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Development and characterisation of a smart cement for CO₂ leakage remediation at wellbores

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Abstract

This paper presents the results of the experimental investigations into the effectiveness of latex based “smart cement” in remediating wellbore related CO₂ leakage. Porosity, N₂ and CO₂ permeabilities, mechanical and elastic properties of the smart cement mixtures developed were determined using core samples. The effectiveness of the smart cement in reducing the cement permeability was assessed through a series of core flooding experiments and by comparing the results with those of Class G Portland cement. A full scale laboratory wellbore test rig was used to investigate the interactions between CO₂ and latex-cement at realistic wellbore conditions. Permeability response of the “smart cement” and microannulus were measured with N₂ and CO₂ at flow rates representative of likely CO₂ leakage rates at storage sites and the results are reported.

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1. Introduction

Experience from oil and gas industry has shown that wells represent the highest risk of leakage in a CO₂ storage project [1]. This is mainly caused by failure of one or more well barrier elements. Leakage could occur due to poorly

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cemented casing, casing failure and improper abandonment [2]. Possible leakage pathways due to cementing problems include: i) micro annuli caused by casing contraction and/or expansion, ii) channels caused by improper mud removal prior to and during cementing, iii) lost circulation of cement into fractured formations during cementing, iv) flow after cementing by failure to maintain an overbalance pressure, v) mud cake leaks, and vi) tensile cracks in cement caused by temperature and pressure cycles [3].

Portland cement is the most widely used cement in the industry. The problem, however, is that Portland cement is not resistant to CO₂. It is not thermodynamically stable upon in contact with CO₂ and will deteriorate over time [4]. Cement containing Ca(OH)₂ reacts with the CO₂ in the air or water phase. This process leads to a lower porosity due to the precipitation of calcium carbonate, which takes up a larger volume than the Ca(OH)₂. When there is excess CO₂ with a low pH, the CaCO₃ will dissolve. The net result is that the porosity increases and the strength deteriorates and leads to a further carbonation of the cement. Therefore, for CO₂ storage over a long period of time, wells with Portland cement may present a leakage risk.

To mitigate or remediate wellbore leakage of CO₂ either through the casing-cement or cement-rock interfaces, or through the fractures within the cement itself, new cement types with components that swell upon contact with CO₂ have been proposed in the literature. Such materials could enable self-healing of fractures in the casing-cement or cement-rock interfaces, as well as fractures in the cement itself. These cements, such as those developed by Halliburton (ExpandaCem™, LifeCem™, LifeSeal™) are mainly water or hydrocarbon swellable materials.

The smart cement or latex-cement mix developed in this study represents a self-activating leakage prevention technique, and its injection via the main CO₂ injector would cause the latex to react instantly with any CO₂ present, preventing it from reaching the leakage point. However, it could be used as cement-fill between the casing and surrounding caprock overlying the storage reservoir and has to be placed during well completion. Therefore, if a leak occurs through a microannulus between the casing and cement, the latex-cement should expand, self-seal and plug the rock matrix above the caprock.

Research into the conditions under which latex solidifies found that: (1) pure latex requires flow through the solution to solidify, (2) nitrogen does not cause latex to solidify, but air and CO₂ do, and (3) mixing latex with brine and subsequently increasing its salinity improves the performance of latex [5]. One such experiment has shown that 5 ml of latex mixed with 5 ml of brine (12% NaCl) solidifies within 4 seconds of exposure to 150 ml/min of CO₂ flow at 80°C [5]. Therefore, it is reasonable to anticipate latex-cement precipitation upon contact with CO₂ flow.

This paper presents a novel mixture of latex-cement material developed and characterised at Imperial College, which can potentially prevent wellbore CO₂ leakages in deep reservoirs. The main objectives of this work were: i) to investigate the effectiveness of the smart cement in mitigation/remediation of wellbore CO₂ leakage either through the casing-cement or cement-rock interfaces, or through the fractures within the cement itself, ii) to characterise the latex-cement mixture for its permeability and mechanical behaviour and strength using core samples, iii) to characterise the permeability of latex-cement under deep reservoir conditions when subjected to CO₂ flow using Imperial College's wellbore test rig, and iv) to compare stress-permeability behaviour of the microannulus of the smart cement with that of Class G Portland cement (100 parts cement/44 parts water).

