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ORIGINAL ARTICLE

Geopolymer as well cement and its mechanical integrity under deep down-hole stress conditions: application for carbon capture and storage wells

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Abstract With regard to the safety, environmental impact and sustainability of carbon capture and storage (CCS) projects, the integrity of injection and production wells plays a major role. In a CCS project, mechanical integrity of well cement should be maintained to sustain the required mechanical strength throughout the life of an oil/gas and CO_2 sequestration well. One of the major issues with existing Portland cement based oil well cement is cement degradation in CO_2-rich environment. On the other hand, geopolymer cement possesses excellent acid resistant characteristics, shows higher mechanical strength and durability and demonstrates lower permeability. Therefore, this research work focused on studying the mechanical integrity of geopolymers under two different down-hole conditions: (1) effect of CO_2 on mechanical behaviour of geopolymers and (2) hydraulic fracturing of geopolymers to study the mechanical integrity under down-hole stress conditions. To study the mechanical integrity under CO_2 rich environment, geopolymers were tested in CO_2 chamber at a pressure of 3 MPa for up to 6 months and compressive strength and microstructural testings were conducted. It was noted that strength values of geopolymers did not change significantly in CO_2 environment for 6 months. There were only about 2 % variations in compressive strength values in CO_2 compared to the initial strength value. Scanning electron microscopy (SEM) test results revealed that there is no significance variation in the microstructure of geopolymer after 6 months in CO_2. For hydraulic fracturing experiment, four different tests were conducted with various injection pressure (P_{in}), axial stress (σ_1), confining pressure (σ_3) and tube length (30 and 40 mm). Geopolymers could not be fractured in any of the four tests, in which maximum values of P_{in} of 23 MPa and σ_1 of 59 MPa were used. There was no fracture development in geopolymers despite maximum ratios of P_{in}/σ_3 of 3.8 and σ_1/σ_3 of 13.3 was tested. Tests could not be repeated with higher ratios of P_{in}/σ_3 and σ_1/σ_3 due to the limitation with the triaxial set-up used. Since there is no fracture development in geopolymers at higher ratios of P_{in}/σ_3 and σ_1/σ_3, it is concluded that required mechanical integrity can be observed when geopolymers are used as well cement.

Keywords Cement degradation · Geopolymer · Greenhouse gases · Hydraulic fracturing · Well cement

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1 Introduction

Fossil fuels, which currently provide more than 85 % of the world's energy requirements, have been the major energy source throughout the 20th and 21st centuries due to their availability, competitive cost, and ease of transport and storage (Bachu 2003; Herzog and Golomb 2004). However, the combustion of fossil fuels emits greenhouse gases (carbon dioxide, methane, nitrous oxide, etc.) to the atmosphere, and this is a serious environmental problem to be addressed. The burning of fossil fuels has brought emissions of carbon dioxide (CO_2) from pre-industrial revolution times of 280 ppm (parts per million) to 400 ppm at present (Wigand et al. 2009; Bala 2013). Greenhouse gas emission can be reduced by some options such as improving the energy conversion efficiency of fossil fuels, shifting energy production to low carbon sources, enhancing uptake by terrestrial and marine biomass, and capturing and storing CO_2 deep underground (Bruant et al. 2002; Vishal et al. 2013). Of all the available solutions, carbon capture and storage (CCS) is a viable method for long-term reduction of greenhouse gases (Westrich et al. 2002; Siggins 2006; Busch et al. 2016; Verma and Sirvaiya 2016). Geological sequestration of CO_2 is the separation and capture of CO_2 and its injection into the geosphere for long-term storage (De Silva and Ranjith 2012).

With regard to the safety, environmental impact and sustainability of CCS projects, the integrity of injection and production wells plays a major role (Chiaramonte et al. 2008), as wellbores are prominent pathways for CO_2 leakage (Carey et al. 2009). One of the major issues with existing OPC- based oil well cement is cement degradation in CO_2-rich environments, leading to increased porosity and permeability, and reduced mechanical strength (Barlet-Gouédard 2007; Liteanu et al. 2009). On the other hand, researchers have found that geopolymer cement possesses excellent acid-resistant characteristics, shows higher mechanical strength and durability, demonstrates lower permeability, experiences little shrinkage, has lower production cost, and possesses higher pump ability compared to OPC (Van Jaarsveld et al. 1997; Nasvi et al. 2013; Singh et al. 2008). Geopolymer is an alumina-silicate cementitious material, which can be synthesized by mixing source material (fly ash, metakaolin, slag, etc.) with a strong alkaline solution (combination of NaOH and Na_2SiO_3). Successful use of geopolymer as well cement has been reported in previous studies (Nasvi et al. 2012, 2013). Therefore, this research focuses on geopolymer as well cement instead of OPC based well cement. The required zonal isolation is provided by the cement used in the wells (Carey et al. 2009), and the integrity of well cement is a key factor in maintaining well integrity to prevent any gas leakage through the wellbore (Newell and Carey 2012). The mechanical integrity of well cement should be maintained to sustain the required mechanical strength throughout the life of a well. This work focuses mechanical integrity of geopolymer well cement under two down-hole conditions: (1) mechanical behaviour of geopolymers in CO_2 rich environment; and (2) Integrity of geopolymer under down-hole stress condition using hydraulic fracturing experiment.

