

Article

Fly Ash-Based Geopolymers as Lower Carbon Footprint Alternatives to Portland Cement for Well Cementing Applications

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Abstract: Ordinary Portland cement (OPC) is currently the preferred material for the creation of barriers in wells during their construction and abandonment globally. OPC, however, is a very carbon-intensive material with some inherent technical weaknesses. These include a low casing-to-cement bond strength which may allow for the formation of micro-annuli, which in turn can become a conduit for greenhouse gas transport (primarily of methane, a powerful greenhouse gas) to surface. Alkali-activated materials (AAMs), also known as geopolymers, have a much lower manufacturing carbon footprint than OPC and can be a good alternative to OPC for primary and remedial well cementing applications. This paper reports on a comprehensive study into the use of Class F fly ash-based geopolymers for a large variety of downhole well conditions, ranging from lower-temperature surface and intermediate casing cementing conditions to much higher temperature conditions (up to 204 °C (400 °F)) that can be encountered in high-pressure, high-temperature (HPHT) wells and geothermal wells. The rheological and mechanical properties of alkali-activated fly ash with six different sodium and potassium-based hydroxide and silicate activators were measured and compared to OPC. The results show that geopolymer formulation properties can be tuned to a variety of downhole cementing conditions. With the application of a suitable alkaline activator, geopolymers exhibit good compressive and tensile strength and an outstanding casing-to-cement bond strength of up to 8.8 MPa (1283 psi), which is more than an order of magnitude higher than OPC. This has important implications for preventing the creation of micro-annuli as a result of casing-to-cement interface debonding, thereby preventing the potential leakage of methane to the atmosphere on future wells that use geopolymers rather than OPC for barrier creation.

Keywords: geopolymer; fly ash; alkali-activated material; zonal isolation; cement replacement; carbon footprint reduction



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1. Introduction

Almost every major energy company has announced plans to achieve net zero emissions before or by 2050 [1]. To achieve such goals, current practices and materials will need to be modified, and new ones will have to be adopted and implemented. As an example for the subsurface energy industry, shifting towards renewable energy sources such as geothermal energy and adopting carbon capture and underground storage are major steps toward reaching net zero goals [2,3]. Additionally, maintaining proper zonal isolation inside and outside wellbores is essential to prevent leakage incidents (see for instance [4]), which can release large quantities of greenhouse gasses (GHG) to the atmosphere. The concern revolves primarily around leakage of methane (CH₄), which has 86 times the GHG effect of carbon dioxide (CO₂) over a 20-year time period [5]. Ordinary Portland cement (OPC) is used extensively in the well construction industry for establishing cemented well barriers, but this comes at the cost of a large carbon footprint. The cement manufacturing

industry is responsible for 5–8% of global CO₂ emissions [6]. OPC also has several technical weaknesses, which include low casing–cement bond strength, low tensile-to-compressive strength ratios, and failure behavior without significant re-healing effects when cement fractures under the influence of applied loads (e.g., cyclic loads, geomechanical and geochemical loads acting on the wells during their entire lifetime [7,8]). A low carbon footprint cementing material that can effectively address the weaknesses of OPC and provide zonal isolation and lost circulation control in a wide range of wellbore conditions is therefore highly desirable on the road towards reduced—and eventually net zero—emissions.

Several studies have been dedicated to the use of alkali-activated materials (AAMs), also known as geopolymers, as an alternative cementing material for wellbore cementing applications [7,9–15]. Geopolymers are formulated by mixing an aluminosilicate precursor powder (examples are fly ash, slag, or metakaolin) with an alkaline activating solution. The most common activators used in geopolymer formulations are sodium or potassium hydroxides and silicates. Class F fly ash-based geopolymers have shown desirable properties for cementing applications in previous investigations. They exhibit a high tolerance to contamination with drilling fluids [16–18], good resistance to acid attack [19], self-healing abilities [20–23], and lower shrinkage sensitivity at elevated pressure and temperature [24]. Moreover, high temperature stability up to 800 °C was observed for geopolymers activated with silicate activators [25,26], which is particularly useful when considering application in high-pressure/high temperature (HPHT) oil and gas wells as well as geothermal wells [27]. Most importantly for the present study, a well-cited study by Duxson et al. [28] indicates that geopolymer binders can deliver an 80%-or-greater reduction in CO₂ emissions compared to OPC. This is mainly because OPC manufacturing requires the high-temperature calcination (up to 1400 °C) of cement clinker, which not only consumes a large volume of fossil fuels to supply the necessary energy but also releases CO₂ as a reaction product. Such a calcination step is absent from geopolymer synthesis of ashes or slags [28]. Moreover, geopolymers yield additional environmental benefits compared to OPC associated with a lower water requirement (of particular importance in dry regions of the world where non-renewable water use may be a significant issue) and a limited requirement to use super-plasticizing agents which contribute to the cost and CO₂ footprint associated with the use of OPC [28,29].

