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A STUDY ON THE THICKENING TIME OF CLASS F FLY ASH GEOPOLYMER CEMENT FOR OIL WELL CEMENTING

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ABSTRACT

With the increasing awareness towards global warming, there is a dire need to develop a green cement to replace the conventional Ordinary Portland Cement (OPC). Geopolymer cement has been identified as a potential replacement for the OPC and its suitability for oil well cementing applications are being studied extensively. The determination of thickening time is crucial for oil well cementing to avoid catastrophic incidents due to premature cement setting. This research investigates the thickening time of class F fly ash based geopolymer cement at different densities (low, medium and high) according to the industrial standards with and without the addition of retarders. Three formulations with different ratios of Sodium Hydroxide (NaOH) to Sodium Silicate (Na_2SiO_3), molarity of NaOH, Fly Ash to Alkali ratio, and water content were used to come up with cement densities of 11ppg, 15ppg and 17ppg. The thickening time was determined using a High Pressure High Temperature (HPHT) consistometer at pressure and temperature of 2000 psi and 60 ^oC respectively. The results shows that the medium density formulation of fly ash geopolymer cement resulted in the longest duration of thickening time compared to the low and high density formulations. In addition, it was found that addition of retarder contributed to less than 10% of the increment in thickening time for all three cement densities.

Keywords: fly ash, geopolymer cement, oil well cement, thickening time.

1. INTRODUCTION

Oil well cementing process involves displacing cement slurry down the casing to a predetermined depth in the well. The primary objective of oil well cementing is to provide zonal isolation by restricting fluid movement between the formations. In addition, cementing is also crucial in supporting the casing by forming a bond between the formation and the casing. The composition of the cement used for its application in oil well cementing plays a pivotal role in ensuring that the cement achieves an adequate compressive strength after it reaches its targeted depth. However, prior to the setting of the cement, the cement slurry must remain pumpable long enough until it reaches its targeted depth. Hence, the control of thickening time, which is the time after the cement is mixed and can no longer be pumped is crucial in oil well cementing process. A longer than optimum thickening time will result in delays which involves higher rig costs and a shorter than optimum thickening time will result in the failure of the cement to reach its required targeted depth.

Comprising different chemical and physical standards depending on their application, the oil and gas industry generally adheres to the classifications in accordance with the American Petroleum Institute (API). Currently, the most common type of cement used in the oil and gas industry is the Class G Ordinary Portland Cement (OPC) [1-3]. Approximately one ton of Carbon Dioxide (CO_2) is released to the atmosphere for the production of one ton of Portland cement whereby the calcination of Calcium Carbonate ($CaCO_3$) releases 0.53 tons of CO_2 and another 0.45 tons of CO_2 is emitted if carbon based fuel is used as the energy source for the production of Portland cement [4]. Apart from the environmental concerns, studies have also shown that there are other critical problems associated with the use of OPC such as degradation, strength reduction, shrinkage and susceptibility to chemical reactions [5]. Although researches have confirmed that geopolymer cement possesses superior properties compared to OPC in the aspects of compressive strength, chemical durability and cement shrinkage [5-8], more studies on thickening time of geopolymer cement has to be done to enable its application in oil well cementing process.

2. FLY ASH BASED GEOPOLYMER CEMENT

Geopolymers are materials which are formed under high alkaline condition from alumina silicate polymers and alkali silicate solutions which consist of amorphous and three dimensional structures through the geopolymerization of alumina silicate monomers in alkaline solution [7]. Upon the geosynthesis, geopolymers will consist of alumina and silica tetrahedral which are interlinked in an alternating manner, sharing oxygen atoms the alumina and silica atoms. Upon introduction of the alumina silicate polymers in the alkaline solution, the geopolymerization takes place and hardens quickly. The short settling and hardening time which enhances its mechanical properties is due to its tightly packed polycrystalline structure. Materials which contains Alumina and Silica in its amorphous form are suitable to be used as geopolymer cement. The source of alkaline chemicals are usually $Ca(OH)_2$, NaOH, Na_2SiO_3, the combination of NaOH and Na2SiO3, the combination of KOH and NaOH, K_2SiO_3 and its combination, and $NaCO_3$. The properties associated with the geopolymer cement is highly dependent on the combination of alkaline solution used. Some of the common types of geopolymer cement includes slag based, rock based and also fly ash based geopolymer cement.

