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# MASTER'S THESIS

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# Abstract

Historically and up to date, ordinary Portland cement (OPC) or a slight variation is the most widely used material for permanent Plug & Abandonment operation. However, there are several challenges related to cement usage. Apart from the placement of the product and the displacement of the fluid in place which will not be considered in this work, there is also the concern of long-term sealing capability. Also cement lack adequate mechanical properties such as compressive strength and has high shrinkage, to mention just a few. Therefore, the question has always been, does there exist or is it possible to develop an alternative material that can be placed easily and can develop very high compressive strength with eternity in view and that might possibly allow for a shorter plug length.

The motivation behind this thesis experimental work is not just to develop a preferred alternative material to well plugging and abandonment, but to investigate how essential mechanical properties like compressive strength and tensile strength is developed and investigate how the mechanical integrity of aplite-based geopolymer material is impacted by compositional ratio of admixtures. Very few literature exist that discusses aplite-based geopolymer material. Therefore to extend the work done by previous researchers, we used a well-known retarder in oil well cement by applying it on the slurry design and see how it will delay the setting time. This thesis findings are of great practical importance to the drilling industry because the effect of adding additional micro silica was also investigated and reported.

A scan electron microscopy (SEM) will further reveal the intermolecular counteraction of the geopolymer grain and how they contribute to strength of the material. After two months of laboratory experimental work and analysis of the results, it was discovered that sucrose addition to aplite-based geopolymer could retard the setting-time. Whereas addition of excess silica above a certain degree could prevent hardening of the geopolymer irrespective of the application of heat.

# Nomenclature

| | |
|---|---|
| P&A | Plug and Abandonment |
| HSE | Health Safety and Environment |
| NCS | Norwegian Continental Shelf |
| OPC | Ordinary Portland Cement used for well cementing |
| NORSOK | An abbreviation for Norsk Sokkels Konkuranseposisjon |
| CT | Coiled tubing |
| CBF | Cement free binders |
| GGBFS | Ground granulated blast furnace slag |
| CFA | Class C fly ash |
| FFA | Class F fly ash |
| ASTM | American Society for Testing and Materials |
| SEM | Scan Electron Microscopy |
| OGUK | Oil and Gas UK |
| E | Mixing energy (kilo-Joules) |
| K | $6.1 * 10^{-8} m^5/s$ (found experimentally) |
| t | Mixing time (seconds) |
| w | Rotational speed (radian/sec) |
| m | Mass of the slurry (kilogram) |
| V | Volume of slurry in the slurry cup (Liters) |
| S | Compressive strength |
| F | Force (Newton) required to crush the core |

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# 1   Introduction

Currently, some wells in the Norwegian continental shelf are in their final stage of production. That is true for a number of reasons; when oil and gas reservoirs are being depleted and the reservoir pressure decreases, it is more often than not observed that maintaining the wells will eventually be less economical and the well will be prepared for plug and abandonment (P&A). Also, when there are well integrity problems such as corrosion in the lower section of the production tubing or casing and abandoning the well is considered the best economic option, the well will be prepared for P&A. In addition, most wells in recent times are being considered for P&A, at least temporarily if not permanently because of the dwindling oil prices. So, P&A is an inevitable reality in the life cycle of every well. Or in other words, one day every well will be plugged and abandoned. Plug and abandonment is the final stage of a well's lifetime, and according to regulations that are applicable to the Norwegian Continental Shelf (NCS), the objective of a permanent P&A operations is to seal the well with eternity in view. Hence, special emphasis on long-term integrity of well barrier materials.

P&A operations in the Norwegian Continental Shelf and all over the world, face a long list of global challenges; including skyrocketing costs, Health Safety and Environmental (HSE) issues and concerns, and rapidly growing demand. Traditional tools, materials and methods are frequently unable to address these concerns. For example, ordinary Portland cement have always been used by the industry for years despite the challenges encountered both during production of cement and with the use of cement, viz.: $co_2$ emission, inability to withstand high temperature, inability to withstand corrosive environment thereby jeopardizing the long term integrity, inability to develop high enough compressive strength for long-term durability. Also, it is well known that the effectiveness of a permanent abandonment plug is measured by its ability to bridge the wellbore cross section, both vertically and horizontally, including all annuli, with a plugging medium that can withstand the harsh environment to which it is exposed. Therefore, tireless efforts have gone into the improvement of plug and abandonment of oil and gas wells.

Solutions to P&A challenges are being found in new technologies and development of new materials and equipment that are capable of improving efficiency and performance.

In recent times, most of the advances in P&A centers on the development of versatile and compact rigless intervention and well abandonment systems. These systems are fit for purpose only and can include hydraulic pulling and jacking units, cantilever systems with light duty work decks, and casing jack configurations [1]. Lightweight and modular and with a minimal footprint, these systems provide new levels of mobilization and flexibility. They are at the core of a suite of technologies that provide a scalable P&A solution ranging from casing jacks to light-duty work deck and cantilever systems, to full-function pulling and jacking units.

Further integration with a larger scope of service draws on multiple resources including wellhead diagnostics, running bridge plugs, tubing cutting and removal, and remedial cementing to improve safety and efficiency. These technologies and capabilities combined provide the tools for innovative, engineered solutions that improve performance on a range of P&A applications[1]. A very important part of P&A operations includes sealing and isolating the annular space between casing and formations and isolating the reservoir and the wellbore as well. It is therefore very important that we briefly understand the concept of P&A and certain regulations that apply.

## 1.1   Plug and Abandonment Background

Plug and Abandonment refers to set of activities /operation carried out to prepare a well to be closed permanently, usually after either logs determine there is insufficient hydrocarbon potential to complete the well, or after production operations have drained the reservoir.

In this section, most reference will be made from the NORSOK standard D-010[2]and the Oil & Gas UK (OGUK) guidelines for the suspension and abandonment of well and also cost estimation (2012) [3]. These two regulations do not apply to the USA, Middle East and Asia. The individual states in the United States of America, for example, have various regulations that apply. Also in the Middle East, there are regulations that also apply specifically to them. I will for the purpose of this thesis focus on standards and regulations governing the operation in the North Sea which by extension can also be applied to other parts of the world with slight modifications.

### 1.1.1 Definition of Plug and Abandonment terms

#### 1.1.1.1 Potential source of inflow

Formation with permeability, but not necessarily a reservoir.

#### 1.1.1.2 Reservoir

Permeable formation or group of formation zones originally within the same pressure regime, with a flow potential and/or hydrocarbons present or likely to be present in the future.

#### 1.1.1.3 Barrier

Up to date, well barriers have been defined as either cementitious or mechanical device used to prevent leakages and reduce the risk associated with drilling, production and intervention activities. According to NORSOK D-010, the following are properties of a permanent well barrier.[2, 3]

- Impermeable.
- Long term integrity.
- Non-shrinking.
- Ductile – (non-brittle) – able to withstand mechanical loads/impact.
- Resistance to different chemicals/ substances (H2S, $CO_2$ and hydrocarbons).
- Wetting, to ensure bonding to steel.

The concept of barriers leads us to well barrier element and well barrier envelop, primary barrier and secondary barrier.

- **Well barrier element:** Object that alone cannot prevent flow from one side to the other side of itself [3].
- **Well barrier:** Envelope of one or several dependent barrier elements preventing fluids or gases from flowing unintentionally from the formation into another formation or to surface[3]. In unequivocal terms, a well barrier has one or more well barrier elements.

- **Primary Well Barrier** is the first object that prevents flow from a source. The primary barrier is the first source of pressure containment as it prevent unintentional flow to the environment or other formations.
- **Secondary Well Barrier** is the second object that prevents flow from a source. The secondary barrier is to prevent unintentional flow if the primary barrier fails. It is like a backup to the primary.

### 1.1.1.4　Unintentional flow:

This is any flow of fluid (liquid or gas) in or out of the well through a failed barrier.

### 1.1.1.5　Independent barrier:

Each type of mechanical closing barrier in/on a well shall be able to be closed and contain the well bore fluids by its own control system irrespective of any power failure.

### 1.1.2　Phases of Well Abandonment

According to OGUK, there are three phases of abandonment depending on the work-scope, equipment required and the duration [3]. These are; (1) Reservoir abandonment, (2) Intermediate abandonment and (3) wellhead and conductor removal.

### 1.1.2.1　Reservoir Abandonment:

Reservoir abandonment of a P & A operation is the first phase of abandonment and can be both complex and challenging. In this phase of abandonment, full well control is required. It can be challenging when needing to reestablish barriers as a result of poor cement jobs behind casing. This could lead to milling operation which is often times not desired. Activities covered in this phase include: setting Primary and secondary permanent barriers to isolate all reservoir producing or injecting zones. The tubing may be left in place, partly or fully retrieved. It is complete when the reservoir is fully isolated from the wellbore [3] .

### 1.1.2.2　Intermediate Abandonment

This is the second phase and the set of activities that it encompasses includes: isolating liners, milling and retrieving casing, also setting barriers to intermediate hydrocarbon or water-bearing

permeable zones and potentially installing near-surface cementitious material. The tubing may be partly retrieved, if not done in Phase 1 as described. The Intermediate abandonment is complete when no further plugging is required [3].

### 1.1.2.3 Wellhead and conductor removal.

This is the third phase of abandonment and the activities that are carried out in the phase includes; retrieval of wellhead, conductor, shallow cuts of casing string, and cement filling of craters. Complete when no further operations is required on the well[3].

## 1.1.3 Types of Plug and Abandonment

There are broadly two types of well P&A that applies. These include the Temporary plug and abandonment and permanent plug and abandonment. We will now discuss these in detail.

### 1.1.3.1 Temporary plug and abandonment

According to NORSOK D-010 standard, temporary abandonment is defined as a well status in which the well has been temporarily plugged where the BOP or XT has been removed, and the well barriers **are not** continuously monitored.

Temporary P&A can be classified as a suspension when the well is temporarily plugged, XT is installed, and the well barriers **are** continuously monitored. Suspension of a well under construction or intervention is defined as a well status, where the well operation is suspended without removing the well control equipment. A very good example of well suspension is when drilling operation is halted due to wait-on weather (WOW). It is a necessary requirement to have the possibility to re-enter a temporarily abandoned well at a later stage in a safe manner**.** Integrity of the materials that is used in a temporary abandoned well must withstand at least double its planned period of abandonment. In some cases a mechanical well barrier may be accepted, based on the planned abandonment period and subsurface environment.

### 1.1.3.2 Permanent plug and abandonment.

According to NORSOK D-010 standard, permanent abandonment is defined as a well status in which the well has been plugged and abandoned with an eternal perspective taking into account the effects of any unforeseen or foreseeable chemical and geological processes [2].

Figure 1.1 shows a schematic of best practice applicable to permanent plug and abandonment.



**Best practices**

Height of 500ft MD, containing at least 100 ft MD of good cement.

Plug depth determined by formation (impermeability and strength) and primary cementation

Pipe stand-off

Support to prevent cement movement, slumping and gas migration while setting

Good bond, clean surfaces, water wet

**Barrier elements**

Sealing abandonment plug

Tubing sealed with cement, in cement

Casings, tubing embedded in cement

Sealing primary cementations

Formation: impermeable and adequate strength to contain future pressures

*Figure 1.1 permanent abandonment schematic showing best practice shown in orange boxes to the right and best practice shown in the boxes to the left according to OGUK [3].*

According to NORSOK (2013)[2], eternal perspective with regards to re-charge of formation pressure shall be verified and documented [2]. Table 1.1 gives a summary of primary and secondary barrier function and requirement to depth position including Well barrier between reservoirs and well open to the surface.

*Table 1.1 Examples of well barriers, their function and minimum requirement*

| Name | Function | Requirement to Depth position |
|------|----------|-------------------------------|
| Primary well barrier | First well barrier against a potential source of inflow | Minimum formation stress at the base of the barrier shall be in excess of the potential pressure below |
| Secondary well barrier | Back-up to the primary well barrier. Applies also where the potential source of inflow is also a reservoir. | Minimum formation stress at the base of the barrier shall be in excess of the potential pressure below |
| Well barrier between reservoirs | To permanently isolate reservoirs from each other. Can also function as primary barrier for the reservoir below. | Minimum formation stress at the base of the barrier shall be in excess of the potential pressure below |
| Open hole to surface well barrier | To permanent isolate an open hole from surface exposed after casing cut. (This formation can be (i) impermeable or (ii) permeable with no HC and less/equal to normal pressure). | As deep as possible in the surface casing and with the top minimum 50 m above the shallowest permeable zone. |

### 1.1.4   Minimum requirements for barrier placement

The following are the minimum requirement for barrier placement. Which is an indication of best practice as shown in Figure 1.2. There we can see best practice as it is able to prevent crossflow and ensures proper isolation and also poor placement of well barrier as it only prevent vertical flow and not horizontal flow. The following are minimum requirements for barrier placement [2];

- There shall always be two tested barriers identified to prevent flow to the environment. Both will be risk assessed, verified and monitored during any operation on the well.

- In principle, tested and approved barriers shall not have a leak rate greater than 0, before any work is conducted. The owner of the well may accept alternative test criteria to gain assurance that the barrier is secure.

- The owner of the well may accept deviation of the test from this requirement in certain circumstances. The deviation shall as a minimum be specified and documented including: such as; Mitigation actions and responsibilities are identified, in place and fully understood by all staff. Deviation note is approved by a senior person of the well owner management accountable for well integrity.

- If bonded shale formation is to be used as a barrier element, its location shall be identified and sealing ability verified by logging and leak testing respectively.

- Bonded shale formation cannot be predicted. Therefore during any planning phase (construction, production, P&A, etc.), it shall be planned for using cement as barrier element outside casings. However, once collapsed formation is proven in place and qualified it can be used, and is preferred used in permanent P & A.

- At all times, the following should be clearly understood by personnel working on a well:

  1. The consequence of barrier failure and unintentional flows to the environment or to other formations.

  2. The components in a well that are the primary and the secondary barriers during the specific work on the well.

  3. That the specification of the components are suitable for the intended use.

  4. That the verification process for the installation of these components is understood.

  5. The acceptance criteria are available for the successful location, and testing for these components.
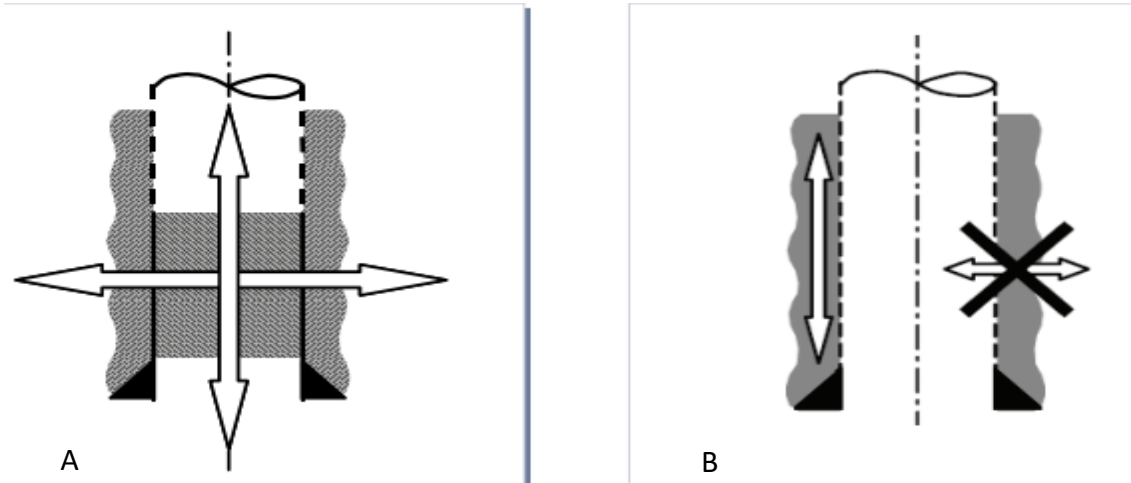
*Figure 1.2 schematic showing well barrier requirement of crossflow. Figure 2.2 (A) indicates best practice as it is able to prevent crossflow and ensures proper isolation. Figure 2.2 (B) indicates poor placement of well barrier as it only prevent vertical flow and not horizontal flow.*

## 1.1.5  Functional Requirement for Permanent Barriers Qualification

In this subsection, the idea is to reproduce important and more general requirements for the qualification of new technology. These were defined in the Det Norske Veritas (DNV) document Qualification procedures for new technology (DNV RP-A203, 2001)[4].

