

Combined Effect of Temperature and Salinity on the Triaxial Mechanical Behaviour of Geopolymers: An Experimental and Numerical Study

M.M.A.L.N. Maheepala, R.L. Hewavitharana and M.C.M. Nasvi

Abstract: Well cement plays a major role in providing the required wellbore integrity of carbon capture and storage projects. Geopolymers have gained recent attention as a low-cost and environmentally friendly substitute to ordinary Portland cement (OPC) based well cement to overcome the wellbore integrity issues related to OPC. Therefore, fly ash based geopolymer was used as well cement in the present research. As a typical well cement is exposed to a variety of temperatures, salinities and confinements under down-hole conditions, this research focused on the combined effect of temperature and salinity on the triaxial mechanical behaviour of geopolymers. The research work comprised: (1) experimental work where a series of uniaxial compressive strength (UCS) tests were performed on geopolymer samples cured at different temperature and salinity combinations; and (2) numerical work where a model was devised using COMSOL software and the model was validated based on the laboratory scale uniaxial stress-strain behaviour. The model was then extended to predict the triaxial mechanical behaviour of geopolymer under varying confinements. Results revealed that the resulting failure strength of geopolymers increases with increasing salinity, confinement and temperatures up to 60 °C. A maximum average failure strength of 66.4 MPa was obtained for the possible worst combination (temperature of 80 °C, salinity of 30% NaCl and confinement of 25 MPa) which satisfies the strength requirement for a typical well cement. On the whole, the combined effect of temperature and salinity acts favourably for geopolymers and they can be successfully used as well cement.

Keywords: Alkaline activator, Carbon capture and storage, Confining pressure, Geopolymer, Salinity, Well cement

1. Introduction

Carbon capture and storage (CCS) is identified as one of the most promising technologies among the methods through which the atmospheric greenhouse gas content could be reduced [1, 2]. Wellbore integrity should be maintained for the success of a CCS project. Well cement plays a major role in providing the required wellbore integrity. Well cement is injected in between the steel casing and the geological formations in borehole wells with the intention of providing zonal isolation.

Although ordinary Portland cement (OPC) based cement has been used in most of the sequestration projects, it has been found that OPC is unstable in CO₂ rich environments as it undergoes strength reduction, degradation due to acidic attacks and is subjected to shrinkage due to high pressures and temperatures which result in a lower durability [3-6]. On the contrary, fly ash based geopolymers which are durable, anti-corrosive, chemically inert, less permeable and adaptive to pressure variations have been recognized as a good replacement to

OPC, under aggressive curing temperatures, varying salinity concentrations and increasing confinements in earth's down hole, due to its abundant availability and ability to address waste management issues [3, 7 - 11].

Geopolymer cement, also known as alkali-activated cementitious material, is an inorganic binder that can be polymerized from materials rich in silica and alumina. These cements primarily constitute two basic components:

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cementitious source material (kaolinitic clays, fly ash, metakaolin, blast furnace slag etc.) and an alkaline activator (Ca(OH)_2 , NaOH , Na_2SiO_3). It has been found that low cost geopolymers could be synthesized using fly ash from industrial waste that has a highly stable structure compared to metakaolin geopolymers [7, 12, 13]. Fly ash can be broadly categorized according to calcium (Ca) content as low (ASTM class F) and high (ASTM class C) calcium fly ash. Ca content in class F fly ash is less than 10% while that of class C fly ash is higher than 10%, which is the primary difference between the two classes [14]. Low calcium (ASTM class F) fly ash is preferred as a source material than high-calcium (ASTM class C) fly ash since the presence of calcium in high amounts may interfere with the polymerization process and alter the microstructure of geopolymer [15]. Hence, this study focused on the low calcium ($\text{Ca} < 10\%$) fly-ash based geopolymer cement (ASTM class F) as well cement.

For a CCS project to be technologically feasible, wellbores should run to a depth of at least 800 m so that the stored CO_2 remains in a supercritical state [16]. Hence, due to the geothermal gradient ($30\text{ }^\circ\text{C/km}$), well cement will be exposed to a variety of temperatures and confining pressures, and saline concentrations under downhole conditions. Well cement should meet the necessary strength requirements and other material properties in order to provide the required integrity of wellbore in the short-term as well as in the long run. Thus, the mechanical behaviour of well cement with the variation in temperature, salinity and pressure needs to be investigated.

There are many studies [4, 10, 16-21] focusing on the mechanical behaviour of geopolymer based well cement under different salinity and temperature conditions. Sindhunata et al. [21] studied the effect of curing temperature on fly ash based geopolymerization. It was found that an increase of curing temperature from 30 to $75\text{ }^\circ\text{C}$ leads to a higher rate of reaction until the time of setting is reached, beyond which the temperature-controlled kinetics are inhibited. The increased reaction rate was observed through the well-developed mesoporous structure which is a resemblance of well reacted fly ash based geopolymers. According to Lloyd & Rangan [19], longer curing times result in increased compressive strength for fly ash based geopolymer, where a rapid rate of

strength gain was observed up to 24 hours and the rate of strength gain declined thereafter thus establishing the fact that minimum curing time of 24 hours is sufficient in practical applications with geopolymer concrete.

Nasvi et al. [20] compared the mechanical behaviour of geopolymer and OPC at different temperatures and it was found that the optimum curing temperature for higher mechanical strength for both low calcium fly ash based geopolymers and class G (OPC) cement was in the range of $55 - 60\text{ }^\circ\text{C}$. Geopolymer possessed high strength compared to OPC at elevated temperatures, whereas the strength of class G (OPC) cement is higher than that of geopolymer at low temperatures ($< 36\text{ }^\circ\text{C}$). Nasvi et al. [17] conducted a numerical study on the triaxial mechanical behaviour of geopolymers at different curing temperatures ($23 - 80\text{ }^\circ\text{C}$) using the COMSOL multiphysics software. They concluded that the resulting failure strength increases with the confining pressure due to the closure of pore voids. The deviatoric strength also increased for all confinements up to $60\text{ }^\circ\text{C}$ and then reduced beyond $60\text{ }^\circ\text{C}$ to $80\text{ }^\circ\text{C}$. The initial strength increment is due to the increased reaction rates with the rapid dissolution of Si and Al in alkaline materials and the nucleation rates slow down beyond $60\text{ }^\circ\text{C}$, hence no further strength increment with the curing temperature was observed.

Nasvi et al. [10] conducted a research to analyse the mechanical properties of geopolymer cement in brine and the study found that the compressive strength of fly ash based geopolymer reduces in saline water and the reduction rate is less in samples saturated at 15% brine water (BW) compared to those at 5% BW because a higher NaCl content will lead to more reactions with geopolymer and it provides more resistance to alkali leaching. Giasuddin et al. [16] observed a strength increment for geopolymer samples cured in saline water compared to those cured in normal water due to the significantly less leaching of alkaline solution and metal cations in the presence of saline water. Additionally, saline water cured samples were associated with lower sorptivity, that indicated a lower level of porosity and micro-crack density which leads to higher compressive strength. Balinee et al. [4] studied the mechanical behaviour of geopolymer and OPC in saline water. It was found that the compressive strength of geopolymer increases with the salinity level

due to the restricted alkaline leaching from the sample with the excess Na^+ ions in the surrounding curing solution.

Thirumakal et al. [18] compared the mechanical behaviour of geopolymer and OPC based well cement in saline water based on experimental and numerical techniques. It was found that the uniaxial compressive strength (UCS) of geopolymer is 6 - 66% higher compared to OPC-based well cement depending on the salinity condition (0 - 30% NaCl), and for a given salinity, the UCS of geopolymer was always observed to be higher than that of OPC. With regard to the triaxial mechanical behaviour, the failure strength of geopolymer was 3 - 61% higher than that of OPC in saline water for a given confining stress condition.

2. Research Significance

There are many studies conducted to determine the mechanical behaviour of geopolymer with varying temperature and salinity conditions. However, most of these studies have focused on either the effect of salinity or temperature. To date, no studies have been carried out on the combined effect of temperature and salinity on the triaxial mechanical behaviour of geopolymers. Hence, the aim of this research is to analyse the combined effect of temperature and salinity on the triaxial mechanical behaviour of geopolymers.

The research comprised both experimental and numerical work which are detailed in the following sections. The UCS of geopolymer samples was determined at different temperature and salinity combinations during the experimental stage. Data thus obtained were used to validate the uniaxial stress-strain behaviour of geopolymers using a numerical model after which the validated numerical model was extended to simulate the triaxial mechanical behaviour of geopolymers. It should be noted here that laboratory based triaxial experiments were not conducted in this research as the existing laboratory triaxial set up at the Department of Civil Engineering, University of Peradeniya, Sri Lanka could not fail samples under high confining pressures. Therefore, a numerical modelling approach was chosen to predict the triaxial mechanical behaviour of geopolymers under the combined effect of temperature and salinity conditions.