2. Background

In a previous study, the authors investigated the permeability response of the microannulus and Class G Portland cement to interaction with CO₂ under different pressure, temperature and salinity conditions representative of three different reservoirs: i) Sleipner type, ii) Ketzin type, and iii) deep North Sea type [6]. The Sleipner and Ketzin fields are both relatively shallow, therefore any behavioural difference between the two experiments is a result of a change in salinity, whereas the deep North Sea reservoir represents the effects of depth, and thus high temperature and pressure. These experiments have shown that, in the long-term, the permeability of microannulus decreases when exposed to CO₂ under Sleipner and Ketzin type conditions, displaying a self-healing behavior of the Portland cement [6]. However, under the high pressure and temperature conditions of the deep North Sea environments, the microannulus permeability was found to remain constant.

Furthermore, other studies also found that, after six months of exposure to CO₂, Portland cement can exhibit spalling and, despite initial self-sealing via carbonation, the cement eventually undergoes dissolution [7]. In this case,

it was concluded that for carbon storage purposes, Portland cement is not resistant enough to either CO₂-saturated water or wet supercritical CO₂ [7].

3. Characterisation of the smart cement samples

In this research, a latex-based sealant (Caffélatex™) produced by Effeto Mariposa, which is used in the cycling industry as a tyre sealant was selected to prepare the smart cement mixture. It has been reported that Caffélatex™ foamed into a rigid sealant when exposed to CO₂ [3], due to the behavior of its constituent components: water, latex and ammonia. Since the alkalinity of ammonia keeps latex suspended in solution, when water in the system becomes acidic upon reaction with CO₂, it can no longer retain the diluted latex and precipitation occurs [5]. In this study, the latex was used as an additive for Portland cement, mixed into the cement slurries when fluid and then cured. The latex-cement is expected to swell when in contact with CO₂, subsequently plugging the cement matrix and the microannulus, blocking further flow.

Core flooding experiments were carried out using samples of smart cement with 2% latex. The Class G Portland cement core samples were also tested for comparison (Fig. 1). The freshly prepared cement mixtures were poured into the casts and, after 24 hours, placed in water to be cured for 28 days. The cylindrical samples were then cored out of cast cement blocks. The cores were dried at 60°C in an oven for 24 hours, followed by vacuum for 24 hours.

The porosity of the samples was measured using a pre-calibrated Boyle's law pycnometer. In order to investigate the effect of CO₂ on permeability of both latex-smart cement and Class G Portland cement, single phase N₂ and CO₂ permeabilities of the core samples were measured in a Hassler-type core holder under low confinement enough to seal the samples. Details of the experimental setup can be found elsewhere [8,9]. After N₂ permeability measurements, samples were saturated with CO₂ for one hour and CO₂ and N₂ permeability tests were carried out. These results are presented in Table 1.

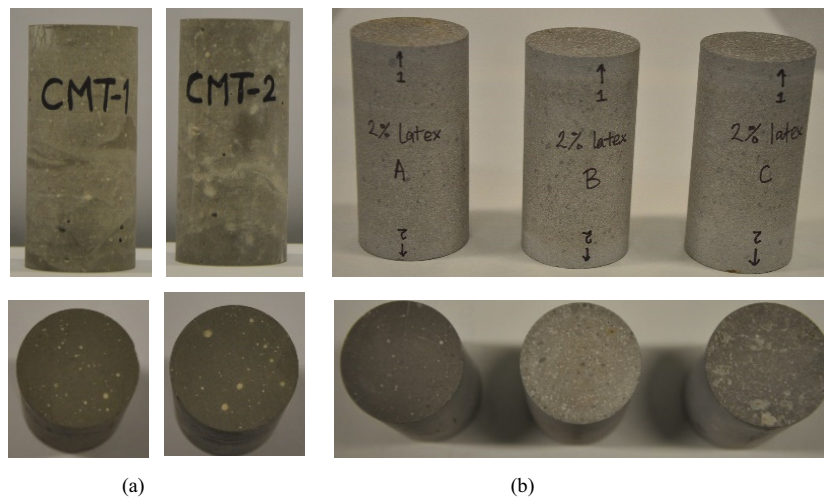


Fig. 1. Cement samples used in characterising the flow, mechanical and elastic properties of: (a) Class G Portland cement and (b) 2% latex-cement.

In the case of latex-cement samples, initial CO₂ injection resulted in a rapid decrease in permeability of the cement samples due to the expansion of latex and its sealing effect. Elevation in cement temperature was also observed which was attributed to the reactions between CO₂ and latex component. After the confining pressure was removed and samples were relaxed at ambient conditions for some time, the permeability measurements were repeated. The cores have yielded higher N₂ and CO₂ permeability values. It is believed that subsequent cooling and relaxation of the samples have led to the latex to expand further, and/or become brittle and fracture the cement, thus increasing the permeability of the samples.