We will make reference to permanent barriers, although functional requirements of temporary barriers do not differ from those of permanent barriers except possibly for a relaxed time scale of required durability.

A permanent barrier should be able to perform the following functions effectively;

### 1.1.5.1  Sealing

The main function of a permanent barrier is to provide an eternal seal against migration of hydrocarbon. However, permeation of some kind is possible through most materials. Such fluid movement follows well understood natural processes. Within the context of permanent barrier materials it must, therefore, be recognized that it is inevitable that a fluid within the well will ultimately migrate past a barrier, but at a low rate.

Thus, appropriate barriers are those through which the rate of permeation is acceptably low. Since cap rock/seal restoration is also possible by means of a cementitious seal/barrier, it is expected that leakage of fluids at the same or a lower rate than the cap rock. The permeability of cap rock is typically within the range 0.001-1 microdarcy. However, good quality cementitious material, typically with a permeability of 10 microdarcy (µd) is deemed acceptable on the basis of historical industry experience, and on the grounds that barrier length is a controllable parameter (as long as it is opposite the caprock) and the cross sectional area is considerably smaller than that of the caprock [3].

A permanent barrier requires: continuous material, or sequence thereof, with low-permeability; and an appropriate length along the well bore.

### 1.1.5.2  Position

It is expected that position of the barrier should not move, either along the well bore or in a lateral direction. This means, for instance, that the barriers should not be pushed upwards by pressure developing below from the reservoir. The barrier material is required to remain bounded to the steel and the rock it has been placed against  [3]. Figure 1.3 shows the forces acting on a cement barrier which can influence its position. This is achieved through sealing stresses normal to the casing, friction stress, bonding at the interface, weight and dimensional stability, or a combination of these forces [3].
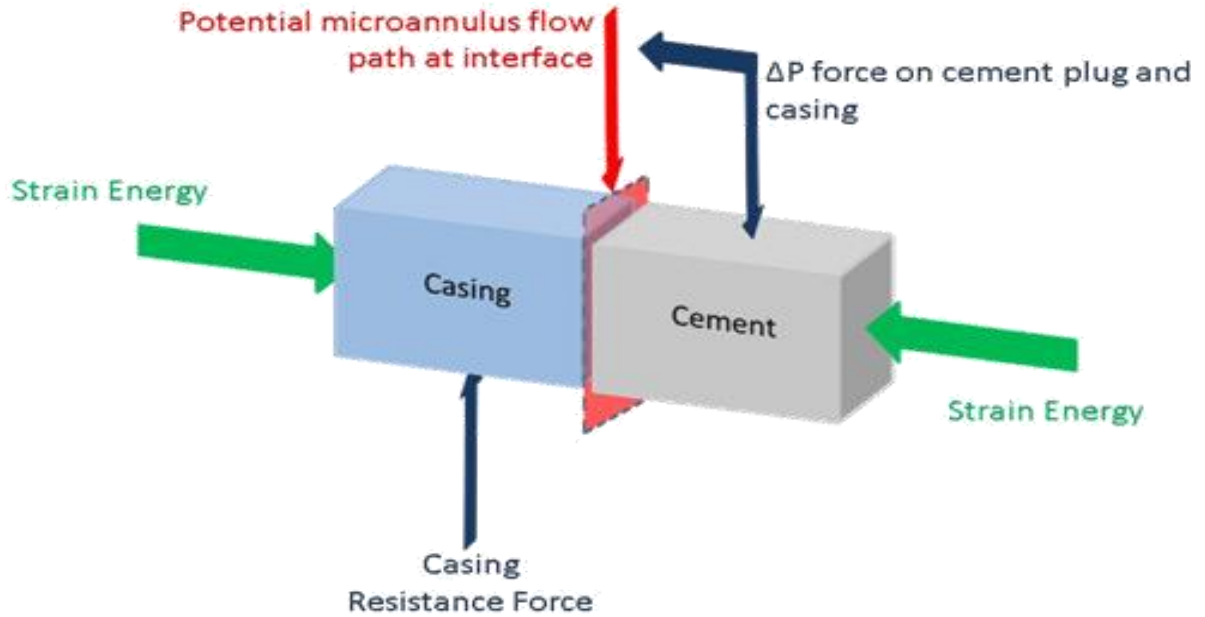
*Figure 1.3 Forces acting to maintain the seal and position of a barrier. OGUK* [3]

### 1.1.5.3  Placeability/ Pumpability

It is a functional requirement that the permanent barrier material should have the capability to be placed in a wellbore at any specified depth interval and is subsequently able to perform its required function [3].

The material should have appropriate properties that allow it to be pumped, placed and displace the existing fluids and form a continuous sealing medium, even when taking the possibility of its contamination into account. The material may be circulated in place to replace the present fluid. This will require a work string, such as drill pipe, tubing or coiled tubing [3].

Where a barrier material undergoes a transformation from a liquid to a solid, this period of transformation must be sufficiently short to prevent escape of fluid and unacceptable disruption of the barrier. Wells may be positioned at an angle to the vertical, and the placement technique employed should take this into account. A means of verifying that the placement of the permanent barrier has been successful is required.

### 1.1.5.4 Durability

A permanent barrier material should not degrade placing its sealing capability at risk. For temporary abandonment an anticipated timescale may be specified [4]. Permanent well abandonment has an eternal perspective, meaning that the mindset for design is in terms of geological timescales, which span millions of years. It will not be possible to quantify such a time requirement, and it is clearly not feasible to qualify materials for this timescale.

In order to define testing criteria against a quantified service life, a service life of an arbitrary number of a million days (about 3,000 years) is proposed in the context of this document. This is of the same order of magnitude as requirements for the storage of $CO_2$, which refer to timescales of thousands of years, although it has been suggested that an expectation of more than 30 years will be difficult to prove for most materials [5]. The estimation of long-term performance through ageing testing should be considered also.

### 1.1.5.5 Removal options

As stated above, a key objective of permanent well abandonment is that the well should be sealed with eternity in view. However, due to uncertainties, a leak might occur through a barrier. A permanent barrier should have removal options. Therefore, there should be a method to remove the barrier(s) in order to remedy the leak. This is in line with the mindset of $CO_2$ storage projects [4] .

## 1.1.6 Potentially Suitable Barrier Materials

In this section, we will review some materials that are recommended as potentially suitable well barrier materials. The materials are divided based on their chemistry and physical nature. Table 1.2 summarizes some of the materials [3].

*Table 1.2 List of material types for permanent barrier.(taken from OGUK, 2011)* [3]

| Type | Material | Examples |
|------|----------|----------|
| A | Cements / ceramics (setting) | Portland API class cement, Pozmix, slag, phosphate cements, hardening ceramics, geopolymers. |
| B | Grouts (non-setting) | Sand or clay mixtures, bentonite pellets, barite plugs, calcium carbonate and other inert particle mixtures. |
| C | Thermosetting polymers and composites | Resins, epoxy, polyester, vinylesters, including fibre reinforcements |
| D | Thermoplastic polymers and composites | Polyethylene, polypropylene, polyamide, PTFE, Peek, PPS, PVDF and polycarbonate, including fibre reinforcements |
| E | Elastomeric polymers and composites | Natural rubber, neoprene, nitrile, EPDM, FKM, FFKM, silicone rubber, polyurethane, PUE and swelling rubbers, including fibre reinforcements |
| F | Formation | Claystone, shale, salt. |
| G | Gels | polymer gels, polysaccharides, starches, silicate-based gels, clay-based gels, diesel / clay mixtures |
| H | Glass | |
| I | Metals | Steel, other alloys such as bismuth-based materials |

It is important to note that in the case of composite materials, assignment of material type should be for the material acting as the matrix, unless it can be demonstrated through testing that another constituent of the composite defines the behavior of the material to a greater extent.

Barrier configurations employing discrete multiple materials which are interdependent in providing a seal are assigned to multiple types, but require function testing in the envisaged configuration. Multiple barriers comprising different materials should be tested individually [3].

It must be verified that a suitable shale formation is present that will act as a barrier before such can be classified as a barrier.

Many materials can be used in a foamed condition. Where it is intended that a barrier material is to be used in such a way, it is essential that testing is carried out on the foamed material to ensure that it can withstand sufficiently high temperature and pressure [3].

### 1.1.6.1    Material properties of permanent barriers

The performance requirements of a permanent barrier within a given set of operating conditions means that it is capable of carrying out its intended purpose. Therefore, it is necessary to characterize certain properties of a prospective barrier material to ensure that it is appropriate for the application. Some of these properties, along with further definitions, and a discussion of their significance in relation to their potential failure modes, are listed in Table 1.3.

However, very little in comparison have been said on the improvement of cementitious material used for creating a well barrier envelop which is the main material characterized for the NCS for zonal isolation during well plugging and abandonment.

*Table 1.3* Properties of barrier materials. Definition and Significance.(OGUK, 2012) [3]

| Property | Definition | Significance |
|---|---|---|
| Permeability | Transmit fluids under a pressure differential. Units = Darcy | Allows estimation of lag time between placing and break- through and rate of release of fluid below a given length of barrier under a given pressure differential |
| Hydrostatic yield | Hydrostatic stress (i.e. stress applied uniformly in all directions) at which plastic deformation occurs. Units = Pa = $Nm^{-2}$ | Indicates the onset of pore collapse in granular materials. This failure mode is plastic and results in irreversible deformation. Beyond this stress level the material will gradually lose cohesion and hence load-bearing capacity |
| Tensile strength | Stress at failure under a tensile load. Units = Pa = $Nm^{-2}$ | Gives maximum tensile stress that can be withstood by barrier |
| Unconfined compressive strength | Axial compressive stress at which a material fails. Units = Pa = $Nm^{-2}$ | Gives maximum compressive stress that can be withstood by barrier |
| Hardness | Ability of a material to resist penetration of its surface | Easy quality assurance / quality control test. For certain materials, hardness can be related to yield strength |
| Shear bond Strength | Stress at which bond between two materials fails under shear loading. Units = Pa = $Nm^{-2}$ | Allows calculation of pressure differential that can be withstood by the barrier before movement takes place |
| Tensile bond Strength | Stress at which bond between two materials fails under tensile loading. Units = Pa = $Nm^{-2}$ | Gives maximum tensile stress that can be withstood at the barrier – casing interface |
| Density | Mass per unit volume. Units = $kg/m^3$ | Easy QA/QC test. Allows assessment of likelihood of barrier moving as a result of imbalance between densities of barriers and well fluids |
| Poisson's ratio | Ratio of lateral to axial strain in a material loaded uniaxially in the axial direction. No units. | Allows calculation of lateral deformation of barrier under a given pressure (in combination with modulus of elasticity) |
| Modulus of elasticity | Ratio of uniaxial stress to uniaxial strain. Units = Pa = $Nm^{-2}$ | Allows calculation of magnitude of deformation of barrier under a given pressure. |

## 1.2 Geopolymer Background

Several materials have been proposed by researchers and authors as being more suitable than the traditional Ordinary Portland Cement (OPC). For the most part, while a blend of Portland cement with some inorganic materials have been observed to generally improve the behavior of cement, the search for a suitable improvement is an ongoing one. Below are a review of some.

Saasen et al. [6] considered a material for permanent abandonment of a north sea well. Using unconsolidated Bingham plastic material with high solid concentration as Well-Plugging and abandonment material. With this Bingham plastic material, they attempt to address well integrity issues caused by the traditional OPC such as shrinking of cement after hardening or those caused by gas migration during setting. Fracturing after setting or long term degradation caused by exposure to degradable chemicals and substances in the well [6] . More interestingly is the fact that the newly developed material complied with the Norwegian requirement for permanent P&A as stipulated by NORSOK [7]. However, a solid foundation is necessary for material to be used.

Ian S. Barclay et al.[8] presented Petroleum Development of Oman's (PDO's) use of an unconventional new expanding, flexible sealant system on a P&A project, conveying the flexible sealant with a coiled tubing (CT) unit. The new sealant presented was reported to have improved elastic and expansion properties to meet PDO's requirement for a long-term mechanical durability and zonal isolation. The presence of expanding material leads to an optimum configuration to prevent loss of zonal isolation resulting from changes in downhole conditions over time. The presence of flexible and expanding materials increases the elasticity and decreases compressibility and permeability of the flexible sealant while retaining good compressive strength[8] . However, shrinkage which may affect the seal stability seem to be a challenge. Also, there exist doubt about long-term durability. Packer fluid in contact with those flexible sealant may pose a problem.

Hyun Cho et al. [9] also carried out an extensive research which reveals that certain pozzolanic materials can be retarded like OPC when slurries are made out of it and it can be pumped and placed like cement with coiled tubing instead of employing a rig [9]. They studied the chemical

compositions, size distribution, compressive strength, thickening time, durability, and rheology of the materials. They also studied the effects of various additives on the materials [9] . Although there were improved mechanical properties as compared to cements without fly ash, fly ash grout was suspected to be contributing to corrosion because it reacts with the hydroxide used.

ChevronTexaco in 1999 [10] also pioneered research into the use of compressed sodium bentonite as an alternative to cement for permanent well plugging. Their objective was to identify a process to reduce plugging costs by at least 30% to encourage the expeditious abandonment of the growing back-log of wells. Following pilot studies in California, over 500 wells across the USA have been abandoned using highly compressed sodium bentonite as well plugging material [10] .

Despite the above, OPC or a slight variation of it is being used as the most common well barrier material for permanent P&A. Although its durability and survival have for decades raised dust and has been questioned by many researchers. In addition to that, there are also environmental concerns with respect to production of Portland cement. Although it is invaluable in a lot of applications, production of OPC is not just resource exhausting and energy intensive process but it releases large amounts of the greenhouse gas $CO_2$ into the atmosphere. According to sources, production of 1 ton of OPC, for example, requires about 2.8 tons of raw materials, including fuel and other materials. As a result of de-carbonation of lime, 1 ton of carbon dioxide which is a greenhouse gas is released from production of about 1 ton of Portland cement [11] .

This is indeed alarming considering developing countries that need a lot of cement and concrete for building houses to meet the need for their growing population.

In addition to the above, strict regulatory requirements such as greenhouse $CO_2$ mitigation have necessitated the search for a more reliable P&A techniques including materials used and therefore P&A is becoming increasingly important in the whole well planning process. As a result of this increased importance, the cost of P&A consist of a major part of well planning. It is estimated that P&A activities in recent times have contributed about 25% to 30% of the total costs of drilling exploration wells in the NCS [12] .

