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Effects of Storage of CO_2 on Multiaxial Mechanical and Hydraulic Behaviours of an Oilwell Cement

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ABSTRACT

The storage of CO_2 is an expected solution by the oil industry: using the petroleum wells as geological reservoirs is a very important and new research field. Durability of such storage has an importance to be predicted. This paper deals with the carbonation of an oilwell cement ("Class G" type) under temperature (90°C). In a first part, we will explain the protocol of fabrication of our samples and the conditions in which we realized our tests. We focus then on the evolution of cement carbonation over time. In a second part, we will present the results obtained by triaxial mechanical tests with permeability measurements at 90°C. Mechanical evolutions obtained for different confinement pressures show a remarkable decrease in permeability and an important increase of multiaxial strengths, which may exceed 100%. Some long-term tests will be also necessary to evaluate the effect of CO_2 on the chemical stability of cement.

INTRODUCTION

The objectives of this study are to obtain experimental characterisation of the effect of CO_2 on the multiaxial mechanical behaviour and on transport properties in oilwell cement under high temperature (in particular 90°C). This study is integrated in a general project for the sequestration of acid gases (for instance CO_2 and H_2S) in oil reservoirs developed by TOTAL E&P. Wells are normally constituted of steel tubes encircled with a cement casing. Cement is also used to stop the gas increase in the steel tube. Therefore, the degradation of this cement could provide a way of leakage of gases towards the surface, which can be considered harmful for the environment. This paper deals with the carbonation of oilwell cement ("Class G" type) under temperature.

The carbonation of a cement paste corresponds to physical and chemical mechanisms which result from the instability of portlandite and C-S-H phases in cementitious material under the influence of carbon dioxide CO_2. The dissolution of CO_2 in interstitial fluid causes a decrease of the concentration of OH^- ions, which in turn decreases the pH of pore solution. The carbonation of portlandite takes place as follows:

- Dissolution of portlandite to compensate the decrease of alkalinity

$Ca(OH)_2 \rightarrow Ca^{+2} + 2OH^-$ (1)

● Formation of calcite

$Ca^{+2} + CO_3^{-2} \rightarrow CaCO_3$ (2)

The global reaction can be written as follows:

$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$ (3)

The carbonation of the C-S-H leads to the formation of calcite and silica gel according to the reaction below [Thiery, 2005]:

$C_xS_yH_z + x\ H_2CO_3 \rightarrow x\ CaCO_3 + y\ SiO_2.t.H_2O + (x-t+z)\ H_2O$ (4)

The initial carbonation of portlandite is usually faster than that of the C-S-H but after some time this becomes no longer true because of the formation of microcrystal layers of $CaCO_3$ on the surface of $Ca(OH)_2$. [Thiery et al, 2007]. Formation of crystalloid forms of calcite (Calcite, Vaterite and Aragonite) is accompanied with an increase of solid phases in the cementitious material as these forms have higher molar volumes than portlandite. Therefore, precipitation of carbonates of calcium will help to fill the pores spaces as a result condensing the cement paste. Many authors have proved that carbonation leads to a drop of porosity in cementitious materials. Arandigoyen [Arandigoyen et al, 2005] found that the porosity was decreased of about 10% after the carbonation and that distribution of the pores sizes trends towards smaller pores. The volumetric reduction of pores was proportional to the quantity of carbonated $Ca(OH)_2$. Houst [Houst, 1993] studied the effect of carbonation on the porosity and on the volumetric mass for cement pastes in function of the water by cement (W/C) ratio: the effect of carbonation on the porosity becomes weaker as well as on the volumetric mass. Johannesson [Johannesson et al, 2001] observed that the carbonation modifies the specific surface slightly. The specific surface obtained for a carbonated and non-carbonated mortar was 29.4 and 31.8 m²/g respectively. Houst [Houst, 1993] has calculated the specific surface for carbonated and non-carbonated hardened cement pastes in taking into consideration a variable relative humidity between 9% and 44%. The obtained results are graphically plotted figure 1. The porosity of cement paste is modified by carbonation. What are the effects on porosity, permeability and mechanical behaviors with the temperature increase ?

Thiery [Thiery, 2005] found that the carbonation has a slight influence on the cementitious material permeability. The author attributes this effect to the creation of capillary macroporosity, which conceals the effect of the decrease of porosity. On the other hand, Garcia [Garcia et al, 2007] found that the carbonation decreases water permeability of concrete. This could be explained by the creation of finer and more disconnected pores in carbonated samples. De Schutter [De Schutter et al, 2004] also concluded that the carbonation reduces the permeability of concrete made by Portland cement, and it is exactly the contrary for concretes based on cement with slag. There are no sufficient studies in this domain. Furthermore, very few authors have studied the impact of temperature on the carbonation process. Lo [Lo et al, 2007] found that hot curing leads to a carbonation rate higher than that of a normal temperature curing, maybe because long time normal curing confers to concrete denser pores than in the case of hot curing due to good hydration of cement.

