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Observations of Thermal Cracking Propagation in Geopolymer Curing

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ABSTRACT

Geopolymers are a growing potential alternative of study to traditional Portland cement applications. With this increase in interest of the material, additional scrutiny of the material is needed to verify applicability in more environmentally challenging applications. It is the goal of this work to further the understanding of previously identified surface cracking of geopolymer samples cured under high-heat conditions.

To capture the full nature of the apparent sample cracking of high curing temperature geopolymers, new sample cubes are generated at high temperatures and pulled from curing at set times. As well as temperature variation, samples will also be cured in both a wet and dry environment. Unlike traditional cement testing, where the intervals of curing grow larger, for this test samples will be pulled from the heating environment every day for 14 days. This allows for the highest level of insight on the nature of the propagation of the cracks. The samples will undergo controlled, high-resolution photography in order to best catalogue the nature of the cracks. Additionally, all samples will be subjected to uniaxial UCS testing, biased to the direction of the apparent crack, to see if the failure plane is that of the crack. This generates insight into the depth of the crack, as they are typically too small to measure from the surface.

The images collected as a result of this experiment are compared in both temperature and timeline conditions. It is expected that the cracking will onset, expand, and fail the sample faster in higher heat environments. These images will be paired with the corresponding UCS test values and trendlines for the UCS will be adopted. It is expected that if the propagation of thermal cracking is significant to the mechanical strength of the sample, there will be a notable point at which the UCS meaningfully deviates from the time trend, and optimistically this occurs before sample failures begin to occur in the curing environment.

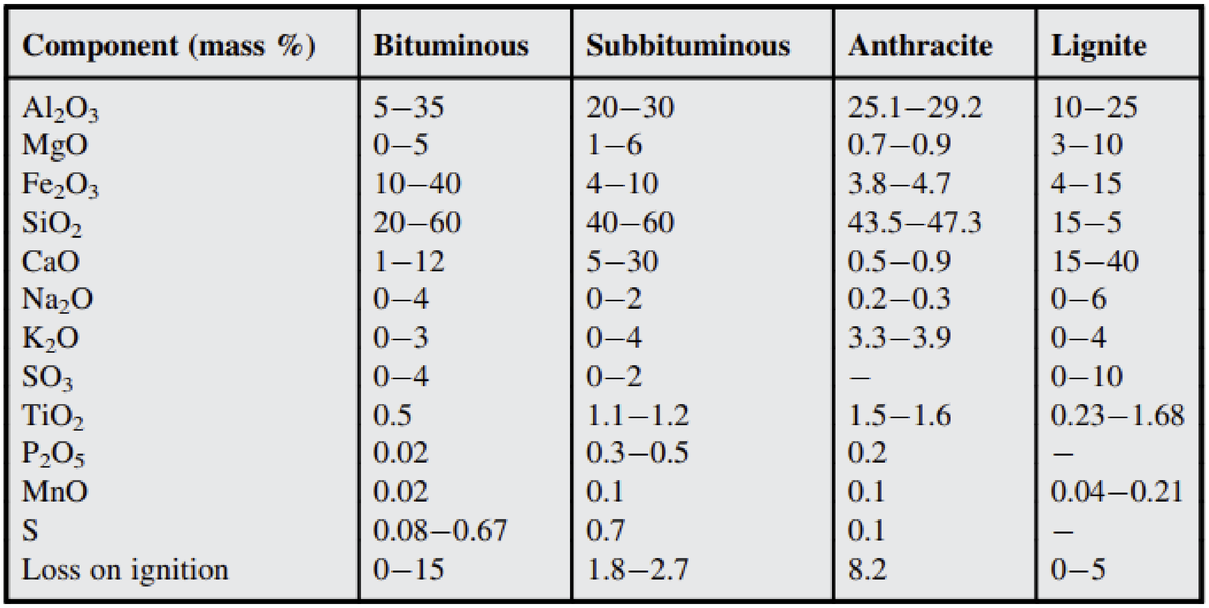
Details into the surface integrity, as well as the general thermal integrity, of geopolymers are relatively sparce at the time of this experiment. It is the hope that this work can serve as a foundation for the establishment of more detailed experiments which better characterize the nature of the cracking phenomenon.

