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Novel Cementing and Lost Circulation Solutions for Geothermal Wells based on Class F Fly Ash Geopolymers

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Keywords

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ABSTRACT

The advancement of geothermal energy has been challenged by the need to achieve good zonal isolation in harsh downhole environments and to control lost circulation events. Alkali-activated materials (AAMs), also known as geopolymers, have unique properties that make them excellently suited for cementing and lost circulation control purposes for high temperature geothermal well applications. Geopolymers created from low calcium fly ashes, a waste product, and a suitable alkaline solution exhibit good compressive and tensile strength, and excellent casing bond strength (in excess of 7 MPa, more than an order of magnitude higher than conventional cements). In addition, they exhibit extraordinary temperature stability, with certain formulations being stable at geothermal wells conditions (temperatures higher than 200 °C) without strength retrogression.

1. Introduction

With increasing calls for reduction of greenhouse gas emissions due to climate change, the energy industry is shifting towards renewable sources such as solar, wind, and geothermal energy (Hosseini & Wahid, 2016). Geothermal energy has continued to attract attention as a baseload-capable renewable source of energy that is less affected by external conditions and weather fluctuations (Kagel et al., 2005). Although the worldwide production of electricity from geothermal energy more than doubled over the past two decades (6833 MWe in 1995 to 15950 MWe in 2020) (Finger & Blankenship, 2010; Huttrer, 2020), the advancement and widespread use of geothermal energy has had to deal with challenges in construction and completion of geothermal wells. Such challenges include achieving long-term zonal isolation in harsh downhole environments (i.e. temperature 200 – 400 °C) and lost circulation control. Currently, lost circulation represents up to 10% of the total cost of a geothermal project (Saleh et al., 2020). A suitable material for geothermal well cementing should have high temperature stability at geothermal conditions. In addition, to provide zonal isolation and lost circulation control, the cementing material should have sufficient compressive strength, high tensile strength, and high bond strength to the casing (Finger & Blankenship, 2010).

The current established practice is to use ordinary Portland cement (OPC) to construct a physical barrier outside the steel casing to provide the required zonal isolation. However, several studies have shown that OPC yields poor performance under the extreme conditions that exist in higher temperature wells in addition to having a high carbon footprint due to CO_2 emissions during manufacturing (Chan et al., 2015; Duguid et al., 2011; van Oort et al., 2019). Thus, studies were conducted to investigate the development of alternative cementing materials for geothermal applications. In the 1990s, calcium phosphate cement was introduced as an alternative cementing material for high temperature applications (> 200 °C) such as steam injection wells and geothermal wells (Fuenmayor et al., 2014; Sugama, 2006). Although CaP shows desirable properties for geothermal applications (such as high thermal stability, suitable rheological properties, low density, and sufficient toughness), it still shares significant drawbacks with OPC, including low bond strength to casing (< 0.6 MPa) and brittle failure behavior (Sugama, 2006).

The use of alkali-activated materials (AAMs), also known as geopolymers, as an alternative cementing material to OPC has been the focus of several studies (Khalifeh et al., 2018; Salehi et al., 2019; van Oort et al., 2019). Geopolymers are made by mixing an aluminosilicate precursor powder (e.g. fly ash, slag cement, or metakaolin) with an alkaline activating solution. The most common activators used in geopolymer formulation are sodium/potassium hydroxides and silicates. Geopolymers made from Class F fly-ash (FA) precursor material have shown desirable properties for cementing application in a variety of well applications, including high-temperature wells. Class F fly ash-based geopolymers were found to have high tolerance to contamination with non-aqueous drillings fluids (NADF) (Ahdaya & Imqam, 2019; Liu et al., 2019), making them useful for lost circulation control in wells drilled with such fluids. In addition, geopolymers were found to be highly resistant to attacks by various acids (Rostami & Brendley, 2003). Geopolymers were also found to have self-healing abilities (Liu 2017; Ross 2020) and lower shrinkage sensitivity when subjected to elevated pressure and temperature (Panchmatia et al., 2020). Moreover, silicate-activated geopolymers have shown remarkable temperature stability up 800 °C (Colangelo et al., 2017; Kong & Sanjayan, 2010). In addition, the production of FA-based geopolymers resulted in equivalent carbon emissions up to 28% lower than OPC (Chan et al., 2015). In this study, the feasibility of using geopolymers in cementing applications in geothermal wells was investigated. The viscosity, thickening time, and mechanical properties (i.e. compressive strength, tensile strength, and bond strength) of geopolymer slurries were measured and compared to OPC.

