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Impact of Admixtures on Pumpability and Short-Term Mechanical Properties of Rock-Based Geopolymer for Zonal Isolation and Well Abandonment

By

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Abstract

Ordinary Portland Cement (OPC) is the primary binder material used for primary cementing and plug and abandonment (P&A). This material has many advantages and some shortages, and it is well-studied when it comes to its properties. However, OPC consumes a large amount of raw material and energy for the calcination of limestone. It is responsible for a considerable amount of carbon dioxide (CO_2) emission and other greenhouse gasses. Hence, OPC is not an environment-friendly binder; several studies and investigations have been done to find a greener and suitable alternative for OPC.

Geopolymers are inorganic polymers and have binding properties with a network structure of aluminum and silicate. Studies have shown that geopolymer is an excellent alternative for OPC, thus having properties such as stability at elevated temperatures, lower Young's modulus, longer durability, a lower degree of chemical shrinkage, and lower permeability compared to OPC. However, controlling its pumpability is the current limitation that keeps geopolymers from being applied in the oilfields. For removing this current limitation and improving pumpability of the geopolymer slurry, retarding admixtures are added to delay the thickening of the slurry, while minimizing its setting time.

This study presents the impact of admixtures on pumpability and short-term mechanical properties of rock-based geopolymer cement (GPC). The properties that are analyzed include workability, setting time, and uniaxial compressive strength. Following additives are investigated throughout this study:

- Magnesium oxide (MgO)
- Sucrose
- Zinc & Potassium (Zn & K)
- Alumina oxide (Al_2O_3)

Acronyms

Al_2O_3	Aluminum Oxide
API	American Petroleum Institute
AABC	Alkali Activated Based Cement
BHCT	Bottom Hole Circulating Temperature
BHST	Bottom Hole Static Temperature
CO_2	Carbon Dioxide
GPC	Geopolymer Cement
GGBFS	Ground Granulated Blast Furnace Slag
HPHT	High Pressure High Temperature
MgO	Magnesium Oxide
OFITE	OFI Testing Equipment
OPC	Ordinary Portland Cement
P&A	Plug and Abandonment
RPM	Revolutions Per Minute
UCS	Uniaxial Compressive Strength
ZKS	Zinc, Potassium and Sucrose

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1 Introduction

Drilling process begins with reservoir discovery done by geophysicists where well location is identified, and objectives are summarized by petroleum engineers. The drilling process starts with site preparation to ensure the area is clear and ready for the rig. This follows up with setting up the conductor casing, which secures loose formations close to the mud line. Once the conductor casing is in place, the drilling is resumed, and surface casing is run and cemented into the formation. This process continues throughout the whole well construction.

After every casing is run into the well, primary cementing is necessary. Primary cementing is the process of placing cement slurry around the casing to support and protect the casing while preventing any migration and penetration of fluid in the system and annulus. Primary cementing is performed by pumping the slurry into the well and displacing the drilling fluid in the annular space between the formation and casing. The cement is placed in between wiper plugs to prevent mixing with drilling fluid and then pushed down with the help of drilling fluid. The slurry is pumped down with the plugs to the wellbore's bottom and then squeezed in between the casing and formation.

When a well has produced all of its capacity and its lifetime is over, it has to be permanently plugged and abandoned, also knowns as P&A operation. This operation usually undergoes by injecting Portland cement plugs in the well to isolate and seal fluid from the reservoir and formation. There has been recently an increase in the number of old wells in areas such as the Gulf of Mexico and the North Sea. Therefore, P&A has gotten great interest in making it safer, more environmentally friendly, and cost-efficient. [1] This has been intensified by the Deep Water Horizon incident when consequences of leaks to the environment and human beings were experienced.

Portland cement is a crucial material used in plenty of stages of both drilling and P&A operations, and therefore it is the most studied and common zonal isolation and P&A material. It got developed first time in England by Joseph Aspdin in the early 19th century. Fine powder Portland cement is usually produced by heating limestone and clay minerals and placing them in a type of oven called kiln to form solid material known as cement clinker; finally, these clinkers are ground, and 2 to 3 percent gypsum is added. There are several types of Portland cement available today, but the most common one is, without a doubt, Ordinary Portland cement (OPC).

1.1 Ordinary Portland Cement (OPC)

OPC is a binder that is mainly used for construction to produce concrete. It is also a crucial component in drilling operation and P&A. One of the shortcomings of OPC is its low durability when exposed to downhole chemicals and under high temperature, which is due to containing high calcium concentration. Another major negative impact of OPC is its role in global warming. OPC consumes a large amount of energy for the calcination of limestone, and it follows up with CO_2 release. Nitrogen oxide and SO_3 are also emitted into the atmosphere, which can result in acid rain. One metric ton OPC produces between 650 - 1100 kg CO_2, and about 1500 million tons of cement is yearly produced worldwide. These numbers are alarming; therefore, finding a suitable alternative is crucial to minimize CO_2 emission and energy consumption. There have been many investigations for greener cement production while improving the OPC properties, and as a result, the geopolymer cement has taken great interest [2-5].

1.2 Geopolymer

Geopolymers are inorganic polymers and a class of cementitious materials, introduced in 1978 by Joseph Davidovits. Geopolymer cement (GPC) has a calcium concentration less than 15 percent, which is the factor that differentiate it from other OPC alternatives such as alkali-activated based cement (AABC). The low calcium concentration of GPC results in an environment-friendly manufacturing process, high compressive strength, long-term durability, and high corrosion and sulfate attack resistance making it a sustainable alternative [6, 7].

Geopolymers have binding properties with a network structure of aluminum and silicate. It is produced by introducing a liquid phase known as the "hardener" to a solid phase (known as precursors), which is rich in aluminum and silicates (tetrahedral aluminosilicate). The hardener is an alkali silicate solution. Mixing the hardener and precursor phases results in creating long repeating chains of molecules made up of Si-O-Al-O bonds. The solid phase is an industrial waste material, and many alternatives can be used, including clays, fly ash, slag, rice husk ash, natural rocks, and zeolite. It is important to note that aluminosilicates are a very abundant compound in the earth's crust, giving geopolymer technology a great advantage. As hardener, sodium metasilicates and potassium metasilicates are the most used ones [4, 6].

1.2.1 Synthesis of Geopolymer

Whenever a geopolymer slurry is prepared, it goes through a chain of reactions before it sets and becomes a geopolymer cement. These reactions undergo three mechanisms, including dissolution, transportation/orientation, and polycondensation/geopolymerization [2].

The first phase of the reaction is dissolution, and it occurs when OH- ions in the hardener dissolve the precursor. This follows up with forming of Si—O—Si and Si—O—Al through the hydrolysis of aluminosilicates into alkaline solutions by the action of hydroxide ions. Precursor ions can then convert into monomers where Al^{+3} partly replaces Si^{+4}. This replacement allows bonding with positive charges from alkali silicate solution (K^+ or Na^+) to reach an equilibrium state. When monomers react with each other, oligomers with different structures during the process of nucleation are created. This phase of the reaction is called transportation, which is also known as orientation. Oligomers are small molecules and are known as the crucial unit to form a geopolymer. At last, polycondensation (also known as geopolymerization) occurs and results in 3D aluminosilicate networks due to the interaction of oligomers with each other. The degree of polymerization can depend on the size and charge densities of various alkaline cations as it affects the crystallization and formation of aluminosilicate chains. For example, K^+ cation has a large size and lower charge density than Na^+, which will result in a higher degree of polymerization. It is important to note that in the polymerization process, water is produced, unlike OPC, in which water is consumed [2, 8, 9].

Figure 1- Mechanism and synthesis of geopolymer [10]

1.2.2 Raw Materials – Precursors

The main elements for producing geopolymer slurry are alkali silicate solution and raw material (i.e., hardener and precursor). However, additives are added to improve the properties of the slurry. The raw material is used as a binder, and therefore it should be rich in aluminum and silicates to be eligible and produce geopolymer. Industrial waste, general waste (recycle waste), and natural materials are three raw materials with different characteristics, availability, application, and cost. There has been some investigation on the mechanical strength of the different raw materials where they concluded that industrial waste has the highest mechanical strength among the other two types of raw materials. There are, however, many parameters that can affect this statement, such as Si/Al ratio and curing condition.

