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Geopolymer as well cement and its mechanical behaviour with curing temperature

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Abstract: Carbon capture and storage (CCS) technique is found as a best solution to reduce the emission of CO_2 to the atmosphere. In this technique, the CO_2 emitted from large industries is captured, and pressurized, and finally injected into deep underground reservoirs. In a geological sequestration project, integrity of injection well play an important role. It means the well cement is a key factor that affects the well integrity. In typical injection wells, Ordinary Portland cement (OPC) based cement is used as well cement and it has been found that it undergoes degradation in CO_2 rich environment. Geopolymer can be a good alternative to existing OPC based well cement as it has been found that geopolymer possess high strength and durability compared to OPC. Geopolymer is a binder produced through the process called geopolymerization of alumino- silicate materials and alkaline activators. In the sequestration wells, well cement is exposed to different curing temperatures with a geothermal gradient of 30°C/km. Therefore, it is important to study the mechanical behaviour of well cement with curing temperatures expected deep under the ground. Therefore, this research aims to study geopolymer as well cement and its mechanical behaviour at different curing temperatures (25, 40, 50, 60, 70, 80 °C). In addition, effect of ageing on the mechanical behaviour was also studied. The OPC samples were tested for the comparison of results with geopolymer. The results showed that the optimal curing temperature for higher strength of geopolymer and OPC are 60 °C and 50 °C respectively. Geopolymer possess highest strength at elevated temperatures whereas OPC possess higher strength at ambient temperatures. Moreover, at elevated temperature curing, geopolymer develops ultimate strength within short curing period and it does not gain significant strength with further ageing.

Keywords: CO_2 sequestration, geopolymer, greenhouse gases, well cement

1. Introduction

Emission of greenhouse gases is a major problem in the world. Of all greenhouse gases, CO_2 is responsible for 64% of the greenhouse gas effects [1]. There are so many ways to reduce the emission of greenhouse gases; such as minimizing fossil fuel consumption in industries and vehicles, increasing the energy conversion efficiency of fossil fuels, switching energy sources in to renewable energy sources such as wind energy, wave energy and solar radiation and capturing and storing carbon dioxide in deep under the ground [1, 2]. Of all the proposed methods, carbon capture and storage (CCS) technique is found as a good solution to reduce CO_2 emission to atmosphere [3].
The lifetime of CCS projects depends on many factors and within these well integrity plays an important role. Well cement is the major factor that affects well integrity and, in the injection wells, Ordinary Portland Cement (OPC) based cement (class G, H) is used as well cement. According to previous studies [4, 5], OPC undergoes degradation in CO_2 rich environment due to the reaction with dissolved CO_2 in brine. Kutchko et al [4], found that when OPC based well cement exposed to a CO_2 rich environment, it undergoes carbonation followed by cement degradation. Three distinct zones were identified in degraded cement, the outer most zone was fully changed as calcium bicarbonate and that is an easily solluable substance. The second zone is calcium carbonate which was the results of the reaction between $Ca(OH)_2$ and dissolved CO_2 and the third zone is unaltered cement. In addition, various other researchers [5, 6, 7] have also found that OPC based well cement experiences degradation exposed to CO_2 rich environment.
This paper examines geopolymer as well cement since, geopolymer possess high strength, excellent acid resistance characteristics and high durability [8, 9]. Davidovits, [10] proposed that an alkaline liquid could be used to react with the silicon (Si) and the aluminium (Al) in a source material of

geological origin or in by-product materials such as fly ash and rice husk ash to produce binders and he termed these binders as geopolymers. Any alumino-silicate material can be used as raw material to produce geopolymer binder. When the alumino-silicate materials mixed with alkaline agent and the polymerization process will initiate. A generalized formula for geopolymer is as follows:

$$M_n[-(SiO_2)_z - AlO_2]_n . w H_2O$$

where z is 1, 2 or 3; M is an alkali cation, such as potassium or sodium, and n is the degree of polymerization [10, 11].

There are many advantages by using geopolymer in construction of injection wells compared to OPC. The manufacture of geopolymer emits 90 % less CO_2 and consumes 50 % less energy compared to OPC [12]. Furthermore the geopolymer concrete manufacture costs 10-30 % less than that of OPC concrete [13].

