GEOPOLYMER AS WELL CEMENT AND VARIATION OF ITS MECHANICAL PROPERTIES UNDER DIFFERENT CURING TEMPERATURE AND CURING MEDIUMS

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Abstract

Geo sequestration of carbon dioxide (CO_2) has been found to be one of the best solutions to reduce anthropogenic amount of greenhouse gases to the environment. Well integrity of sequestration wells should be maintained for the success of any sequestration projects. Well cement plays a vital role in well integrity for any sequestration projects, and ordinary Portland cement (OPC) based well cement has been used in underground wells. There are many problems, such as cement degradation, chemical attacks, durability issues, leakage, etc., associated with OPC based well cement. One of the best replacements for OPC based well cement would be the use of geopolymer cement, as it is economical in production, sustainable in reducing waste products, consumes less energy, doesn't undergo chemical attacks, durable, resistive in acidic environments and possess higher strength compared to OPC. This paper will review suitability of geopolymer as well cement under downhole conditions, and analyse the advantages of using geopolymer over OPC-based well cement. Moreover, well cement will be exposed to range of temperatures, pressures and fluid medium from the ground surface to sequestration depths of more than 1 km. Therefore, this paper aims to study the mechanical behaviour of geopolymer under different curing temperatures (from 23 ºC to 80 ºC) and curing mediums (brine, water and CO_2 saturated brine). It has been found that optimum curing temperature for higher strength is 60 ºC and geopolymer exhibits high strength compared to class G cement above ambient temperature. In addition, water saturated samples showed higher strength reduction compared to brine saturated geopolymer samples.

Keywords: alkaline activator, geopolymer, carbonation, degradation, well cement

1. Introduction

Anthropogenic emissions of greenhouse gases have been one of the major problems for the global nations. The Intergovernmental Panel on Climate Change (IPCC) estimates that under a "business-as-usual" energy scenario, global CO_2 emissions will reach approximately 77Gt/ yr by 2100, and the average atmospheric CO_2 concentration will reach approximately 750 parts per million by volume (ppmv). Global CO_2 emission should be reduced to reach 15 Gt/ yr less than the business-as-usual projection in 2050, and by 2100, emissions will be 50 $GtCO_2$ / yr less (Bruant et al., 2002). Of all greenhouse gases, CO_2 is responsible for 64% of the greenhouse gas effects (Bertier et al., 2006). 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. Of the above solutions, the best solution to reduce greenhouse gases in the near term would be to inject carbon dioxide (CO_2) into deep underground wells such as coal seams, saline aquifers, and depleted oil and gas reservoirs. This method will help to capture and store CO_2 from power generation, iron and steel production, cement manufacture, and oil and natural gas production and refining, which collectively contribute approximately one third of the total CO_2 emissions (Bruant et al., 2002).

Well cement plays vital role in the success of any sequestration project. When CO_2 is injected through bore-hole wells it should not leach through the surrounding formation as it may cause many problems to the existing system. Therefore, these wells should be constructed using a concrete which is durable, anti-corrosive, chemically inert, adaptive to pressure variations, and less permeable, in order to maintain well integrity, and to avoid any leakage of CO_2. To date, ordinary Portland cement (OPC) based well cement have been used and there are many problems with OPC, when used for CO_2 sequestration. The detailed behaviour of OPC based well cement under sequestration conditions are discussed in chapter 3. According to an EOR survey, out of the total of all CO_2 EOR wells (16,348) only 0.15% use non-Portland cement CO_2 zones.

2. Literature review

This section discusses about geopolymer cement, advantages of geopolymer compared to OPC and relative performance of OPC and geopolymer under CO_2 sequestration conditions.

2.1 Geopolymer cement

Geopolymer is a type of amorphous alumina-silicate cementitious material with high strength, excellent volume stability, durability and resistance to acids. Geopolymerization can be a profitable way of recycling materials and using previously unused materials (Van Jaarsveld et al., 1997). The term was first defined by Davidovits in the early 1970s to describe inorganic materials with polymeric Si-O-Al bonds. Geopolymer can be defined as "the material that

results from the geosynthesis of polymeric alumina-silicates and alkali silicates, yielding a three-dimensional polymeric frame work of linked SiO_4 and AlO_4 tetrahedra" (Kriven and Bell, 2004). Fly ash, metakaolin, silica fume, recycled concrete slug, etc. have been used as the raw material for geopolymer production. Metakaolin is refined kaolin clay that is fired (calcined) under carefully-controlled conditions to create an amorphous aluminosilicate that is reactive in concrete. Kaolin is the by-product of oil sands operations. Metakaolin particles are 10 times smaller than cement particles, and produce more durable and impervious concrete. Although metakaolin is widely used for geopolymer applications, its usage is decreasing, due to its high water demand caused by its plate-like particle shape and higher porosity. Fly ash is one of the best alternatives in place of metakaoiln as it gives a sustainable solution for waste management. 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). Fly ash increase concrete strength, improves sulphate resistance, decreases permeability, reduces the water ratio requirement, and improves the workability of the resulting concrete (Badur and Chaudhary, 2008). The role of alkaline activator is to activate the raw materials to take part in the polymerization process. The polymerisation process is very rapid in the presence of alkali solution. The alkali activator is most commonly an alkali hydroxide or alkali silicate solution. Strong alkalis are required to activate Si and Al to form a compacted composite. The most common activators used are NaOH, Na_2SO_4, waterglass, Na_2CO_3, K_2CO_3, KOH, K_2SO_4 and various combinations of them (Khale and Chaudhary, 2007).