2. Materials

Two types of cementitious materials were used in this study: Class H ordinary Portland cement (OPC) and Class F fly ash (FA). The chemical compositions of both OPC and FA are shown in Table 1. Geopolymer slurries were formulated using six different activators, namely Liquid Sodium Hydroxide (LSH), Liquid Potassium Hydroxide (LPH), Liquid Sodium Silicate (LSS), Solid Sodium Silicate (SSS), Liquid Potassium Silicate (LPS), and Solid Potassium Silicate (SPS). The hydroxide-based activator solutions were prepared in such a way as to maintain a concentration of alkali (i.e. Na or K) at 8M. For silicate-based activator solutions, the SiO_2/M_2O weight ratio (where M is either Na or K) was maintained at 0.12. Activating solutions were prepared by mixing appropriate amounts of commercially-available sodium / potassium silicate solutions with deionized water (18 MΩ-cm). Following this, appropriate amounts of sodium / potassium hydroxide pellets (98% purity) were added to the solution.

The OPC slurry was prepared with a water-to-cement ratio by mass (w/c) of 0.385 following the procedure described in API RP 10B-2 (2010) using a high shear mixer. To overcome the strength retrogression reported in OPC slurries subjected to high temperature, an additional OPC mix incorporating silica flour (SF) was investigated (Pyatina & Sugama, 2019). The OPC/SF mix was prepared by replacing 30% of the cement wright with silica flour while maintaining the w/c at 0.385. For geopolymer slurries, the M_2O/FA weight ratio was selected to achieve an 8M alkali concentration in the activator solution, while the water-to-solid weight ratio was maintained at 0.33. Geopolymer slurries were prepared by initially hand-mixing FA into the activating solution to obtain a uniformly blended mixture, which was then mixed with a high-speed overhead paddle stirrer for 30 sec. Mixture design parameters for slurries are summarized in Table 2.

Table 1: Chemical compositions of Class H OPC and Class F FA used in this study.

Oxide	**Content (%)**	
	Class H OPC	**Class F FA**
SiO_2	22.1	44.7
Al_2O_3	2.7	23.2
Fe_2O_3	4.5	24.2
CaO	64.4	3.2
MgO	2.5	0.8
SO_3	2.8	0.6
Total alkali as Sodium Oxide, Na_2O_{eq}	2.0	1.0
Loss on Ignition (LOI) at 750°C	1.1	0.4

Table 2: Mix design parameters of OPC and Geopolymers slurries.

Mix ID	**Activator**	**W/S**	**SiO_2/M_2O**	**M_2O/FA**
OPC	DI Water	0.385	---	---
OPC/SF	DI Water	0.385	---	---
LSH	8M Liquid Sodium Hydroxide	0.33	---	---
LPH	8M Liquid Potassium Hydroxide	0.33	---	---
LSS	Liquid Sodium Silicate	0.33	0.12	0.1
SSS	Solid Sodium Silicate	0.33	0.12	0.1
LPS	Liquid Potassium Silicate	0.33	0.12	0.2
SPS	Solid Potassium Silicate	0.33	0.12	0.2

3. Experimental Methods

3.1 Viscosity

Viscosity testing was used to characterize the rheological properties of geopolymer and OPC slurries immediately after preparation following API RP 10B-2 (2010). Three viscosity tests were conducted for each slurry at 23°C using a viscometer equipped with an R1B1 rotor and bob configuration and an F1 Spring. The rheological constants (including yield stress and apparent viscosity) of tested slurries were calculated by curve fitting the shear stress vs. shear rate data using the Herschel-Bulkley Yield Power Law (YPL) rheology model given by:

$$\tau = \tau_y + K\dot{\gamma}^n \tag{1}$$

where τ is the shear stress (Pa), τ_y is the yield stress (Pa), K is the consistency index, n is the fluid behavior index, and $\dot{\gamma}$ is the shear rate (1/s).

