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Dossier

Closure and Abandonment of Oil and Gas Wells
Fermeture et abandon des puits de pétrole et de gaz

Well Technologies for CO_2 Geological Storage: CO_2-Resistant Cement

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Résumé — Technologies de puits pour le stockage géologique du CO_2 : ciment résistant au CO_2 — Le stockage souterrain du CO_2 est actuellement considéré comme la voie la plus efficace pour une séquestration sure et à faible coût. Cette nouvelle application exige une étanchéité du puits à très long terme. La rupture de la gaine de ciment dans l'intervalle entre le cuvelage et la formation géologique peut créer des chemins préférentiels favorisant la fuite du CO_2 vers la surface avec des vitesses probablement supérieures à celles pouvant être provoquées par les fuites au travers des formations géologiques. Il en résultera une perte économique, une réduction de l'efficacité du stockage de CO_2 et la remise en cause du champ pour le stockage de CO_2. Ce risque potentiel de fuites soulève des questions quant à la bonne isolation du puits à long terme et à la durabilité du ciment hydraté utilisé pour isoler l'annulaire entre les intervalles de production et d'injection dans les puits de CO_2. Nous proposons une nouvelle procédure expérimentale et une méthodologie pour étudier la réactivité des systèmes CO_2-Eau-Ciment en simulant les interactions du ciment pris avec le CO_2 injecté à l'état supercritique dans des conditions de fond de puits. Les conditions utilisées pour ces expériences sont de 90°C et 280 bars. L'évolution des propriétés mécaniques et physico-chimiques du ciment Portland est mesurée dans le temps sur une période maximale de six mois. Les résultats sont comparés à ceux obtenus par une étude similaire sur un nouveau ciment résistant au CO_2, la comparaison étant prometteuse pour ce nouveau matériau.

Abstract — Well Technologies for CO_2 Geological Storage: CO_2-Resistant Cement — *Storing carbon dioxide (CO_2) underground is considered the most effective way for long-term safe and low-cost CO_2 sequestration. This recent application requires long-term wellbore integrity. A CO_2 leakage through the annulus may occur much more rapidly than geologic leakage through the formation rock, leading to economic loss, reduction of CO_2 storage efficiency, and potential compromise of the field for storage. The possibility of such leaks raises considerable concern about the long-term wellbore isolation and the durability of hydrated cement that is used to isolate the annulus across the producing/injection intervals in CO_2-storage wells.*

We propose a new experimental procedure and methodology to study reactivity of CO_2-Water-Cement systems in simulating the interaction of the set cement with injected supercritical CO_2 under downhole conditions. The conditions of experiments are 90°C under 280 bars. The evolution of mechanical, physical and chemical properties of Portland cement with time is studied up to 6 months. The results are compared to equivalent studies on a new CO_2-resistant material; the comparison shows significant promise for this new material.

INTRODUCTION

Storing carbon dioxide underground is considered as the most effective way for long-term safe and low cost CO_2 sequestration (Sarmiento and Gruber, 2002; Gielen, 2003). There are three main types of geological reservoirs with sufficient capacity to store captured CO_2: depleted oil and gas reservoirs, deep saline aquifer reservoirs and unminable coal beds (Bachu, 2000). The reservoirs need to be at a depth typically greater than 800 m so that the CO_2 is in a supercritical state *i.e.* at a temperature and a pressure above its critical point (31.6°C, 7.3 MPa). Piping CO_2 for underground injection is not a novel concept and is already often used for the purposes of enhanced oil and gas recovery (Power *et al.*, 1989; Mizenko, 1992; McDaniel Branting and Whitman, 1992). However, this application of CO_2 injection is not intended for long-term storage, which is a more recent concept requiring a long-term wellbore integrity strategy to be developed.

The construction of CO_2 injection wells starts with drilling followed by well completion before starting CO_2 injection operations. In the framework of well completion, the cementation phase guarantees well isolation from the reservoir to the surface and isolation between geological formations. A crucial technical problem in CO_2 sequestration is the chemical resistance of cement to CO_2 over time. Conventional materials used for well isolation for oil or gas production are Portland-based cement systems. These systems present the advantage of being low cost and efficient for conventional well construction. However, cement is known to be thermodynamically unstable in CO_2-rich environments. It tends to degrade rapidly, once exposed to such acid gases by reacting with calcium hydroxide formed from hydrated calcium silicate phases (Bruckdorfer, 1986). As carbonates are dissolved in low pH environment, the cement-carbonation process will not become a self-plugging effect in the cement sheath. Some data have been already published under this type of environment (Onan, 1984). Moreover, recent analysis on one cement sample collected in CO_2 enhanced oil recovery well (SACROC) have been done. Although a similar carbonation process is mentioned, the cement sample demonstrates that at least in one location, Portland cement has retained its structural integrity after 30 years in near-CO_2-reservoir environment (Carey *et al.*, 2006). Furthermore, recent experimental studies on the interfaces cement/formation and cement/casing were led and showed that similar chemical reactions are involved (Jacquemet *et al.*, 2005; Duguid *et al.*, 2006).

Long-term isolation and integrity of CO_2 injection wells clearly must be improved to ensure long-term environmental safety. In processes involving the injection of CO_2 for enhanced oil recovery, a number of failures have been reported due to poor cement properties. Failure of the cement, in the injection interval and above it, may create preferential channels for carbon dioxide to migrate back to the surface. This may occur on a much faster timescale than geological leakage.