In this study, the potential of class F fly ash based geopolymer cement is studied for its use in oil well cementing applications. This is because, among the

available types of geopolymer cement, fly ash is the best option as it provides the most sustainable solution for waste management [5].Besides that, fly ash is the preferred raw material in the manufacturing of geopolymer cement because the life cycle expectancy and durability of the structure was found to be superior in comparison to the other available raw materials [9]. Moreover, its availability in abundance worldwide and low utilization rate is also another factor why fly ash would be the preferred raw material for the synthesis of geopolymers [6, 9, 10].In addition, fly ash based geopolymer cement exhibits higher workability and mechanical properties with one fourth of the water consumption required to produce metakaolin based geopolymers [10].Besides that, the ASTM Class F Fly Ash is preferred compared to the low-calcium fly ash, ASTM Class C Fly Ash in the synthesis of geopolymers since the presence of the calcium element in huge amounts would affect the polymerization process adversely [11].

Formulation of fly ash based Geopolymer cement

The chemicals used to formulate fly ash based geopolymer cement in the experiments conducted in this research were class F fly ash, Na_2SiO_3, NaOH, dispersant, retarder and water. The Na_2SiO_3 / NaOH ratio was maintained at 0.25 and the molarity of NaOH used was 8M. Three different samples were prepared to obtain low, medium and high density mixtures of geopolymer cement. Tables 1 and 2 illustrates the composition of the mixtures with retarder and without retarder. For the low density mixtures, water was added to the mixture until the desired density was obtained. The water added is not inclusive of the water added to dilute NaOH pellets to achieve a molarity of 8M. On the other hand, for the high density mixtures, barite was added to increase the density until the desired density was obtained.

Table-1. Sample composition for low, medium and high density cement mixtures with retarder.

Composition	A	B	C
Density	11.3 ppg	15 ppg	17 ppg
Fly Ash (g)	400	720	720
Alkali (g)	300	360	360
Water (g)	100	120	120
NaOH (g)	240	288	288
Na_2SiO_3 (g)	60	72	72
NaOH Molarity	8	8	8
Na_2SiO_3/NaOH Ratio	0.25	0.25	0.25
Dispersant (g)	5	3	6
Retarder (g)	6	6	6
Barite (g)	-	-	400

Table-2. Sample composition for low, medium and high density cement mixtures without retarder.

Composition	D	E	F
Density	11.3 ppg	15 ppg	17 ppg
Fly Ash (g)	400	720	720
Alkali (g)	300	360	360
Water (g)	100	120	120
NaOH (g)	240	288	288
Na_2SiO_3 (g)	60	72	72
NaOH Molarity	8	8	8
Na_2SiO_3/NaOH Ratio	0.25	0.25	0.25
Dispersant (g)	5	3	6
Barite (g)	-	-	400

3. EXPERIMENTAL METHODOLOGY

Slurry preparation

The experiments were conducted in accordance to the API cement testing guidelines. The materials were weighed according to the formulation stipulated in Tables 1 and 2. The NaOH pellets were diluted with water to achieve a molarity of 8M. Na_2SiO_3 was then added to the mixture according to the proportion given and mixed for 50 seconds at a constant speed. Fly ash was then added to the mixture before adding dispersant and water to the mixture. Barite was added to samples C and F to achieve high density. In addition, the measured amounts of retarders were added to samples A, B and C according to the design of the experiment.

Density measurement

The density of the cement slurries were measure using a pressurized mud balance. In order to expel the air inside the container, a small amount of cement was allowed to overflow from the pinhole of the lid. The rider at of the mud balance was then adjusted until it was on level with the balance before the reading was taken.