3.2 Mechanical Properties

3.2.1 Curing Conditions

All samples tested in the mechanical properties investigations (i.e. compressive strength, tensile strength, and bond strength) were cured in a high-pressure high-temperature (HPHT) curing chamber following the curing procedure described in API RP 10B-2 (2010). A bottomhole static temperature (BHST) of 204.4 °C and bottomhole pressure (BHP) of 20.68 MPa were selected to represent bottomhole geothermal well conditions. The temperature of the curing chamber was increased from a surface temperature of 23 °C to a bottomhole circulating temperature (BHCT) of 130 °C in 3 hours, then to a BHST of 204.4 °C in 10 hours. The pressure was increased from atmospheric pressure (101.3 kPa) to 20.68 MPa in 30 seconds at the beginning of the curing procedure and maintained at that value during the entire duration of the curing process. At the end of the curing period, the pressure and temperature were ramped down to atmospheric pressure and 32.2 °C, respectively, in 30 minutes.

3.2.2 Compressive Strength

3 cylinders (51 mm diameter and 102 mm height) made from each slurry were tested following ASTM C39/C39M (2021). Samples were cured following the curing condition given in section 3.3.1 for 3 days. All samples were loaded using a universal testing machine until failure, and the compressive strength was calculated based on the recorded peak load.

3.2.3 Tensile Strength

Tensile strengths of OPC and geopolymer slurries were determined using a modified Brazilian Split Tension test following ASTM C496/C496M (2017). 3 cylinders (51 mm diameter and 102 mm height) made from each geopolymer and OPC slurry were cured following the curing condition in section 3.3.1 and tested at the age of 3 days.

3.2.4 Bond Strength

The bond strengths of OPC and geopolymer slurries were measured using a push-out test. A clean stainless steel rod with a diameter of 12.7 mm was placed in the center of a 51 mm diameter cylindrical mold. Slurry was then cast around the rod to a height of 102 mm. 3 samples of each mixture were cured following the curing conditions outlined in section 3.3.1 and tested at the age of 3 days using the test setup shown in Figure 1. Steel rods were loaded with a load rate of 50 N/sec until deboning between the rod and the cementing material (i.e. OPC and geopolymer) was observed. Bond strength was calculated by:

$$f_b = \frac{P}{\pi l d} \tag{2}$$

where f_b is the bond strength (Pa), P is the peak load (N), l is the height of the slurry (m), and d is the diameter of the rod (m).

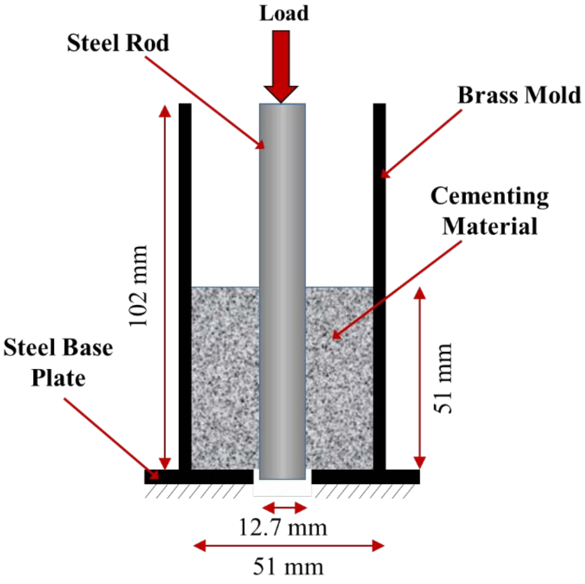

Figure 1: Schematic diagram of the push-out test setup used for cement-casing bond strength testing.

3.3 Thickening Time

Thickening time of all slurries was measured using an HPHT consistometer following the procedures described in API RP 10A (2019) and 10B-2 (2010). The test temperature was increased from a surface temperature of 23 °C to a BHCT of 135 °C in 3 hours and then kept constant at 135 °C for the rest of the test. The pressure was increased immediately from atmospheric pressure to 6.89 MPa, and then to 20.68 MPa over a period 3 hours. It was subsequently kept constant at 20.68 MPa until the end of the test. Thickening time is defined as the time required for the slurry to achieve a consistency of 70 Bearden consistency (Bc) units, after which the slurry is considered to be unpumpable. Each slurry was tested three times, and the average values and range of measured thickening times were reported.

