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Laboratory Investigation of High Performance Geopolymer based slurries

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Abstract

The purpose of this study is to develop environmental friendly fly ash based geopolymer mixtures as substitute for ordinary Portland cement. This study involved conducting rheological and compressive strength, thickening time and free fluid tests on the geopolymer slurry mixtures.

The study here presents geopolymer slurries that have high compressive and shear bond strength, enhanced thickening time and high durability. Slurries developed in this work show durability when prone to sulphate/chloride or any other acid attack that might be encountered during cementing operations. Class F fly ash geopolymers were used for developing samples with different mix designs in this work. Class H Portland cement was used a controller on all the tests conducted in this work. Tests conducted in this research include Unconfined Compressive Strength (UCS), shear bond strength, thickening time and durability tests. Results indicate temperature as crucial factor affecting thickening time of Geopolymer mix slurry. More than four hours thickening time was achieved by optimizing mix design and application of developed mix of superplactisizer and retarder. UCS testing indicates a high compressive strength after one and fourteen days of curing for Geopolymer mixtures. This indicates gaining strength with time for Geopolymer mixture where time retrogression effects are observed for Portland cements. Results also indicate higher shear bond strength for Geopolymer mix which can better tolerate de-bonding issues. Additionally, more ductile material behavior and higher fracture toughness were observed for optimum geopolymer mixes. Final observations confirm applicability of these materials for oil and gas well cementing with circulating temperatures up to 250o F. These mixtures also show very good durability when compared with Portland cement mixtures. Higher durability will facilitate application of these materials for HPHT and corrosive wells where Portland cement shows poor performance.

Based on results from this study, Geopolymer mixtures show potentials for replacing Portland cement if they can be successfully tested in field applications. These materials can be produced cheaper with less environmental impact. The tangible benefits of the new products would be cost saving on well construction materials for operators with achieving long-time wellbore integrity goals and meeting regulators criteria for zonal isolation.

Introduction

Geopolymers are a relatively new group of binding materials, which were first developed by Joseph Davidovits in 1978 (Davidovits, 1994). These geopolymeric binders are synthesized by alkaline activation of aluminosilicate base materials such as fly ash, granulated blast furnace slag, silica fumes or calcined clays like metakaoline and has the potential for a wide range of engineering applications. Since the last decade, fly ash based geopolymers are receiving more attention due to their economic and environmental advantages.

Geopolymerisation involves processes such as dissolution, diffusion, polycondensation, and hardening. This complex system requires systematic optimization study of a number of synthesizing parameters as well of their interactions. These interactions are extremely important issues for geopolymers because fly ash from different sources show different levels of reactivity under specific geopolymer synthesis conditions, which subsequently affects its final properties. To be more precise about the reasons to study the interactions of fly ash geopolymer binders, to manufacture a high performance geoplymer binder, it is necessary to understand the effects of a various synthesis parameters and their relationships with mechanically clinical properties and microstructures.

The geopolymer mix composition is normally controlled by adjusting the alkali and silicate content of activating solution. Using silica powder (SiO_2) as an additive is useful for improving basic composition of fly ash as it increases SiO_2/Al_2O_3 molar ratio. This SiO_2/Al_2O_3 molar ratio is an important parameter, which has major influence on the physical and mechanical properties of geopolymeric microstructures. A systemic study is necessary to develop guidelines in this regard (Igbojekwe et al., 2015, Salehi et al., 2016). These issues have not received much attention in the past and the literature that is available for study are limited in number and a study on the feasibility of low calcium based Fly Ash Geopolymers is required due to the various solutions it brings to the table of the problems that are faced with OPC.

The cement slurry are subjected to very high pressures reaching over 200 MPa (30000 psi) depending on the height and density of the column of material above it. Thus, oil/gas well cementing operations face additional challenges in contrast to common cementing work above ground. Strength retrogression is another problem that is faced by Portland Oil Well Cement. The temperatures in excess of 110°C result in phase transformation of cement, significantly decreasing its compressive strength. In addition to the high pressure and temperature, the OWC must be able to contend with weak or porous formations, corrosive fluids, etc. Likewise, there is still a lack of information in the open literature regarding the effects of various chemical admixtures, such as new generation superplasticizers, on the rheological, physical and other engineering properties of cement-based materials at high temperatures relating to low calcium based Fly Ash. Finally, there are limitations with OPC and low calcium based Fly Ash can overcome these limitations and a study should be conducted to see if it can be potentially employed as a greener alternative to OPC in oil well cementing.

