Comparison of mechanical behaviour of geopolymer and OPC-based well cement cured in saline water

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Abstract

Well cement plays a vital role in maintaining wellbore integrity in a carbon capture and storage project. To date, ordinary Portland cement (OPC)-based well cement has been used and there are contrasting research findings on its suitability as well cement. This research aims to use geopolymer as well cement, and major aim of this work is to analyse the mechanical behaviour of both geopolymer and OPC subjected to various down-hole conditions including different salinity (0–30% NaCl) and confinements (0–15 MPa). This research comprises experimental and numerical works. Under the experimental work, series of unconfined compressive strength (UCS) test were conducted for geopolymer and OPC samples cured in saline water with 0–30% NaCl salinity for a period of 45 days. COMSOL multiphysics software was used for the numerical study, and first, laboratory scale uniaxial stress–strain behaviour of both geopolymer and OPC was validated numerically. The model was then extended to study the triaxial mechanical behaviour under different salinity (0–30% NaCl) and confining pressures (0–15 MPa) conditions. Based on the results, it was noticed that UCS of geopolymer increases with salinity due to the high resistance against alkali leaching in saline water compared to fresh water. The UCS of OPC increases with salinity up to 10% NaCl, and then it reduces with any further increase in salinity. The UCS of geopolymer is 6% to 66% higher than that of OPC depending on the salinity conditions and geopolymer possesses higher UCS than OPC for any given salinity condition. COMSOL multiphysics numerical software predicted the stress–strain behaviour of geopolymer and OPC accurately up to yield point. Failure strength of geopolymer in saline water is 3% to 61% higher than that of OPC for a given confining pressure. Findings of this research indicate that geopolymer can be a good alternative for OPC based well cement under deep down-hole conditions.

Keywords Geopolymer · Ordinary Portland cement · Salinity · Triaxial · Well cement

1 Introduction

Carbon capture and storage (CCS) is found out to be the most efficient and effective method to reduce the anthropogenic emissions of greenhouse gases into the atmosphere [1, 2]. Geological reservoirs, depleted oil and gas reservoirs, deep saline aquifers and un-mineable coal beds are good candidates for the CCS process [3]. The captured CO₂ is injected through borehole wells and cement is used as the primary sealant in injection wells. The well cement

is poured between the casing and the formation (annular cement) and into the casing (cement plug) to provide the required zonal isolation in the wellbore [4]. The success of the long-term geological sequestration of CO₂ depends on wellbore integrity and it is a condition that maintains the isolation of vertical formations and prevents vertical migration of fluids. The integrity of well cement is a key factor in maintaining wellbore integrity to prevent any gas leakage through the wellbore.

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To date, most of the sequestration wells are cemented with ordinary Portland cement (OPC)-based American Petroleum Industry (API) Class G and Class H cements [5, 6]. The OPC-based cement undergoes cement degradation, strength reduction, shrinkage and increase in permeability and porosity under down-hole conditions [7–11]. In addition, failures in OPC under down-hole conditions include radial cracks within the cement sheath, formation of micro-annuli at the cement-casing interface and flow channels through the cement [11, 12]. In contrast to OPC, it has been found that geopolymer cement possesses excellent mechanical properties, experiences little drying shrinkage and low creep, has excellent resistance to sulphate attack and possesses prolonged durability [9, 13]. Geopolymer is formed by the alkali activation of the alumina-silicate source materials such as fly ash, metakaolin, and slag with a strong alkaline liquid. Generally, combination of sodium silicate and sodium hydroxide is used as the alkaline activator for geopolymer production [6]. Production of geopolymer is economically feasible and sustainable compared to the production of OPC [4, 13, 14].

In the CCS wells, the CO_2 is injected at supercritical state (pressure > 7.8 MPa and temperature > 31.8 °C) and a minimum depth of 800 m is required to have the supercritical conditions to increase the storage capacity [7, 15]. A typical borehole well experiences range of temperatures, confinements and salinity from the surface to the injection point [15, 16]. Temperature in a typical borehole well increases with the depth with a geothermal gradient of 30 °C/km and the salinity of the brine water at these depths is generally higher depending on the geological location (0–40% NaCl) [9, 17]. In addition, pore pressure and the confining stress also increase with the depth applying different stresses to the formation rock and well cement. Therefore, the mechanical behaviour of well cement should be studied under these down-hole conditions to predict the mechanical integrity of the well cement.