The polymerisation process includes a fast chemical reaction under alkaline conditions on Si-Al minerals, resulting in a three-dimensional polymeric chain and ring structure consisting of Si-O-Al-O (poly (sialate)) bonds, as follows:

$$Mn\ [-(SiO_2)\ z-AlO_2]\ n.\ wH_2O$$
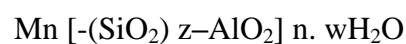
Where: M = the alkaline element or cation such as potassium, sodium or calcium; the symbol indicates the presence of a bond, n is the degree of polycondensation or polymerisation; and z is ratio of Si/Al, which is 1, 2, 3, or higher.

Some of the related frameworks (Davidovits, 1994) are given below;

1. Poly (Sialate) Si: Al = 1, having (-Si-O-Al-O-) as the repeating unit

2. Poly (Sialate-Siloxo) Si: Al = 2, having (-Si-O-Al-O-Si-O-) as the repeating unit

Poly(sialate-siloxo)
(-Si-O-Al-O-Si-O-)

3. Poly (Sialate –disiloxo) Si: Al = 3, having (-Si-O-Al-O-Si-O-Si-O-) as the repeating unit
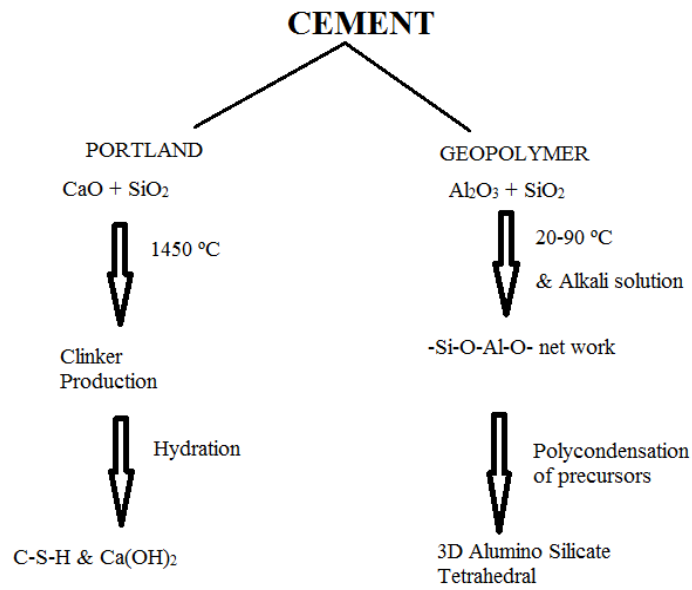
Poly(sialate-disiloxo)
(-Si-O-Al-O-Si-O-Si-O-)

2.2 Advantages of geopolymer compared to OPC

The usage of concrete is second only to water usage in the world, and the production of one tonne of OPC emits approximately one tonne of CO_2 to the atmosphere (Yang et al., 2009). One tonne of geopolymeric cement generates 0.184 tonnes (approximately $1/6^{th}$) of CO_2 (Davidovits, 2002). The production of cement is increasing by 3% annually. The manufacture of geopolymer cement emits approximately 90% less CO_2 and requires 50% less energy in production due to its low process temperature compared to OPC (Hewayde et al., 2006). Furthermore, the cost of geoplymer concrete manufacture is 10-30% less than that of OPC concrete (Lloyd and Rangan, 2010). If the manufacture of the two cements is compared, as shown in Fig 1, geopolymer has the following advantages:

1. The presence of alumina silicate materials in geopolymer provides more resistance to chemical attack
2. Since there is no calcination step, there is no release of CO_2.
3. Total energy consumption for production is lower than for OPC.

CEMENT

PORTLAND	GEOPOLYMER
$CaO + SiO_2$	$Al_2O_3 + SiO_2$
↓ 1450 °C	↓ 20-90 °C & Alkali solution
Clinker Production	-Si-O-Al-O- net work
↓ Hydration	↓ Polycondensation of precursors
C-S-H & $Ca(OH)_2$	3D Alumino Silicate Tetrahedral