3. Experimental Work

3.1 Materials

Low calcium ($\text{Ca} < 10\%$) fly ash (ASTM Class F) samples were collected from Lakwijaya coal power plant, Norochcholai, Puttalam, Sri Lanka whose specific gravity was 2.12. Composition of fly ash used in the experiment is shown in Table 1. A combination of 15M Sodium hydroxide solution ($\text{Na}_2\text{O} = 30.0\%$) with a specific gravity of 1.45 and commercially available Sodium Silicate solution ($\text{Na}_2\text{O} = 14.7\%$, $\text{SiO}_2 = 29.4\%$) with a specific gravity of 1.53 were used to prepare the alkaline activator solution. Sodium hydroxide solution was prepared by mixing sodium hydroxide pellets with water in the solid: water ratio of 1:1.64 just before the preparation of geopolymer samples.

Table 1 - Composition of Class F Fly Ash

Constituents	Percentage composition (%)
SiO_2	52.03
Al_2O_3	32.31
Fe_2O_3	7.04
CaO	5.55
MgO	1.30
SO_3	0.07
K_2O	0.68
Cl	1.00

3.2 Mix Design

Activation of fly ash has been researched as being affected by several factors from which Activator modulus (AM) (Equation 1) and the Na_2O dosage (Equation 2) have been recognized as having a significant impact on the strength of geopolymers [22]. Therefore, previous researchers [22, 23] have used AM and Na_2O dosage as design variables to optimize the mix design for low calcium (ASTM Class F) fly ash based geopolymers. Hence, this research utilizes a mix design based on AM and Na_2O dosage (absolute volume method as detailed in Gunasekara et al. [22]). As per literature, an optimized reference mix design based on AM was used to determine the proportions of each material to be mixed in order to acquire the desired strength parameters. The reference mix design used is

shown in Table 2. The AM was maintained at 1.25 while Na₂O dosage was fixed at 15%.

$$AM = \frac{SiO_2 \text{ in Alkaline Activator}}{Na_2O \text{ in Alkaline Activator}} \quad (1)$$

$$Na_2O \text{ Dosage} = \frac{Na_2O \text{ in Alkaline Activator}}{\text{Mass of Fly Ash}} \quad (2)$$

Table 2 - Reference Mix Design using Absolute Volume Method for AM = 1.25

Constituent	Mass ratio of materials
Fly ash	1
Sodium silicate	0.638
Sodium hydroxide	0.188
Water	0.027
Water/Solids	0.370

3.3 Specimen Preparation, Curing and Testing

First, PVC moulds with a diameter of 38 mm and a height of 100 mm were used to cast the geopolymers samples. Subsequently, the samples were cut to a height of 76 mm once demoulded, to maintain the height to diameter ratio of 2.0. Mould oil was applied thoroughly on the inner surface of the moulds for the convenient demoulding of the samples. Alkaline activator solution was prepared by mixing 15M Sodium hydroxide solution with the Sodium silicate solution as per the design specifications. Alkaline activator solution was made ready just before the geopolymer cement mix was prepared. Activator solution, fly ash and added water were thoroughly mixed for 15 minutes using a mechanical mixer to prepare the geopolymer paste. Immediately after mixing, the paste was placed in the PVC moulds in three approximately equal layers where each layer was vibrated using a vibration table for one minute to remove the trapped air bubbles. Figure 1 shows a set of cast geopolymer paste samples.



(a)



(b)

Figure 1 - (a) Geopolymer Paste Sample in the PVC Mould and (b) Prepared Geopolymer Samples

Curing temperatures used in this study were 25 (room temperature), 40, 60 and 80 °C and the salinity levels used were 0, 10, 20, 30% NaCl by weight. First, the prepared geopolymer samples were cured in the respective temperatures for a period of 24 hours and then the samples were de-moulded from the PVC moulds. The samples were covered with a polythene while being oven cured to prevent excessive loss of moisture. The NaCl measured as a proportion of the total weight of each solution, was mixed with distilled water to prepare the brine solutions. The de-moulded samples were immersed in brine solutions of concentrations 0, 10, 20, 30% NaCl and they were cured at prescribed temperatures (25, 40, 60 and 80 °C) for 7 and 28 days. For instance, samples cured at 40 °C were cured under different salinity conditions for 7 and 28 days. This way it was ensured that samples were exposed to the combined effect of temperature and salinity during the curing period. For each specific condition, four samples were tested to ensure reproducibility and hence a total of 128 samples were prepared. The brine solution was stirred

at frequent intervals to avoid the precipitation of NaCl at elevated temperatures which may lead to the retardation of the polymerization reaction.

Uniaxial compressive strength (UCS) test (zero confining pressure) was performed using a Universal testing machine (Avery with a capacity of 60,000 lb) available at the Materials and Metallurgy Laboratory, Department of Civil Engineering, University of Peradeniya, Sri Lanka with a stress-controlled loading rate of 0.2 MPa/sec. The end faces of the samples were ground to ensure purely axial loading during the test.

4. Numerical Work

Well cement is subjected to an increasing confining pressure with depth and the typical injection depth is more than 1 km below the ground surface. Since there are no sophisticated facilities available at the laboratory to support higher confining pressures to simulate the triaxial behaviour, triaxial mechanical behaviour of well cement was replicated numerically using COMSOL multiphysics finite element method-based software (version 5.5). First, the model was developed under uniaxial stress condition (zero confining pressure) and the validation of the model was done based on the experimental UCS test results. Once the model was validated, it was extended to predict the triaxial mechanical behaviour of geopolymers under different salinity, temperature and confining pressure combinations. COMSOL multiphysics has a comprehensive simulation software environment with a wide range of applications. It acts as a simulation platform that has all the steps in a modelling workflow, from defining geometries, assigning material properties, physics for solving and producing accurate, and trustworthy results. Users can shift between simulating electromagnetics, acoustics, fluid flow, structural mechanics, heat transfer, or any other physics modelled by a system of partial differential equations in a single environment using the various modules in COMSOL. The software suggests available study types such as time dependent or stationary solvers upon the selection of a particular physics interface. The structural mechanics module (solid mechanics) and stationary study type was used to model the stress-strain behaviour of geopolymer in this study. The material models within this module include linear elastic, linear viscoelastic,

piezoelectric and models for creep, viscoplasticity, soil plasticity, concrete, rock etc., from which the linear elastic material model was adopted in our numerical model. UCS, Young's modulus, Poisson's ratio, uniaxial tensile strength (UTS), biaxial compressive strength (BCS) and density of geopolymer paste (1800 kg/m^3) were used as the input material properties to the numerical model [17]. Poisson's ratios at the corresponding curing temperatures were adopted from a previous research study conducted by Nasvi et al. [24] for geopolymer paste samples.

Several basic assumptions were incorporated for the model as follows: (1) Geopolymer cement is a linearly elastic, isotropic and homogeneous material (no aggregates used); (2) UTS is 10% of UCS and BCS is 116% of UCS [17]; (3) Poisson's ratio doesn't change with the salinity; and (4) The amount of vertical displacement experienced by the sample is same under the uniaxial and triaxial stress conditions. A 2-D axisymmetric geometry was used with a fixed boundary at the base, a prescribed displacement on top, axial symmetry from left and a boundary load as the confining pressure (0 - 25 MPa) from the right. The model geometry and the boundary conditions used for the modelling are shown in Figure 2. Two parametric sweeps were used in this study as follows: (1) Parametric sweep 1 - the prescribed displacement was increased by maximum displacement times parameters from 0.05 to 1 in 0.05 intervals (maximum displacement $\times$ range (0.05, 0.05, 1)) and (2) Parametric sweep 2 - the confining pressure was varied from 0 to 25 MPa in steps of 5 MPa. A pre-defined 2-D mapped mesh with 'finer' elements, where the length of the largest grid is fixed at 2.7 mm, was utilized for modelling. The assumed mapped mesh and the mesh quality plot is shown in Figure 3, illustrating a good quality mesh which perfectly fits the modelled geometry. The parameters of the mapped mesh are given in Table 3. The Bresler-Pister criterion, which is a function devised to predict the strength of concrete under multiaxial stresses, was used as the failure criterion for the model. This yield criterion is an extension of the Drucker-Prager criterion, widely used in applications related to confined concrete.

