The Role of MgO as Swelling Cements Admixtures under CO$_2$ Attack on API Class-G Cement

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Abstract. API Class-G Portland cement commonly put in as zonal isolation material in oil and/or gas well. Corrosion against the well zonal isolation material could lead to potential leakage of formation fluid such oil, gas, or water. It is widely known that ordinary Portland cement is thermodynamically unstable in CO$_2$ rich environment, which can be found in the CO$_2$ geological sequestration. CO$_2$ attack on API Class-G cement had been observed through experiments that simulate the down hole condition of Geological Sequestration of CO$_2$. Some of the experiment reveal the detrimental effect of CO$_2$ such as increase of porosity and permeability of cement sheath corroded by CO$_2$ attack. The degradation of API Class-G cement by CO$_2$ involves emergence and crystallization of CaCO$_3$ from Ca(OH)$_2$ which is formed during hydration of cement. In this experiment, we examine the role of addition of MgO swelling cement by weight fraction to mitigate the corrosion caused by CO$_2$ against downhole hardened API Class-G cement thus inhibits the occurrence of leakage path of CO$_2$. Observation for characterization and analysis by XRD, optical microscope, and cement paste uniaxial volumetric expansion presented in this paper. The conclusion will provide insights into design of carbonation resistant cement slurries using swelling cements admixtures.

1. Introduction
American Petroleum Institute (API) Specification 10A classifies Portland cement. One of them is Class-G which is the most common Portland cement applied for downhole zonal isolation in oil/gas well. Presence of CO$_2$ in the vicinity of well is inevitable in some geological formation especially in CO$_2$ geological sequestration. Rich CO$_2$ environment tend to corrode Portland cement and have been studied through experiments[1-8]. When Portland cement contacts with rich CO$_2$ environment, portlandite (Ca(OH)$_2$) or C-S-H phase in the Portland cement is carbonated to form calcium carbonate (CaCO$_3$) by following chemical reactions:

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

\[
\text{C-S-H} (\text{CaSiO}_r\text{H}_O) + y\text{H}_2\text{CO}_3 \rightarrow \text{Ca}_r\text{SiO}_r\text{yH}_O + y\text{CaCO}_3 + 2y\text{H}_2\text{O}
\] (2)

The emergence of solid CaCO$_3$ reduces cement permeability and improves its compressive strength thus creates blockade effect to further CO$_2$ attack [9]. This effect is possible due to their
emergence, CaCO$_3$ crystal need volume space for expansion as the CaCO$_3$ crystal occupy a larger volume than their precursor (portlandite)[7].

Above described that occupancy of void (pore) space by solid CaCO$_3$ is effective to blockade the further CO$_2$ 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 (figure 1):

1. An increase in cement porosity;
2. A decrease in the exterior dimensions of the cement body, the so-called matrix or bulk volume, comprising 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 CO$_2$ attack since it allows more carbonated water diffuses into cement matrix. The higher the starting porosity/permeability, the higher the penetration of CO$_2$[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 CO$_2$ attack) may occur along existing or introduced pathway (micro annulus) as illustrated in figure 2. The pathway may be widened by degradation of CO$_2$ attack[3].

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**Figure 1.** Practicable consequences of hydration volume shrinkage (boundary cases)[3].

**Figure 2.** Schematic indicating corruption by matrix dissemination through flawless cement (left) vs CO$_2$ infiltration along a pre-existent gaps between the cement rock and cement-casing interfaces (right) of a hypothetical wellbore [3].

In our study, we introduce MgO swelling cement admixtures into ordinary Portland cement in order to occupying the pore space in cement matrix, thus reduces the occurrence of pore space and compensates the shrinkage volume of the cement matrix. Ghofrani R et. al.[10] had observed the expansion behavior of cement paste admixed with CaO and MgO and suggested that pre-requested for real matrix expansion is the forming 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 (figure 3):

Case a: At high hydration rate of the swelling additive, crystallization occurs mainly in the fluid phase of the cement. In this state, the cement slurry provides no support for the crystallizing swelling additive. The components of the cement slurry merely displace one another; expansion of the exterior dimensions is either very slight or entirely absent.

Case b: If the hydration rate of swelling additive is lower than that in case “a”, hydration occurs mainly in the late plastic phase and at the beginning of cement hardening. The spatially stable matrix which forms provides a support for the crystallizing swelling additives.
During expansion in the initial phase of hardening, sufficient cement material capable of hydration is still available for mutually recombining the particles of binding agent which have been driven apart by the crystallization pressure of the swelling additive.

Case c: At a hydration rate of the swelling additive which is considerably lower than that for case “b”, the expansion occurs mainly in the hardening cement. With increasing degree of hydration in the cement, the hazard of matrix destruction by the crystallization pressure of the swelling additive thereby augments. If the triaxial strength is locally exceeded, macrocracks are formed and can no longer be closed, since no more or hardly any cement material capable of hydration is available.

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].