Barlet-Gouedard et al. (2010) studied the degradation characteristics of metakaolin-based geopolymer in CO_2 by placing geopolymer samples in wet super-critical CO_2 and CO_2-saturated water for 15 days at 90 °C under 28 MPa fluid pressures. It was noticed that the geopolymers showed excellent mechanical strength in wet super-critical CO_2 and CO_2-saturated water after 15 days. Scanning electron microscopy (SEM) test results revealed that there was no sign of degradation of geopolymers in the CO_2-rich environment, and it was concluded that geopolymers can be used in CO_2 injection wells. Apart from the study reported by Barlet-Gouedard et al. (2010), there are no studies focusing on the mechanical behaviour of geopolymers saturated in CO_2, and hence first part of this study focuses on an experimental program on the mechanical integrity of fly ash-based geopolymer in CO_2-rich environments (Experiment 1). Fly ash is a finely divided residue resulting from the combustion of ground or powdered coal, and consists of fine oxide particles such as quartz, hematite, mullite and amorphous particles (Temuujin et al. 2009). The worldwide production of fly ash was predicted to reach 800 million tons per year in 2010 and the development of new technologies to recycle this large amount of fly ash has led to the production of geopolymer cement (Izquierdo et al. 2009). Currently, about 70 % of the fly ash produced worldwide ends up in landfills (Haynes 2009). In Australia, 10 % of the fly ash is utilized, while the rest is buried under the ground causing land pollution problems (Wang and Wu 2006). Australian industries produce 13 million tons of fly ash per annum (Yunusa et al. 2006) and this is more than the domestic need if all the required cement is to be produced using fly ash. The use of fly ash based geopolymers produce less CO_2 than OPC (one tonne of geopolymeric cement generates 0.184 tonnes (approximately 1/6th compared to OPC) (Davidovits 2002), thus the reuse of fly ash to form well cement holds powerful carbon reducing synergies to CCS. The use of fly ash as source material provides sustainable solutions to the waste management and environmental protection, and hence fly ash was used as the source material for geopolymer.

The second part of this study focuses on mechanical integrity of geopolymers using hydraulic fracturing to simulate the down-hole stress conditions (Experiment 2). Hydraulic fracturing is a technique employed in pressurising a wellbore used in oil and gas wells to induce a tensile fracture perpendicular to the least principle stress (Zoback et al. 1977; Bohloli and De Pater 2006). In this process, fluid is injected at high pressure through the wellbore to overcome in situ stresses and to fail the rock to create a fracture in the reservoir (Hossain et al. 2000; Wanniarachchi et al. 2015). Hydraulic fracturing has been studied based on comprehensive laboratory experiments and models. The available models include the classical breakdown model, the poroelastic model, the fracture mechanics model, the shear failure model and the point stress model (Zoback et al. 1977; Rummel 1987; Ito and Hayashi 1991; Guo et al. 1993a; Hossain et al. 2000; Papanastasiou 2006). A summary and comparison of these models are shown in Table 1. Each of the models mentioned in Table 1 has their own advantages and limitations depending on the type of hydraulic fracture analysis. Most of these models cannot predict high breakdown pressures, with the exception of the fracture mechanics model. However, that model also includes certain assumptions such as fracture length and fluid pressure distribution in the fracture. It has been concluded that none of these models can predict the breakdown pressures observed under different conditions, including low and high injection rates, sample size, different types of fracture fluids and the stress field (Guo et al. 1993b).

Previous researchers (Zoback et al. 1977; Guo et al. 1993b, c; Bohloli and De Pater 2006; Zhou and Xue 2011) have experimentally studied the effects of stress level, borehole pressurization rates, fluid rheology, fluid injection rates, and sample size on the hydraulic fracturing behaviour of rocks. Bohloli and De Pater (2006) focused on fluid rheology and confining stress on the fracture propagation behaviour of soft rocks using Newtonian fluids and cross-linked gel. They noted that Newtonian fluid and cross-linked gel lead to infiltration associated with wellbore expansion. In addition, the ratio of maximum injection pressure to confining pressure required for fracturing decreased from 12 to 3 when the confining pressure was increased from 0.8 to 7 MPa. Guo et al. (1993b) conducted hydraulic fracturing experiments with Gypstone artificial rock samples using gear oil as the injection fluid, and concluded that specimen size has no effect on the breakdown pressure of rocks. In the same study, Guo et al. (1993c) tested the effect of least principle stress (σ_3) and injection rates on hydraulic fracturing of rocks. It was noted that σ_3 controls the magnitude of breakdown pressure and higher values of σ_3 lead to higher breakdown pressure values. According to hydraulic fracturing theory, breakdown pressure (for a vertical fracture) occurs when the minimum effective stress ($3\sigma_3-\sigma_{hmax}$) on the wall of a well becomes equal to the tensile strength of the rock. However, Guo et al. (1993b) noted that breakdown pressure relies more on least principle stress (σ_3) rather than $3\sigma_3-\sigma_{hmax}$.