The compressive strength and workability of fly-ash geopolymer concrete were affected by the ratios and characteristics of the constituent materials (Rangan, 2010). Higher concentration of sodium hydroxide solution increased the strength of the fly-ash geopolymer concrete. Increase in the ratio of sodium silicate solution to sodium hydroxide solution, increased the compressive strength of the fly-ash geopolymer. Palomo, investigated the effect of different fly-ash samples activated with sodium hydroxide solution of molarity ranging from 8M-12M (Palomo et al., 1999). The samples cured at 185°F for 24 hours produced a compressive strength between 5076 – 5801psi. Curing time had profound effects on the fly-ash geopolymer strength. Longer curing time improved the polymerization process, giving higher compressive strength (Hardjito & Rangan, 2005).

The primary difference between geopolymer concrete and Portland cement concrete is the binder. The silicon and aluminum oxides in the low-calcium fly ash reacts with the alkaline liquid to form the geopolymer paste that binds the loose coarse aggregates, fine aggregates, and other un-reacted materials together to form the geopolymer concrete. As in the case of Portland cement concrete, the coarse and fine aggregates occupy about 75 to 80% of the mass of geopolymer concrete. The influence of aggregates, such as grading, angularity, and strength, are considered similar to the Portland cement concrete (Lloyd & Rangan, 2009). Therefore, this component of geopolymer concrete mixtures can be designed using the tools currently available for Portland cement concrete. Studies have been carried out on fly ash-based geopolymer concrete.

Numerous lab and field studies were carried out to characterize the behavior of cement in low pH environments. Jain and Neithalath (2009) conducted experiments to evaluate the behavior of neat and modified cements in pure water. Additives like silica fume, fly ash, and fine glass powder were added to the modified cement samples. These batch experiments were done with deionized water at a liquid-solid ratio of 1000 for 90 days with intermittent sample analysis. Porosity of all cement samples increased with respect to leaching duration. At the end of the experiment, the neat cement was found to be of highest porosity, while the glass powder of modified cement was found to be of lowest porosity. The two authors believed that the Na_2O might have provided NaOH that buffered the cement. The dissolution of CH was lower in modified fly ash and glass powder modified cement compared to neat cement. The authors confirmed CH dissolution as the main cause of porosity increase, but stated that C-S-H decalcification contributed as well (Jain & Neithalath, 2009).

Experimental Methodology

A comprehensive experimental program has been undertaken to evaluate the engineering properties of low calcium fly ash based Geopolymer (ASTM Class F) at elevated temperatures of 150°F, 175°F, 200°F and 250°F. The composition of the Geopolymer mix in different test series was adjusted by varying quantities of different ingredients such as the ratio of akali to fly Ash, the ratio of Sodium Silicate (Si) to Sodium Hydroxide (NaOH) and the dosages of retarder and plasticizer. The curing conditions were set according to the parameters studied, and the curing procedures complied with API 10B. With positive performance observed from the materials tested, we believe Class F fly ash Geopolymer materials can be deployed for cementing oil and gas wells in addition to well abandonment purposes.

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.

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 cured at different temperatures.

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

Results

UCS tests were conducted in compressive uniaxial loading using closed loop servo-hydraulic machine, manufactured by material testing system (MTS). Compressive strength tests were performed for mixtures cured at temperatures ranging between 150^{o}F to 250^{o}F. Triplicate samples were prepared at three different concentrations of sodium hydroxide (NaOH) i.e. 8M, 10M and 12M solutions. Average results of UCS tests at three different molarities and two different silicates to hydroxide ratios are shown in the Figure 2 and Figure 3. It is observed that concentration of hydroxide solution is in direct relation with UCS up to 10M solutions. However, 12M solution did not show significant improvement in UCS. The statistical analysis of data at 10M and 12M tests revealed that p-value of the t-test is 0.11, which is fairly higher than the alpha value of 0.05. This proves that there is not enough evidence to reject null hypothesis; therefore, there is no significant difference between the UCS values of 10M and 12M solutions. This proves that 10M is the percolation point for this mixture after which no significant improvement were observed in UCS values.