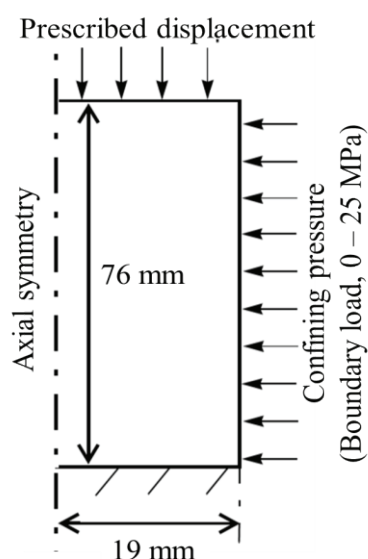


Figure 2 - Model Geometry and Boundary Conditions

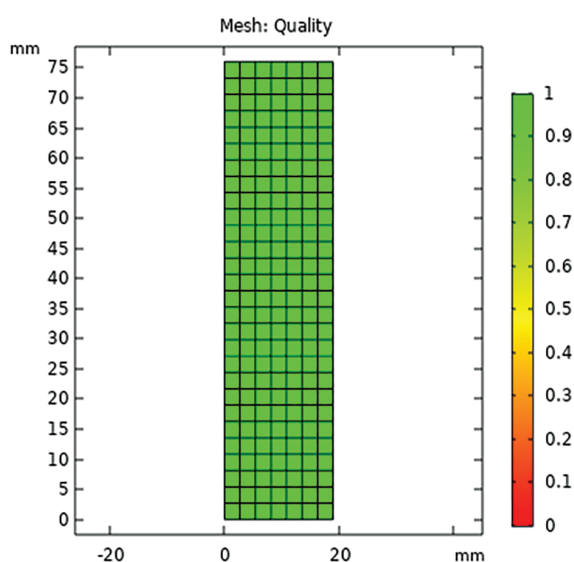


Figure 3 - The Mapped Mesh and the Mesh Quality Plot

Table 3 - Meshing Parameters

Parameter	Value
Number of degrees of freedom	1318
Number of rectangular elements	196
Number of nodes	232
Number of boundary elements	70
Element size (mm)	2.7 x 2.7

5. Results and Discussion

5.1 Experimental Results on the Mechanical Behaviour of Geopolymer Under Uniaxial Stress Condition

Variation of UCS of geopolymer with salinity for 7 days and 28 days are shown in Figures 4 and 5, respectively. The standard deviation of the results varies in the range of 0 to 3.5 MPa and 0 to 4.2 MPa for 7 and 28 days, respectively. Generally, the UCS shows an increasing trend with the salinity levels. The percentage increase in the UCS with salinity at 7 and 28 days are 3 to 91% and 0.5 to 39%, respectively, depending on the curing temperature. During saline water curing, since there is an abundance of Na^+ ions in the surrounding curing solution, the tendency for the cations in the geopolymer sample (Na^+) to leach out is at a minimal stage. Hence, the excess cations in the curing medium and in the sample actually promote the geopolymerization reaction, thereby increasing the resulting strength at higher salinity levels [4, 6, 10].

On the contrary, there has been a significant leaching of alkali activator solution and other useful reactants from the sample to the surrounding water in normal water cured samples (0% NaCl), which leaves a considerable number of unreacted particles in the samples that ultimately affects in strength reduction [4]. These conclusions could be further backed by the findings of Giasuddin et al. [16] where saline water cured geopolymer samples were found to have lower sorptivity than normal water cured samples which indicates less porosity or micro-crack density. According to Giasuddin et al. [16], water cured samples appeared to have a relatively large number of unreacted particles and pores rooted in the geopolymer matrix whereas the brine cured samples showed a fairly homogeneous matrix with more reacted components. Further, Nasvi et al. [6] observed that geopolymer samples undergo higher saturation in brine water than in normal water which can also testify to the lower leaching rates from geopolymer in saline water.

Figures 6 and 7 show the variation of UCS with the curing temperature at 7 and 28 days, respectively. The UCS shows a generally increasing trend with increasing temperature up to 60 °C and thereafter decreasing to reach 80 °C for all salinity levels. Geopolymers gain strength with the curing

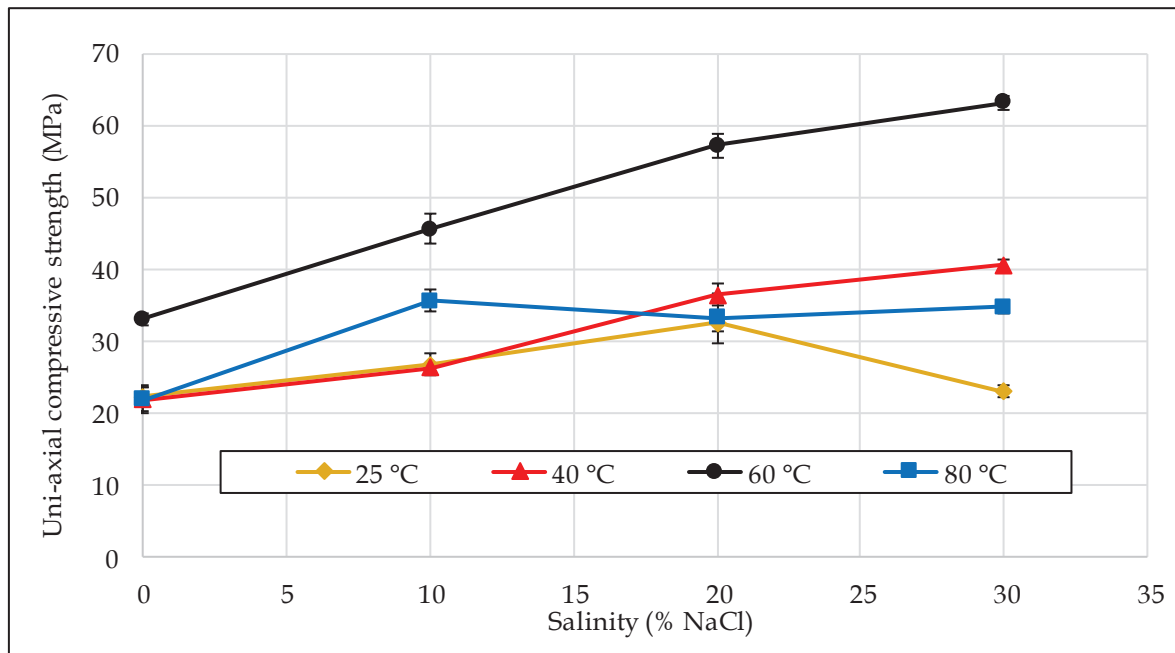


Figure 4 - Variation of UCS with Salinity at 7 Days Curing

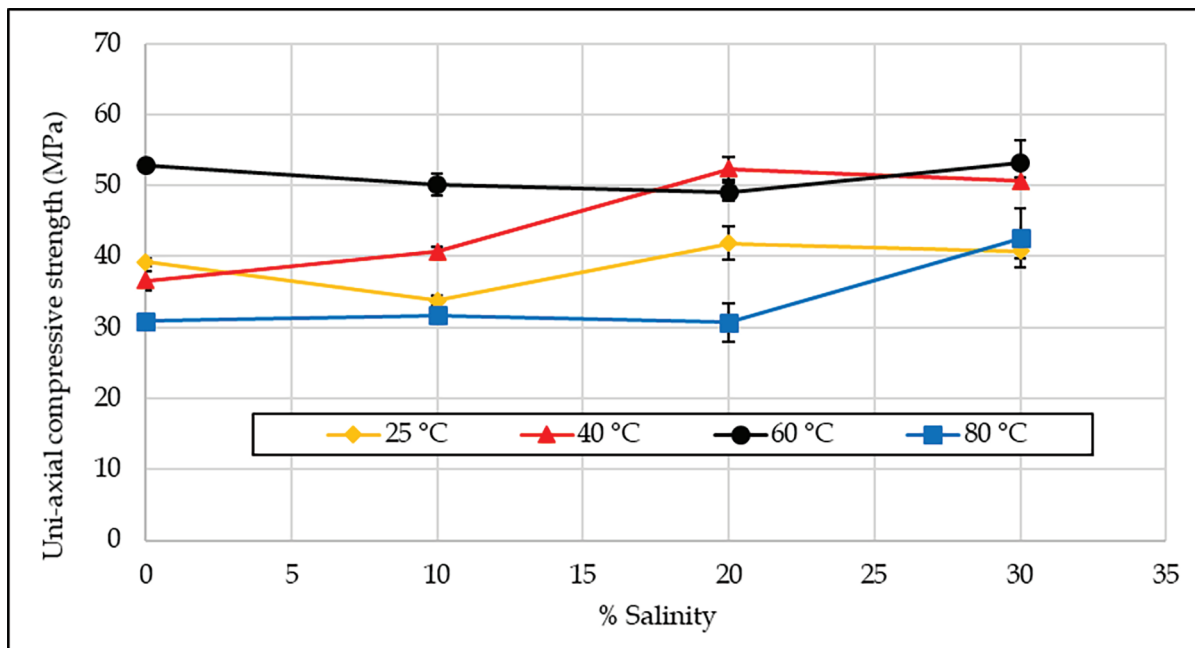


Figure 5 - Variation of UCS with Salinity at 28 Days Curing

temperature due to the rapid dissolution of Si and Al from the source material, which improves the chemical reactions [20]. At lower temperatures, the dissolution of Si and Al from the source materials takes place at a retarded pace and the geopolymer gel develops at a slower rate. The amounts of Si and Al dissolved are insufficient for polymerization and hence the UCS shows minimum values at lower curing temperatures. Elevating the curing temperature is associated with the increased dissolution of Si and Al and accelerated formation of a hard structure at the early stages