One of such materials that have attracted a lot of attention to cement development are geopolymers. Geopolymers are a class of inorganic materials made by reacting alumino-silicate rich materials such as fly ash, aplite, ground granulated blast furnace slag (GGBFS), and metakaolin with an alkaline solution such as sodium hydroxide or potassium hydroxide.

These mineral polymers have empirical formula: $M_n$ $[-(SiO_2)_z-AlO_2]$ $_n$ $wH_2O$, where the subscript z is 1, 2 or 3; $M$ is an alkali cation, such as potassium or sodium, and the subscript $n$ is the degree of polymerization [13], [14] and [15]. It has a wide range of usage. It is used for coatings and adhesives, binders for fiber composites, waste encapsulation, additives in cement and new cement for concrete. The properties and uses of geopolymers are being explored in many scientific and industrial disciplines: modern inorganic chemistry, physical chemistry, colloid chemistry, mineralogy, geology, and in all types of engineering process technologies [16]. Joseph Davidovits seemed to have been the first person to use the word "geopolymer" or at least it was credited to him [16] . Geopolymers are believed to possess desirable properties which are to be looked out for in any cementitious material: like long-term integrity (eternal perspective), Impermeable, non-shrinkage, able to withstand mechanical loads/impacts (ductile), resistance to different chemicals/substances ($H_2S$, $CO_2$ and hydrocarbons), ensure bonding to steel (wetting) and not harmful to the steel tubulars integrity, to mention just a few [12] .

Geopolymer cements are also acid-resistant cementitious materials with zeolitic properties that can be applied to the long-term containment of hazardous and toxic wastes [12] .

Many literatures have addressed geopolymers. For instance, Temuujin et al. [17] referred to all geopolymers without cement as cement free binders (CFB) [17]. They studied the composition of geopolymer raw materials and the different alkaline solution used as activators including percentages and pH value and how it affects the final strength of the geopolymers. In their publication, they showed that the amount of aluminous silica present in the starting material plays a significant role in activation reactions and the properties of the geopolymer formed [17]. The compressive strengths of geopolymer concretes have been seen to increase with increase in activator concentration. Also geopolymers made using ground granulated blast furnace slag (GGBFS) as the starting material showed higher compressive strengths compared to those made

with fly ash because of the self-cementing property of GGBFS and higher binder content used [17]. Temuujin et al. also showed that the presence of calcium oxide in the source material also influences the properties, especially because of the formation of more than one reaction product[17] .

Criado et al. [18], in 2007 , carried out an investigation using a class F fly ash (FFA) from the compostilla steam power plant in Spain . In their experiment, they complied with the ASTM standard C6128–03 for preparing fly ash of that type, consisting primarily of $SiO_2$ and $Al_2O_3$. He studied the effect of the soluble silica content in the activating solution on the reaction rate of the "ash-activator" system and the nature of the reaction products including their impact on mechanical development in the material. It was seen that the mechanical strength development of these types of materials depends not only on the reaction degree, but also on the nature and composition of the reaction products, the aluminosilicate gel being the main product of reaction inducing the mechanical properties. Higher alkaline solution-to-fly ash ratio and longer thermal curing durations were reported to produce more crystalline reaction products [18].

Bakharev et al. [19] in 2005 also studied FFA. They investigated the effect of increased temperature on the curing, on phase composition, microstructure and strength development in geopolymer materials prepared using FFA and sodium silicate solution and sodium hydroxide solutions. They reported the effect of storage at room temperature before the application of heat on strength development and phase composition. Although heat is an important factor for the activation of fly ash, because of the activation barrier, which it has to overcome for the reaction to take place. They reported that long precuring at room temperature is beneficial for strength development of geopolymeric materials utilizing fly ash and cured at elevated temperature as it allows shortening the time of heat treatment for achievement of high compressive strength [7].

Activation of aluminosilicate materials with alkalis generally requires heat curing for the formation of geopolymers especially when the activating solution does not contain soluble silica. A wide range of temperatures ranging from 40 C to 90 C have been reported in order to produce alkali-activated binders with appreciable mechanical properties [20], [21], [22], [23].

For example, Chindaprasirt et al. [20] carried out an experiment on lignite based fly ash and sodium silicate solution with sodium hydroxide (NaOH) as activating reagents. They reported that the strength development was dependent on the ratio by mass of sodium silicate to NaOH and the concentration of NaOH [20] .

Dimitrios et al.[23] investigated effect of the water, sodium hydroxide and sodium silicate contents in the synthesis of class F fly ash (FFA) based geopolymers obtained from the Greek Public Power Corporation S.A. and derived from lignite combustion. They investigated how the water, sodium hydroxide and sodium silicate contents affect their compressive strength. It was observed that water content was a crucial parameter in the synthesis of fly ash-based geopolymers for the development of mechanical strengths. Water plays important roles during dissolution, polycondensation and hardening stages of geopolymerization. In their observation, they reported that sodium hydroxide content in the synthesis of geopolymers was found to affect significantly their compressive strength. Sodium hydroxide concentration in the aqueous phase of the geopolymeric system acts on the dissolution process, as well as on the bonding of the solid particles in the final structure. Geopolymers synthesized with either too low or too high NaOH concentration in the aqueous phase developed lower compressive strength. The amount of sodium silicate solution in the synthesis of geopolymers was evidenced to have a substantial effect on the obtained compressive strength. Sodium silicate solution was observed to control the soluble silicate concentration and the predominant silicate species in the geopolymeric system, improving the mechanical strength of the produced materials [23]

Khalifeh et al. [24, 25] also showed usability of class C fly ash (CFA) geopolymer for oil well cementing. In their experiment, they showed that the curing temperature affects the early compressive strength development. For the particular CFA that they used for their experiment, they observed that as the temperature rises from $87^0C$, to $125^0C$, a consecutive reaction takes place at the higher concentrations of NaOH which decrease the compressive strength at the higher temperature. [24]. They employed ultrasonic cement analyzers (UCA) to investigate the instantaneous strength development of the geopolymeric slurries. They further studied the

internal structure using scan electron microscopy (SEM) and it was found that there was a change in the morphology of the samples at 125 $^0C$ using a higher concentrations of alkali.

Another interesting work done on geopolymer studies was by Nasvi et al.[26], [27], they studied the permeability of class F fly ash (FFA)-based geopolymers for $CO_2$ sequestration wells. The prepared geopolymers were cured for 24 hours at 50 $^0C$ and ambient pressure. Their findings show that, depending on the mix compositions of the geopolymers, the apparent $CO_2$ permeability of geopolymers is lower than ordinary Portland cement (OPC) and class G cement which was also tested for comparison[26]. Their experiment found great application in leakage and degradation problems associated with OPC based oil well cement, and geopolymers can be used for different depths of the injection well by adjusting the mix compositions.

In general, it is immediately obvious that there have been hundreds of literatures on fly ash (both CFA and FFA) based geopolymers. However, very little have been said about other materials rich in aluminum and silica. For example, geopolymer made from rock as a major starting material that also has promising future applications.

One of the earliest work done on the applicability of aplite based geopolymer was by Khalifeh. Khalifeh et al. [28] suggested the possible utilization of aplite-based geopolymer for cap rock restoration in permanent plug and abandonment operations. They found the compressive strength suitable for use for zonal isolation and well plugging activities [28]. Kalifeh's work on aplite-based geopolymer is a motivation for discovering further mechanical properties of aplite based geopolymers and hence this thesis work.

Cementitious materials used for P&A are generally retarded and the setting time increased to allow for full section pumpability before the material starts to develop compressive strength. Also especially where cement returns are expected on surface. Many retarders have been patented and used for decades by well cementing companies. Interestingly, research have shown that the effect of simple carbohydrates on the thickening time of cement slurries can be both positive and negative depending on the concentration and the dosage used. By simple sugars, I mean monosaccharides, disaccharides, trisaccharides and the oligosaccharides – containing 1, 2, 3, and 4 or more monosaccharide units respectively [29].

In the case of OPC, retardation mechanism is still not so clear. However it is believed to follow these four principal theories [28]:

- **Adsorption Theory**: Retardation is due to the adsorption of the retarder onto the surface of the hydration products, thereby inhibiting contact with water.

- **Precipitation Theory**: The retarder reacts with calcium and/or hydroxyl in the aqueous phase, forming an insoluble and impermeable layer around the cement grains.

- **Nucleation Theory:** The retarder adsorbs on the nuclei of hydration products, poisoning their future growth.

- **Complexation Theory**: Calcium ions are chelated by the retarder, preventing the formation of nuclei.

    Some of this theories have also been used to explain retardation in geopolymers made from fly ash and also other materials. This is also seen from the present study.

## 1.3  Objectives

In this experimental work, attention is turned to rock as starting materials in synthesis of aplite-based geopolymer because of the impressive mechanical properties like compressive strength. More importantly in this laboratory experimental work/ thesis is an attempt to include addition of a retarder (a disaccharide with general formula $C_{12}H_{22}O_{11}$) to aplite based geopolymer and to study the effect of sucrose  on the setting time and investigate how it affects the compressive strength. Also because previous studies on geopolymer is more focused on the compressive strength, there is a need to also carry out a tensile test on the test sample because in real life situation , certain forces is exerted by the casing on the cement plug thereby placing it in tension. Furthermore, scan electron microscopy (SEM) was used to investigate the internal structure of the crushed sample. Also novel to these series of research is the addition of tensile strength test on aplite-based geopolymer and also the addition of excess microsilica to see what effect excess microsilica will have on aplite-based geopolymer.

# 2   Experimental Procedures

The main process difference between OPC and geopolymer is that the former relies on a high-energy manufacturing process that imparts high potential energy to the material via calcination, therefore making it possible for low energy material such as water to be used to cause chemical reaction to take place. Whereas, the later uses  very low energy materials, like fly ashes, GGBFS, aplite and other industrial wastes and a small amount of high chemical energy materials (alkali hydroxides) to bring about reaction only at the surfaces of particles to act as a glue [30] The materials used in this experiment are measured to specific amount and ratios to tailor the product to specification. We will now consider some of these materials used in this experiment in detail.

## 2.1   Materials

### 2.1.1   Aplite

In the context of geological studies on the origin, composition, distribution and structure of rocks the term aplite is the name given to intrusive rock in which quartz and feldspar are the dominant minerals[31]. Quartz is the main consistent of the aplite used in experiments. Aplite seem to have pozzolanic properties. The Table 2.1 shows the composition by percentage of the aplite used in this experiment.

*Table 2.1 Composition of Aplite used in this experiment showing main components*

| Components | % by mass |
|---|---|
| Silicon Dioxide ($SiO_2$) | 83.4 |
| Magnesium Oxide (MgO) | 0.06 |
| Titanium oxide($TiO_2$) | 0.03 |
| Barium oxide (BaO) | 0.02 |
| Aluminum Oxide ($Al_2O_3$) | 8.29 |
| Sodium Oxide ($Na_2O$) | 2.16 |
| Manganese Oxide (MnO) | 0.02 |
| potassium oxide ($K_2O$) | 2.86 |
| Iron Fe or ($Fe_2O_3$) | 0.9 |
| Loss on Ignition | 0.8 |

From Table 2.1, it is clear that aplite is silicon dioxide (quartz) dominated. To be suitable for usage in geopolymer preparation, the rock needed to be ground to fineness. It is the aluminum and silica content coupled with the pozzolanic properties that combines to make aplite a suitable starting material for geopolymer.

### 2.1.2   Ground Granulated Blast Furnace Slag

GGBFS as a byproduct of iron or steel industry is a non-metallic product consisting essentially of calcium silicates and other bases that is developed in a molten condition simultaneously with iron in a blast furnace[31]. When the iron ore, which is made up of iron oxides, silica, and alumina, come together with the fluxing agents, molten slags and iron are produced.

When the resulting molten slag is quenched rapidly using water jets, it then produces a granular glassy aggregate. The molten slag could also be air-cooled. Air-cooled slag has a rough finish and larger surface area when compared to aggregates of that volume which allows it to function as a good binder.

GGBFS can be used as a replacement for, or be blended with, Portland cement. When mixed with OPC, GGBFS has shown improvements in some properties in the cement, like being more resistant to chemical attacks and having both environmental and economic benefits. Table 2.2 shows some essential components of GGBFS. It is worthy of note that the composition of GGBFS is not constant but varies slightly depending on how and where the iron ore is gotten.

**Table 2.2 composition of GGBFS by mass percentage [32]**

| Components | % by mass |
|---|---|
| Calcium Oxide (CaO) | 37.16 |
| Silicon Dioxide (SiO$_2$) | 35.94 |
| Aluminum Oxide(Al$_2$O$_3$) | 12.06 |
| Magnesium Oxide (MgO) | 7.59 |
| Iron Fe or (Fe$_2$O$_3$) | 0.5 |
| Manganese Oxide (MnO) | 0.44 |
| Sulfur( S) | 1.4 |
| Sodium Oxide ( Na$_2$O) | 0.4 |
| Loss on Ignition | 0 |

Also the type of GGBFS may be varied due to the cooling process. Slow cooling will crystallize the molten slag into a material having virtually no cementitious properties, while rapid cooling will form a glass that is "latent hydraulic cement". Latent hydraulic cement means that it requires more than only water to set, it requires a chemical activation[33]. The different chemical activators that can be used include but not limited to the following; sodium hydroxide, sodium carbonate, sodium silicate, potassium hydroxide, sodium sulfate, calcium sulfate potassium silicate solution.

### 2.1.3  Potassium silicate solution

Potassium silicate solution (K-silicate) also called liquid glass or water glass is a glass forming silicate salt. K-silicate is water-soluble and has a general formula $K_2SiO_3$. It has a molar mass of 154.28 g. $mol^{-1}$. K- Silicate has a white crystal appearance but also exist in solution.

Potassium silicate and sodium silicate are produced by the direct fusion of precisely measured portions of pure silica sand ($SiO_2$) and soda ash ($Na_2CO_3$) or potash ($K_2CO_3$) in oil, gas or electrically fired furnaces at temperatures above 1000 °C according to the following chemical reaction:

$$X_2CO_3 \; + \; ySiO_2 \longrightarrow X_2O \,.\, y\,SiO_2 \; + \; CO_2 \tag{1}$$

**(where *x* =Na or K; *y*= coefficient)**

Potassium silicate solutions are similar to solutions of sodium silicate. However, one significant difference, however, is that potassium silicate solutions are somewhat more viscous(low pour) than corresponding sodium silicate(high pour) solutions at equal concentrations. But, like sodium silicate, the viscosity of solutions is affected by ratio, concentration, and temperature. The addition of soluble silicates to the alkaline activator is expected to increase the dissolution of silicate ions from the aggregate into the geopolymer binder phase.

### 2.1.4  Deionized Water

Deionized water was used throughout the experiment. The importance of water among many reasons might be seen in the hydration process and also to be able to achieve a well-mixed homogenous solution within the given mixing time.

### 2.1.5  Potassium Hydroxide

Potassium hydroxide are white pellets alkali salts and inorganic compounds that are often used in the liquid form as bases to carry out chemical reactions. The Potassium hydroxide (KOH) used for this experiment was produced in the laboratory by mixing accurately measured KOH pellets with deionized water to prepare 4 M KOH solution. 4M KOH was used with a combination of k-silicate as activator for the geopolymer mixture.