1. INTRODUCTION

The oil and gas industry is one that is simultaneously under direct scrutiny to continuously push technological boundaries while simultaneously expected to operate under the safest possible conditions. During the well planning portion of the operations, considerations for safety and environmental concerns are coupled with the mechanical requirements of adhering the tubulars to the surrounding annular space, the importance of which was indicated by Bellabarba et. al (2008). The material most commonly utilized to achieve mechanically and environmentally secure the tubulars is Portland Cement, specifically American Petroleum Institute (API) grade Portland Cement. API, through updates to API specification 10B, ensures a level of expected reliability of the seven grades of cement by maintaining a standardization of mechanical property testing and material composition. While this material, and corresponding standard practices document, withstand historical scrutiny as an appropriate material for zonal isolation and mechanical strength, the generation of Portland Cement accounts for the largest anthropogenic contribution of carbon dioxide in the atmosphere as detailed by Humphreys and Mahasenan (2002). As such, there is rapidly growing interest in determining a carbon-friendly or carbon-neutral replacement for currently utilized Portland Cement. One such identified material, first described near the end of the 20th century by French Scientist Davidovits (1991), are geopolymers. Geopolymers are the result of the reaction between aluminosilicates and alkaline solutions such as potassium-hydroxide or sodium-hydroxide.

The type of chemical bonding present in pozzolanic material determines the primary structural distinction between geopolymers and cement. Geopolymers are composed of 3D covalent bonds because of polycondensation of inorganic aluminosilicate solution, whereas cement is constructed on hydration and ionic bonding, shown by Humairah et al. (n.d.). Moreover, the chemical composition and activation mechanism of these compounds account for the main performance variations. Geopolymers, as opposed to Portland cement, are created by the alkaline activation of aluminosilicate-based materials like fly ash, as shown in the work by Salehi et al. (2016). However, the chemical composition of fly ash may vary one from to another, and this mainly depends on the type of coal that was used in the combustion and the combustion technology used for this purpose. Information on this variance can be seen below in **Table 1**.

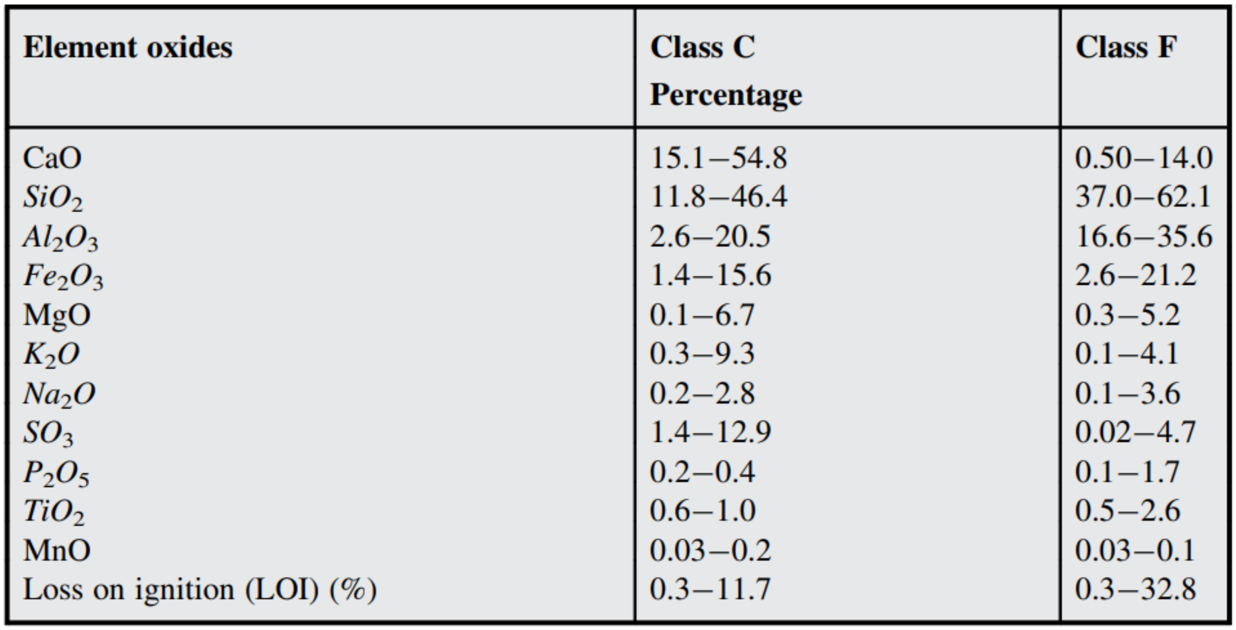
Table 1 Composition of fly ash obtained from different coals (Gollakota et al., 2019)