of geopolymerization. The gel continues to grow while filling the larger pores (macro pores) available in the geopolymer matrix by significantly increasing the mesopore volume [21, 25], thus allowing an increasing trend in the UCS values with the curing temperature up to 60 °C. Nasvi et al. [20] also found that the optimum curing temperature for low calcium fly ash based geopolymers is 60 °C, above which the compressive strength gradually reduces.

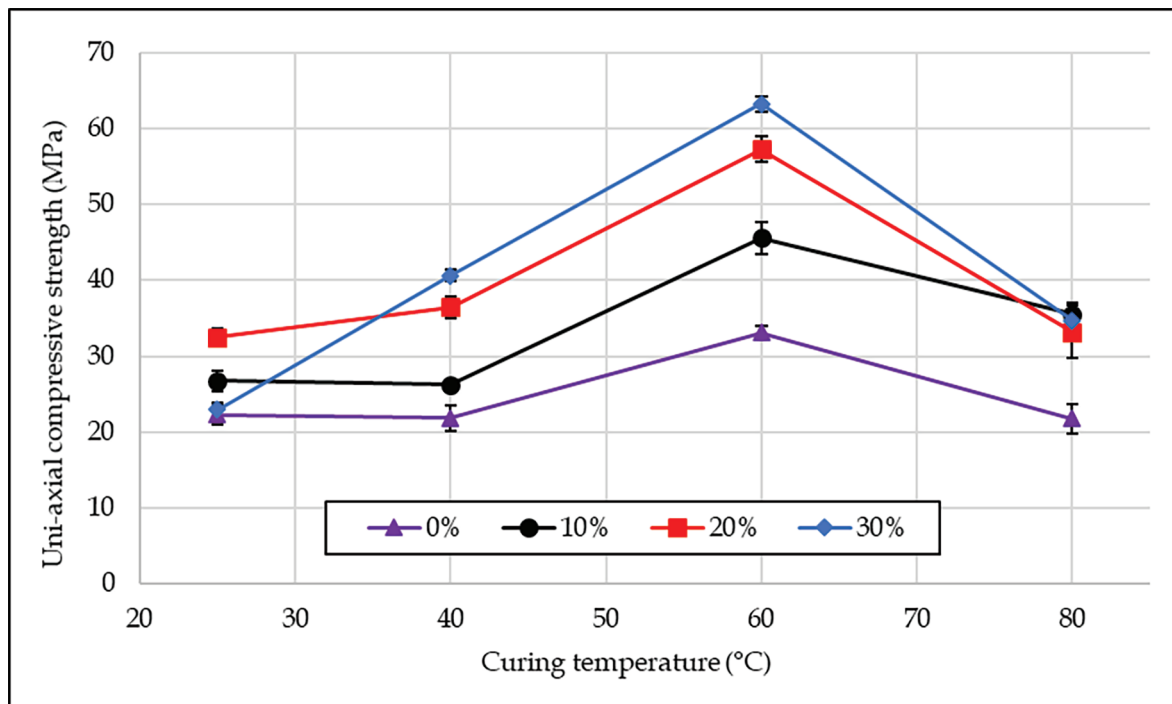


Figure 6 - Variation of UCS with Curing Temperature at 7 Days Curing

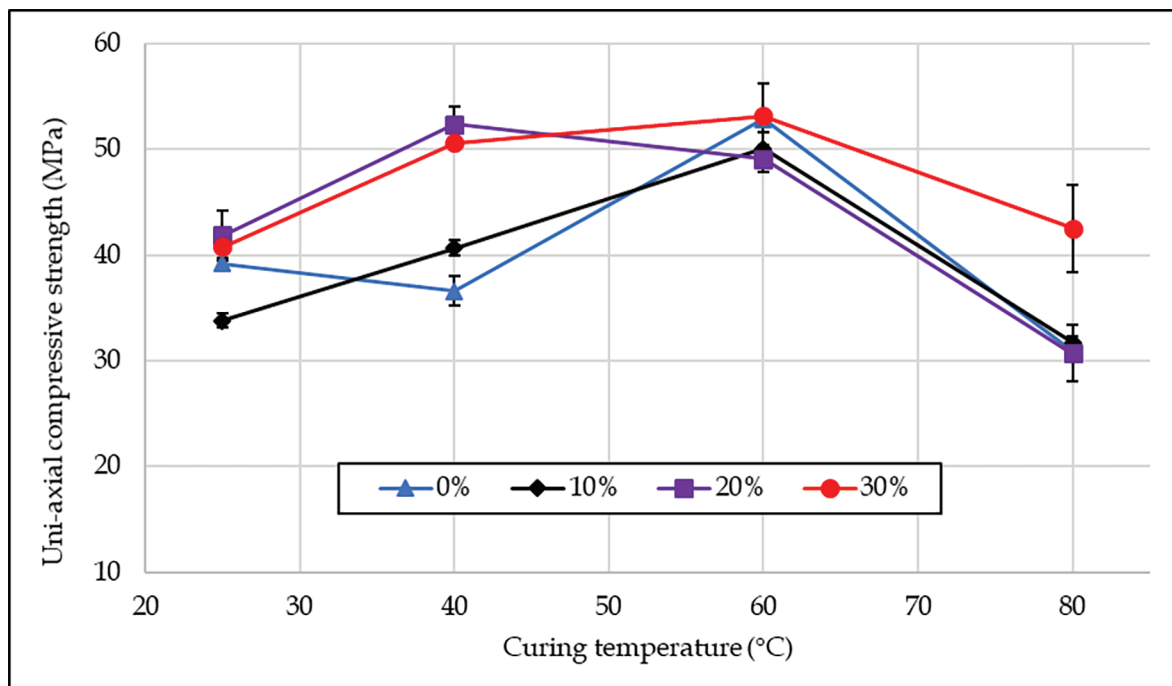


Figure 7 - Variation of UCS with Curing Temperature at 28 Days Curing

When the curing temperature reaches around 80 °C to 100 °C, the viscosity of the mixture increases rapidly at the inception of polycondensation where Al and Si released by the dissolution of the source material react immediately. This increases the setting speed of geopolymer slurries from which the unreacted particles are shielded, thereby constraining further dissolution of the source material. However, the optimum temperature depends on many other factors, including especially the

source material. Further, the calorimetric curves corresponding to the heat evolution during the geopolymerization reaction show three distinct peaks linked with the dissolution of source material, formation of oligomeric species and polymerization/condensation reactions [26]. At lower temperatures (30 – 50 °C), the heat evolved at the first two peaks is low, implying that the dissolution and formation of oligomeric species are not complete or efficient, while at higher temperatures (75 – 90 °C), the time taken

to attain the first two peaks is shortened suggesting that the time needed to break the source material and to form the oligomers and alumina/silica-hydroxy species is not enough. However, the total heat evolved reaches a peak at 60 °C where optimum compressive strength values could be observed, beyond which it gradually reduces. In addition, geopolymer needs moisture for polymerization, but the exothermic reactions cause a rapid loss of water at elevated temperatures leading to the formation of micro cavities thereby increasing the porosity, hence, contributing to the strength reduction at very high temperatures [24, 26]. With respect to enlightenments above, it can be concluded that the optimum curing temperature of geopolymer to be around 60 °C.