There are many studies [5, 6, 11, 16, 18–22] focusing on the mechanical behaviour of well cement under different down-hole conditions including different salinity, temperature and stress conditions. Gowthaman et al. [5] studied the effect of salinity on the mechanical behaviour of OPC-based well cement. It was found that both the UCS and Young's modulus reduce with salinity due to the retardation in the hydration in saline water. Balinee et al. [6] studied the mechanical behaviour of fly ash-based geopolymer and OPC in the saline water. It was found that compressive strength of geopolymer increases with the increase in salinity and the reason for this is the enhanced rate of reaction and lower leaching rates in saline water compared to fresh water. On the other hand, strength of OPC increases in saline water up to 10% NaCl and then it reduces with any further increase in the salinity beyond

10% NaCl. The reason for the initial increase is the faster water movement across the membrane in saline water up to 10% NaCl that leads to a rapid increase in the formation of spines which increases the compressive strength. At higher salinity levels (beyond 10% NaCl), the NaCl is dispersed in C–S–H and $\text{Ca}(\text{OH})_2$ in the form of micro-crystallite precipitates. This lowers the activation energy required for the decomposition of $\text{Ca}(\text{OH})_2$ leading to retardation of the hydration process. Due to the retardation of the hydration process, the compressive strength decreases beyond 10% NaCl salinity. Ahdaya et al. [11] investigated the performance of fly ash Class C-based geopolymer for oil well cementing applications. Based on the findings, it was concluded that geopolymers possess excellent rheological and mechanical properties compared to OPC-based well cement. Due to the high mechanical strength, long-term wellbore integrity and zonal isolation is ensured with the use of geopolymer well cement.

Nasvi et al. [16] studied the triaxial mechanical behaviour of fly ash-based geopolymer cured at different temperatures (23–80 °C) using COMSOL multiphysics numerical software. They concluded that the failure strength increases with confining pressure for a given temperature and it is due to the closure of pore voids with increased confinement. In addition, deviatoric strength increased by 300% when the temperature was increased from 23 to 60 °C. This is due to the increased polymerization of geopolymer as more Si and Al are leached out from the source material with the increase in the temperature. In addition, for a given temperature, volume of geopolymer experiencing plastic deformation increases with the confining pressure. Nasvi et al. [18] compared the mechanical behaviour of fly ash-based geopolymer and Class G (OPC) cement at down-hole temperature conditions (20–80 °C). The optimum temperature for higher strength for both geopolymer and OPC was in the range of 50–60 °C. Class G cement showed higher strength and stiffness values at ambient conditions, whereas geopolymer exhibited higher strength and stiffness values at elevated temperatures. Failure strain behaviour of the samples was predicted using the ARAMIS software and the results revealed that failure strain does not vary significantly with curing temperature for Class G cement and the mode of failure was shear failure. On the other hand, failure strain of geopolymer reduces with the increase in temperature and the failure mode changes from shear failure at ambient conditions to splitting failure beyond 40 °C curing temperature. Giasuddin et al. [19] studied the strength of fly ash-based geopolymer cured in saline water in the ambient conditions. It was found that curing of geopolymer in saline water leads to high compressive strength and low

sorptivity compared to normal water cured samples at ambient temperature and pressure conditions.

Subaha et al. [20] investigated the combined effect of salinity (0–40% NaCl) and temperature (25–80 °C) on unconfined compressive strength (UCS) of OPC samples cured for 7 and 28 days. Their findings state that UCS of OPC samples initially increases up to 10% salinity due to the microcrystal absorption. Thereafter, it reduces towards 40% salt content as the formation of Ca(OH)_2 retards the strength gain at high salinity levels. When considering the effect of temperature, the compressive strength initially increases with temperature due to the increased rate of hydration. The C–S–H (Calcium Silicate Hydrate) bond becomes denser and it cannot occupy the capillary pore space at elevated temperatures and hence the compressive strength drops with increase in the temperature. Salehi et al. [21] studied the feasibility of using low calcium fly ash-based geopolymer for oil and gas well cementing applications. It was concluded that geopolymers can perform better than OPC-based well cement and they possess good morphology and shear bond strength between casing and cement. Based on the findings of Salehi et al. [22], low calcium fly ash-based geopolymers can achieve required mechanical and flow characteristics under down-hole conditions including high thickening time of more than 5 h, high bond strength between casing and cement to avoid deboning issues, more ductile behaviour and high fracture toughness values compared to API Class H well cement.