As early as 1930s, alkalis, such as potassium hydroxide, were originally used to test iron blast furnace ground slag to determine if the slag would set when added to Portland cement. It was discovered that the alkali addition produced a rapid-hardening binder [16].

KOH has accelerating effect when used with OPC. This means that they act as accelerators to shorten the setting time of the hydration process, or to accelerate the hardening process or both [34].

### 2.1.6  Sucrose

Sucrose is a disaccharide obtained from dehydrolysis of glucose and fructose units with an acetal oxygen bridge, as shown by the structure in Figure 2.1. When used with OPC in certain proportion, sucrose was observed to have retarding effect. However due to the fact that the degree of retardation is very sensitive to small variation, sucrose are commonly not used.
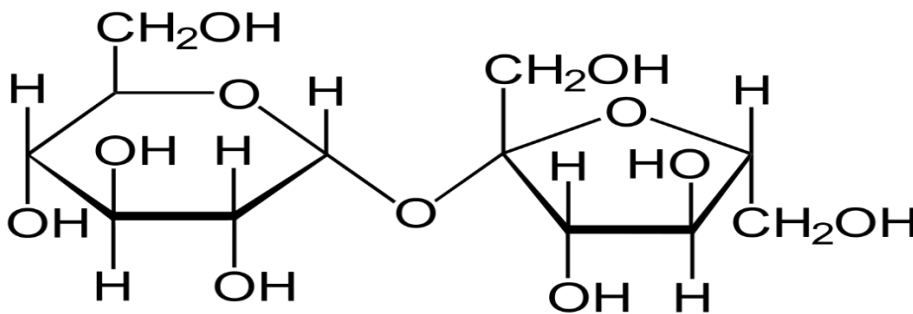


**Figure 2.1 Sucrose molecular structure. glucose + fructose**

It is important to note that one key reason why sucrose is widely used as a retarder at very low dosage is because of its osmotic rupture and formation of hydration sheath [35]. However, using sucrose at high dosage may cause flash setting. It is of interest to note that some well-known accelerators can act as retarders depending on its concentration, particularly at low concentration [35].

Sucrose, as a chemical admixture in this experiment was utilized in the third, fourth and fifth mix designs in an attempt to see the effect as a retarder to delay the setting time and extend the working period of the binder phase.

## 2.2 Specimen Mixing Procedure

The same mixing procedure was used when preparing samples for both the UCA and UCS tests to ensure uniformity. Prior to the preparation of the aplite-based geopolymer slurry, KOH solutions of the desired concentrations (4M) was prepared at approximately 24hours before usage.

The mixing procedure involved initial mixing of the solid phases (aplite, GGBFS or/and micro-silica). Using a woven wire mesh sieve that is most widely used for all types of laboratory sampling, the sieve was used as a quality to keep particle size below a certain size (63 micrometer). Larger aggregates, if any, are removed. The solid phase partially mixed is poured into a stainless steel container. The liquid phase components (KOH and K-silicate) are also measured accurately using the mettler Toledo mass balance. And then poured into a separate empty and clean stainless steel container. Figure 2.2 shows a mass balance that was used for this experiment.



*Figure 2.2 A Mettler Toledo mass balance that was used for accurately weighing the materials*



*Figure 2.3 An Ofite blender/mixer used for Mixing the solid and liquid phases*

An OFITE Model 20 Constant Speed Blender shown in Figure 2.3 that is used for oil well cements testing according to the guidelines stated within API 10-B [36] was used for the mixing of the solid and liquid phases. An ofite blender/mixer is suitable for this purpose because it is equipped with stainless steel mixing blades, stainless steel mixing container, rotational speed which is maintained at set point with microprocessor, timing relays which automatically control mixing times at required revolutions per minute (RPM), digital instrumentation which provides excellent readability and also two preset mixing speeds and variable speed for Cement, viz; 4,000 RPM and 12,000 RPM. The mixing process is exothermic and the energy required to do this is called mixing energy. Mixing energy as expressed in equation (2) is a function of rotational speed, time and mass of the slurry.

Mixing energy can be mathematically expressed as;

$$E_m = \frac{E}{M} = \frac{K\omega^2 t}{V} \tag{2}$$

Where:

$E_m$ =Mixing energy (kJ)

k=6.1 ´ 10-8m5/s (found experimentally)

t=mixing time (s)

w=rotational speed (radian/sec)

m=mass of the slurry (kg)

V=volume of slurry in the slurry cup (L)

The ofite blender was turned at automatic mode where it was preprogrammed to run for 4000 RPM for 15 seconds and 12,000 RPM for 35 seconds. The liquid phase is poured into the blender and then the blender is turned on. The solid phase is then gradually added. It is very important to ensure that there was no residual solids left over on the wall or in the bottom of the container, and if there was, a spatula is used to remove it while the blender is still rotating. However if the

mixer stopped rotating while some materials were still left in the cup, the materials were stirred into the mixture with a spatula to ensure that the slurry is properly mixed.

The mixture is then poured into a consistometer slurry cup for conditioning. An atmospheric consistometer is used for conditioning the slurry for approximately 20 minutes. Initially, atmospheric consistometers were designed to be used for low temperature cement system. But nowadays, it is used for conditioning slurries before testing. All slurries that was used for my experiment both UCA, UCS and tensile test was conditioned for the same amount of time. The basic purpose of employing an atmospheric consistometer at this stage is to ensure that proper homogenous mixing and a good interaction between the particles of the mixtures. Figure 2.4 shows the atmospheric consistometer that was used for this experiment.



*Figure 2.4 Atmospheric consistometer used for conditioning the slurry.*

After conditioning, due to the fact that some of the geopolymers had short setting time, it was important to put the slurry into the relevant container as soon as possible after being mixed. For the UCA test, the slurry was poured into the slurry chamber of the UCA equipment used. For the UCS and tensile test, the slurry was poured into cylindrical molds of length 92.00 mm and diameter 52.00 mm approximately.

## 2.3 Equipment and Apparatus

### 2.3.1 Ultrasonic Cement Analyzer

An ultrasonic cement analyzer (UCA) was used to measure the compressive strength of the geopolymer slurry over time as it sets and develop strength in the equipment. UCA employs a non-destructive test method that measures the change in velocity of an ultrasonic signal under simulated downhole temperature and pressure conditions. Figure 2.5 shows the UCA used for testing mix design #1, #2, #4 and #5. Figure 2.6 shows the UCA that is used for testing mix design #3. The temperature and pressure conditions for the system was set at 70$^{\circ}$C and 2200 psi using a precision quizix pump.
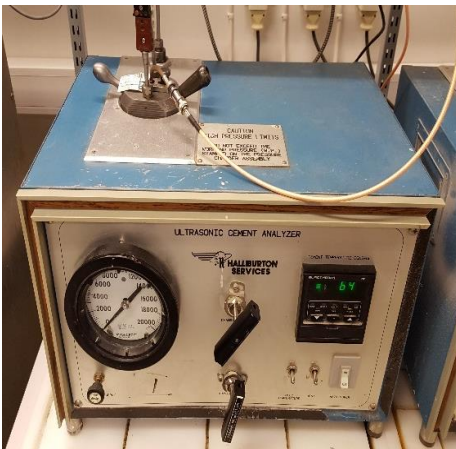


*Figure 2.5 Ultrasonic cement analyzer (UCA) used for testing.*
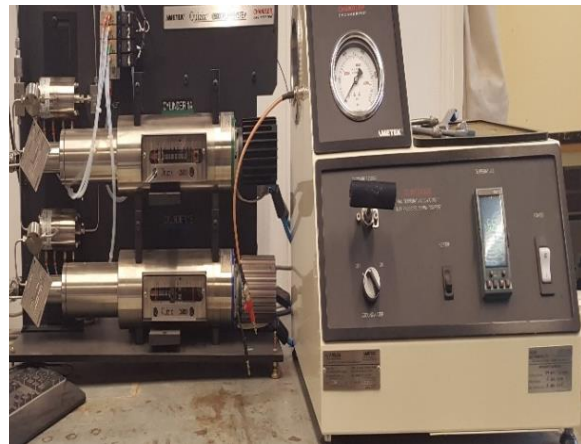
*Figure 2.6 Ultrasonic Cement Analyzer. MPRO model powered by a Quizix pump*

After conditioning the geopolymer slurry for 20 mins, the slurry is immediately placed in a sample holder. Afterwards the holder is placed in the UCA system and the sonic receiver and thermometer connected. The temperature ramping up of the UCA is immediately started and the pressure regulating system is also connected and pressurized to the required pressure rating.

A computer program, Chandler 5270 Data Acquisition and Control System version 2.0.152 was used to record the readings of transit time, temperature, compressive strength and time. As the ultrasonic waves are continuously sent though the sample the ultrasonic waves are detected and the information are recorded.

**Advantages**

- Non-destructive: the geopolymer samples are not destroyed during testing

- Flexible: More than one parameter can be measured at the same time

- Realistic: the temperature and pressure are set to simulate downhole conditions

- Accurate data: the unique technology gives a clean signal leading to more accurate times and data

- Computer controlled: data is instantly available and shown at the computer for easy analysis

**Disadvantages**

- UCA system does not take into account the tri-axial loading that the test sample will experience in the wellbore, meaning the failure stresses may be different from those observed in the UCA test.

- UCA system also do not account for the shear strength of the casing to cement or the casing to formation bond.

### 2.3.2 Toni Technik Unconfined Compressive Strength Equipment

Toni Technik equipment is used to conduct the unconfined compressive strength (UCS) test, a destructive testing method. This means that the geopolymer samples are destroyed during testing at deformation. After conditioning for 20 minutes in an atmospheric consistometer as discussed from the previous section, the slurry was poured into cylindrical molds of length and diameter of approximately 92.00 mm and diameter 52.00 mm respectively. It is then put in a core holder where it is pressurized up to 2200+/-10 psi using the same pressure chamber that is used to supply pressure to the UCA. After which it is put in an oven for temperature treatment for up to 70$^{\circ}$C.

The samples were kept in the oven for 1, 4, 5 and 7 days respectively for each mix design following the same mix design as was used in the previous case. After each of the period is complete, the

sample is removed and carefully taken out of the core holder. The top of the core samples is cut off using a diamond blade cutter and the samples are taken to the lab for axial loading until failure of the sample is observed. Figure 2.7 and Figure 2.8 shows the oven used and the Toni Technik equipment used.



*Figure 2.7 Oven used for curing the samples at the required bottom hole temperature.*



*Figure 2.8 A Toni Technik UCS equipment used for crushing the geopolymer samples.*

It is important to note that to be able to obtain an even load distribution and get accurate results, a smooth top and bottom of the sample is important. For that purpose was the top of the sample cut off. Sometimes the bottom of the sample might be cut off also. It is also important to ensure an evenly distributed applied force throughout the sample and for that reason, the sample is placed in a centralized position in the UCS equipment. A computer program is started to record the strength required to deform the core sample. It records the applied force given the length and diameter of the core sample.

### 2.3.3   Zwick Z020 Equipment for Tensile Strength Test

For the tensile test, a Zwick Z020 universal testing equipment shown in Figure 2.9 was used to carry out a Brazilian test and measure the splitting tensile strength. The samples were kept in the oven for 7 days only for each mix designs #1, #2 and #3 following the same mix design as was used in the previous case. After 7 days, the sample was removed and carefully taken out of the

core holder. The top of the core samples is cut off using a diamond blade cutter and the samples are taken to the lab for axial loading until failure of the sample is observed.

The load is applied normal to the length rather that normal to the cross sectional area as was the case of compressive strength. The loading rate was kept constant at 50mm/min. For the tensile loading, two forces were observed and recorded. The first was during fracture initiation or splitting and the second during complete failure of the core plug.

### 2.3.4  Scan Electron Microscope

The scan electron microscopy test was carried out using a ZEISS SUPRA 35VP scan electron microscope equipped with EDX to provide high resolution images of samples and elemental analysis. The scan electron microscope is used to reveal the structure and composition of materials on a nanometer scale. Figure 2.10 shows the ZEISS SUPRA 35VP series scan electron microscope that was used.

*Figure 2.9 Zwick Z020 manufactured by Zwick GmbH Germany used to perform a Brazillian test*
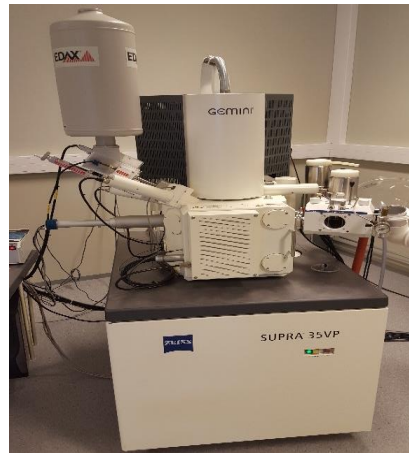
*Figure 2.10 A ZEISS SUPRA 35VP series Scan electron Microscope*

Before taking the sample for scan electron microscopy (SEM) analysis, a small section of the crushed sample from the UCS test has to be prepared first. Preparation of crushed sample for SEM analysis involve mounting and coating the sample and then introducing the sample into the vacuum chamber. After sufficient vacuuming of the sample, it is then mounted on a microscope tray. Thereafter, a computer program is started which automatically controls the microscope.

# 3    Results and Discussion

## 3.1    Sonic measurements

In the section that follows, we will get a presentation of the Ultrasonic Cement Analyzer (UCA) results for the various mix designs. The UCA is designed to use an empirical relationship between the velocity of an acoustic pulse through a cement sample and the sample's compressive strength. UCA allows for estimation of compressive strength development with time at typical well temperatures and pressures. The ability of UCA to perform strength measurements at downhole temperature and pressure and generate a continuous stream of measurements over time are key advantages of UCA instruments. The UCA tests were conducted at 70 °C (+/- 1) and a pressure of 2200 psi (+/- 100). This temperature and pressure correspond to the bottom-hole temperature and pressure respectively.

By comparison, UCA instrument is more effective than cylindrical UCS tests for analyzing standard cement slurries and geopolymers prepared according to API 10-B recommended standards[36]. This is because the UCS test introduce many errors to the system and it also destroys the sample at the end of the experiment. Therefore, the UCS test generates only single data points per sample. Also, the test is performed at atmospheric conditions rather than at downhole temperature and pressure. Table 3.6 presents the mixing proportion of the mix design #1 to #5.
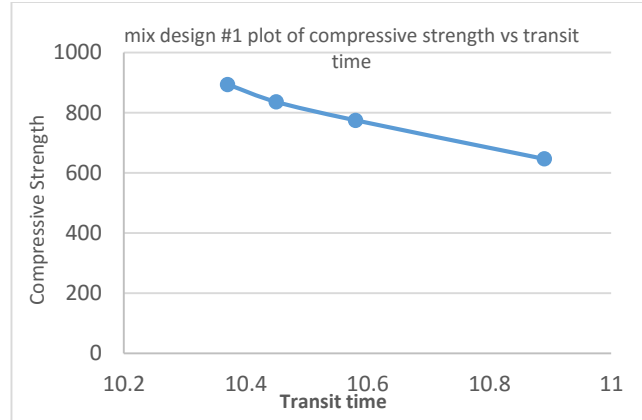
**Mix design #1-#5**

After seven (7) days, the compressive strength and the transit time was extracted for 24, 96, 120 and 168 hours which corresponds to 1, 4, 5 and 7 days respectively. Compressive strength and transit time were extracted for these times and a graph of compressive strength vs. transit time was plotted as seen in Figure 3.1 to generate an equation that best describe our particular aplite-based geopolymer slurry system.

