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Geopolymers, Are They Consistent Enough for Geothermal?

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ABSTRACT

In the constantly evolving renewable energy market, there are constant efforts to ensure technological developments match the growing energy demand. In the geothermal energy sector, well designs much be considered for both high temperature and high-pressure conditions, with some wells expected to be functional for over 50 years. This makes the understanding of the cement barrier between the casing and the environment critical, as it provides structural support and prevents potential fluids communications that could be environmentally detrimental. In an effort to bring new solutions to the market, ongoing investigations into geopolymers, specifically those made using type F fly ash, are suggesting the general superiority of this new class of cementing material over traditional API or Portland cement-based solutions. This work aims to scrutinize these investigations by subjecting many of the geothermal cement recipes analyzed in literature to API testing standards and recording characteristics of the samples in the same manner as normal API testing would.

The testing in this work focuses on uniform testing conditions for Class F Fly ash geopolymer testing, only changing conditions to match published works that suggest improvements to UCS. Over 30 geopolymer samples are tested for times ranging 1 to 31 days, and the resultant testing of the samples yielded UCS results far more variant than classic API class G, C, or H cement, with many samples failing to show strengths superior to traditional cement classes. Further investigation of the variations suggests that not only are these variables variant across samples from the same Fly Ash source but very with both setting environmental temperature and pH.

1. INTRODUCTION

In the Oil and Gas Industry, the utilization of Portland cement is critical in the completion of oil and gas wells as it provides not only the cementing for affixing the downhole tubulars to the annulus but also inhibits zonal flow in the annulus as well as provide essential confining pressure around the tubular as highlighted by Bellabarba et al (2008). This material is well understood, and the testing and performance of the material are standardized within the oil and gas industry by API 10B. This standardization ensures that there is a metric that all testing, both laboratory and field samples, can be compared to in a fair and repeatable way. The primary issue with the material is that it is Portland cement, and cement production is that the process accounts for 5% of global anthropogenic CO2 emissions, as shown by Humphreys and Mahasenan (2002). With recent studies highlighting the importance of minimizing the emissions of all greenhouse gases, efforts have been made to find ways of reducing contributions towards these emissions wherever possible. One recent discovery that may help the oil and gas industry reduce this CO2 contribution comes in the form of a cementing alternative. At the end of the 20th century, an alternative cementing material called a geopolymer was conceived by Davidovits (1991). The benefits of this material were two-fold, as not only did it theoretically function superiorly to standard Portland cement but was also sourced from coal ash; another material the planet is currently producing a large amount of without much in the way of properly disposing of it; noted by the fact that roughly 80% of the material is currently disposed of hazardously in landfills (Joshi and Lothia 1997, Ahmaruzzaman 2010). Since the discovery of this material, several industries have begun detailed works to further the understanding of the behavior of this new cementing material.

Despite the potential benefits of the material, there is much regarding the nature of geopolymer, especially in downhole applications, that is left unknown. A primary reason for this is that the current standard for the composition of fly ash is determined by the American Society for Testing Materials, and the composition is only broken into two types: Class F and Class C; a breakdown primarily dependent on the concentration of lime. Another method of differentiating the types was addressed by Ahmaruzzaman (2010) when they proposed a 3-category breakdown shown in **Table 1** based on the original coal source.

Sakmeier et al (2018) have pointed out that although the main ingredient of a cement slurry (the cement) is accurately defined and standardized (i.e. Class A, B, C, D, E F, G, H) the type of recipe to be used for a given well configuration is not. The fact that the base material is highly standardized allows the users to create reference data that can be used for better recipe design. The need of a comprehensive reference repository has been documented by Ichim and Teodoriu (2017) and Abraham et al. (2021). This reference information are also necessary for geopolymer materials I order to increase their suitability for the wellbore applications.

Table 1: Typical composition of Fly Ash based on its coal source

Component (wt.%)	Bituminous	Sub-bituminous	Lignite
SiO_2	20–60	40–60	15–45
Al_2O_3	5–35	20–30	10–25
Fe_2O_3	10–40	4–10	4–15
CaO	1–12	5–30	15–40
MgO	0–5	1–6	3–10
SO_3	0–4	0–2	0–10
Na_2O	0–4	0–2	0–6
K_2O	0–3	0–4	0–4
LOI	0–15	0–3	0–5

Although the industry is taking steps towards to improve the standing classification system, it still leaves large levels of composition variance among many of the components. This is an issue as the work done by Duxson et al. (2005) suggests significant variance in critical parameters, primarily UCS, among variations in fly ash component ratios. This problem is compounded by the fact that the majority of fly ash is sourced as a by-product from other industries, leading to a potentially high variance in sample composition. Additionally, when compared to the short mix time of API grade cement, research conducted by Rattanasak and Chindaprasirt (2009) highlights the necessity for long mix times in order to generate high UCS values. However, they continued this work, suggesting that high enough inclusions of liquid glass could reduce the effective mix time by a factor of 10. The inclusion of the material is present in many works investigating geopolymers, such as the work by Salehi et al. 2017b. The high inclusion rate of this material across literature suggests that it should be included at a base level. If this is to be the case, it would also mean that geopolymer would need two liquid additives that are potentially hazardous as opposed to OPC, which only needs water.