However, to date, there are very limited number of studies comparing the salinity dependent mechanical behaviour of geopolymer and OPC-based well cements. Specifically, there are no studies comparing the triaxial mechanical behaviour of geopolymer and OPC-based well cements in saline water. Therefore, aim of this research is to analyse the mechanical behaviour of geopolymer and OPC cement in saline water with different salinity levels (0–30% NaCl). This research comprises experimental and numerical work. Under the experimental work, a series of UCS tests were carried out for both geopolymer and OPC to determine the UCS of the samples. It should be noted that laboratory triaxial experiments were not conducted in the present study. The triaxial mechanical behaviour was predicted numerically using COMSOL multiphysics numerical software, and the results of geopolymer and OPC were compared. The numerical modelling approach was selected to study the triaxial behaviour since the existing triaxial set-ups cannot fail cement samples under high confinements due to lack of stiffness of the loading frame.

2 Experimental work

2.1 Materials and mix design

The OPC-based well cement samples were prepared using high sulphate resistance OPC cement, and the cement sample was purchased from Insee Cement, Colombo, Sri Lanka. The reasons for selecting high sulphate resistant OPC instead of Class G cement are two folds: (1) API Class G cement is not available in Sri Lanka and (2) It has been found that high sulphate resistance OPC cement possesses similar chemical composition as Class G cement, as shown in Table 1 [5]. Hence, high sulphate resistance cement can be used instead of Class G cement. It should be noted here that the main feature of API Class G cement compared to other API Class cement types is it is OPC-based cement with high sulphate resistant characteristics [23]. Neat well cement paste samples were prepared in cylindrical moulds of 38 mm diameter and 76 mm height. The OPC neat samples were prepared with a water-to-cement ratio of 0.44 based on API 10B specification [19].

Geopolymer samples were prepared using fly ash as the source material and a combination of Na_2SiO_3 and 12 M NaOH as the alkaline activator. Low calcium Class F fly ash was obtained from Lakvijaya coal power plant, Norochcholai, Sri Lanka and the chemical composition of the fly ash used is given in Table 1. According to American Society for Testing Materials [24, 25], Class F fly ash contains more than 70% by weight $\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$ and the lime content is very low (< 12%). On the other hand, Class C fly ash contains $\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$ between 50 and 70% by weight and possesses high lime content (as high as 30–40%). In this research, Class F fly ash was selected to prepare geopolymer samples due to the following reasons: (1) The type of fly ash produced at Lakvijaya coal power plant in Sri Lanka is Class

Table 1 Comparison of the Chemical composition of high sulphate resistance OPC, API Class G cement and low calcium Class F fly ash

Constituents	Percentage (%)		
	OPC	API Class G cement	Fly ash
CaO	64.40	64.70	8.40
SiO_2	20.38	22.91	45.55
Fe_2O_3	3.26	4.75	3.07
Al_2O_3	4.79	3.89	33.48
MgO	0.98	1.80	1.59
SO_3	2.21	0.74	0.81
K_2O	0.04	0.64	0.71
Na_2O	–	0.10	0.62

F and Class C fly ash is not commercially available in Sri Lanka, and (2) since Class C fly ash is rich in calcium, it is more suitable in Portland cement production. On the other hand, low calcium fly ash is rich in alumina-silicate materials and it is pozzolanic in nature facilitating the polymerization reaction in the presence of alkaline liquid [4, 25].

The specific gravity of the fly ash used was 2.12, and the surface area determined from Brunauer–Emmett–Teller (BET) method by N_2 absorption was $1495 \text{ m}^2/\text{kg}$. Both Na_2SiO_3 and NaOH were purchased from Glochem industries private limited, Colombo, Sri Lanka. The NaOH was obtained in the pellet form and Na_2SiO_3 obtained has a silicate modulus (ratio of SiO_2 to Na_2O) of 2.0. Geopolymer neat samples were prepared using an alkaline liquid (AL) to Fly ash (FA) ratio of 0.6 and the ratio between Na_2SiO_3 /NaOH in alkaline liquid was kept to 2.5, as it has been found that Na_2SiO_3 /NaOH ratio of 2.5 provides the highest compressive strength for fly ash-based geopolymer paste samples [26]. The mix proportion used for OPC and geopolymer pastes are shown in Table 2.