Component (mass %)	Bituminous	Subbituminous	Anthracite	Lignite
$\mathrm{Al_2O_3}$	5–35	20–30	25.1–29.2	10–25
MgO	0–5	1–6	0.7–0.9	3–10
$\mathrm{Fe_2O_3}$	10–40	4–10	3.8–4.7	4–15
$\mathrm{SiO_2}$	20–60	40–60	43.5–47.3	15–5
CaO	1–12	5–30	0.5–0.9	15–40
$\mathrm{Na_2O}$	0–4	0–2	0.2–0.3	0–6
$\mathrm{K_2O}$	0–3	0–4	3.3–3.9	0–4
$\mathrm{SO_3}$	0–4	0–2	–	0–10
$\mathrm{TiO_2}$	0.5	1.1–1.2	1.5–1.6	0.23–1.68
$\mathrm{P_2O_5}$	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

Additionally, the chemical composition of the fly ash can vary depending on the final use of this one, having class C fly ash and class F fly ash, having a big variation of percentages in the oxide elements that are present in it as seen in **Table 2.**

Table 2 Element oxides are present in Class C and Class F fly ash. (Hemalatha and Ramaswamy, 2017)



Element oxides	Class C Percentage	Class F
CaO	15.1–54.8	0.50–14.0
SiO_2	11.8–46.4	37.0–62.1
Al_2O_3	2.6–20.5	16.6–35.6
Fe_2O_3	1.4–15.6	2.6–21.2
MgO	0.1–6.7	0.3–5.2
K_2O	0.3–9.3	0.1–4.1
Na_2O	0.2–2.8	0.1–3.6
SO_3	1.4–12.9	0.02–4.7
P_2O_5	0.2–0.4	0.1–1.7
TiO_2	0.6–1.0	0.5–2.6
MnO	0.03–0.2	0.03–0.1
Loss on ignition (LOI) (%)	0.3–11.7	0.3–32.8

However, some authors have demonstrated that despite the heat being an enhancer for the geopolymerization of fly ash, when it surpasses 100 °C the compressive strength of this material starts to decrease, due to the excessive loss of moisture, generating cracks in the specimens. (Okoye et al., 2015) The American Society for Testing and Materials commonly divides fly ash into two classes: Class C fly ash (high calcium) and Class F fly ash (low calcium) (ASTM) (T. Hemalatha, 2022) Due to its widespread availability and additional technical benefits including decreased heat of hydration, bleeding, segregation, permeability, enhanced sulfate resistance, acid resistance, etc., low calcium fly ash is utilized extensively. Nevertheless, there have also been observed drawbacks with low calcium fly ash in concrete, such as poorer carbonation resistance and higher water absorption. (Rashad, 2015)

While this material has seen early experimental potential in fields ranging from petroleum engineering to civil engineering, characterizations of geopolymer materials have not been conducted anywhere near the magnitude they have been for Portland Cement. While this is true primarily as a symptom of time, over four centuries of recorded lime-based cement utilization, it does not allow for reductions in safety or environmental considerations. Compounded with concerns of the understanding of geopolymer material when compared to Portland Cement in the realm of oil and gas drilling, global uptick in geothermal energy drilling and interest is only increasing the demand for cementitious materials. Compared to traditional oil and gas operations, the cementing material utilized in geothermal drilling must not only be able to withstand increased high-temperature high-pressure conditions, but also the onset of thermal cycling (Grant and Bixley, 2011). It is the aim of this work to inspect macroscopic effects of thermal conditions on two different recipes of geopolymer samples for the purpose of furthering the understanding of geopolymer potential in geothermal wells.