A typical underground well is constructed from ground level to the required depth depends on the injection reservoir level and it may vary from 800 m to 2 km. As the temperature is varying with depth with a geothermal gradient of 30 °C/ km [2], the well cement is exposed to different temperatures varying up to approximately 80 °C. Therefore variation of mechanical behaviour of geopolymer at different down-hole temperature conditions need to be studied in order to predict the behaviour of geopolymer cement during the life time in the down-hole conditions. This paper investigate geopolymer as well cement and its mechanical behaviour with curing temperature from ambient level (27 °C) to 80 °C. Testings such as X-Ray Diffraction analysis (XRD), Uniaxial Compressive Strength (UCS) and Scanning Electron Microscope (SEM) analysis were conducted to study the behaviour of well cement at different temperature conditions.

2. Materials and Methodology

To date most of the researches on geopolymer concrete was done with geopolymer paste with aggregates and also for elevated temperature curing to study fire resistance properties. In this research, geopolymer paste was used instead of concrete as the annular space in typical well is between 30- 80 mm. in addition, the sole purpose of well cement is to provide zonal isolation (low permeability) and required mechanical strength. Hence, cement paste is used in wells instead of mortar or concrete.

2.1 Materials

Geopolymer paste samples was prepared using fly ash as the alumino-silicate material and combination of NaOH and Na_2SiO_3 as alkaline activator. The ASTM class F fly ash (low calcium) which is produced at Nuraichcholai coal power plant, Puttalam, Sri Lanka, was obtained from Holcim Lanka (Pvt) ltd. 8 M NaOH solution was mixed with Na_2SiO_3 with a ratio of Na_2SiO_3 to NaOH of 2.5 to obtain higher strength [14]. The ratio of alkaline activator to fly ash used was 0.4 for all the mix design. In addition, sulphate resistant OPC samples was tested to compare the results. Sulphate resistance OPC was obtained from Holcim Lanka (Pvt) Ltd. For the mix of OPC samples, a w/c ratio of 0.44 was used as it is found to be the optimum to achieve higher strength [15].

The mix compositions of fly ash and OPC was obtained from X-Ray Diffraction (XRD) test and the results are shown in Table 1.

Table 1: Compositions of fly ash and OPC

Constituents	Percentage (%)	
	Fly ash	OPC
SiO_2	52.03	20.38
Al_2O_3	32.31	4.79
Fe_2O_3	7.04	3.26
CaO	5.55	64.4
Mgo	1.3	0.98
SO_3	0.07	2.21
K_2O	0.68	0.04
Cl	1	0.01

2.2 Sample preparation and experimental methodology

Geopolymer paste was prepared by mixing fly ash with alkaline activator in above proportions. The NaOH pellets was mixed with distilled water to prepare 8 M NaOH solution. This was mixed with Na_2SiO_3 with above proportions and the alkaline activator was prepared. PVC pipes with 50 mm diameter were cut into 100 mm height pieces to make the casting moulds. These cylindrical moulds were fixed on plywood vertically and the connections were sealed by silicon paste. Figure 1 shows the casting moulds used to cast the samples. Fly ash was mixed with alkali solution using a mechanical concrete mixture for 3 minutes and the mixture was poured in to the prepared mould in three layers. Then the samples was placed on the vibrating table for 2 minutes in order to remove

Figure 1: PVC moulds used to caste cement samples

This work includes two types of curing to study the effect of curing temperature and ageing time. To study the effect of curing temperature all the samples were cured at different curing temperatures (27- 80 °C) for 48 hours and then they were allowed to cool at room temperature (RT) for another 24 hours before testing. Based on this test, optimum temperature for high strength

any air voids present in the sample. Then the top of the mould was covered with polythene in order to avoid the moisture loss.

was observed. Effect of ageing was studied by exposing samples to two different temperatures (27 °C and the optimum temperature) for prolong curing periods of 2, 7, 14, 28 and 45 days.

After curing both side of the samples was grinded using by the mechanical grinding wheel and capped with sulphur capping. Figure 2 shows the samples prepared for testing.

