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Characterization, morphology and shear bond strength analysis of geopolymers: Implications for oil and gas well cementing applications

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ABSTRACT

The aim of this paper is to present results of testing class F fly-ash and its potential application for oil and gas cementing applications. The main challenge in applications of these material is due to lack of research in understanding how these materials react in downhole conditions. Therefore, the methodology followed in this paper is based on experiments to understand geopolymer reactions with activator(s) and second compare some of their properties such as morphology and shear bond strength with Portland cement samples. Furthermore, we investigate the effects of chemical changes of alkaline activators on the shear bond and compressive strength and to analyze the microstructure and morphology of the slurry through SEM (Scan Electron Microscopy), and EDS (Energy Dispersive Spectroscopy). Experimental workflow includes testing several mix designs of geopolymers with different molarity. Observations from experiments confirmed increase in the specimen strength as the molarity increases. In addition, the analysis of the microstructure through SEM and EDS indicated that the Al and Si had considerable influence on the structure of the slurry. Further, we present results for shear bond tests conducted on two different pipe surfaces. Test results showed geopolymers have potentials to be applied for cementing pourposes with good morphology and shear bond strength Albeit, mix design plays a key role where excessive plasticizer concentration is determental to their performance. Additionally, an increase in Shear Bond Strength of fly ash-based geopolymer with a molar concentration of NaOH from 8 M to 10 M.

1. Introduction

Geopolymers are a relatively new group of binding materials, which were first developed by Joseph Davidovits in 1978 (Davidovits, 1999). These geopolymer 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 such as being used construction and sealing materials. Since the last decade, fly ash based geopolymers are receiving more attention due to their economic and environmental advantages.

geopolymerisation involves different processes such as dissolution, diffusion, polycondensation, and hardening (Davidovits, 1999). This complex system requires systematic optimization study of a number of synthesizing parameters in addition to their interactions. These interactions are extremely important issues for geopolymers because fly ashes from different sources show different levels of reactivity under specific geopolymer synthesis conditions, which subsequently affects its final properties. Due to complexities involved in geopolymer's reactions, it is vital fly ash geopolymer geopolymerto 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 significant impact on the physical and mechanical properties of geopolymeric microstructures. An intensive laboratory study is required to develop guidelines in this regard. Hence a systemic study on the feasibility of low calcium based Fly ash geopolymers is required due to the various solutions that these materials can have when compared with ordinary Portland cement (OPC).

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The cement slurry is subjected to very high pressures reaching over 200 MPa (30,000 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 OPC. The temperatures in excess of 110 °C result in phase transformation of cement, significantly decreasing its mechanical properties. In addition to the high pressure and temperature, the oil well cement must be able to contend with weak or porous formations, corrosive fluids, and so forth. Likewise, there is still a lack of information in the current literature regarding the effects of various chemical admixtures, such as new generation superplsticizers, on the rheological, physical and other engineering characteristics of cement-based materials at high temperatures relating to low calcium based Fly ash. Furthermore, various limitations associated with OPC can be overcome with low calcium based Fly ash geopolymers which needs to be studied to see if it can be potentially employed as a greener alternative to OPC in oil well cementing.

A study on the microstructure development of alkali activated fly ash cement using canning electron microscope (SEM) by Palomo et al. (2004) indicated importance of understanding the microstructural development over time. It was found that the elemental composition of reacted products, and rate of activation reaction were dependent on the elemental composition of fly ash and distribution of particles. Final chemical structures and physical properties of fly ash based geopolymers were studied by Van Jaarsveld et al. (2003). It was observed that zeta potential of fly ash particles and calcium content had an effect on both setting time and hardening time of the geopolymer. Also the setting time, strength development and workability of the mixture were shown to be affected by calcium-containing compounds such as calcium-silico-aluminates, calcium silicates, and calcium aluminates hydrates. The shapeless nature (Amorphous) of the geopolymer and the amount of CaO in fly ash were also shown to affect the compressive strength of geopolymers. Sindhunata et al. (2006) showed that a fully reacted fly ash based geopolymer displayed a mesoporous structure (3.6–50 nm). The increase in curing temperature and silicate helped in the development of mesoporous structure.

