PROCEEDINGS, 49th Workshop on Geothermal Reservoir Engineering
Stanford University, Stanford, California, February 12-14, 2024
SGP-TR-227

Effect of Gilsonite on the Mechanical Properties of Geopolymer Cement

Miguel Leonardo Romero Tellez, Khizar Abid, Catalin Teodoriu

Mewbourne College of Earth and Energy, The University of Oklahoma, Norman, OK, USA

cteodoriu@ou.edu

Keywords: Geopolymer Cement, Compressive Strength, Long Term Testing, Gilsonite

ABSTRACT

Global warming has become one of the most prominent issues at present. In that respect, the emission of greenhouse gases into the atmosphere plays a vital role. Among all the greenhouse gases, Carbon Dioxide (CO_2) is considered the most harmful. Therefore, many countries have pledged to reduce the exhaust of CO2 into the environment and have set a "net zero goal".

One of the most significant emissions of CO2 gases comes from the cement factory. It is found that to produce 1 pound of cement, almost 0.9 pounds of CO2 is produced. Hence to lower the effect of CO_2 on the climate the use of Portland cement should be reduced. As for the petroleum industry, cement plays a vital role because it assures the integrity of the well. In order to decrease the dependency on cement in the petroleum industry many companies and researchers are focusing their attention on the use of geopolymer in well cementing.

One of the most important properties that a geopolymer cement should have is good compressive strength so that it can have the capacity to bear different loads present in subsurface conditions. Hence, this study focuses on preparing the neat geopolymer cement (only Class F Fly Ash) and compares its results with the geopolymer cement composite having 5% gilsonite in its ingredient. The tests are focused on long term behavior of selected recipes.

The samples were cured in a water bath at 75°C for the time period of six months. It was found that the samples that had gilsonite as an additive showed better compressive strength than the neat geopolymer cement since the start of curing days and continued the trend throughout the time of the experiment window. Hence, it can be said that gilsonite can be used as a strength enhancer in geopolymer cement.

1. INTRODUCTION

The world's population has increased significantly over the last three decades, triplicating the size of the population in the mid-1900s. By mid-November 2022, the count had risen from 2.5 billion in 1950 to 8 billion, a gain of 2 billion since 1998 and an extra 1 billion since 2010. According to UN estimates for 2023, this growth pattern is predicted to continue, with an additional 2 billion people added to the world population by 2050, and a peak of roughly 10.4 billion people by 2085 (United Nations, 2023)..

As per the U.S. Energy Information Administration (EIA), the rise of consumption of electricity usage globally is surpassing the growth rate of the global population. This tendency leads to an increase in the average electricity consumption per individual, commonly referred to as per capita electricity consumption, as highlighted in the 2023 report by the Energy Information Administration (Energy Information Administration, 2023). Where a significant share of the energy production comes from conventional (oil and gas) and renewable sources (BP, 2022.)

This emphasizes how important it is to develop innovative technology in order to extend the life of both new and existing wells and maintain their integrity while producing oil and gas. These technologies can also help them in their future transition to geothermal energy or carbon capture and storage, which will eventually result in well abandonment (Romero Tellez, 2023). As a result, the oil and gas industry must continually push out the limits of technology while upholding the most rigorous safety regulations (Romero et al., 2022). Therefore, the industry is assessing a large amount of resources for the advancement of well-cementing technologies such as geopolymers and additives like gilsonite.

Geopolymers are a low-carbon option for Portland cement; according to Humairah et al., (2021). The emissions from geopolymer cement, such as fly ash, can be as much as ten times lower than those from conventional Portland. This will help reduce the CO_2 releases in the atmosphere, as cement production is an intensive CO_2 emission source. It is given that for the production of 1 pound of cement, almost 0.9 pounds of CO_2 is released into the atmosphere. Therefore, many oil and gas companies are focusing on using geopolymer in their wells, which will help different countries achieve the net zero emission goal. Therefore, it is crucial to understand the different properties of geopolymer cement, especially the mechanical properties before being fully adopted by the petroleum industry.

Fly ash is one of the main components of geopolymers, a byproduct generated during coal combustion in coal-fired thermal power plants. It poses a substantial disposal challenge, with approximately 750 million tons produced yearly. Fly ash is created when coal is burned between 1200°C and 1700°C. It is made up of both organic and inorganic materials. Fly ash's complex composition, wide range of particle sizes and shapes, fine texture, and variety of components make it challenging to identify, specify, characterize, and use (Kar, 2022). Despite being a crucial source of engineering materials, fly ash has yet to be fully exploited (Kabir et al., 2016)

Romero et al., 2022 have observed that the chemical composition and activation of the components inside geopolymers are the primary factors that affect their performance variability. In contrast to cement, which is dependent on hydration, geopolymers are created by alkalinizing materials based on aluminosilicates, including fly ash (Salehi et al., 2016). It is crucial to recognize, that the chemical composition of fly ash can differ from batch to batch based on the type of coal burned (as seen in Table 1) and the particular combustion technique utilized (Kar, 2022).