To date, most of the hydraulic fracturing experiments have been conducted with rocks under various testing conditions. However, during the hydraulic fracturing operation, the well cement in the annulus also experiences extreme stress exposures. In a typical wellbore, the main purpose of well cement is to provide the required cement integrity at any given depth of the well. One of the causes of loss of cement integrity may be the cracks formed in the cement during extreme stress exposure conditions like hydraulic fracturing. Therefore, scope of the second part of this paper is to conduct hydraulic fracturing experiments on geopolymer cement samples to predict their mechanical integrity under extreme down-hole stress conditions.

2 Experimental procedure

2.1 Sample preparation and test procedure for Experiment 01—effect of CO_2 on mechanical integrity of geopolymers

Geopolymer samples 38 mm in diameter and 76 mm in height were prepared using low calcium fly ash

Table 1 The comparison of different hydraulic fracturing breakdown models

Model	Breakdown pressure (P_b) formula	Assumptions and description
Classical breakdown Eq. (1)*	$P_b = T + 3\sigma_3 - \sigma_1 - P_o$	Rock is isotropic and linear elastic stress analysis; fracture is initiated when the minimum tangential compressive stress in the wall is equal to the tensile strength of the rock; rock is impermeable to fluid penetration; predicted break down pressure is too low
Poroelastic Eq. (2)*	$P_b = \frac{3\sigma_3 - \sigma_1 + T - \alpha\frac{1-2v}{1-v}P_o}{1+\beta-\alpha\frac{1-2v}{1-v}}$	The model concept is same as classical break down model; However, stress analysis is based on Biot's Poroelasticity theory; effective for low porosity rocks; include effect of fluid penetration on the breakdown pressure, and however it reduces the predicted breakdown pressure value
Shear failure Eq. (3)*	$P_b = c\cos\emptyset + (1+\sin\emptyset)\frac{T}{2} + (1+\sin\emptyset)\sigma_3$	Breakdown occurs when fracture starts unstable extension; predicts lower breakdown pressure values; applicable when the injection rates and viscosity of the injecting fluid is very low
Point stress Eq. (4)*	$P_b = \frac{T-\sigma_\theta-P_0}{\frac{1}{2}\left[1+\frac{1}{\left(1+\frac{d}{a}\right)^2}\right](2-A)} + P_o$	Linear elastic stress analysis; fracture is initiated when the minimum effective stress is equal to the tensile strength of the rock at a point which is not on the wellbore; proposed breakdown pressure is fracture initiation, and however the actual break down pressure is much higher compared to this prediction
Fracture mechanics Eq. (5)*	$P_b = \frac{1}{h_o+h_a}\left[\frac{K_{lc}}{\sqrt{a}} + \sigma_1 f + \sigma_3 g\right]$	Breakdown occurs when the stress in the wall reaches shear strength of the rock; considers stable and unstable crack propagations; predicts high breakdown pressure values; size effect on breakdown pressure is included; promising model compared to others

* T is tensile strength; σ_1 and σ_3 is major and minor principle stresses; P_o is pore pressure; α is Biot's coefficient; v is Poisson's ratio; β is compressibility; c is cohesion; $\emptyset$ is friction angle; σ_θ is circumferential total stress; d is characteristic length; A is a constant; a is well radius; h_o, h_a, g, f are function of fracture length and well radius, and K_{lc} is fracture toughness

(ASTM Class F) as the source material and a combination of 10 M NaOH and Na_2SiO_3 as the alkaline liquid. An alkaline liquid/fly ash ratio of 0.4 and Na_2SiO_3/NaOH ratio of 2.5 were used in the geopolymer mix. All the ingredients and their proportions used for geopolymer sample preparation are shown in Table 2. Geopolymer samples were prepared by mixing the source materials in the correct amounts and the samples were oven-cured for a period of 24 h at 50 °C. Then the end surfaces of all the samples were machine ground prior to placement in a CO_2 chamber (Fig. 1), in which CO_2 can be saturated at a maximum pressure of 3 MPa. Uniaxial compression testing was conducted for geopolymers saturated in CO_2 for periods of 2, 4 and 6 months, and the control samples were tested without any saturation to compare the results. Three samples were tested for each data point and the average compressive strength values were taken, provided that the standard deviation did not vary more than 5 %.

2.2 Sample preparation and test procedure for Experiment 02—hydraulic fracturing of geopolymer well cement

The hydraulic fracturing experiment was conducted for geopolymer samples with a diameter of 38 mm and a height of 76 mm using water as the injection fluid. Geopolymer samples were prepared using ASTM class F fly ash as the source material and a combination

Table 2 Ingredients and their proportions used for geopolymer sample preparation

Ingredient	Mix composition (kg/m^3)
Fly ash	1571.4
Na_2SiO_3 solution	419.0
NaOH pellets	56.4
Amount of water added to make NaOH solution	123.2