Table 2 Mix proportion for OPC and geopolymer pastes

Mix Proportion ratios	OPC	Geopolymer
Water/Cement	0.44 (API 10B specifications)	–
Alkaline liquid/Fly ash	–	0.6
Na_2SiO_3 /NaOH	–	2.5
NaOH pellet/Water for 12 M NaOH	–	0.5625

2.2 Fabrication of specimens and testing

Cylindrical PVC moulds of 38 mm diameter and 76 mm height were used to cast the samples (Fig. 1a) and cement paste was poured into the mould in three layers and each layer was vibrated for a period of 2 min on a vibrating table. A set of casted geopolymer paste samples is shown in Fig. 1b. Once the samples were casted, they were covered with polythene to prevent any moisture loss and then they were placed in the oven at 50°C for 24 h. A typical borehole well experiences range of temperatures from 20 to 80°C and typical subsurface temperature is about 50°C at a depth of 1 km [27]. Therefore, curing temperature of 50°C was chosen for this research study and all the samples were cured at this temperature. After oven curing the samples for 24 h, they were subsequently cured at room temperature in saline water with different salinity levels until being tested. The NaCl was mixed with distilled water (by weight proportions) to prepare the saline water and the salinity of the saline water used were changed from 0% NaCl (fresh water) to 30% NaCl in 10% NaCl intervals and the samples were cured in saline water for 45 days. Set of control geopolymer and OPC samples were tested soon after heat curing (after 24 h of initial curing) to compare the results with the saline water cured samples. Prior to the uniaxial compression test, sulphur capping was applied to the top and bottom surfaces of the sample (Fig. 2) to ensure that the end surfaces of the samples are parallel so that the loading is purely uniaxial. Uniaxial compression test was conducted for all the samples with a stress control loading rate of $1.2 \text{ MPa}/\text{min}$. For each data point, at least three samples were tested to obtain a reliable set of data and the average compressive strength of the three samples was taken as the final compressive strength of

Fig. 1 Sample preparation procedure: **a** splitted PVC tubes mounted on plywood board and **b** casted geopolymer samples

Fig. 2 Sulphur capped cement sample

the sample. The load and the axial displacement were recorded continuously during the test and the stress was calculated from the load while strain was calculated from the displacement readings. The stress–strain curves of the three samples were combined to obtain the average stress–strain curve for a given testing condition.

3 Numerical analysis

In the present study, only the unconfined compression test was conducted and triaxial experiments were not conducted in the laboratory as the existing triaxial equipment at Department of Civil Engineering, University of Peradeniya, Sri Lanka, cannot fail samples under confined loading due to lack of stiffness of the loading frame. Therefore, a numerical modelling approach was chosen to predict the triaxial mechanical behaviour of geopolymers and OPC-based well cement samples. First, laboratory unconfined compression test results were used to validate the numerical model under uniaxial loading condition and then the validated numerical model was extended to predict the triaxial mechanical behaviour of both geopolymers and OPC under different salinity and confining stress conditions.

Finite element method (FEM)-based numerical software, COMSOL multiphysics (version 4.4), was used for the numerical modelling. It utilizes conventional physics-based user interfaces and systems of partial differential equations in the modelling approach. COMSOL

multiphysics is a partial differential equations and finite element analysis-based numerical software that can be used to solve various engineering problems. There are different modules in COMSOL including acoustics, chemical engineering, earth science, heat transfer and structural mechanics. User can use one of these modules or can couple several modules together to solve the problem. Since the structural mechanics module can solve problems related to structural and solid mechanics, it was used to model the stress–strain behaviour of both geopolymer and OPC. Materials including isotropic, anisotropic, orthotropic and nonlinear materials can be modelled in structural mechanics module and another attractive feature of this module is it can be coupled with any other modules in COMSOL. Of the available material models including elastoplastic, hyper elastic and viscoelastic, the elastoplastic material model was used for the current study. In order to develop the model, some basic assumptions were made as follows: (1) Both geopolymer and OPC can be considered as linear elastic isotropic material; (2) since the neat cement samples without any aggregate were modelled, both OPC and geopolymer can be assumed to be homogeneous materials; (3) the uniaxial tensile strength (UTS) of both geopolymer and OPC were assumed to be 10% of their UCS values [16]; (4) the biaxial compressive strength (BCS) of both geopolymer and OPC are assumed to be 16% higher than their UCS values [28]; (5) Poisson's ratio of the cement samples does not vary with the salinity, and (6) for both geopolymer and OPC, the values of the vertical displacement that samples experience are assumed to be the same under uniaxial and triaxial stress conditions.

A 2-D axisymmetric geometry was chosen for the modelling as the sample used for experimental work is a cylindrical sample and the boundary conditions used were similar to the testing conditions employed in the laboratory. In the experimental work, the bottom base is fixed and the top platen is moved down to apply the loading, and hence the bottom of the sample was modelled as a roller support while the top platen was moved down with a prescribed displacement until sample reaches the maximum displacement recorded in the experiment. The right boundary was modelled as free with radial stress (confining pressure) and the left boundary was modelled using the axisymmetric condition. The boundary condition at the right boundary was changed according to the loading condition (uniaxial/triaxial). The confining stress was increased from 0 MPa (uniaxial loading) to 15 MPa (triaxial loading) and a boundary load was applied to the right boundary to simulate the confining stress on the sample. Two different parametric sweeps were used as follows to change both the applied confining pressure and the prescribed displacement on the sample: (1) Confining pressure on the sample was increased from 0 to 15 MPa in 5 MPa steps, and (2) the

prescribed displacement was increased by maximum displacement times parameters from 0.05 to 1 in 0.05 steps (maximum displacement $\times$ range (0.05, 0.05, 1)). The model geometry and the boundary conditions used for the modelling are shown in Fig. 3.