To analyse the combined effect of temperature and salinity on the mechanical behaviour of geopolymer, the solubility of NaCl with the temperature needs to be considered. The solubility of NaCl doesn't increase appreciably

with the temperature. Maximum solubility of NaCl in water at 25 °C is 357 mg/ml, while at 100 °C it is 384 mg/ml. According to Bharmoria et al. [15], slow exchange of solvated water molecules with bulk water due to the formation of stable NaCl-water clusters, highly perturbed water hydrogen bonding network with reduced capacity to solvate ions/ion pairs, and high rigidity of aqueous NaCl saturated solution preventing penetration of sodium chloride further into the solution are the probable reasons behind the nearly constant solubility of sodium chloride as a function of temperature. Therefore, the impact of the solubility of NaCl on the increasing UCS values with the curing temperature could be neglected. According to the results, the effect from the increasing salinity act favourably on the resulting strength at all temperatures and the increasing temperature shows favourable consequences only up to 60 °C which is apparent from the average UCS values recorded at different salinity and temperature combinations shown in Figure 8 and Figure 9.

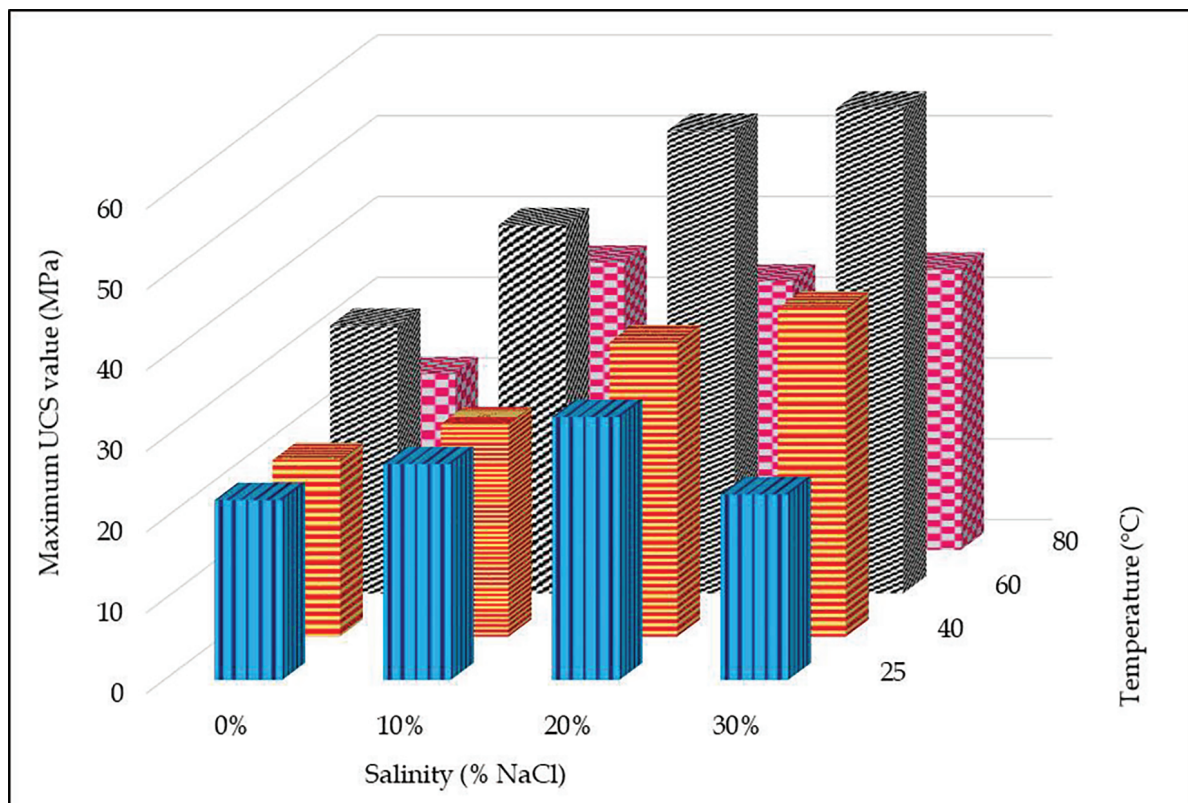


Figure 8 - Average UCS Values at different Salinity and Temperature Combinations after 7 Days of Curing

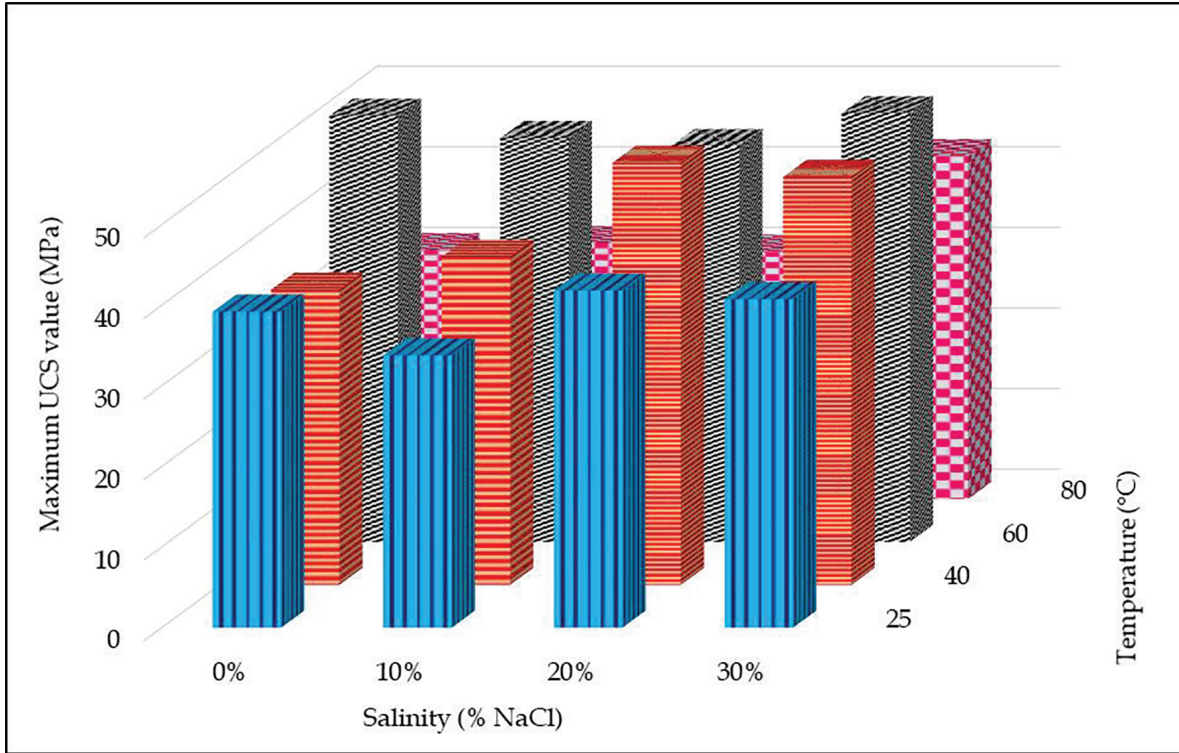


Figure 9 - Average UCS Values at different Salinity and Temperature Combinations after 28 Days of Curing

5.2 Numerical Results

5.2.1 Model Validation

The numerical model was validated against the experimental results under uniaxial stress conditions to assure the credibility of the new model, for which the experimental stress – strain curve values obtained for uni-axial compression were used as the reference. In order to calculate the vertical resultant force over the entire sample caused by the prescribed displacement, the integral operator “intop1” was applied (Eq. 3). As the reaction force is defined only at nodes, “summation over nodes” was chosen as the integration method (Eq. 4). The deviatoric stress was calculated by the difference between the resulting stress and the confinement stress. Once the model was validated, the same model was further extended to investigate the triaxial mechanical behaviour of geopolymer.

$$F_{res} = \text{intop1}(\text{solid}.RFz) \quad \dots(3)$$

$$F_{res} = \int \sigma_z \cdot 2\pi r \cdot dr \quad \dots(4)$$

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

Overall comparison of the stress-strain curves for geopolymer samples cured for 28 days (a) at 40 °C for all salinity levels (0-30% NaCl) and (b) at 30% NaCl salinity for all the temperatures (25 – 80 °C) are shown in Figures 10 and 11, respectively. Geopolymer is a brittle material and experimental stress-strain curve did not show any plastic behaviour with the loading rate used. Since linearly elastic material was assumed for the numerical model, the model accurately predicts the stress strain variation up to the yield point after which a perfectly plastic behaviour is assumed by the model. According to Figures 10 and 11, it is evident that the experimental and modelled curves are consistent with each other up to the yield point. Based on Figures 10 and 11, the percentage difference between the model predicted failure strength and the experimental failure strength values for geopolymer is between 0.01 - 0.64%. Similar to Figures 10 and 11, there was a good correlation between the experimental and numerical stress-strain curves for all the temperature and salinity combinations. Hence, it was concluded that the developed numerical model is valid for the existing experimental results.