Optimization of advanced systems allowing long-term well isolation is critical to allow safe and efficient underground storage for carbon dioxide and thus keep the greenhouse gas out of the atmosphere for long duration.

This article presents the results of a comprehensive study on the degradation of cement in simulating the interaction of the set cement with injected supercritical CO_2 under downhole conditions. The methodology and the equipment are described for testing conventional Portland cement and measuring the evolution of its alteration process with time under CO_2 conditions. The results are compared to equivalent studies on a new CO_2-resistant material.

1 EXPERIMENTAL PROCEDURE

1.1 Sample Preparation

The effects of carbonic acid on hydraulic Portland cements are studied using cylindrical samples of 1.27 cm diameter × 2.54 cm length and 1.27 cm diameter × 5.08 cm length.

All cement slurries are prepared according to API Specification 10, Section 5 (Recommended Practice for Testing Well cements, 1997) and using fresh water. Before mixing the slurry, an antifoam agent, a dispersant and a retarder are added to the mix water to optimize the main slurry properties. The cement samples are cast by slowly pouring the degassed slurry down the cubic mold before launching the curing chamber. The samples are cured for 72 hours at 207 bars and 90°C. The cubic samples are removed from the moulds and placed in water. Then the cubic samples are cored to obtain 1.27 cm diameter cylindrical samples. Finally, the core samples are cut to 2.54 cm or 5.08 cm length.

1.2 Experimental Reactor

Cement carbonation is performed under static conditions using the following experimental set-up and procedure. The static conditions are considered as realistic simulation of the CO_2-exposure conditions at the formation/cement sheath interface, except around the perforations where the exposure is under a dynamic state during CO_2 injection. So static conditions have been selected as representing downhole conditions. Water with a pH of about 8 is used rather than saline solution to provide more severe conditions as CO_2 is highly soluble in pure water (Spycher and Pruess, 2005).

The experimental set-up accommodates temperatures from 30°C to 300°C and pressure from 1 to 500 bars to cover the targeted application ranges. Experiments with wet supercritical CO_2 and with water saturated by dissolved CO_2 are performed in a titanium vessel *(Fig. 1)*. The cell volume is 126 ml, the ratio of sample volume/water volume is 1.2, and the one of sample volume/CO_2 volume is 0.7. The samples are collected all together at the end of each experiment. Therefore, these ratios are constant during each CO_2 test at each duration. The CO_2 pressure is monitored and maintained constant during the whole test duration by CO_2 injections if pressure drops of a few bars. More technical features of this CO_2-equipment are described in details in Barlet-Gouédard *et al.* (2006). The test conditions are fixed for all experiments to 90°C and 280 bars. The tests are performed at different durations: half-day (13 hrs), 2 days (44 hrs), 4 days (88 hrs), one week (188 hrs), 3 weeks (523 hrs), 6 weeks (1006 hrs) and 3 months (2033 hrs). For each experiment, the volume content of water is about half of the volume of injected CO_2 at atmospheric pressure and room temperature. There is no fluid mixing in the vessel. At 90°C and 280 bars, water is liquid while CO_2 is supercritical (Hollister, 1981; Blencoe *et al.*, 2001; Blencoe, 2004). At these conditions, the water mole fraction in the supercritical CO_2 phase is about 1.8‰ and the CO_2 mole fraction in water is 2.25% (Spycher *et al.*, 2003). Furthermore, some experimental data available in the literature show that pH of water saturated with CO_2 is comprised between 2.8 and 3 under such severe conditions (Toews *et al.,* 1995)

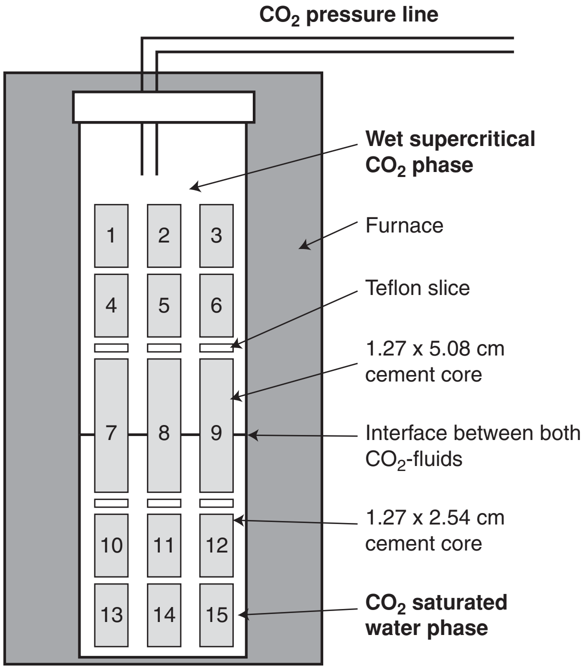

Figure 1

View of the three levels of the 1.27 cm diameter cylindrical core samples for CO_2 experiments in the titanium simple cylinder vessel. Note that the three cores at the middle are not cut in order to study the interface between wet supercritical CO_2 and CO_2-saturated water fluids.

1.3 Test Procedure

The experimental set-up is designed to get a quick overview of the behavior of cements with supercritical CO_2. The set-up simultaneously obtains data for the three situations: CO_2 dissolved in water (lower part of the reactor), water dissolved in CO_2 (upper part of the reactor), and interface between the two media. For this experiment, core samples are disposed in three crowns *(Fig. 1)*. The samples located in the lower part of the reactor (six samples of 1.27 cm diameter × 2.54 cm length) are submerged in water while the upper crown (six samples of 1.27 cm diameter × 2.54 cm length) is completely exposed to CO_2. The intermediate crown simulates the conditions at the water-CO_2 interface. This crown is made of three samples of 1.27 cm diameter × 5.08 cm length, allowing studying the interface between both CO_2-fluids *(Fig. 1)*. The pressurization and depressurization phases of the CO_2 experiments follow a well-defined procedure described by Barlet-Gouédard *et al.* (2006).