The effect of variation of Sodium Silicate to Sodium Hydroxide ratio ($Na_2O_3Si/NaOH$) in the slurry on UCS are illustrated in Figure 3. It can be observed that up to 40% improvement in UCS was achieved per each 0.25 increase in normalized ratio of the mixture. This proved that silicates play vital role in strength improvement of geopolymers. This is due to the availability of silicates to react and form silicate gels, which inevitably improved the strength. However, it is worth mentioning that although higher ratio can lead to higher compressive strength; this may have adverse effect on thickening time. Therefore, a proper optimization of mix design is required.

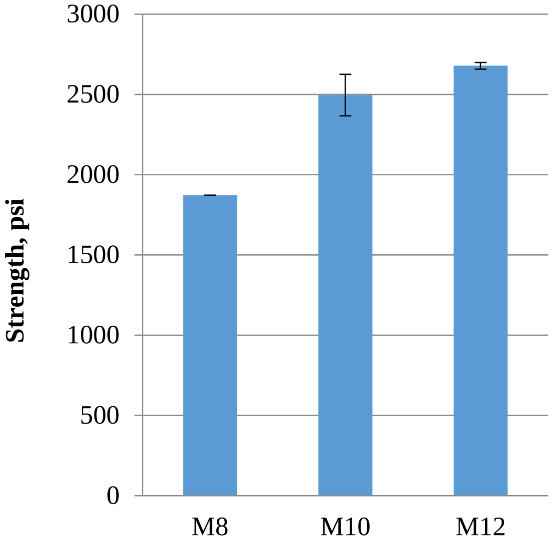

Figure 2. Effect of Molarity of Alkaline on Fly Ash slurry compressive strength

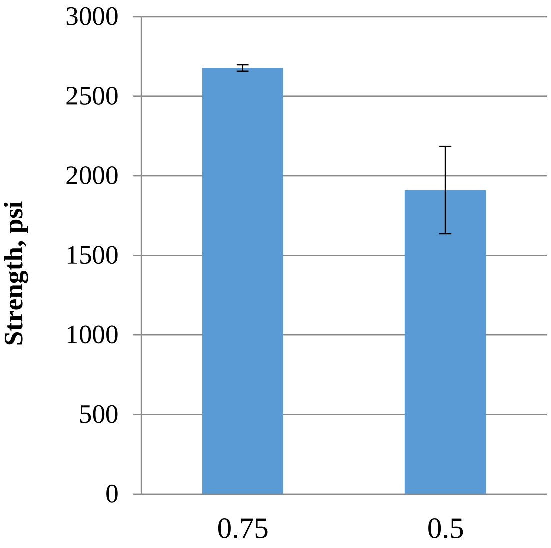

Figure 3. Effect of silicates to hydroxide ratio on compressive strength

In order to see effect of curing time on the compressive strength, triplicate samples were cured at each curing time. Four different curing times were selected to conduct UCS including 1, 3, 7, and 14 days. Results of strength tests are shown in the Figure 4. It can be observed that compressive strength can be directly related to curing time. Especially, after 7 days, the strength of the mixture showed significantly higher improvement. This is due to completion of geopymerization process and hardening process within 14 days. These results show that geopolymers show consistent improvement in strength within first 14 days of curing.

