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Development of a New Geopolymer Based Cement: Laboratory Investigation

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Abstract

A compromised cementing operation integrity can hinder the long term production capability of the well and can also result in some environmental concerns. Ordinary Portland cement used in well cementing has shown to perform ineffectively in adverse conditions.

The purpose of this study is to develop environmental friendly fly ash based geopolymer material as substitute for ordinary Portland cement. This study involved conducting rheological and compressive strength, test on the optimized substitute material.

The optimized fly ash geopolymer mix showed an increase in the compressive strength as the curing temperature increases, whereas increasing the temperature decreases the compressive strength in ordinary Portland cement. At 300°F, the compressive strength of fly ash based geopolymer increased to about 4100psi while that of Portland cement decreased to about 1400psi. In terms of toughness and rate of crack propagation, Fly ash based geopolymer showed an overall better performance than Portland cement.

The result and observations from the test conducted shows that with further study and improvement, fly ash based geopolymer can effectively be used as an alternative to ordinary Portland cement in oil and gas well.

Introduction

Ineffective zonal isolation or cement integrity failure may lead to problems in the well and the well may not operate at its expected producing potential. The rheological property of the cement slurry as well as the mechanical property of the set cement must be optimized in order to achieve an effective cementing operation.

Wellbore cement integrity failure can occur as a result of poor cement/casing bonding due to mudcake, fluid breakout and channeling in the cement and high permeability in the set cement. Another mechanism of cement integrity failure can occur after the setting of the cement sheath, which can be as a result debonding of the casing/cement/formation due to tensile stresses and temperature changes, fractures and cracks induced and propagated in the set cement and corrosion of set cement (Nygaard et al. 2014).

Ordinary Portland cement (OPC) is primarily used as oil and gas well cementing material. The brittle nature of set Portland cement makes it susceptible to cracking when exposed to pressure and thermal induced loads (Jackson and Murphey 1993, Godwin and Crook 1990). The phenomenon of strength retrogression experienced when Portland is subjected to high temperatures is a great concern. The reduction in strength at high temperature is usually accompanied with increase in porosity and permeability (Eiler and Root 1974). Increase in permeability makes the internal micro structure of the set cement sheath accessible by corrosive fluid present in the formation. Portland cement can suffer further degradation when exposed to these corrosive fluids like CO2, H2S and stimulation acids and sulfates, which can lead to ineffective zonal isolation (Brady et al. 1989, Krilov et al. 2000).

Aside the susceptibility of Portland cement in adverse environment, the production of Portland cement poses a great environmental and energy concern. During the calcination of limestone and combustion of fossil fuel to generate energy needed to heat the kiln, about one ton of CO2 is generated in the production of one ton of Portland cement (Davidovits 1994, McCaffrey 2002).

Recently, there has been a lot of research geared toward using environmental friendly material to replace Portland cement, most of the research and study carried out so far has been in the concrete and construction industry, while the oil and gas industry, which primarily uses Portland cement in her cementing operation, is almost being left out. The environmental unfriendliness and enormous energy required in the production of Portland cement as well as its ineffectiveness to provide zonal isolation in adverse condition cannot be overemphasized.

This paper presents the performance of Fly ash Based geopolymer when compared to ordinary Portland cements. The compressive strength as well as the fracture energy and modulus of fly ash based geopolymer and ordinary Portland cement at various condition of curing has been reported in this paper.

Experimental Methodology

Alkaline Activator

A combination of sodium silicate and sodium hydroxide is selected as the alkaline activator. The selection is based on previous research that shows that a combination of both alkaline solutions provides a better strength for fly ash based geopolymer and it is cheaper than their potassium counterpart. The water composition of the solution is >60% while the sodium silicate is <40% by weight.