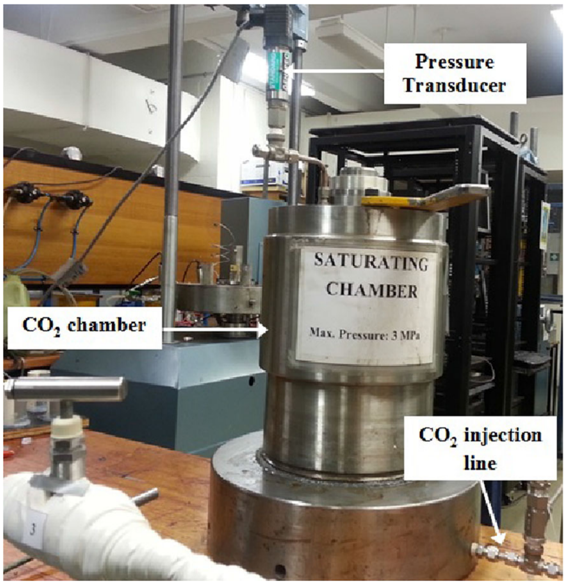


Fig. 1 The CO_2 chamber used to saturate geopolymers

of 8 M NaOH and Na_2SiO_3 as the alkaline activator. The ratios of Na_2SiO_3/NaOH and alkaline liquid to fly ash used were 2.5 and 0.4 respectively. The mix design for Experiments 1 and 2 are the same except the concentration of NaOH. For this experiment (Experiment 02), lower concentration of NaOH (8 M NaOH) was used (instead of 10 M NaOH as used in Experiment 1) to get reduced values of compressive strength and increase the possibility of fracturing. It should be noted that increase in NaOH concentration increase the compressive strength of geopolymer (Hardjito et al. 2005). The mix composition of the ingredients for Experiment 2 is similar to Experiment 1 (see Table 2), except the amount of NaOH pellets (47.1 kg/m^3) and water used to prepare NaOH solution (132.5 kg/m^3). For the hydraulic fracturing experiments, geopolymer paste was cast with a 3 mm diameter stainless steel tube at the centre of the PVC mould to simulate the borehole, and the length of the tube inside the geopolymer was 30 mm (See Fig. 2). The high pressure triaxial set-up (Fig. 3) was used for hydraulic fracturing experiments. This set-up is capable of delivering fluid injection pressures up to 50 MPa, confining pressures up to 70 MPa, axial loads up to 100 kN and temperatures up to 70 °C (Ranjith and Perera 2011).

Before placing the samples in the tri-axial cell, industrial-grade silicon was pasted along the longitudinal surface of the sample and it was allowed to harden for 24 h. A 2 mm gauge and 37.5 mm internal diameter nitrile membrane was inserted into the silicon-pasted sample using compressed air to prevent contact between the confining oil and the sample. Once the membrane inserted sample was mounted on the bottom pedestal, two 2 mm thick O-rings were inserted into the top and bottom ends of the samples. The bottom pedestal was modified by drilling an axial hole at the centre to fix the steel tubing, to enable fluid injection into the geopolymer. A schematic view of the geopolymer mounted on the cell base with the applied loadings (P_{in} is water injection pressure, σ_1 is axial stress and σ_3 is confining pressure) is shown in Fig. 4. The water injection system is connected to the steel tubing in the sample and the maximum water pressure that can be injected is 50 MPa. The confining pressure to the sample was applied by compressing the oil in the cell barrel using a hand pump. The undrained triaxial experiment was conducted for different injection, confining and axial stress values, and the downstream pressure (breakdown pressure) was monitored for each experiment.

The hydraulic fracturing test procedure included the following steps: (1) The confining pressure (σ_3) was increased up to the desired value; (2) The axial stress (σ_1) was increased to a certain value considering the required σ_1/σ_3 ratio; (3) once the external stresses on the sample were stabilized, the water was injected

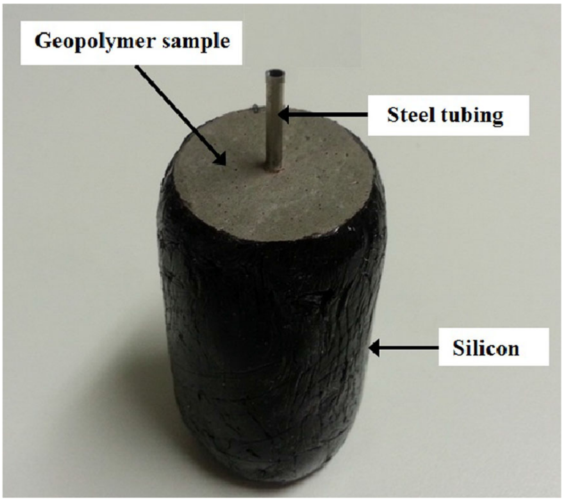


Fig. 2 Silicon pasted geopolymer with steel tubing at the centre

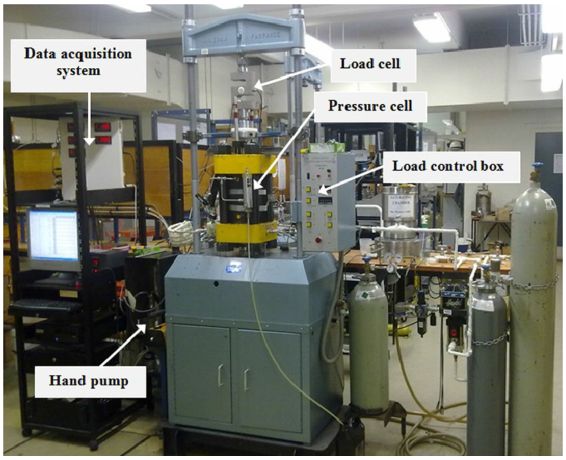


Fig. 3 The high pressure triaxial set-up used for hydraulic fracturing experiment