Table 1. Porosity and permeability characterisation of cement core samples.

| Cement type | Porosity (-) | N ₂ Permeability ($\times 10^{-15} \text{m}^2$) | CO ₂ permeability under confinement ($\times 10^{-15} \text{m}^2$) | CO ₂ permeability relaxed and re-confined ($\times 10^{-15} \text{m}^2$) | N ₂ permeability relaxed and re-confined ($\times 10^{-15} \text{m}^2$) |
|-------------------------|--------------|--|---|---|--|
| Class G Portland Cement | 0.04 | 0.40 | 0.15 – 0.17 | - | - |
| 2% latex smart cement | 0.2 | 0.18 – 0.23 | 0.07- 0.09 | 0.17 – 2.46 | 0.63 – 5.46 |

The mechanical and elastic properties of the smart cement samples were determined in the laboratory using a four column 2000kN capacity rock testing unit manufactured by ESH Testing Limited. The uniaxial tests have been carried out to measure the peak strength and deformability of the core samples. Complete axial stress - axial strain curves were obtained and Young's Modulus of the samples determined from the axial stress - axial strain graphs (Fig. 2).

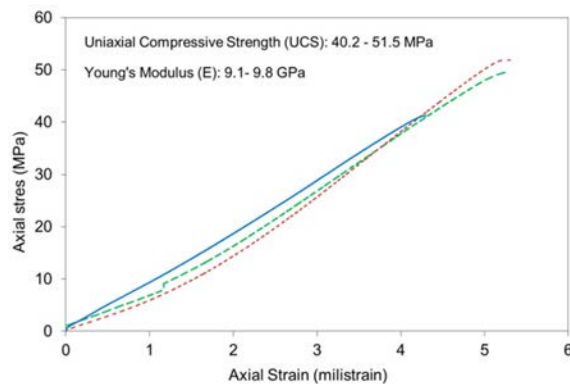


Fig. 2. Complete uniaxial stress-strain data for the smart cement core samples with 2% latex.

In general, the peak strength of the smart cement was found to be similar to that reported for the normal Class G Portland cement (36 - 64 MPa) [10]. On the other hand, its Young's Modulus was found to be lower than that (12 - 16 GPa) reported by Teodoriu et al. [10].

4. Wellbore experimental rig and test procedure

Fig. 3 shows the full scale wellbore experimental rig constructed for use under elevated pressure and temperature conditions encountered in typical CO₂ storage sites, which was used to investigate the interactions between CO₂ and latex-cement to characterise non-reactive flow through the microannulus and to determine its stress-dependent permeability. The rig comprises of two concentric stainless steel rings, each 9 cm deep: the inner ring acts as the well casing, whilst the outer ring represents the stiffness of reservoir rock with a shear modulus of 3.4 GPa, representing a relatively weak geological formation [6]. The Central Loading Mechanism (CLM) inside the inner ring has four shoes powered by hydraulically controlled precision jacks, which apply uniform radial load onto the well casing. A 4 MPa hydraulic pressure applied by the CLM displaces the casing around its circumference by 12 μm . As illustrated in Fig. 3, the cell contains other auxiliary elements to enable pore fluid flow. The experiments were conducted in a laboratory oven as a temperature-control and a safety enclosure. The cement-fill used was API Class G Portland cement and the smart cement developed and presented here respectively.

In order to create a microannulus, the cement mix was poured into the annulus whilst the CLM applied 35 MPa pressure onto the casing and, after allowing the cement to set for one day, the load was removed so that the casing retracted and caused a displacement of 102 μm . The cement was then cured in water for 28 days under ambient temperature and then placed in the rig and fitted with the auxiliary equipment.