2. EXPERIMENTAL METHODOLOGY

To test macroscopic effects of thermal environments on geopolymer samples, samples had to first be generated and then subsequently subject to varying thermal environments. The recipe utilized for the geopolymer sample generation is maintained from the previous work, with the inclusion of samples with added sodium silicate. The exact recipe material recipe for the sample is displayed below in **Table 3.**

Table 3 – Breakdown of the Geopolymer Slurry Compositions

Name of the slurry	Fly ash	Fly ash 50%-50%
Fly ash (g)	500	500
Sodium Hydroxide (g)	250	125
Natium silicate (g)	0	125

The samples were prepared in the same manner as the previous work, Devers et al. (2022), which is in accordance with the API standards. This methodology was selected due to it is the only standard practice for the testing of any cementitious material within the oil and gas industry. Once the samples are generated, they are monitored with observational equipment in a thermally active environment. The curing temperature was set at 75°C to avoid prematurely degradation as mentioned by other authors (Okoye et al., 2015).

2.1 Sample Preparation

As stated previously, the samples are all generated under the API mixing practices. This dictates that samples must be mixed in an API regulation blender such as the one shown in **Figure 1**. The liquid materials are first measured out in the appropriate amount, in this case 250 grams of sodium hydroxide for the neat recipe or 125 grams of sodium hydroxide and 125 grams of sodium silicate for the non-neat recipe. Then the solid materials are measured out, in the case of both recipes this is 500 grams of class F fly ash. Once all of the materials are weighed out, the liquids are transferred to the API blender cup and the blender is engaged. The liquids will undergo a low-shear rate mixing (4000 rpm) process for 15 seconds. During this time, the solid material is slowly introduced to the blender cup and the blender cup lid engaged. At the conclusion of the 15 seconds and introduction of solid material, the blender automatically increased the shear to a rate of 12000 rpm for an additional 35 seconds. Once the high-shear mixing is complete, the slurry has been generated and is ready to transfer to molds such as those shown in **Figure 2**. The molds are made of PTFE to avoid hard bonding between mold and the fly ash slurry.

Figure 1 API Blender used to prepare all geopolymer slurries

Figure 2 Plastic molds used to cure all geopolymer samples

Once the molds are filled with the geopolymer slurry, they are transferred to an oven set to 75°C. After a 24 hour period, the molds are removed from the oven so that the cubes may be extracted. Once the cubes have been extracted, they are returned to the oven until the designated curing time has been reached.

2.2 FRACTURE MONITORING

The samples are stored in a large oven capable of holding temperatures at the target temperature of 75°C, shown in **Figure 3**. The temperature of the oven was monitored using an independent thermometer rated up to 150°C, shown in **Figure 4**. Additionally, the oven was retrofitted with heat-distributing fans, shown in **Figure 5** to ensure a consistent internal temperature inside the oven. To closely observe if and when the samples begin to experience surface cracking, a real-time camera was fixed outside the oven facing the clear windows and transmitted a live feed of the oven to a nearby computer (**Figures 6** and **7**). As a final precaution, the entire experimental apparatus was stored inside of a larger insulated chamber with controlled humidity. This was done in order to mitigate the potential for long-term thermal degradation of the environment or outside influence from potential short-term power outages, shown in **Figures 8 and 9.**.