1.4 Alteration Measurements

Carbonic-acid corrosion on the core samples is indirectly measured: the pH of water in equilibrium with the cement sample (*i.e.* the pH of the pore solution) measured at atmospheric pressure and ambient temperature, the weight and volume change of the cores, the change in density and porosity, the evolution of compressive strength, the thickness of the carbonation front, and microscopic measurements.

The alteration front is determined in cutting each core sample to prepare a thin section in the axial plane. The front is measured both directly and with a scanning electron microscope averaging several zooms.

The microscopic evolution is determined by scanning electron microscopy (SEM) and back-scattered electron (BSE) analysis through the entire core section. Additional SEM-EDS (Energy Dispersion Spectroscopy) analyses and X-ray imaging are performed in the same material with a quantitative EDS device (Quantex on Hitachi 2500).

Compressive strengths are determined with an ADAMEL press. As length-to-diameter ratio of the cylindrical samples was always equal to two, the resulting strengths are directly used. The compressive strength of each core sample is measured before and after CO_2 attack without additional treatment.

The porosity variation is measured with a mercury-porosimetry instrument. Mercury intrusion porosimetry (MIP) estimates the pore size over a wide range (theoretically from 0.003 μm to 360 μm). MIP measurements were carried out by two different laboratories on 1.27 cm diameter by 2.54 cm length cylindrical samples, dried at 100°C at standard atmosphere during 60 hours. It is noteworthy that these measurements are performed on whole sample core and not only in the altered zone. Two intrusion-extrusion cycles were

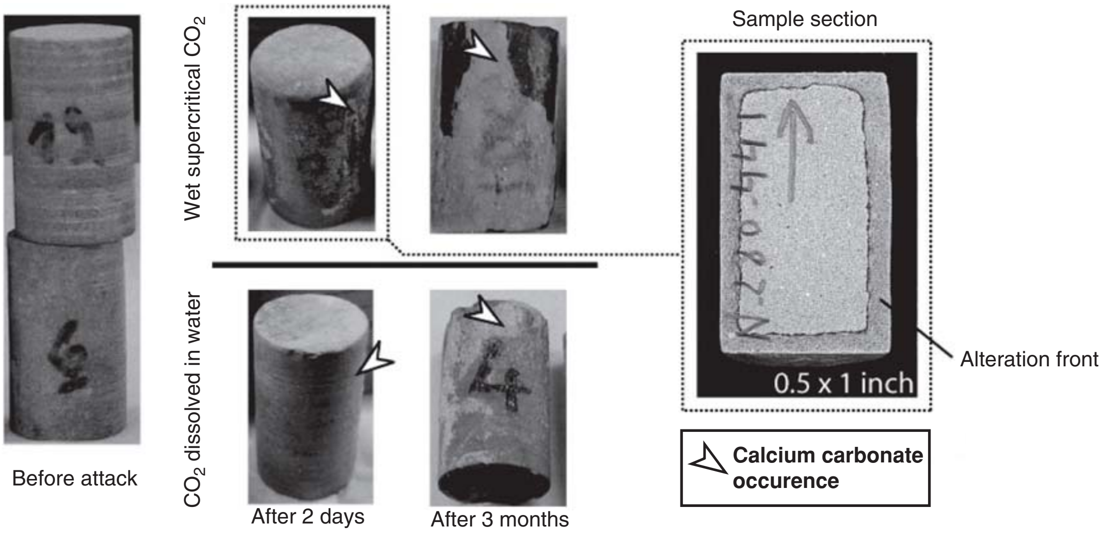

Figure 2

Core integrity and alteration front observed with Portland cement at 1.9 g/cm^3 after two days and three months at 90°C and 280 bars in carbon dioxide fluids.

performed to determine irreversible and reversible intrusion volumes. After an additional extrusion-intrusion cycle, the initial volume was always reached to within a small error, indicating that no significant damage occurred to the sample during the first intrusion. The maximum intrusion pressure is 2 kbar (corresponding to a minimum pore entrance size of 6.2 nm), and the equilibrium time is 20 seconds.

2 RESULTS

We present in this chapter the results of our kinetic study on conventional Portland cement (class G, density equal to 1.9 g/cm^3) and a first generation of CO_2-resistant cement (density range between 1.5 and 2.0 g/cm^3) tested under CO_2 exposure up to 3 months. Preliminary results on samples tested during 6 months are also shown.

2.1 Alteration Process

Alteration of Portland cement during CO_2 attack is a very effective process. A sharp alteration front is clearly observed at the rim of the samples already after half-day of CO_2 attack. The thickness of this alteration front increases with time from about 1-2 mm after 44 hrs *(Fig. 2)* to 5-6 mm after 3 weeks of attack. After 6 weeks, the front reaches the central part of the samples (~7 mm deep). After 3 months, the significantly carbonated samples exhibit a strong degradation as attested by cracking occurrences *(Fig. 2)*. After 6 months, a high deterioration is observed in both CO_2 fluids: a spalling effect is observed on the sample core *(Fig. 3)*.