***Table 3.1 Extracted transit time and compressive strength.***

| Time (days) | comp. strength(psi) | Transit time(**micsec/in**) |
|---|---|---|
| 1 | 647 | 10.89 |
| 4 | 775 | 10.58 |
| 5 | 836 | 10.45 |
| 7 | 894 | 10.37 |



***Figure 3.1 A plot of compressive strength vs. transit time for extracted time interval.***

From the graph of compressive strength vs transit time for mix design #1, the following equation (3) was generated to convert transit time into compressive strength;

$$\boldsymbol{\Phi = -49.888\Psi^2 + 602.15\Psi} \qquad (3)$$

Equation (3) is a polynomial equation of the second order and it was imputed into the algorithm section of the UCA data acquisition software. This was done by following some basic steps.

By clicking on the "test properties" icon and then the "calculated values" tab of the 'chandler 5270 data acquisition and control system' software which was used for the analysis. Finally, double click on compressive strength and a display similar to Figure 3.2 provides the input window for our algorithm.

*Figure 3.2 A description of the input window for equation 2*

Data were generated for Time (days), Transit time (microseconds/in), Temperature (degree Celsius) and Compressive strength (psi). From the given data, the following were plotted.
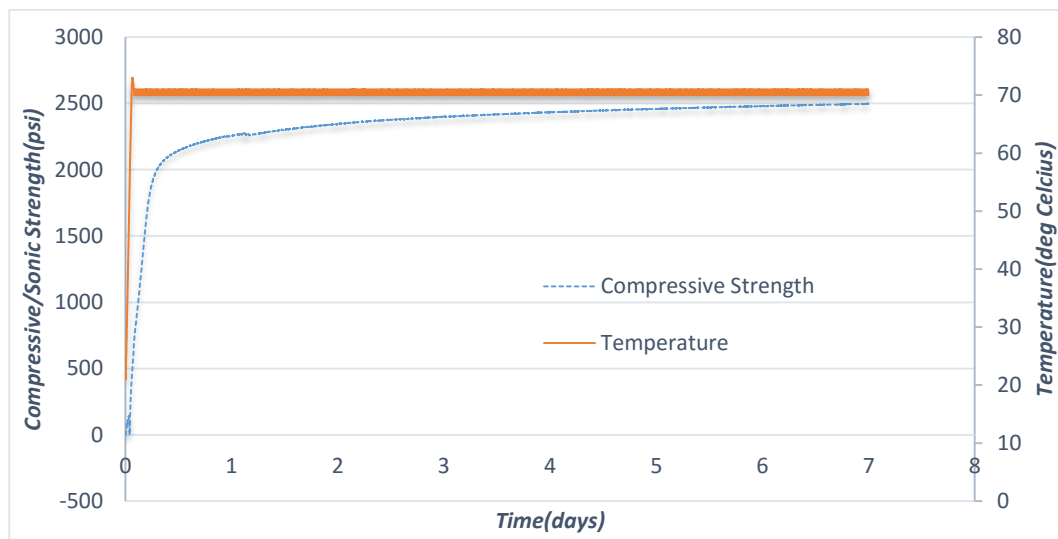


*Figure 3.3 A plot of temperature and compressive (sonic) strength vs. time*

*for mix design #1.*

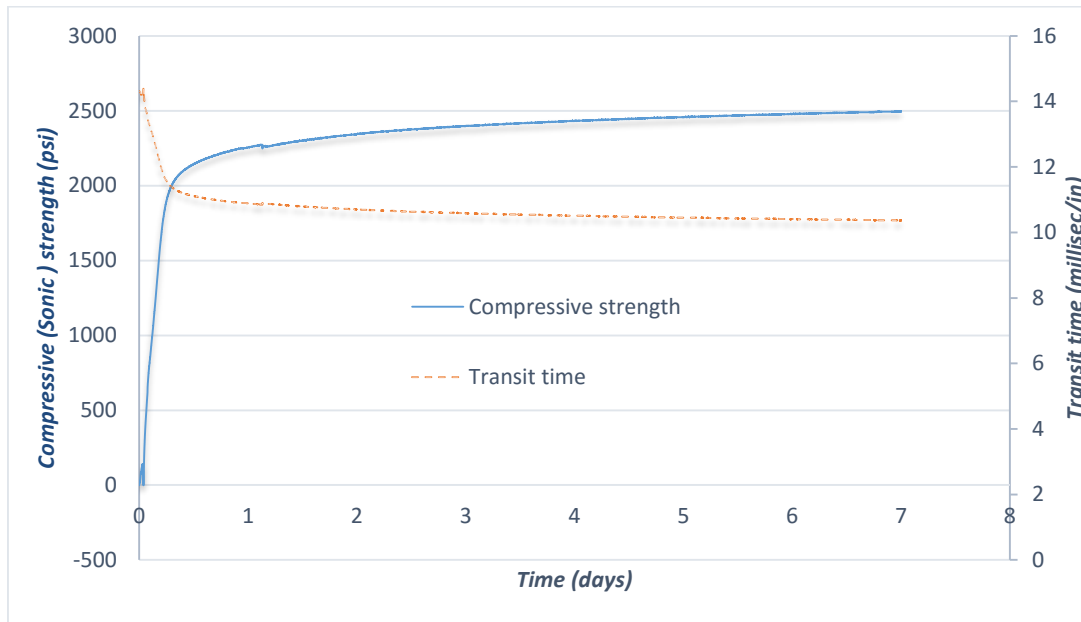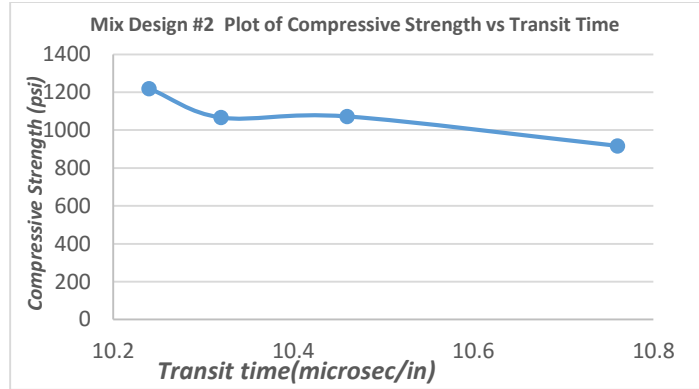*Figure 3.4 A plot of transit time and compressive (Sonic) strength vs. time*

From the plots of compressive strength (sonic) vs time, we see the strength development with time. The temperature ramps up to 70ºC in less than two hours and also at same time the most significant drop in transit time was observed.  After 1 day, 4 days, 5 days and 7days, the compressive strength was 2255 psi, 2433 psi, 2458 psi and 2496 respectively. Significantly, 90% of the strength was developed after 24 hours as can be seen from Figure 3.3 and Figure 3.4. Also the effect of temperature in compressive strength development is seen from Figure 3.3. As the temperature increases, the compressive strength was observed to increase also. The higher early strength which developed can be attributed to the suddenness of this reaction at an early stage caused by the high-temperature curing [37].

Table 3.2 and Figure 3.5 shows the extracted measured uniaxial compressive strength and transit time at selected time interval for mix design #2.

**Table 3.2 Extracted transit time and compressive strength for mix design #2.**

| Time (days) | comp. strength(psi) | Transit time(micsec/in) |
|-------------|---------------------|-------------------------|
| 1 | 917 | 10.76 |
| 4 | 1072 | 10.46 |
| 5 | 1066 | 10.32 |
| 7 | 1219 | 10.24 |



**Figure 3.5 A plot of compressive strength vs. transit time for extracted time interval for mix design #2.**

The following correlation in equation (4) was generated to convert transit time into compressive strength;

$$\Phi = -56.663\Psi^2 + 694.36\Psi \qquad (4)$$
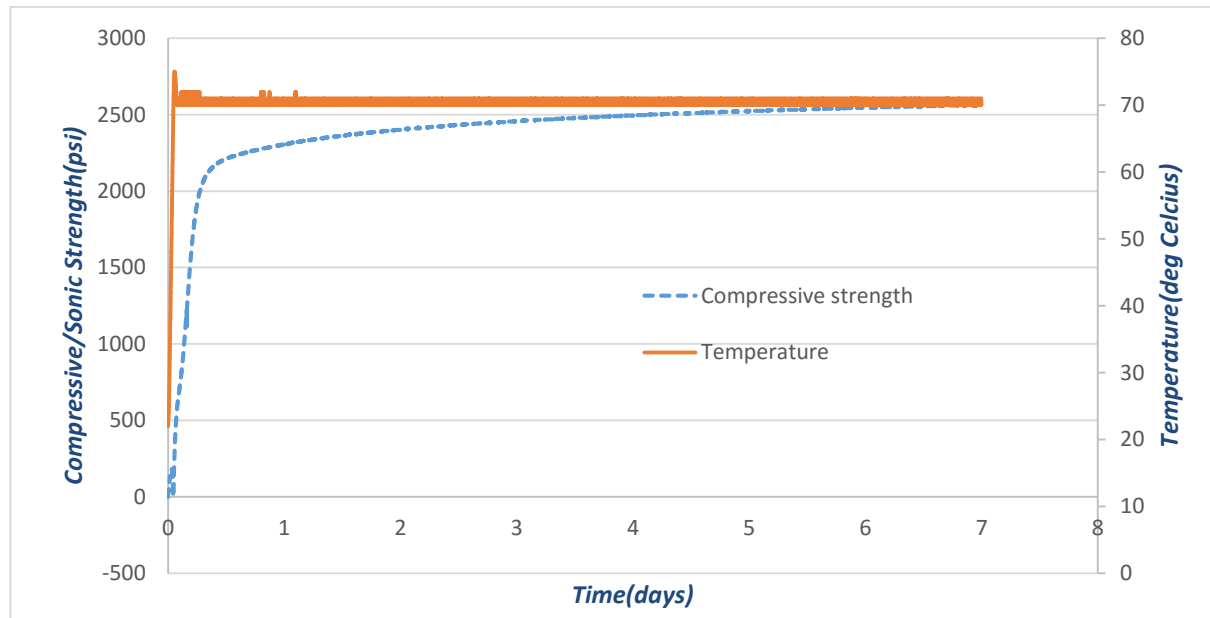


**Figure 3.6 A plot of temperature and compressive strength vs time for mix design #2**
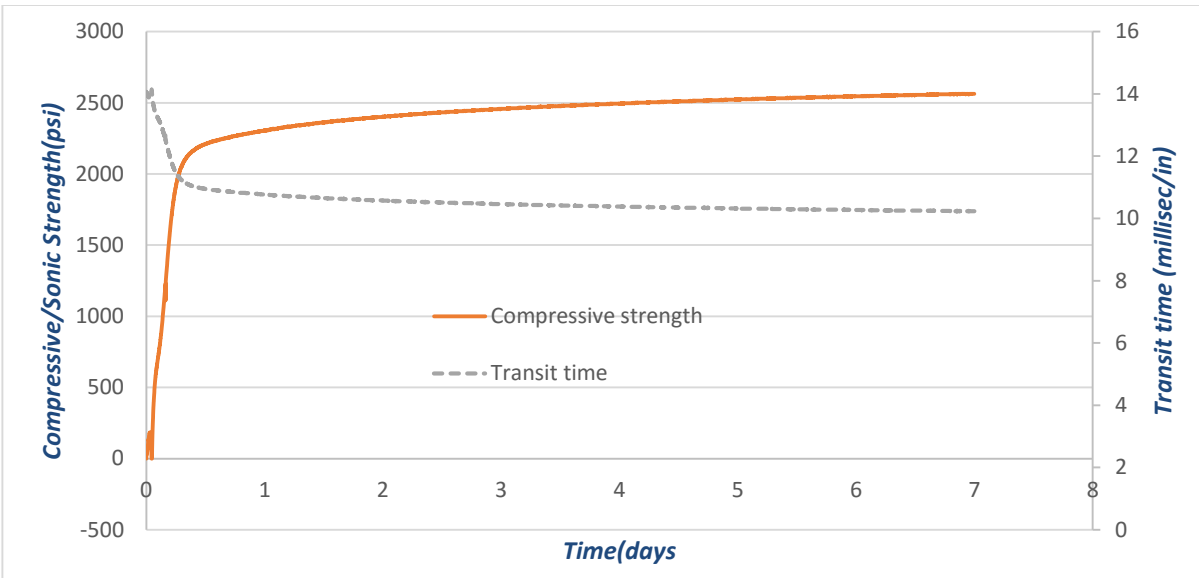
**Figure 3.7 A plot of transit time and compressive (sonic) strength vs time for mix design #2**

From Figure 3.6 and Figure 3.7 of temperature, transit time and Compressive (Sonic) strength vs time for mix design #2. The compressive strength was seen to rise rapidly after day 1 to 2307 psi. After 4 days, 5 days and 7days, the compressive strength was 2494 psi, 2523 psi, 2458 psi and 2563 respectively. Significantly, approximately 97 percent of the strength was developed after one day as can be seen from Figure 3.6. It is immediately observable that there is an increase in compressive strength as compared with the base case. Also the temperature ramps up quite fast although at same rate. It appears from Table 3.1 and Table 3.2 that the sonic strength of mix design #2 is greater than sonic strength of mix design #1 which is likely because of the effect of the added sucrose. This caused a slower initial formation of geopolymer product which most likely gives them more opportunity and more time to align or organize themselves in the matrix.

Table 3.2 and Figure 3.5 shows the extracted measured uniaxial compressive strength and transit time at selected time interval for mix design #3. After seven (7) days, the compressive strength and the transit time was extracted for 1, 4, 5 and 7 days.