The Bresler–Pister criterion was used as the failure criterion for concrete due to the following reasons [16, 29]: (1) This criterion is the extension of the Drucker–Prager criterion for brittle material, (2) of the available yield functions for concrete, the Drucker–Prager criterion is most widely used for confined concrete, and (3) due to its simplicity in involving only two parameters. Since the assumed geometry is a rectangular one with four boundary segments,

Fig. 3 Boundary condition used for the FEM analysis

a 2-D mapped mesh with finer mesh was used for the modelling (Fig. 4). The distribution was introduced to mapped meshing by specifying the number of elements to each side. The convergence of the model is affected by the mesh refinement and it is required to ensure that the mesh size used is the optimum for the convergence. A mesh convergence analysis was performed by analysing the effect of the mesh size (length of the largest grid of the rectangular mesh) on the failure strength of geopolymer cured in 10% NaCl saline water under uniaxial loading condition and the results are shown in Fig. 5. Model results presented in Fig. 5 clearly show the mesh dependency of the results. When the length of the mesh is reduced from 15.2 mm (extra course) to 2.7 mm (finer), corresponding failure strength increases from 35.02 to 35.35 MPa and any further reduction in the mesh size beyond 2.7 mm does not cause any noticeable change in the failure strength. Hence, it is assumed that the obtained solution is converged. Based on the results and in order to reduce the computation time, the length of the largest grid of the rectangular mesh was fixed to 2.7 mm. Table 3 provides the meshing parameters used in the model. The model parameters used for geopolymer and OPC for the modelling are shown in Tables 4 and 5, respectively. The UCS and Young's modulus (E) values were obtained from the experimental results and UTS and BTS values were derived from the UCS values. Poisson's ratio value of both geopolymer and OPC was assumed to be constant with the salinity and a value of 0.26 was used for geopolymer cured at 50 °C based on the findings of Nasvi et al. [16]. Poisson's ratio value used for OPC was 0.25 based on the literature for OPC paste samples [30].

4 Experimental results on unconfined compressive strength of geopolymer and OPC in saline water

Table 6 shows overall UCS results of both geopolymer and OPC with the standard deviation (SD) for each condition. According to Table 6, SD values of geopolymer and OPC vary in the range of 7.5–12.8% and 1.9–14.1%, respectively, depending on the salinity condition. Variation of UCS of geopolymer and OPC in saline water is shown in Fig. 6. The average compressive strength value of the control geopolymer sample (soon after heat curing for 24 h) was 42.9 MPa. Compared to the control geopolymer samples, all the geopolymer samples cured in the saline medium (Fig. 6) show a strength reduction and it is due to the alkali leaching initiated with the ageing [9]. The percentage reduction varies from 14 to 35% depending on the salinity level. Based on Fig. 6, it can be seen that UCS values of geopolymer

Fig. 4 Mesh quality plot for the assumed mapped mesh **Fig. 5** Variation of resulting strength with the length of the longest grid of the rectangular mesh **Table 3** Meshing parameters used in the model

Property	Value
Number of degrees of freedom	1318
Number of internal degrees of freedom	8820
Number of elements (rectangular)	196
Number of nodes	232
Number of boundary elements	70
Element size (mm)	2.7 × 2.7

Table 4 Model parameters used for geopolymer

Salinity (%)	UCS (MPa)	UTS (MPa)	BCS (MPa)	E (GPa)
0	27.9	2.8	32.4	0.9
10	35.9	3.6	41.7	1.3
20	32.3	3.2	37.4	1.2
30	37.1	3.7	43.0	1.1

generally increases with salinity from 0 to 30% NaCl and the percentage increase is 33%. Previous researchers [6, 19] have also concluded that strength of fly ash-based

Table 5 Model parameters used for OPC

Salinity (%)	UCS (MPa)	UTS (MPa)	BCS (MPa)	E (GPa)
0	26.3	2.6	30.5	0.76
10	26.9	2.7	31.3	0.91
20	21.3	2.1	24.7	0.55
30	22.2	2.2	25.7	0.63

geopolymer increases with the increase in salinity of the saline water. Leaching of alkalis and other reactant materials from the samples is significant for normal water curing compared to saline water curing. The Na^+ ions from the NaCl and Ca^{2+} ions in the geopolymer give resistivity against weakening and they are less prone to leaching compared to fresh water. In fact, this excess amount of Na^+ helps to enhance the reaction rate in saline water. This is the reason for increased strength with the salinity [15, 19].