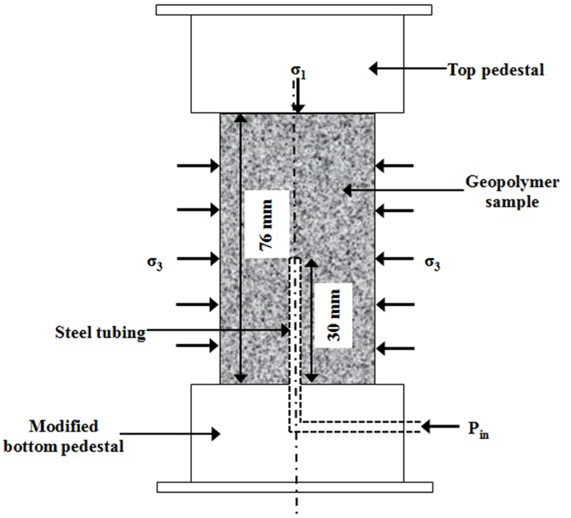


Fig. 4 Schematic diagram of the sample mounted on the *bottom* pedestal

into the sample through the steel tubing; and (4) the data acquisition system recorded the downstream pressure (breakdown pressure), other applied stresses, and axial and radial displacement values with the time. The test was started with injection pressure (P_{in}) of 15 MPa, axial stress (σ_1) of 25 MPa and confining pressure (σ_3) of 12 MPa, and the subsequent pressure values were chosen based on the fracture behaviour of geopolymer with the initial pressure conditions employed.

3 Results and discussion

3.1 Mechanical behaviour of geopolymers in CO_2 environment

The overall compressive strength test results is shown in Table 3. The variation of average compressive strength and Young's modulus of geopolymer with time in CO_2 is shown in Fig. 5, and the corresponding stress–strain plot is shown in Fig. 6. The standard deviation of compressive strength values of the control, 2, 4 and 6 months were 0.66, 0.42, 1.16 and 0.72 MPa respectively. According to Figs. 5 and 6, the compressive strength and Young's modulus values of geopolymers do not vary significantly in CO_2 up to 6 months. These findings are consistent with the findings of Barlet-Gouedard et al. (2010) as they concluded metakaolin-based geopolymer does not experience any degradation or strength loss in a CO_2-rich environment. The compressive strength value reduces slightly up to 4 months and then it tends to increase towards 6 months, and it should be noticed that the compressive strength value after 6 months is slightly higher than that of control samples. However, the variations in compressive strength values are not significant as the reduction after 4 months is 2.4 %, while the increment after 6 month is 2 %, compared to the compressive strength of the control geopolymer sample. Generally, compressive strength of geopolymer in CO_2 increases with the curing time except for 4 months curing period. At this stage, authors are not very sure as to why there is a drop in the compressive strength from 2 to 4 months curing period. However, it should be noted that the maximum variation in compressive strength with the curing time is 2.4 % compared to the compressive strength of the control geopolymer sample, and hence it can be concluded that fly ash based geopolymer does not experience significant strength degradation in CO_2 rich environment.

SEM testing was conducted to characterize any microstructural changes in CO_2 using a MCEM Nova NanoSEM 450 scanning electron microscope, and the corresponding SEM images of control and 6 months CO_2 saturated geopolymer samples are shown in Figs. 7 and 8, respectively. According to Figs. 7 and 8, there is no considerable variation between the SEM images of control and 6 months CO_2 saturated geopolymers. However, some mild carbonate deposits are

Table 3 The overall uniaxial compressive strength (UCS) test results of geopolymer saturated in CO_2

Curing time (months)	Sample no.	UCS (MPa)	Mean UCS (MPa)	Standard deviation (MPa)	Young's modulus (GPa)	Average Young's modulus (GPa)	Standard deviation (GPa)
Control sample	1	91.40	90.87	0.66	14.95	14.55	0.57
	2	90.12			13.90		
	3	91.08			14.80		
2	1	92.58	92.10	0.42	15.08	14.89	0.43
	2	91.89			14.40		
	3	91.82			15.19		
4	1	88.60	88.73	1.16	15.58	15.60	0.48
	2	89.95			16.09		
	3	87.64			15.13		
6	1	93.34	92.55	0.72	15.78	15.13	0.59
	2	92.36			14.95		
	3	91.94			14.65		