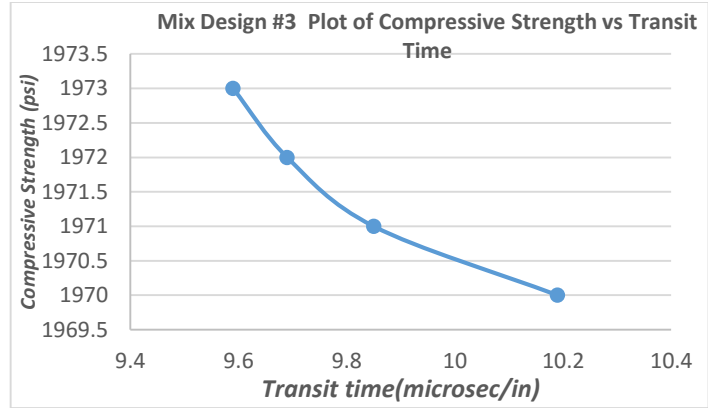*Table 3.3 extracted transit time and compressive strength for mix design #3.*

| Time (days) | comp. strength(psi) | Transit time(micsec/in) |
|---|---|---|
| 1 | 1970 | 10.19 |
| 4 | 1971 | 9.85 |
| 5 | 1972 | 9.69 |
| 7 | 1973 | 9.69 |



*Figure 3.8 A plot of compressive strength vs. transit time for extracted time interval for mix design #3.*

For this case, the following polynomial in equation (5) was generated to transform transit time to compressive strength.

$$\Phi = 2.9299\Psi^3 - 78.625\Psi^2 + 690.29\Psi \tag{5}$$
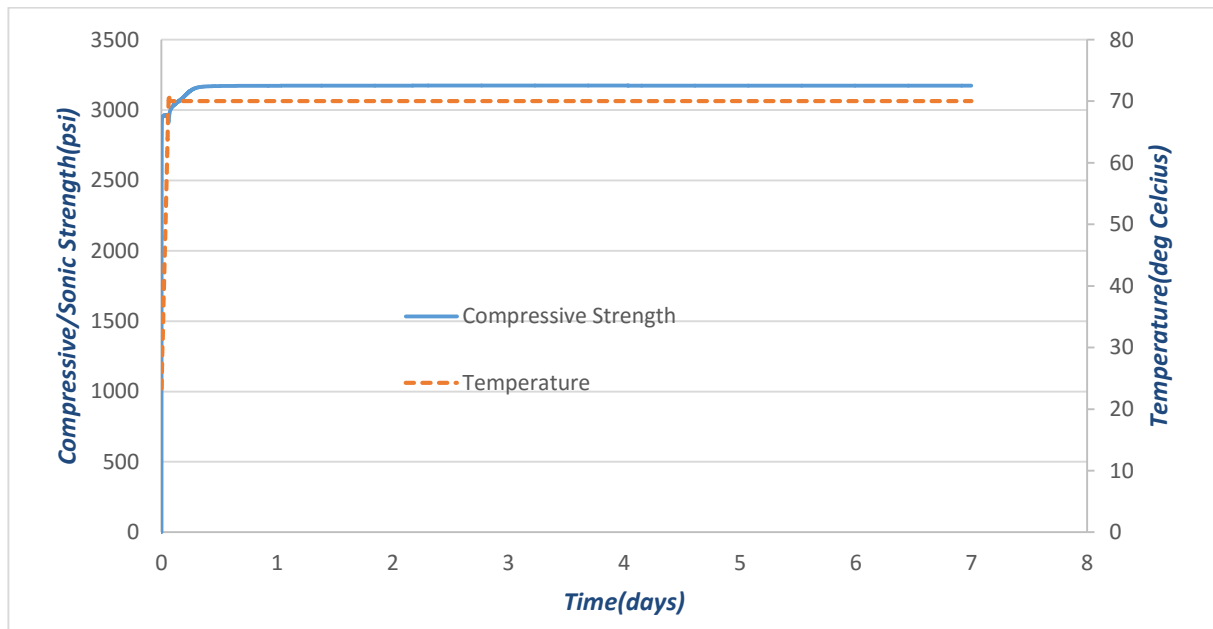


*Figure 3.9 A plot of temperature and compressive strength vs time for mix design #3*
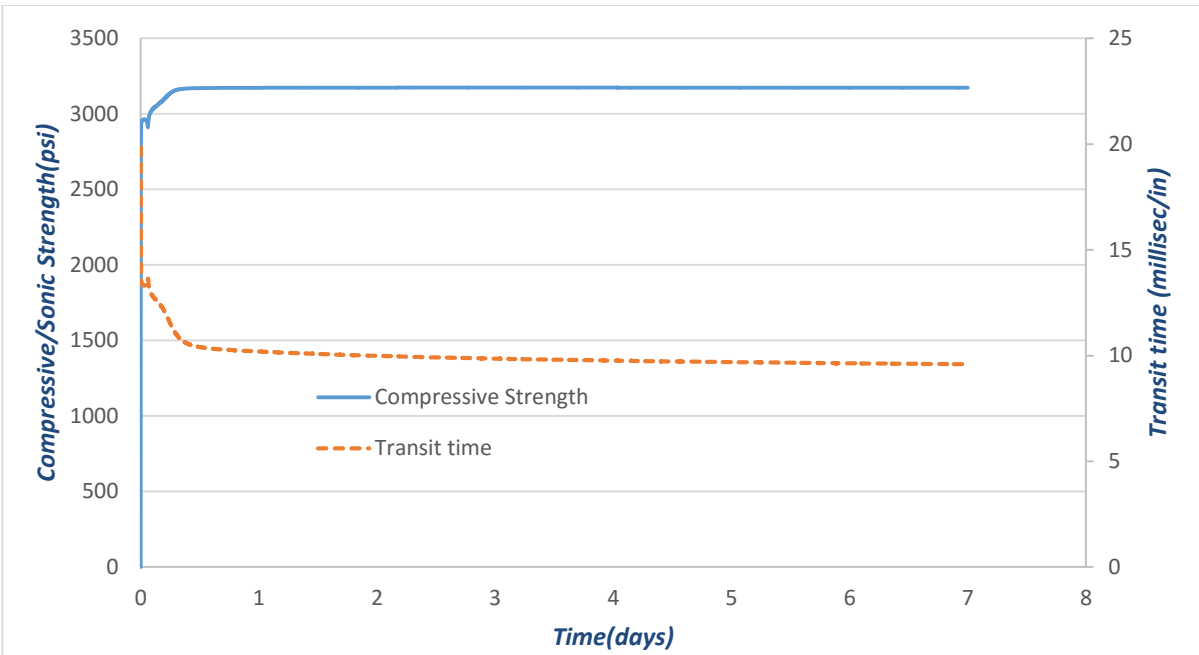
*Figure 3.10 A plot of transit time and compressive (Sonic) strength vs time for mix design #3*

The obtained compressive strength for the third mix design is obviously greater than the second and the first. But will be made clearer with a comparison of the plots. The compressive strength peaked at 3173 psi after 7 days.
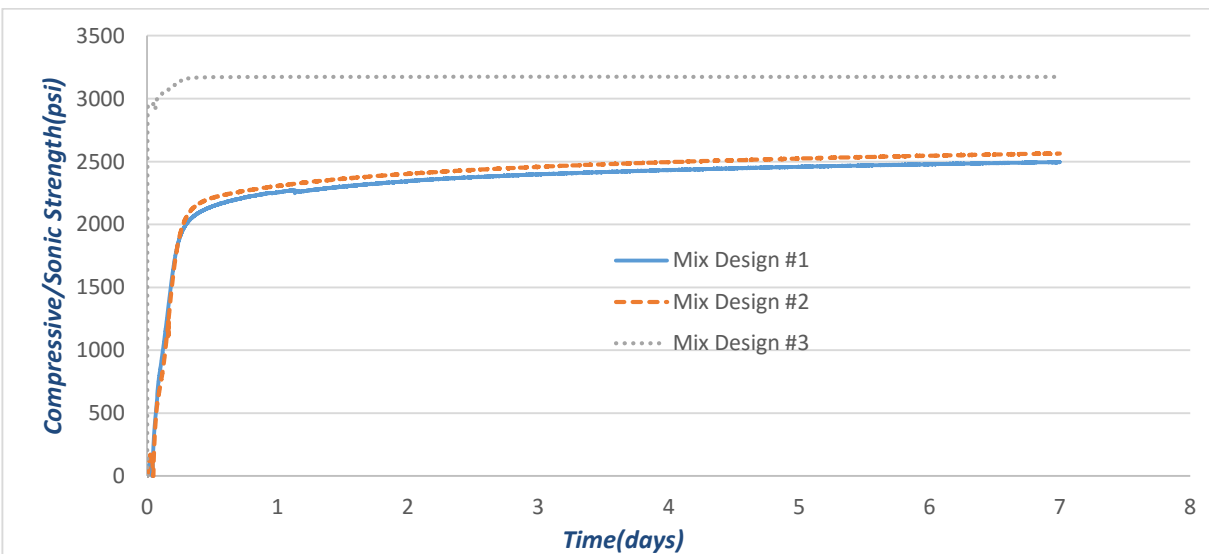


*Figure 3.11  A graph of result comparison of UCA test for mix design #1,#2 and #3*

From the Plot of Figure 3.11, it is immediately obvious that there was an improved strength in the case of mix design #2 and #3 with compressive strength of 2653 psi and 3173 psi respectively after 7 days.  This might be owing to the fact that a sufficiently high dosage of sucrose was added to the system. The results show that sucrose at a certain dosage could significantly affect the synthesis of aplite based geopolymer as it tend to increase the initial setting time of the geopolymer paste, hence acting as a retarder. The sucrose added to mix design #2 was observed to retard the strength development. For example after 4 hours of curing in the UCA, the compressive strength of mix design #2 was 1154 psi whereas the compressive strength of the base case was 1339 psi. Also increasing the amount of sucrose added in mix design #3 was seen to accelerate the reaction with the addition of temperature. After 4 hour of curing, the compressive strength was observed to be 3162 psi.

Mix design #4 and #5 has a solid-to-liquid ratio of 1.95 and 1.99 respectively. For mix design #4 and mix design #5, it was observed that the slurry developed no strength after 7 days as shown in Table 3.4 and Table 3.5. After 7 days, they developed no compressive strength and the sample was removed from the UCA and it looks like in Figure 3.12. This shows that it developed no compressive strength.

*Table 3.4 extracted compressive strength and transit time at selected time interval for mix design #4.*

| Time (days) | comp. strength(psi) | Transit time(**micsec/in**) |
|---|---|---|
| 1 | 0 | 14.42 |
| 4 | 0 | 14.47 |
| 5 | 0 | 14.43 |
| 7 | 0 | 14.44 |

*Table 3.5 extracted compressive strength and transit time at selected time interval for mix design #5.*

| Time (days) | comp. strength(psi) | Transit time(**micsec/in**) |
|---|---|---|
| 1 | 0 | 14.42 |
| 4 | 0 | 14.47 |
| 5 | 0 | 14.43 |
| 7 | 0 | 14.44 |

**A**



**B**
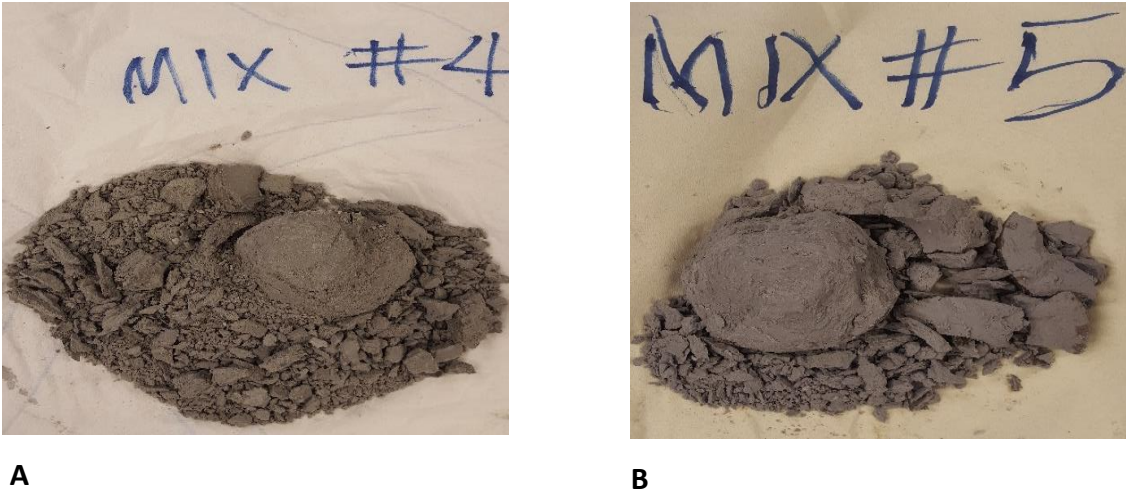
*Figure 3.12  Samples from mix design #4 and #5 recovered from the UCA equipment after 7 days with heat curing at 70⁰C.*

*Table 3.6 Compositional ratio used for mixing the slurry.*

| Sample | Alkali solution/ Alkali silicate solution by weight | Distilled water/ Activator ratio by weight | Solid/ Total solid fraction by weight | | | | Liquid/ solid ratio by weight |
|---|---|---|---|---|---|---|---|
| | | | Sucrose | Micro-silica | GGBFS | Aplite | |
| Mix design #1 | 0.431 | 0.097 | - | - | 0.303 | 0.697 | 0.514 |
| Mix design #2 | 0.431 | 0.097 | 0.012 | - | 0.299 | 0.689 | 0.507 |
| Mix design #3 | 0.431 | 0.097 | 0.018 | - | 0.298 | 0.685 | 0.504 |
| Mix design #4 | 0.431 | 0.097 | 0.012 | 0.015 | 0.294 | 0.678 | 0.500 |
| Mix design #5 | 0.431 | 0.097 | 0.017 | 0.029 | 0.289 | 0.665 | 0.490 |

## 3.2   UCS measurements

Uniaxial compressive strength (UCS) test is unquestionable the oldest technique for compressive strength quantification. Therefore, in the following section, you will get a presentation of the UCS measurement which in the present experiment involves a known procedure of pouring a sample of the aplite based geopolymer slurry into a cylindrical mold with approximate diameter of 52.00mm and curing it according to recommended API standards and not compromising real downhole conditions of temperature and pressure.

As stated earlier, UCS tests is also referred to as destructive testing because at the end, the material is deformed by crushing. In this case, it was prepared according to API 10B-4 recommended practice[36].

A total of 45 different samples was prepared (repeated experiments not included). Three (3) different samples were prepared for every specific recipe or mix design (labelled as mix design #1, #2, #3, #4 and #5). The specimen was placed in a core holder and pressurized to 2200 psi to mimic bottom-hole conditions. The core holder together with the samples now pressurized is placed in an oven and the temperature ramping up of the oven was started. The temperature ramps up from ambient temperature of 23 degree Celsius $(^0C)$ to 70 degree Celsius $(^0C)$  and then held constant for the rest of the experiment.  70 degree Celsius $(^0C)$   is the bottom-hole temperature. For each set of experiment, the oven was turned off, the core holders allowed to cool down and the specimens were removed after a 24 hours, 96 hours, 120 hours, and 168 hours, which corresponds to 1 day, 4 days, 5 days and 7 days respectively.

A SIMEX uniaxial compression machine located in the Civil engineering laboratory was used to crush the test samples.  Before proceeding with each test, a record of the diameter and the length of the core is made using a vernier caliper. A record the maximum axial force required to break the specimen is noted and then the compressive force calculated. Proper measurement is essential to ensure accuracy of calculated results.