Most of the studies conducted on the use of geopolymers as alternative materials for wellbore cementing applications have focused on relatively low-temperature applications (i.e., bottom hole static temperature (BHST) of less than 77 °C (170 °F)) or have used sodium-based activators [10,12,13,30–32]. This paper reports on a comprehensive investigation into the use of Class F fly ash-based geopolymers as cementing materials for various wellbore applications, including higher temperature conditions than previously studied. Potassium activators were also explored in addition to the more traditional sodium activators. Geopolymers formulated with six different activators, i.e., sodium and potassium-based hydroxide, as well as liquid and solid sodium and potassium silicates, were tested at different conditions, including relatively low-temperature conditions (BHST 77 °C (170 °F)), simulating surface and intermediate casing cementations; elevated temperature conditions (BHST 135 °C (275 °F)), representing deep intermediate and production casing cementations; and high-temperature conditions (BHST up to 204 °C (400 °F)), more representative of conditions in HPHT and geothermal wells. 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

2.1. Cementitious Materials

Two types of cementitious materials were used in this study: Class H OPC and Class F fly ash (FA). The oxide contents of both OPC and FA are shown in Table 1. The chemical composition of the FA used in this study is representative of a Class F FA as defined by the

ASTM C618 standard, while the composition of the OPC is representative of a Class H OPC in accordance with the API 10A standard.

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

Oxide	Content (wt%)	
	Class H OPC	Class F FA
SiO ₂	20.9	44.7
Al ₂ O ₃	3.6	23.2
Fe ₂ O ₃	6.3	24.2
CaO	63.3	3.2
MgO	1.0	0.8
SO ₃	3.0	0.6
Total alkali as sodium oxide, Na ₂ O _{eq}	0.55	1.0
Loss on ignition (LOI) at 750 °C	1.2	0.4
Insoluble residue/other	0.15	1.9

2.2. Mixtures Preparation

Table 2 shows the mixture design parameters for all OPC and geopolymer slurries. OPC slurries were prepared with a water-to-cement solids ratio by mass (W/S) of 0.385 following the procedure described in API RP 10B-2 using a high shear mixer. To overcome the strength retrogression reported in OPC slurries subjected to high temperature, an additional OPC mixture incorporating silica flour (OPC/SF) was investigated [33,34]. The OPC/SF mixture was prepared by replacing 30% of the cement weight with silica flour while maintaining the W/S ratio at 0.385.

Table 2. Mix design parameters of OPC and geopolymer slurries.

Mix ID	Activator	W/S	M ₂ O	SiO ₂ /M ₂ O	M ₂ O/FA
OPC	DI Water	0.385	—	—	—
OPC/SF	DI Water	0.385	—	—	—
LSH	8M Liquid Sodium Hydroxide	0.33	8M	—	—
LPH	8M Liquid Potassium Hydroxide	0.33	8M	—	—
LSS	Liquid Sodium Silicate	0.33	8M	0.12	0.1
SSS	Solid Sodium Silicate	0.33	8M	0.12	0.1
LPS	Liquid Potassium Silicate	0.33	8M	0.12	0.2
SPS	Solid Potassium Silicate	0.33	8M	0.12	0.2

Geopolymer slurries were formulated using six different activators, including 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 slurries were prepared by initially hand-mixing dry components into the activating solution until a uniformly blended mixture was obtained, followed by mixing with a high-speed overhead paddle stirrer for 35 s. A constant W/S ratio of 0.33 was used for all geopolymer slurries.

For liquid hydroxide-based geopolymers, the activator solutions were prepared by dissolving appropriate amounts of sodium/potassium hydroxide pellets (98% purity) into deionized water (18 MΩ-cm resistivity) to reach an Na or K-based alkali concentration of 8 M.

Silicate-activated geopolymers had a constant SiO₂/M₂O weight ratio (where M represents either Na or K) of 0.12 and M₂O/FA weight ratio of 0.1 or 0.2, depending on the

activator used, to achieve an 8M alkali concentration in the mixture. For the liquid silicate-based geopolymers, the solutions were prepared by dissolving solid sodium/potassium hydroxide pellets in deionized water, followed by mixing in commercially available sodium/potassium silicate solutions at the appropriate amounts. For the solid silicate-based geopolymers, the solutions were prepared by dissolving the required amount of solid sodium/potassium hydroxide pellets in deionized water, while sodium/potassium solid silicate powders were dry-mixed with the fly ash prior to mixing with the activating solution.

3. Experimental Methods

3.1. Viscosity

Viscosity testing was used to measure the rheological properties of geopolymer and OPC slurries. Following the API RP 10B-2 recommended practice, the slurries were tested immediately after preparation using a rotational viscometer. Three viscosity tests were conducted for each slurry at 23 °C using an Ofite Model 900 rotational viscometer equipped with an F1.0 spring and an R1B1 rotor and bob configuration. All geopolymer slurries were modeled using the Yield Power Law (YPL) rheology model shown in Equation (1) to determine the rheological constants:

$$\tau = \tau_y + K\dot{\gamma}^n \quad (1)$$

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

3.2. Mechanical Properties

3.2.1. Curing Conditions

A high-pressure high-temperature curing chamber (Model M5-700-8-2 by CTE with 371 °C (170 °F) and 5000 psi temperature and pressure limits) was used for three curing schemes, summarized in Table 3, to create all samples prepared for mechanical property determination. The schemes were chosen to reflect a wide range of wellbore conditions from a relatively low temperature of 77 °C (170 °F), representing conditions typically encountered during surface and intermediate casing cementations, to high temperature conditions of 204 °C (400 °F), more representative of HPHT and geothermal well cementation conditions. The bottomhole static temperature (BHST), bottomhole circulating temperature (BHCT), and bottomhole pressure (BHP) values for these curing schemes were selected following curing procedures and schedules given in recommended practice API RP 10B-2. All samples were cured for a period of 3 days, after which the temperature and pressure were ramped down to 32 °C (90 °F) and atmospheric pressure, respectively, in 30 min.