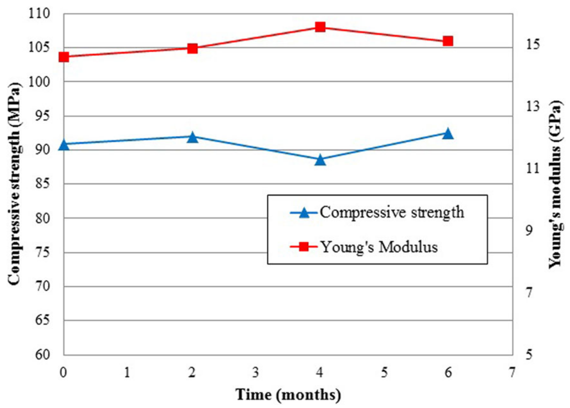


Fig. 5 Variation of strength and Young's modulus of geopolymer in CO_2

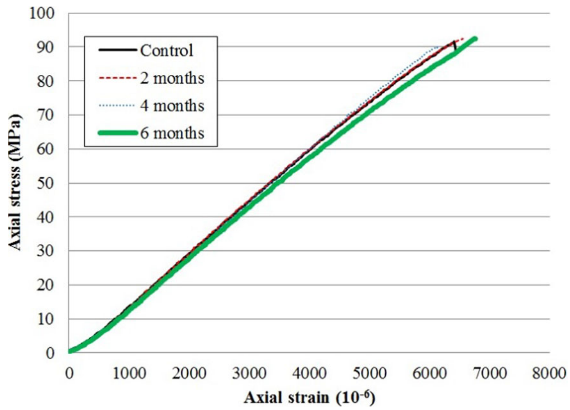


Fig. 6 Stress-strain variation of geopolymer in CO_2

observed in geopolymer saturated in CO_2, as shown in Fig. 9, and this might be the reason for the small strength increment in geopolymer after 6 months of CO_2 saturation. Barlet-Gouedard et al. (2010) also did not observe any significant changes in the microstructure of metakaolin-based geopolymer in CO_2. Previous researchers (Criado et al. 2005; Lecomte et al. 2006) have also concluded that geopolymers are less sensitive to carbonation than OPC, due to the absence of crystalline or semi-crystalline phases (calcium hydroxide) in geopolymers.

On the other hand, some researchers (Barlet-Gouedard et al. 2010; Duguid 2009; Liteanu et al. 2009) have found that OPC-based oil well cement experiences cement degradation within a short time period, leading to increased porosity and reduced mechanical strength. Compared to OPC, geopolymer shows enhanced mechanical integrity, as there is no sign of either strength reduction or cement degradation in CO_2-rich environments after 6 months. Therefore, geopolymers are a good replacement for traditional OPC-based well cement to provide long-term sealing capacity in injection/production wells.

3.2 Mechanical integrity of geopolymers using hydraulic fracturing

Four different hydraulic fracturing experiments (test 1–test 4) were conducted for geopolymer with different loading values. The variation of applied stresses

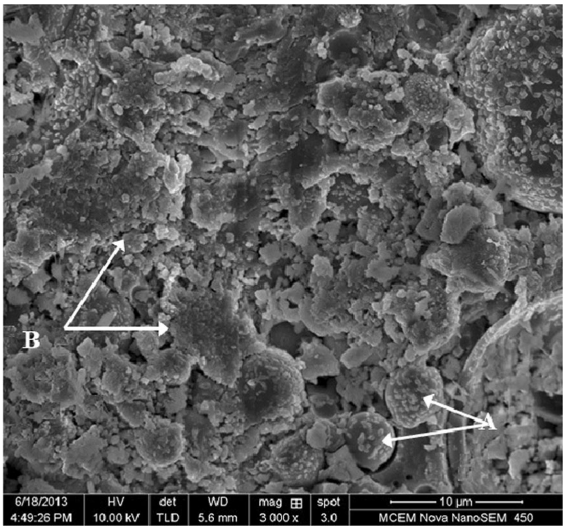


Fig. 7 SEM image of control geopolymer sample: *A* indicates unreacted fly ash particles, and *B* shows amorphous gel phase

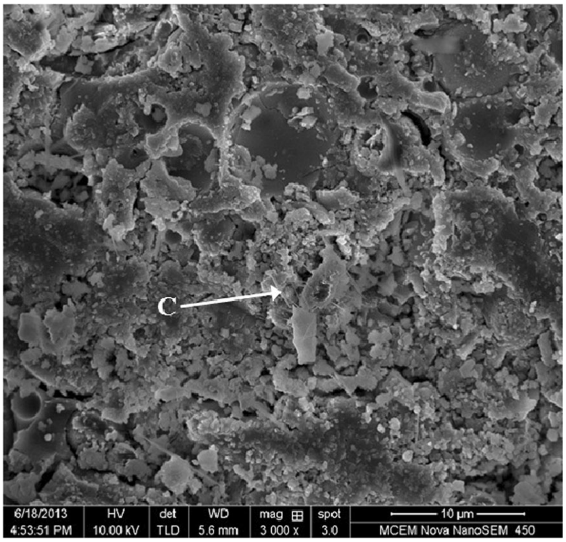


Fig. 8 SEM image of geopolymer saturated in CO_2 for 6 months: *C* denotes some mild carbonate deposits

during test 1 is shown in Fig. 10a. Even though the fluid injection was continued at various pressure conditions for approximately 40 min during test 1, there was no sign of fracture and downstream pressure development throughout the test duration. At the beginning of the test, the ratios of injection pressure/confining pressure (P_{in}/σ_3) and axial stress/confining pressure (σ_1/σ_3) were 0.8 and 2.1 respectively. As there was no sign of either fracture or downstream pressure development, the P_{in} and σ_1 values were increased up to 22.5 and 36 MPa respectively, making the ratios of P_{in}/σ_3 and σ_1/σ_3 1.9 and 3 respectively. The confining pressure remained constant throughout the test and there was no sign of fracture after approximately 40 min of water injection.