The plots from Figure 3.13 - Figure 3.16 show the results of the UCS test. And the compressive strength was calculated using the expression for calculating compressive strength found in equation (6):

$$S = \frac{F}{A} = \frac{4F}{\pi * d^2} \qquad (6)$$
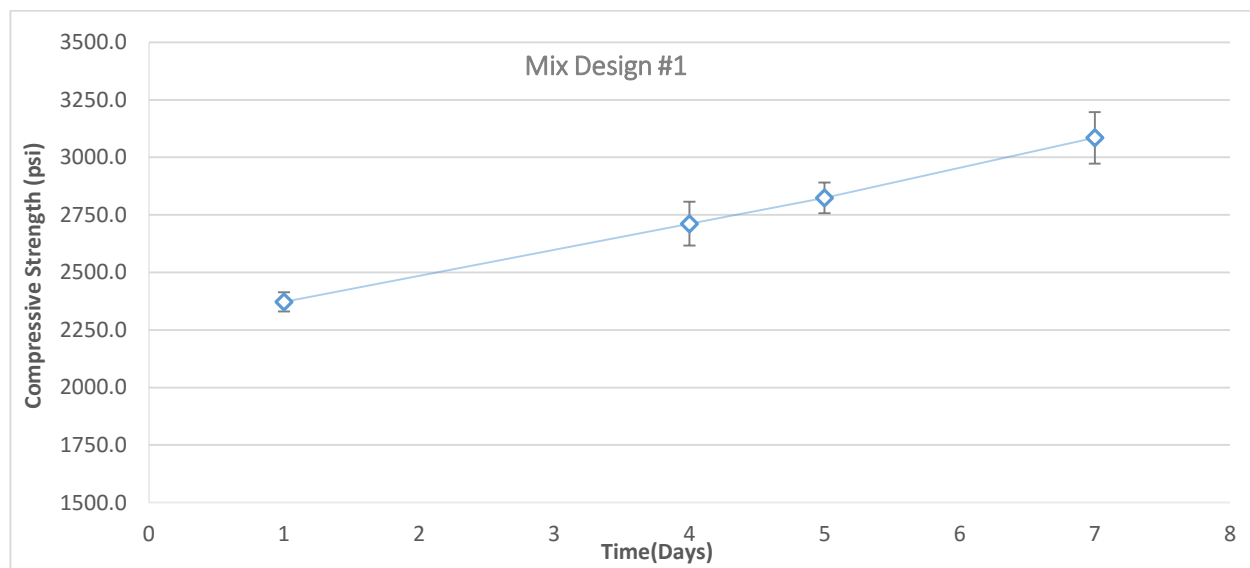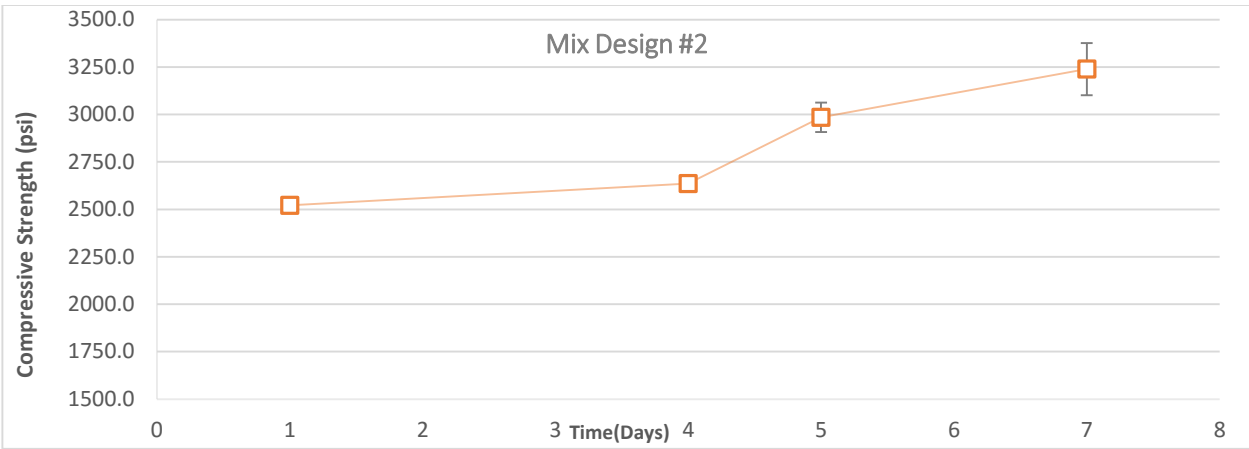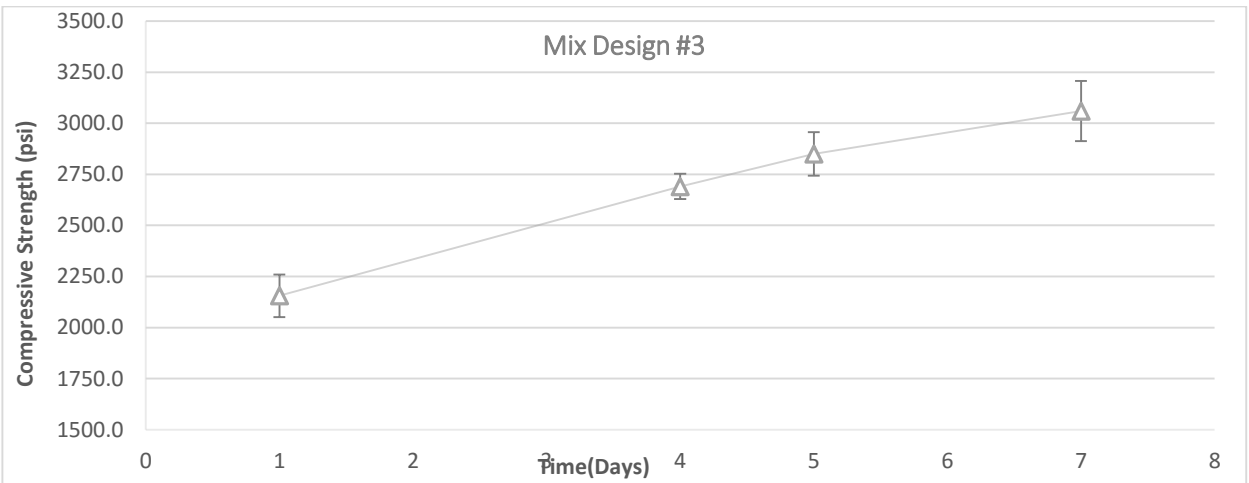
Where

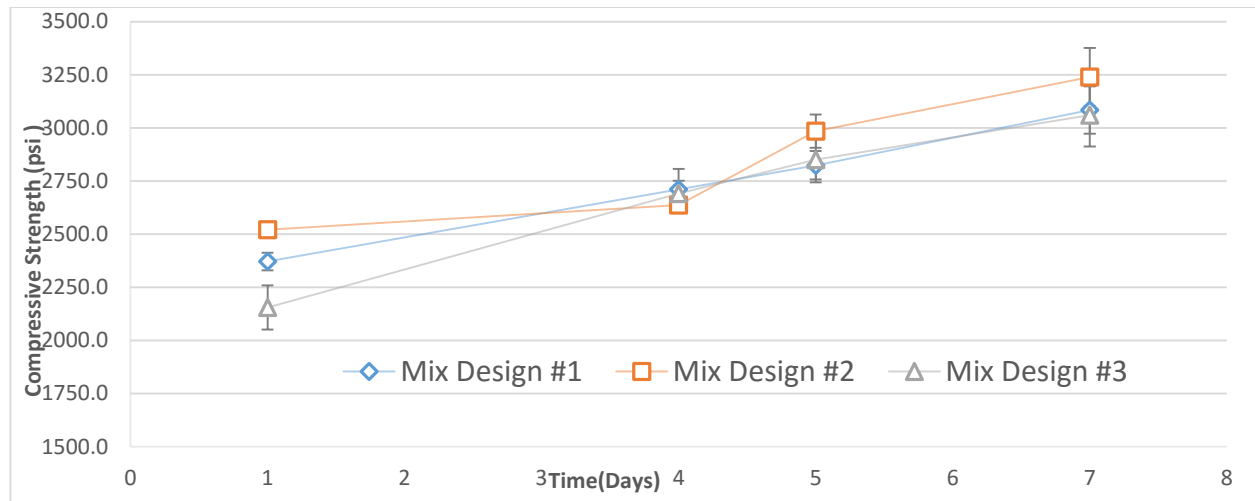S= compressive strength

F= force (N)

A= area (m)

d= diameter (m)



*Figure 3.13 compressive strength development versus time for mix design #1*

*Figure 3.14 compressive strength development versus time for mix design #2*



*Figure 3.15 compressive strength development versus time for mix design #3*

*Figure 3.16 Comparison of the compressive strength of the three mix design #1, #2 and#3.*

## 3.3 Tensile test measurements

For the tensile test, the Brazilian test was used to determine the indirect tensile strength of the cylindrical sample of the material. It was subjected to a diagonal compressive line load (splitting test). The setup was illustrated in Figure 2.9. The average of three tested specimens each mix design #1, #2, #3 was taken and reported as the representative strength of the corresponding mix.

*Table 3.7 Tensile properties of geopolymer mix design #1 -#3 after 7 days of curing*

| Sample | Li(mm) | Di(mm) | Fi(N) | Tensile strength (N/mm2) | Tensile strength (Psi) |
|---|---|---|---|---|---|
| SAMPLE #1-1 | 40.5 | 52 | 2450 | 0.74 | 107 |
| SAMPLE #1-2 | 37 | 52 | 2400 | 0.79 | 115 |
| SAMPLE #1-3 | 35 | 52 | 3400 | 1.19 | 172 |
| SAMPLE #2-1 | 37 | 52 | 2400 | 0.79 | 115 |
| SAMPLE #2-2 | 37 | 52 | 1700 | 0.56 | 82 |
| SAMPLE #2-3 | 38 | 52 | 2000 | 0.64 | 93 |
| SAMPLE #3-1 | 30 | 52 | 1500 | 0.61 | 89 |
| SAMPLE #3-2 | 39 | 52 | 2500 | 0.78 | 114 |
| SAMPLE #3-3 | 39 | 52 | 1955 | 0.61 | 89 |
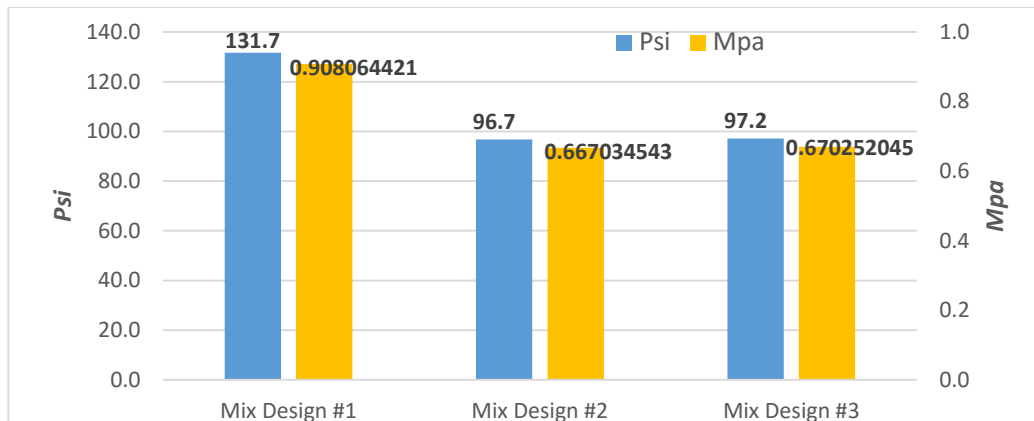
*Figure 3.17 Splitting tensile strength of three mix designs in psi and Mpa*

The variation of the split tensile strength of mix design #1, #2 and #3 aplite based geopolymer cured for 7 days is shown in Figure 3.17. From the bar diagram it is clear that the geopolymer concrete blended with sucrose shows a reduced split tensile strength values. However mix design #1 which was assumed base case showed the highest split tensile strength.

## 3.4   Scan Electron Microscopy analysis

The micrograph of aplite based geopolymer of mix design #1, #2 and #3 is shown in Figure 3.18, Figure 3.20 and Figure 3.22 respectively. All samples were cured at 70°C for 7 days at same pressure of 2200 +/- 10 psi. The orange spot is an actual spot from which EDAX analysis was made. Analysis areas can actually be as small as 1/2 a micron in size. Importantly, to observe the elemental distribution of aplite based geopolymer, the geopolymerized solidified product was studied using SEM mapping as can be seen in Figure 3.24 and observing the distribution of major elements like Al, Si, Ca, mg, K.
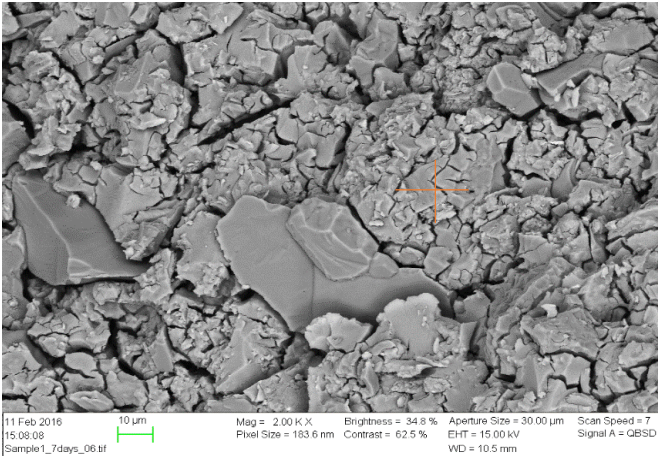
**Figure 3.18 Scan electron microscope (SEM) image of mix design #1 magnified 2000 times**
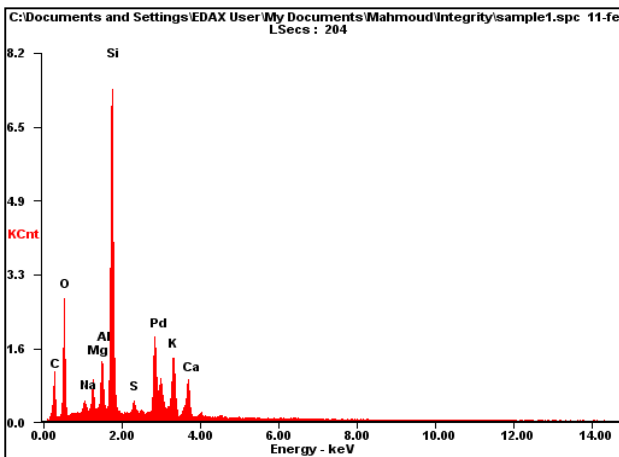


**Figure 3.19 Energy dispersive X-Ray (EDAX) spectroscopy analysis of mix design #1 for elemental analysis performed on the small orange-box region indicated in the figure. A gaussian fit of the elemental peaks selected is performed. From this peaks, it calculates the area under the peaks. From this, the atomic and weight percent are calculated and tabulated in table 3.8.**

**Table 3.8 A standardless quantitative analysis performed on sample.**

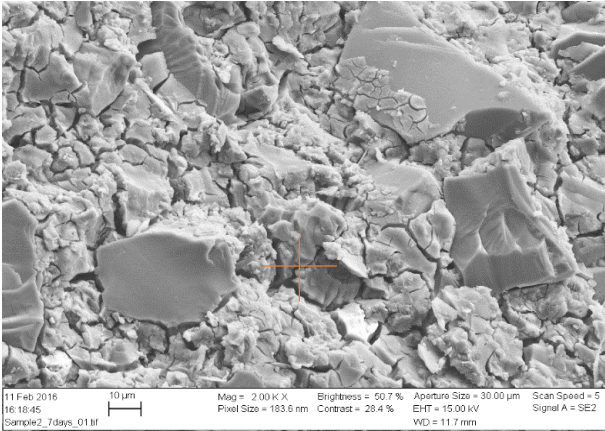| Element | Wt % | At % |
|---------|------|------|
| C K | 31.58 | 54.37 |
| NaK | 01.15 | 01.04 |
| MgK | 02.80 | 02.38 |
| AlK | 04.63 | 03.55 |
| SiK | 34.76 | 25.59 |
| S K | 01.84 | 01.18 |
| K K | 11.53 | 06.10 |
| CaK | 09.82 | 05.06 |
| TiK | 00.63 | 00.27 |
| FeK | 01.27 | 00.47 |

**Figure 3.20 Scan electron microscope (SEM) image of mix design #2 magnified 2000 times.**



**Figure 3.21 Energy dispersive X-Ray (EDAX) spectroscopy analysis of mix design #1 for elemental analysis performed on the small box area indicated the in figure. A gaussian fit of the elemental peaks selected is performed. From this peaks, it calculates the area under the peaks. From this, the atomic and weight percent are calculated and tabulated in table 3.9.**