Fig 1: Comparison of OPC and geopolymer manufacture

## 2.3 Relative performance of OPC and geopolymer under sequestration conditions

Kutchko et al., (2007) published their work on class H neat samples (w/c =0.38) cured in (1% Nacl) brine solution under four different curing conditions [0.1MPa and 22 °C, 0.1MPa and 50 °C, 30.3 MPa and 22 °C, and 30.3 MPa and 50 °C], and all the samples were saturated with brine for 9 days. A series of rings was found as shown in Fig 2.
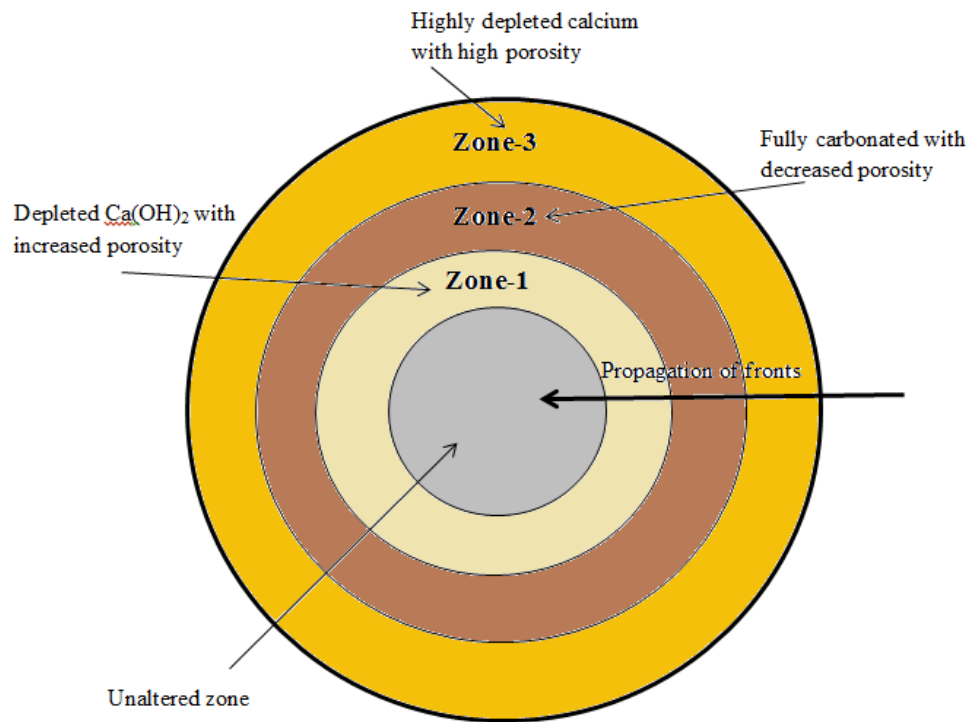
Fig 2: Formation of different zones due to the dissolution of calcium as observed by Kutchko et al. (2007) and Duguid (2010) modified.

Duguid et al. (2009) observed that under geological sequestration conditions (50 ℃), well cement exposed to carbonated brine may lose its sealing properties within a short period of time. Duguid et al. (2010) conducted experiments on class H neat samples and 6% bentonite containing samples with influent pH of 2.4 and 3.7 and temperatures of 23 ℃ and 50 ℃. The samples were initially cured for 3 hours, and then placed in the brine solution for 12 months. They observed five different layers in the samples reacted with a pH of 2.4 at 50 ℃ by X-ray diffraction (Duguid et al., 2010): 1.An orange layer at 50 ℃, depleted by calcium hydroxide and calcium silicate hydrate (C-S-H); 2.An outer brown layer at room temperature; 3. A white layer precipitated with calcium carbonate; 4.A grey layer with depleted calcium hydroxide, and 5. A dark grey core of un-reacted sample.

In all the above findings, it has been observed that OPC-based well cement cannot survive in acid rich environment. However, geopolymer has excellent properties in adverse conditions compared to OPC cement. Since geopolymer has excellent acid-resistant properties (Uehara, 2010) it can be used in CO_2-rich environments. Uehara (2010) conducted experiments by immersing OPC and geopolymer samples in 10% H_2SO_4 solution. He observed that the OPC sample collapsed after four months, whereas the geopolymer sample indicated no significant change as shown in Fig 3. This indicates that geopolymer cement can be used in acid- rich environments like CO_2 sequestration conditions.
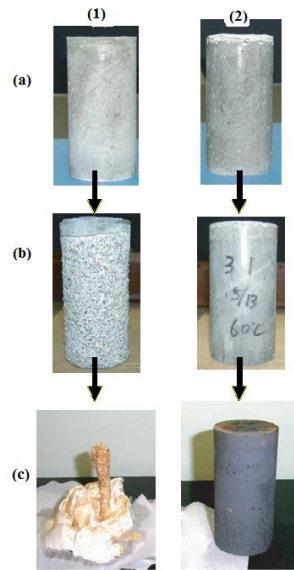
Fig 3: Geopolymer mortar and OPC mortar soaked in 10% H2SO4 (Uehara, 2010);
(1) OPC Sample (2) Geopolymer sample
(a) Before soaking (b) One week later (c) Four months later