4. Results and Discussion

4.1 Viscosity

Table 3 shows the average values of the rheological constants for OPC and all geopolymer slurries. OPC and OPC/SF slurries were found to have fluid behavior index of 0.46 and 0.61, respectively, which reflects YPL behavior. This behavior can also be observed in the shear stress vs. shear rate plots shown in Figure 2. For geopolymer slurries, it was found that slurries with all types of activators behaved like Bingham plastic fluids with a fluid behavior index close to 1.0 ($0.95 < n < 1.05$). In addition, it was found that all geopolymer slurries had yield stress values lower than OPC slurry. Moreover, all geopolymers slurries activated with sodium-based activators were found to be too viscous, such that the apparent viscosity could not be measured by the viscometer (> 0.32 Pa.s). However, the use of LPH and LPS-based activators resulted in pumpable geopolymer slurries (apparent viscosity ~ 0.2 Pa.s) with acceptable rheological properties.

Table 3: Rheological constants for all OPC and geopolymer slurries tested.

Mix ID	**Apparent Viscosity @ 300 rpm (Pa.s)**	**Herschel-Bulkley model constants**		
		Yield Stress τ_y (Pa)	**Fluid Behavior Index n (dimensionless)**	**Consistency Index K (Pa.s^n)**
OPC	0.13±0.03	6.70±0.37	0.46±0.06	3.87±0.73
OPC/SF	0.12±0.02	6.63±2.91	0.61±0.11	2.30±0.72
LSH	> 0.32	2.87±0.21	1.00±0.05	0.84±0.30
LPH	0.21±0.06	2.62±0.98	1.02±0.08	0.18±0.09
LSS	> 0.32	1.05±0.72	1.00±0.01	2.04±0.48
SSS	> 0.32	4.31±2.40	1.02±0.05	1.69±0.51
LPS	0.21±0.09	0.57±0.93	1.01±0.10	0.19±0.05
SPS	0.30±0.03	3.20±1.05	1.04±0.04	0.22±0.04

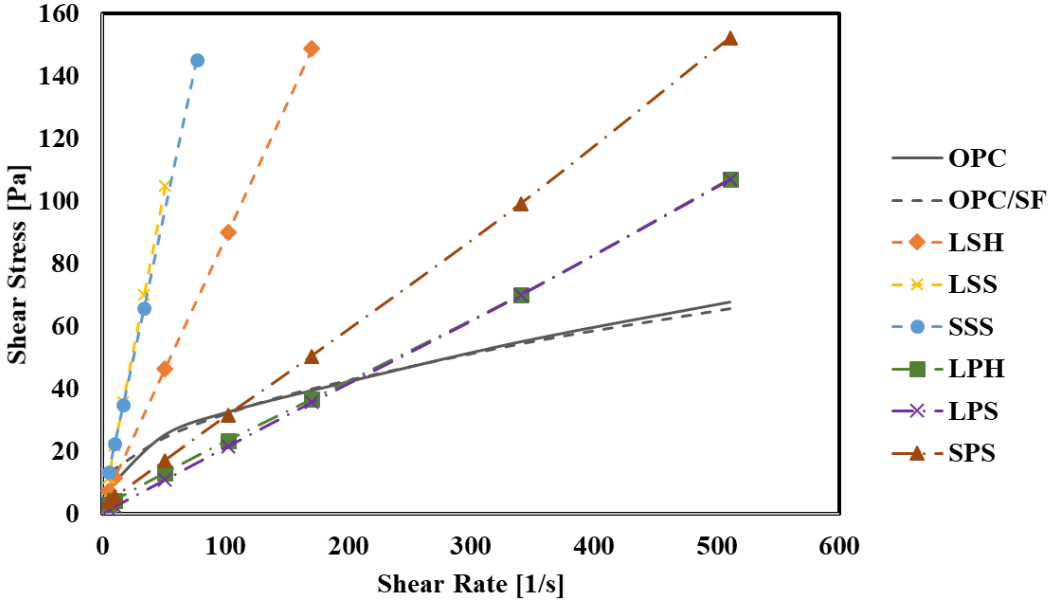

Figure 2: Viscosity profiles for OPC and geopolymer slurries.