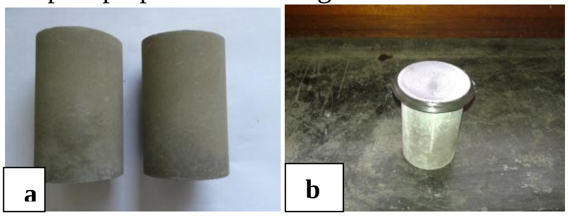

Figure 2: (a) Oven cured geopolymer samples, (b) sulphur capped sample

UCS test was conducted on the samples with a stress controlled loading rate of 0.2 MPa/ s. Schematic view of the UCS testing set-up used is shown in Figure 3. A total number of 32 samples of geopolymer cement and 32 samples of OPC were tested in this research. For each data point, two samples were tested to ensure reproducibility.

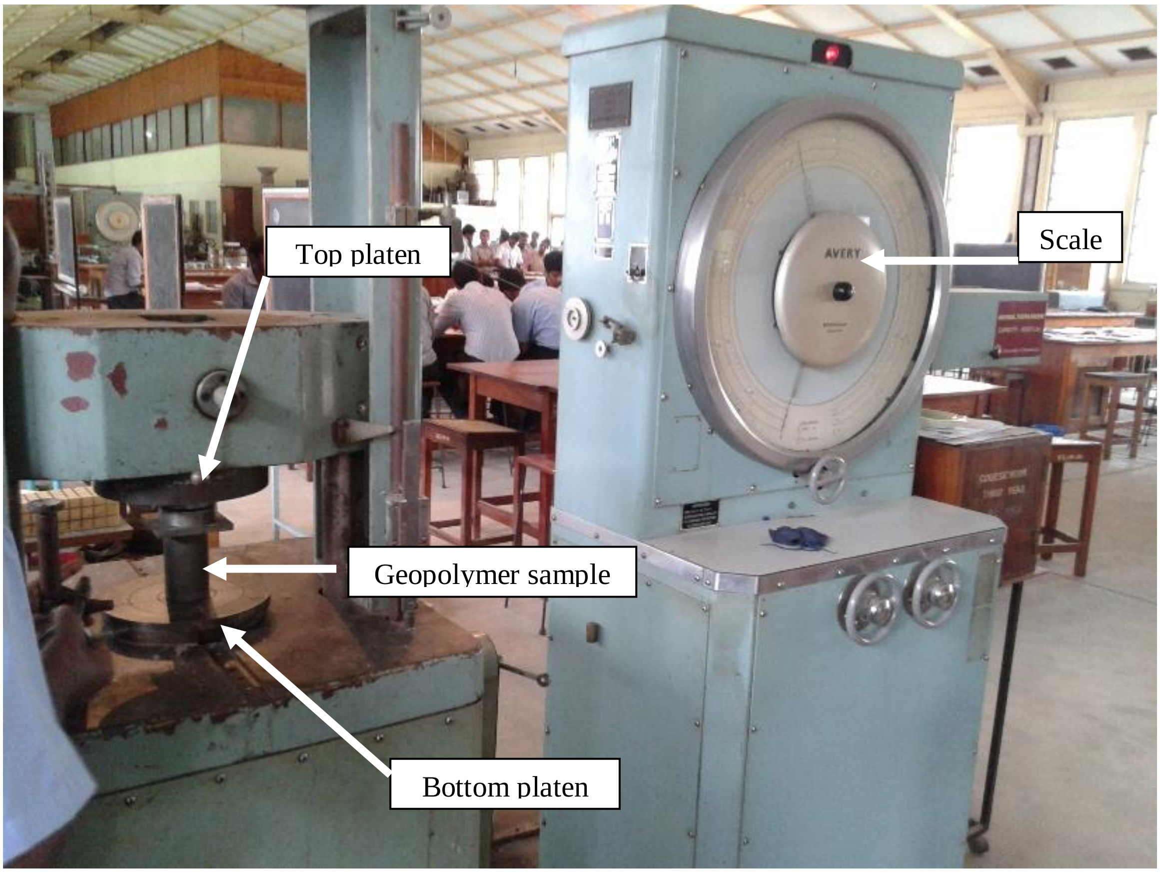

Figure 3: schematic view of UCS testing machine

To study the microstructural behaviour of geopolymer cement with temperature variations and the curing duration, SEM analysis was performed. The geopolymer samples was crushed and samples of approximately 1 mm^3 was mounted on the test plate in the machine. The samples was coated with Au (gold) to make the sample conductive. Magnification factor up to × 25000 can be used in this machine. Figure 4 shows the SEM testing machine

Figure 4: SEM testing machine used

3. Results and Discussions

3.1 Effect of curing temperature

Well cement is exposed to different temperature conditions (from ambient level to 80 ºC). Therefore, the failure stress of geopolymer paste and OPC motar was tested at different curing temperature for 48 hours of curing. Figure 5 shows the strength variation with curing temperature for both geopolymer and OPC.