On the other hand, Saleh and Teodoriu (2017, 2021) have clearly shown that mixing energy gained during the cement slurry blending process is critical for Portland cements and should be considered when different recipes are compared. For example, cements mixed according to API 10B (15s plus @ 4000 RPM and 35 s @ 12000 RPM) do not have similar properties as for example cements mixed at low RPM for a long time. Teodoriu et al. (2017) have shown that laboratory and field mixing of normal Portland cements does not necessary lead to similar cement properties, especially for the short-term curing. It is also worth to mention that added salt the Portland cement will sometimes delay cement setting up to 21 days (Teodoriu and Assambe 2015) which in a way can be comparable with geopolymers that are cured at room conditions such as those for civil engineering applications.

However, these concerns can be mitigated by thorough research into the material from a fundamental level and advancing from there. The work in this paper primarily focuses on testing geopolymer samples without the inclusion of liquid glass in nature as identical to the testing of current API grade cement would be tested. This is done in order to generate testing equivalencies to current standard materials and begin to draw fair comparisons across the materials.

2. EXPERIMENTS AND RESULTS

A systematic method of testing multiple samples from the same fly ash source was developed to generate a stronger understanding of Class F Fly Ash. This method was designed to be as in-line with standard API OPC testing as possible. This was done by preparing the Class F geopolymer samples in the same way API cement would be prepared and subsequently tested. Before testing began, 10M Sodium Hydroxide solution was generated in half-liter quantities. This was done as the generation of sodium hydroxide solution generates heat and therefore requires a cooling period. Once the sodium hydroxide solution returned to room temperature, it was transferred to long-term storage containers for testing. All samples were made by first measuring 250 grams of the 10M sodium hydroxide solution into a standard API blender. After the liquid portion was measured out, 500 grams of Class F fly ash was measured into a measuring cup and prepared to be transferred into the API blender. The ratio of solid to liquid and the selected molarity were selected based on the work of Salehi et al. (2018). The solid material was then transferred into the API blender during a second period during which the fluid was undergoing low-rpm blending as prescribed by standard API cement blending. After 15 total seconds of fluid agitation have occurred, all solid material transferred, and the blender lid replaced, the rpm of the blender elevated to a high-speed for a remaining 35 seconds to result in a total of 50 seconds of fluid agitation. After the conclusion of the blending process, the slurry was transferred into a 3-cube mold, as shown in **Figure 1**. Once the slurry was fully transferred into the cube mold, the mold was placed into a 75C water bath. From this point, slight variances in the process take place; but most samples were removed from their molds at the 3-day mark and either immediately tested or returned to the hot water bath, seen in **Figure 2.**