1.2.3 Alkali Silicate Solution - Hardener

In the periodic table of elements, alkaline activators are divided into alkaline earth metals and alkaline metals. Earth metals have two active electrons in their outer shell; on the other hand, alkaline metals have only one. This factor makes the alkaline metals more reactive than alkaline earth metals; thus, they are often used as an alkaline activator [9]. Na_2SiO_3 and K_2SiO_3 are some of the common hardeners used in the geopolymer mixture. To adjust the molar ratio (SiO_2/M_2O) of hardener NaOH or KOH may be introduced. Potassium silicate solution is the alkaline activator used in this study.

1.2.4 Characterization of Geopolymer Properties

Geopolymer has many advantages when it comes to strength, durability, and chemical resistance over the most used binder in the world, OPC. Many studies have shown that geopolymer has high resistance to chemicals and corrosion. Moreover, it has high early strength, ductility, durability, and compact structure. Besides, geopolymer is more resistant at high pressure and temperature and has less contamination with oil-based mud.

1.2.4.1 Durability

The durability of cement can be described as the resistance of the material against sulfate, acid, chloride, and thermal stability over long time. Sulfate attack as an example is one of the well-known durability problems of OPC, leading to cracks, mass loss, and reduction of mechanical properties. The hydration product of OPC paste is calcium silicate hydrate (CSH), while in a geopolymer system, unlike OPC, the hydration product is an alumina-silicate matrix. Therefore, geopolymers react differently in an aggressive environment. It has shown in several

studies that geopolymers with fly ash and slag as their precursors have shown superior performance compared to OPC regarding durability and resistance against acid attack, alkali-silica reaction (ASR) of aggregates, freeze and thaw, and sulfate-rich solutions [11, 12].

1.2.4.2 Acid Resistance

Acid penetrates cement by dissolving both anhydrate and hydrated compounds of cement in addition to the calcareous aggregate. This reaction causes forming of water-soluble calcium, which is later leached out. Generally, siliceous aggregates are more resistant to acid attacks, and that is the particular reason for geopolymers being more reliable against acids.

1.2.4.3 Thermal Stability

Studies have indicated that OPC lacks thermal resistance and its mechanical properties is reduced at elevated temperature, which is due to chemical and physical alterations. As cement is a heterogeneous material, elevation in temperature penetrates both cement paste and aggregates. The strength of OPC can be affected significantly by elevated temperature due to limited thermal conductivity and phase separation. If the temperature rises to 400 °C, the hydration product of OPC, which is calcium hydrate, decomposes into water and calcium oxide. When the temperature is risen higher than 400 °C, dehydration of calcium hydroxide and rehydration of calcium oxide occurs, resulting in loss of strength. On the other hand, how geopolymers react to elevated temperatures depends on factors such as the type of precursors and the Si/Al ratio. However, in several scenarios and studies where fly ash and the rock-based precursor are used, an increase in compressive strength is observed up to 800°C [13].

1.2.4.4 Porosity

Porosity can be defined as the pore volume of cement to the bulk volume of it. Many factors affect the porosity of cement, such as cementing material, packing, variable grain size, overburden stress, and particle angularity and sphericity. According to previous studies, geopolymers have several types of porosity, either macroporous, mesoporous, or microporous. The factor that differs these types of porosity is variation in their pore's diameter in their solid phase [14]. The pore diameter for each type is:

- Microporous: Pores smaller than 2 nm in diameter

- Mesoporous: Pores larger than 2 nm in diameter

- Macroporous: Pores larger than 50 nm in diameter

1.2.4.5 Shrinkage

Every cement particle has hydration product around them, and between them are pores filled up with water. If these pores face loss of water, shrinkage occurs. That is due to the surface tension water molecules have. This tension fights to keep the molecules together, but it causes shrinkage and eventually cracks the concrete during water loss in the pores. In other words, shrinkage can be described as the process of volume reduction with time. Four different shrinkage types can occur on hardened concrete, including drying shrinkage, autogenous shrinkage, chemical, and carbonation shrinkage. On the other hand, there is only one potential shrinkage that can occur during concrete's plastic phase, which is called plastic shrinkage [15].

Shrinkage of GPC is very dependent on which precursor or hardener is used. In a study done by S.E. Wallah and B.V. Rangan, it has been shown that using potassium silicate solution instead of sodium silicates will result in a lower autogenous shrinkage in both ambient and high pressure and high temperature (HPHT) conditions. Another factor that impacts the shrinkage of the concrete is the size of the pores. It is important to note that water is produced during the chemical reaction of geopolymers. The water product will either evaporate or enter the pores of the hardened concrete. Since GPC is microporous, the induced drying shrinkage is also very low [16].

1.2.5 Retarding Admixture

After all the explanation and description above, it is safe to say that geopolymer might be an ideal alternative for OPC. It has greater properties such as stability at elevated temperatures, lower Young's modulus, longer durability, a lower degree of chemical shrinkage, and lower permeability than OPC. On the other hand, the neat recipe for geopolymer still needs prolongation of pumping time long enough for safe primary cementing and P&A applications. To improve properties and solve such problems, chemical admixtures are added to the system. Chemical admixtures that extend the workability (pumping time) of the slurry are called retarders.

Counting geopolymer as a young aged technology compared to cement, there is no scientific explanation of how retardation occurs in the system or how the mechanism is. However, some theories give a brief imagination of how retardation occurs. When the geopolymer slurry is prepared, there are many free hydrogens and hydroxides in the system. When these hydrogen atoms get anticipated to create Si-O-Al-O, the paste will set and become cement. If these hydrogens are captured by additives and then released later on, that additive will act as a

retarder. This is a theory that needs investigation furthermore; however, it cannot be looked aside. Retarders can be produced from two following types of material:

- Inorganic materials: oxides of Zn, magnesium salts, oxides of Pb, phosphate, borates and fluorates.
- Organic materials: hydroxycarboxylic acids, carbohydrates, salts of lignosulphonate acid, Ca, Na and NH_4.

Retarders can affect the geopolymer slurry in two different ways. It can have an impact on both workability and setting time of the slurry and each of them have different mechanism and functions.

1.2.5.1 Magnesium-Oxide

Magnesium-oxide (MgO) has shown in several studies that it had a great impact on the short-term mechanical properties of AABC. The result indicates that reactive MgO reduces chemical shrinkage, autogenous shrinkage, and drying shrinkage significantly. The particular reason for this circumstance is forming of $Mg(OH)_2$ crystals, which produce expansion. The expansion refines the pore size of pastes, which results in compressive and flexural strength increase [13]. Studies have also shown that adding MgO accelerates the hydration process of AABC in early ages due to rapid reaction, which also causes an increase in compressive strength and high early strength [17-20].

$$MgO + H_2O \rightarrow Mg(OH)_2$$
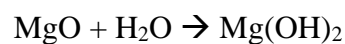
Majority of the studies have added MgO with different reactivity and weight percentage to AABC pastes. Most studies concluded that 7.5% of high reactive MgO made the most improvement on the mechanical properties such as shrinkage compressive strength and thermal conductivity. Very few studies have shown the impact of MgO on workability and setting time of geopolymer slurry. The role of Mg^{2+} on polymerization of hardener is a concern that has been less explored. Therefore, it is interesting to observe the effect of MgO on the workability of rock-based geopolymer slurry.

1.2.5.2 Sucrose

Sucrose also known as sugar is a well-known retarder for OPC and there are numerous studies regarding this. Sugar is used to delay the setting-time and extend the workability of the slurry. This retardation occurs due poisoning of nucleation site, which follows with delay of

cement hydration. This means that the production of hydration products such as calcium silicate hydrate (C-S-H) is reduced and retarded [21].

There have been several studies on both geopolymers and AABC covering the effect of sucrose on their setting time, workability and compressive strength. Studies have shown that sucrose also acts as a retarder and delays the polycondensation and results in longer workability. They have also added that sucrose does not have significant change on compressive strength but observing decrease in it is possible. Khalifeh [22] have indeed studied effect of sucrose on rock-based geopolymer and concluded with that up to 2wt% of sucrose have retardation effect on the system and does not affect the compressive strength of the cement. Another effect of sucrose, which has been observed in the previous studies is that it has potential to delay the setting time significantly dependent on the composition of the system. A strong retardation effect on setting-time is not ideal since as mentioned, an ideal cement for drilling operation must have a controllable workability and rapid setting time [23-25]. However, if delay in setting time is observed it can be accelerated with other additives.