Table 1. Element oxides are present in Class C and Class F fly ash. (Hemalatha and Ramaswamy, 2017).

Component (mass %)	Bituminous	Subbituminous	Anthracite	Lignite
Al_2O_3	5–35	20–30	25.1–29.2	10–25
MgO	0–5	1–6	0.7–0.9	3–10
Fe_2O_3	10–40	4–10	3.8–4.7	4–15
SiO_2	20–60	40–60	43.5–47.3	15–5
CaO	1–12	5–30	0.5–0.9	15–40
Na_2O	0–4	0–2	0.2–0.3	0–6
K_2O	0–3	0–4	3.3–3.9	0–4
SO_3	0–4	0–2	–	0–10
TiO_2	0.5	1.1–1.2	1.5–1.6	0.23–1.68
P_2O_5	0.02	0.3–0.5	0.2	–
MnO	0.02	0.1	0.1	0.04–0.21
S	0.08–0.67	0.7	0.1	–
Loss on ignition	0–15	1.8–2.7	8.2	0–5

On the other hand, according to (Boden, 2014), gilsonite is a very pure solid hydrocarbon that occurs naturally and can be obtained from the Uinta Basin in Colorado and Utah. It was first used as a lost circulation material for water-based drilling fluids in the petroleum sector. Later, it was discovered to be useful as an addition to low-density lost circulation cement. Slagle and Carter, (1959), concluded that the main goal of gilsonite was to decrease borehole collapses in water-sensitive shales. While (Clemens & Lasance, 2001) showed that the cement's Unconfined Compressive Strength (UCS) decreases as the concentration of gilsonite increases over 5%, rendering it unsuitable for use in cement applications. However, no study has shown the effects of gilsonite on geopolymer cement such as fly ash cement, in the short and long term. Therefore, this study compares the compressive strength results of the neat geopolymer with the geopolymer that had 5% gilsonite in its composition.

2. MATERIALS AND METHOD

2.1 Sample Preparation

The measurement of the weight of materials is the first step in sample preparation utilizing a digital balance. For this study, two different recipes were used. For preparing the neat geopolymer cement, which is also a control sample, 500 grams of Class F fly ash and 250 grams of an aqueous solution of sodium hydroxide (NaOH) were used. For the second sample, the same recipe of the neat geopolymer was used in which 5% of gilsonite was added. The fly ash and the gilsonite were mixed by hand for 5 minutes so that they were properly mixed. Table 2 shows the compositions of the sample used in this study. Then, the Ofite high-shear mixer, as depicted in Figure 1, is turned on after all the materials have been measured. The pure fly ash or the pre-blended mixture (Fly Ash+Gilsonite) is gradually added to the mixer, which is set at a shear rate of 4000 RPMs, during the first 15 seconds of operation. After this, the lid was closed, and high shear mixing began for the next 35 seconds at 12,000 RPMs.

Table 2. Composition of the samples used in this study

Sample	Materials		
	Fly ash (g)	Gilsonite (g)	Sodium Hydroxide (g)
Fly ash	500	-	250
Fly ash + 5% Gilsonite	500	25	250

Figure 1: Ofite high shear mixer

2.2 Sample Curing

After the specified amount of time for mixing, the resultant slurry is put into plastic molds Figure 2 that have been lubricated beforehand. Following API-10B2 requirements and corroborated by research by Rincon (Rincon et al., 2022), these molds are designed to produce three 2" x 2" cubes. This selection is consistent with the findings of Rincon, indicating that cylindrical samples would not accurately reflect the mechanical properties of the cement or properly correlate with UPV-UCS (Ultrasonic Pulse Velocity - Unconfined Compressive Strength) measurements. Once the molds have been filled with the slurry, they are put into water baths set at 75 °C for 1, 2, 3, 4, 5, and 6 months.

Figure 2. Plastic molds used to cure all geopolymer samples

2.3 Compressive Strength Measurement

The CM-2500 compression testing equipment is used in a destructive test to ascertain the unconfined compressive strength of the two geopolymer cement in this study, as shown in Figure 3. The manufacturer claims that this machine, which was made and calibrated by Test Mark Industries, has a precision level of ± 0.5%. The CM-2500 measures the force required to cause permanent deformation in the cement composite sample by applying a uniaxial load at a constant rate of 72 kN ± 7 kN per minute. Then, by dividing the highest point of applied force by the sample's surface area, the unconfined compressive strength is calculated. The resulting values are then presented with a 0.3 MPa rounding error. When possible, an average is obtained from three samples that came from the same batch by applying the rules outlined in API RP 10B-2. For any data point to be validated, a minimum of 3 samples of the same slurry batch were tested. Additionally, another three extra samples were prepared to corroborate the previous test's data to avoid any inconsistency.