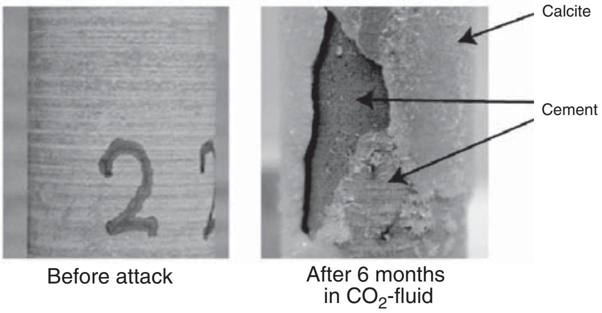

Figure 3

Portland cement samples before experiment and after 6 months at 90ºC and 280 bars in carbon dioxide fluids (sample located at the interface between both CO_2 fluids). Note the spalling effect observed on the sample core after 6 months of test.

Portlandite [$Ca(OH)_2$] and Calcium Silicate Hydrates (CSH) of set cement are progressively consumed to produce calcium carbonates (aragonite, vaterite and/or calcite), silica amorphous gel and water. Back-scattered electron images allow distinguishing different zones in the attacked Portland cement *(Fig. 4)*. This geometry in different concentric zones is systematically observed at all test durations. From the rim towards the core of the sample, the cement sample consists of a carbonated zone, a carbonation front, a dissolution front and a non-carbonated zone. Such geometry has also been deciphered with SEM images (Kutchko *et al., 2006*).

The carbonated zone contains calcium carbonate, silica gel and calcium-depleted calcium silicate phases. Then, the carbonation front is a thin front (50 to 100 μm-large) of very

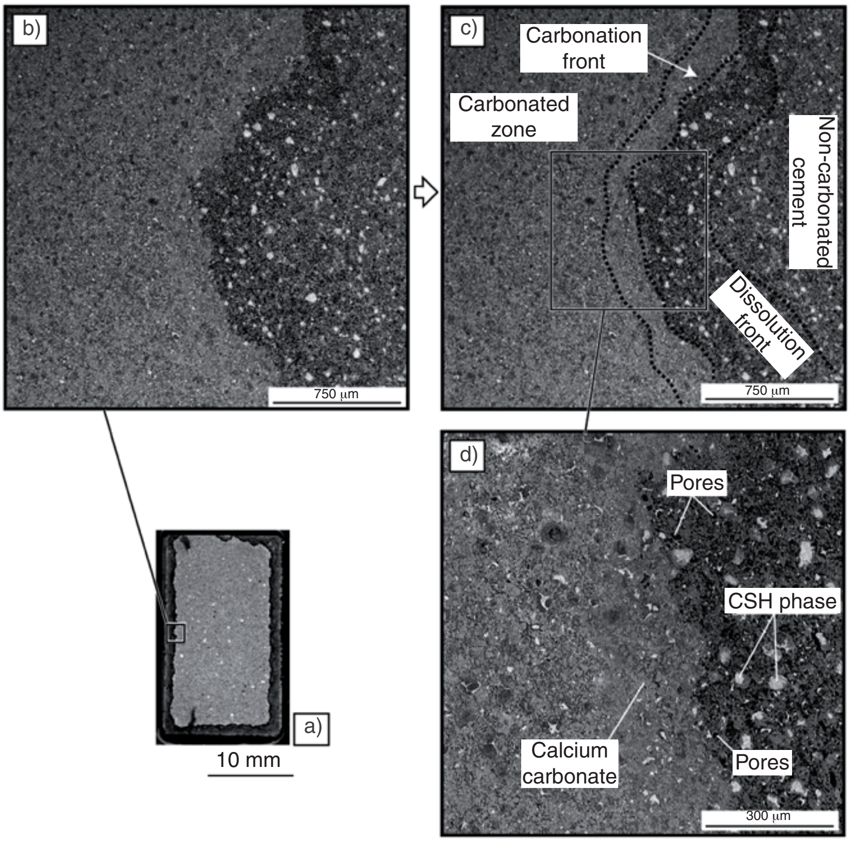

Figure 4.

a) Section of a Portland cement core tested during two days at 280 bars and 90°C in CO_2-saturated water. Note the occurrence of the concentric carbonated zone.
b), c) Back-scattered electron image showing the different zones in a Portland cement sample after CO_2 attack. See text for explanations.
d) Zoom on the low-porosity carbonate front and the high-porosity front that are chemical reaction fronts.

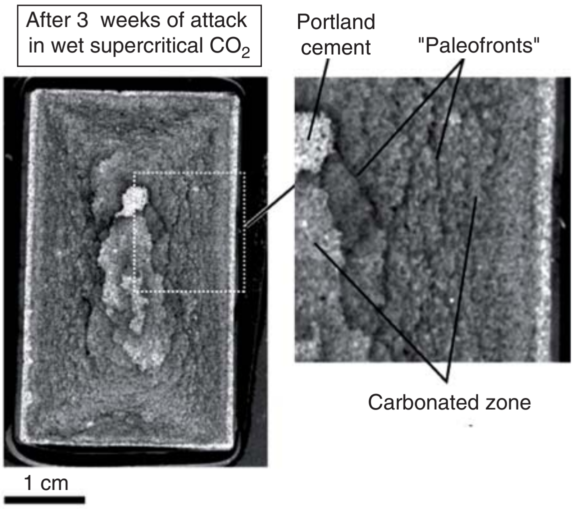

Figure 5

Section of a Portland cement sample tested during 3 weeks at 280 bars and 90°C in wet supercritical CO_2 fluid. The occurrence of carbonation front and dissolution front relicts (the so-called "paleofronts") is highlighted.