The behaviour of OPC and geopolymer was also compared at elevated temperatures using the equivalent OPC paste finding of Mendes et al. (2008). It was found that geopolymer gained strength with the temperature, whereas OPC showed a considerable drop with the increase in temperature (see Fig. 4). The geopolymer attained peak strength of 77 MPa at 300 ºC, and then showed a gradual decrease. Since down-hole conditions are always under higher pressure and temperature, use of geopolymer as well cement will ensure no strength reduction during sequestration phases.
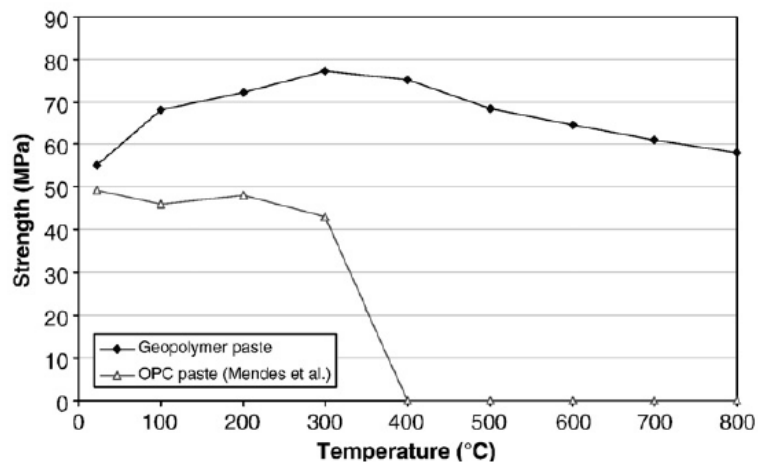
Fig. 4: Comparison of compressive strengths of OPC and geopolymer at elevated temperatures (Kong and Sanjayan, 2010).

Temperature and pressure variations in the down-hole conditions affect CO_2 attacks on well cement. Arina et al. (2010) conducted experiments on Class G well cement by changing pressure (105 bars and 140 bars) and temperature (40 ℃ and 120 ℃) to study the effect of pressure and temperature on the degradation properties of well cement. Cement degradation was evaluated under wet supercritical CO_2 and CO_2 saturated brine (0.01M NaCl) solutions for different curing periods of 24 hours, 72 hours and 120 hours. It was observed that loss of compressive strength was higher at elevated temperatures as well as at higher pressures, as shown in Fig 5.a. It was also noted that samples exposed to wet supercritical CO_2 showed 2% to 7% more mass increase compared with CO_2 saturated brine. Samples exposed to elevated temperatures showed higher depths of penetration, whereas at higher pressures the depth of penetration was lower, compared with low pressure conditions (See Fig 5.b).
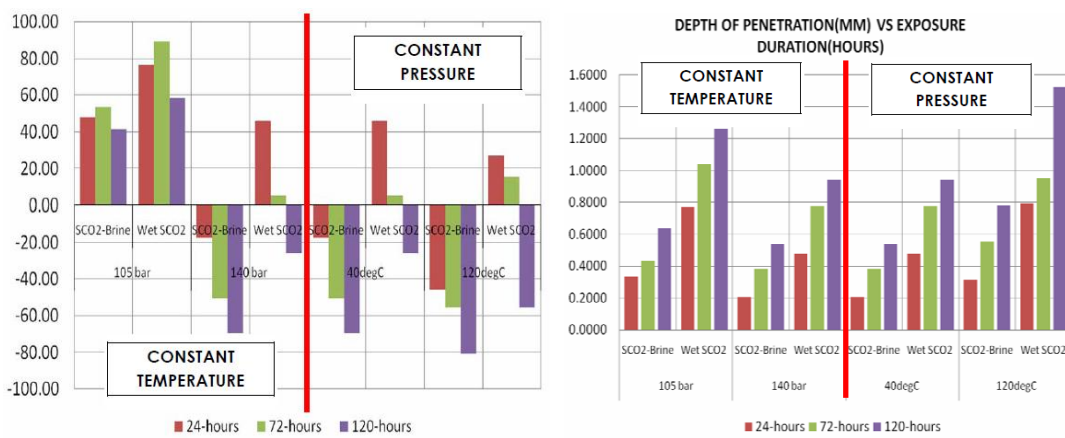
(a) *(b)*

Fig 5: (a) Compressive strength evolution (%) at different pressure and temperature conditions; and (b) Depth of penetration (mm) at different pressure and temperature conditions (Arina et al., 2010).