The average UCS of the control OPC sample was 17.3 MPa. Normally, OPC develops high compressive strength values when it is cured at room temperature conditions for a period of 28 days. It can be argued that the

compressive strength value of 17.2 MPa obtained in this research would be little high given that the curing temperature used was high (50 °C) and the curing time was only 24 h. However, previous researchers [18, 31–33] have obtained a compressive strength values of 12–50 MPa for API Class well cements (Class G and H) within 24–72 h when the samples were cured at elevated temperatures (50–93 °C). This is well expected because API Class G and H cements have been designed for a depth range of 0 to 2440 m and temperatures up to 93 °C [23]. According to Marvoudis [34], at wellbore temperatures of less than 230 °C, the C–S–H gel is a very good binding material. At temperatures above 230 °C, the C–S–H gel is subjected to metamorphism, which decreases the compressive strength and increases the permeability of the cement.

The UCS values of OPC samples are higher than that of control OPC sample as the strength of OPC samples increases with the time due to hydration process. During hydration process in OPC, the tobermorite gel is formed around cement grains. The initial product of hydrates acts as a semi-impermeable membrane through which water from the background solution is drawn in due to osmotic pressure. With this developed pressure, spines grow and

Table 6 Overall compressive strength (MPa) results of Geopolymer and OPC

Sample	Salinity (% NaCl)							
	0		10		20		30	
	Average UCS	SD (%)	Average UCS	SD (%)	Average UCS	SD (%)	Average UCS	SD (%)
Geopolymer	27.9	12.8	35.9	7.5	32.3	10.4	37.1	7.8
OPC	26.3	2.1	26.9	14.1	21.3	1.9	22.2	2.5

Fig. 6 Variation of UCS of geopolymer and OPC with salinity

occupy around cement grains increasing its compressive strength [6]. The UCS of OPC increases with salinity up to 10% NaCl salinity level and then it starts to decrease towards 30% NaCl salinity condition. The initial increment is due to the absorption of NaCl micro crystallites which cause the strength reduction. Previous researchers [6, 20] have also found that the maximum strength of OPC-based well cement is obtained at 10% NaCl salinity condition. The strength reduction beyond 10% salinity level is due to the reaction between the Ca^{2+} ions in the C-S-H and Cl^- ions in the NaCl. At high salinity levels, Cl^- ions penetrate into cement matrix and the reaction forms the insoluble $\text{Ca}(\text{OH})_2$ which retards the rate of hydration. This leads to reduce the compressive strength of OPC at high salinity levels [35].

When the UCS trend of geopolymers and OPC is compared in saline water (Fig. 6), it can be seen that geopolymers possess higher UCS than OPC for a given salinity condition. The UCS of geopolymer cement is 6% to 66% higher than that of OPC depending on the salinity level and this indicates that geopolymer performs better than OPC in saline water. Typical well cement should have a compressive strength value of at least 20 MPa and the required compressive strength value will vary depending on the depth, underground environment and application [7, 36]. Based on the results, it can be seen that both geopolymer and OPC satisfy the minimum strength requirement for well cement, and however geopolymer has higher mechanical strength than OPC at any salinity level. This indicates that geopolymer cement can

replace existing OPC-based well cement for borehole well applications.

Variation of average Young's modulus of geopolymer and OPC with different salinity levels is shown in Fig. 7. According to Fig. 7, the trend of Young's modulus variation of geopolymer with salinity is similar to the trend of UCS variation with the salinity. Young's modulus values of saline water cured geopolymer samples are higher than that of fresh water cured samples. This is due to the reduced rate of leaching of alkali elements and other reactants in saline water compared to fresh water which in turn increases the stiffness of geopolymer in saline water. Nasvi et al. [15] have also noticed that stiffness of geopolymer increases in saline water compared to fresh water. According to Fig. 7, Young's modulus of OPC increases in saline water up to 10% NaCl due to the formation of spine in saline water and then it reduces with any further increase in salinity. At high salinity levels ($> 10\%$ NaCl), NaCl content degrades the samples and reduces the stiffness of OPC [5].