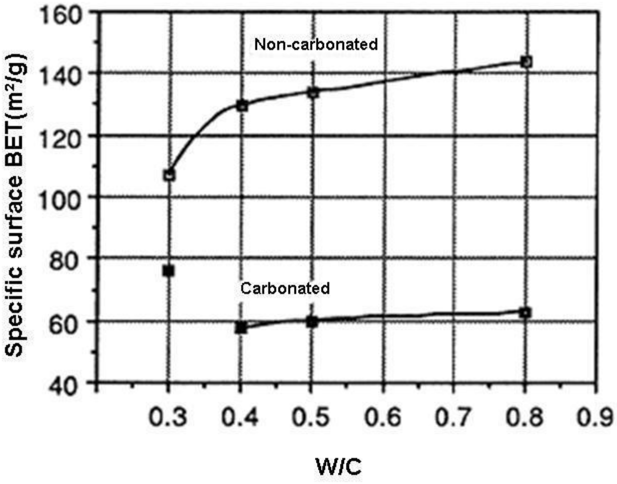


Fig. 1. Specific Surface for Carbonated and Non-Carbonated Hardened Cement Pastes vs. W/C Ratio [Houst, 1993].

In a first part, we will explain the protocol of fabrication of our samples and the conditions in which we realized our tests. We will focus then on the evolution of cement carbonation over the time by using the phenolphthalein indicator to detect carbonated zone. In a second part, we will present the results obtained by the way of triaxial mechanical tests with permeability measurements, performed at a temperature of 90°C. We will make a comparison between these results and we will give at the end some conclusions extracted from curves.

II. PROTOCOL OF FABRICATION

The study was realized on classic cement used in petroleum domain. The composition of the cement paste is illustrated in the table 1. Two additives, an antifoaming and a dispersant were added for the fabrication of the cement paste.

Table 1. Composition of the Cement Paste

Component	Quantity (Kg/m3)
Cement G class	1308.3
water	578.5
D175 (antifoaming)	5.2
D 80 (dispersant)	8.1
Water/Cement ratio	0.44

Cement and additives were supplied by TOTAL©. Special moulds of stainless steel were used (figure 2). 96 samples (Ø36, H=100 mm) were obtained from the same batch, of which we get later 210 samples (Ø 20, H 22 mm).

Fig. 2. Moulds Used for Obtaining Samples of (Ø36, H=100) mm

After a mixing at ambient temperature, the moulds were kept for 72 hours in distilled water at 90°C saturated with lime; this temperature is chosen to simulate the real conditions in wells where the gas is supposed to be stocked. After a rapid demoulding, samples were kept also in distilled water at 90°C saturated with lime for one month; this period of maturation for one month has been adopted for getting a stabilization of the microstructure, of the evolution of mechanicals properties and a quasi-complete hydration of samples.

III. PHASE OF CARBONATION

Experimental setup:

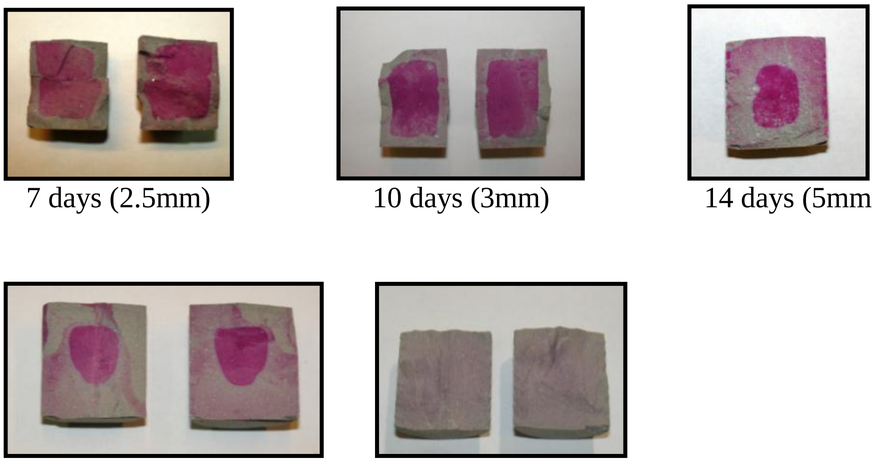
The process of carbonation was performed in a climatic chamber where both temperature and relative humidity are controlled at the same time. In addition, this type of chamber allows the attachment of a bottle of gas, which is necessary to realize this test of accelerated carbonation (figure 3).