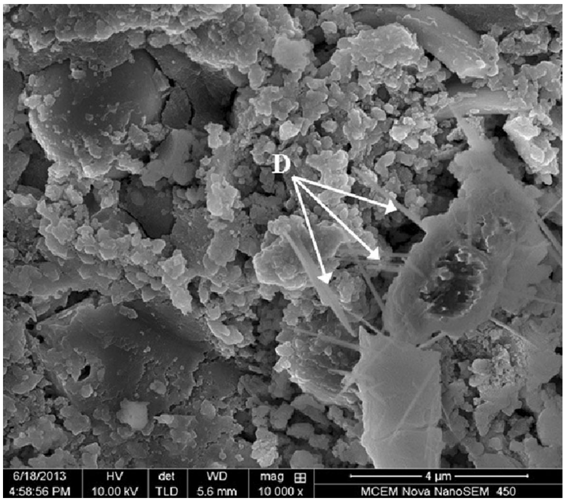
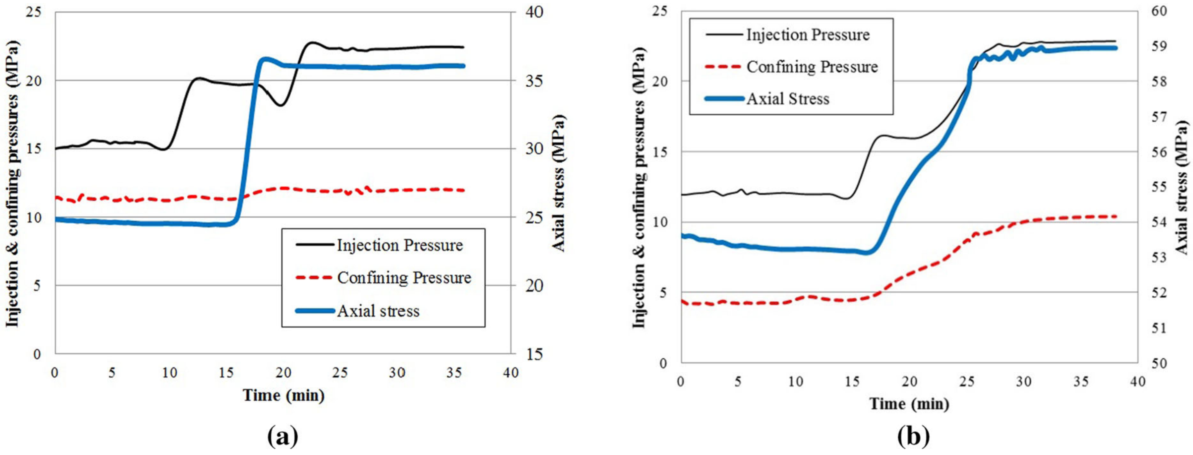


Fig. 9 Magnified SEM image of 6 months CO_2 saturated geopolymer showing mild carbonate deposits (*D*)

Therefore, the subsequent set of experiments (test 2–test 4) was conducted by changing the applied stress values and the tube length. To increase the possibility of fracture, P_{in} and σ_1 values were increased, while σ_3 values were reduced. In addition, the tube length was increased from 30 to 40 mm. The applied stresses against time for test 4 are shown in Fig. 10b, while Table 4 shows the overall results of all the four tests conducted. There was no sign of either fracture initiation or downstream pressure development even after test 4 (Fig. 10b), in which higher values of P_{in} and σ_1 were used. Compared to test 1, test 2 was conducted with a low confinement and higher P_{in}/σ_3 and σ_1/σ_3 ratios (Table 4). As there was no sign of fracture after test 2, the tube length and stress values were changed for test 3 and the ratios of P_{in}/σ_3 and σ_1/σ_3 were increased up to 3.8 and 11 respectively, while the tube length was increased to 40 mm.

During tests 3 and 4, the ratios of P_{in}/σ_3 and σ_1/σ_3 values were lower for higher P_{in} and σ_1 values, whereas higher ratios were observed at lower P_{in} and σ_1 values (Table 4). This is because there was an increase in confining pressure during test 3 and test 4 as the P_{in} and σ_1 values were increased (Fig. 10;



(a)
(b)

Fig. 10 Variation of applied stresses with injection time for: **a** Test 1 and **b** Test 4

Table 4 Overall hydraulic fracturing experimental results of geopolymer

Test	Stages	P_{in} (MPa)	σ_1 (MPa)	σ_3 (MPa)	P_{in}/σ_3	σ_1/σ_3	Tube length (mm)
Test 1	First	15	25	12	1.3	2.1	30
	Last	22.5	36	12	1.9	3	30
Test 2	First	12	35	6	2.0	5.8	30
	Last	22	36	6	3.7	6	30
Test 3	First	15	44	4	3.8	11	40
	Last	22	48	8	2.8	6	40
Test 4	First	12	53	4	3	13.3	40
	Last	23	59	10	2.3	5.9	40

Table 4). The increase in confining pressure is due to the infiltration of water into the surrounding confining oil. The test could not be continued beyond test 4 due to the limitations of the triaxial set-up as the maximum axial load is restricted to 100 kN, and hence the geopolymer could not be fractured. Based on the physical inspection of the sample after test 4, it was observed that there was no sign of clear fracture on the surface of geopolymer (Fig. 11).

