Evaluating the Feasibility of Fly Ash-Based Geopolymer as an Alternative to Portland Cement for Oil Well Cementing Operations

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Abstract: Portland cement has been used in oil well cement during drilling operation. It has numerous disadvantages related to operational failure at high thermal well and environmental hazards during production and manufacturing of Portland cement. Geopolymer cement (GPC) is an organic aluminosilicate binder which possess high compressive strength. Geopolymer examined as a prospective material to replace Portland cement due to high compressive strength and durability. This study presents an investigation to evaluate the feasibility of fly ash of the Thar power plant as a substitute for Portland cement. Thirty samples of geopolymer were designed by varying the concentration of alkaline activators. The effect of sodium silicate, sodium hydroxide and their concentration ratio in fly ash was determined through compressive strength measurement at varied curing time and temperature. The experimental results of XRF analysis revealed that fly ash of Thar power plant contains high calcium oxide and classified as Class C type. Furthermore, the study exposed that alkali activators have a promising influence on fly ash. Geopolymer compressive strength was increased by increasing sodium silicate and sodium hydroxide concentration. Moreover, the designed geopolymer cement showed high compressive strength and enhanced by increasing the curing time and temperature. Based on the experimental result, it is revealed that geopolymer exhibited superior thermal resistance and mechanical properties as compared to the class G cement. Fly ash of the Thar power plant can be use as an alternate of OPC with the addition of other additives that further enhance the properties of geopolymer.

Keywords: Fly ash, Compressive strength, Sodium hydroxide, Sodium silicate. Cementing

1. INTRODUCTION

The main purpose of oil well cementing is to prevent the migration of fluids from the formation, to secure the casing string from corrosion and to anchor the casing string on the wellbore. Among other things, it provides zonal insolation and prevent fluids from moving between successive formations[1], [2]. The loss of regional isolation can lead to severe operational difficulties and environmental problems with high restoration costs. During displacement of cement slurry, it is important to maintain the rheological parameters of the cement slurry[3]. Once hardened, the mechanical properties are important to determine compressive strength, tensile strength, durability, stability, and permeability. These qualities must be controlled to achieve optimized, low-permeability cement lining in the well. The best way to achieve a good cement slurry formulation with the desired and improved properties is through laboratory testing. It entails testing several formulations of cement and additives and selecting the appropriate components for cementing operation. Ordinary Portland cement (OPC) is being widely used for cementing operation in petroleum industry[4]. In most cases, various grades of OPC and additives based on desired well conditions have been used for cementing operation. Beside of this, in production process, one kilogram Portland cement emits approximately 0.82 kg of carbon dioxide into the atmosphere, accounting for 5-7% of worldwide anthropogenic carbon dioxide emissions. These emissions are projected to increase with an average atmospheric concentration of about 750 parts per million by volume [5]. The cement manufacturing process requires huge amounts of fuel and involves the decomposition of the limestone, leading to substantial carbon dioxide (CO_2) emissions [6] [7]. Therefore, Portland cement has a serious environmental effect during the manufacturing process.

It is important to develop sustainable cementing technology with superior performance compared to OPC for oil well cementing. Geopolymer is considered a new economic and environment friendly material having similar properties to cement. Geopolymer has found advantages over OPC due to their smaller carbon footprint [5].

Geopolymer is an inorganic material which is made of binder (alumina silicate) and alkaline activator that produces polymer network of Si-Al-O[8], [9]. In geopolymer preparation, raw materials of pozzolanic compound such as metakaolin, slag, fly ash, kaolinitic clays; combination of these materials or source of rich silica and alumina have been utilized [10]. The geo polymer is formed by using these raw materials in the presence of an alkaline solution which acts as a source of geo polymer activator. The alkali solution has been used to activate the raw material, to take part in polymerization process and form a compact composite having same properties of cement [11]. Geopolymer has a wide range of qualities depending on the raw material, processing conditions, and synthesis, such as strong compressive strength, low shrinkage, low permeability, and low heat conductivity [12].

Currently, the properties of geopolymer have been explored for use as a substitute for Portland cement. The work published in this research area has shown good results in considering geopolymers as an alternate for Portland cement. At varied alkaline solution concentrations and polymerization settings, geopolymers with appropriate compressive strength may be produced [13]. The concentration of alkali activator has a huge impact on geopolymer properties to enhance the compressive strength. Sugumaran investigates the influence of water-to-sodium-hydroxide ratio on geopolymer[14]. Suppiah investigates the compressive strength of geopolymer cements with variable NaOH concentrations and silicate/hydroxide ratios. Their findings reveal that mechanical properties increase with the concentration of sodium hydroxide [15]. In another study Salehi utilized low calcium fly ash and compared geopolymers properties with Portland cement. The results revealed that geopolymers improves the compressive strength faster than Portland cement [16]. Furthermore, the binding strength of geopolymers was found to be greater than that of Portland cement, which is consistent with the results[17]. Aside from adhesive strength, geopolymer viscosity and density increases with NaOH concentration in fly ash. Furthermore, other qualities like surface roughness, durability and high temperature stability are also considered important to characterize geopolymers[18].