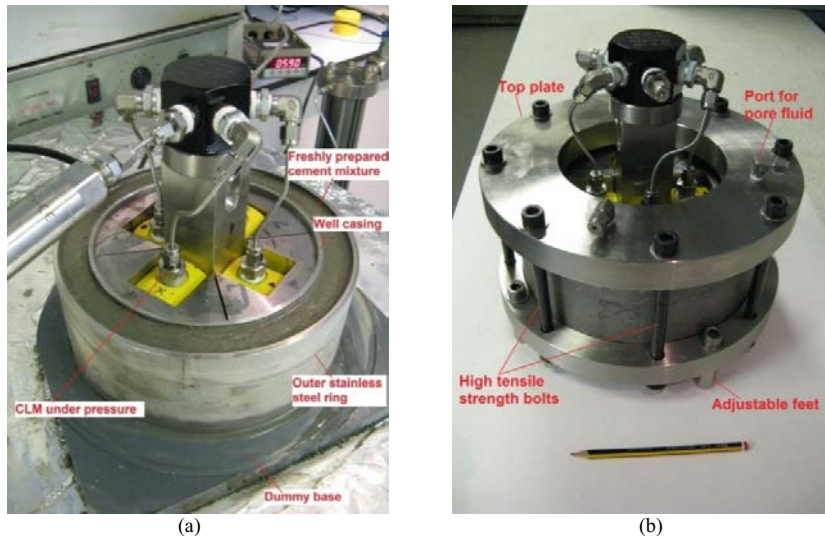


Fig. 3. Details of experimental set up for the wellbore test rig: (a) central loading mechanism, casing, outer stainless steel cylinder and the annular space with cement poured in; and (b) complete wellbore rig assembly.

4.1. Stress-dependent permeability of the microannulus

Prior to CO₂ injection experiments, stress dependency of the microannulus was assessed by means of increasing the confining load using the CLM. The stress in the CLM was increased up to 35 MPa in several steps in order to characterise the stress dependent permeability behaviour of the microannulus. At this stage, permeability was measured using N₂ as the pore fluid. Fig. 4 illustrates the decrease in permeability of the microannulus with increase in stress applied by the central loading mechanism for Class G Portland cement and smart cement respectively.

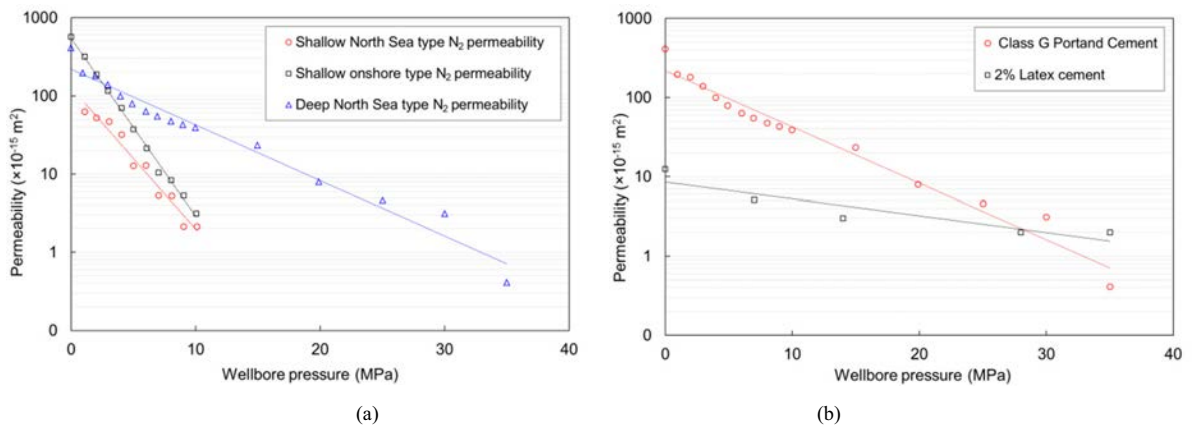


Fig. 4. Stress-N₂ permeability behavior of the microannulus using: (a) Class G Portland cement for three different reservoir pressure and temperature conditions (onshore shallow reservoir conditions: T=34°C, P=7.3 MPa, 25.0% salinity; North Sea shallow reservoir conditions: T=40°C, P=10.0 MPa, 3.5% salinity; North Sea deep reservoir conditions; T=92°C, P=35.0 MPa, 12.5% salinity); and (b) smart cement and Class G Portland cement in two different wellbore cement experiments carried out under the deep North Sea reservoir pressure and temperature conditions (T=92°C, P=35.0 MPa, 12.5% salinity).

The measurements illustrated in Figs. 4a and 4b indicate that, as hydraulic pressure increases, wellbore permeability decreases. The exponential decrease of permeability with stress is a characteristic phenomenon, observed in flow through fractures. In the case of smart cement, however, the initial permeability of the microannulus at low wellbore pressure was over an order of magnitude lower than that for Class G cement, and remained lower until the wellbore pressure applied was over 28 MPa. This behavior was attributed to the effect of latex on N_2 permeability of the cement, which was also observed in core flooding experiments (Table 1).