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Slurry Preparation

The sequence developed for mixing the component of the geopolymer was basically developed from a trial study. Sodium hydroxide and sodium silicate solutions were mixed at the appropriate ratios and allowed to sit for at least 30mins
The alkaline solution was poured into the fly ash and mixed slowly for about 2minutes and later mixed faster for about 10mins in order to obtain a homogenous slurry.

Fly Ash Based Geopolymer Optimal Mix Design

The optimal mix for the fly ash based geopolymer applicable in oil and gas well was determined based on the rheology of the slurry and compressive strength gained after 24 hours at 140°F.

The variables considered in the optimization include the Alkaline to fly ash ratio (alkaline/Fly ash), sodium hydroxide concentration (NaOH (M)), Sodium Silicate to sodium hydroxide ratio (Na2SiO3/NaOH). The experimental mix designs were strategically selected to capture the effect of the variables on the compressive strength and viscosity. The result of the optimal study was used to predict the effect of the variables on the compressive strength

Rheology Test

Rheology test characterizes the flow of the slurry. It helps determine the viscosity of the slurry. The viscosity gives an indication of the workability of the slurry.

OFITE Model 800 viscometer was used for the rheology test. The viscometer determines the flow property of the slurry in terms of the shear rate and shear stress at atmospheric pressure. For this test, an R1B1 bulb and an F5 rated spring was used because of the viscous nature of the slurry. The Viscosity is estimated by the equation below:

$$Viscosity\ (cp) = \frac{k\ factor * spring\ factor * dial\ reading}{RPM}$$

Compressive Strength Test

The compressive strength test was carried out with 810 Material Test System. The testing system can supply a load up to (20KIP). The samples were tested at a rate of 0.02inch/min. For each compressive test, 3 samples were tested and the average is obtained.

A plot of the stress against deformation was used to estimate the fracture energy and modulus of the sample. The fracture energy is estimated using the area under the stress-deformation curve, while the modulus is estimated from the slope of the curve. The bottom part of the curve was corrected while estimating the slope and is due to the effect of the capping material which appears to be softer than the actual sample. In this study, the slope (modulus) of the curve was estimated from the origin to about 40% of the total compressive strength.

Result and Discussion

Evaluation of Fly ash based Geopolymer

The performance of Fly ash based geopolymer as oil well cement was carried out. A Class G Oil well Portland cement was used as a base case in making comparison. The mix design for the study is shown in table 1.

Table 1: Mix design for performance characterization

Mix	Density (ppg)
Geopolymer A (Optimal Mix)	14
Geopolymer B (modified mix)	14
Class G Portland Cement w/c = 0.44	16.8

Effect of Curing Temperature on compressive Strength

Fig 1 shows the effect of temperature on the compressive strength. The compressive strength test was carried after curing the samples at the various temperatures for 24 hours.

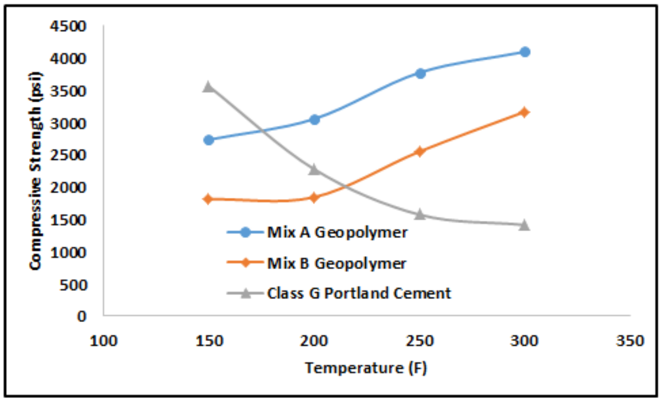

Fig. 1: Compressive strength development at various curing temperature

From the figure, Class G Portland cement showed higher strength than Geopolymer A and B at 150°F. As the temperature increases, the strength of Geopolymer A and B increased while that of Class G cement decreased. At 300°F the compressive strength of Geopolymer A and Geopolymer B were 4100psi and 3200psi respectively. The strength of Class G cement at 300°F deteriorated to about 1400psi.