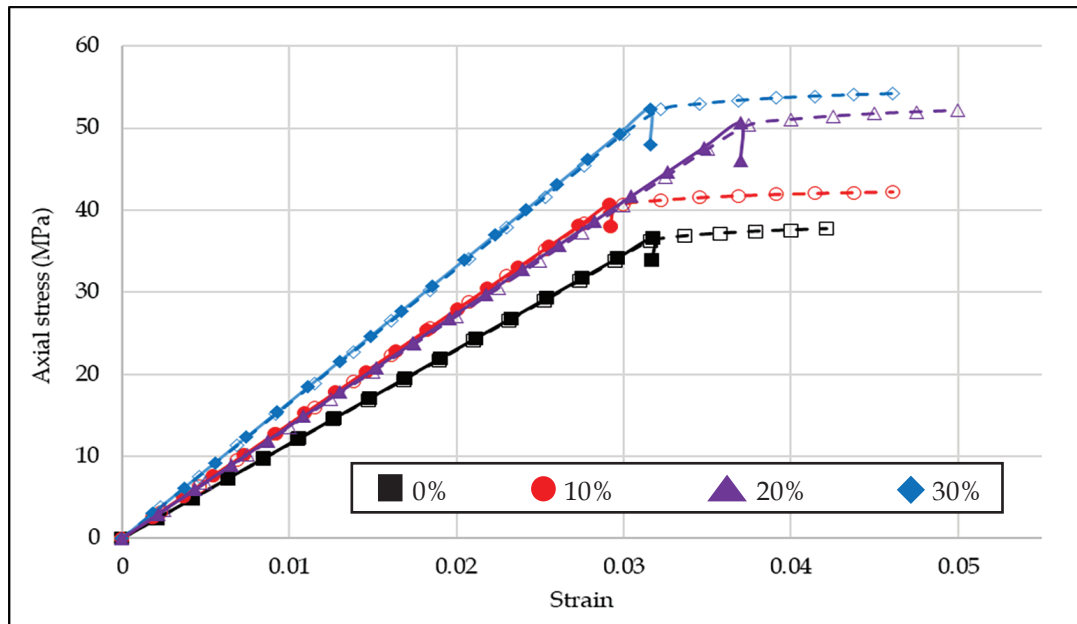


Figure 10 - Overall Comparison of Stress-Strain Curves of Geopolymer Cured at 40 °C for 28 Days (Solid Points - Experimental Results, Hollow Points - Numerical Results)

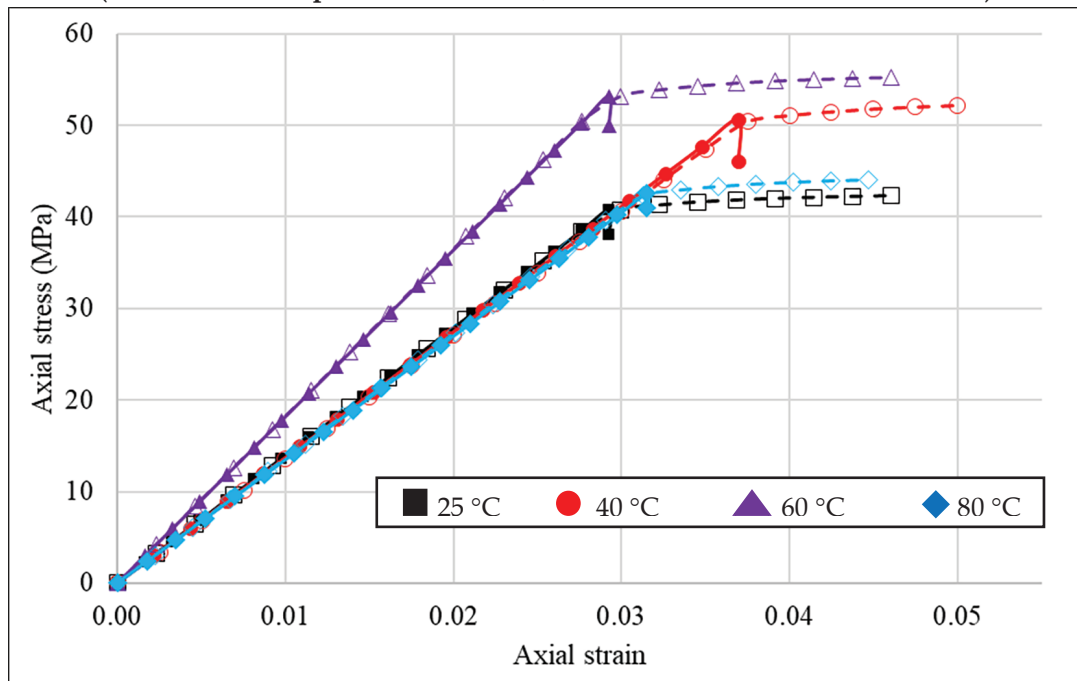


Figure 11 - Overall Comparison of Stress-Strain Curves of Geopolymer Cured at 30% NaCl Salinity for 28 Days (Solid Points - Experimental Results, Hollow Points - Numerical Results)

5.2.2 Triaxial Mechanical Behaviour of Geopolymers Under the Combined Effect of Temperature and Salinity

Variation of resulting strength with the axial strain for geopolymer cured at 40 °C and 30% salinity level at 28 days are shown in Figure 12. Based on Figure 12, the resulting strength corresponding to the strain after which no considerable strength gain was recorded was considered as the failure strength of geopolymer under each condition. Figure 13 shows the variation of failure strength with the confining stress for geopolymer cured at 40 °C

and 30% salinity levels at 28 days. It can be seen that the failure strength increases with the confining pressure. The pores in the geopolymer paste deteriorate its micro structure, hence dropping the mechanical strength. However, with the increasing level of confinement, these pore voids close, reducing the permeability and the percentage of voids, thereby increasing the mechanical strength [27]. Therefore, the maximum resulting strength is obtained at the highest level of confinement (25 MPa).

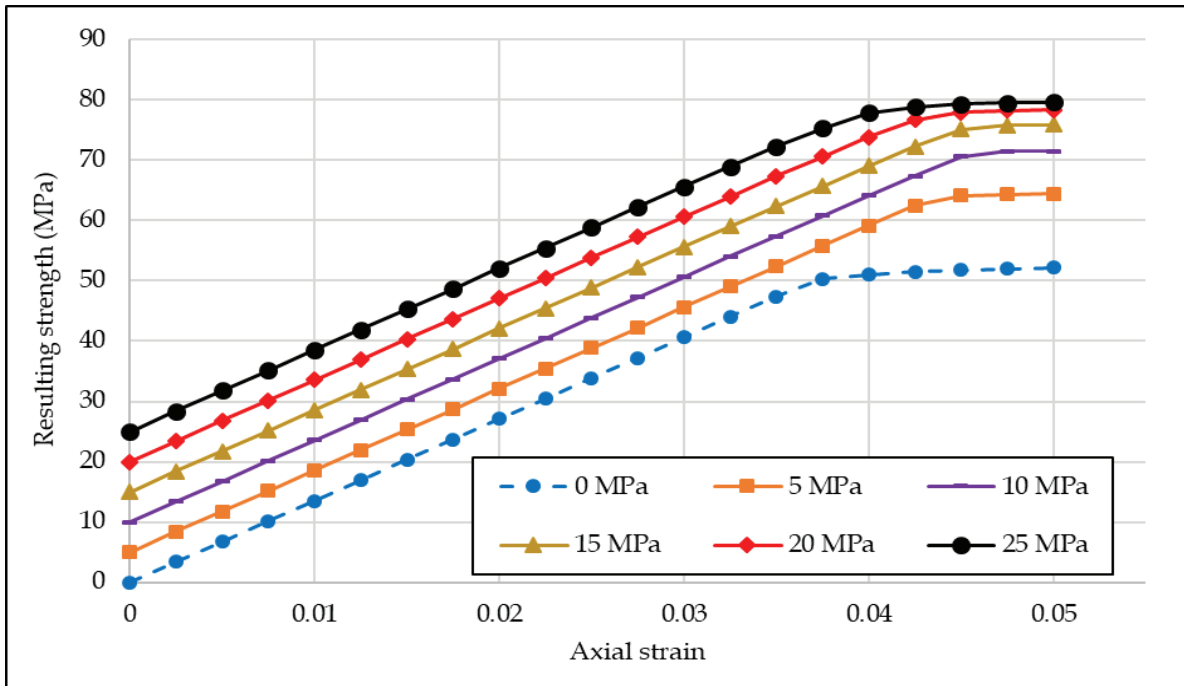


Figure 12 - Variation of Resulting Strength with Different Confining Pressures for Geopolymer Cured at 40 °C and 30% Salinity Level for 28 days