The geopolymer could not be fractured in the hydraulic fracturing experiment even at higher pressure values ($P_{in} = 23$ MPa and $\sigma_1 = 59$ MPa) with a tube length of 40 mm (tube/sample length ratio of 0.53). The maximum values of P_{in}/σ_3 and σ_1/σ_3 of 3.8 and 13.3 could not fracture geopolymer, and this shows the mechanical integrity of geopolymer under down-hole stress conditions. An attempt was made to predict the breakdown pressure values of geopolymer using three different models (classical breakdown model, poroelastic model and shear failure model) described in Table 1. The parameters required for the above three models were taken from the experiments and relevant literature, and the values used are given in Table 5. The point stress and fracture mechanics models were not considered due to lack of data for those models. The maximum breakdown pressure values predicted based on the first three models for test 1–4 were 8 MPa (Eq. 1), 5.4 MPa (Eq. 2) and 24.8 MPa (Eq. 3) respectively. However, no sign of fracture was observed for the maximum injection pressure of 23 MPa used in test 4. This indicates that both the classical breakdown and poroelastic models highly under-predict the breakdown pressure values, as concluded by previous researchers (Guo et al. 1993a). Although the shear failure model showed little higher breakdown pressures than the maximum injection pressure used, it has been concluded that the shear failure model also under-predicts the breakdown pressure values (Guo et al. 1993a).

Fig. 11 Geopolymer sample after test 4

At any given depth of the casing in a typical wellbore (surface casing, intermediate casing and production casing levels), the main objective of the annular cement is to provide the required subsurface zonal isolation (API 2009). Fracture through the cement is one of the dominant pathways for CO_2 leakage (Celia et al. 2004), and the down-hole stresses are the major cause of cement fracture. Stress exposure on cement is due to factors such as in situ conditions (depth, pressure and temperature), injection history, and higher stresses caused during hydraulic fracturing (Pedersen et al. 2006; American Petroleum Industry (API) 2009). As geopolymer shows good mechanical integrity under extreme stress exposure conditions like hydraulic fracturing, it can provide the required mechanical integrity and zonal isolation under deep down-hole conditions.

4 Conclusions

When geopolymers are used as the primary sealant in injection/production wells, it may be exposed to different stress and saturation mediums deep under the ground. Therefore, this paper focused on the mechanical integrity of geopolymer well cement under two different scenarios: (1) mechanical behaviour of geopolymers in CO_2 rich environment; (2) Hydraulic fracturing of geopolymers to study its mechanical integrity under deep down-hole stresses. The following conclusions are drawn based on the experimental findings:

1. There are no significance changes in compressive strength and Young's modulus of geopolymer in CO_2 after 6 months. Scanning electron microscopy (SEM) testing on CO_2 saturated geopolymers also revealed no significance variation in the microstructure of geopolymer after 6 months of CO_2 exposure. As geopolymers show no significant strength variation in CO_2, they can be used as well cement in CO_2 sequestration well for long-term application.
2. Hydraulic fracturing experiment on geopolymer samples with various water injection pressures (P_{in}) (12–23 MPa), axial stresses (σ_1) (25–59 MPa), confining pressures (σ_3) (4–12 MPa) and tube lengths (30 and 40 mm) showed no sign of any fractures in geopolymer, even though maximum ratios of P_{in}/σ_3 of 3.8 and σ_1/σ_3 13.3 were used. This shows that geopolymers can provide the required mechanical integrity in CO_2 injection wells, as the absence of fractures in geopolymer

Table 5 Parameters used in different models (classical breakdown model, poroelastic model and shear failure model)

Parameter	Value
Uniaxial compressive strength (UCS) (Nasvi et al. 2012)	80 MPa
Tensile strength (T) = 10 % of UCS (Labbane et al. 1993)	8 MPa
Poisson's ratio (v) (Nasvi et al. 2012)	0.26
Biot's coefficient (α) (Ulm et al. 2004)	0.7
Compressibility (β) (Zhang et al. 2009)	0
Cohesion of geopolymer (c) from triaxial test	20.6 MPa
Friction angle of geopolymer ($\emptyset$) from triaxial test	20°

under extreme stress conditions eliminates one of the possible CO_2 leakage pathways.

3. The breakdown pressure values of geopolymer obtained from classical breakdown model, poroelastic model and shear failure model were 8, 5.4 and 24.8 MPa, respectively. Since there was no sign of fracture at 23 MPa injection pressure, it is proved that these three models under predict the break down pressure values, and this finding is consistent with previous findings on these models.
4. On the whole, geopolymers can be a good alternative for existing ordinary Portland cement (OPC) based well cement, as they show excellent mechanical integrity under deep down-hole stress conditions.

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