Figure 3 Heating environment for monitoring thermal cracking of geopolymer samples

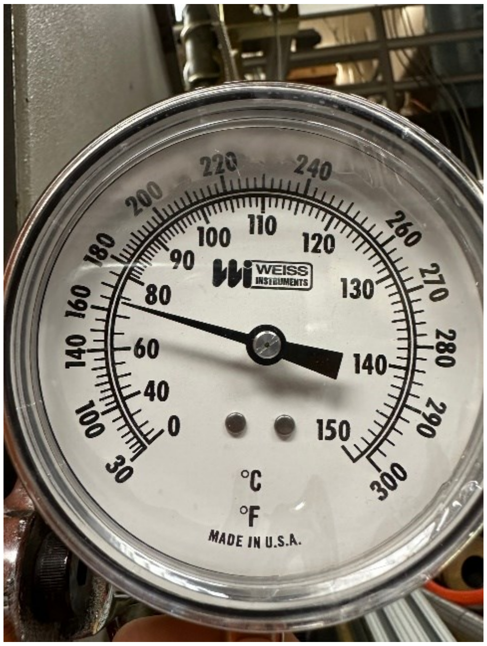


Figure 4 Thermometer fixed to heating unit to closely observe temperature

Figure 5 Circulation fan installed within heating chamber to ensure uniform temperatures

Figure 6 Camera used to monitor thermal cracking onset continuously

Figure 7 Video feed of the samples under heating

Figure 8 Larger oven used to house the entire experimental setup

2.3 MECHANICAL TESTING

A subset of samples, once at the completion of the set curing interval, are removed from the heating environment and their physical dimensions taken. Note this is only possible if the sample is mechanically stable, such as in the case of no cracking or surface-only cracking. Several samples experienced virtually total failure in the heating environment and therefore cannot be measured or tested mechanically. After measurements are collected, including weight in air and water for purposes of determining density, samples are transferred to a calibrated unit for uniaxial crush testing. The system applies force via a piston, and continues to apply the force until the sample experiences total mechanical failure. The corresponding compressive strength is recorded and presented graphically for interpretation.

3. EXPERIMENTAL RESULTS

The section below depicts image results of the thermal cracking onset as well as additional data from mechanical testing,

3.1 PHOTO RESULTS

Figures 10 and 11 show the samples in the oven after the crack in the neat geopolymer samples have shown cracking (see figure 10). The sodium silicate doped samples remain stable until day 8, while currently several tests are still ongoing.

Figure 9 Neat geopolymer samples after 2 days in heating conditions, note thermal cracking on all 6 samples