However, geopolymer gain higher strength under high pressure and temperature conditions. Hardjito et al. (2004) and Palomo et al. (1999) found that increasing the curing temperature increased the compressive strength of geopolymer. Since sequestration depth is above 800 m, the pressure and temperature will be always higher. This will enable geopolymer to gain strength and reduce permeability, which can form tight joints to prevent CO_2 migration upward. Another important factor affecting the degradation of cement is the P^H gradient. Since there is a difference between the P^H of pore water in un-reacted cement (~12.3) and the surrounding aqueous solution (~2.9), the system will be in disequilibrium until the cement degrades completely (Kutchko et al., 2007). If the P^H is above 10.5, carbonate will be dominant by blocking the connected pores, and thus reducing the permeability. When P^H is reduced further as the calcium hydroxide and alkali phases are depleted, carbonate will not have the predominant phase, and bicarbonate will become predominant. This will cause calcium to deplete out of the cement, leading to porous silica gel (Duguid et al., 2009). When geopolymer is used, it produces Na_2CO_3 or K_2CO_3, and pH will drop only up to 10-10.5, providing strong resistance to corrosion. This will ensure no degradation or porosity increment taking place in geopolymer matrix.

3. Variation of mechanical properties of geopolymer with different curing temperatures

3.1 The variation of Uni-axial compressive strength (UCS) with curing temperature

This experimental works analyse the variation of compressive strength of geopolymer from low temperature ranges (23 ℃) up to 80 ℃. In addition, similar plot was obtained for class G cement, which is currently used in the petroleum industry. Geopolymer neat samples (without aggregate) were prepared using ASTM Class F Fly ash (low calcium) based on the mix design. Density of the geopolymer cement slurry was assumed to be 1800 kg/m^3, and the ratio of alkaline liquid/ fly ash selected was 0.40 as this will give optimum strength according to the literature (Hardjito et al., 2009). A combination of 10M sodium hydroxide (NaOH) and sodium silicate (Na_2SiO_3) was used as the alkaline activator. NaOH was obtained in pellet form having 32% of pellet and 68% of water. Na_2SiO_3 with 44% silicate solid and sodium salt, and 56% of water was used. In addition, Na_2SiO_3/ NaOH = 2.0 was selected, based on previous studies. On the other hand, class G cement was observed from Adelaide Brighton Cement Ltd, Adelaide, Australia.

The mixtures were mixed in a mechanical concrete mixer for a period of 8 minutes, and then samples were poured in to the cylindrical moulds of height 100 mm and diameter 50 mm in two layers. The samples were then vibrated on a vibrating table for 2 minutes to remove any air voids. Then the samples were directly transferred to the oven for curing. Curing temperatures of 80, 70, 60, 50, 40, 30 ℃ and ambient temperature (23 ℃) were selected. Samples were cured in the oven for 24 hours, and then cured at ambient condition for another 48 hours before testing. Prior to testing, the end faces of the samples were machine ground to ensure purely axial load during the testing. Vertical and horizontal strain gauges were used to measure the strain. The compression testing apparatus was used was a Shimadzu 300 kN Uniaxial Testing Machine and the test was performed on the samples with a displacement control loading rate of 0.2 mm/min. The variation of UCS with the curing temperature is shown in Fig 6. At the ambient condition (23 ℃), samples could not be tested after 48 hours due to poor geopolymerisation. However, samples cured under ambient conditions were tested after 7 days, and the UCS value was 29.4 MPa, which is higher than normal OPC concrete. Also, it was observed that the optimum curing temperature for higher strength is 60 ℃, and compressive strength tended to reduce when cured beyond 60 ℃. This may be due to the weakening of the microstructure at elevated temperature or the formation of micro-cracks.
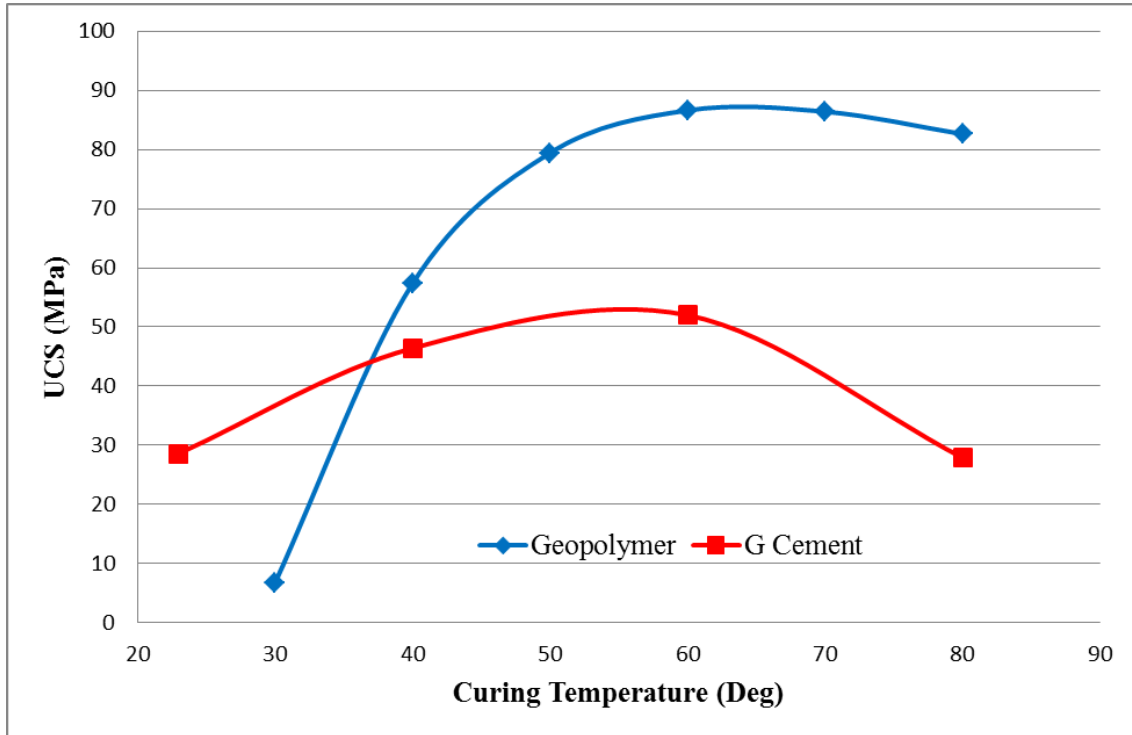
Fig 06: The comparison of UCS of geopolymer and G-cement samples with curing temperature