1.2.5.3 Aluminum-Oxide

As is mentioned, geopolymer is a system with a network structure of aluminum and silicate. It is also important to note that the ratio of silicate and aluminum plays a big factor in the mechanical properties of the geopolymer. According to many articles adding alumina-oxide to this system will lower the Si/Al ratio and affect the mechanical properties of the geopolymer. H.Tchakoute Kouamo et al.[26] have previously studied the effect of alumina on geopolymers with metakaolin and volcanic ash as their precursors. In this study, they have mainly focused on the compressive strength and microstructure of the geopolymer. They concluded that alumina increases compressive strength and "improves the mechanical properties of the material by increasing the geopolymeric phase of the material, which helps to imprison the unreacted/partially reacted crystalline phase of the material starting material." However, when the amount of alumina was increased to 40wt%, compressive strength got reduced [27]. Some other studies done by De Silva et al [28] on high calcium fly ash-based geopolymer system concluded that increasing Al_2O_3 content decreases the setting time and workability. In addition, no significant changes were observed on its compressive strength.

The reason alumina-oxide is an interesting additive to study and analyze, is to observe how decrease in Si/Al ratio affects the workability, setting time and compressive strength of rock-based geopolymer system. This study will also give a brief explanation of how other additives

that decrease the Si/Al ratio will affect workability and setting time. Besides, it is also a study that has not been specifically done before.

1.2.5.4 Zinc & Potassium

Salt metals are generally known to be retarders for OPC. Previous studies have confirmed that zinc oxide manipulates the hydration process of OPC and acts as a retarder in the system. Some studies have shown that zinc oxide has also performed as a retarder in high and low calcium alkali-activated materials (slag and metakaolin systems, respectively). By adding zinc to the system, some delays in the activation process were observed and therefore based on previous studies, potassium can be added to solve this delay. Hence, colleagues' previous observations and studies, the combination of zinc and potassium, are interesting additives to study. The main goal of this study is to observe a significant retardation effect; therefore, sucrose is added to the zinc and potassium combination [15, 29].

1.3 Geopolymer and Alkali Activated Based Cement (AABC)

Since greenhouse gas and CO_2 emission has become a genuine concern, there have been many studies regarding finding an alternative to Portland cement resulting in great interest in geopolymers and AABC. Unfortunately, there are many misunderstandings regarding the theory and concept of geopolymers and AABC, and it is important to note that geopolymers and AABC are not the same technologies.

It has shown that geopolymers and AABC have different chemical reactions and structures. The chemical reaction of geopolymerisation produces potassium or sodium aluminum silicate hydrate (K-A-S-H or Na-A-S-H) gels, and the alkali cation (K^+ or Na^+) is placed inside the 3D network. On the other hand, AABC chemical reaction results in calcium aluminum silicate Hydrate (C-A-S-H) gels, and the placing of alkali cation (K^+ or Na^+) are outside of the structure. Calcium concentration is also a factor that separates these two technologies. AABC has a calcium concentration above 20 percent, and on the other hand, geopolymer has a calcium concentration under 20 percent, making it more environmental-friendly with less CO_2 footprint. Another factor that differs these two technologies from each other is their sodium and potassium hydroxide (NaOH, KOH) concentration. A concentration above twenty percent of these chemicals makes the material AABC and not geopolymer [6, 30].

2 Objective

Geopolymer technology is young aged and still has not been used in oilfields. This is mainly due to its setting time, workability, making it not the optimal material for primary cementing and P&A. However, studies have shown that using additives can solve these downsides and improve its properties without affecting the long-term mechanical properties of the cement. The goal is to have controllable workability and setting time while having sufficient early compressive strength.

There are many additives such as MgO, Zn, and sucrose used for improving OPC properties in the industry. Hence GPC has a different composition; these additives might not have a similar effect on this system. This study aims to analyze the impact of different additives that are expected to act as a retarder based on previous studies, on the short-term mechanical properties of rock-based geopolymer cement (GPC). The properties that are analyzed are workability, setting time, and uniaxial compressive strength, and the following additives are studied throughout this study:

- Magnesium oxide (MgO)

- Sucrose

- Zinc & Potassium (Zn & K)

- Alumina oxide (Al_2O_3)

3 Methodology

In this part of the study, the materials and dosage of them are mentioned. This chapter will also have a great focus on introducing the used equipment and describe the procedures. This thesis follows research done by the University of Stavanger and Safe Rock AS, and the data is confidential. Therefore, the recipes and materials used cannot be described in detail.

3.1 Materials

There are mainly two components that are base of a geopolymer, the precursors, and the hardener. The precursor is from a source material and is rich in silica and aluminum. In this study, a specific rock was used to produce a rock-based geopolymer. Commercial aluminosilicate minerals were added to normalize the chemical composition of the used rock. The hardener, on the other hand, is silicate-rich and used as an alkaline activator. Hardener is the component that is mainly responsible for the dissolution of the minerals and binding them. In this study, potassium silicate was used as a part of the hardener. As mentioned above, every sample has two main components, which are the precursors and the hardener. The total weight of the slurry is around 1057 grams, where 700 grams is composed of precursors and the rest 357 grams as the hardener. The component of solid phase content is displayed in Table 3.

Table 3 - Solid Phase Content

Solid Phase Content	
Precursors	**Wt%**
SiO_2	60.02
Al_2O_3	10.88
Fe_2O_3	0.58
CaO	15.04
MgO	8.07
Na_2O	1.84
K_2O	1.62
TiO_2	1.15
MnO	0.01
SrO	0.01
BaO	0.01
S^{2-}	0.61
LOI	0.15
Total	100

3.2 Equipment

Many tools are used in this study to prepare and analyze the geopolymer slurry. Each piece of equipment has its own procedure and functions.

3.2.1 Mettler Toledo Scale

Mettler Toledo scale is used for measuring the weight of the different components of the mixture. This scale has an accuracy of +/-0.01 g. Figure 3 shows the specific scale used for this project.
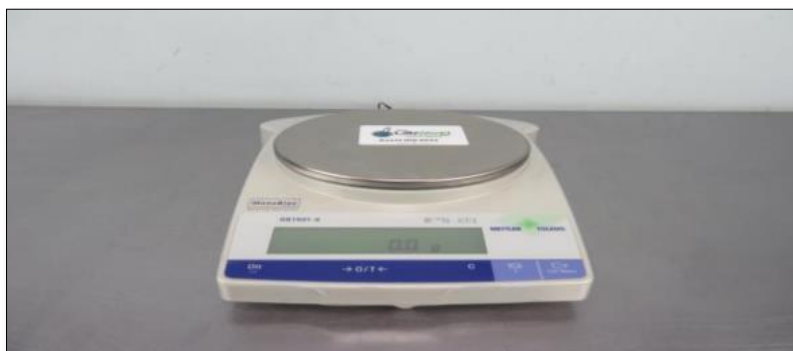
Figure 3 - Mettler Toledo Scale

3.2.2 OFITE Model Commercial Blender

This equipment is used to mix the precursor and hardener and prepare the slurry. There are two speed levels used to prepare the slurry following API procedure standards. For preparing and mixing the hardener, 4000 RPM speed level is used. When it comes to introducing the precursors, a preprogrammed setting is used, which automatically varies the speed during mixing. Mixing of the hardener and precursors has a 50 second duration which the 15 seconds of that is on 4000 RPM and for the rest 45 seconds it goes up to 12000 RPM. The first 15 seconds is when the precursor is added to the hardener, and the reason for lower speed at this section is to prevent and minimize losses and dust. The used blender in this study is present on Figure 3.1.

Figure 3.1 - OFITE Commercial Blender

3.2.3 Molds

Molds are cylindrical plastic-shaped containers showed on Figure 3.2 used to contain samples for curing. These molds prevent absorption of moisture and oxidation of the specimens.

Figure 3.2 - Molds Used to Store Samples

3.2.4 Atmospheric Consistometer

Atmospheric Consistometer is one of the most used equipment in this project, and it follows API standards spec 10A/10B2. This equipment consists of the machine itself, cells, and blades that are placed inside the cells. This equipment provides a simulation of bottom hole circulation at atmospheric pressure with temperature ramp up. The consistometer is used for two purposes. The first one is for measuring the consistency of the slurry in Bearden units of consistency (Bc) which refers to measuring workability and setting time. The second purpose of using the ATM-consistometer is to condition the slurry for measurements, including rheology, viscosity, and compressive strength. The equipment is connected to a computer with LabVIEW2018 installed to collect and save the measured data. Figure 3.3 displays of the consistometers used in this project.