Fly ash is the biggest source of geopolymer all over the world. In Pakistan, coal-fired thermal power plants are major producer of fly ash. One of them is the Thar Coal Power Plant, which contains around 7-10% ash and generates approximately 1344 tons of ash per day. Currently, the Thar Coal Power Plant produces around 24502.6 tons of fly ash each month[19]. The fly ash of the Thar power plant has cementitious qualities and could be used as an alternate of Portland cement for petroleum industry. Further, in literature, most of the studies were presented on class F type fly ash and limited literature is found for assessment of class C type fly ash geopolymer [20]. Therefore, the purpose of this article is to evaluate the performance and feasibility of Class C fly ash to replace the OPC for well cementing. The fly ash produced from Thar power plant is classified as "Class C" which contains high calcium oxide contents. This is the first assessment of the viability of utilizing Thar power plant fly ash for oil well cementing application. The compressive strength of designed slurry was determined to evaluate the feasibility of geopolymer at various concentrations of alkali activator, curing time and temperature. This study will open the window for the oil industry to utilize fly ash efficiently in placement of OPC and reduce the cost of operation.

2. MATERIALS AND METHODS

2.1. *Materials*

Fly ash from the Thar power plant was used for geopolymer preparation. Class "G" Portland cement was obtained from OGDCL, Pakistan for testing purpose. The chemical composition of fly ash and Class G cement was determined using X-ray fluorescence (XRF). The chemical constitution of both materials is presented in Table.1. Based on composition the fly ash is classified as Class "C" due to its higher contents of calcium oxide. The specific gravity of fly ash was 2.1 and specific gravity of Class G cement was 3.20. Sodium hydroxide (NaOH) pellet 97 % purity and Sodium Silicate solution (Glass water) was purchased from DaeJung Chemicals & Metals, Korea. Both materials are used as alkaline activators to prepare geopolymer.

Table. 1: Chemical composition of fly ash and class G cement in percentage.

Chemical composition	Al_2O_3	Fe_2O_3	CaO	SIO_2	MgO	K_2O	Na_2O
Fly ash	14.25	16.58	15.97	37.25	3.41	0.1	1.52
Class G Cement	3.85	4.57	65.04	21.08	2.31	0.31	0.28

2.2. Geopolymer and Cement slurry Preparation Method

Sodium hydroxide solution of 8M,10M,12M (molarity) was prepared and mixed with glass water to prepare alkaline activator. The mixing procedure began with the input of tap water to the constant speed mixture (blender), which was followed by the addition of fly ash. For 15 seconds, the blender was set to low speed. The alkaline solution was then added to the constant speed mixture. The geopolymer slurry was stirred for 15 seconds at low rpm speed and 35 seconds at high rpm. Class G cement was prepared in accordance with API specifications. The procedure began with the addition of distilled water to the blender, followed by the addition of dry cement. For 15 seconds, the blender was set to 4000 rpm. The blender was then covered and increase the rpm upto12000 for 35 seconds. Total thirty geopolymer samples were prepared by changing SS/SH ratio, alkali/fly ash ratio, NaOH molarity. Further, the density of slurry was kept at 13.5 ppg. The density of the slurries was maintained by varying the amount of tap water and barite during preparation of geopolymer. The designing of geopolymer slurries is presented in Table 2.

Table. 2: Geopolymer slurry design with their concentration.

AA / FA	Fly-ash (gm)	SS / SH	SH-Solution (gm)	SS-Solution (gm)
0.3	400	0.20	100	20
	400	0.60	75	45
	400	1.0	60	60
	400	1.5	48	72
	400	2	40	80
0.6	400	0.20	200	40
	400	0.60	150	90
	400	1.0	120	120
	400	1.5	96	144
	400	2	80	160

2.3. Compressive Strength Test Procedure

The cement and geopolymer slurries were poured into 2x2x2 inch molds separately and left at room temperature for 24 hours. After curing at specified time periods and temperature, the cubic samples were removed and tested for compressive strength measurement**.**

3. RESULTS AND DISCUSSION

The feasibility of geopolymer for cementing is based on compressive strength measurement. Therefore, the compressive strength was determined to evaluate the effect of alkaline activators, temperatures and curing period to make fly ash of Thar coal power plant feasible to use in oil well cementing. The effect was evaluated by altering the ratio of AA/FA, SS/SH, and molarity of sodium hydroxide.