Table 3. Curing parameters for the three curing schemes used in this study.

Scheme	Initial Temp.	BHCT	Ramp Time	BHST	Ramp Time	BHP
1	23 °C (73.4 °F)	52 °C (125 °F)	120 min	77 °C (170 °F)	600 min	20.7 MPa (3000 psi)
2	23 °C (73.4 °F)	100 °C (212 °F)	150 min	135 °C (275 °F)	600 min	20.7 MPa (3000 psi)
3	23 °C (73.4 °F)	135 °C (275 °F)	180 min	204 °C (400 °F)	600 min	20.7 MPa (3000 psi)

3.2.2. Unconfined Compressive Strength (UCS)

Unconfined compressive strength (UCS) tests were carried out using cylinders (51 mm (2 inches) in diameter and 102 mm (4 inches) in height) created from geopolymer and OPC material following standard ASTM C39/C39M. Three cylinders were cured for each of the three curing schemes given in Table 3 for all mixtures discussed in this paper. After curing for 3 days, the cured materials were uniaxially loaded using a Forney-250 compression machine until failure with a load rate of 667 N/s (150 lbf /s) to determine UCS values.

3.2.3. Tensile Strength

The tensile strength of geopolymers and OPC samples was characterized using a split tension test following standard ASTM C496. Three cylinders of 51 mm (2 inches) in diameter and 102 mm (4 inches) in height were cured for each of the three curing schemes given in Table 3 for all mixtures discussed in this paper. Samples cured 3 days were then loaded using a Forney-250 compression machine to tensile failure with a load rate of 155 N/s (35 lbf/s).

3.2.4. Bond Strength

The shear bond strength of the geopolymer and OPC materials to steel was investigated using a pushout procedure, as described by [20,35]. A clean stainless-steel rod 12.7 mm (0.5 inches) in diameter was concentrically placed in a cylindrical mold with a 51 mm (2 inches) diameter. Geopolymer or OPC slurry was then cast around the rod to a height of 51 mm (2 inches). Three samples of each geopolymer or OPC mixture were cured following each of the three curing schemes in Table 3 and tested for bond strength after curing for 3 days. Bond strength was obtained by loading the steel rods using a Forney-250 compression machine at a load rate of 53 N/s (12 lbf/s) until debonding between the rod and the geopolymer or OPC material was observed. Bond strength is given by:

$$f_b = \frac{P}{\pi l d} \quad (2)$$

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

3.3. Thickening Time

An Ofite Model 2040 automated HPHT cement consistometer was used to determine thickening times of all slurries following the API standards RP 10A and 10B-2. During testing, temperature was raised from a surface temperature of 23 °C (73.4 °F) to the BHCT value in the corresponding ramp-up time for each wellbore condition as summarized in Table 3. Temperature was then kept constant at the BHCT value for the remainder of the test. Pressure was raised immediately from atmospheric pressure to 6.89 MPa (1000 psi) and then further increased to the BHP value in the corresponding ramp time as summarized in Table 3. Pressure was then kept constant at the BHP value for the remainder of the test. Note that thickening time is defined as the time required for the slurry to reach a consistency of 70 Bearden consistency (Bc) units, after which the slurry is considered to be unpumpable. The average value and range of the thickening time was obtained by testing each slurry three times.

4. Results and Discussion

4.1. Viscosity

The shear stress versus shear rate plots for OPC and geopolymer slurries are presented in Figure 1. The viscosity profiles were modeled using the YPL model (given in Equation (1)) and rheological constants (yield stress, fluid behavior index, and consistency index) were calculated. The average rheological constants and apparent viscosities at 300 rpm are summarized in Table 4. The results show that OPC (solid gray line) and OPC/SF (dashed gray line) slurries have similar viscosity profiles. The fluid behavior indices (n -values) of OPC and OPC/SF were found to be 0.46 and 0.61.