According to Figure 5, at room temperature, the strength of the geopolymer is considerably low and it is because of the poor rate of geopolymerization process. The rate of geopolymerization is high at elevated temperatures [8, 9]. The optimum temperature for high strength for geopolymer and OPC are approximately 60 and 50 °C respectively.

Geopolymer gains strength with curing temperature as Si and Al from the source material readily dissolves with the increase in curing temperature up to 60 ºC. After that the strength decreases with the temperature. However, some of the researches [14, 16] found that the optimum strength is between 70- 80 ºC. The optimum temperature may vary depends on the source of fly ash, type of curing, sample compositions and the mix compositions [14].

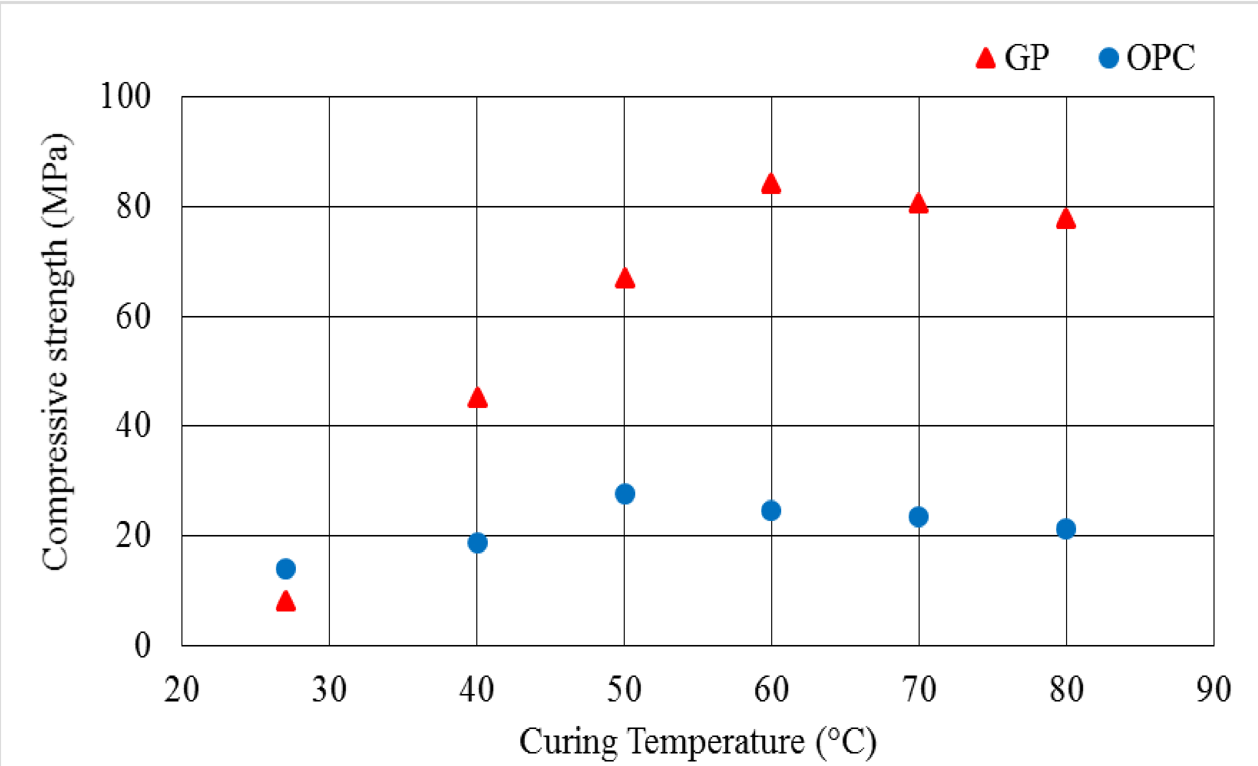

Figure 5: Variation of UCS with curing temperature for geopolymer and OPC

For geopolymer, strength is decreasing beyond 60 °C. This may be due to the weakening of microstructure at elevated temperatures or the formation of micro cracks [9]. For the geopolymerization process presence of moisture also important and at higher temperatures moisture might be vaporized and because of that strength reduction may occur. According to Figure 5, strength of the OPC is increasing with curing temperature up to 50 ºC and after that the strength decreases. The increase of strength is because of the rate of hydration increases with the temperature increment. The optimum temperature is 50 ° C, and however optimum temperature vary with the w/c ratio and the type of OPC [17].