Most of the previous work on application and use of geopolymers are reported in the concrete and civil industry. Unfortunately, due to lack of research on application of these materials in the oil industry, these materials are not very well received and applied in the oil and gas wells. Some of the previous work includes application of Class C fly ash for well abandoning purposes (Khalifeh et al., 2014; Shah, and Jeong, 2003). Some of the recent research shows relevant testing for application of geopolymers in Oil and Gas wells (Salehi et al., 2016a, 2016b). The main challenge is the short thickening time of geopolymer binders. It is shown that geopolymerisation process gets accelerated as the temperature increases. The mix design, type and concentration of plasticizer and retarder used, and type of alkali activator are contributing factors controlling geopolymers performance.

Shear Bond strength in the oil and gas well is the shearing force between the casing and the surrounding cement binder. The bond between cement and casing is a fundamental factor for mechanical and chemical stability of oil wells. Bonding of steel to cement is best described as adhesion since the material surfaces are dissimilar and cling together. The five mechanisms of adhesion proposed to explain why dissimilar materials stick together are as follows: physical absorption, chemical bonding, diffusion, electrostatic, and mechanical interlocking. As far back as 1962 Evans and Carter (1962) and Carter and Evans (1964) investigated factors influencing bonding properties of cement to casing under laboratory conditions. They also investigated the relationship between compressive strength and shear bond strength and came up with guidelines for determining bond strength with known compressive strength.

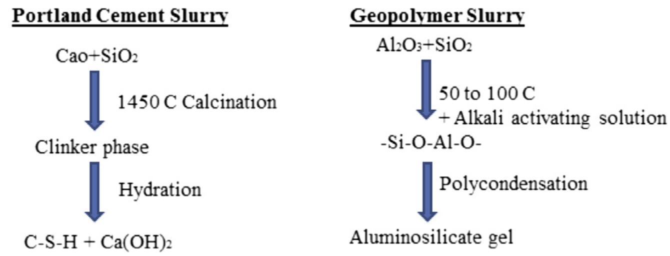

Fig. 1. Comparison of OPC slurry versus geopolymers slurry.

Table 1
Elemental ratios of fly ash geopolymers used in this study.

Oxide	Ratio
SiO_2/Al_2O_3	1.7–9.2
Al_2O_3/CaO	1.2–5.4
Fe_2O_3/SiO_2	0.1–0.9

Table 2
Experimental design matrix.

Temperature, °F	Mix designs
150	8 M, 2.5% Plasticizer, 0.5 Alkaline/Fly ash Ratio
	8 M, 5% Plasticizer, 0.5 Alkaline/Fly ash Ratio
	10 M, 0% Plasticizer, 0.5 Alkaline/Fly ash Ratio
	10 M, 2.5% Plasticizer, 0.5 Alkaline/Fly ash Ratio
	12 M, 2.5% Plasticizer, 0.5 Alkaline/Fly ash Ratio
	12 M, 2.5% Plasticizer, 0.6 Alkaline/Fly ash Ratio
	12 M, 2.5% Plasticizer, 0.6 Alkaline/Fly ash Ratio, 1:1 Silicate
200	8 M, 0% Plasticizer, 0.5 Alkaline/Fly ash Ratio
	8 M, 5% Plasticizer, 0.5 Alkaline/Fly ash Ratio
	10 M, 0% Plasticizer, 0.5 Alkaline/Fly ash Ratio
	10 M, 5% Plasticizer, 0.5 Alkaline/Fly ash Ratio
	10 M, 10% Plasticizer, 0.5 Alkaline/Fly ash Ratio
	12 M, 5% Plasticizer, 0.5 Alkaline/Fly ash Ratio

1.1. Reaction mechanism

The key difference in performance of fly ash based geopolymer materials lies in their chemical structure and activation mechanism. Unlike, OPC, geopolymers are synthesized by alkaline activation of aluminosilicate based materials such as fly ash, granulated blast furnace slag, silica fumes or calcined clays like metakaoline. A simple comparison of OPC and geopolymers is illustrated in the Fig. 1. OPC are composed of calcium hydroxide and calcium silicate hydrate whereas geopolymers are based on aluminosilicate gel.

1.2. Material selection and design

Low Calcium Fly ash geopolymers (ASTM Class F) were used as base material in this research work. The ratio of the constituent elements is described in the Table 1.

The material also composed of other oxides such as calcium oxide, magnesium oxide and sulfur oxide. The particle size distribution of the fly ash shows that the specific surface area is 0.196 m^2/g. The particle size ranges from 0.2 to 150 μm, the material has a uniformity of 0.875. The geopolymer mixture was prepared using dry fly ash and alkaline activator in combination of sodium hydroxide and sodium silicate solution. Later on different types of