Figure 3.3 - Atmospheric Consistometer

3.2.4.1 Workability

It should be assured that the slurry that is being used in the oilfield is capable of being pumped in a certain period. This certain period is known as workability and is a key and sensitive factor. If the predicted workability is unstable, it can cause serious problems. Workability is measured by using an ATM-consistometer. A slurry is pumpable when its consistency is lower than 40 Bearden units of consistency (Bc); thus, the time it takes for a slurry to reach 40 Bc is considered the workability of the slurry. The 40-100 Bc is called risky and it is showing the gel development of the slurry.

3.2.4.2 Setting time

Setting time is considered as the time it takes for the slurry to set after it is no longer pumpable. In another way, it can be described as the time it takes for the slurry to go from 40Bc to 100Bc. Both workability and setting time can be variable and easily affected by regulating liquid to solid ratio and alkaline activators concentration.

3.2.5 pH-Meter

In this study, Inolab pH 7110 was used to measure pH of the slurry. Electrode of the pH meter is kept in a 3M KCl fill solution to maintain a constant potential of the Ag/AgCl electrode. The electrode is cleaned with deionized water before and after measurements. Figure 3.4 shows the exact pH-meter used in this project. This equipment is not the most ideal choice for pH measurement of a slurry since according to previous studies, using fiber optic sensors and embedded metal/metal oxide electrodes is the most effective non-destructive method for monitoring pH of slurries. [31]

Figure 3.4 - pH meter used in this study

3.2.6 D-Series Syringe Pumps

Teledyne ISCO D-Series single-pump systems consist of a pump module and controller. This equipment is used to pressurize the curing cells and keep a constant pressure during the curing time. The machine pressurizes the cell by pumping in water with a constant flow. In this study, the samples are pressurized to 2000 psi and kept at the same pressure throughout the curing process. It is essential to increase the pressure flow gradually to not shock the samples and affect their properties.

Figure 3.6 - Cells Used For Curing

Figure 3.5 - Teledyne ISCO D-Series Single-Pump

3.2.7 Cutting Machine

Samples that are cured in molds must be evened before it gets crushed for uniaxial compressive strength measurements. To get reliable data and minimize the error in the measurements, the force must be distributed evenly along the whole surface of the sample. Thus the demolded samples must have perpendicular and flat ends on each side.

Figure 3.7 - Cutting Machine

3.2.8 Hydraulic Press Machine

After curing and cutting, the samples are brought to the hydraulic press machine to measure their uniaxial compressive strength. Toni Technik-H's equipment, the hydraulic press machine used in this study, applies force to the sample until it fails to handle the force and breaks. The loading rate of this machine is 36 KN/min, and it is directly connected to a computer with the TestXpert software, which executes the uniaxial compressive strength. Data collected from this equipment is used to measure Young's modulus and compressive strength.

Figure 3.8 - Equipment Used to Measure UCS

3.2.8.1 Conditioning of the slurry

The process of a UCS test begins by conditioning the slurry. The goal by doing conditioning is to simulate the slurry's conditions when it is pumped into the wellbore and placed around the casing. The OFITE atmospheric consistometer is used for this simulation which provides high-temperature applications and homogenous mixture with the blade placed inside of the cell.

3.2.8.2 Curing time

It has shown in several studies that the curing time of the sample significantly affects the progress of geopolymer strength development. The strength develops as time goes, and that is due to alkaline saturation and product densification. When a geopolymer slurry is made, the reaction begins immediately and begins to thicken. It has been estimated that the GPC gains approximately 85% of its compressive strength after the first few hours [9]. Khalife [11] has indeed studied the mechanical properties of a rock-based geopolymer in 2016 and confirmed that his system could have an increase in mechanical properties up till one year, dependent on

the curing environment and temperature. It is also important to note that type of raw material, and alkali solution or water content are factors that must be considered for getting an optimum condition for curing.

3.2.8.3 Curing temperature

Curing temperature can have a significant effect on the workability of the geopolymer slurry. Pavel [32] concluded that the workability of a metakaolin-based geopolymer was increased from four hours at ambient temperature, to four days after it was treated with low temperature (10˚C). The same concept goes on when the sample's temperature is risen. When a geopolymer cement is treated with high temperature, the workability will decrease, and the early compressive strength will increase according to previous studies. One should note that there is no linear relationship between temperature and setting time of geopolymeric slurries. The goal of condition and curing is to simulate the environment that cement will have in the wellbore. In this study, the samples are cured with dry heat at 70°C BHST and conditioned at 50°C BHCT.

3.3 Procedures

3.3.1 Mixing

There are different ways to prepare and mix the solid and liquid phases. Not having a similar mixing procedure for every sample increases the error and gives unreliable data. Therefore, it is crucial to be consistent with the mixing procedure and follow the same step for all samples. Following procedure is followed throughout the whole project:

1. Preparing and weighting every element of the mixture
2. Prepare the precursor by mixing solid phase components at dry condition
3. Prepare the hardener by adding the additive to the liquid phase components and mixing it for 15 seconds at 4000 RPM using OFITE Model Commercial Blender
4. Turning on the blender by using the automatic button which as previously described consist of a 50 second mixing program which the first 15 seconds are at 4000 RPM and the rest at 12000 RPM according to API RP 10B-2 standards.
5. The solid phase should be introduced during the first 15 seconds of the mixing process.
6. At last a spatula is used to clean around the cup while it is mixing to minimize loss of solid phase.

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3.3.2 Consistency measurement

The techniques for consistency measuring according to API Spec 10A/10B2 standards are:

1. ATM consistometer contains a cell with a hole at the bottom which a blade (paddle) is placed into it.
2. Pouring the slurry into the cell to the maximum limit which is marked on the inside of the cell.
3. A specific lid is placed on the cell which the top of the paddle in the cell connects to its torque shaft.
4. The cell is afterwards placed into a bath of mineral oil in the machine. The mineral oil helps to transfer the heat to the cell and then the slurry.
5. The string is then connected to the lid on the cell. This string transfers the amount of torque applied which is afterwards converted to consistency.
6. The main, motor and heat button can now be switched on. Once the motor is turned on the cell will rotate with speed of 150 RPM.
7. The temperature is then set as desired. After every five minutes the temperature will raise five degrees.
8. Once the consistency is closing to 90Bc, the cell filled with slurry is removed.
9. The slurry is then poured into a mold and placed in the oven at 70°C to make sure it sets as expected. The remaining slurry is disposed.

3.3.3 Conditioning

The techniques for conditioning are similar to measuring of consistency however there are some difference between them, which are:

1. For conditioning it is not required to connect the string to the lid since there is no need for consistency measurement.
2. After the slurry is reached the desired temperature, it will be in the machine for 10 minutes and then be taken out. The slurry is not taken out when it is closing to set, however it is taken out when the slurry is well conditioned at desired temperature.

3.3.4 Curing

After the sample are conditioned, following procedure is applied for curing:

1. Small hole is drilled on the lid of the molds for letting water pressurize the samples in the cell.
2. Conditioned slurry is poured into the molds.
3. The curing cell is filled with hot spring water to avoid any temperature shock to the slurry.
4. The molds are placed in the cell.
5. The cell is then properly closed to prevent any pressure leakage.
6. At last the cell is pressurized and then placed in the curing oven.

3.3.5 pH Measurement

1. The electrode is taken out from the 3M KCl fill solution.
2. The electrode is cleaned with deionized water and dried gently with tissue.
3. The electrode is place into the slurry and it is important that the electrode is not touching surface of the cell or container.
4. After few minutes, the pH meter will be stabilized, and the electrode can be taken out.
5. The electrode must be then cleaned with deionized water and placed back into the 3M KCl fill solution.

4 Results and Discussion

The data collected from the different additives are compared, presented and discussed below.