The surface of Geopolymer A and B and Class G cement after curing at 150°F and 300°F for 24 hours is shown in Fig 2.

It can be observed that the surface of Geopolymer A shows some form of roughness at 300°F while that of Geopolymer B containing water and plasticizer appears very smooth at 300°F. Class G cement which is an oil well Portland cement showed a high degree of surface deterioration at 300°F. This surface damages also plays a part in the reduction in strength of Portland cement in at higher temperature. The surface of fly ash based geopolymer can be said to be more stable than ordinary Portland cement when exposed to heat. This implies that fly ash based geopolymer can be more suitable in High temperature wells.

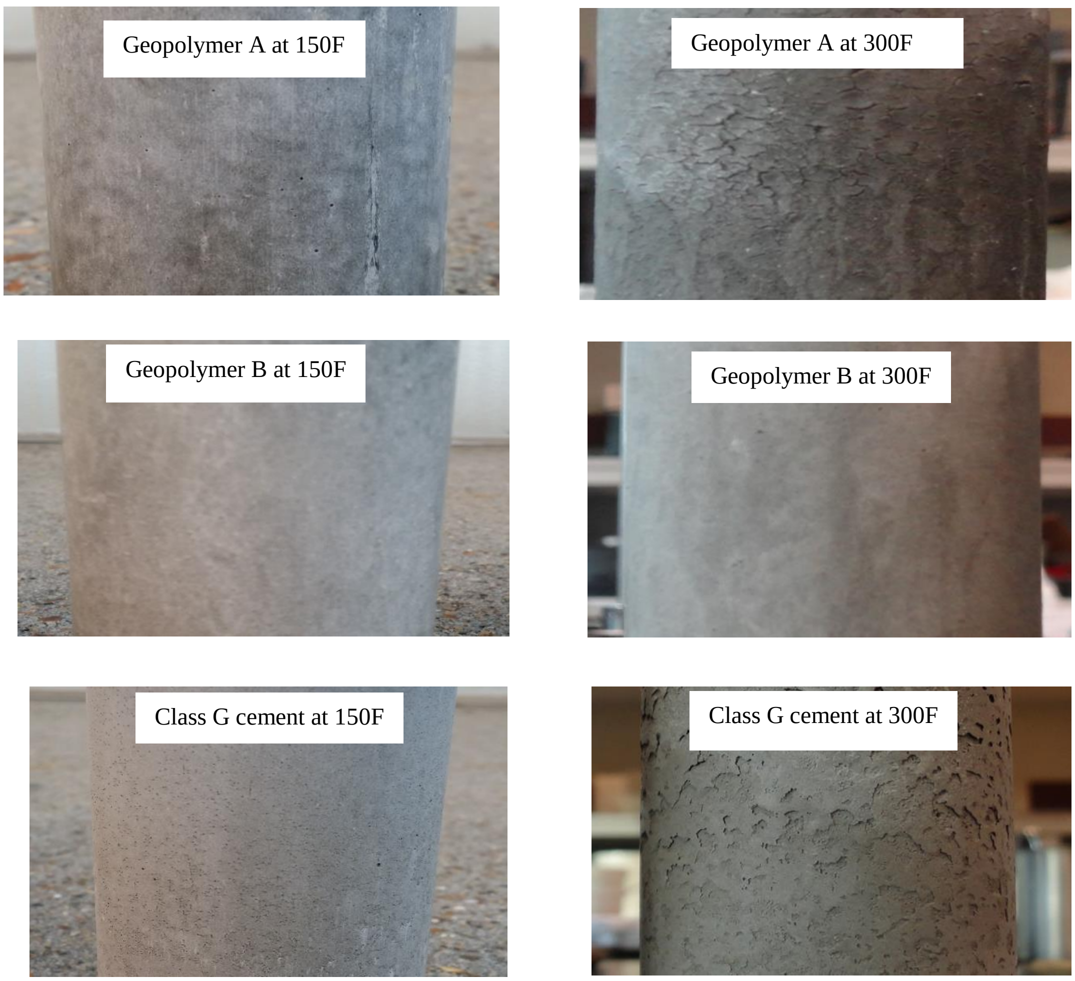

Fig 2: Surface of Geopolymer A and B and Class G cement at 150°F and 300°F

Free Fluid Test

Free fluid test investigates the free fluid content of the slurry and the tendency to cause channeling when the fluid breaks out. Excessive free fluid in the slurry can be detrimental to cement sheath quality and effectiveness to create zonal isolation. The free fluid test of fly ash based geopolymer slurry (Mix A and B) and class G Portland cement is shown below:

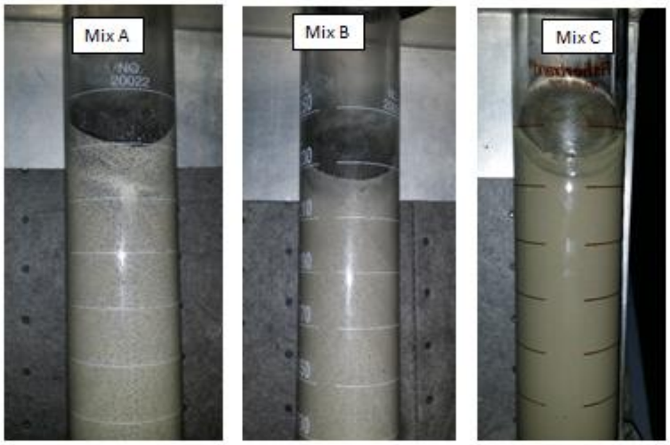

Figure 3. Detailed view of the free fluid test

From Figure 3, it can be seen that Portland cement without an additive shows high tendency of fluid breakout. Fly ash geopolymer slurry (Mix A and B) show zero free fluid breakout. The free fluid breakout of an oil well cement slurry to a great extent indicates the slurry stability. Extreme fluid breakout can result to uneven strength of the set cement