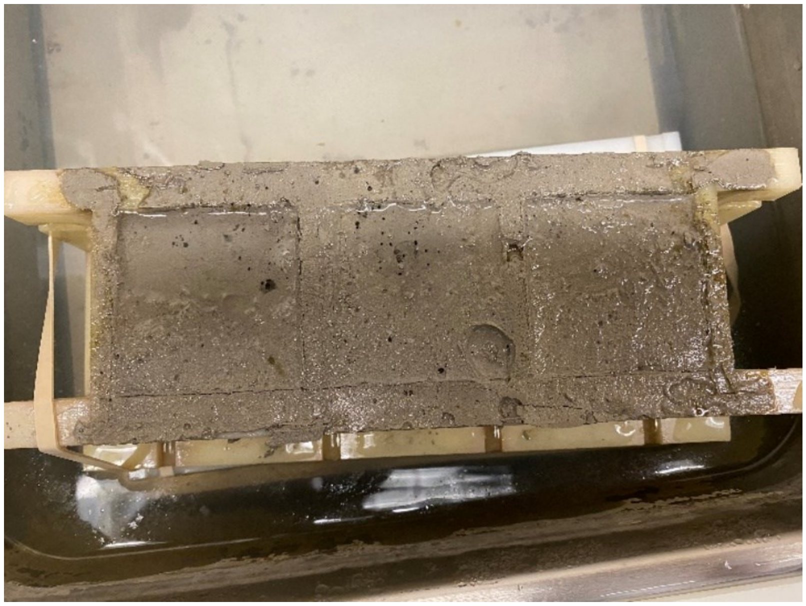

Figure 1. Geopolymer slurry poured into a mold

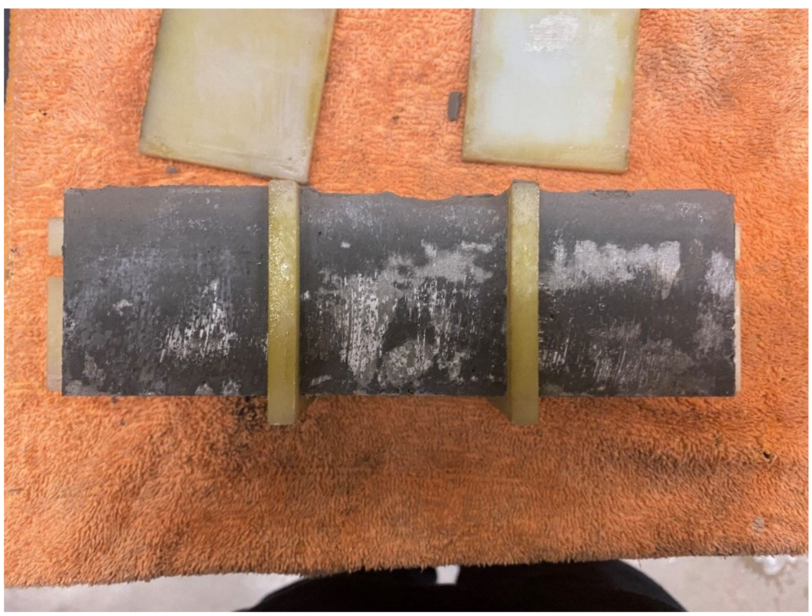

Figure 2. Geopolymer samples removed from mold

Once the molds were recovered from the hot water bath after the planned aging period, the samples were removed from the hot water bath and placed out to cool off just long enough to be handled. Once they could be handled, they were transferred to a testing station in which all samples had their lengths and widths tested three times and had the average taken. Additionally, the samples weights in air then in water were taken. Then, after weighing, the samples UPV was measured before being subjected to UCS testing. The taken measurements and testing results were then catalogued into a laboratory book and then subsequently transferred to a digital format. Once the information was transferred to digital format, the results were plotted in a variety of ways.