4.1 Workability and Setting time

As mentioned previously, for measuring how long the geopolymer slurry is pumpable (workability) and how long it takes for it to set (setting-time), ATM consistometer is used. Workability is defined as the time it takes for the slurry to reach 40 Bc. On the other hand, the setting-time is addressed as the time it takes for the slurry to ramp up from 40 to 100 Bc. The temperature during measurements is increased from ambient 23°C to 50°C, and it is ramped up five degrees celcius every fifth minutes. After the data is collected, it is transformed and plotted on to excel.

All the plots have time in minutes as the x-axis and the consistency in Bc as y-axis, and in addition, the temperature ramp-up is shown on the plots with a black colored line. Looking at the presented graphs, it is essential to pay attention to how long it takes for the slurry to reach 40 Bc and if the end of the graph is right-angled or not. The initial consistency is also analyzed; hence it is ideal for primary cementing to have a slurry with low consistency for less complex pumping operation.

4.1.1 Magnesium-Oxide

MgO is an additive that several studies had been done on its effect on compressive strength of GPC and AABC. However, very few studies have covered the effect of this additive on workability and setting-time of a rock-based geopolymer. By considering the expected chemical reaction, it is expected that the MgO captures the free hydrogens in the geopolymer system and acts as a retarder. This means recipes with MgO should be pumpable for a longer period compared to the neat recipe. MgO being a pH stabilizer is also a factor that gives such expectations. The MgO used for this study is a 99% pure MgO in powder form from Schlumberger, and it is added to the neat recipe with seven different concentrations starting from one (MP-1) to seven (MP-7) percent of the solid phase total weight (wt%). Figure 4 contains the data collected from this test.
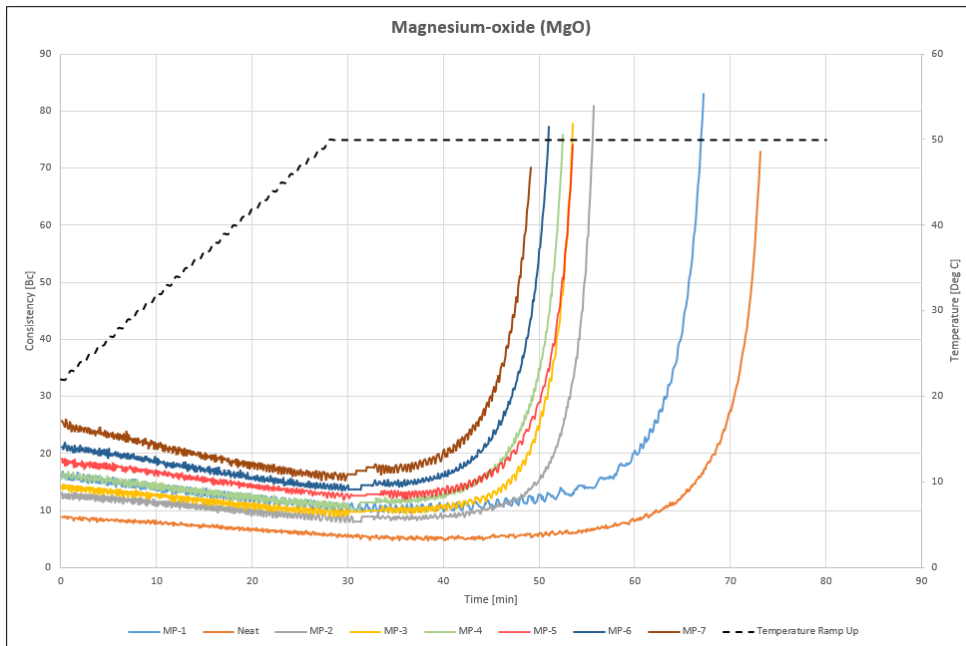
Figure 4 – MgO Consistency Data

Table 4 – MgO Concentration

Recipe	MgO [wt%]
MP-1	1
MP-2	2
MP-3	3
MP-4	4
MP-5	5
MP-6	6
MP-7	7

As shown in Fig.4, MgO has acted as an accelerator. Every extra percent of MgO has pushed the graphs to the left side of the neat recipe. The neat recipe reaches 40Bc after approximately 73 minutes. On the other hand, by adding 7wt% reactive MgO, the workability gets reduced to 47 minutes. The reduction is significant; thus, it is safe to say that MgO acts as an accelerator in this system. Besides, MgO has an effect on the viscosity and thickness of the slurry. By analyzing the initial consistency, it is observed that this factor is increased significantly. The neat recipe starts at 9 Bc; that said, the recipe with 7wt% MgO has an initial consistency of 25 Bc. This change results in an increase in viscosity and thickness of the paste. This effect is also observed during the mixing process of the slurry. The setting time, however, stayed constant throughout all the recipes.

The question now is, why does adding MgO result in such data when it was expected to act as a retarder? Well, it is not easy to analyze and describe the exact chemical reaction that occurs by adding MgO, but there is a potential explanation for it. MgO has two free capacity, with atomic number of 12. It is a large atom and can engage several silicates present in the alkali silicate solution. This can release Mg^{2+} as result of chemical interaction between the hydrogen groups (OH^-) and aluminosilicates present in the slurry. This theory is not confirmed thus needs further investigation.

Since MgO is known to be a pH stabilizer in drilling fluids, the consistency measurement is paused when the slurry reaches $50°C$ (after 30 minutes) to measure slurry's pH. Trace of pH measurements are visible on Fig.3 at 30 minutes range. The pH is also measured before (t=0) and after (pH final) consistency measurement. By comparing these pH values, it is possible to observe if MgO is able to minimize pH reduction after increase in temperature and circulation in the atmospheric consistometer. Since taking out the samples from the consistometer can harm the consistency data, pH measurement time is minimized. Hence the pH measurements are subjected to small uncertainty. Following table presents pH measurements for the samples.

Table 4.1 – MgO pH Measurements

Recipe	pH at t=0	pH at t=30 min	pH Final	pH Reduction
Neat	13.02	12.85	12.70	0.32
MP2	13.00	12.92	12.70	0.30
MP3	12.92	12.80	11.92	1.00
MP4	13.03	12.80	12.30	1.00
MP5	13.04	12.77	12.40	1.00
MP6	13.04	12.81	12.63	0.41
MP7	12.70	12.40	12.01	0.69

Higher pH value provides a better dissolution mechanism in the system, which is a factor that is favored. Since the system has already a high pH, it is ideal with a minimized pH reduction when the slurry undergoes increase in temperature. As it is shown in table 4.1, MgO has not reduced the pH reduction. According to the collected data, the neat recipe had the lowest pH reduction and adding MgO even resulted in increase of pH reduction which is opposite of what was expected. This means that the hydrogen concentration of the system has increased by elevating slurry's temperature. Particular reason for these unexpected results can be the unique composition of the system. As mentioned, MgO has not been previously used as an admixture in a rock-based geopolymer system.

4.1.2 Sucrose

Sucrose is a well-known retarder for OPC, and it has shown in some studies that it can have the same effect on GPC and AABC. The retardation occurs by delaying the hydration process of the system. Therefore, it is expected that sucrose acts as an effective retarder. For analyzing this effect, different concentrations of sucrose are added to the neat recipe starting from 1wt% (SP-1) to 4wt% (SP-4). The result is presented in Figure 4.1.
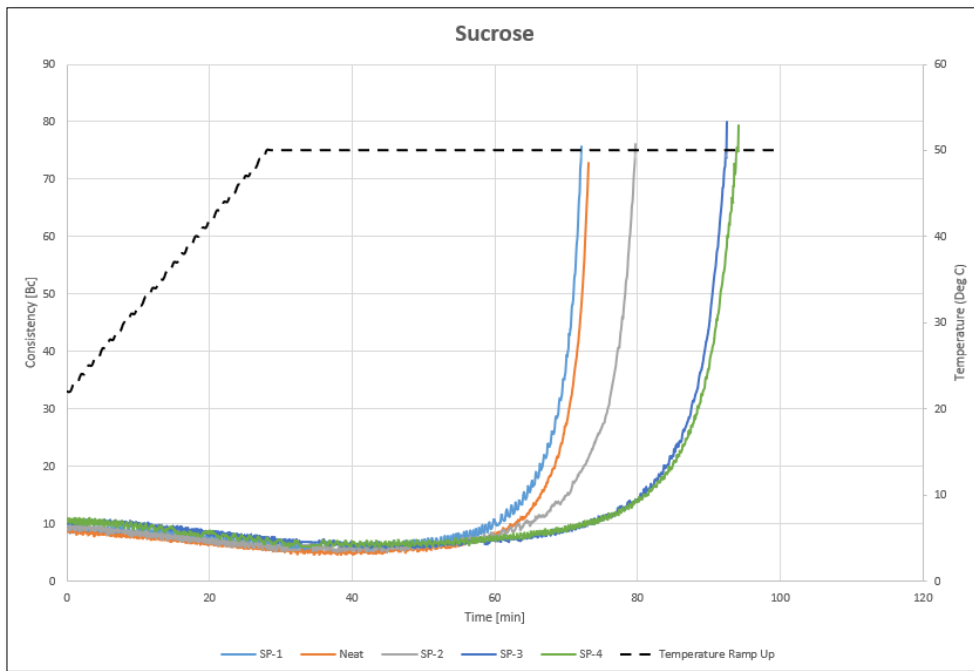

