaSiO}_2_2,\text{H}_2\text{O}) + y\text{H}_2\text{CO}_3 \rightarrow \text{Ca}_{x_3}\text{SiO}_{2_2,y}\text{H}_2\text{O} + y\text{CaCO}_3 + 2y\text{H}_2\text{O} \quad (2)
\]

The formation of solid CaCO₃ decreases cement permeability and increases its compressive strength thus creates barrier effect to further CO₂ attack [9]. This effect is plausibly due to the fact that during
their growth, CaCO₃ crystal need volume space for expansion as the crystal occupied a larger volume than their precursor (portlandite) [7].

As described above, the occupancy of void (pore) space by solid CaCO₃ is effective to inhibits the further CO₂ attack. Pore space occurs because the volume of chemically occluded water and the physically attached water occupy only 75% of the sum of the original volumes for all participating components (water, cement clinker minerals, and hydration products) [10]. Two limiting shrinkage cases are distinguished as possible consequences for bodies of cement (see figure 1), i.e. (1) a development in cement porosity, and (2) a shrinkage of bulk volume where the so-called matrix or bulk volume comprises the volumes of the cement components and of the water- or gas-filled pores.

Increased cement porosity is one of contributing factor to increase the rate of CO₂ attack since it allows more carbonated water diffuses into cement matrix. The higher the initial porosity/permeability, the higher CO₂ is penetrated [5]. Decrease in the exterior dimensions of the cement body is also not desired since it creates micro annulus between cement-casing and/or cement-rock contact. The most significant alteration (due to CO₂ attack) may occur along existing or introduced pathway (gap) as illustrated in figure 2. The pathway may be broadened by degradation of CO₂ attack [3].

In our study, we introduce CaO swelling cement admixtures into ordinary Portland cement in order to occupying the pore space into cement matrix, and thus reduces the occurrence of pore space and compensates the shrinkage volume of the cement matrix. Ghofrani et.al [10] has observed the expansion behavior of cement paste admixtures with CaO and MgO and suggested that prerequisite for real matrix expansion is the formation of a spatially stable matrix by gelation and stiffening. The hydration rates of the swelling additives and structure-forming phase must be mutually harmonized with respect to time. In this conjunction, a distinction is made among three cases. See table 1 for the description and figure 3 for its visualization.

The objective of this study is to observe the effect of the presence of CaO swelling cement admixtures in the ordinary Portland cement paste against CO₂ attack (carbonation) under certain pressure and temperature.

![Development of total porosity](image1.png)
![Shrinkage of bulk volume](image2.png)

**Figure 1.** Conceivable consequences of hydration volume decrease (limit cases) [3].

![Formation rock Cement Casing CO₂ Perforation hole Gaps Desired CO₂ flow CO₂ infiltration into cement](image3.png)

**Figure 2.** Schematic indicating corruption by matrix dissemination through flawless cement (left) vs CO₂ infiltration along a pre-existent gaps between the cement rock and cement-casing interfaces (right) of a hypothetical wellbore [3].

**Tabel 1.** Three cases of sequential conditions in the structure-forming of cement Portland.
At high hydration rates of swelling additives, most crystallization is formed in the liquid phase of cement. In this situation, cement slurry does not support the crystallized swelling additives. The observed expansion is relatively small, or even none at all.

If the rate of hydration of the additive swelling is smaller than in the "case a", hydration occurs at the end of the plastic phase and at the beginning of the hardening period. Cement bodies that begin to harden can support crystallized swelling additives. When expansion occurs in the initial phase of cement cementing, non-hydrated cement is still available which can reunite the cement body which is previously separated by the additive swelling additive pressure.

At the rate of swelling additive which is relatively much lower than the rate in "case b", most expansion occurs at the phase where the cement has hardened. With increasing cement hardness, the risk of cement body cracking due to additive swelling additive pressure increases. If a crack occurs, then there is no more unhydrated cement that can reunite the cracked cement.

**Figure 3.** Instances of sequential conditions between gel quality advancement of the concrete (X), hydration rate of the swelling added substance (Y), and development conduct (Z) [3].

**Table 2.** Composition of cement pastes.

| Sample Number | Class-G Cement (gr) | %BWOC\(^a\) | CaO (gr) | 35%BWOC (gr) | 0.5WHSR\(^b\) (gr) |
|---------------|---------------------|-------------|----------|--------------|------------------|
| 1             | 300.0               | 0.0         | 0.0      | 0.0          | 132.0\(^c\)      |
| 2             | 300.0               | 5.0         | 15.0     | 105.0        | 157.5            |
| 3             | 300.0               | 10.0        | 30.0     | 105.0        | 165.0            |
| 4             | 300.0               | 15.0        | 45.0     | 105.0        | 172.5            |
| 5             | 300.0               | 20.0        | 60.0     | 105.0        | 180.0            |

\(^a\)BWOC : by weight of cement  
\(^b\)WHSR : water-hydratable solid-ratio  
\(^c\)Due to no presence of swelling cement WHSR = 40%
2. Experimental Methods

2.1. Sample preparation and design
Cement pastes used in this study were prepared from API Class-G oil well cement, distilled water, CaO powder and silica fumes. The composition of the pastes was described in table 2. The cement and/or admixtures pastes were mixed according to American Petroleum Institute Recommended Practice 10B (API RP 10B).