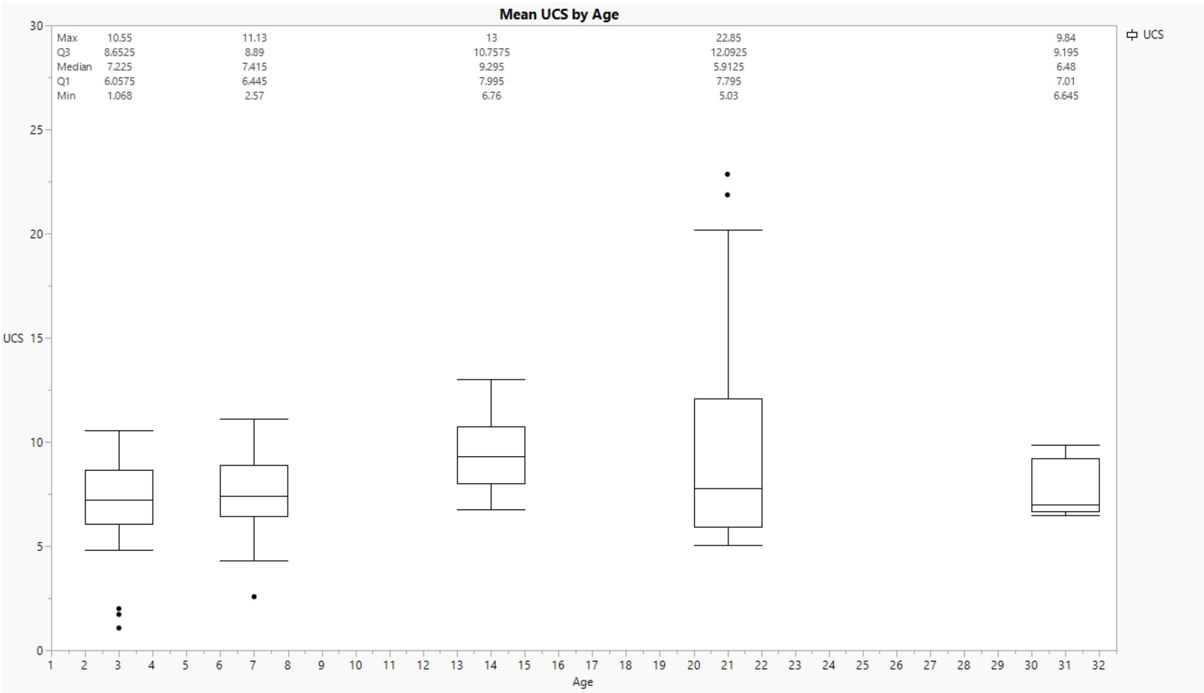

Figure 3. Box and Whisker chart for UCS of tested Samples by Age

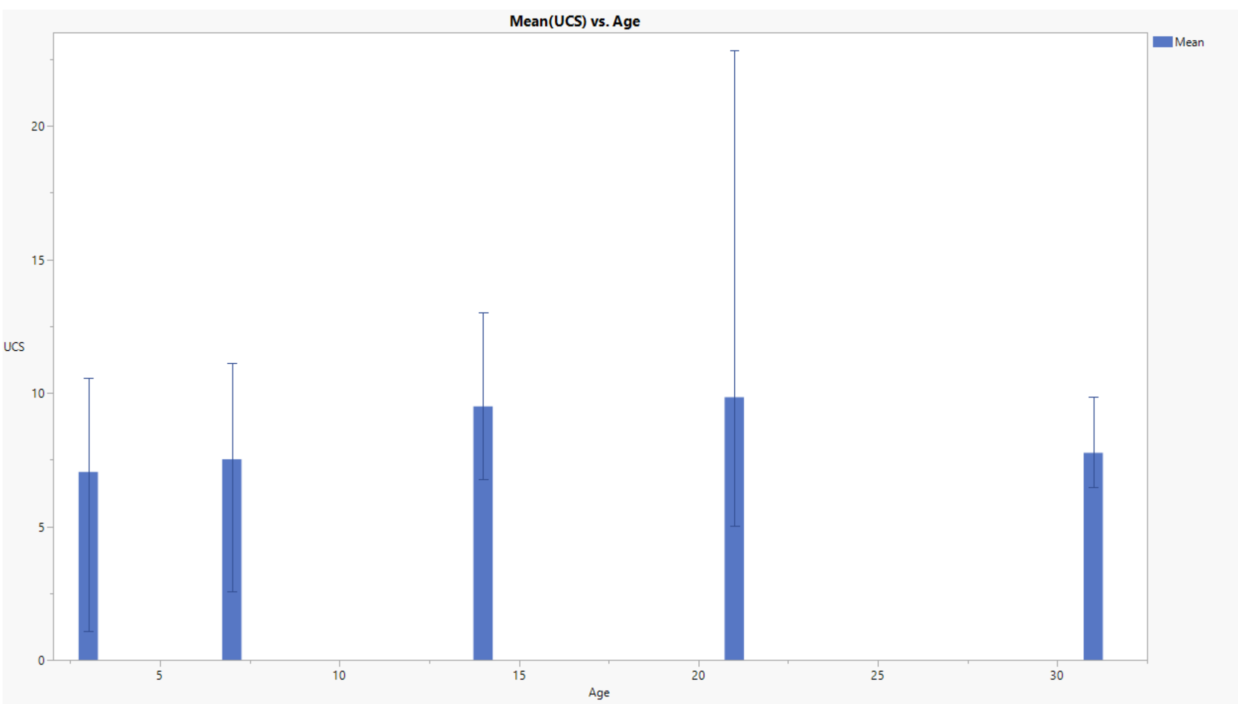

Figure 4. Histogram of UCS by Age with error bars

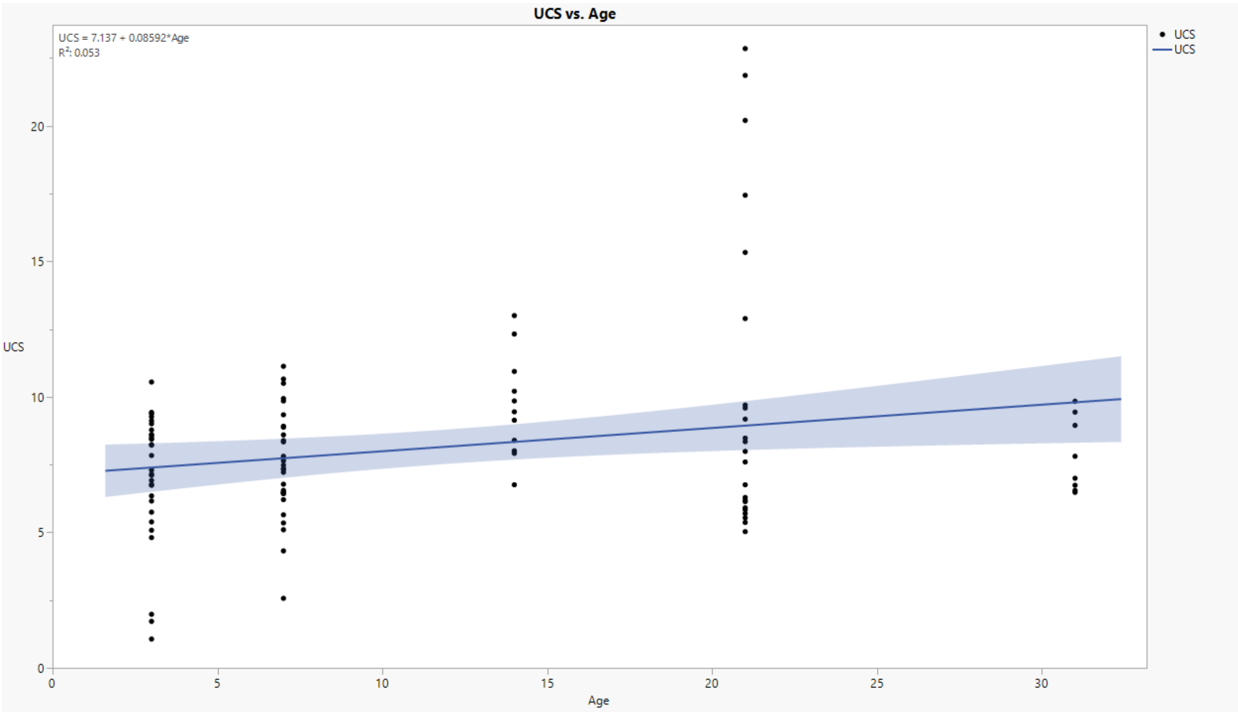

Figure 5. Linear projection of UCS as a function of Age

3. DISCUSSIONS

The initial box- and-whisker chart displayed in **Fig 3** shows clearly that there is little time-based difference between the curing age of the samples. This is counter to the expected behavior of classical neat, Portland based cement product. Both **Figs 3 and 4 s**how similar averages in UCS across testing ages and show considerable variation among testing at the same age group. The UCS results are more in line with the work done by Salehi (2017a), as opposed to some of the work that includes considerable amounts of additional liquid glass. The work does have some similarities to the work done by Mehta and Siddique (2017), who were studying the influence of additional additives. However, the UCS was much higher. **Figure 5** shows a slight increase of UCS with age, but the trend is more linear, unlike Portland cement where a logarithmic tendency is noted. The range of this issue is made apparent when the data is broken out into binned histograms, as is done in **Figures 6-10**. For clarity, the histograms are binned in ranged of .5 MPa, with the number of included samples denoted in the top right of the graphs.