4.2 Mechanical Properties

The compressive strengths of OPC and geopolymer formulations are summarized in Figure 3. The compressive strength of OPC slurry subjected to geothermal well conditions was found to be 12.3±1.8 MPa, which exceeds the minimum required strength for wellbore cementing. However, this value was significantly lower than the compressive strength of OPC slurries with similar w/c under typical wellbore conditions (i.e. BHST of 75 °C to 95 °C) reported in the literature (Krezinski et al., 2021; Li et al. 2015). Incorporating SF in OPC mixtures eliminated the strength retrogression and increased the compressive strength by 278% to 46.6±11.5 MPa, as expected. Geopolymer formulations activated with an LPS activator showed compressive strengths to OPC without SF of 11.7±1.1 MPa, which still met minimum requirements. Moreover, geopolymer formulations activated with LPH and SPS activators were found to have higher compressive strengths of 23.3±1.1 MPa and 22.0±0.6 MPa, respectively. All geopolymer formulations activated with sodium-based activators were found to have compressive strengths lower than 2.1 MPa. Such a low compressive strength does meet the minimum required strength for wellbore cementing.

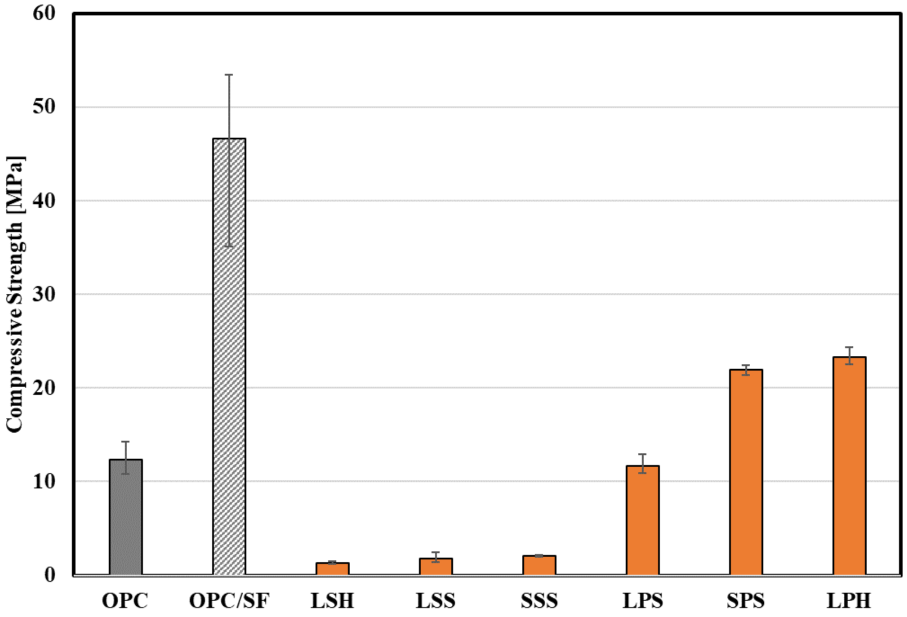

Figure 3: 3-day compressive strengths of OPC and geopolymer formulations cured under geothermal well conditions (204.4 °C and 20.68 MPa). Error bars represents the range of compressive strengths values measured for each mixture.

As expected, the tensile strengths of OPC and geopolymer formulations follow the same trends as the compressive strengths, as shown in Figure 4. However, the increase in tensile strength due to the incorporation of SF was limited to 175% compared to the 278% increase in compressive strength. In addition, geopolymer formulations activated with LPH and SPS were found to have relatively high tensile strengths of 2.2±0.4 MPa and 1.8±0.3 MPa, respectively. The tensile strengths of all geopolymer formulations with sodium-based activators were found to be very low and did not exceed 0.25 MPa.