sheath. Fluid breakout is usually accompanied by longitudinal fluid channeling which can impair proper sealing of the annulus. Water channeling challenge is more pronounce in deviated well where by a continuous fluid channel is formed at the upper side of the annulus and thus affects the sealing and setting quality of the cement. Alkaline activated fly ash geopolymer slurry has a very low tendency of producing fluid breakout or channeling when compared to Portland cement as show in the test result.

Sedimentation Test

Sedimentation test was carried to investigate the settling tendency of the solid components of fly ash geopolymer slurry. The sedimentation test result is shown below:

Table 2: Specific gravity of various portions of geopolymer

position	suspended weight (g)	Total weight (g)	Specific gravity
1	16.91	32.18	1.90
2	11.57	22.16	1.92
3	12.39	23.58	1.90
4	9.65	18.37	1.90
5	8.37	15.78	1.89

Figure 4. Fly ash geopolymer cured at 150oF and 3000psi divided into 5 unequal portions

The specific gravity of the various portion of fly ash geopolymer as shown in Table 2 is approximately equal. The result shows that the settling tendency of the fly ash geopolymer is very minimal. A considerable variation in the specific gravity of any portion of a set cement can result in variation in the mechanical properties of the portions.

Fracture Energy and Modulus

The fracture energy gives an indication of the toughness of a material while the modulus is related to the stiffness of the material. The fracture energy and modulus of Geopolymer A and B and Class G Portland cement at different curing temperatures was estimated from the compressive stress vs deformation curve.