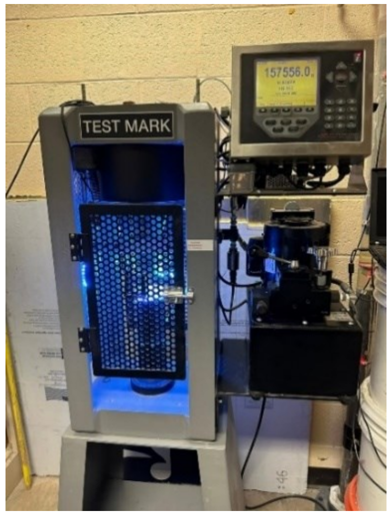

Figure 3. Test Mark CM-2500

3. RESULTS

3.1 Compressive Strength of Neat Geopolymer

The neat geopolymer that was cured at a high temperature of 75°C showed a compressive strength of approximately 21 MPa when tested for 1 month. Likewise, it was possible to see a little erratic development of the compressive strength throughout the experiment; however, the values obtained from 1 to 6 months were close to the error bars. By month 6 the control samples reached an approximate value of 31 MPa, as seen in Figure 4.

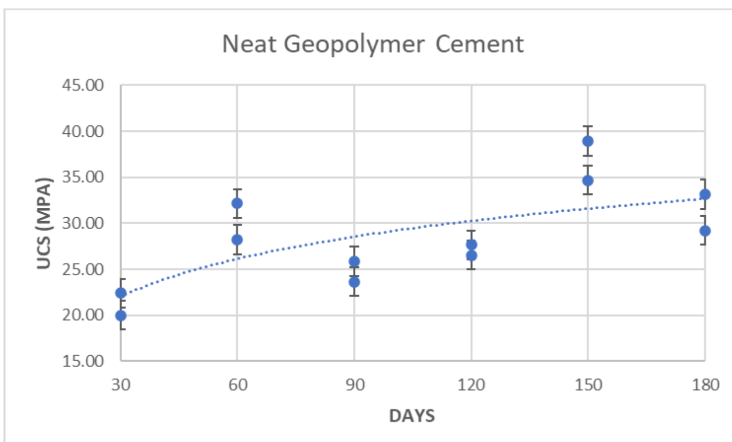

Figure 4. Compressive strength of the neat geopolymer cement after six months of curing

3.2 Compressive Strength of Neat Geopolymer+5% Gilsonite

On the other hand, when gilsonite is added to the mixture at 5% by weight and cured at high temperature, the development of the compressive strength was a little erratic for the length of the experiment. However, within the samples tested on the same day, the values were close to each other, having an approximate value for the compressive strength of 43 MPa when tested at one month, and 48 MPa at the six-month mark, as presented in Figure 5.

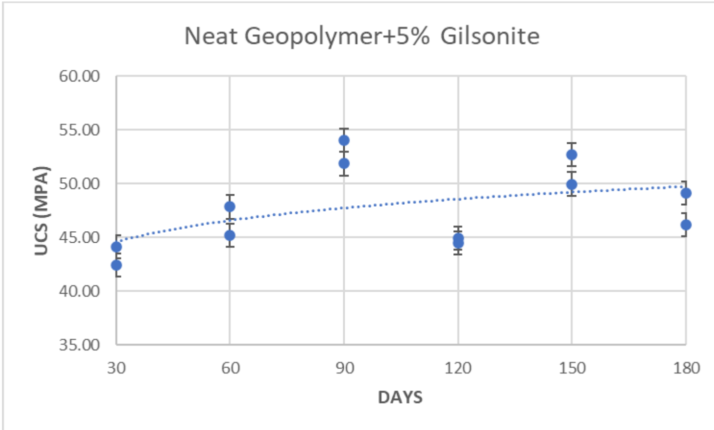

Figure 5. Compressive strength of the neat geopolymer + 5% gilsonite after six months of curing

3.3 Combined Results

Overall, the samples with 5% gilsonite in the mixture showed better compressive strength development from the beginning to the end of the experiment than the neat geopolymer cement (Fly Ash). Nonetheless, both samples showed similar behavior, and no significant change in the compressive strength was observed from 1 to 6 months of curing, as shown in Figure 6.