low porosity, and mainly made of calcium carbonates. It contrasts with the dissolution front that is a zone of high porosity where calcium silicate phases progressively dissolve. Finally, the uncarbonated zone is the internal part of the cement. It is noteworthy that the dissolution front and the carbonation front are chemical reaction fronts. The dissolution front is the zone in which Portland cement phases (portlandite and calcium silicate phases) react with CO_2 to form calcium carbonates forwards in the carbonation front. At longer test duration, this particular geometry of reaction fronts is translated towards the central part of the samples, and relicts of these fronts are commonly observed backwards in the carbonated zone. This complex series of "paleofronts" *(Fig. 5)* marks several physical discontinuities in the sample and participate to the weakening of Portland cement in terms of mechanical properties.

A first generation of CO_2-resistant material tested under similar conditions contains a reduced amount of Portland cement and CO_2 - inert particles. Samples of different density (between 1.5 and 2.0 g/cm^3) have been tested in both CO_2-fluids. In contrast with Portland cement, a low amount of calcium carbonate precipitates in the samples of 2 g/cm^3,

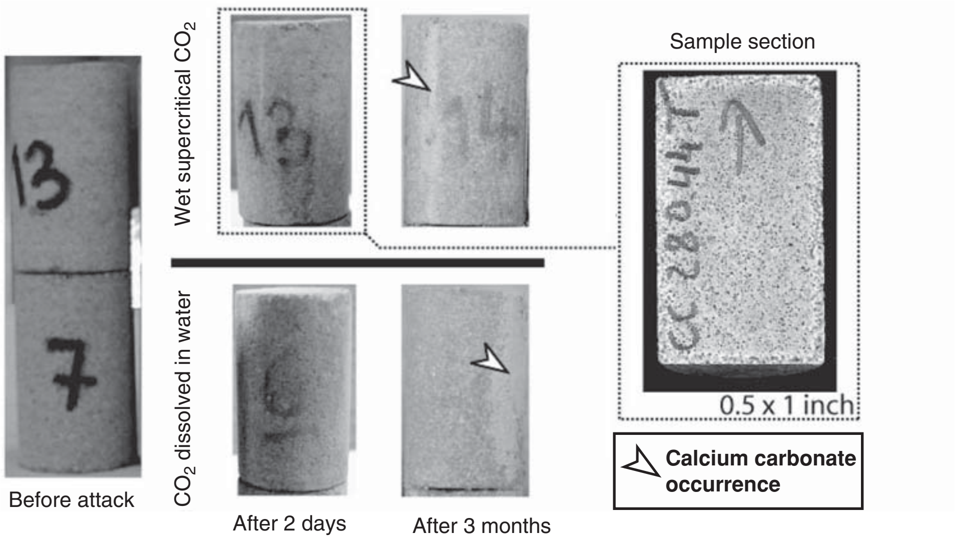

Figure 6

Core integrity and section of the CO_2-resistant cement at 2 g/cm^3 after two days and three months at 90ºC and 280 bars in carbon dioxide fluids.

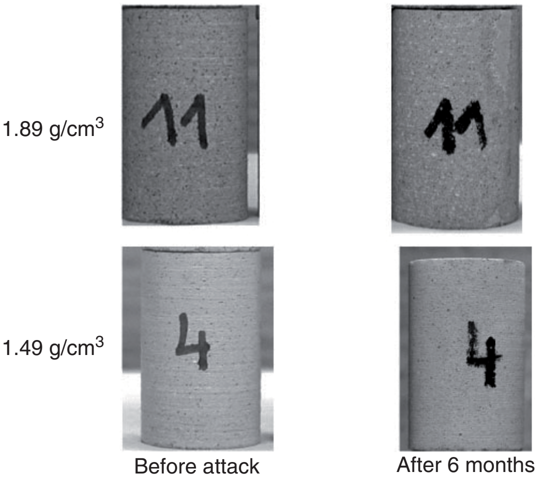

Figure 7

CO_2-resistant cement integrity at 1.49 and 1.89 g/cm^3 before attack and after 6 months at 90ºC and 280 bars in CO_2-saturated water. Note that in the wet supercritical CO_2 phase, the samples are identical to those shown here.

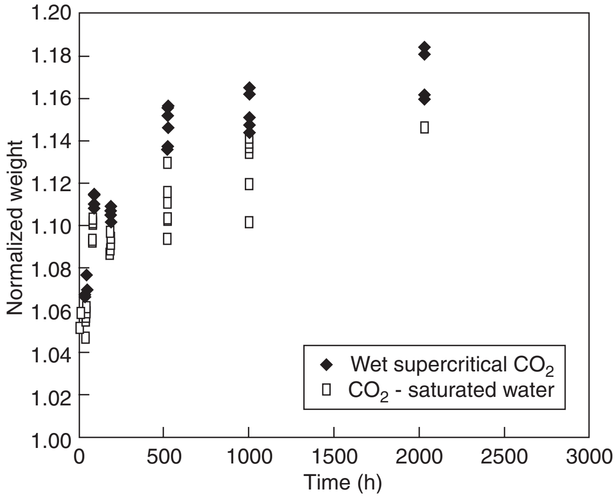

Figure 8

Weight variation of Portland cement samples (density = 1.89 g/cm^3) with time in wet supercritical carbon dioxide fluid and in carbon dioxide saturated in water at 90°C under 280 bars, up to 3 months of experiment.

even after 3 months of CO_2-attack *(Fig. 6)*. Furthermore, the cement mass keeps a good integrity after 3 months of experiment and does not show microcracking at any test duration *(Fig. 6)*. The CO_2-resistant cement cores at other density as 1.49 or 1.89 g/cm^3 show the same behavior up to six months in both CO_2-fluids *(Fig. 7)*. At the microscopic scale, this new cement exhibits a homogeneous pattern of carbonation with a low amount of calcium carbonate, in contrast with pure Portland cement.