Table 4.2 – Sucrose Concentration

Recipe	Sucrose [wt%]
SP-1	1
SP-2	2
SP-3	3
SP-4	4

Figure 4.1 – Sucrose Consistency Data

Sucrose fulfilled the expectation. By looking at the graph, sucrose has clearly acted as a retarder, and its effect has increased for every weight percent sucrose added to the system. However, by adding 3wt% sucrose, the system got somehow saturated, and the retardation effect got reduced. Therefore, it is safe to say that 3wt% sucrose gave the best retardation effect. By adding this amount of sucrose, the workability is increased by approximately 20 minutes. It is also interesting to observe that 1wt% sucrose did not affect the system and that there is no effect on the initial consistency.

When 3 and 4wt% sucrose is added to the system, some setbacks in the setting-time are visible at 75-80 Bc. The degree of these setbacks is increased in samples with zinc and potassium, which will be presented further in chapter 4.1.4. The latter retardation effect has also been observed on many other samples with sucrose as an additive. Hence, it is proved that sucrose acts as a late retarder, which weakens the right-angle set. This counts as an adverse

effect for well-cementing usage. However, adding another additive can improve and solve this negative effect. Following chemistry structures presents the three possible reaction mechanisms of sucrose with the geopolymer system:
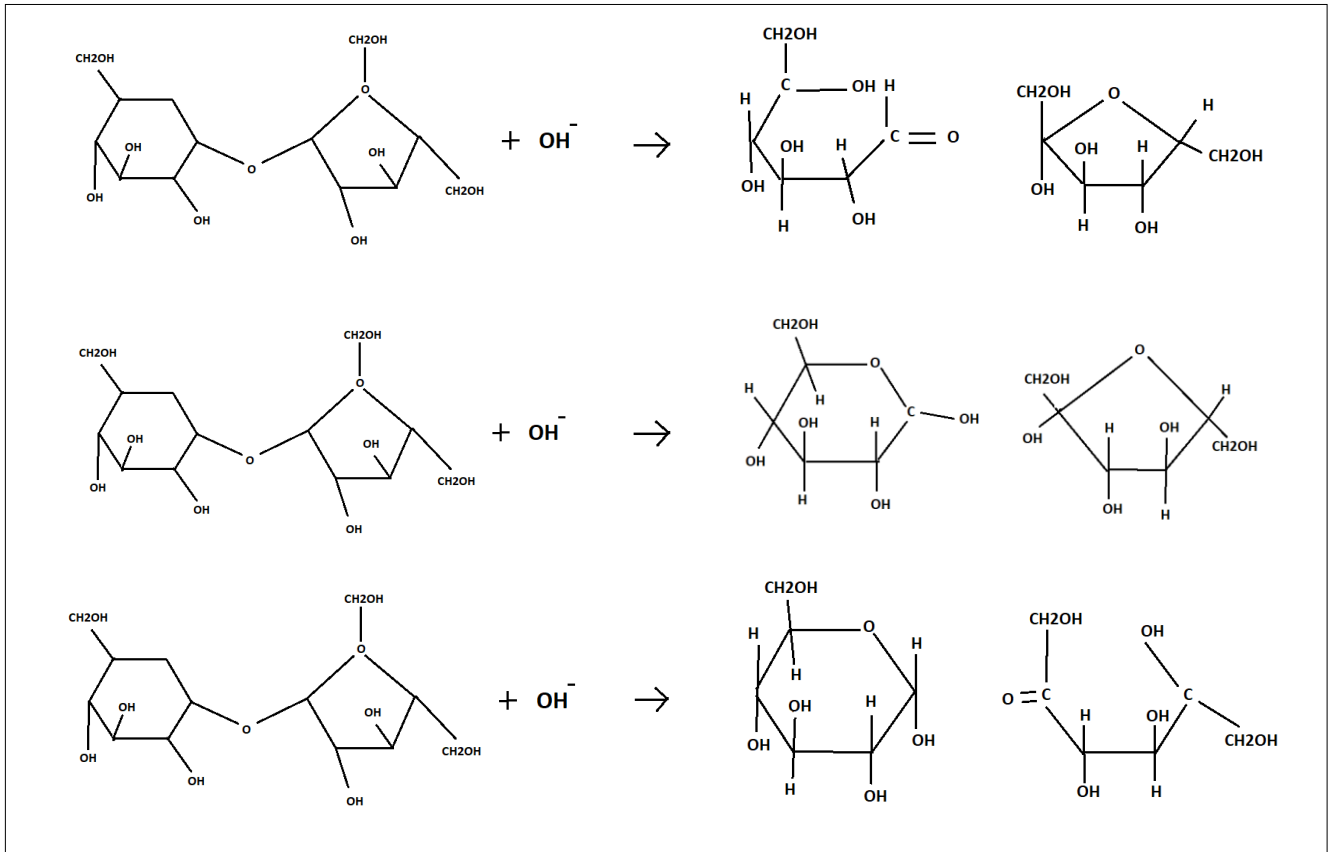

Figure 4.2 – Potential Reaction Mechanisms of Sucrose

4.1.3 Aluminum-Oxide

Several studies have shown that Al_2O_3 increases compressive strength and improves the mechanical properties of GPC. However, there is no studies showing its effect on rock-based geopolymer. As Al_2O_3 has an oxygen atom in its structure, it is expected that, it captures hydroxyl (OH^-) in the system and acts as a retarder. Al_2O_3 is added with two concentrations of 1wt% (AP-1) and 3wt% (AP-3) to the neat recipe and collected data is presented in Figure 4.3.
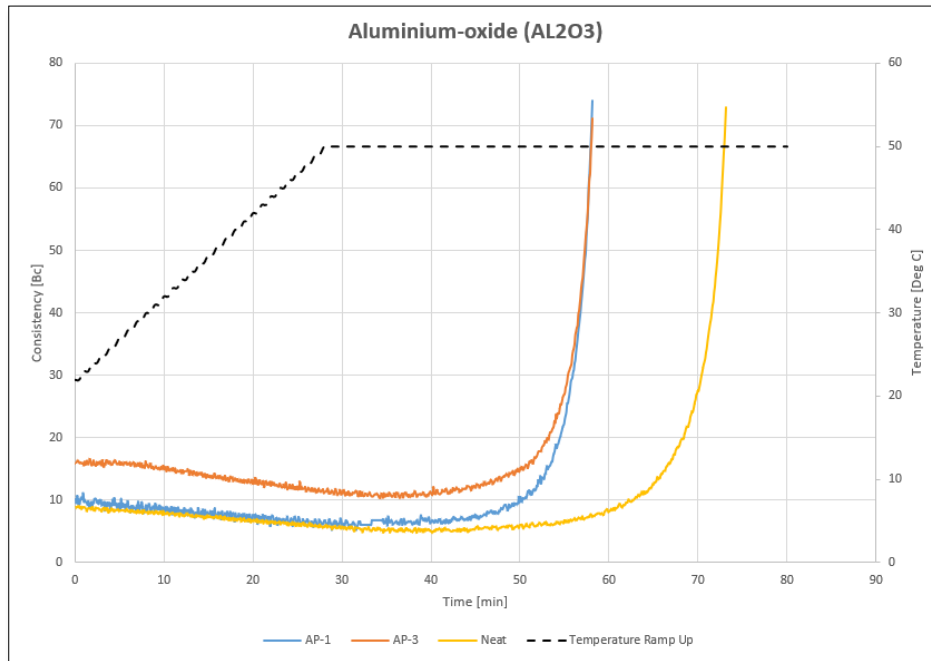