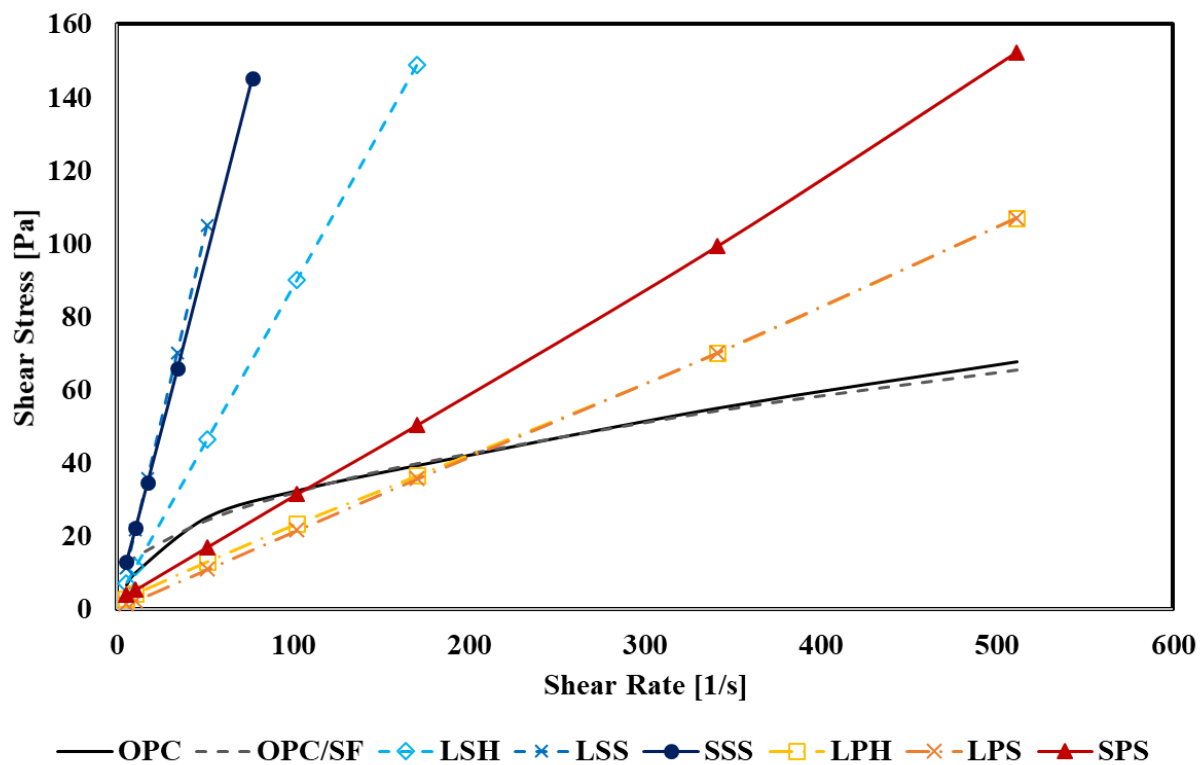


Figure 1. Viscosity profile for OPC and geopolymer slurries.

Table 4. Rheological model parameters for OPC and geopolymer slurries.

Mix ID	Apparent Viscosity at 300 rpm (Pa·s)	YPL Model Constants—See Equation (1)		
		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

For geopolymer slurries with all types of activators, it was found that their rheological behavior can be approximated as a Bingham Plastic because they have fluid behavior indices very close to 1.0 (i.e., in the range $0.95 < n < 1.05$). Moreover, the yield stresses of all geopolymer slurries were found to be lower than those of OPC slurries. All geopolymer slurries activated with sodium-based activators (represented by blue lines in Figure 1) were found to have high viscosities such that the apparent viscosity could not be measured by the viscometer (i.e., apparent viscosity values larger than $0.32 \text{ Pa}\cdot\text{s}$). It was also found that the sodium hydroxide-based activator resulted in a slurry with a higher viscosity than slurries activated with sodium silicate-based activators. On the other hand, geopolymer slurries activated with potassium-based activators (represented by red, orange, and yellow lines in Figure 1) were found to have lower viscosities than those made with sodium-based activators. Liquid potassium activators were found to yield pumpable slurries (apparent viscosity $\sim 0.2 \text{ Pa}\cdot\text{s}$) with good rheological properties without the needs for thinners. In

addition, the slurry with the liquid potassium activator showed lower viscosity than the solid potassium silicate-activated geopolymer.

4.2. Mechanical Properties

4.2.1. Unconfined Compressive Strength

The compressive strengths of OPC and geopolymer formulations cured under different curing schemes are summarized in Figure 2. At a curing temperature of 77 °C (170 °F), OPC was found to have a compressive strength at 3 days of 46.2 ± 2.3 MPa (6705 $\pm$ 337 psi). Incorporating SF in the OPC mixture reduced the compressive strength by 30%, which agrees with similar observations reported in the literature [36]. All the geopolymers had lower compressive strengths than OPC. In general, sodium-based geopolymers had higher compressive strengths than potassium-based geopolymers, with the highest geopolymer compressive strength at a value of 34.3 ± 1.2 MPa (4982 $\pm$ 173 psi) observed when using LSS as an activator. It was also found that silicate-based geopolymers showed higher compressive strengths than hydroxide-based geopolymers.