Fig.3. Climatic Chamber Attached with a Bottle of CO_2

The climatic chamber has been regulated at a temperature of 90°C and a relative humidity of 65%, which are optimal conditions to get a faster and maximal carbonation. The process of carbonation was launched by injecting 100 cm^3/min of CO_2 in the climatic chamber; this rate was adopted according to literature [Sisomphon and al, 2007]. One sample was regularly taken from the climatic chamber to control the development of the carbonation front.

Kinetics of carbonation:

The aim is to detect the progress of carbonation over time. For this purpose, samples were split according to their longitudinal axis and then, phenolphthalein is applied as an indicator which change into pink if the pH>9.5, and it remains colorless in the carbonated zone where the pH is less than 9.5, because of the decrease of alkalinity due to the decomposition of portlandite. Figure 4 shows the evolution of carbonation over time in samples by using the phenolphthalein.



7 days (2.5mm) 10 days (3mm) 14 days (5mm)

21 days (6mm) 28 days (10mm)

Fig. 4. Evolution of Carbonation over Time

The evolution of carbonation is represented in figure 5, which gives the speed of carbonation in addition. Carbonation depth was measured by taking the average of the four sides of every sample according to phenolphthalein indicator. A quasi-linear relation between the depth of carbonated front and the time is remarked; this means that carbonation process was not hindered by the formation of the calcite, perhaps because the radius of samples (10 mm) is not enough to let us remark a slowing-down of carbonation speed. In literature, carbonation is proportional to square root of time [Parrott, 1987] but this is in case of atmospheric carbonation that may take many years.

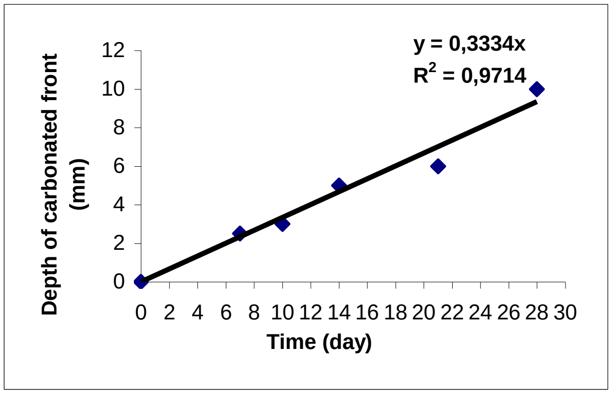


Fig. 5. Evolution of Carbonation over Time

IV. MULTIAXIAL MECHANICAL CHARACTERIZATION

This stage aims to detect the influence of carbonation on the evolution of hydro-mechanical behavior of oilwell cement paste at a temperature of 90°C. Samples used for triaxial tests were subjected to radial carbonation by covering their upper and lower surfaces with aluminum scotch tape. Tests were realized on samples carbonated at different rates (3, 6, and 10 mm), besides, on sound samples. For every rate of carbonation, four triaxial tests were carried out correspond to four values of confining pressure (Pc=0, 3, 10 and 20 MPa). An interstitial pressure of 2.5 MPa was applied for tests with confinement different from zero and the permeability was measured in these cases just before applying deviatoric stress.

Experimental devices

The Experimental devices, developed by our laboratory, are represented in figures 7 (a, b, c). The set of devices is composed of:

- A triaxial cell
- An oven
- Three Gilson's pumps for the application of confinement and deviatoric pressure, and also for the injection of interstitial fluid.
- A data acquisition system.

a. Set of Devices for Triaxial Tests

b. Three Pumps Gilson

c. Triaxial Cell in the Oven

d. Installation of a Sample in the Cell

Fig. 6. Experimental Devices Used for the Realization of Triaxial Tests and Permeability

Axial strains were measured by means of 2 displacement transducers (LVDT); on the other hand, we used a circumferential collar in order to measure lateral deformations. The figure 7 (d) shows the installation of LVDTs and a collar on a sample for measuring its deformations.

Protocol of tests realization:

The same stages were adopted for all tests in order to get all the results in the same conditions.
The protocol consists of the following steps:

- Putting the sample, preserved at 90°C in the climatic chamber, in a sheath of Viton then in the cell.
- Installing the collar and LVDT with the calibration.
- Filling the cell by the oil for confinement then closing it.
- Installing the cell in the oven regulated at 90°C.
- Waiting for the homogenization of temperature in the whole cell within 24 hours.
- Application of confining pressure.
- Injection of distilled water at 2.5 MPa and measuring the permeability after getting a stable flow.
- Turning off the valve of fluid exit in order to get a homogenate interstitial pressure (2.5 MPa).
- Finally, application of the deviatoric stress.