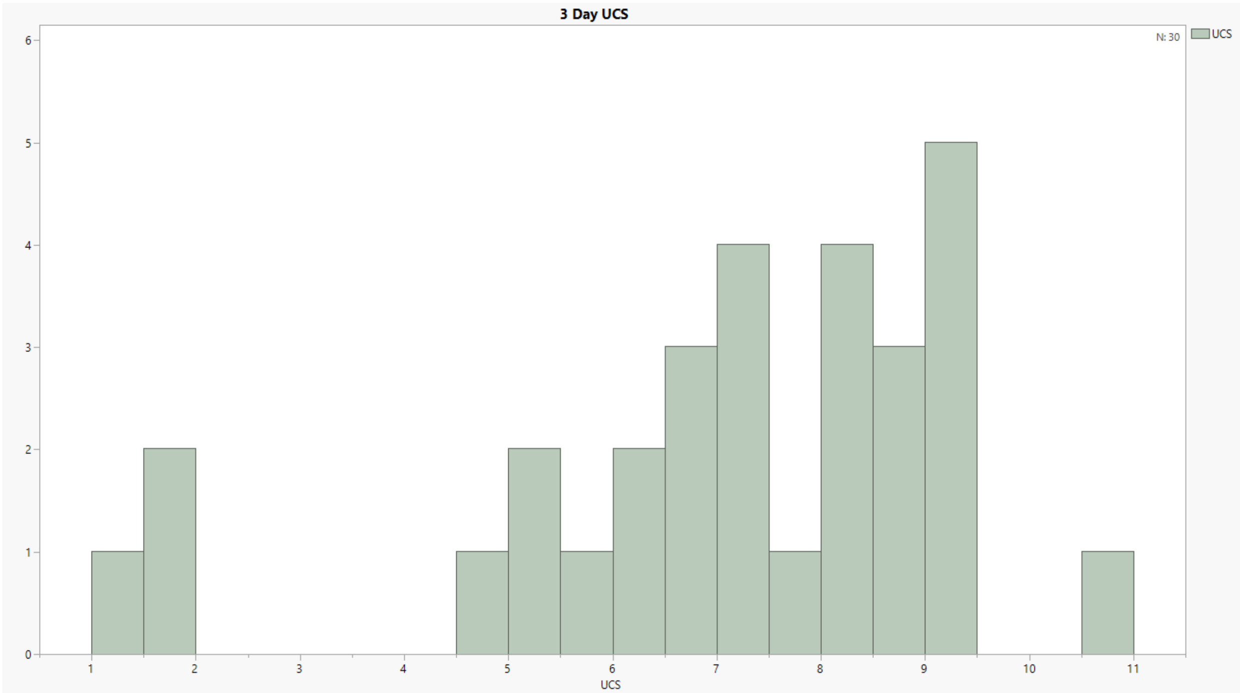

Figure 6. 3 Day UCS Histogram

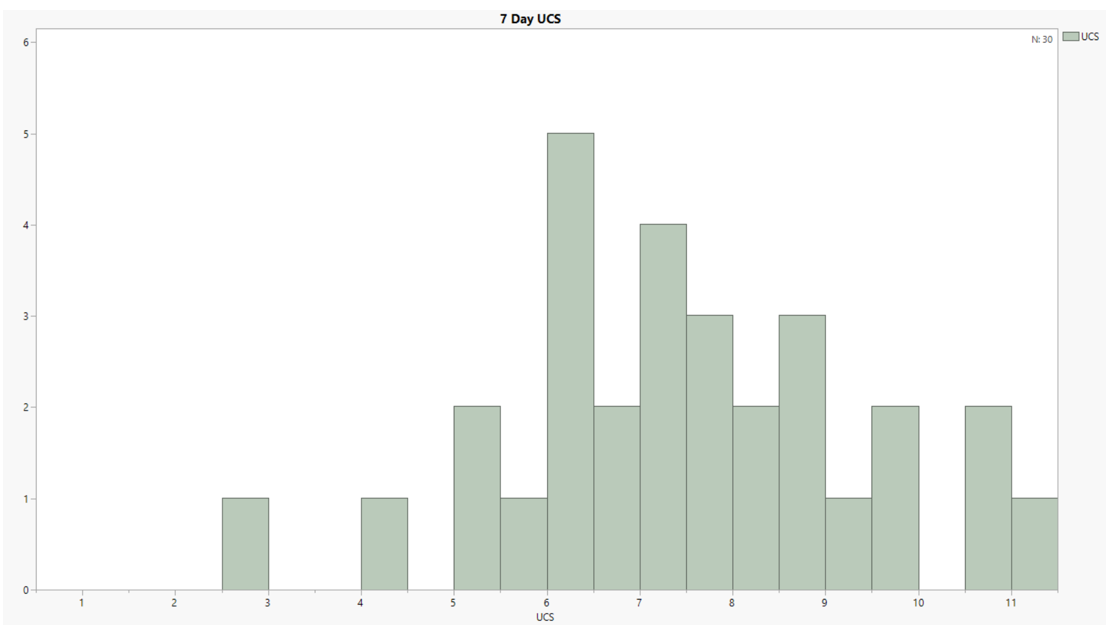

Figure 7. 7 Day UCS Histogram

Figure 8. 14 Day UCS Histogram