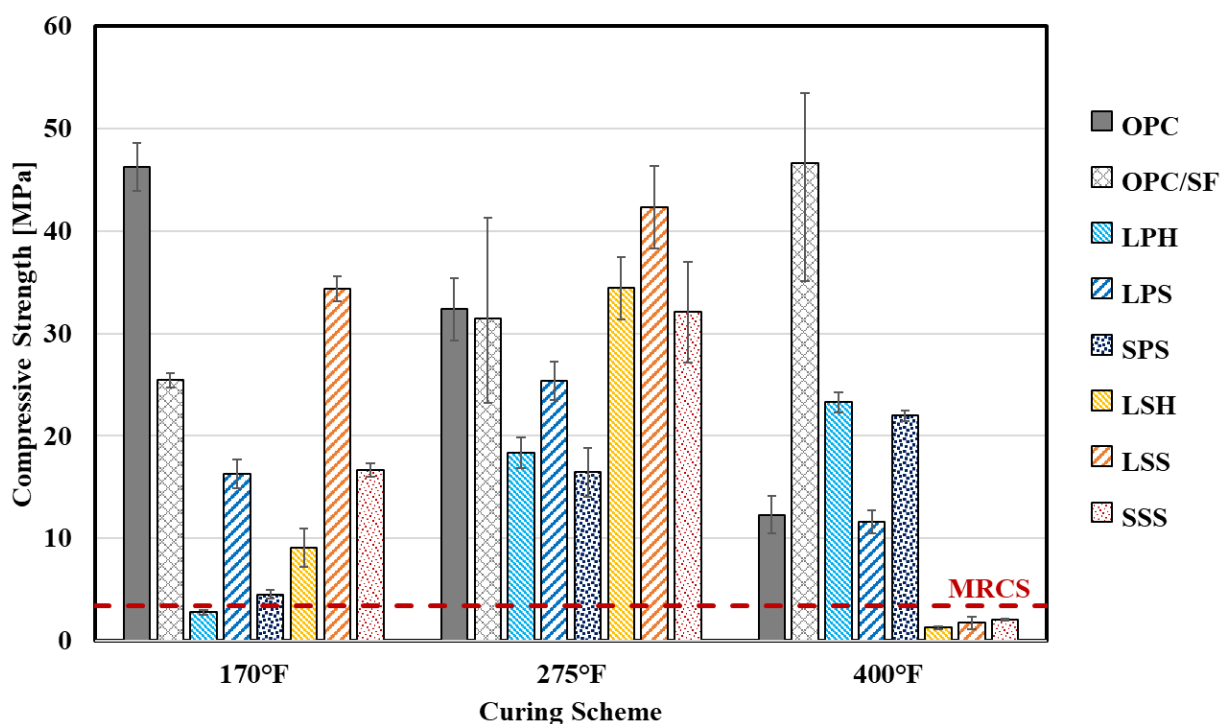


Figure 2. Three-day compressive strength for OPC and geopolymer formulations cured with different curing schemes (indicated by BHST value, see Table 3). Error bars represents the range of compressive strengths values measured for each mixture. Minimum Required Compressive Strength (MRCS) in accordance with standard API 10A is indicated by a dotted line.

When the curing temperature was increased from 77 °C (170 °F) to 135 °C (275 °F), the average compressive strength of OPC slurry decreased from 46.2 MPa (6705 psi) to 32.4 MPa (4693 psi). Incorporating silica flour (SF) into the OPC mixture cured at elevated temperature (135 °C (275 °F)) did not statistically significantly change its strength, resulting in a comparable strength to OPC alone. These results are consistent with expectations of strength retrogression from the literature [34,37]. Increasing the curing temperature from 77 °C (170 °F) to 135 °C (275 °F) resulted in an increase in the compressive strength for all geopolymer formulations. Although the potassium-based geopolymers had lower compressive strengths than OPC, LPS activation yielded a compressive strength up to 80% of the compressive strength of OPC. All geopolymers activated with sodium-based activators were found to have compressive strengths higher than geopolymers activated with

potassium-based activators. Additionally, LSH and SSS were found to have compressive strengths comparable to OPC, while LSS had a compressive strength more than 30% higher than OPC.

Increasing curing temperature to the highest value tested (204 °C (400 °F)) reduced the average compressive strength of the neat OPC slurry to 12.3 MPa (1785 psi). However, the mixture incorporating silica flour (SF) in OPC showed a significant strength increase at this temperature, confirming the ability of silica flour addition to overcome strength retrogression [34]. In potassium-based geopolymer formulations, increasing the curing temperature to 204 °C (400 °F) resulted in increasing compressive strengths of geopolymers activated with LPH and SPS, while strength retrogression was observed in LPS. On the other hand, increasing the curing temperature to 204 °C (400 °F) resulted in a significant reduction of the compressive strengths of geopolymer formulations activated with sodium-based activators, such that they did not meet the minimum required compressive strength (MRCS) for cementing applications of 3.45 MPa (500 psi) according to the API 10A standard.

4.2.2. Tensile Strength

As expected, the tensile strengths of all formulations, as shown in Figure 3, followed trends similar to the compressive strengths. At 77 °C (170 °F), OPC was found to have a tensile strength of 1.8 ± 0.2 MPa (264 ± 30 psi). This result is consistent with the tensile strength of OPC cured at similar conditions reported in the literature [38]. In addition, no change in the tensile strength was observed when SF was added to the OPC mixture. Similar to compressive strength, the tensile strength values of potassium-based geopolymers were found to be lower than that of OPC. On the other hand, the tensile strength of geopolymers activated with sodium-based activators were found to be generally higher than those of geopolymers activated with potassium-based activators. The highest tensile strength amongst geopolymers at the low temperature condition was observed while using the LSS activator and was found to be similar to the tensile strength of OPC. In addition, it was observed that silicate based-geopolymers had higher tensile strengths than hydroxide-based geopolymers cured at 77 °C (170 °F).