Permeability- protocol of measurement:

Measurements of permeability were carried out in function of confining pressure, the permeability has been always measured before the application of deviatoric stress. It is obtained by the application of Darcy’s law, which is correct in case of a laminar flow in saturated porous media. No physical or chemical interaction is supposed between the fluid and the media. In our case, fluid used for measuring the permeability is distilled water. Permeability is deduced from equation 5:

$$K = \frac{\mathrm{Q}}{\mathrm{S}} \cdot \frac{\Delta \mathrm{X}}{\Delta \mathrm{P}} \cdot \mu \qquad (5)$$

where K is the intrinsic permeability (m²), ($1\mathrm{m}^2 = 10^{+12}$ darcy), Q the volumetric flow (m^3/s), S the cross section of the sample (m²), ΔP/Δx the gradient of pressure (2.5 Mpa / 22 mm in our case), μ the dynamic viscosity of fluid (0.000315 Pa.s for water at 90°C).
The values of permeability for different carbonation rates and different confining pressures are summarized in table 2. Tests made on sound samples give results very close to those of 3 mm carbonated samples. No changes of permeability were observed between the two cases. This means that the rate of carbonation was not enough to have remarkable changes in permeability, or because big pores are not yet filled by the calcite.

Table 2. Values of permeability in function of carbonation rate and confinement pressure

	Pc=3MPa	Pc=10MPa	Pc=20MPa
3mm of carbonation	K=1.61E-18 m²	K=9.5E-19 m²	K=5.98E-19 m²
6mm of carbonation	K=7.97E-19 m²	K=4.07E-20 m²	K=1.79E-20 m²
10mm of carbonation	K=4.94E-20 m²	K=1.32E-20 m²	K=8.82E-21 m²

The decrease of the permeability with the increase of the confinement is due to the diminution of the space of flow of the fluid and maybe also because of the reduction of degree of interconnection of the porous network. The reduction of permeability over carbonation comes from the creation of finer and more disconnected pores.The variation of permeability in function of confining pressure and with the state of material is graphically illustrated in the figure 7. It has been well noted the high influences of carbonation on permeability: a diminution of 97% is obtained for a confining pressure of 3 MPa. The confining pressure has a slight effect on the permeability of completely carbonated samples because of the low porosity of these samples, so that the circulation of fluid is very limited in the pores.

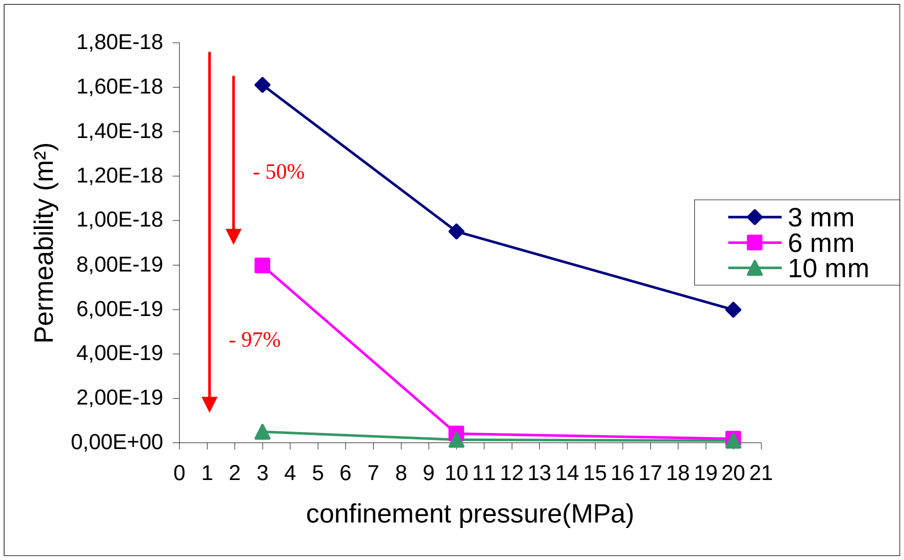


Fig. 7. Evolution of Permeability in Function of Confining Pressure and Carbonation Ratio.

Triaxial mechanical tests at 90°C

Uniaxial and triaxial mechanical tests have been performed [(0, 3, 10 and 20) MPa of confining pressure] in order to characterize the multiaxial mechanical behaviour of studied cement at a temperature of 90°C and under an interstitial pressure Pi=2.5 MPa.