When the behaviour of OPC and geopolymer is compared, it can be seen that at room temperature conditions, OPC has higher strength compared to geopolymer. This is because of the poor geopolymerization rate for geopolymer at room temperature. On the other hand, at elevated temperatures, geopolymer possesses high strength compared to OPC. Rate of strength increment of geopolymer from room temperature to optimum temperature (60 °C) is 90 % while the rate of increment of OPC is 49 %. The increment rate is much high for geopolymer than OPC. However, the reduction rate is low to geopolymer compared to OPC. The rate of strength reduction beyond the optimum temperature is 8 % for geopolymer while it is 23 % for OPC. Based on this, it can be concluded that the geopolymer cement is suitable for the constructions where the down-hole temperature conditions is above 40 °C.

Figure 6 shows the variation of Young's modulus with curing temperature for geopolymer and OPC. The variation of young's modulus also follow the same pattern as variation of strength. At the higher temperatures, the geopolymer is stiffer than OPC whereas at lower temperatures OPC is stiffer than geopolymer cement.

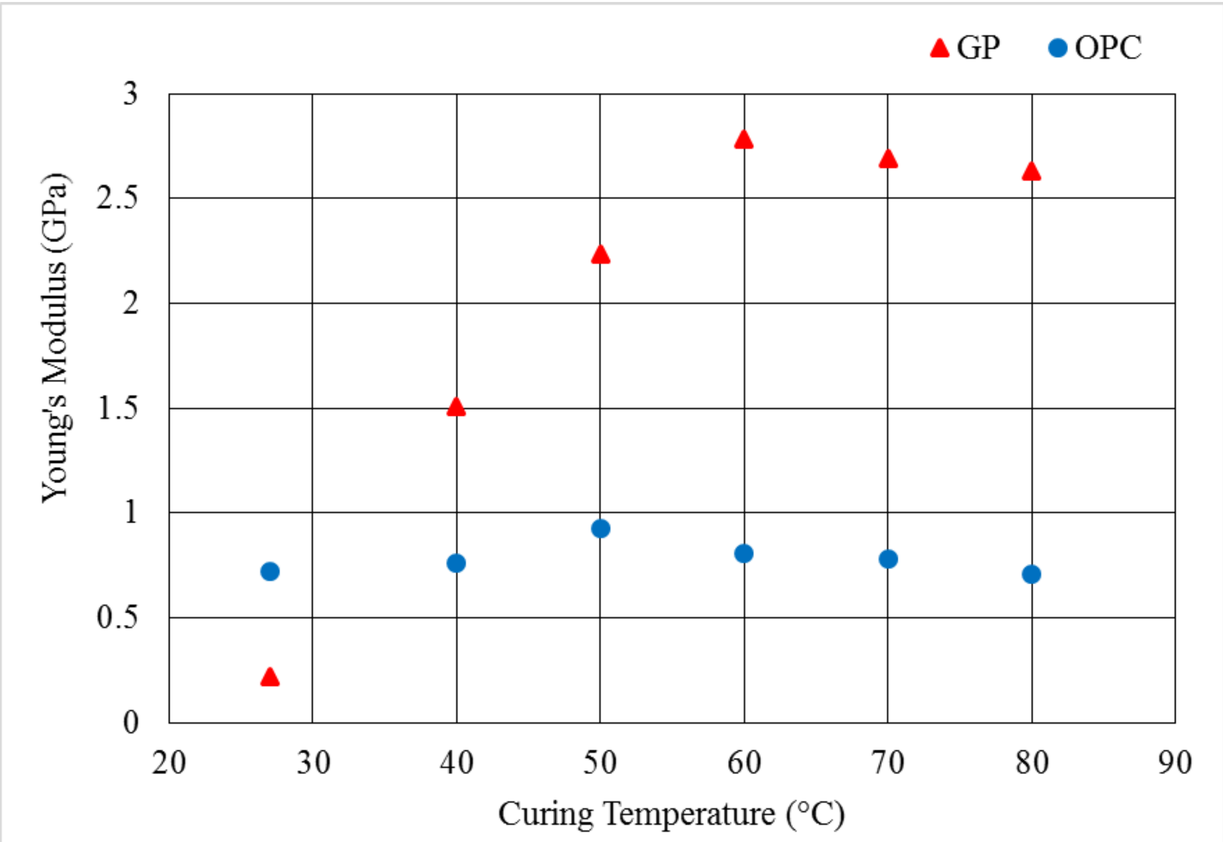

Figure 6: Variation of Young's modulus with curing temperature

3.2: Effect of ageing

To study the effect of ageing, OPC and geopolymer samples were cured at room temperature and optimum temperature (60 °C) for different curing periods. Figure 7 shows the variation of UCS of OPC and geopolymer with the ageing.