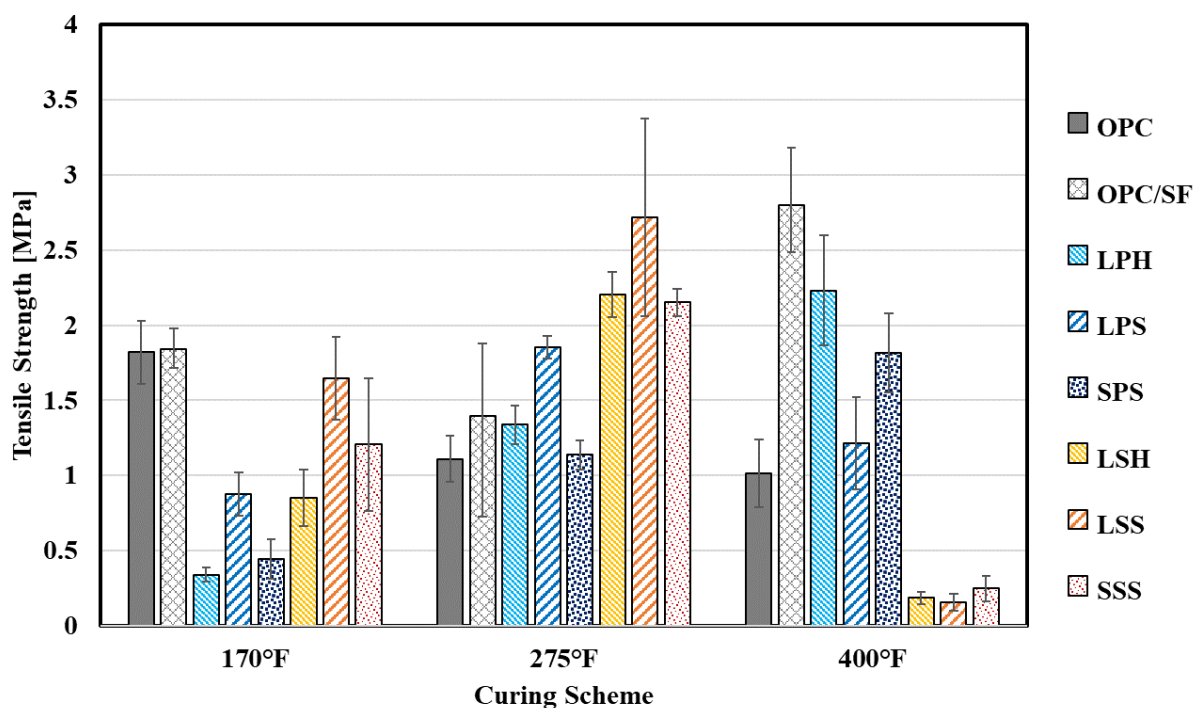


Figure 3. Three-day tensile strength for OPC and geopolymer formulations cured with different curing schemes (indicated by BHST value, see Table 3). Error bars represent the range of tensile strengths values measured for each mixture.

As the curing temperature increased to 135 °C (275 °F), a reduction of the tensile strength of OPC by 39% was observed compared to the lower curing temperature. Furthermore, incorporating SF had no significant impact on the tensile strength of OPC cured at the elevated temperature of 135 °C (275 °F). Increasing the curing temperature to 135 °C (275 °F) resulted in increasing the tensile strength of all geopolymer formulations. It was found that all sodium-based geopolymers had higher tensile strengths than potassium-based geopolymers. The highest tensile strength amongst geopolymers of 2.7 ± 0.7 MPa (394 ± 94 psi) was observed in LSS and was about 1.5 times higher than OPC cured at 135 °C (275 °F).

At the highest temperature tested of 204 °C (400 °F), no further reduction in the tensile strength of neat OPC compared to samples cured at 135 °C (275 °F) was observed. Furthermore, incorporating SF resulted in an increase of the tensile strength of OPC cured at the high temperature of 204 °C (400 °F) of 176%, which agrees with similar observations reported in the literature [39]. For geopolymer formulations, the increase of curing temperature from 135 °C (275 °F) to 204 °C (400 °F) resulted in a significant increase in the tensile strength of LPH and SPS-activated materials, while some strength reduction was observed for LPS-activated material. For all sodium-based geopolymers, high curing temperature resulted in low tensile strengths of less than 0.25 MPa (36 psi).

4.2.3. Bond Strength

The bond strength results for all OPC and geopolymer formulations cured at different curing conditions are summarized in Figure 4. For samples cured at 77 °C (170 °F), the bond strength of neat OPC was found to be 1.7 ± 0.08 MPa (247 ± 12 psi), which falls within the range of bond strengths reported in the literature [40,41]. Moreover, incorporating SF resulted in a 50% increase in the bond strength of OPC cured at 77 °C (170 °F). For geopolymer formulations, it was found that silicate-based geopolymers had higher bond strengths than hydroxide-based geopolymers. Moreover, the highest bond strengths amongst geopolymers at this temperature were observed in LSS and LPS and were found to be similar to the bond strength of OPC.