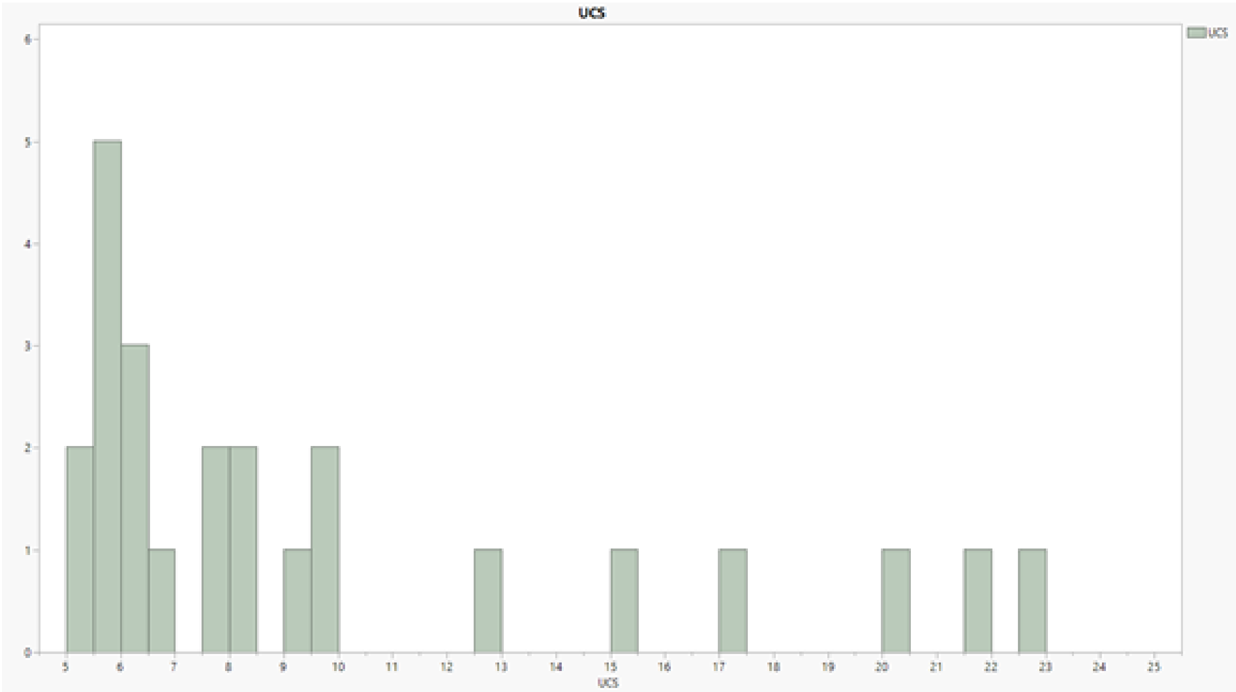

Figure 9. 21 Day UCS Histogram

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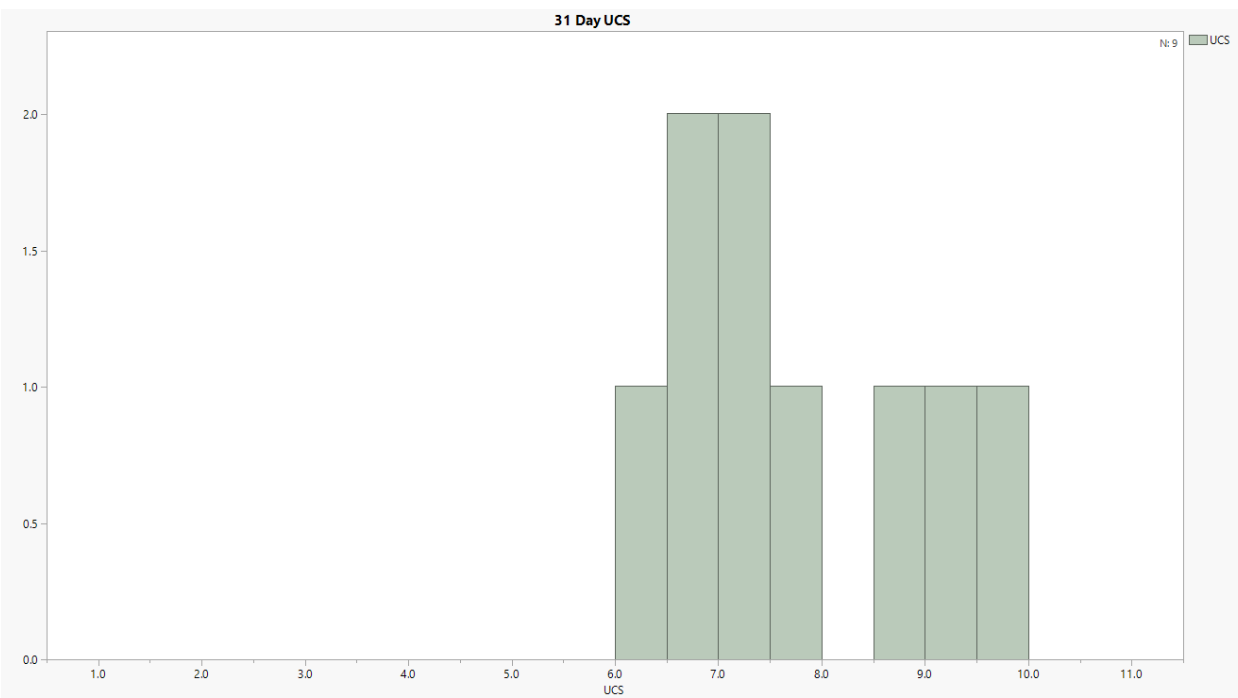