3.1 Effect of AA/FA Concentration on Compressive Strength

The compressive strength of geopolymer samples was determined at 0.3 and 0.6 concentration ratio of alkali activator to fly ash. It was observed that the compressive strength of geopolymer samples was increased by increasing AA/FA ratio as shown in Figure.1. The compressive strength of 0.3 AA/FA and 0.20 SS/SH ratio was 947psi. Similarly, 1442 psi compressive strength was obtained for 0.6 AA/FA concentration ratio. The increase in compressive strength was due to the increase in quantity of alkali activators. In 0.6 AA/FA based geopolymer, the quantity of alkali activators becomes double, and it creates high strength during polymerization.

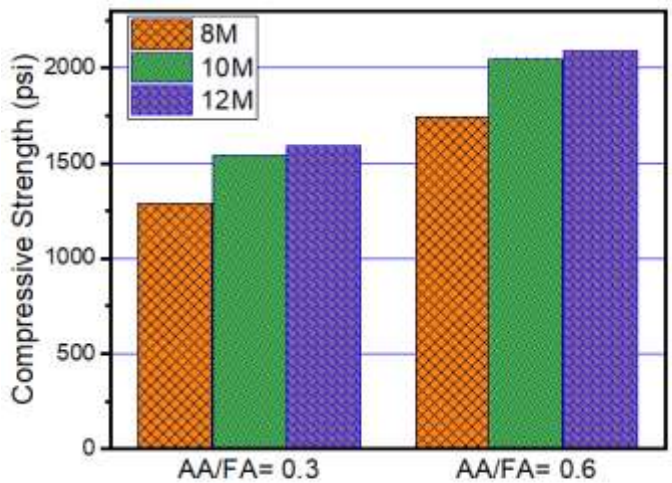

Figure 1. Compressive strength of geopolymer w.r.t AA/FA concentration.

3.2 Effect of SS/SH Concentration on Compressive Strength

The compressive strength results of all prepared geopolymer samples are presented in Table.3. The compressive strength of AA/FA ratio of 0.3 and 0.6 at different concentration and molarity is shown in Figure. 2 and Figure.3.

Table. 3: Compressive strength of designed geopolymer w.r.t change in concentration.

Parameter	AA/FA	SS/SH	NaOH Concentration		
			8M	**10M**	**12M**
Compressive strength (psi)	0.3	0.20	947	1157	1202
		0.60	1151	1382	1418
		1.0	1291	1547	1593
		1.5	1425	1721	1753
		2	1571	1884	1917
	0.6	0.20	1442	1692	1746
		0.60	1621	1878	1915
		1.0	1741	2054	2096
		1.5	1905	2197	2231
		2	2083	2313	2354

Experimental results show that the compressive strength was increasing w.r.t increase in concentration of SS/SH. The samples contain 02 SS/SH ratio (80gm/40gm) have maximum compressive strength. The increase in compressive strength from 947 psi to 1571 psi for 08M NaOH solution was due to the increase in sodium silicate concentration. The result shows that sodium silicate plays a vital role to increase the compressive strength. The compressive strength of geopolymer also increases as the concentration of sodium hydroxide increased from 08M to 12M as shown in Figure.4. A magnificent change was observed from 08M to 10M, while the compressive strength was also increased 1157psi to 1202 psi by changing Molarity 10M to 12M, but it was not rapid and high. The leaching of aluminum and silicate is the main cause of increase in compressive strength [21]. The high compressive strength of slurry was due to the alumina-silica gel formation between the silicate and alumina which is forms during geo polymerization [22].

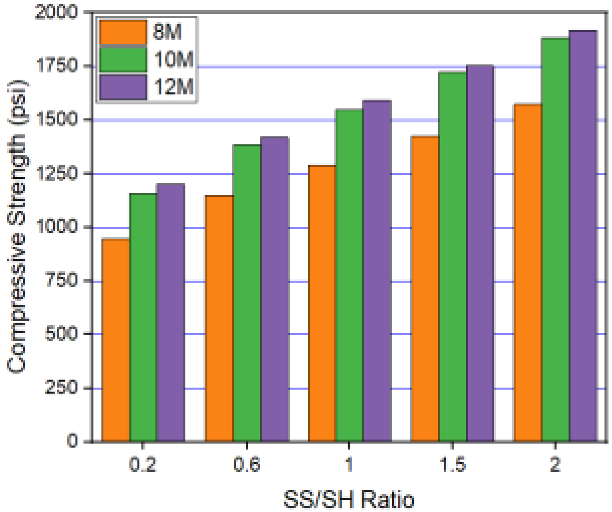

Figure 2. Compressive strength of 0.3 AA/FA based geopolymer at different concentration ratios of SS/SH.