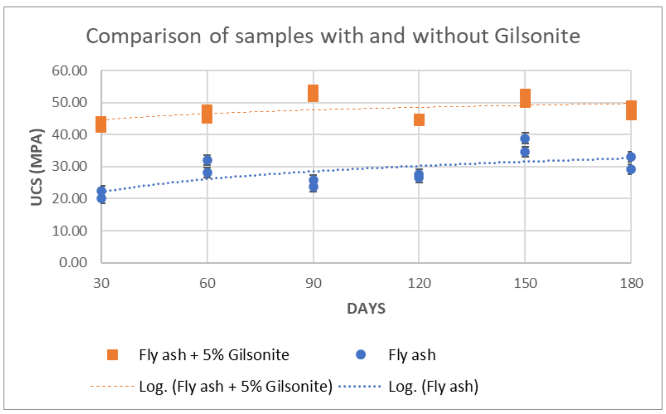

Figure 6. Combined results of the compressive strength of sample with and without gilsonite

4. DISCUSSIONS

The results of this study highlight the possible benefits of adding gilsonite to geopolymer cement formulations. According to the preliminary data, the geopolymer cement significantly increased its compressive strength, showing a remarkable 50% rise after a month of curing at 75 °C in comparison to control samples made entirely of pure fly ash (neat geopolymer).

This observed increase in compressive strength holds true throughout the sample testing in the following months, suggesting that gilsonite has a long-lasting beneficial effect on the mechanical characteristics of the geopolymer matrix. Nonetheless, it is worth noting that as the research continues, the advantageous effects of gilsonite on the geopolymer cement gradually decrease between the fourth and sixth months of testing, with a difference of almost 33% compared to the neat geopolymer samples.

This fluctuation in gilsonite's effectiveness points to a tendency for sample behaviors to converge over a prolonged curing period, pointing to a complex link between curing time and gilsonite's reinforcing effects in geopolymer cement. To fully grasp the temporal dynamics and maximize the use of gilsonite in geopolymer technologies, more investigation and in-depth analysis are required.

5. CONCLUSIONS

This work has established a background for a mechanically reliable (long-term properties) geopolymer cement which is also an environmentally sustainable material for drilling and completion operations for oil, gas, and geothermal wells. Overall, the addition of gilsonite has enhanced the mechanical integrity of the geopolymer cement, increasing the compressive strength of all the samples that were tested during this study. However, the lack of characterization and understanding of the interaction between gilsonite and fly ash gives space for further research in order to have a better understanding of these two materials to unveil their true potential for the industry.

6. ACKNOWLEDGMENTS
The authors of this research would like to thank the Well Integrity Laboratory at OU for the cement repository that allowed to conduct this research and the Mewbourne School of Petroleum and Geological Engineering for the facilities.

REFERENCES

BP. (2022). bp Energy Outlook 2022.

Boden, T. (2014). Utah Geological Survey. Retrieved from Utah Geological Survey: https://geology.utah.gov/map-pub/survey-notes/utah-still-supplying-gilsonite-to-the-world-after-125-years/

Clemens , J., and Lasance, M. (2001). The thermal conductivity of unfilled plastics.

Slagle, K. A., and Carter, L. G. (1959). Gilsonite-a Unique Additive for Oil-Well Cements.

Humairah, S., Rahman, A., Medvedev, A., Yakovlev, A., Yon, S. ;, Sazali, A., Research, P., Bhd, S., Jain, B., Hassan, N., and Thompson, C. (2021). IPTC-21371-MS Development of New Geopolymer-Based System for Challenging Well Conditions. http://onepetro.org/IPTCONF/proceedings-pdf/21IPTC/4-21IPTC/D041S016R002/2424510/iptc-21371-ms.pdf

Kabir, I. I., Sorrell, C. C., Mada, M. R., Cholake, S. T., and Bandyopadhyay, S. (2016). General model for comparative tensile mechanical properties of composites fabricated from fly ash and virgin/recycled high-density polyethylene. Polymer Engineering and Science, 56(10), 1096–1108. https://doi.org/10.1002/pen.24342

Kar, K. K. (2022). Handbook of Fly Ash.

Rincon, F., Abid, K., Arbad, N., and Teodoriu, C. (2022). A comprehensive analysis of class H cement Unconfined Compressive Strength using cubical and cylindrical samples. Journal of Petroleum Science and Engineering, 215. https://doi.org/10.1016/j.petrol.2022.110692

Romero, M., Devers, C., and Teodoriu, C. (2022). Observations of Thermal Cracking Propagation in Geopolymer Curing. https://pangea.stanford.edu/ERE/db/GeoConf/papers/SGW/2023/Romero.pdf

Romero Tellez, M. L. (2023). Study On The Mechanical And Thermal Properties Of Class G Cement Composites. https://shareok.org/handle/11244/340042

Salehi, S., Khattak, M. J., Ali, N., and Rizvi, H. R. (2016). IADC/SPE-178793-MS Development of Geopolymer-based Cement Slurries with Enhanced Thickening Time, Compressive and Shear Bond Strength and Durability. http://onepetro.org/SPEDC/proceedings-pdf/16DC/3-16DC/D031S025R007/1390118/spe-178793-ms.pdf/1