4.2. Effect of CO_2 on permeability of the microannulus

Subsequent to stress-permeability characterisation of the microannulus, the CO_2 flow-through experiments were carried out using the same wellbore set up at high temperature and CLM pressure at a constant CO_2 flow rate of 300 ml/min. The pressure on the CLM was set at 35 MPa and the experimental set up was maintained at $92^\circ C$ to simulate CO_2 storage conditions in deep North Sea depleted oil and gas reservoirs/saline aquifer conditions. During the first hour of CO_2 flow through experiments, rapid decrease in gas flow rate was observed due to reactions between the latex (smart) cement and CO_2 . Next, the wellbore cement was saturated with CO_2 and both upstream and downstream valves closed. After 24 hours, N_2 flow through experiments were carried out to measure changes in microannulus permeability after CO_2 injection and compare with the Class G Portland cement behaviour. Fig. 5 illustrates the changes in N_2 permeability of the system before and after CO_2 flow through and compares this with the Class G cement. The figure clearly demonstrates that the microannulus permeability was reduced by an order of magnitude once it is exposed to CO_2 at both low and high wellbore pressure conditions and high temperatures.

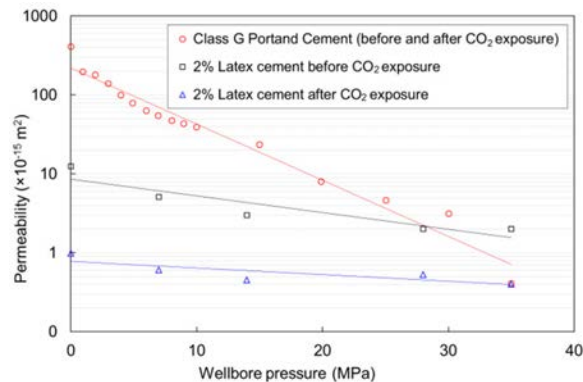


Fig. 5. Change in microannulus N_2 permeability with wellbore pressure, before and after CO_2 exposure, and comparison with that of Class G Portland cement.

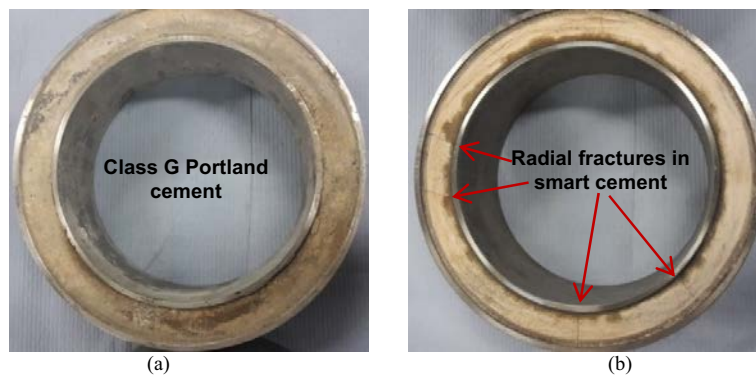


Fig. 6. Wellbore cement samples after CO_2 injection and stress relief: (a) Class G Portland cement; and (b) smart cement with 2% latex.

Fig. 6 shows the wellbore cement samples of both Class G Portland cement (Fig. 6a) and smart cement (Fig. 6b) after the N₂ and CO₂ injection experiments. As shown in Fig. 6b, several radial fractures have appeared in the smart cement sample once the confining load (CLM) was lifted, *i.e.* the unloading process. This effect was also observed in core flooding experiments where the permeability of the smart cement was increased after removing and re-applying the confining pressure, which can be due to structural damage from expansion of the latex and microfracturing of the cement matrix.

5. Conclusions

This paper presented a novel mixture of latex-cement material developed and characterised with the objective of self-sealing under high pressure and temperature conditions when exposed to CO₂. Core flooding experiments carried out under low confinement (Table 1) have shown that the addition of latex to Portland cement at a concentration of 2% volume can reduce the permeability of the cement by up to 42% and, after CO₂ flow-through experiments, the permeability was reduced by a further 60%.

Laboratory wellbore experiments under deep North Sea reservoir conditions have illustrated that stress-dependent N₂ permeability of the microannulus with 2% latex cement is up to an order of magnitude lower than that of Class G cement. The same experiments suggested that, once exposed to CO₂, the permeability of microannulus is further reduced by an order of magnitude, which can be up to two to three orders of magnitude lower than that of Class G cement N₂ permeability. Once stress relieved (unconfined), the permeability of 2% latex cement increases significantly as a result of structural damage and microfracturing of the cement matrix due to expansion of the latex.

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