2.2 Weight Evolution

The weight of Portland cement increases of 17% in wet supercritical CO_2 and 14% in CO_2-saturated water after 3 months of experiment, and its evolution does not stabilise at this duration *(Fig. 8)*. In contrast, a good weight stability is observed for the CO_2-resistant material up to 3 months either in wet supercritical CO_2 or in CO_2-saturated water phase, after an initial weight increase around 4-5% *(Fig. 9)*.

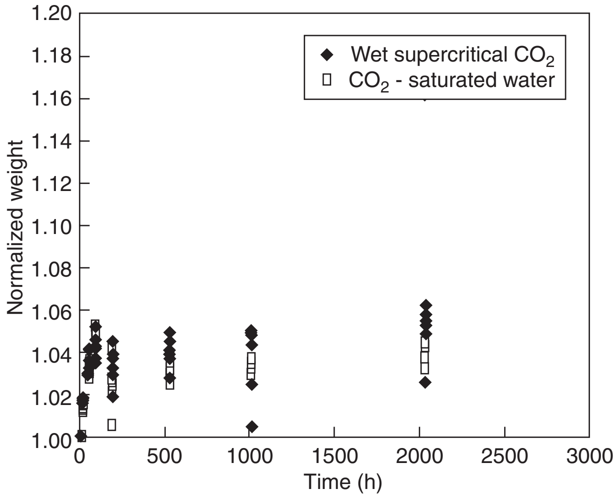

Figure 9

Weight variation of CO_2-resistant cement samples (density = 2 g/cm^3) with time in wet supercritical carbon dioxide fluid and in carbon dioxide saturated in water at 90°C under 280 bars, up to 3 months of experiment.

2.3 pH Evolution

The pH of water in equilibrium with Portland cement cores initially equals to 13. After CO_2 attack, core samples are stored in water and the pH is measured at equilibrium. After each duration of CO_2 attack, the new equilibrium pH is around 7 up to 3 weeks and decreases again up to 6 after six weeks and 3 months of experiment *(Fig. 10)*. Such CO_2 attack-related decrease of pH has already been reported in the literature (Van Gerven *et al*., 2004a; 2004b). This decrease results from the reaction between CO_2 and calcium from the calcium silicate phases or portlandite coming from Portland cement hydration. As for Portland cement, the pH data obtained with CO_2-resistant cement also decrease from 11-12 initially to 6-7 after CO_2 attack *(Fig. 10)*.

2.4 Mechanical Properties

Figure 11 shows the compressive-strength results of Portland cement samples tested at several durations in CO_2 fluids, under similar pressure-temperature conditions. After six