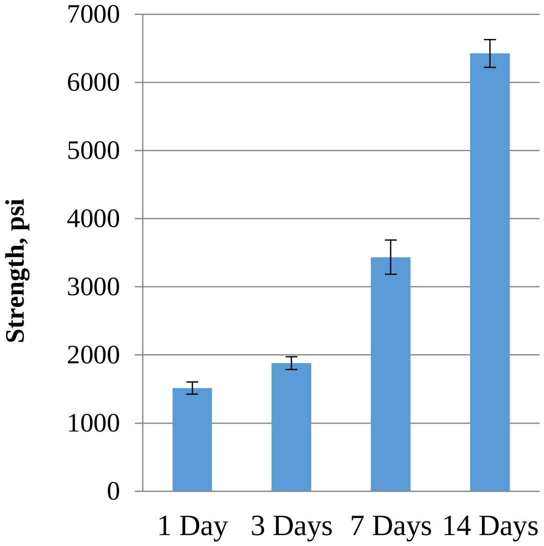

Figure 4. Compressive strength comparison at different curing times

Thickening Time Tests

Thickening time is an important property that indicates application of a material in downhole conditions and its pumpability. The improvement in the thickening time was the key breakthrough achieved in this research. A Chandler Model of 7222 rated to 25,000 psi (170,000 kPa) at a maximum temperature of 400° F (200° C) was used in measuring thickening time. All the tests were conducted according to API-10B standards at pressure of 5,700 psi and temperatures ranging from 150° F to 250° F. Different mix designs and addition of various superplasticizers and retarders were utilized to improve the thickening time. The mixture designs included changes in alkali content (Na_2O/Al_2O_3), silica content (SiO_2/Al_2O_3), water to binder ratio, alakali to fly ash ratio as well as curing conditions and curing temperatures. Water plays an important role in geopolymerization process including dissolution, polycondesntion, and hardening stages. The water level should be optimized to control the thickening time which is a key parameter for downhole applications.

Here, results of thickening time tests are presented. Figure 5 indicates thickening test results for mixtures at temperature of 200°F for two mix designs of slurries with addition of a polycarboxymetyle superplasticizer (dashed black) and no plasticizer or retarding agent (red curve). Although slurry without of plasticizer or retarding agent seems to have acceptable thickening time, observations from visual inspection of actual slurry from consistometer showed severe gelling and balling effect (Figure 6). Slurries with addition of a mixed polycarboxymetyle superplasticizer and retarder were still thin and pumpable at the end of test (5.5 hours) with acceptable BC value of 33. This indicated unreliability of BC values without further inspecting the slurry inside consistometer for geopolymer mixtures.

Several tests were conducted in various temperatures to understand physics of geopolymers pumbaility. Results are illustrated in the Figure 8. It indicates that temperature has an important impact on setting time of Geopolymer mixtures. With approximately one hour of thickening time test, geopolymerization starts where BC values abruptly increase at this time and they smooth out later in the test (Figure 7). At temperature of 250° F due to early activation of Geopolymer, a sudden peak was observed which continues to increase with final BC value of 54. Inspecting samples at the end of thickening test show complete gelation of the mixtures at this temperature. All the mixtures tested have 2% of polycarboxymethyl superplasticizer. It indicated that addition of this superplasticizer is effective up to 200° F temperature. To further improve the thickening time of mixtures at high temperature, combinations of different commercial superplasticizer and retarders were tested. Many of the tests were unsuccessful; therefore, it was decided to investigate in-house developed mixtures of superplasticizer and retarders. Rheology tests were conducted to investigate viscosity changes before testing the thickening time. The final developed additive mixture of superplasticizers and retarders was successful in improving thickening time and preventing gelation of Geopolymer mix at 250° F. Results are illustrated in Figure 9. The newly developed additive successfully lowered the consistency value to less than 30 BC and the mixture was still pumpable with more than 4 hours thickening time. The mix formula of the new additive is currently patent pending by the inventors therefore cannot be disclosed in this paper (Salehi and Khattak, 2015).