Figure 10. 31 Day UCS Histogram

From this breakdown, we can begin to see that the samples not only have a large range in UCS but have no ‘normal’ distributive behaviors. First addressing the samples that were tested after the 7-day mark, we see that the 14 day and the 31-day testing times have the tightest grouping of material, both displaying 7 subgroups across 12 tests. The 21-day mark has a better bins-to-samples ratio, having 8 subgroups across 24 samples, however, the grouping is far worse. This is the best bins to samples ratio, however as both the 3- and 7-day tests are comprised of 30 samples but have 13 and 14 bins, respectively. While UCS poorly functions with time, UPV shows a much stronger correlation with time, displaying a quadratic trend between the two with an R^2 of .51, which still is lower than anticipated. The interesting piece of note here that UPV has a moderate trend with time while UCS has no discernable relationship. One reason for this could be due to the relationship between density and UPV, while UCS has a higher dependence on the internal bonding of the material, however the work of Abd Rahman et al. (2020) suggests the density of the slurry has a notable level of influence on the UCS.

There was concern that the testing environment may have been having an adverse effect on the final tested samples due to the pH of the heating water being too high. To verify this, samples were heated with fresh, deionized water, and compared to the previous 3- and 7-day data that had reused water. This testing was confined to 3- and 7- day testing, with overall results in Figure 11 and individual results in Figures **12** and **13**.