Thickening time measurement

After the density test was done, the cement slurry was then poured into a slurry cup and sealed before it was placed into the HPHT Consistometer. The pressure and temperature of the HPHT Consistometer was set at 2000psi and 60 ^{o}C, simulating oil well conditions downhole.

4. RESULTS AND DISCUSSIONS

Thickening time is referred as time taken for the cement slurry to change from fluid state to solid state. The thickening time test is performed to know when a composition of slurry has reached a consistency where it cannot be further pumped downhole. The time taken to reach the consistency is referred to as the thickening time. In this study, the consistency was set to 100Bc in

accordance to the API guidelines [12]. Table 3 and Figure-1 illustrates the results obtained from the experiments conducted.

Table-3. Thickening time results.

Composition	A	B	C	D	E
Thickening Time (hours)	4.10	6.00	4.23	3.85	5.63

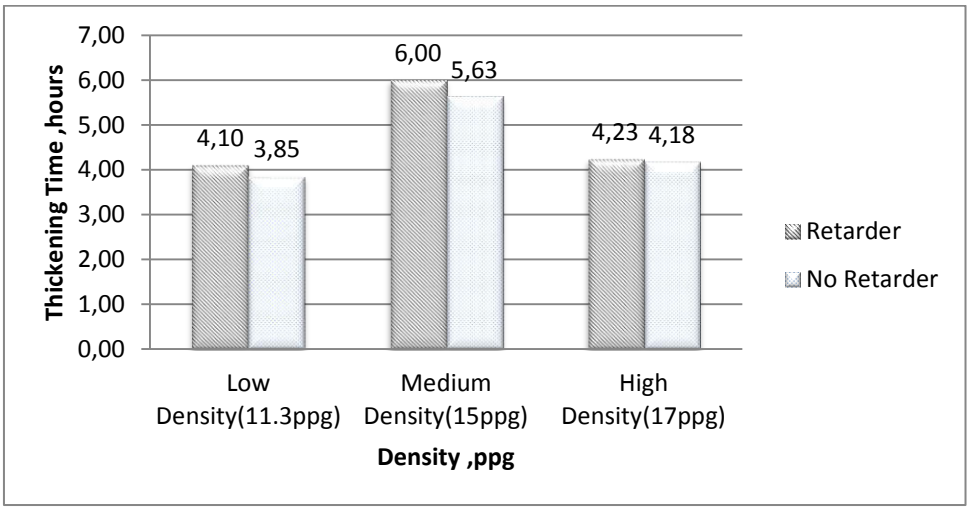

Figure-1. Thickening time for compositions A, B, C, D, E and F.

From Table-3 and Figure-1, it is evident that the medium density mixture is the optimum mixture with the highest thickening time of 6.00 hours and 5.63 hours with and without retarder respectively. The quantity of fly ash, water content and addition of barite are the three variables manipulated in achieving the required density for a particular slurry mixture. Water was used to reduce the density of the slurry and barite was used as a heavyweight agent to increase the density of the mixture. From the results obtained, it is evident that the addition of water and barite slows the geopolymerization reaction taking place. In addition, it was found that the addition of retarder delays the thickening time by 6.49%, 6.57% and 1.12% for low, medium and high density cement slurries respectively. The addition of retarder is significant in the low and medium density slurries but it is insignificant for the high density slurry. The addition of barite is believed to affect the ability of the retarder to form a barrier layer around the reacting geopolymer cement molecules, thus not making it an effecting hindrance for the geopolymerization process to take place.

5. CONCLUSIONS

In this research, three different densities (11.3ppg, 15ppg and 17ppg) of geopolymer cement slurries were studied in accordance to the density requirements of conventional oil well drilling practices. It was found that the three formulations used met the requirements of conventional oil well cementing process with thickening time of 3-8 hours depending on the depth. It can be deduced that the density of the cement slurry and the addition of retarders affects the thickening time of class F fly ash geopolymer cement. The medium density cement slurry resulted in the longest thickening time duration. Besides that, the addition of retarders was found to be ineffective in prolonging the thickening time of high density cement slurries with the presence of barite which was used as a weighting agent to increase the density of the slurry.

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