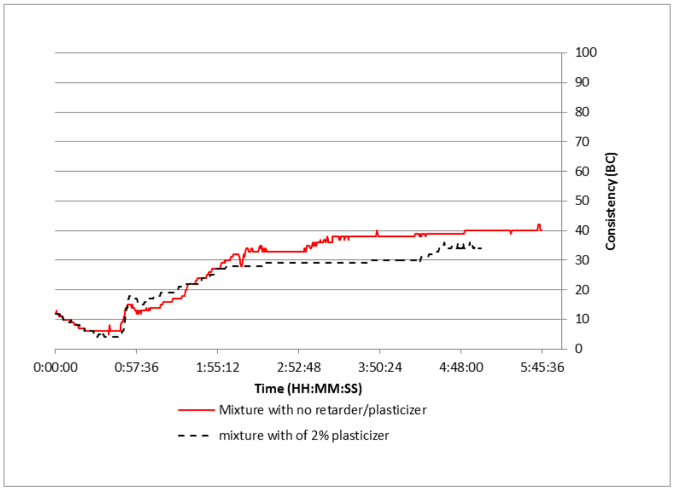

Figure 5. Thickening time test results of the slurry at 200° F degree with and without addition of retarder/plasticizer

Figure 6. **Gelling around Paddle for slurries tested at high temperature without addition of superplasticizer**

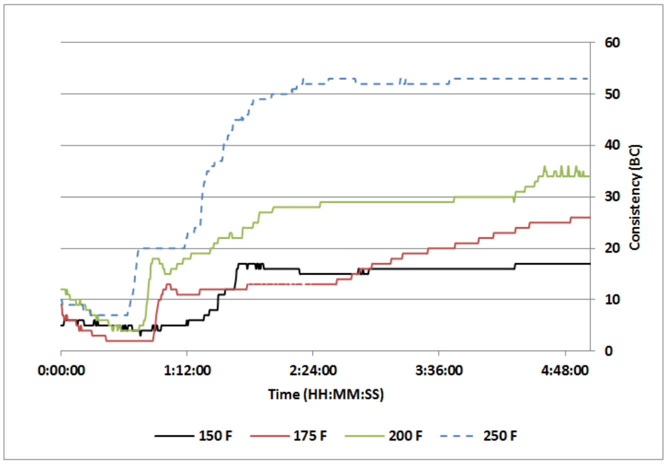

Figure 7. Thickening time comparison for slurries at different temperatures

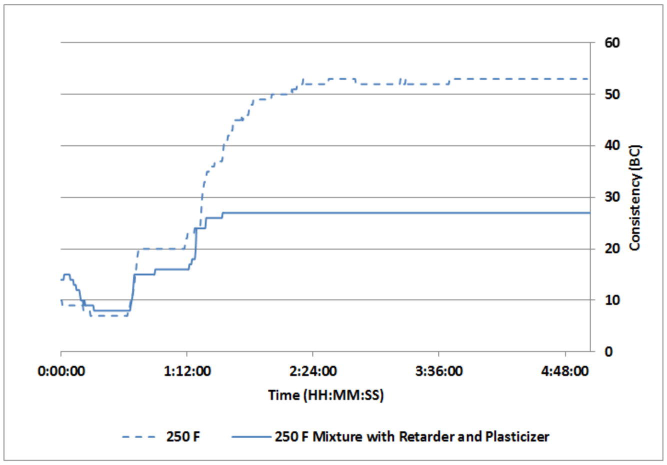

Figure 8. Thickening time results for the comparison of the base mix and mix with addition of superplasticizer and retarder

Durability Tests

Chemical resistance is a necessary property when cementing oil and gas wells. In Portland cement, calcium oxide is one of the oxides in the cement. The Calcium is easily attacked by acids will cause more strength loss in Portland cement. The main purpose of durability test is to see how the cements will resist chemical attacks. Three different chemicals were prepared in solutions for chemical attack resistant test. The chemicals were anhydrous salt of sodium sulphate in granular form, carbonic acid (98% by purity) and sulphuric acid (98% by purity). 10% by solution of sulphuric acid and 50% by solution of carbonic acid were prepared while 0.1M of sodium sulphate was also prepared. The different cement slurries were prepared according to experimental design matrix and cured for 24 hours at a temperature of 200^{0}F using API curing standard. Samples were soaked in chemicals for 28 days and their properties (mass, length and strength) were measured and compared with the situation after 28 days. None of the geopolymer samples exposed to Na2SO4 showed significant surface degradation. However, the surface of Portland cement was degraded. Exposure of geopolymeric samples to H_2CO_3 did not reflect any physical change in the appearances of the specimens. Exposure of Portland cement to H_2CO_3 reflected white particles on the concrete. This occurs due the process of cement corrosion in the presence of H_2CO_3. During the hydration of Portland cement, calcium-silicate-hydrate (C-H-S) phases are formed which give the strength and portlandite "(Ca(OH)2" which is a fragile link in the cement medium. It was further observed that reaction of Portland cement in the presence of carbonic acid is a carbonation process where H_2CO_3 infiltrates into the cement medium and reacts with portladite. This process leads to the conversion of portlandite to calcium carbonate ($CaCO_3$), as shown in the Figure 10.