3.2 Damage behaviour of geopolymer using acoustic emission (AE)

Crack closure, crack initiation and crack damage stages were studied for the samples cured at different curing temperatures with acoustic emission method. The stress thresholds obtained for the samples cured 80 ℃ is shown in Fig 7. All the crack propagation stress threshold values obtained for samples cured from 23 ℃ to 80 ℃, using stress-strain and AE analysis is displayed in Table 1. Although, samples cured at 30 ℃ were tested, they did not show any AE events. This may be due to the non-brittle behaviour at that curing temperature with the short curing period of 48 hours. According to the results obtained, samples cured at ambient conditions (23 ℃), 40 and 80 ℃ doesn't show crack closure phase in AE event. However, crack closure stress threshold increases with curing temperature from 19.4 MPa at 50 ℃ to 32.3 MPa at 70 ℃. This is due to the increase in the compressive strength with the curing temperature, which leads to a proper geopolymerisation. Similarly, crack initiation thresholds also follow the same trend, showing an increase with the curing temperature, whereas crack damage is higher at 70 ℃ compared to 80 ℃. Crack initiation threshold increases from 10.2 MPa at ambient curing (23 ℃) to 64.6 MPa at 80 ℃ curing, whereas crack damage increases from 23.9 MPa at ambient curing (23 ℃) to 85.7 Mpa at 70 ℃, and then dropped to 71.7 MPa at 80 ℃. This indicates that crack initiation threshold increases with the curing temperature, while crack damage threshold increases with the compressive strength. Compressive strength increases up to 60 ℃, and further increase in curing temperature causes the strength to reduce slightly. Crack damage threshold

also follows the trend of compressive strength, and hence it can be concluded that crack damage threshold is strength dependant.
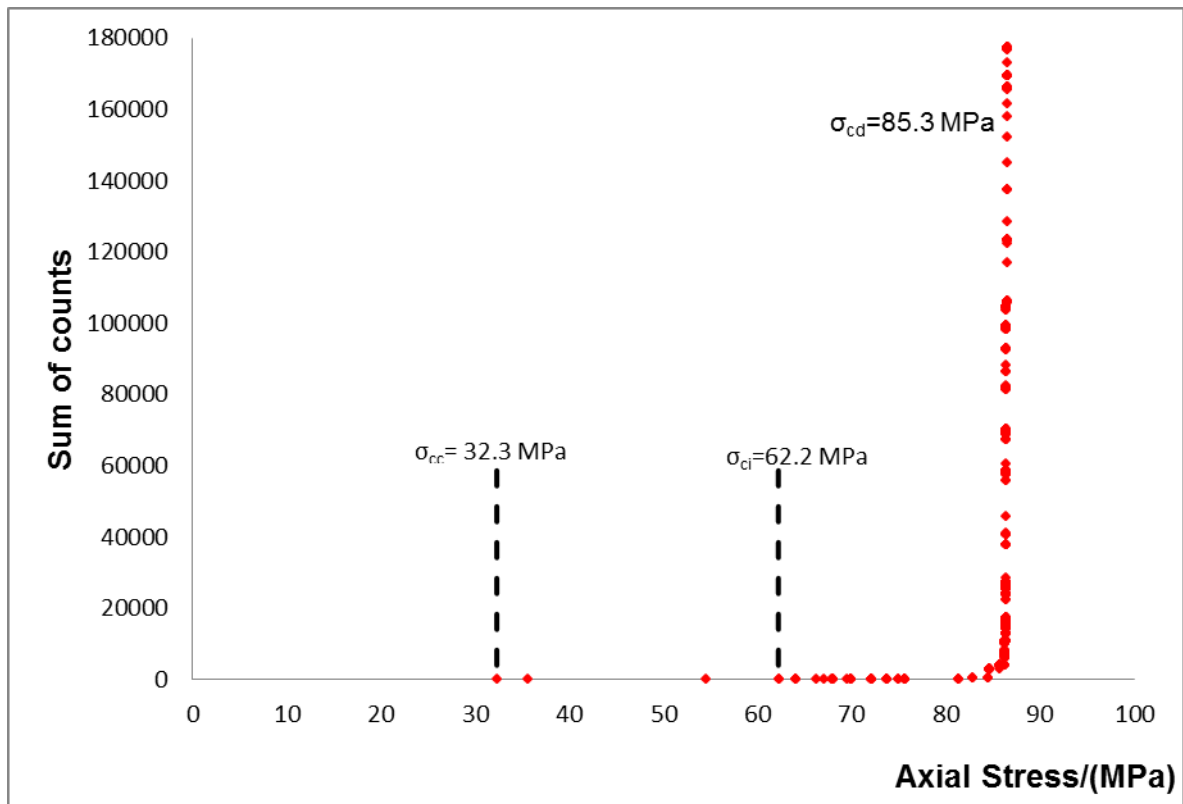
Fig 7: Stress threshold obtained for the sample cured at 70 ºC from AE analysis