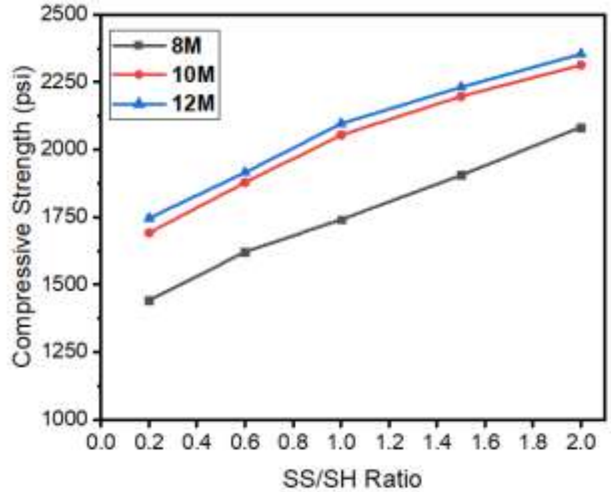

Figure 3. Compressive strength of 0.6 AA/FA based geopolymer at different concentration ratios of SS/SH.

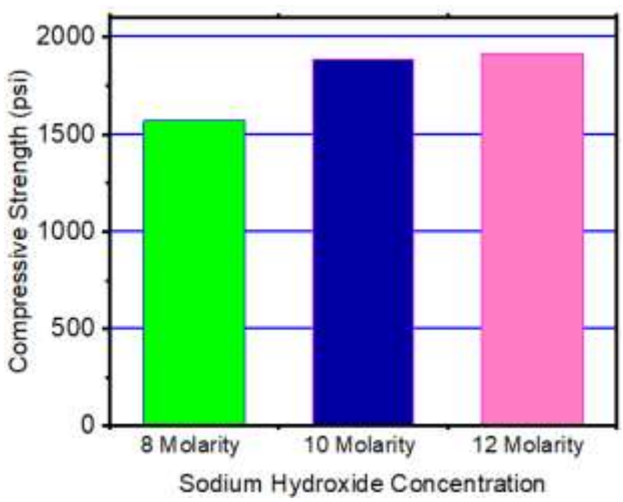

Figure 4. Compressive strength at different molarity concentration.

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3.3 Effect of Curing Time on Compressive Strength

To observe the effect of curing time on compressive strength, the samples were cured at given time of 1 day, 03,07 and 14 days. The results of compressive strength of geopolymer sample having 10 M concentration of sodium hydroxide are provided in Table 4. It is observed from Figure.5 that the compressive strength of geopolymer samples was increasing by increasing curing time. A good difference was observed in compressive strength at 07 days and 14 days curing time. The high increase in compressive strength at 14 days was due to the completion of geo polymerization process. On the other side, it was observed that the compressive strength of class G cement started to decrease after a certain time of curing. The compressive strength was increased from 3405 psi to 3874 psi by curing 1 day to 03 days.

Table. 4: Compressive strength of specified geopolymer at various curing time.

Parameter	AA/FA	SS/SH	Curing Period			
			1 Day	3 Days	7 Days	14 Days
Compressive strength of fly ash (psi)	0.3	0.20	1157	1371	1912	4183
		1.0	1547	1769	2306	4837
		2	1884	2124	2692	5319
Compressive strength (psi) of Class G cement		-	3405	3874	3695	2914

Afterward the compressive strength starts to decrease, and compressive strength reduced up to 3695 psi for seven days and 2914 psi for 14 days curing time as shown in Figure 5. The decrease in compressive strength for class G cement was due to excess water loss during curing.