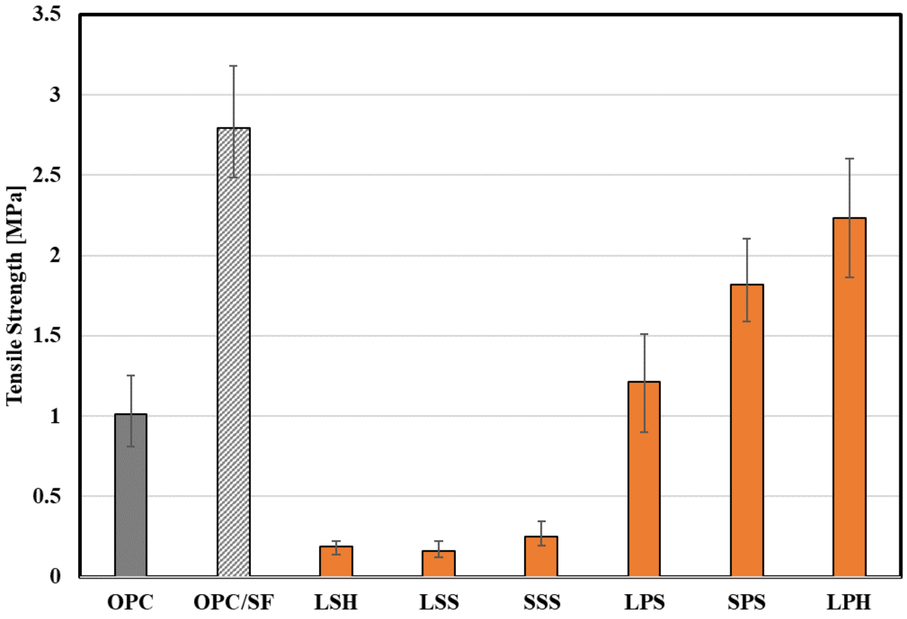

Figure 4: 3-day tensile strengths of OPC and geopolymer formulations cured under geothermal well conditions (204.4 °C and 20.68 MPa). Error bars represents the range of tensile strengths values measured for each mixture.

The push-out bond strength results for OPC and geopolymer formulations activated with potassium-based activators are shown in Figure 5. OPC and OPC/SF mixes were found to have low bond strengths of 0.66 ±0.46 MPa and 0.88±0.21 MPa, respectively, with no statistically significant difference between the two mixtures. Potassium-based geopolymer formulations subjected to geothermal well conditions, on the other hand, were found to have much higher bond strengths of 7.2±0.3 MPa, 7.2±0.5 MPa, and 7.7±0.3 MPa for LPH, LPS, and SPS geopolymers, respectively. Such remarkably high bond strengths were not observed with other cementing slurries and are some of the highest bond strengths ever recorded. All geopolymer formulations activated with sodium-based activators were found to have such low bond strengths (< 0.1 MPa) that they could not be accurately measured. Their results were therefore omitted in Figure 5.

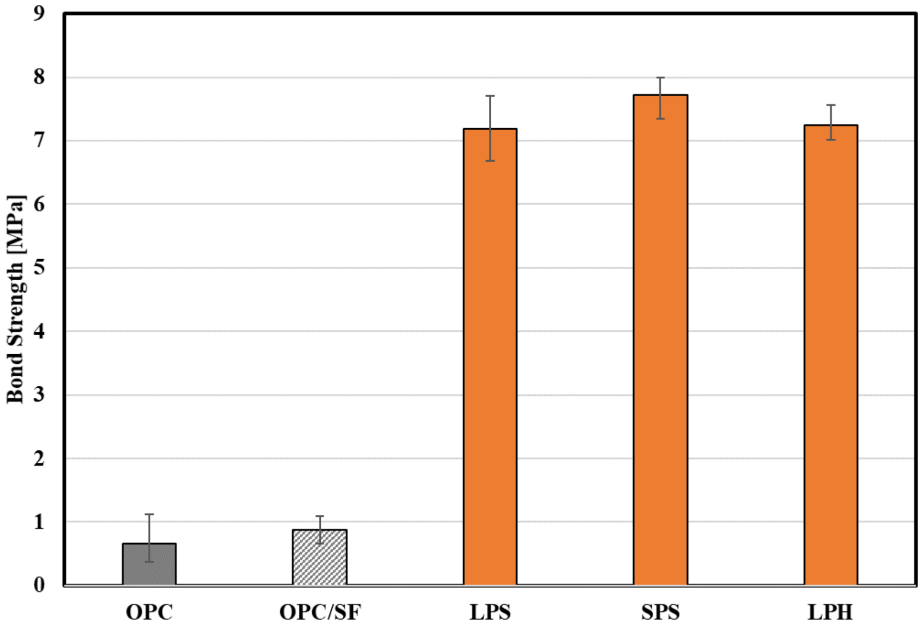

Figure 5: 3-day bond strengths of OPC and potassium-based geopolymer formulations cured under geothermal well conditions (204.4 °C and 20.68 MPa). Error bars represent the range of bond strengths values measured for each mixture.