Besides the compressive strength, the toughness and stiffness are some other properties that is considered in the selection of a material. From Fig. 5, Class G ordinary Portland cement showed higher compressive strength than Geopolymer A and B at 150^{o}F. The fracture energy of Mix A is approximately equal to that of Mix C. In terms of the stiffness, Geopolymer A showed a lower modulus than Mix C at 150^{o}F while Geopolymer B developed the lowest modulus. A high toughness and a low stiffness is desired in oil well cement as the development and rate of propagation of crack will be slower. At 150^{o}F, the rate of propagation of crack will be higher in Class G cement than in Geopolymer A.

As the Temperature is increased to 200^{o}F as shown in Fig 6, Geopolymer A showed an overall better property than Class G Portland cement. Geopolymer A showed higher compressive strength and toughness and lower modulus than Class G cement.

At 250^{o}F the compressive strength of Class G cement deteriorates further and the toughness decreases drastically. The compressive strength of Geopolymer A and B increased further while there is a slight decrease in their toughness.

Based on the toughness and stiffness estimated for fly ash based geopolymer and glass G Portland cement, fly ash based geopolymer might be able to provide better long term integrity and performance especially at higher temperature as a result of its low stiffness and higher toughness.

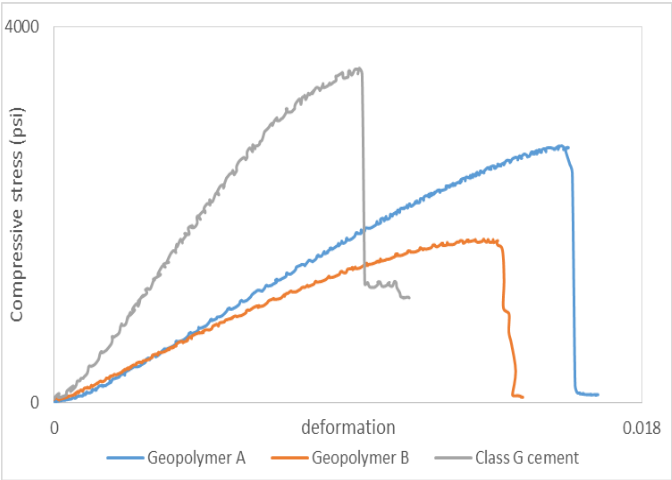

Fig. 5: Compressive stress vs deformation for Geopolymer A and B and Class G cement cured at 150°F

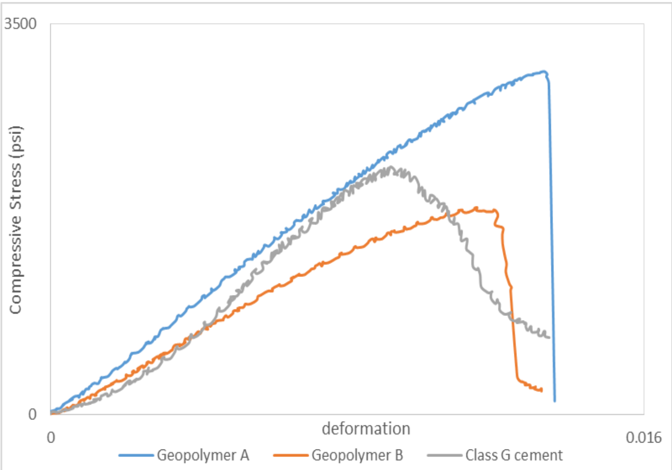

Fig. 6: Compressive stress vs deformation for Geopolymer A and B and Class G cement cured at 200°F

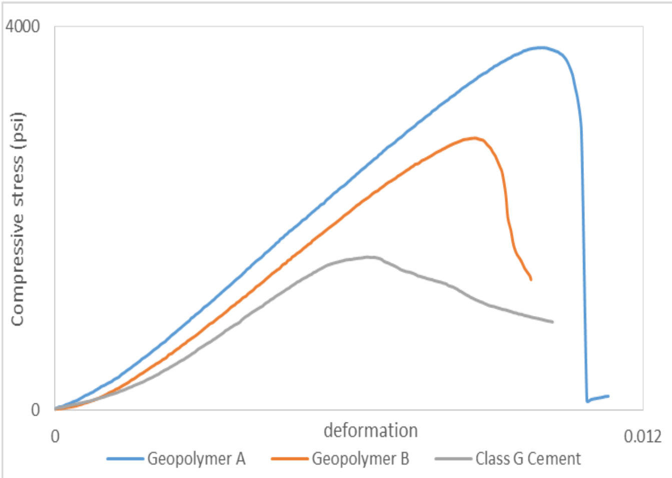

Fig. 7: Compressive stress vs deformation for Geopolymer A and B and Class G cement cured at 250°F