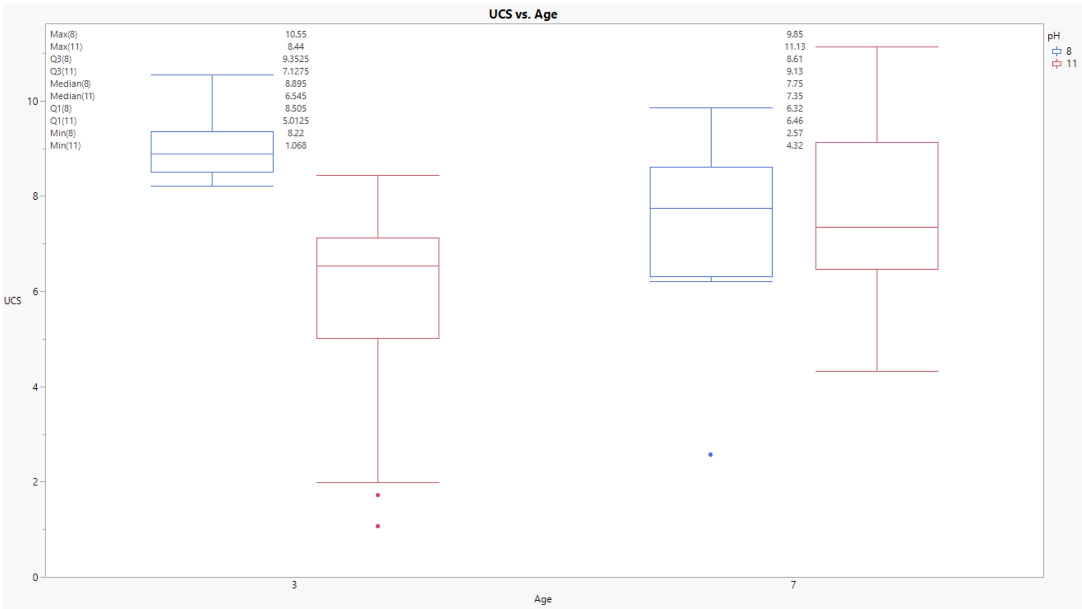

Figure 11 Box and Whisker of 3- and 7-day tests by pH

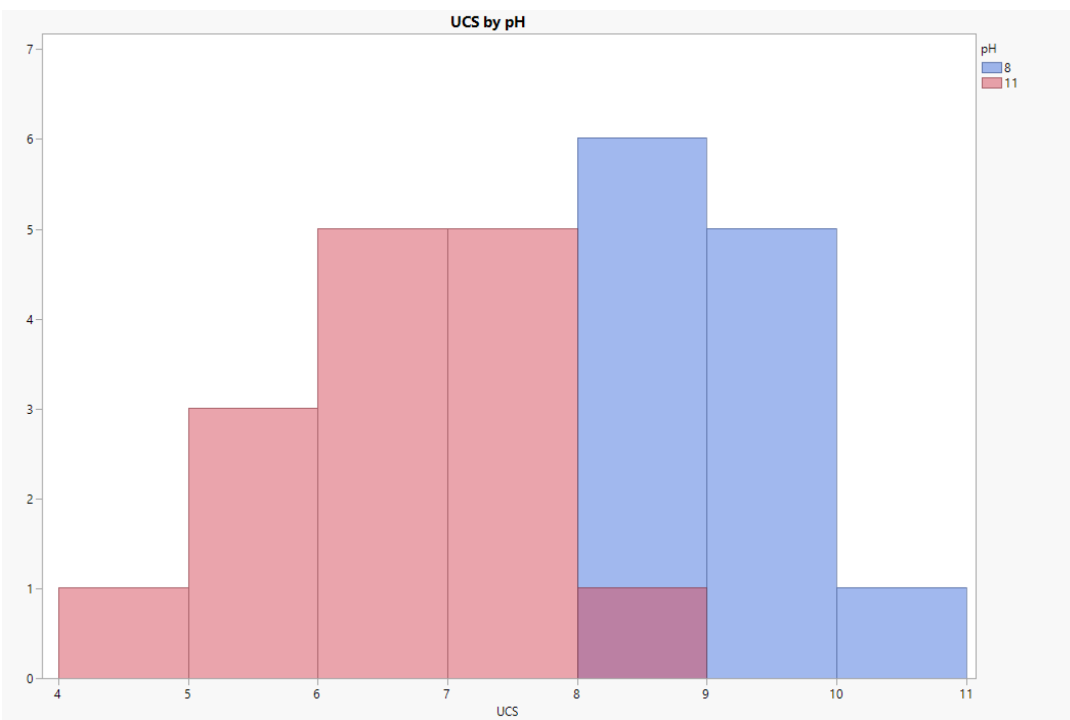

Figure 12. 3-Day UCS by pH

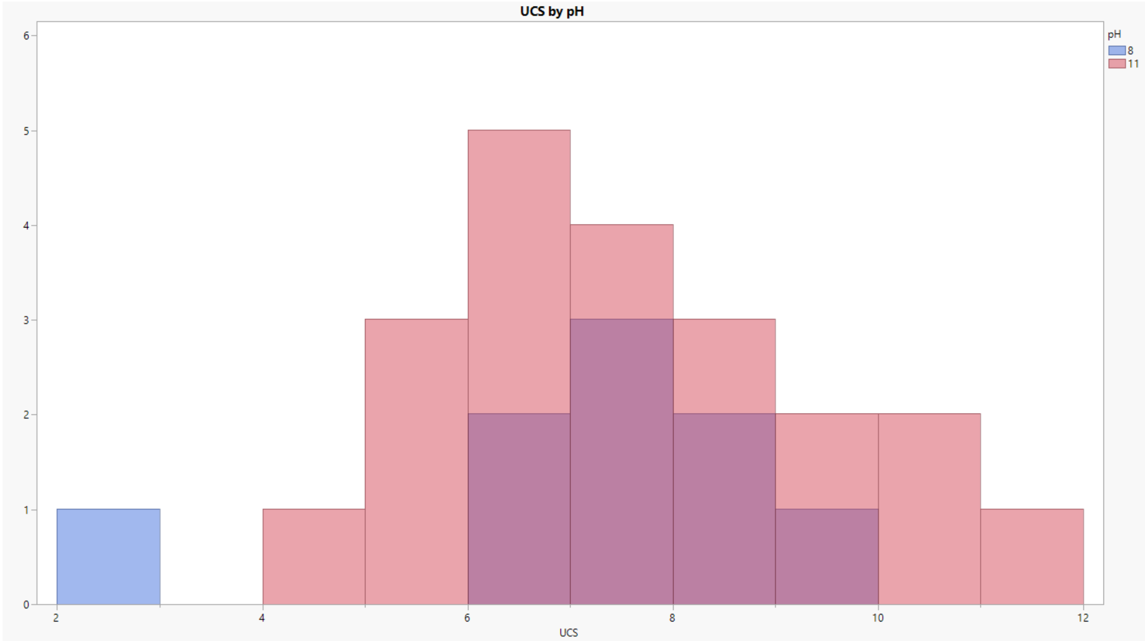

Figure 13. 7-day UCS testing by pH

When looking at the influence of the pH on the testing, the results are fairly improved from earlier analysis. In the 3-day testing, there is a clear improvement in samples tested in freshwater as opposed by the used water. While the UCS is improved, the range of results is not, with over a 30% variation in UCS even among freshwater testing samples. When reviewing the 7-day testing samples, we see that the, baring one outlier, that the freshwater samples have a much higher concentration of UCS. In contrast, the used water had over a 250% sample variation. This is highly concerning as natural wellbore conditions have water contaminated by natural compounds and may have a large range of potential pH values.

4. CONCLUSIONS

Portland cement is the current standard for wellbore cementing operations, with the material highly scrutinized by API standards. However, the production of this material is a notable, if not dominant, a contributor to the CO_2 in the planet's atmosphere. Because of this, the search for an appropriate alternative material has begun.

One material that shows promise, not only because it is potentially as strong as the incumbent but also because it is sourced from recycled materials, is fly-ash sourced geopolymers. However, these materials are not water activated and have no organization scrutinizing the testing or sourcing of the material like OPCs.

To better understand the material in comparison with API graded cement, this work generated and tested over 100 samples of geopolymer samples from the same original fly-ash source by API testing standards. The results of these tests were then displayed graphically in several methods.

A review of the results shows no relation between curing time and UCS highly different from Portland cements, but samples tested under identical conditions and curing times have large variation in UCS. Concerns in testing methodology with regards to the pH of the testing environment were investigated, revealing a potential influence of pH on UCS, but not a significant impact on the range of sample strength.

The large range in UCS, the potential influence of pH on the geopolymer slurry curing process, and potentially hazardous materials utilized in the mixing of the geopolymer slurry, raise significant concern for utilization of this material downhole without additional investigation and standardization.

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