After exposure to Na_2SO_4, all the specimens exhibited mass loss with Portland cement recording the highest value. The mass after immersion in chemicals was compared to the mass before immersion. Average percent loss of Portland cement in Na2SO4 was 9.1% while the highest recorded in geopolmeric concretes was less than 7.0%. Unconfined compressive strength testing was performed for three samples of each specimen before conducting durability tests and 28 days after. Portland cement samples lost an average of 2.5% strength during this period where as the average strength reduction for Geopolymer samples was less than 1.5%. All the durability tests were conducted with consistent procedure and same equipment to minimize testing errors. Exposure of all specimens to $H2_{S}O_4$ for 28 days increased amount of compressive strength's degradation. Portland cement samples had a great amount compressive strength loss after 28 days of exposure to sulhuric acid environment. Portland cement samples lost an average of 7.2% of its compressive strength after 28 days of exposure to sulphuric acid whereas this was less than 4.0% for Geopolymer samples. Based on durability tests

Conducted results indicate higher durability for Geopolymer samples in harsh chemical environments compared to Portland cement, however, more testing is recommended at different temperatures to draw specific conclusions.

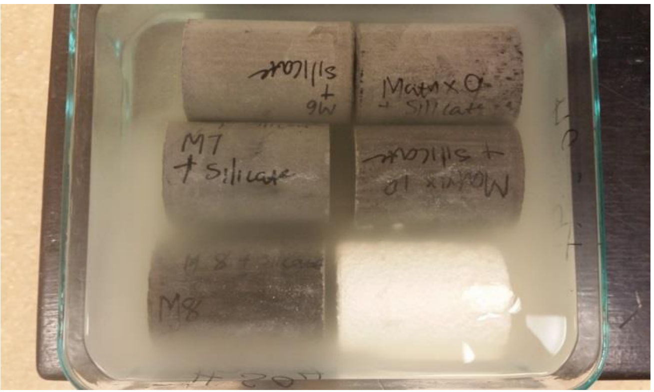

Figure 9. Samples soaked for 28 days durability tests

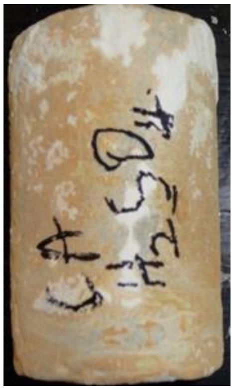

Figure 10. Portland cement after exposure to H_2SO_4

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 (different slurry mixtures) and class G Portland cement are shown in Figure 11.

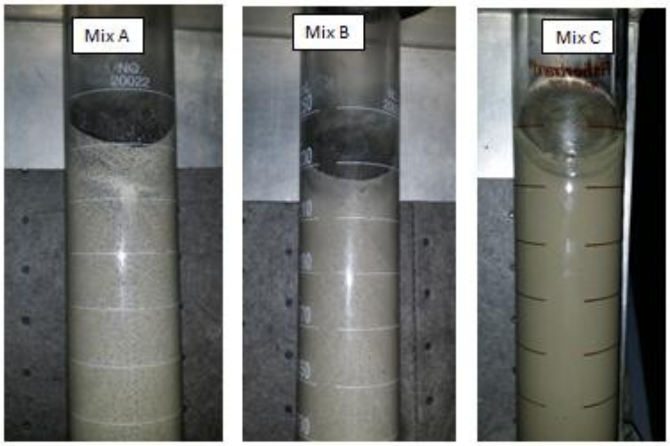

Figure 11. Detailed view of the free fluid test

From Figure 11, it can be seen that Portland cement without an additive shows high tendency of fluid breakout. Fly ash geopolymer slurry (Mix A and B of geopolymers) show zero free fluid breakout. The free fluid breakout of an oil well cement slurry 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.