Table 1: Crack propagation stress thresholds for all the samples from stress-strain and AE analysis methods.
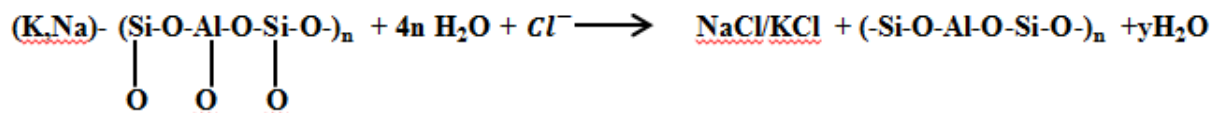
| Curing Temperature (deg)	Crack closure (MPa)	Crack Initiation (MPa)	Crack Damage (MPa)
Ambient (23)	na*	10.2	23.9
40	na*	36.2	56.9
50	19.4	50.8	78.8
60	24.2	51.3	85.8
70	32.3	62.2	85.3

| 80 | na* | 64.6 | 71.7 |

'na*'- not applicable

4. The variation of mechanical strength of geopolymer under water and brine saturation

When geopolymer is placed as well cement, it will undergo range of mediums such as water, brine water, CO_2, etc. Therefore, an experiment was conducted to study the mechanical behaviour of geopolymer paste, saturated under fresh water (FW) and Brine water (BW). The BW was prepared by adding 15% NaCl by weight to distilled water. The samples used were 54 mm diameter and 108 mm height and the mix design and method of sample preparation were as discussed in section 4. All the samples were oven cured for a period of 24 hours, and then allowed to cool at ambient temperature for another 6 hours. Then they were transferred to saturation buckets containing FW and BW except the control samples. The control samples were kept at room temperature from the oven for a period of 14 days. The saturated samples were tested for 14d, 30d, 60d and 90d. The degree of saturation by mass for both the saturation mediums is plotted in Fig 8. It can be seen that samples saturate under BW quickly and then follows the same trend as water. The variation of UCS with different saturation mediums are shown in Fig 9. It can be seen from Fig 9 that the UCS of geopolymer reduces under FW and BW. The reduction rate is lower for 15% BW saturated samples compared to W and 5% BW samples. The samples saturated in water shows 18-26 % of strength reduction, whereas it is lower [< 10 %] in 15% BW. When geopolymer is saturated in brine water, the following reaction may happen;

$$(K,Na)\text{-}(Si\text{-}O\text{-}Al\text{-}O\text{-}Si\text{-}O\text{-})_n + 4n\ H_2O + Cl^- \longrightarrow NaCl/KCl + (\text{-}Si\text{-}O\text{-}Al\text{-}O\text{-}Si\text{-}O\text{-})_n + yH_2O$$