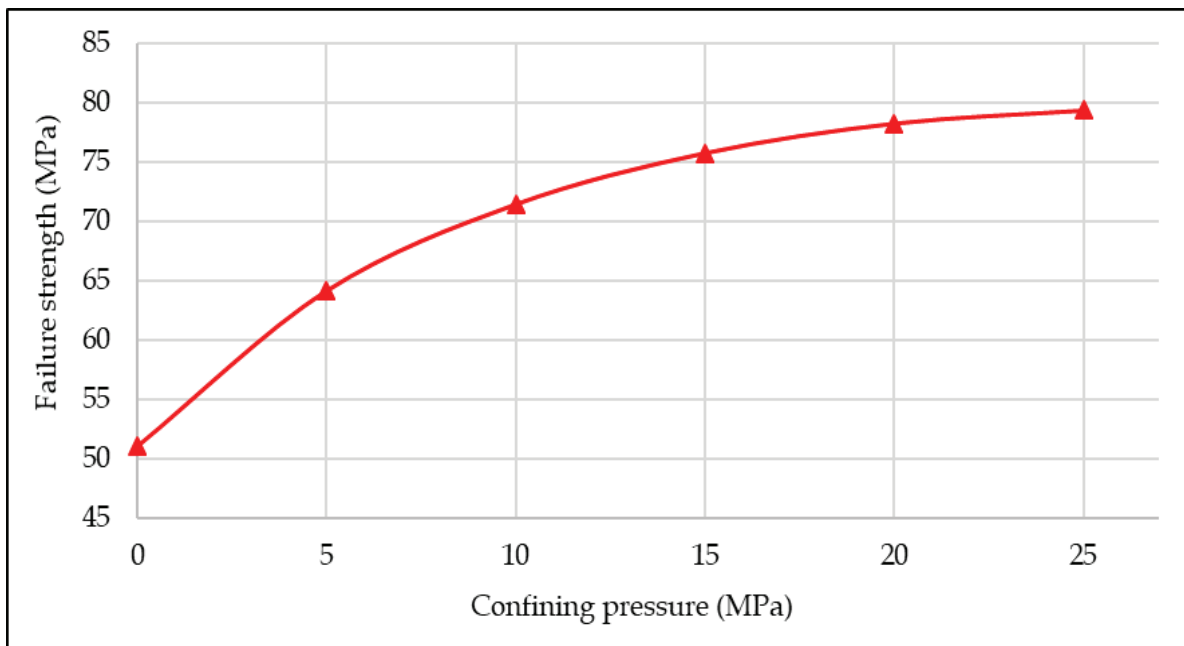
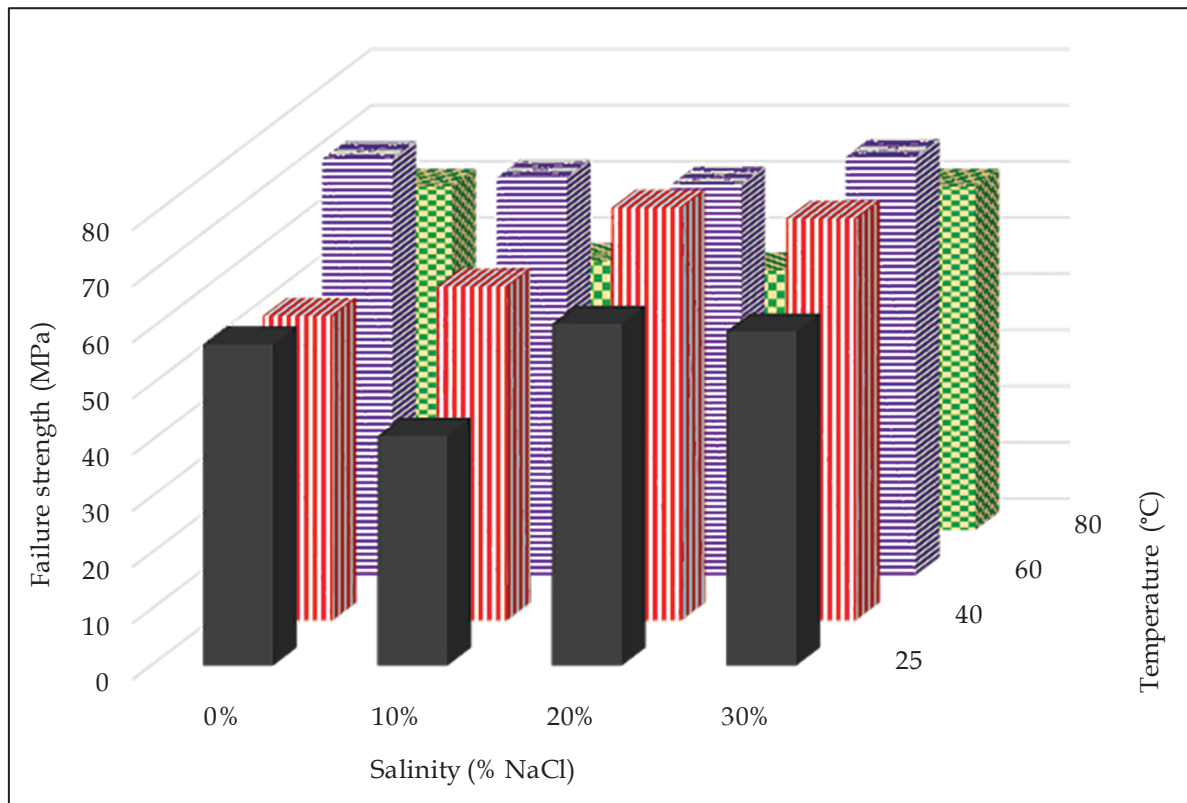


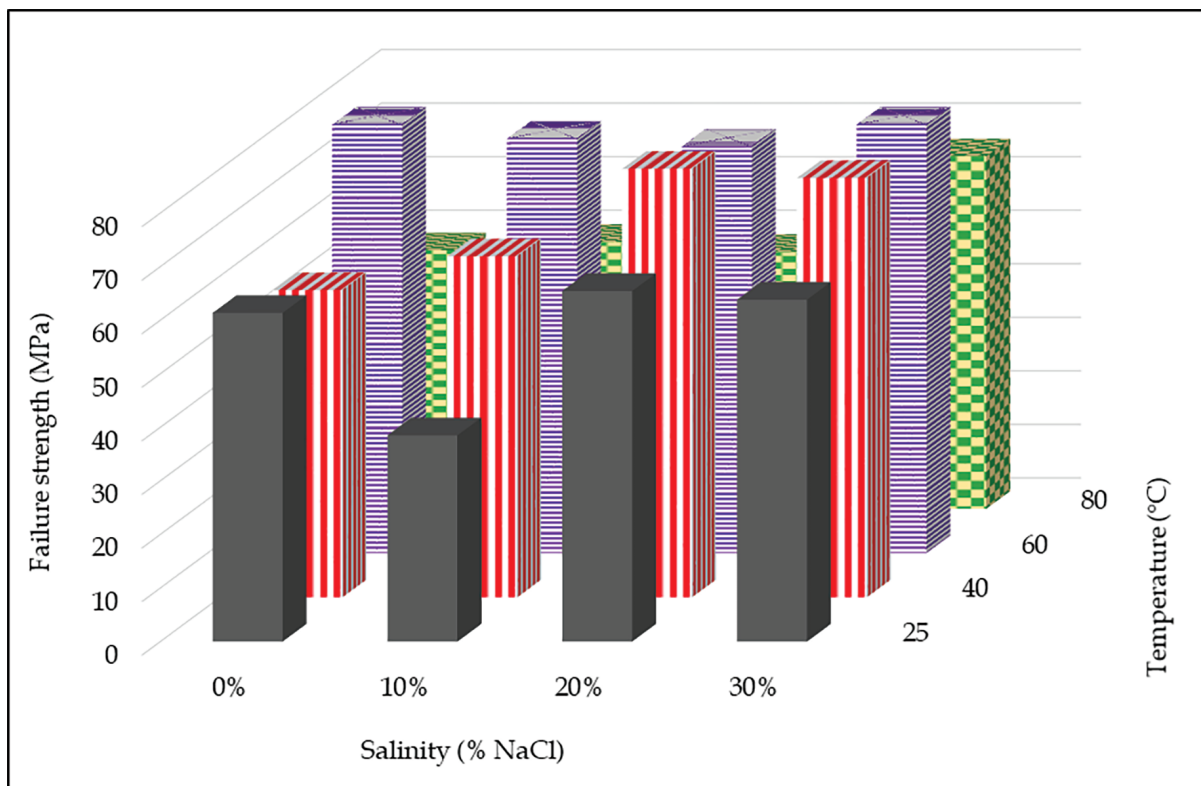
Figure 13 - Variation of Failure Strength with Confining Pressures for Geopolymer Cured at 40 °C and 30% Salinity Level for 28 Days