Conclusions

Study here presented results of laboratory testing for Class F fly ash based geopolymers. The tests were conducted at different temperatures and curing times. Following specific conclusion can be drawn:

- Results of compressive strength shows increased compressive strength by curing time where more than 6000 psi compressive strength by two weeks curing is developed for fly ash Geopolymer mixtures in this work. Additionally, a very high compressive strength was achieved after one day of curing. Furthermore, higher the ratio of sodium silicate to sodium hydroxide, higher was the compressive strength of Geopolymer mixtures.
- Geopolymer mixtures showed increase in strength as the curing temperature increases while Portland cement samples showed strength retrogression by temperature.
- Thickening time results of geopolymers reveal strong effect of temperature on the thickening time of fly ash Geopolymer mixtures where temperatures above 175oF are critical for thickening time and there is a need for addition of retarders and/or superplasticizers.
- Results of thickening time shows more than four hours thickening time for all the mixtures tested up to temperature of 250oF. This was achieved by optimizing mixture design and addition of in-house newly developed mix of retarders and superplasticizers.
- It is very important to visually inspect Geopolymer slurry after thickening time tests. Due to gelation and different physical mechanisms of geopolymer slurries in consistometer, BC values may stay low and be misleading.
- Results of durability tests indicate better durability of Geopolymer mixes when compared to class H Portland cement. Portland cement samples had more reductions in compressive strength after 28 days of exposure to sulfuric acid environment. Portland cement lost an average of 7.2% of its compressive strength after 28 days of exposure to sulphuric acid whereas this was less than 4% for Geopolymer samples.

Acknowledgement

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References

1. Davidovits, J. (1978). Ancient and modern concretes: What's the real difference? Concrete International, pp. 23-35.
2. Davidovits, J. (1994). Properties of geopolymer cements. Presented in First international conference on alkaline cements and concretes, Vol. 1, pp. 131-149.
3. Hardjito, D., S.E. Wallah, D.M.J. Sumajouw & B.V. Rangan (2005). Fly Ash-Based Geopolymer Concrete. Australian Journal of Structural Engineering, Vol. 6, No. 1, pp. 77-85.
4. Igbojeckwe, S., Salehi, S. and Khattak, M.J. 2015. Development of a New Geopolymer Based Cement: Laboratory Investigation. Presented at 2015 AADE conference, AADE-NTCE-07
5. Jain, J., Neithalath, N. (2009). Analysis of calcium leachingbehavior of plain and modified cement pastes in pure water. Cement and Concrete Composites, 31(3), pp. 176-185.
6. Lloyd, N., Rangan, V. (2009). Geopolymer concrete-sustainable cementless concrete. ACI Special Publication, 261, pp. 33-54.
7. Palomo, A., Fernández-Jiménez, A., López-Hombrados, C., & Lleyda, J. L. (2004). Precast Elements Made of Alkali-Activated Fly Ash Concrete. Presented in 8th CANMET/ACI International Conference on Fly Ash, Silica Fume, Slag and Natural Pozzolans in Concrete, Las Vegas, USA. Supplementary Volume, pp. 545.
8. Palomo, A., Grutzeck, M. W., & Blanco, M. T. (1999). Alkali-activated fly ashes: a cement for the future. Cement and concrete research, 29(8), 1323-1329.
9. Rangan B. V. (2010). Fly ash based geopolymer concrete. Presented at the proceedings of the International Workshop on Geopolymer Cement and Concrete (pp. 68-106). Mumbai, India: Allied Publishers Private Limited.
10. Salehi, S., Khattak, M.J., Ali, N., and Rizvi, H. (2016). Development of Geopolymer-based Cement Slurries with Enhanced Thickening Time, Compressive and Shear Bond Strength and Durability. SPE 178793 presented SPE/IADC Drilling Conference and Exhibition, Fort Worth, Tx.