When brine is added to geopolymer Cl^- will react with Na or K and will produce NaCl or KCl. The (-Si-O-Al-O-Si-O-) will not have any reaction with Cl^- as both are acidic. The higher content of NaCl in 15% BW may give more resistivity again weakening under brine water compared to fresh water. Fresh water saturated samples leach more alkalis and cause higher strength reduction.
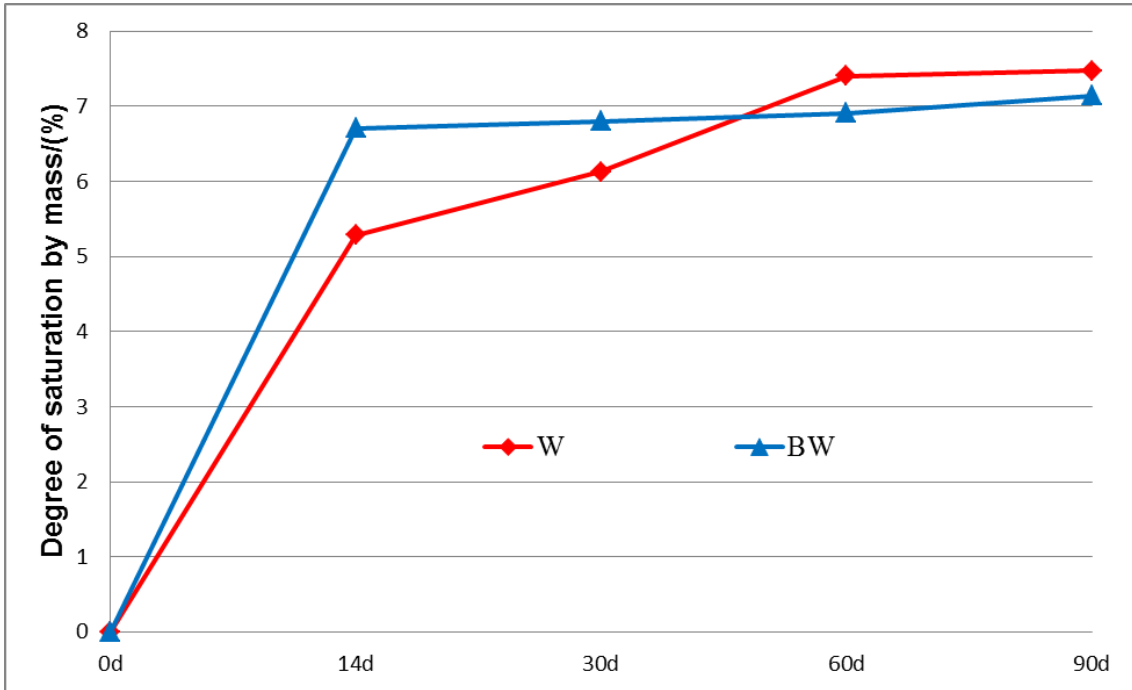
Fig 8: The degree of saturation (by mass) of geopolymer under FW and BW
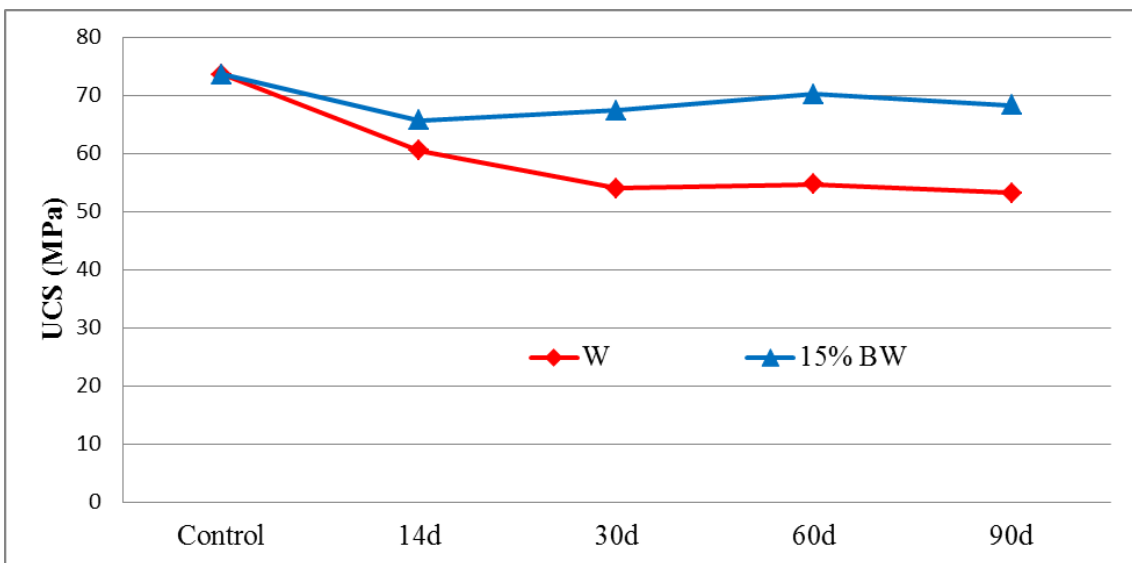
Fig 9: The variation of UCS geopolymer saturated under FW and BW

5. Conclusions

Based on the current study, the following conclusions were drawn,

1. Since geopolymer has many advantages over OPC in production and shows a better behaviour under sequestration conditions, it will be one of the best replacements for existing OPC-based well cementing system.

2. Under sequestration conditions, OPC based well cement undergoes cement carbonation followed by cement degradation, strength reduction, permeability increment, shrinkage, etc. On the other hand, geopolymer doesn't deteriorate under acidic environment, possess higher strength, less shrinkage compared to OPC and doesn't undergo alkali aggregate reaction (AAR).

3. The optimum curing temperature of geopolymer for higher strength is 60 ℃, and it possesses higher strength compared to class G cement above ambient temperatures.

4. The crack propagation stress thresholds such as crack closure, crack initiation and crack damage generally increases with the curing temperature

5. When geopolymer is saturated under FW and BW, the strength reduction rate is higher in FW compared to BW. This is due to the leaching of more alkali ions in FW compared to BW.

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