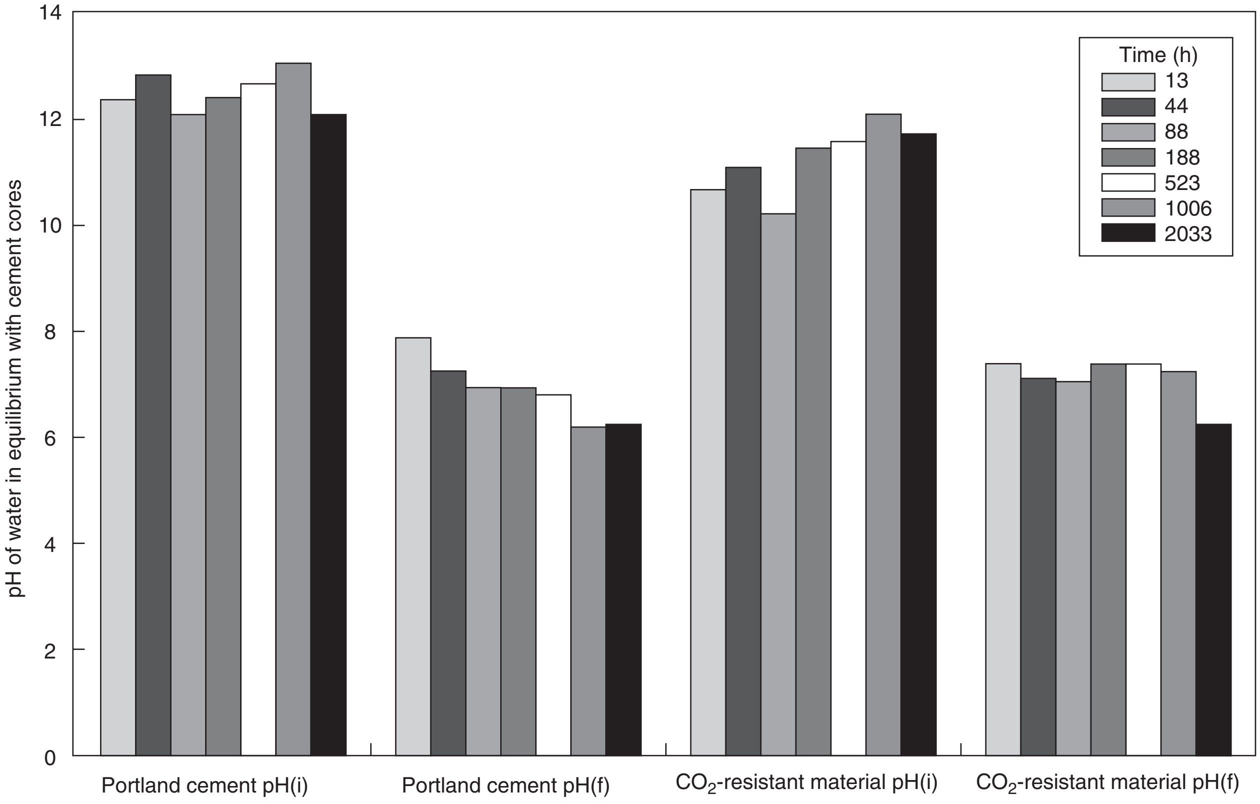

Figure 10.

Evolution of pH of water in equilibrium with cement samples, at each test duration (up to 3 months), for Portland cement and the CO_2-resistant cement. pH(i) = pH before CO_2 attack, pH(f) = pH after attack.

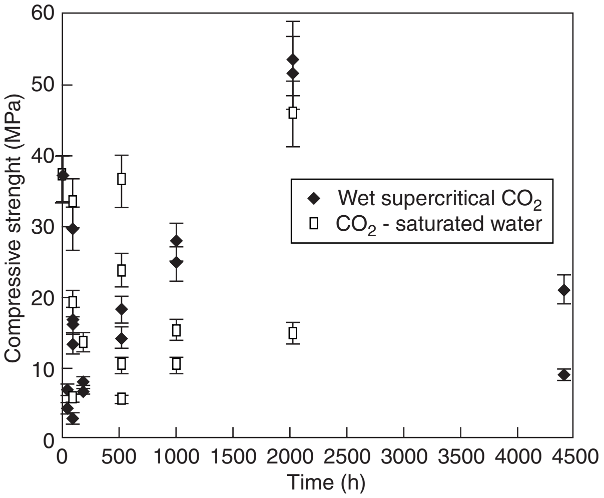

Figure 11

Compressive strength evolution of Portland cement samples with time in wet supercritical carbon dioxide fluid and in CO_2 saturated in water at 90°C under 280 bars. After 6 months in CO_2-saturated water, the compressive strength of Portland cement is not measurable, as most of the samples are highly deteriorated.

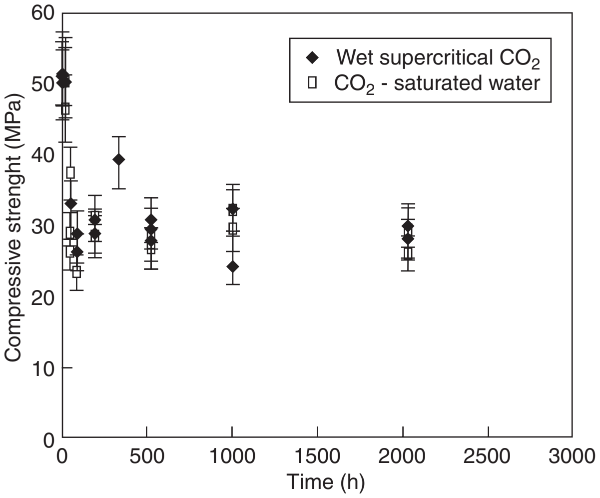

Figure 12

Compressive strength evolution of the CO_2-resistant cement samples (density = 2.0 g/cm^3) with time in wet supercritical carbon dioxide fluid and in CO_2 saturated in water at 90°C under 280 bars, up to three months.

weeks in wet supercritical CO_2 fluid, a strength loss of about 30% is measured. In CO_2-saturated water fluid, the compressive strength loses 65% *(Fig. 11)*. However, compressive strength measurements are very dispersed in both fluids. It may come from the heterogeneity of the samples due to the carbonation process *(Figs 2 to 5)*. During the compressive strength measurements, the carbonation layer cracks. These results cannot be used as absolute compressive strength values but indicate clearly the weakness of the carbonate layer or the interface at this front. After 6 months, the compressive strength of Portland cement is not measurable for the samples located in the CO_2-saturated water phase due to their high deterioration. Some data have been generated for few samples tested in the wet supercritical CO_2 phase, showing also a high decrease of their mechanical properties under these conditions *(Fig. 11)*.

The compressive strength of the CO_2-resistant cement at 2.0 g/cm^3 before and after carbon dioxide attack shows an initial decrease in the first few days, then it stabilizes up to 3 months in both CO_2 phases with a very good repeatability (*Fig.12)*, in contrast to the Portland cement behavior.

Parallel to this kinetic study, compressive strength tests were performed on samples with densities of 1.5 and 1.9 g/cm^3. The results confirm the stable behaviour of CO_2-resistant material over a large density range. For the 1.9 g/cm^3 and the 1.5 g/cm^3 systems, the compressive strength decreases from 50 MPa to 28 MPa and from 38 MPa to about 20 MPa in both fluids after one month respectively. After six months of CO_2 attack, the compressive strength is also comprised between 20 and 30 MPa, whatever the system density.

2.5 Mercury Porosimetry

Water-permeability measurements have been performed on the Portland cement samples and the CO_2-resistant cement samples at different durations. No discrimination has been possible with this method before and after the CO_2 attack because the permeability always remained below the detection limit of 8 microdarcy. The measurement method did not permit to detect any change due to the CO_2 attack.