Figure 14 shows the combined effect of temperature and salinity on the failure strength of geopolymers at 28 days under different confining pressures. For all confinements, failure strength continues to grow with the increasing salinity level (0 - 30% NaCl) and

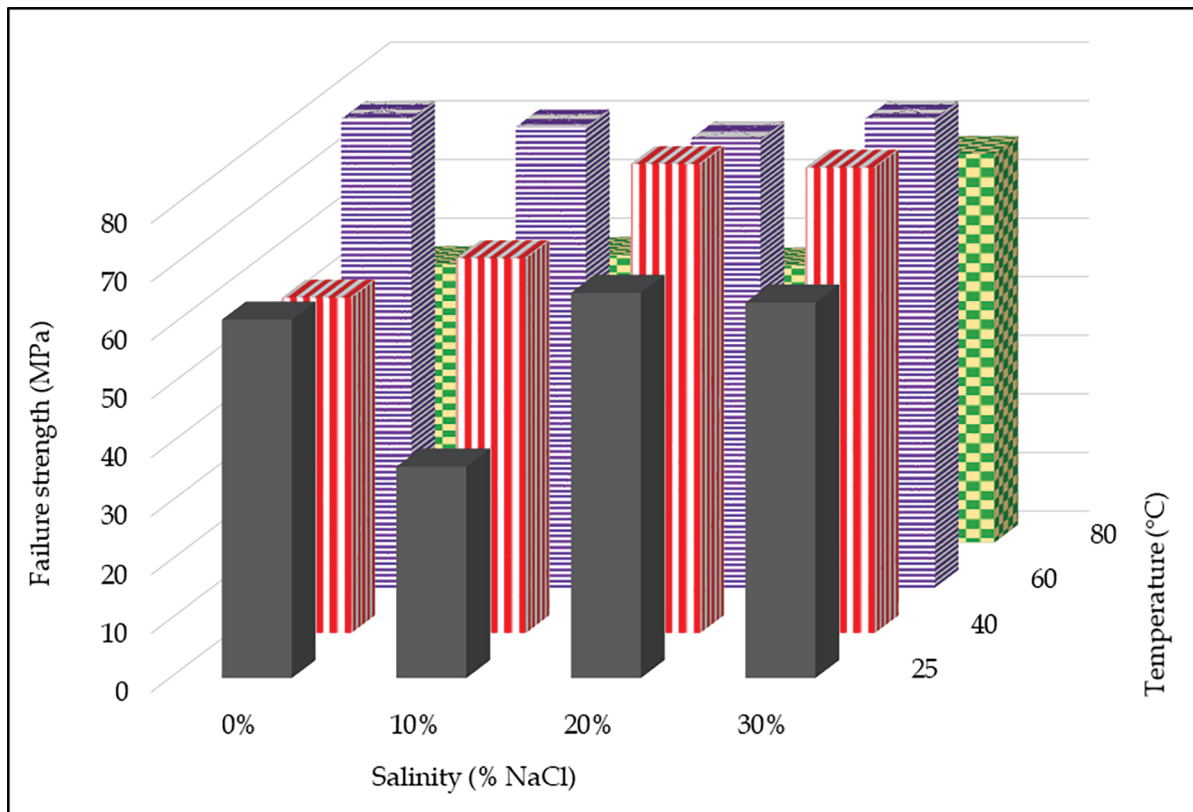
temperatures from 25 - 60 °C. On the contrary, the combined effect has unfavourably affected for geopolymer cured at 80 °C which shows a diminishing trend with the increasing confinements at all sanity levels.



(a) $P_c = 10$ MPa



(b) $P_c = 20$ MPa



(c) $P_c = 25 \text{ MPa}$

Figure 14 - Variation of Failure Strength of Geopolymer with the Combined Salinity and Temperature Conditions at Different Confinements: (a) $P_c = 10 \text{ MPa}$, (b) $P_c = 15 \text{ MPa}$ and (c) $P_c = 25 \text{ MPa}$

Despite the closure of pore voids with the increasing confinement which should result in a higher strength, the adverse effect on the failure strength due to the elevated curing temperature (80 °C) (discussed in section 5.1 above) seems to be playing a dominating role over the confining pressure, thus displaying lower strength values. With the deteriorated microstructure of geopolymer at elevated temperatures, once the higher confinements are applied, samples tend to collapse easily at low strength values. Based on the overall results, the best possible combination of temperature, salinity and confinement that corresponds to the maximum failure strength is at 60 °C, 30% NaCl and 25 MPa, respectively.

According to Figures 9 and 14, when the confining pressure increases from 0 – 10 MPa, the failure strength increases from 20.9 – 97.8% based on the temperature and salinity combination. Increments in failure strength varying between 13.9 – 57.0% and 6.7 – 57.1% were observed at 20 and 25 MPa confinements, respectively, depending on the salinity and temperature combination when compared to their corresponding UCS values. When the

percentage salinity increases from 0 to 30%, compared to the normal water cured samples, failure strength varies from (-28.5) to 35.5%, (-37.3) to 40.57% and (-41.0) to 42.7% for confining pressures of 10, 20 and 25 MPa, respectively, depending on the curing temperature. When the curing temperature increases from 25 to 80 °C, failure strength increment ranges from (-24.1) to 73.1%, (-26.7) to 101.0% and (-28.0) to 118.0% compared to the strength of the samples cured at 25 °C (room temperature) for confining pressures of 10, 20 and 25 MPa, respectively, depending on the salinity. From the above rates it is evident that the curing temperature plays a more dominant role than the salinity, in improving the failure strength of geopolymers.

A typical well-cement should possess a compressive strength of 20 to 50 MPa, depending on the depth, to provide thermal isolation and to avoid mechanical fracturing [4, 12]. On the whole, considering all the three conditions (temperature, salinity and confinement), the failure strength of geopolymer varies in the range of 22 to 83 MPa and the strength obtained under the worst

possible conditions subjected to 30% salinity at 80 °C and 25 MPa confinement is 66.4 MPa, and is beyond the general strength requirement of a typical well cement.

OPC based cement, which is widely used in oil well cementing, has already been diagnosed to provide lower strength values with increasing salinity levels [4]. They are not acid resistant and appear vulnerable to attacks by carbonated brine in CCS projects [5, 20]. OPC based well cement is reported to have higher strength at ambient conditions which declines with increasing temperature. But, based on the output of this study, it is evident that geopolymer possesses favourable properties that could survive the aforementioned extreme conditions in earth's downhole. Therefore, geopolymer could be used as a good replacement for OPC in the sequestration wells with respect to its triaxial mechanical behaviour.

6. Conclusions

An experimental and numerical study was conducted to study the combined effect of temperature (25, 40, 60, 80 °C) and salinity (0, 10, 20, 30% NaCl) on the triaxial mechanical behaviour of geopolymer. The following conclusions are drawn based on the outcomes of this study.

- At a given temperature, the resulting failure strength increases with the level of confinement under triaxial stress conditions for all the salinity levels.
- At a given temperature, both the uniaxial compressive strength (UCS) and resulting failure strength increase with the increase in salinity level.
- At a given salinity level, both the UCS and the resulting failure strength increase with the temperature up to 60 °C and then decrease up to 80 °C. This is due to the increased dissolution of Si and Al from the source material up to 60 °C which accelerates the geopolymerization reaction.
- When the combined effect of temperature and salinity in the failure strength of geopolymer is considered, temperature plays a more dominant role than the salinity and confinement in altering the failure strength of geopolymers. The worst combination in terms of the failure strength

(temperature of 80 °C, salinity of 30% NaCl and confinement of 30 MPa) provided an average failure strength value of 66.4 MPa, which satisfies the strength requirement for typical well cement.

- On the whole, the combined effect of temperature and salinity acts favourably to provide excellent mechanical behaviour under in-situ down-hole conditions and therefore geopolymers can be used as a replacement for ordinary Portland cement (OPC) based well cement.

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