Tests have been always done on samples (Ø 20mm, H 22 mm), classified in four groups:

- Sound samples.

- 3mm carbonated samples.
- 6 mm carbonated samples.
- Completely carbonated samples.

Figure 8 represents the failure strengths obtained for sound and carbonated samples. Each point is obtained by realizing one uniaxial or triaxial test at a temperature of 90°C. For the four groups, the uniaxial resistances are close to those at Pc= 3MPa, because there is an interstitial pressure of 2.5 MPa for the second case. Then, the strengths increase over the increase of confinement pressure and the depth of carbonation front and especially for the completely carbonated samples where the material is more homogeneous. A remarkable increase of resistance between sound and completely carbonated samples for all values of confinement pressure is clearly highlighted. Formation of calcite has a beneficial effect on mechanical properties of cement. In addition, its precipitation in pores reduce both porosity and permeability of cement which in turn increase the compaction of the microstructure, and this leads to a better mechanical resistance.

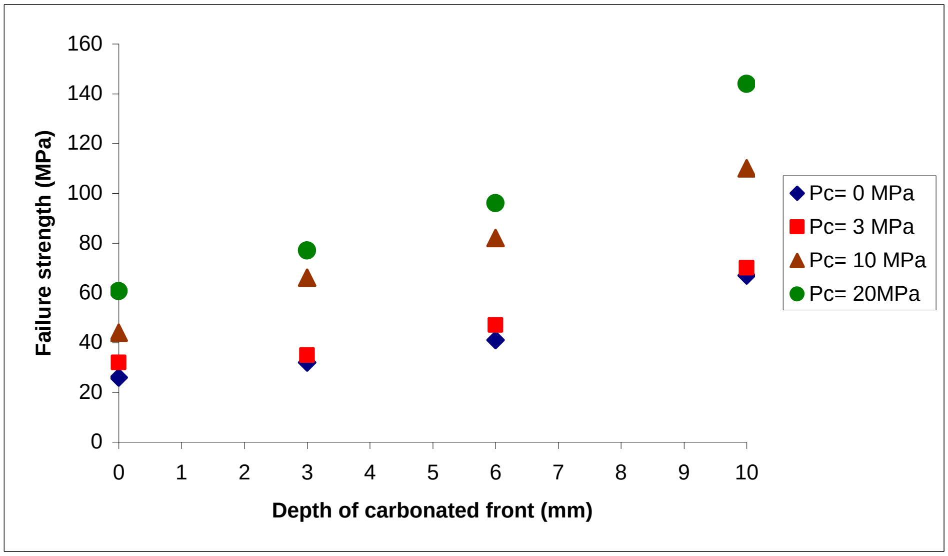


Fig. 8. Maximal Uniaxial and Triaxial Resistance of Oilwell Cement for Different Rates of Carbonation in Function of Confinement Pressure at a Temperature of 90°C

CONCLUSIONS

- The carbonation leads to a microstructure evolution of the hydrated cement, coming from the precipitation of calcium carbonates in the pores of cementitious material, which trends to densify the cement paste.

- For the used oilwell cement in this study, we have shown a remarkable diminution in permeability for samples tested at a temperature of 90°C. This diminution reaches a value of 97% for completely carbonated samples in comparison with the 3 mm carbonated samples. This comes from the consolidation of cementitious material because of the precipitation of $CaCO_3$, which has a molar volume bigger than that of portlandite.

- The permeability decreases when confining pressure increases. This may be due to the closure of micropores and microcracks which in turn reduces the degree of connection between pores. In case of 100% carbonated samples, confining pressure has a little effect on permeability because in these samples, the circulation of fluid in pores becomes very limited to be affected by the confinement pressure.

- The carbonation of our cement has a positive effect on mechanical strength. This may be related to the decrease of porosity in cementitious material and in addition, the formation of calcite which can be considered as a good binder.

- An increase of resistances varies between 100% to 150% when compared with the initial resistance of sound samples, but the biggest gain of resistance is obtained for the 10 mm carbonated samples in comparison with gain obtained between 6 mm and 3 mm carbonated samples. This may be related to the increase of the homogeneity of these samples which are 100% carbonated. This increase exceeds what was mentioned in literature (30-50 %) obtained in ambient temperature [Hornain, 1976, Lea, 1970].

- Some long-term tests will be also necessary to evaluate the effect of CO_2 on the chemical stability of cement. Such results are important to be taken into account in the prediction of long time behaviour of CO_2 storage.

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