Failure patterns of geopolymer and OPC in saline water are shown in Table 7. It can be seen that the failure pattern of both geopolymer and OPC is splitting brittle failure along the sample at any salinity level. This was very evident in the stress-strain curves of these samples as the samples exhibited sudden failure soon after the yield point. Previous researchers [15, 37] have also noticed splitting brittle failure for geopolymers at elevated temperature and high salinity conditions.

Fig. 7 Variation of Young's modulus of geopolymer and OPC with salinity

Table 7 Failure patterns of geopolymer and OPC sample in saline water

Sample type	Salinity (% NaCl)	0	20	30
Geopolymer

Table 7 (continued)

Sample type	Salinity (% NaCl)	
	0	
OPC
	20
	30

Fig. 8 Stress–strain curves for geopolymer (Solid points—Experimental; Hollow points—Numerical)

Fig. 9 Stress–strain curves for OPC (Solid points—Experimental; Hollow points—Numerical)

5 Numerical results

5.1 Model validation

The laboratory scale uniaxial stress–strain curve was validated with the numerical results. It should be noted that the model was validated only under uniaxial loading condition and the validated model was then extended to

predict the triaxial behaviour numerically. The resultant force ($F_{\text{resultant}}$) in the numerical analysis was calculated using Eq. (1). The resultant force was calculated by integrating the z component of the stress tensor (σ_z) at each Gauss point times $2\pi r$, where r is the radius of the geometry in cylindrical coordinates. From Eq. (1), the failure strength was calculated by dividing the resultant force by cross-sectional area of the sample.

Fig. 10 Variation of failure strength with salinity for geopolymer at different confining stresses

$$F_{\text{resultant}} = \int \sigma_z \cdot 2\pi r \cdot dr \quad (1)$$

where $F_{\text{resultant}}$ is the resultant force and $2\pi r$ comes from the integration in cylindrical coordinates.

Comparison of the stress–strain plots for geopolymer and OPC samples from experimental work and numerical analysis are shown in Figs. 8 and 9, respectively. It should be noted that, in Figs. 8 and 9, solid lines denote the experimental results and hollow lines denote the numerical results. Based on Figs. 8 and 9, it can be seen that numerically predicted stress–strain results are consistent with the experimental stress–strain curve. It was not possible to obtain the full plastic region of the stress–strain plot from the experiment as these materials are brittle and showed splitting failure (Table 7). Model predicts

the behaviour well up to yield point and it assumes perfectly plastic behaviour beyond the yield point. The percentage difference between the model predicted failure strength and the experimental strength values for geopolymer and OPC are 0.1–2.4% and 0.1–2.6%, respectively, depending on the salinity conditions.

5.2 Triaxial mechanical behaviour of geopolymer and OPC under different salinity levels

Figures 10 and 11 show the variation of the failure strength of geopolymer and OPC, respectively, with salinity for different confining stresses. As can be seen from Fig. 10, the failure strength of geopolymer increases with salinity as higher NaCl content gives resistivity against leaching of reactants from samples [19]. On the other hand, failure strength of OPC samples increases up to 10% NaCl salinity and then it reduces towards 30% NaCl salinity (Fig. 11). The initial increase is due to the increased rate of formation of spines and the reduction in the failure strength is due to the high salt content, as it degrades the strength gain [35].

Figure 12 shows the comparison of failure strength of geopolymer and OPC at different salinity levels for various confining stresses. According to Fig. 12, for a given salinity level, failure strength of geopolymer is higher than that of OPC for all the confinements. The failure strength of geopolymer is 3% to 61% higher than that of OPC depending on the salinity and confining stress conditions. This indicates that geopolymer can provide higher mechanical

Fig. 11 Variation of failure strength with salinity on OPC under confining stresses

Fig. 12 Comparison of failure strength at different salinity levels for various confining stresses (Solid line—Geopolymer; Hollow line—OPC)

Fig. 13 Variation of failure strength with confining stress of geopolymer under different salinity levels

strength and better mechanical integrity under down-hole conditions compared to OPC.

Variation of failure strength with the confining stress of geopolymer and OPC for different salinity levels are shown in Figs. 13 and 14, respectively. According to Figs. 13 and 14, the failure strength of the geopolymer and OPC samples increases with increasing confining stress for all

the salinity levels. The percentage increase in the failure strength of geopolymer for an increase in confinement from 0 to 15 MPa is in the range of 52.5–57.5% depending on the salinity, while the similar increment for OPC is in the range of 55.40–59.10%. Pore voids in the sample reduce with the increase in confining stress, and as a result, its permeability and the proportion of voids tend to reduce [4,

Fig. 14 Variation of failure strength with confining stress of OPC under different salinity levels