2.2. Samples to be cured in autoclave
For samples to be cured in autoclave, all the above mentioned pastes were poured in 50 mm (length) by 36 mm (diameter) cylinders, cured in atmospheric pressure and room temperature (26 ± 1°C) and demolded after 1 day, then cured in an autoclave filled with CO₂ (purity 99.99%), 1% NaCl (brine) solution at temperature of 50°C and brine pressure of 300 psi. The samples were fully immersed in brine during testing to simulate the environment which could give a severe detrimental effect to the samples due to presence of CO₂. Previous work by Kutchko et. al. [3] reveals that submerged cement sample in brine solution experienced much deeper penetration of CO₂ than unsubmerged cement sample exposed to CO₂ gas. The test duration was 2 days for one set of samples and 4 - 6 days for another set.

2.3. Volumetric expansion/shrinkage and compressive strength development
For volumetric expansion/shrinkage observation, the pastes mentioned in table 2 was poured into atmospheric uniaxial expansion cell immediately after mixing and observed for 24 hours in room temperature (26 ± 1°C). The cement slurry was poured into cylindrical expansion cell (30 mm in diameter) until 30 mm high occupying 21.21 cc of expansion cell. To compare between the volumetric expansion and the compressive strength development as describe in figure 3, the compressive strength of each of CaO added sample was observed using ultrasonic cement analyzer (UCA).

2.4. Characterization and analysis
The samples that cured in autoclave will be sliced and characterized by optical microscope to figure out the deep of carbonation into hardened cement paste. The face of sliced sample was previously sprayed with a 1%wt aqueous phenolphthalein solution to test the alkalinity which would indicate the presence of the unreacted portlandite (Ca(OH)₂). Macro photos of sliced surface of the samples were also obtained as visual observation result. XRD analysis was also conducted for the crushed intact sample and the corroded sample.

3. Results and Discussion

3.1. Volumetric expansion/shrinkage and compressive strength development
Figure 4 shows the result of this observation. Every sample contained CaO showed volumetric expansion. In general, sample with a high content of CaO exhibits low expansion period and high volumetric expansion. Higher composition of CaO also accelerated the compressive strength of cement paste since presence of CaO reduced the composition of silica flour acted as cement retarder.

We also observed that after 10 hours, all samples show a relatively low volumetric expansion rate and hence, it can be considered that volumetric expansion stopped about 14 hours before cement sample demolded. But all samples exhibited continue increasing of compressive strength along 24 hours observation.

3.2. Visual observation
After demolding, no crack was visually observed on the surface of demolded samples. Therefore, we can infer that when they are demolded, the samples were in plastic state because volumetric expansion occurred (confirmed by observation of volumetric expansion described above) while no crack was found.
However, after cured in the autoclave we could see that three samples have crack as shown in figure 5. The crack occurred in the samples which contained relatively high percentage of CaO and cured for relatively long period in the autoclave. The occurrence of crack revealed that: (a) CaO swells continued in the autoclave within the temperature higher than the room temperature, and (b) the samples achieved its hardened-state within autoclave curing period. Thus we can infer that the CaO expansion matched with “case b” described in figure 3. The samples experienced plastic-state expansion period and hardened-state expansion period consecutively.

3.3. Carbonation depth
Carbonation depth of the hardened cement paste was observed using an optic microscope. Figure 6 shows the typical penetration area and front occurred by CO₂ attack against all the samples. In figure 6a, we can see the distinguished CaCO₃ front lied between corroded and intact area for the sample with 5%wt CaO, which was not shown in the sample with 10%wt CaO in figure 6b. This meant that the distinct front of carbonation showed only at sample with 5% CaO admixtures. The higher composition of CaO reduces the composition of ordinary Portland cement, thus reduces the presence of Ca(OH)₂ as the precursor of CaCO₃. The presence of occurred CaCO₃ and the reduced Ca(OH)₂ confirmed by XRD.

As mentioned above, the formation of solid CaCO₃ decreases cement permeability and increases its compressive strength thus creates barrier effect to further CO₂ attack [9]. The consequence is the higher content of CaO, the deeper carbonation depth as revealed by microscopic observation against all samples.

![Graph showing expansion/shrinkage and compressive strength development of cement samples at atmospheric pressure and room temperature (26±2°C) with variation of CaO in %BWOC.](image)

**Figure 4.** Observed expansion/shrinkage and compressive strength development of cement samples at atmospheric pressure and room temperature (26±2°C) with variation of CaO in %BWOC.
Figure 5. External crack observed on hardened cement pastes. (a) Sample contained 15% CaO cured for 2 days in autoclaves. (b) Sample contained 15% CaO cured for 6 days in autoclave. (c) Sample contained 20% CaO cured for 6 days in autoclave.

Figure 6. Cross section of sample (a) 5% CaO and (b) 10% CaO cured for 6 days in autoclave. Note: (A) carbonated area, (B) intact area

4. Conclusions
CaO admixtures can compensate the API Class-G volumetric shrinkage, thus can prevent the formation of gap (microanulus) as path for CO₂ to attack the cement body. However, this kind of volumetric expansion is vulnerable to matrix destruction that leads to the occurrence of crack. Therefore, the volumetric expansion should be controlled to prevent occurrence of crack.

The experiment reveals that presence of CaO swelling admixtures in API Class-G cement slurry cannot reduce the depth of carbonation (CO₂ attack) into hardened cement body. “Case b” expansion mechanism happened in this experiment caused by rapid expansion (swelling) of CaO. Rapid swelling causes the expansion to be occurred in the plastic-state period. Slower swelling rate can give larger opportunity for CaO to swell within hardened-state period (“case c” expansion).

To figure out more about the role of CaO as swelling admixtures in API Class-G cement, a further study is required to compare the properties (i.e porosity, permeability, and mechanical properties) of the altered and unaltered zone of cement body with or without presence CaO admixtures.
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