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

2. Experimental Section

2.1. Sample preparation and design
Cement pastes used in this study were prepared from API Class-G oil well cement, distilled water, MgO powder, and silica fume. The composition of the pastes are described in table 1.

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 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. The test duration was 2 days for one set of samples and 4 and 6 days for another set.
Table 1. Composition of cement pastes.

| Sample Number | Class-G Cement (gr) | MgO %BWOC | Silica Flour 35%BWOC (gr) | Water 0.5WHSR (gr) |
|---------------|---------------------|-----------|--------------------------|-------------------|
| 1.            | 300.0               | 0.0       | 0.0                      | 105.0             | 150.0             |
| 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             |

*BWOC: By Weight Of Cement
*WHSR: Water-Hydratable Solid-Ratio

2.3. Samples for volumetric expansion
For volumetric expansion observation, all the above mentioned pastes were poured into atmospheric uniaxial expansion cell immediately after mixed and observed for 24 hours in atmospheric pressure and room temperature (26±1°C). To compare between the volumetric expansion and compressive strength development as describe in figure 3, the compressive strength of each of MgO 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. Macro photos of sliced surface of the samples also obtained as visual observation result. XRD also conduct to confirm the phases that occurred due to carbonantion.

3. Result and discussion

3.1. Volumetric expansion and compression strength development
Sample number 1 shows volume shrinkage from the beginning of observation and stop shrinked after about 5 hours. Sample number 5 shows volume shrinkage within first 5 hours of observation and then start to expand after 9 hours. The complete result shown in figure 4. The result confirm that the MgO admixtures do swells. But until the end of 24 hours observation, even sample number 5 with 20% BWOC MgO admixtures experienced total volumetric shrinkage. The higher % BWOC of MgO, provides the larger amount of swelling admixture to compensate the shrinkage of hardened cement. Slow swelling rate of MgO admixtures provide enough time for cement to reach its plastic state, so larger period of swelling can continue within cement body. UCA result of all samples shows that compressive strength increased along 24 hours of observation and seems to be continue to increase after 24 hours.

3.2. Visual observation
None of the samples shows crack neither bulge on their surface before and after treated in the autoclave. This result is plausibly due to very small percentage of volumetric expansion occurred. This result also indicated that the swelling of MgO happens within plastic-state period of cement.

3.3. Carbonation depth
Carbonation depth into hardened cement paste was observed through optic microscope. The result is shown in figure 5 to figure 9. The inner face of sliced sample was previously sprayed with a 1% wt aqueous phenolptalein solution to test for alkalinity which would indicate the presence of still unreacted portlandite (Ca(OH)₂).
Figure 4. Observed expansion/shrinkage and compressive strength development of cement samples at atmospheric pressure and room temperature (26±5°C) with variation of MgO in %BWOC.

| MgO, %BWOC | 5 | 10 | 15 | 20 |
|------------|---|----|----|----|
| Expansion/shrinkage | | | | |
| Compressive strength | | | | |

Figure 5. The depth of carbonation on sample number 1 with variable curing time.
3.3.1. Carbonation on sample 1 (no MgO admixtures). The distinct front of carbonation is indicated by grey line between carbonated zone (left side) and unaltered zone (right side). The grey line is crystal of CaCO$_3$ that formed from Ca(OH)$_2$ as in equation (1). The composition of Ca(OH)$_2$ is relatively higher since no other admixtures that can reduce the ordinary Portland cement as the precursor of Ca(OH)$_2$. The solid crystal of CaCO$_3$ fills the leached pore space, thus provides a temporary, less permeable front to the acid attack. The formation of CaCO$_3$ has been reported to
decrease cement permeability and increase its compressive strength and less soluble than Ca(OH)$_2$[11].

3.3.2. **Carbonation on sample contained MgO admixtures.** The higher the composition of MgO, the shallower the penetration of carbonation. All samples containing MgO shows relatively very small carbonated area for 2 and 4 days of carbonation period in autoclave. All the 6 days carbonated samples shows distinguished area between carbonated area and intact area with deeper penetration of carbonation.

4. **Conclusion**

The experiment shows that the MgO admixtures do swells and the swelling occurs in the plastic-state of the cement. Due to slow swelling rate of MgO, the volumetric expansion possibly a “case c” condition as described in figure 3. Even swells, the MgO admixtures with composition 20% BWOC could not compensate the bulk shrinkage. Extended duration of observation needed to figure out whether the swelling of MgO admixtures still continue within hardened-state period of cement or not. Greater percentage of MgO composition can give opportunity for expanded MgO to compensate the bulk volumetric shrinkage. Hence it can applied as well zonal isolation that could prevent occurrence of gaps as described in figure 2.

Shallower carbonation depth in cement with MgO admixtures indicates that presence of MgO can inhibit the penetration of carbonation. However, further study is required to examine the role of MgO against properties (porosity, permeability, thermal deteriorate, and mechanical properties) of altered and unaltered zone of cement body with or without MgO admixtures.

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