Table 4.3 – Al$_2$O$_3$ Concentraion

Recipe	Al2O3 [wt%]
Al-1	1
Al-3	3

Figure 4.3 – Al2O3 Consistency Data

As it is shown on the graph, Al_2O_3 acts as an accelerator, but the interesting part of the result is that there is no difference in workability of the slurry when 1 or 3% of Al_2O_3 is added. Both have approximate workability of 57 minutes, while the neat recipe is pumpable for 72 minutes. This means that the system gets immediately saturated to a small amount of Al_2O_3. Another impressive effect that is observed from this data is that Al_2O_3 improves the right-angle set. By looking closely at the end of the graph, samples with Al_2O_3 have a better right angle set than the neat sample. This effect of Al_2O_3 may be helpful for samples with sucrose where a poor right-angle set is observed. Following chemical reaction describes the chemical interaction between Al_2O_3 and hydrogen groups (OH^-):

$$Al_2O_3 + 2OH^- \rightarrow 2AlO_2 + H_2O$$

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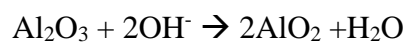
It is important to SP-3 has a higher initial consistency SP-1, because a different consistometer with an 8 Bc error in initial consistency value was used for this sample.

4.1.4 Zinc, potassium, sucrose (ZKS)

Salt of zinc is an inorganic chemical retarder for cement. This additive has not been tested on rock-based geopolymer before, but as mentioned in the introduction, with the data collected by a colleague, he has confirmed that it acts as a retarder in a rock-based geopolymer system. In this test, two retarders (zinc and sucrose) are combined and added to the mix. The pumpability of zinc, potassium and sucrose is independently examined before the pumpability of the complex sample ZKS is analyzed to observe how each admixture affects the neat recipe. Figure 4.4 presents the resulted data.
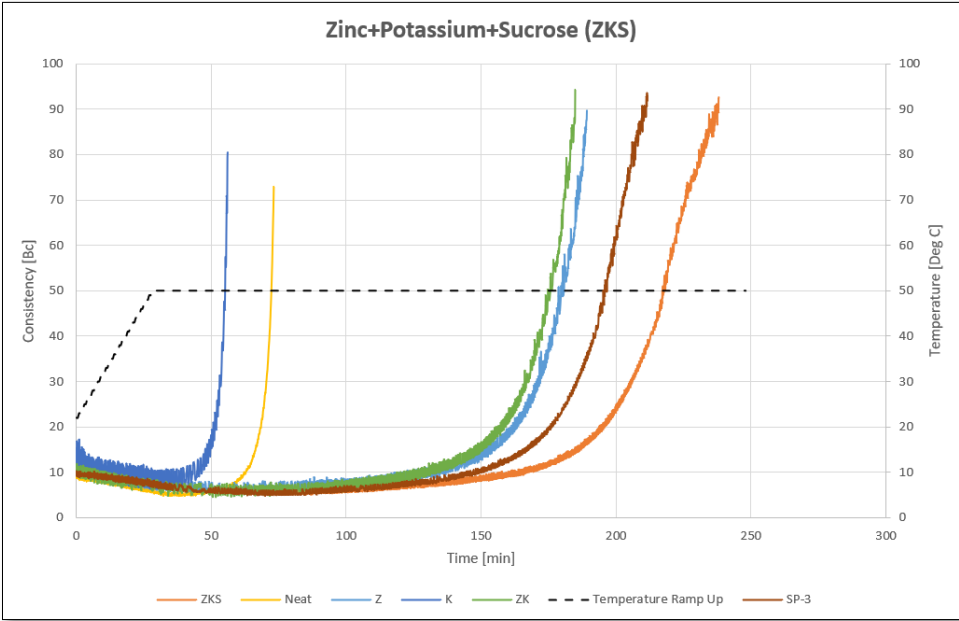

Table 4.4 – ZKS Recipes

Recipe	Potassium [wt%]	Zinc [wt%]	Sucrose [wt%]
K	0.14	X	X
Z	X	0.57	X
ZK	0.14	0.57	X
SP3	X	X	3
ZKS	0.14	0.57	3

Figure 4.4 – ZKS Consistency Data

The potassium acted as an accelerator and has shortened the workability by about 20 minutes. It has also resulted in increased right-angle set, which is the exact reason this additive is added to the system. Furthermore, effect of zinc by itself as an admixture, acted just as expected and increased the workability impressively by 100 minutes. Combination of zinc and potassium resulted in a similar graph to the Z recipe, but with slightly lower workability and increased right-angle set. Recipe ZK has inherent qualities such as low consistency and great right-angle set which gives it a potential to be applied to oilfields; however, its workability must be extended even more and that is why sucrose is added.

By adding sucrose to the ZK recipe, the workability has extended by 50 minutes, and that is not the only effect it had. As discussed above some setbacks are observed at 90 Bc which is the effect of sucrose in the system. These setbacks affect the setting time and delay the slurry to reach 100 Bc. However, all the samples that had right-angle set problem have set after few hours in the heat-oven at 70°C. In conclusion, the sample with zinc, potassium, and sucrose as its additive gave the best retardation effect out of the other samples.

4.2 Uniaxial Compressive Strength

Geopolymer is known to have reasonable uniaxial compressive strength for well cementing and P&A usage; therefore, it is expected that all the samples have the minimum required UCS after seven days of curing. As mentioned previously, for measuring UCS, samples are conditioned and afterward brought to the cutting machine to get the ends of the samples evened. The process is continued by taking samples to the hydraulic press machine for UCS measurements. The force applied on the hardened samples by the hydraulic press machine has a loading rate of 36 KN/min, and the data is collected with unit kN. The data is afterward transported into excel, and its bar diagram is plotted. In addition, the unit is converted to MPa, and error bars are added. In this study, the samples are cured for one and seven days respectively, before they are tested for UCS to observe strength development progression. It is important to note that only one sample for each additive is tested, and for each recipe, three samples are prepared, and its UCS is measured to reduce the error in the results. Samples with 1wt% Al_2O_3, 3wt% sucrose, ZKS, and the neat recipe are tested for UCS. An overview of these samples is presented on table 4.5.

Table 4.5 – UCS Samples

Recipe	Potassium [wt%]	Zinc [wt%]	Sucrose [wt%]	Al2O3 [wt%]
ZKS	0.14	0.57	3	X
Al2O3	X	X	X	1
SP3	X	X	3	X
Neat	X	X	X	X

4.2.1 UCS values after 7 days of curing

Plotted UCS data after seven days of curing is presented in Figure 4.5, and some changes are observed in the UCS values after introducing the chemical admixtures. The first bar graph represents the average UCS value for the neat recipe. The second bar from the left represents the average UCS value for the ZKS recipe, and a 17.1% reduction is observed compared to the neat recipe. This observation was expected; hence both sucrose and zinc can harm the UCS based on previous studies. The third bar displays the average UCS value for the aluminum-oxide recipe, and a 13.37% increase in UCS value is observed. This result was expected; hence some studies had observed acceleration in the hydration process and an increase in UCS value. The bar graph on the right side of the aluminum-oxide graph shows the UCS value for the sample with sucrose as its additive, where insignificant changes are observed compared to the neat recipe. By comparing the ZKS and sucrose UCS values, we can conclude that the combination of zinc-nitrate and potassium has a negative effect on the UCS and sucrose on the other hand, has an insignificant effect.
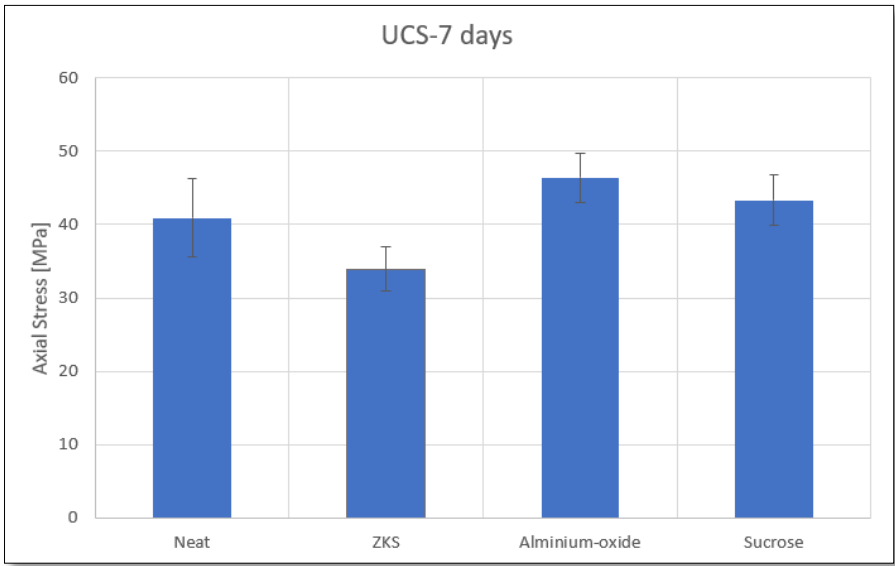
Figure 4.5 - UCS Data After 7 Days of Curing