According to Figure 7, UCS of geopolymer and OPC increases with the ageing time. This is because of the geopolymerization process of geopolymer and hydration process of OPC with ageing. The strength gaining of the geopolymer cured at room temperature is higher than that of OPC cured at same conditions. At room temperature curing the rate of strength increment of geopolymer in 2- 45 days is 92 % while that for OPC is 63 %. This shows that even at low temperatures geopolymer develops higher strength compared to OPC.

For geopolymer cured at 60 °C, the rate of increment in strength is low compared to the samples cured at room temperature. For geopolymer, the geopolymerization process is almost finished within 48 hours of curing for elevated temperature. Hence, geopolymer will not develop significant strength increment with further ageing when cured at elevated temperatures. In OPC, the hydration process is also faster at elevated temperatures and because of that the strength is gained within short period of curing time (48 hrs) [Figure 5]. Due to that the strength increment rate is low for OPC cured at 60 °C than room temperature cured samples. At elevated temperature curing, the rate of strength increment of geopolymer is 8% while that for OPC is 22%.

3.3 SEM analysis

Micrographs of fly ash based geopolymer were obtained using a ZEISS field-emission scanning electron microscope (FESEM) operated at 20 kV. Magnification factors were changed from 500 to 3000. Figure 8 shows the SEM images of fly ash and geopolymer samples cured at different conditions. In Fig 8 (b) and (c), the grey coloured spherical particles (X) are unreacted fly ash particles and more unreacted particles can be seen at low temperature cured samples. This is due to poor rate of geopolymerization. Based on this, it can be concluded that the rate of geopolymerization is high at elevated temperature.