As the curing temperature increased to 135 °C (275 °F), a reduction in the bond strength was observed in OPC compared to the lower curing temperature condition (77 °C (170 °F)). Moreover, incorporating SF had no significant impact on the bond strength of OPC cured at elevated temperature of 135 °C (275 °F). On the other hand, increasing the curing temperature from 77 °C (170 °F) to 135 °C (275 °F) resulted in a significant increase in the bond strength of geopolymer formulations, and all geopolymer formulations were found to have higher bond strengths than OPC. In general, silicate-based geopolymers were found to have higher bond strengths than hydroxide-based geopolymers. In contrast to the compressive and tensile strengths results, geopolymers activated with potassium-based activators and cured at 135 °C (275 °F) showed higher bond strengths than geopolymers activated with sodium-based activators. The highest bond strength amongst geopolymers was observed while using LPS as activator, which had an outstanding bond strength of 8.8 ± 0.35 MPa (1283 ± 51 psi), which is more than an order of magnitude higher than OPC.

Increasing the curing temperature to 204 °C (400 °F) had no statistically significant impact on the bond strength of OPC and OPC/SF compared to samples cured at 135 °C (275 °F). In addition, all geopolymer formulations activated with potassium-based activators cured at 204 °C (400 °F) were found to have similar bond strengths of more than 7.2 MPa (1044 psi). Such remarkably high bond strengths are more than an order of magnitude higher than OPC cured at the same conditions. On the other hand, similar to compressive and tensile strengths, increasing the curing temperature to high temperature of 204 °C (400 °F) resulted in negligible bond strengths (i.e., less than 0.1 MPa (15 psi)) for all geopolymers activated with sodium-based activators.

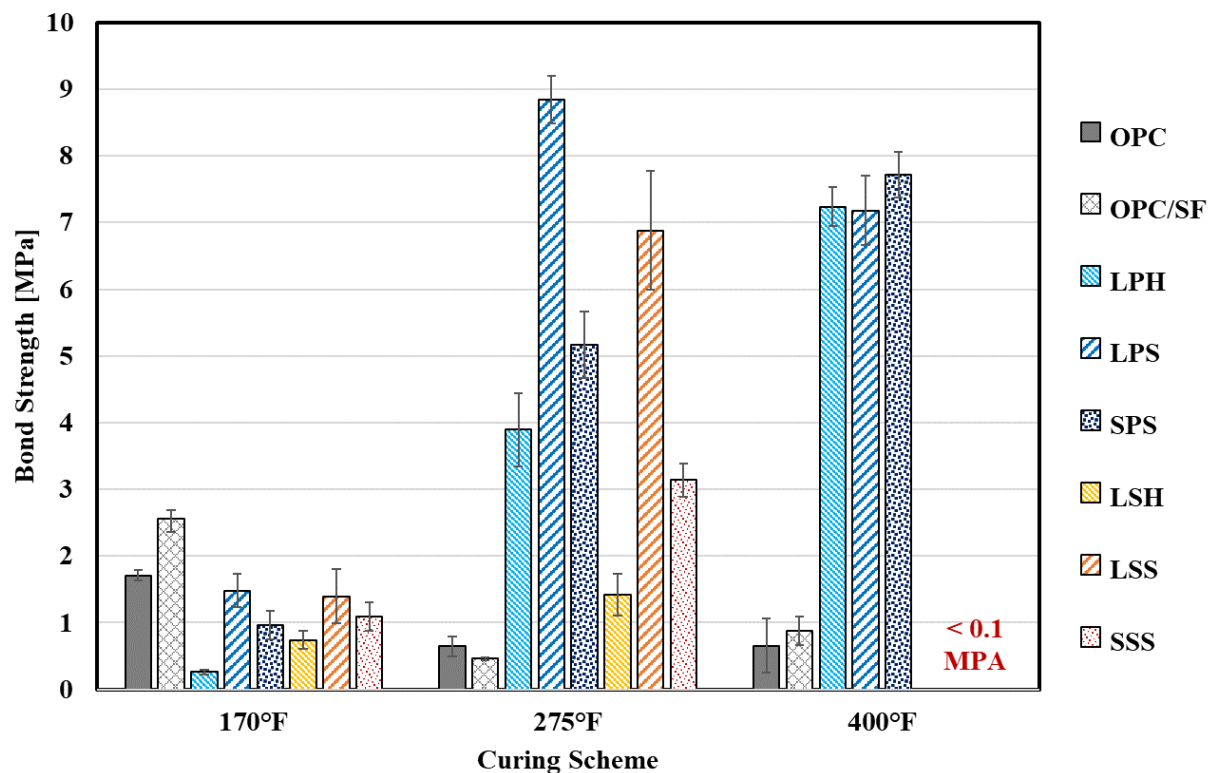


Figure 4. Three-day bond strength for OPC and geopolymer formulations cured with different curing schemes (indicated by BHST value, see Table 3). Error bars represents the range of bond strengths values measured for each mixture. A bond strength of less than 0.1 MPa was observed for geopolymers activated with LSS and SSS at 400 °F conditions.

4.3. Thickening Time

Cementing slurries are required to have thickening times longer than the planned placement time with some safety margins, while a very long thickening time is not desirable as it imposes an unnecessary waiting-on-cement time that translates into additional well cost [41,42]. The minimum required thickening time for most wellbore conditions is 2 h (see e.g., API 10-A and [41]). However, this minimum requirement increases for some applications such as deep HPHT and geothermal wells cementing applications [41,43]. The thickening times for all OPC and geopolymer slurries measured under different conditions are summarized in Table 5. At a BHCT of 52 °C (125 °F), OPC and OPC/SF were found to have similar thickening times a few minutes short of 2 h, which follows the expectations of Class H Cement without the use of retarders. At the same temperature, all potassium-based and sodium hydroxide-based geopolymers failed to reach a consistency of 70 Bc within 24 h, while LSS and SSS showed extended thickening times of 18.7 h and 13.9 h, respectively. With such long thickening times, accelerators will be necessary if geopolymers are to be used at such conditions.