4.2.2 UCS values after 1 day of curing

Figure 4.6 displays data collected from the hydraulic press machine after curing the samples for one day. The goal here is to observe how early the strength develops and if any of the additives delays the beginning hydration process or not. The first bar on the left shows the average UCS of the neat recipe, which is the highest between the four. The second bar from the left represents the UCA for the ZKS recipe, where interesting data was observed. When the

ZKS samples were taken out of the molds, some areas of their surface were soft and contaminated with water. So, it is safe to say that the ZKS recipe does not develop high early strength and has only an average UCS of 1.785 MPa after one day of curing. The third bar from the left displays the UCS value for the sample with aluminum-oxide as its additive. It is clear that 1wt% of Al_2O_3 has not affected the UCS, and it is approximately the same as the neat. On the other hand, the samples with sucrose in their system resulted in a 28% decrease in UCS compared to the neat recipe. The sucrose recipe has developed strength after one day of curing, but it has not fulfilled the seven-day potential strength.
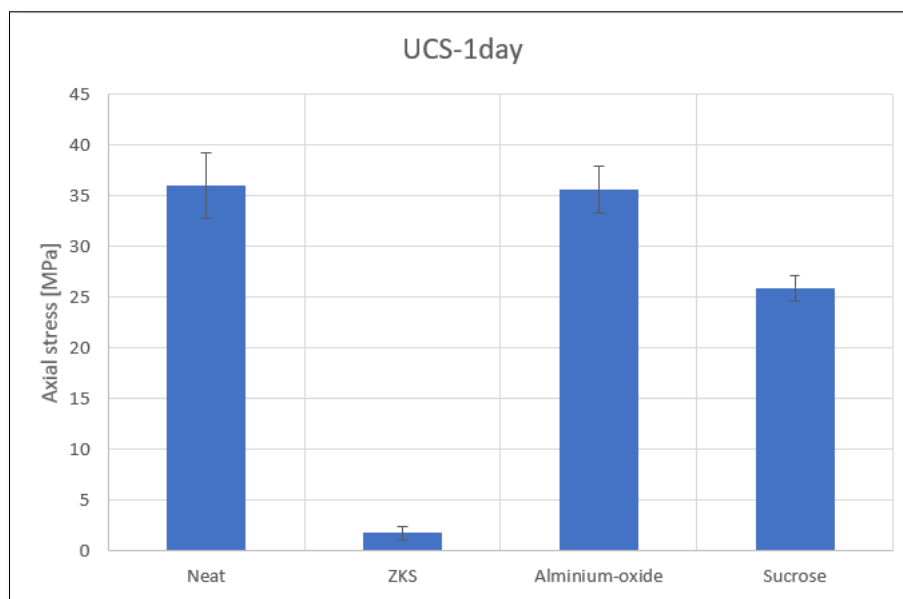

Figure 4.6 - UCS Data After 1 Day of Curing

4.2.3 Comparison of UCS values for 1&7 days of curing

In this chapter, the UCS values of 1 and 7 days are compared for each recipe, and Figure 4.7 demonstrates this comparison. For a more sensible comparison, the samples cured for seven days are counted as the samples with 100% strength development. Hence this statement, by analyzing the neat recipe, it is observed that the cement develops 88% of its seven days strength after the first day. This impressive early strength development of GPC has also been pointed out in previous studies on geopolymers. However, by adding zinc, potassium, and sucrose, the scenario will change. The ZKS sample has developed only 5.3% of its seven-day UCS value, indicating that sucrose, zinc, and potassium delays the hydration process and significantly decrease early strength development. The sample with aluminum-oxide in its system has an impressive early strength development of 76.7% of its seven days UCS value. Based on the results of the ZKS recipe, sucrose has decreased the early strength development as expected;

however, it is not significant. This concludes that either zinc or potassium are the additives that result in a major reduction of UCS in the ZKS recipe, and further investigation is needed to state which additive it is.
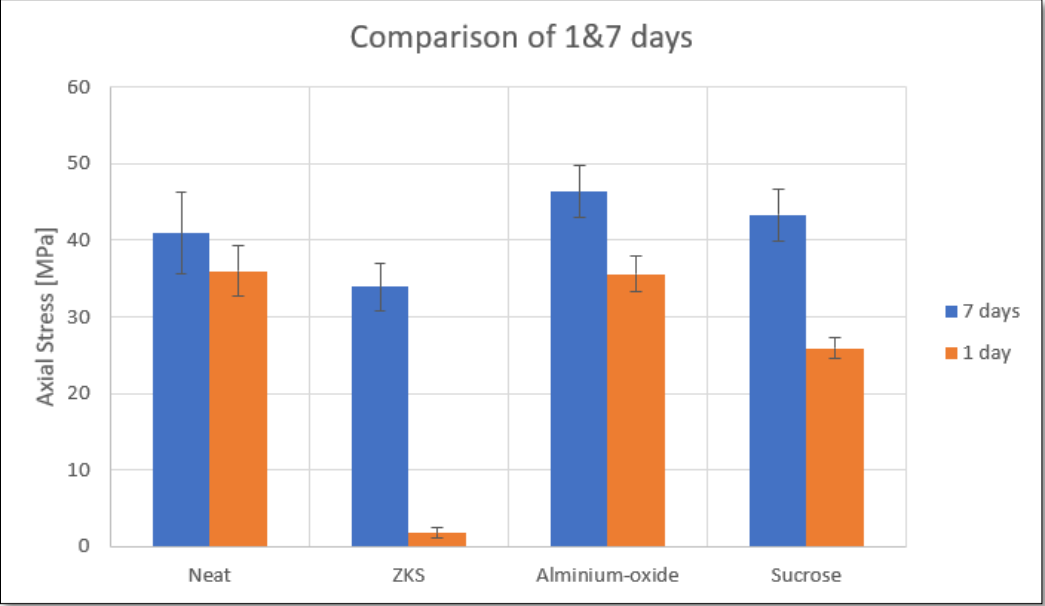

Figure 4.7 – 1&7 Days UCS Data Comparison

5 Conclusion

Hence geopolymer is a young-aged technology; many of the studies done in this project had never been done before on a rock-based geopolymer. Many interesting effects were observed by adding mentioned additives to this system, and some important and provable statements were mentioned. In this part of the thesis, some of the crucial observations are briefly mentioned:

- MgO acts as accelerator in a rock-based geopolymer system. According to previous studies done on other types of geopolymer system, it can reduce shrinkage, increase early strength and improve mechanical properties. To see if these improvements apply in rock-based geopolymer, further investigations are required.

- Sucrose affected the system as expected by delaying the hydration process and acting as a retarder. This retardation affects was not only on slurry's workability, but also on its setting time. However, it was expected to have a negative effect on the compressive strength but the UCS value was not significantly decreased compared to the neat recipe. Other observations that is worth to mention is the setbacks produced at the end of consistency graphs showing some delay on oligomerization process.

- Aluminum-oxide acted as an accelerator on both workability and setting time. This observation can be used to improve the setbacks created by usage of sucrose. The samples with small amount of aluminum-oxide had insignificant changes on their mechanical properties, however some increase in UCS was observed after 7 days of curing.

- Zinc, potassium and sucrose were the additives that had the most impact on the system. ZKS samples had the most retardation effect on both workability and setting time. This concludes that this recipe was more pumpable than the other four recipes. Another interesting impact of these additives were their effect on the mechanical properties. Both UCS and early strength development were significantly decreased compared to the neat sample.

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