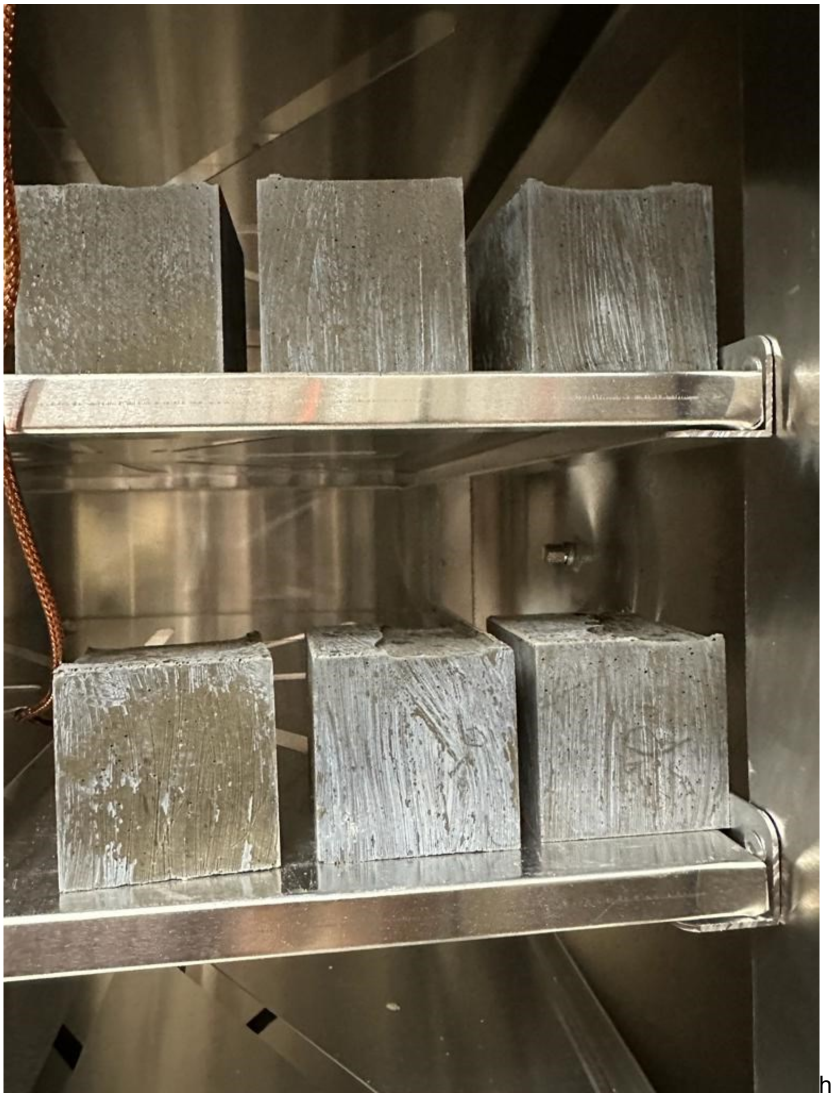


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Figure 10 Sodium Silicate doped samples after 2 days in heating conditions, no signs of thermal cracking

3.2 MECHANICAL TESTING RESULTS

Previously samples used to generate UCS data, have shown similar cracking behavior, but unfortunately crack monitoring was not performed. Hence, we only noticed samples are cracked only at the time of UCS testing, hence after curing period of 3, 7 or 14 days. However as shown in figure 12, cracks in the samples resulted in a non-uniform or erratic UCS development with time. While some this behavior could be attributed to extreme inhomogeneous composition of fly ash, our samples have been created from same fly ash batch and thus the composition non-uniformity may be excluded. As seen in the figure 12, after 3 or 7 days of curing samples show a los of UCS. Please note that our curing temperature is 75°C which is below the threshold found in the literature as being critical for Fly ash based geopolymers. Furthermore, the addition of sodium silicate seems to delay the sample cracking, as noted from figure 12 that only sample 12 showed some cracks at the time of testing.