16]. This results in increase in the failure strength with the increase in the confining stress. It can be seen in Figs. 13 and 14 that some of the strength profiles are overlapping at different salinity levels and the reason for this can be explained as follows. When the variation of strength with the salinity of geopolymer and OPC is considered under uniaxial and triaxial loading conditions, strength of geopolymer generally increases with the salinity (Figs. 6 and 10), whereas the strength of OPC increases up to 10% NaCl salinity condition and then it reduces towards 30% NaCl salinity (Figs. 6 and 11). Although the general trend of the strength variation is as mentioned above, there is a strength fluctuation between two salinity levels for both geopolymer and OPC. For an instance, initially the strength of geopolymer increases from 0 to 10% NaCl salinity (Figs. 6 and 10), and however the strength value at 20% NaCl salinity is little lower than the strength at 10% NaCl salinity condition. On the other hand, strength at 30% NaCl salinity is higher than the strength at 20% NaCl salinity condition (Figs. 6 and 10). The strength fluctuation between the salinity levels (decrease and increase) can be seen under both uniaxial and triaxial stress conditions. The fluctuation of the strength with the salinity between the salinity levels produces these overlapping profiles for geopolymer in Fig. 13. The same explanation can be given for OPC based on Figs. 6, 11 and 14. Therefore, the reason for the overlapping profiles observed in Figs. 13 and 14 is due to the fluctuating trend of the strength with the salinity between the salinity levels under uniaxial and triaxial stress conditions.

Findings of this research study suggest that geopolymers have the potential to replace existing OPC-based well cement as they exhibit better mechanical performance in saline water under uniaxial and triaxial stress conditions. Previous researchers [4, 15, 16, 37, 38] have also concluded that geopolymer can be used as well cement instead of OPC based on their findings on the flow and mechanical behaviour of geopolymers. These studies have shown that apparent CO_2 permeability of geopolymers are two to three orders lower than that of API Class G cement, they possess higher mechanical strength at elevated temperatures and high salinity conditions compared to Class G cement, geopolymers does not undergo cement degradation in CO_2 environment and possesses excellent mechanical integrity under hydraulic fracturing conditions. On the other hand, previous researchers [3, 7–9, 39, 40] have found that OPC is unstable in CO_2 -rich environments and rapid degradation was observed within a short period of time. The problems associated with OPC in CO_2 -rich down-hole conditions are strength retrogression, cement degradation, shrinkage, durability issues, and increased permeability and porosity. All in all, geopolymer-based well cement can be used in CO_2 sequestration wells for long-term application.

6 Conclusions

An experimental and numerical study was conducted to study the mechanical behaviour of geopolymer and ordinary Portland cement (OPC) under different salinity

conditions including 0 to 30% NaCl. A series of laboratory experiments were conducted to obtain the uniaxial stress–strain curves of both geopolymer and OPC in saline water. A numerical modelling technique was employed to validate the laboratory stress–strain behaviour and subsequently the model was extended to predict the triaxial behaviour of both geopolymer and OPC under different salinity and confinement levels. The following conclusions are drawn from the outcomes of this study:

1. Unconfined compressive strength (UCS) of geopolymer increases with salinity of the saline water and it is due to the enhanced resistance against alkali leaching from the sample in saline water compared to fresh water. On the other hand, the UCS of OPC in saline water initially increases up to 10% NaCl salinity and it reduces with any further increase in salinity. The initial increase is due to the increase in formation of spines which in turn increases the compressive strength. The reduction in the UCS beyond 10% NaCl is due to high salt content as it degrades the samples and retards the hydration process.
2. Geopolymer possesses 6% to 66% higher UCS compared to OPC-based well cement depending on the salinity condition, and for a given salinity, the UCS of geopolymer is always higher than that of OPC. As geopolymer possesses higher strength compared to OPC and the UCS values of geopolymer is higher than the UCS value required for typical well cementing application, it can be a good alternative for OPC-based well cement.
3. Triaxial mechanical behaviour of geopolymer and OPC in saline water follows the same trend as their behaviour in uniaxial loading. For a given salinity, failure strength of geopolymer is always higher than that of OPC for any given confining pressure. The failure strength of geopolymer is 3% to 61% higher than that of OPC depending on the salinity and confining stress. In addition, failure strength of both geopolymer and OPC increases with the increase in confining stress and it is due to the closure of pore voids in the cement sample with the increase in confinement leading to increased mechanical strength.
4. On the whole, geopolymer cement provides excellent mechanical behaviour in saline water, and can be a good replacement for OPC-based well cement in CO₂ sequestration wells.

Compliance with ethical standards

Conflict of interest The authors declared that they have no conflict of interest.

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