Thickening Time

The thickening time of cement slurry gives an indication of how long the cement will remain pumpable under specific downhole condition. For this test the thickening time is the time it takes the slurry to get to 70Bc Figure 8 (Bearden unit of consistency). HPHT consistometer set up was used for measuring geopolymer thickening time as shown in Figure 8. Geopolymerization reaction is different from the hydration reaction of Portland cement therefore it is a challenge to increase thickening time of geopolymer based cement. However, using different plasticizer and optimizing the Alkaline activator ratio, thickening time can be improved. Thickening times for an optimized solution with and without plasticizer are represented in the figures 9 and 10. As illustrated in the figures, thickening time was increased to approximately five hours with using a suitable mix of plactisizers.

Figure 8: HPHT consistometer set up used for measuring geopolymer thickening time

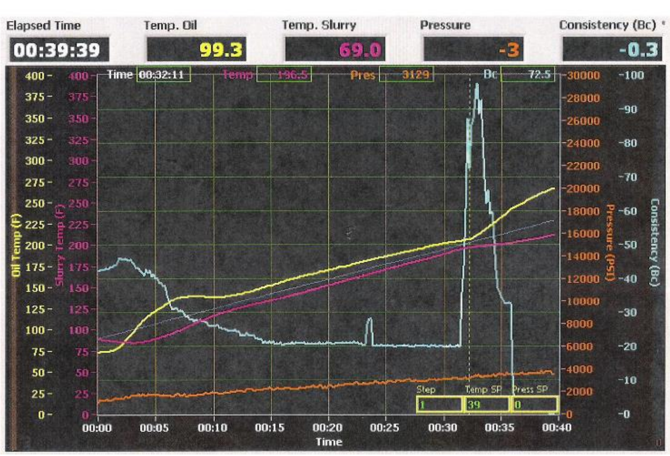

Figure 9: Thickening time results for the sample without placiticizer (39 min)

Figure 10: Thickening time results for the optimized sample using suitable mix of placticizer (5 hrs)

Conclusion

Experimental study of the performance of fly ash based geopolymer for oil and gas well cementing operation has been carried out in this study. The compressive strength, fracture energy and modulus of fly ash based geopolymer was investigated and compared to the conventional Portland cement. Based on the results and observation from the study, the following conclusion can be drawn:

- The compressive strength test shows that fly ash based geopolymer can provide the required strength after 24hrs.
- Increase in the temperature increases the compressive strength of fly ash based geopolymer while the compressive strength decreases in class G Portland cement.
- Higher temperatures has a deteriorating effect on the surface of class G Portland cement while the surface of fly ash based geopolymer is pretty stable. The surface cracks on the Portland cement also contributed to the early failure of Portland cement.
- Fly ash based geopolymer has higher fracture energy (toughness) when compared to ordinary Portland cement, this implies that more energy will be required to fail a unit volume of fly ash based geopolymer.
- Fly ash based geopolymer will exhibit a better resistance to deformation as a result of mechanical and thermal loads in the wellbore due to its plasticity property. Fly ash based geopolymer shows a lower modulus (stiffness) at 150oF which is ideal for oil well cement.
- Based on the tests carried out in this study, fly ash based geopolymer is pumpable has the potential of being used as an oil and gas well cement

- Addition of suitable placticizer can enhance the thickening time of the geopolymer mix

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