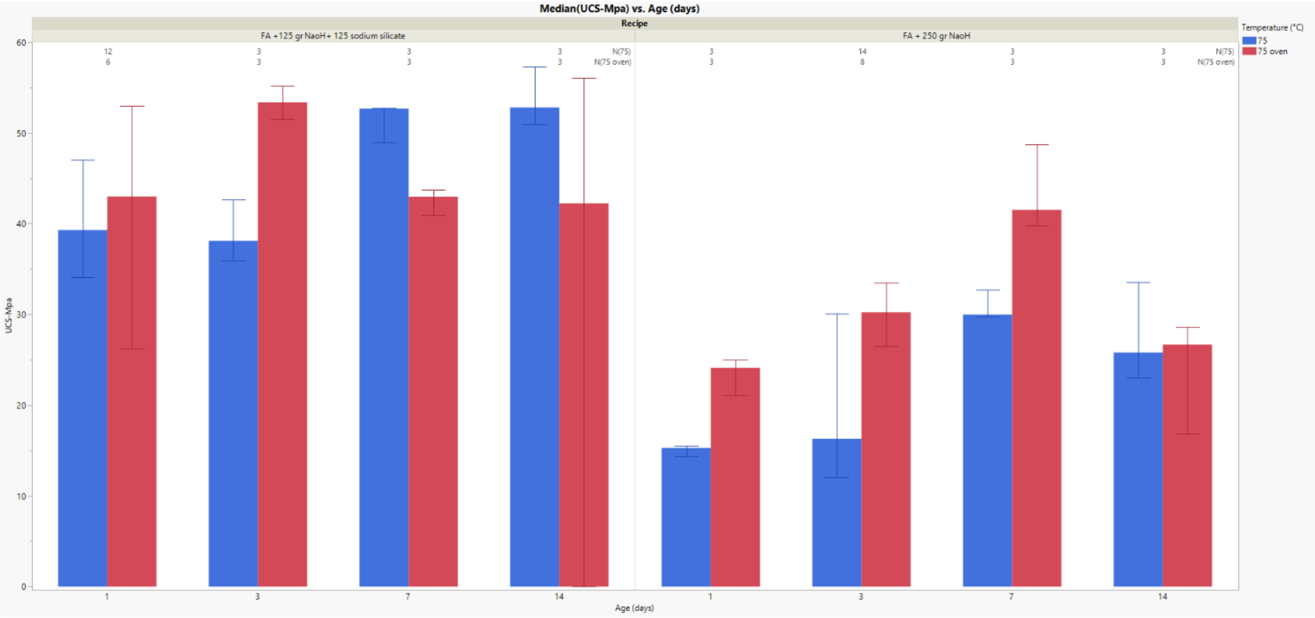

Figure 11 Results of mechanical testing from dry environment combined with results from wet environment in previous work of Devers et a. 2022

4. DISCUSSIONS

Initial optical observations from the dry heating environment suggest that neat fly ash geopolymer samples are more immediately subject to thermal damage than non-neat samples. While the observations are only recorded at the two day mark, all 6 of the observed samples exhibit thermal cracking. These cracks not only propagate across entire interfacial planes, but also in many cases split to make contact with three sides. While the nature of optical testing does not allow for confirmations on propagation depth, the lack of surface level cracking on the non-neat samples suggests the phenomenon is unique to the neat samples in short time intervals. It is also worth noting that there is a significant color difference in the two samples as well. Again, due to the nature of this testing it is unclear if that is due to the chemical difference in the sample giving the color variation, or the presence of residual fluid being higher in the non-neat samples. The appearance of surface level cracking is enough, as studies by Apostolopoulos et al. (2018) observed notable decreases in bonding strength in cementing material by significant quantity. While this work did not test bonding strength of geopolymer samples, the consistent presence of cracking identified by this work has called attention to the need for additional testing of the bonding strength of this material under thermal conditions. In geothermal wells specifically, a review of geothermal well integrity by Allahvirdizadeh (2020) suggests that uniaxial compressive strengths of cement required at the elevated temperatures of geothermal operations is typically higher than that is needed in traditional drilling operations for long-term well integrity. This generates a cause for concern as the neat samples do not achieve strengths typical of neat cement until after the third day of curing, and this is not at the potential height of elevated temperatures in geothermal wells. Additionally, since the material saw a sharp loss in mechanical strength between the 7th and 14th day in an arid heating environment, it could be further suggested that his material is unsuitable for long term geothermal well integrity even before bonding strength failures are considered.

When strictly looking at the difference between the arid environment focused on in this work combined with the results of aqueous heating environments from the previous work by Devers et al. (2022), it is seen that in both recipe cases the mechanical strength suffers as a function of time when subjected to the arid environment over the aqueous one. When transitioning from viewing the graph ordinally with respect to time to continuously, a better understanding of the relationship between the average UCS at each time interval and the curing time in different environments, as shown in **Figure 12**, can be generated.