The mechanical property evaluations showed that geopolymer formulations activated with potassium-based activators have excellent performance under geothermal wells conditions (i.e. temperatures ≥ 200 °C). These results confirm literature observations showing that certain silicate-activated geopolymers exhibit remarkable temperature stability up to 800 °C (Colangelo et al., 2017; Kong & Sanjayan, 2010). With such extraordinary bond strength and relatively high tensile strength to compressive strength ratios, potassium-based geopolymers slurries were found to make excellent cementing material candidates to provide good zonal isolation and lost circulation control in geothermal wells. Sodium-based geopolymers subjected to geothermal well conditions, however, showed significantly lower compressive, tensile and bond strengths in addition to undesirable rheological properties. Hence, such geopolymer formulations were found to be unsuitable for application in geothermal wells.

4.3 Thickening Time

Table 4 summarizes the thickening time of OPC and potassium-based geopolymer slurries measured under geothermal well conditions using an HPHT consistometer without the addition of any retarders. Although it was found that all potassium-based geopolymers have thickening times almost twice the thickening time of OPC mixtures, a longer time may still be needed for specific geothermal applications. Thus, retarders will need to be identified and/or developed for such geopolymer slurries. The high viscosity of sodium-based geopolymer slurries did not allow for an accurate measurement of thickening time.

Table 4: Thickening time for OPC and potassium-based geopolymer slurries.

Mix ID	Thickening Time (Minutes)
OPC	76 ± 4
OPC/SF	78 ± 3
LPH	155 ± 1
LPS	155 ± 14
SPS	152 ± 3

5. Conclusions

In this paper, alkali-activated materials (also known as geopolymers) made from Class F fly ash pre-cursor material are investigated as a primary cementing and lost circulation material in geothermal wells. A bottomhole static temperature (BHST) of 204.4 °C and bottomhole pressure (BHP) of 20.68 MPa were selected as downhole conditions representative for geothermal wells. Six Class F fly ash geopolymer slurries were formulated using different activators (3 sodium-based and 3 potassium-based activators, using hydroxide and silicate anions). The rheological properties of geopolymer slurries were measured to investigate if such slurries can be readily pumped into geothermal wells. Moreover, mechanical properties (compressive strength, tensile strength, and bond strength) of geopolymer slurries were measured and compared to slurries of OPC and OPC incorporating 30% by weight silica flour (SF).

Although potassium-based Class F fly ash geopolymer slurries were found to have higher apparent viscosity than OPC slurries at atmospheric conditions, they were pumpable fluids (apparent viscosity ~ 0.2 Pa.s) with acceptable rheological properties. In addition, geopolymer formulations activated with potassium-based activators subjected to geothermal well conditions were found to have compressive strengths up to 23.3±1.1 MPa and tensile strengths up to 2.2±0.4 MPa. Moreover, potassium-based Class F fly ash geopolymer slurries were found to have extraordinary high casing bond strength (> 7 MPa), which was not observed with other cementing materials. With such excellent mechanical and rheological properties as well as temperature stability, in combination with high resistance to acid attack observed in the literature, potassium-based geopolymers slurries should be excellent candidates for providing sufficient zonal isolation, lost circulation control, and resistance to acid attack in geothermal wells. Literature data suggests that the application range of such geopolymers can be extended beyond our chosen limit of 204.4 °C, which will be a topic of future study. On the other hand, sodium-based Class F fly ash geopolymers subjected to geothermal well conditions showed significantly lower strengths, low temperature stability, and undesirable rheological properties. Hence, geopolymer formulations activated with sodium-based activators were deemed to be unsuitable for geothermal cementing purposes.

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