However, the evolution of the porosity can be well followed with the mercury intrusion porosimetry measurements. The initial Hg-porosity for Portland cement is 33% and is reproducible and repeatable. After CO_2-attack, the porosity evolves during the test period with different behavior in each fluid *(Fig. 13)*.

In wet supercritical CO_2, the porosity continuously decreases, from initially 33% to 15% after 6 weeks. It rapidly decreases from 33% to 27% in the first hours of CO_2-exposure, before the decrease slows down over the next 6 weeks. Then the porosity increases from 15% to 27% between 6 weeks and 3 months of experiment.

In CO_2-saturated water, the porosity also changes in two distinct phases. During the first phase of approximately three weeks, the porosity rapidly decreases from 33% to 9%. At this stage, the carbonation front has quite completely entered the samples. During the second phase after three weeks, the porosity increases from 9% to 28% up to 3 months *(Fig. 13)*. It is here emphasized that this second stage is related to a dissolution process of the neoformed calcium carbonate. After a

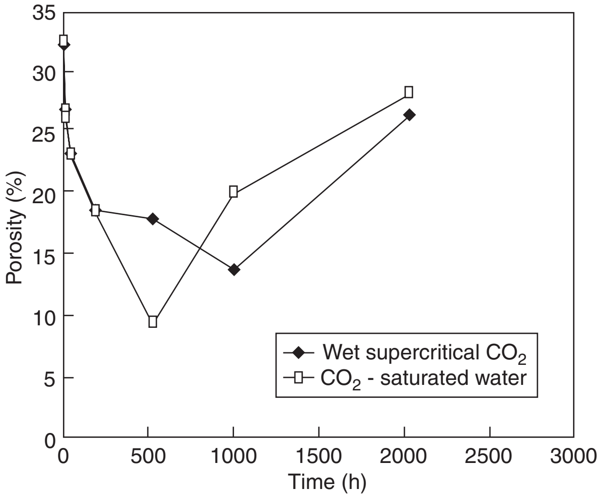

Figure 13

Porosity obtained during the first mercury intrusion in Portland cement core samples at several durations, in wet supercritical CO_2 fluids and in CO_2-saturated water fluid at 90°C under 280 bars, up to three months.

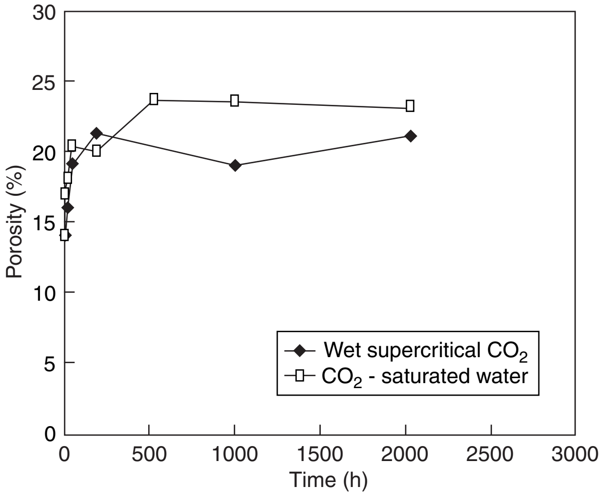

Figure 14

Porosity obtained during the first mercury intrusion in CO_2-resistant cement core samples at several durations, in wet supercritical CO_2 fluids and in CO_2-saturated water fluid at 90°C under 280 bars, up to three months.

complete carbonation of the sample, as CO_2 is in excess in our setup, pH of the fluid within the reactor (pressure and temperature) decreases to 2.8 and 3 (Toews *et al.*, 1995) allowing the dissolution process.

In contrast with Portland cement, the initial Hg-porosity of the CO_2-resistant cement is low and equals to about 15% *(Fig. 14)*. In wet supercritical CO_2 and in CO_2-saturated water, after a slight porosity increase from 15 to 20% in the first two days, the maximal porosity remains stable up to 3 months *(Fig. 14)*.

These porosity results confirm the trend observed with other physical parameters (weight, density, compressive strength, microstructural characterizations), that CO_2-resistant material remains stable after the first two days of exposure. Its behavior is comparable in both wet supercritical CO_2 and CO_2-saturated water.

The CO_2 resistant material exhibits a behavior drastically different from the one observed with Portland cement. Indeed, carbonation occurs very rapidly in the first days of CO_2 attack and is then limited.

CONCLUSION

The conclusions of this study on cement degradation in the framework of CO_2 storage application are the following:

- Portland cement is not resistant enough to wet supercritical CO_2 or to CO_2-saturated water. Its alteration is characterized by a complex series of concentric fronts after CO_2 attack in both fluids. This chemical alteration is a very effective process with a significant pH decrease of interstitial fluid triggering possibly casing corrosion. After six months, the degradation is very high and shows a spalling effect.
- An initial sealing by carbonation is followed by a dissolution stage, which starts earlier in CO_2-saturated water than in wet supercritical CO_2. Indeed, carbonation does not continuously plug Portland cement.
- In contrast, an homogeneous pattern with a limited carbonation threshold is observed with the new CO_2-resistant cement which has a good mechanical behaviour over a wide density range (1.5 and 2.0 g/cm^3). This material remains comparably inert in both wet supercritical CO_2 and CO_2-saturated water phases. Weight, density, compressive strength, microstructural characterizations and Hg-porosity measurements confirm the good stability of the CO_2-resistant cement.

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