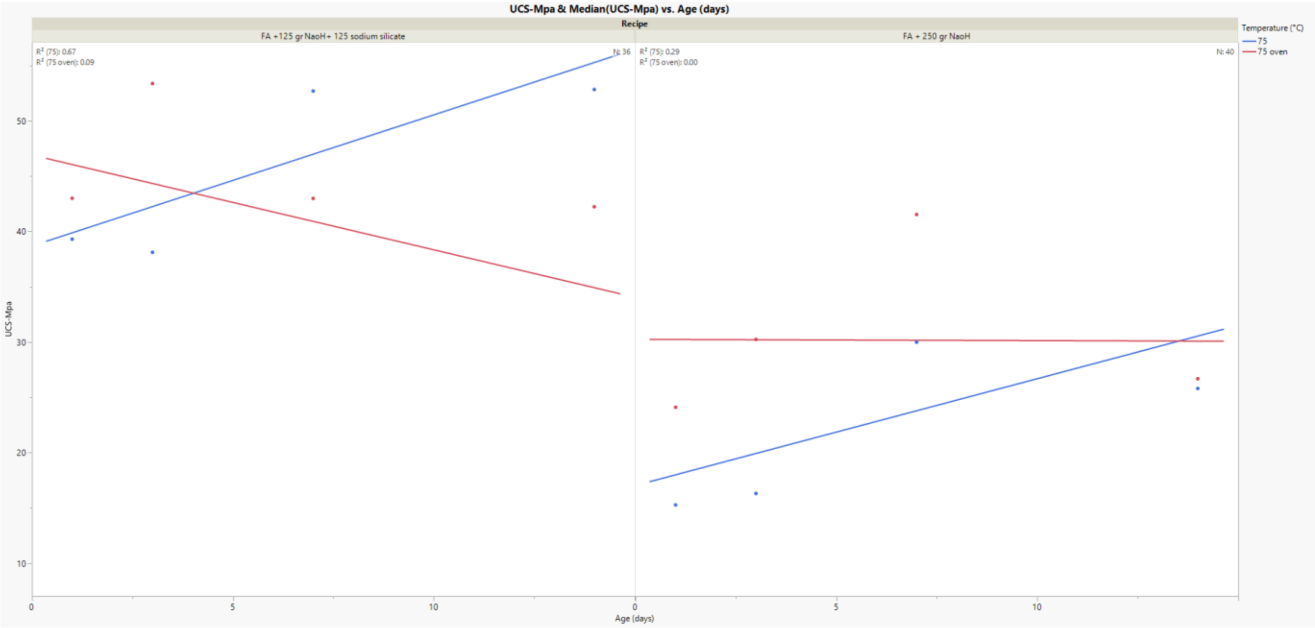

Figure 12 Time trend of sample UCS in different curing environments for each recipe, note that the only trend of value is the aqueous heating of the sodium silicate doped sample

When the data is viewed continuously, the only trend that is even suggestibly acceptable is the case of the aqueous curing of the sodium silicate doped sample. While a linear trend would traditionally be inappropriate for the analysis of UCS as a function of time, especially in the case of traditional Portland cement, it is not necessarily the case for geopolymer pozzolans. Many works, such as those done by Nguyen, et al. (2017), depict that the virtual maximum UCS of geopolymer cement is not reached until 28 days curing. Resultantly, any trend applied to this work would be subject to flux if the experiment continued to include 28-day testing and beyond. Since that is not the intent of this work, the trend only serves to indicate that it would take a considerable amount of over-fitting a trend to account for the influence of time on the mechanical strength of the other three observed conditions. The reason for the weak-to-non-existent trends in the other cases is largely due to the massive relative losses in mechanical strength in the arid condition curing. Even this, however, should be taken with a level of scrutiny as the range of observed UCS values for a given cure-time is large across many of the testing sets. While currently we are aiming to achieve 28 days or longer for sodium silicate doped samples (to identify any cracking tendency) we believe that the use of geopolymers in dry situation require much more attention. A classical dry situation in wellbore could be the annular space between two casings, in particularly the upper zone, where do to the lack o pressure water will vaporize.

5. CONCLUSIONS

This work establishes a background for both the need for a mechanically reliable and environmentally sustainable material for drilling and completions operations. The metrics this material must meet are more elevated in geothermal drilling and completions operations. One potential material candidate, geopolymers, has shown strong candidacy potential in many academic investigations. The lack of characterization experiments or industry standards for the testing or performance of the material, however, leave concerns regarding the material when compared to the current Portland cement standard. In order to further the understanding of the material characteristics specifically for geothermal applications, this work established methodology for observing influences of thermally charged dry environments on geopolymer material and compared these results to existing work and theory. The results of the experimental methodology show weakness induced as a direct result of the type of environment in which the sample is cured in. It is the conclusion of this work that the combined variation of UCS across same cure-times, the surface cracking of neat samples, and the loss of mechanical strength in low-water heated environments are all causes for additional investigation and vetting of the material. Without definitive and proven reasoning for the loss in mechanical strength in thermally active environments, there cannot be confidence in any testing which is able to mitigate the onset of thermal degradation.

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