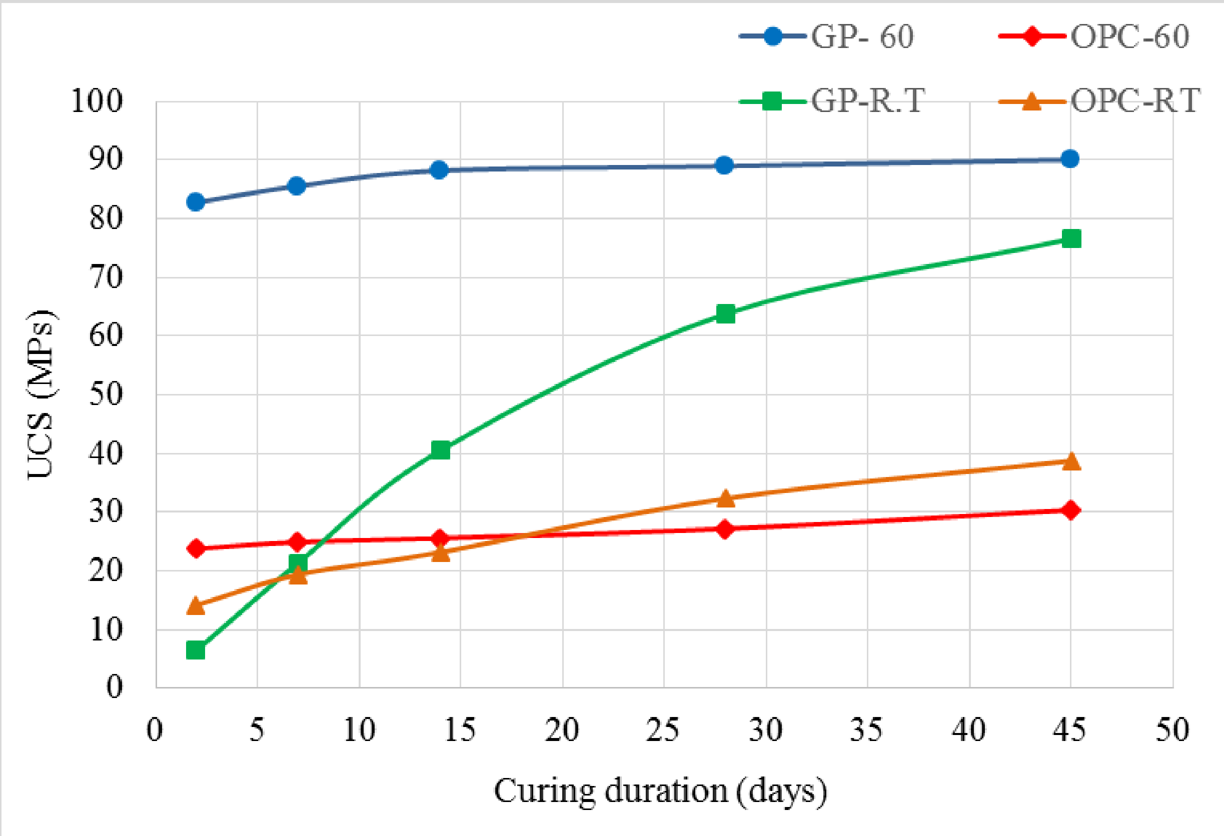

Figure 7: Variation of UCS with ageing for both geopolymer and OPC

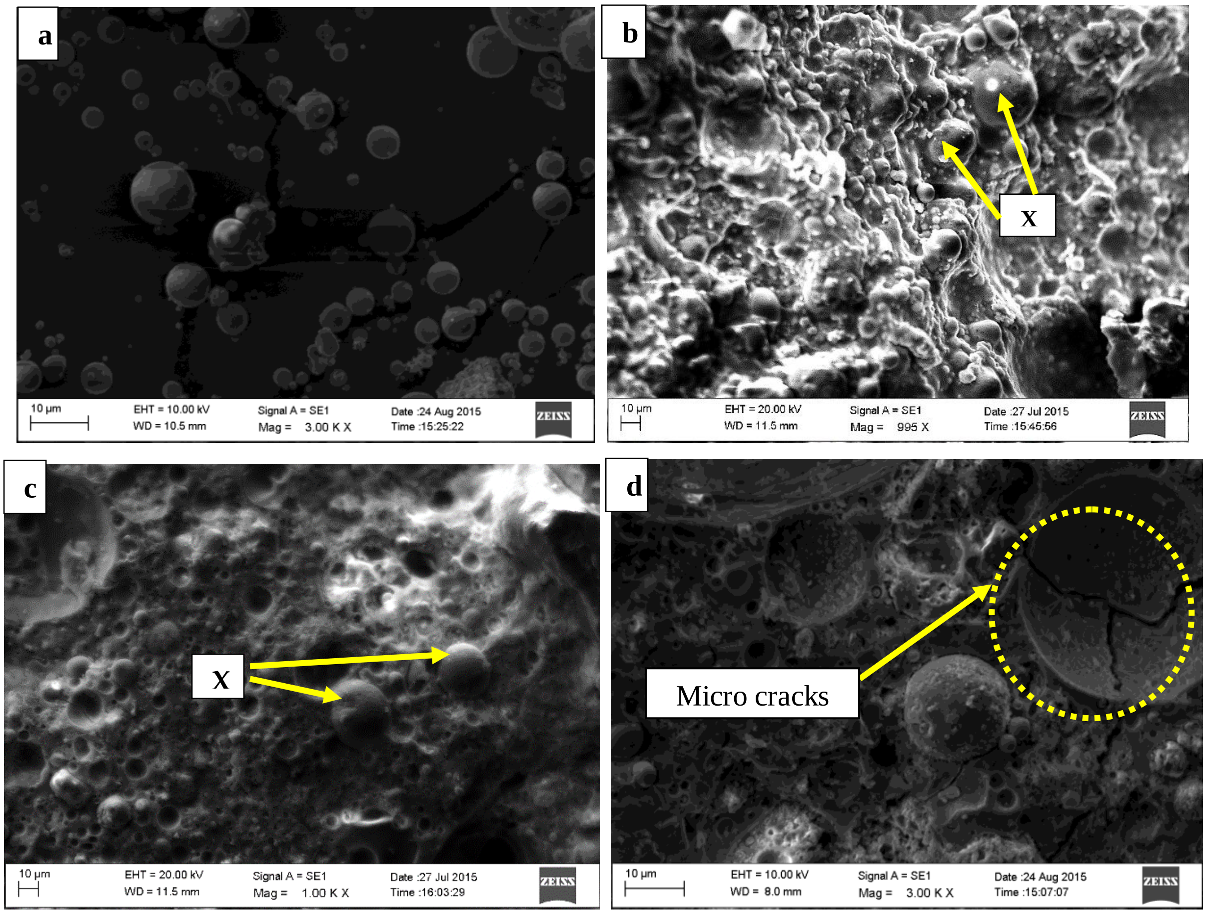

Figure 8: SEM images of (a) fly ash particles (a), geopolymer cured at (b) RT, (c) 60 ºC and (d) 80 ºC

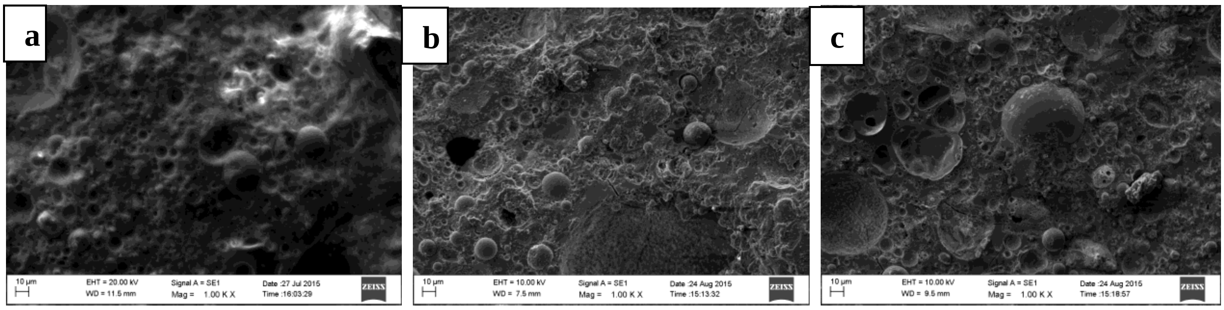

Figure 9: SEM images of geopolymer samples cured at 60 ºC for (a) 2 days, (b) 7 days, (c) 14 days

Figure 8 clearly shows that the different geopolymerization rate between samples cured at R.T and 60 ºC. But there is no significant variation of unreacted particles between samples cured at 60 ºC and 80 ºC. Based on this, it can be concluded that the strength reduction beyond 60 ºC is not due to the variation in rate of geopolymerization. In Figure 8 (d), some micro-cracks can be observed. Hence, it can be concluded that the strength reduction beyond 60 ºC is due to the formation of micro-cracks at elevated temperatures.

Figure 9 shows the SEM images of geopolymer cured at 60 ºC for different durations. There is no much difference in the unreacted particles between samples cured at 60 ºC for 2, 7, and 14 days. Based on this it is concluded that for elevated temperature curing there is no significant strength gain with ageing.

4. Conclusions

Present study focused on geopolymer as well cement and its mechanical behaviour with curing temperature as typical wellbore is subjected to a range of curing temperatures with the depth. OPC was used for the comparison of results. The following conclusions are drawn based on the outcomes of this research.

1. The optimum curing temperature for fly ash based geopolymer is 60 °C and there is no

considerable strength gain after optimum temperature.
2. UCS and Young's modulus of geopolymer increases with curing temperature up to 60 °C and beyond that it decreases.
3. The optimum curing temperature for OPC based well cement is 50 °C and beyond the optimum temperature strength decreases.
4. At lower curing temperatures (below 40 °C), OPC possess higher strength than geopolymer, whereas at elevated temperatures geopolymer possess higher strength.
5. At low temperature curing, both OPC and geopolymer develop strength with ageing and the rate of strength gaining is high for geopolymer compared to OPC.
6. At elevated temperatures, the geopolymer develop its ultimate strength within a short period of curing (48 hours) and it does not develop significant strength increment with further ageing.
7. On the whole, geopolymer is suitable for temperature of above 40 ºC, whereas OPC can be used at shallow depths where temperature is low (< 40 ºC).

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