As expected, an increase of BHCT resulted in a decrease in the thickening time of all slurries [41]. For potassium-based geopolymers, LPH showed an extended thickening time of 6.75 h, while LPS and SPS showed suitable thickening times of 3.25 and 3.5 h, respectively. All potassium-based geopolymers were found to have thickening times of more than 2.5 h at a BHCT of 135 °C (275 °F). A longer time might still be desirable for high-temperature applications, requiring the use of suitable retarders. In general, it was observed that sodium-based geopolymers have lower thickening times than potassium-based geopolymers. In addition, silicate-based geopolymers were found to have lower thickening times than hydroxide-based geopolymers tested at the same BHCT.

Table 5. Thickening time (formatted as hh:mm ± mm) for OPC and all geopolymer slurries. No retarders were used in any of the tests.

Mix ID	BHCT		
	52 °C (125 °F)	100 °C (212 °F)	135 °C (275 °F)
OPC	1:50 ± 2	1:22 ± 1	1:16 ± 4
OPC/SF	1:54 ± 4	1:28 ± 4	1:18 ± 3
LSH	>24:00	1:42 ± 3	N/A
LSS	18:41 ± 54 *	1:32 ± 3 *	N/A
SSS	13:52 ± 98 *	1:38 ± 7 *	N/A
LPH	>24:00	6:43 ± 14	2:35 ± 1
LPS	>24:00	3:14 ± 4	2:35 ± 14
SPS	>24:00	3:30 ± 9	2:32 ± 3

* denotes that the slurries' initial consistency was above 70 Bc.

5. Discussion and Summary

The experimental investigation shows that the type of activator and curing conditions affect the mechanical properties and thickening times of Class F fly ash-based geopolymer formulations. It also shows that such geopolymers can be straightforwardly engineered to provide primary and remedial cementing solutions for different wellbore conditions. For the relatively low temperature of 77 °C (170 °F) or lower, characteristic of conditions encountered when cementing surface and intermediate casing strings, an LSS geopolymer was found to be a viable cementing material. With a slightly lower compressive strength and similar tensile and bond strengths to OPC, LSS can provide similar performance with a lower carbon footprint when compared to OPC. Although it was found to have higher viscosity and extended thickening time at a corresponding BHCT of 52 °C (125 °F), additives such as potassium hydrogen phosphate, potassium chloride, and potassium nitrate may be able to adjust the rheological properties of the LSS formulation without negatively affecting the mechanical properties [6]. It is also possible to lower the viscosity of sodium-activated geopolymers in general by admixing non-aqueous fluids, such as residual oil-based mud or synthetic-based mud left over from the drilling operation, into the formulation, thereby creating a geopolymer-drilling fluid “hybrid” [17,18,20].

At an elevated temperature of 135 °C (275 °F), more common when cementing deeper intermediate and production strings, liquid silicate-activated geopolymers were found to have the best overall performance of all tested formulations. LPS and LSS-activated geopolymer materials were found to have twice the tensile strength and more than 13 times higher bond strength when compared to OPC. Moreover, the LPS geopolymer was found to have desirable rheological properties and thickening time at the corresponding BHCT of 100 °C (212 °F) without the use of additives, while super-plasticizing and retarding admixtures would be required for LSS formulations.

For a high temperature of 204 °C (400 °F), representing cementing conditions in HPHT and geothermal wells, potassium-based geopolymer materials showed high thermal stability. LPH and SPS-activated formulations showed increases in compressive, tensile, and bond strengths when compared to lower curing temperatures, without showing signs of strength retrogression over time. These formulations showed remarkable high casing-to-cement bond strengths that were more than an order of magnitude higher than OPC. Such excellent bonding will benefit zonal isolation and well integrity because the casing–cement bond of high-temperature wells will be able to much better resist the negative impact of cyclic pressure and temperature loading on micro-annulus formation at the cement–casing interface. This will reduce the associated risk of well leakage of methane to the atmosphere. The thickening times of LPH and SPS formulations were found to be on the order of 2.5 h without the use of any retarders. Retarders will be required to further extend the thickening time of geopolymer formulations at high temperature conditions.

6. Conclusions

This study shows the applicability of Class F fly-ash based geopolymers for a wide range of downhole well cementing conditions, ranging from low to high temperatures, making it a suitable, lower carbon footprint alternative to Portland cement. Fine-tuning of properties can be achieved primarily by changing the alkaline activator without changing the base material or having to add a significant number of admixtures, thereby also omitting the carbon footprint of the latter. An important discovery for potassium-activated geopolymer formulations is that they provide a significantly higher casing-to-cement bond strength than Portland cement at elevated and high temperature conditions. This will benefit well integrity and reduce the likelihood of methane leakage to the atmosphere through the de-bonding of the casing-to-cement interface (with the associated formation of a micro-annulus) in wells with compromised zonal isolation and integrity. This, then, adds to the overall carbon footprint reduction achieved by using geopolymers for reliable well barrier formation purposes.

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