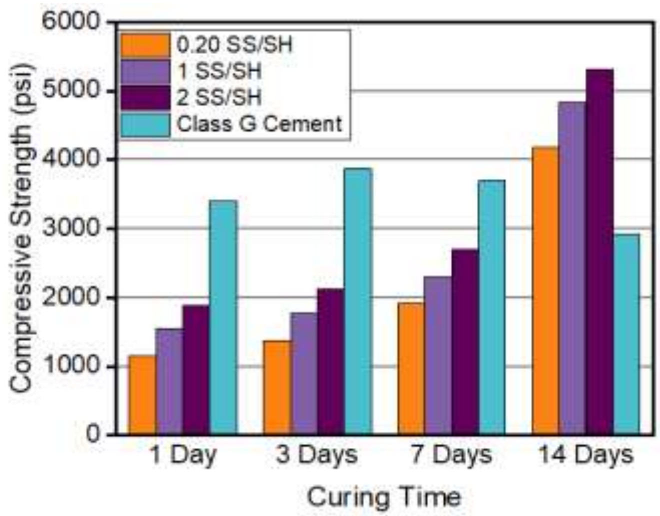

Figure **5.** Compressive strength at different curing times.

3.4 Effect of Temperature on Compressive Strength

To investigate the effect of temperature, additional tests were conducted on specific geopolymer samples. The test was conducted after curing the samples at 30,90,120 and 150 °C temperature. The compressive strength results are shown in Table 5.

Table. 5: Compressive strength of specified geopolymer at various curing temperatures.

Parameter	AA/FA	SS/SH	Curing Temperature				
			30 °C	60 °C	90 °C	120 °C	150 °C
Compressive strength of fly ash (psi)	0.3	1.0	1547	1734	2259	2874	3028
		2	1884	2088	2764	3226	3424
Compressive strength of Class G cement (psi)	-	-	3347	3019	2572	1924	1472

It was observed that the compressive strength of geopolymer samples was increasing with increasing temperature. At 30 °C temperature the compressive strength was 1547 psi and 1884 psi for geopolymer sample. While the increased compressive strength was obtained for same concentration of geopolymers at higher temperatures. High compressive strength of 3028 psi and 3424 psi was achieved at 150 °C temperatures as shown in Figure 6. The class G cement sample showed a higher compressive strength at 30 °C than both geopolymer cement samples. But with increasing temperature the compressive strength starts to decrease and at 150 °C class G cement deteriorated 1472 psi compressive strength. The cement slurry undergoes dihydroxylation process with increasing temperature. It hydrates the water molecules and starts to lose compressive strength with increasing temperature.

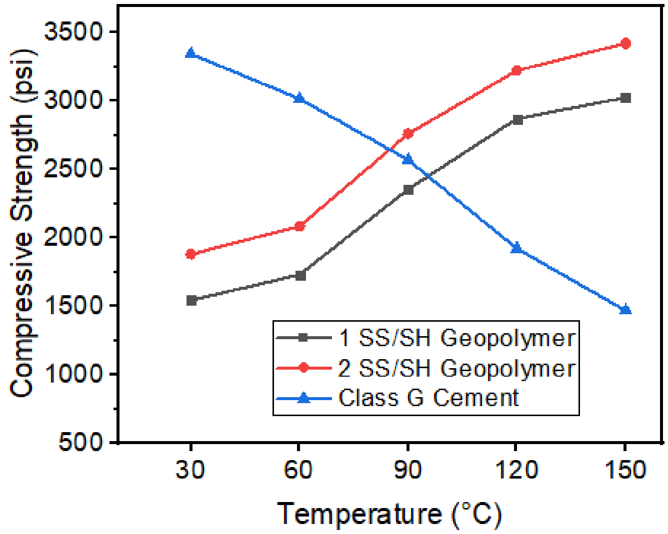

Figure **6.** Compressive strength at different curing temperatures.

4. CONCLUSIONS

Based on the experimental measurement it is concluded that class C fly ash of Thar Power Plant has the same chemical composition of ordinary cement. The alkaline activator plays a decisive role in enhancing compressive strength, as it increases with higher concentration of sodium silicate and sodium hydroxide in term of molarity. The findings of the experiments reveal that a longer curing period, along with a larger concentration of alkaline activator, lead to improvement in compressive strength. The compressive strength of over 5000 psi was attained by utilizing the maximum quantity of alkaline activator and curing the sample for 14 days. Class C fly ash based geopolymer is more thermal stable than class G cement, as it exhibits enhanced strength when cured at high temperature. Fly ash based geopolymer showed low compressive strength for normal temperature conditions and it could be enhanced by adding cement additives. The high thermal resistance and enhanced strength for long curing time property make the fly-ash of Thar power plant suitable, in combination with other additives, for HTHP oil and gas wells for cementing operation with other additives.

The rheological characteristics, fluid loss, and pumpability of API properties will be studied in future investigations. Further, the determination of API characteristics with the addition of various additives will assist in the optimization of for oil and gas well cementing applications.

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DECLARATION OF COMPETING INTEREST

The authors affirm that they have no known financial or interpersonal conflicts that could have influenced their research.

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