*Table 3.9 A standardless quantitative analysis performed based on Figure 3.23*

| Element | Wt % | At % |
|---------|-------|-------|
| C K     | 12.45 | 19.03 |
| O K     | 51.64 | 59.24 |
| NaK     | 00.71 | 00.57 |
| MgK     | 02.45 | 01.85 |
| AlK     | 02.47 | 01.68 |
| SiK     | 18.79 | 12.28 |
| S K     | 00.74 | 00.43 |
| K K     | 05.61 | 02.63 |
| CaK     | 04.56 | 02.09 |
| TiK     | 00.21 | 00.08 |
| FeK     | 00.37 | 00.12 |

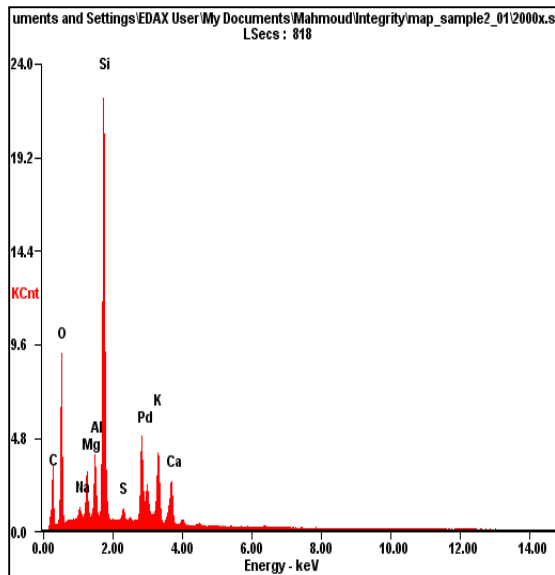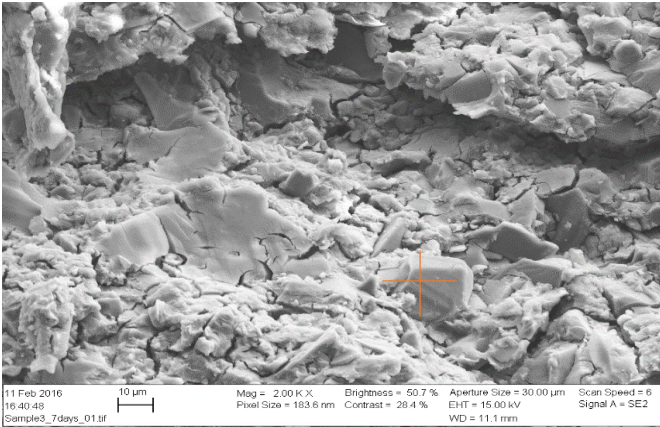**Figure 3.22 Scan electron microscope (SEM) image of mix design #3 magnified 2000.**
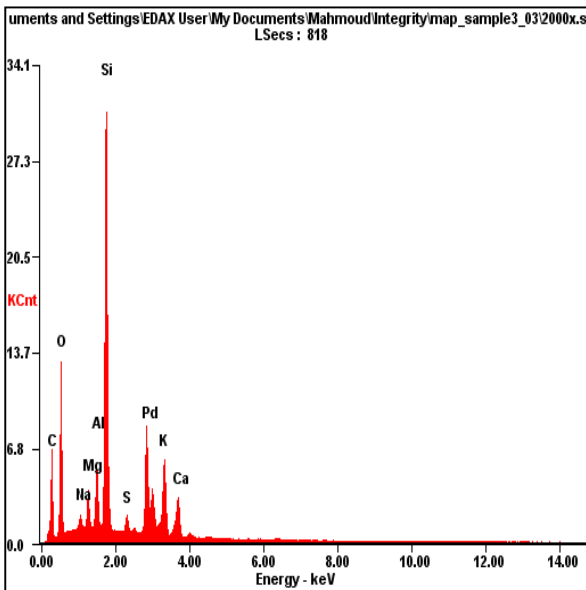


*Figure 3.23 Energy dispersive X-Ray (EDAX) spectroscopy analysis of mix design #1 for elemental analysis performed on the small box area indicated in the figure. A gaussian fit of the elemental peaks selected is performed. From this peaks, it calculates the area under the peaks. From this, the atomic and weight percent are calculated and tabulated in table 3.10.*

*Table 3.10 A standardless quantitative analysis performed on sample based on Figure 8.4*

| Element | Wt % | At % |
|---------|-------|-------|
| C K | 16.35 | 24.30 |
| O K | 50.14 | 55.95 |
| NaK | 00.75 | 00.58 |
| MgK | 01.82 | 01.33 |
| AlK | 02.43 | 01.61 |
| SiK | 17.94 | 11.41 |
| S K | 00.87 | 00.49 |
| K K | 05.35 | 02.44 |
| CaK | 03.98 | 01.77 |
| TiK | 00.07 | 00.03 |
| FeK | 00.31 | 00.10 |
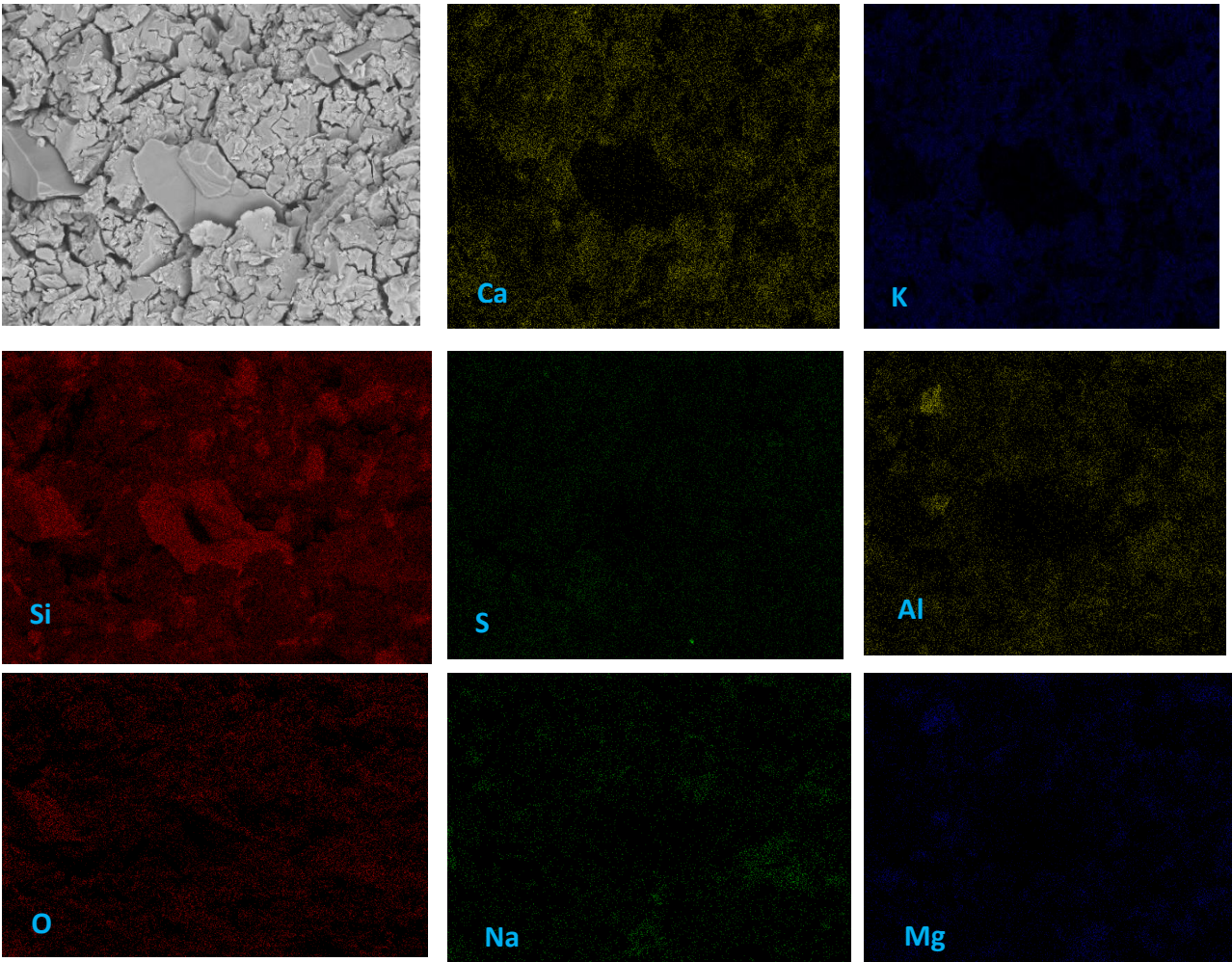
*Figure 3.24 Mapping showing main reaction products of aplite based geopolymer after 7 days*

Advanced mapping was used to identify the main reaction products of the aplite based geopolymer. It is obvious that it was homogenously mixed during the mixing and conditioning phases. These elemental maps agrees with the EDAX spectrographs analysis presented earlier. Note that the magnification is 2000 times and the scale is 10 micrometer.

## 3.5   Discussion

### Workability

Although the rheological properties and behaviors of our aplite-based geopolymer is not included in or rather outside the scope of this study, the aplite-based geopolymer slurry in fresh state was observed to be moderately viscous and the workability was further increased by the deionized water.

### Compressive strength

The compressive strength of the aplite-based geopolymer specimens were determined after 1, 4, 5 and 7 days from manufacture. For the UCS, three specimens for each mix design were crushed in a compression testing machine and the average is reported.  For the UCA, compressive strength were obtained indirectly using a correlation and the data obtained are presented in equation 1.0  and Figure 3.1, Figure 3.5 and Figure 3.8 is a plot from the derived correlation. From the UCS test, Figure 3.13, Figure 3.14, Figure 3.15 and Figure 3.16  are derived plots of compressive strength (psi) vs time (days). As expected, we could see a general compressive strength increment from the samples as the days increases which is a trend that was also observed in the case of the UCA results. However, mix design #2 seems to have developed more compressive strength than mix design #1 and mix design #3 after 7 days. Although the effect of the retarder is not completely obvious from this UCS test result. This could be owing to the fact that the degree of retardation is sensitive to parameters like concentration and temperature [34]. Also because the UCS test measures discrete points and not a continuous measurement as in the case of the UCA test.

### Effect of microsilica

It is important to note the effect of micro-silica on mix design #4 and #5. Micro silica has a higher reactivity especially at early age of the reaction firstly because it has a higher silicone dioxide ($SiO_2$) content and secondly, because of its small particle size. However, typical temperature of $60^oC$ to $90^oC$ is needed for heat activation in early strength development. Interestingly, it was observed that for mix designs #4 and mix design #5 where microsilica was added 1.5 and 2.9 %weight excess, and heat curing for up to $70^oC$, a reverse trend was noticed.

The compressive strength of the aplite-based geopolymer with excess microsilica increased the silica content so much that 4M concentration of KOH solution could not effect an alkali activation. However because of the corrosive nature of potassium hydroxide, the concentration could not be increased. Mix design #1 aplite-based geopolymer without any sucrose addition in this research would start to set after 20 minutes as observed from the computer logs, but with addition of sucrose, and every other parameters kept constant, the setting time could be delayed until after 1 hour. Inclusion of sucrose also provide positive effect to the concrete strength.

In terms of adsorption, it was observed that increasing the silica content of the fresh geopolymer by adding micro silica with large surface area due to its fineness, there was an increased water adsorption process in early phase. Free water not involved in the reaction is adsorbed to the large surface area of the microsilica and hence the free water left in the mix cannot bleed to the surface since the micro particles also blocks the pores in the fresh geopolymer mix so that free water does not come to the surface. As a result, there was no compressive strength developed as can be seen in Figure 3.12. A similar interesting result was observed by D. Adak et al. (2014) [38] where, addition of microsilica to a fly ash based geopolymer mortar up to above 6% of fly ash seems to provide a reduction in compressive strength [38] .

### Split tensile strength

The results of the tensile test is given and the corresponding plots in Figure 3.17.  It is observed from the test results that the splitting tensile strength of the geopolymer concrete is varying from 131.7 psi to 97.2 psi. From the comparative study, it can be shown that the splitting tensile strength of the geopolymer concrete is also increasing proportionately to the compressive strength. The observed trend showed that the tensile strength is only a fraction of the compressive strength. It is however difficult to get a correlation to express the relation between the tensile and compressive strength because of limited data. Further studies could be able to show this.

For mix design #1, it is expected that the splitting tensile strength falls within the range of 95 psi to 97 psi. However, it is also possible that there was error introduced in the system either during the curing phase of the geopolymer since there could be a pressure variance in the system or the

loading rate used for the first was different which must have affected the higher value gotten. Again, the position of the core may not have been centralized causing an uneven loading on the sample. However, the main shortcoming of Brazilian test is that the stress state at the center of the testing disc is not a purely tensile mode. The source of the error is not clear but the evidence of error is customarily indicated by the error bars.

## Microstructure analysis

The SEM images only give confirmation to the findings with respect to the elements present and the compositional analysis. Using a fractured surface, we gain information on the different phases present. Figure 3.18 - Figure 3.22 showed the micrograph of mix design #1, #2 ad #3 aplite-based geopolymer cured for 7 days at 2000 psi. It showed the particles being homogenously mixed, with very little porosity as is obvious from very narrow cracks. These narrow cracks may have been as a result of water evaporation, applied force on the core sample while crushing or due to incomplete reaction. The micrograph of Figure 3.20 and Figure 3.22 are very similar. It can be generally seen that there is no major differences in their appearance since they contain dosages of sucrose in 1.2 wt. % and 1.7 wt. % respectively. EDAX spot analysis on the sample as can be seen from Figure 3.18, Figure 3.20 and Figure 3.22. The resulting elemental composition is displayed in Figure 3.19 , Figure 3.21 and Figure 3.23 where we observe that the Si/Al ratio is 7.51, 7.61 and 7.38 for mix design #1, #2 and #3 respectively. This closely agrees with the Si/Al ratio of the starting material when compared.

# 4   Conclusion

The mechanical property of aplite-based geopolymer have been studied and investigated by conducting compressive strength tests using two methods and also a splitting tensile test using the Brazilian test method. Interestingly, the compressive strength increased steadily with age (days) as the trend showed after 7 days. By extrapolation it can be proved that the strength increment could go indefinitely making it suitable for use in permanent P&A operations.

The addition of up to 1.2 wt. %   of sucrose to the total constituents showed a retarding effect in the early stage of the reaction as can be seen from the UCA test results. A delay of about 3 hours was observed.  Although sucrose have been observed to be stable in alkaline geopolymer slurries, it exhibits selective adsorption at hydrating silicate surfaces but not at aluminate surfaces as was noticed by the addition of sucrose and excess microsilica. Therefore sucrose can serve as a hydration inhibitor in low concentration and thus as a retarder when added in the right proportion of 1.2 wt. % as was observed from the results of this experiment.

The addition of 1.5 wt. % and 2.9 wt. % of additional microsilica to mix design #4 and #5 respectively introduced more silicate to the system and was seen to prevent bleeding of excess water to the surface, water that was not involved in the reaction. This is due to increased adsorption of water molecules to the silica surface and thus no compressive strength was developed after 7 days. Therefore, excess of silicon in the form of microsilica could hamper strength development.

Also from the spot compositional analysis, Mix design #2 and #3 showed the inclusion of sucrose in the mixture as shown in the elemental analysis.

# 5   Future works

With increased importance on geopolymers, it is vital that future experiments be focused on other types of retarders that can efficiently retard aplite-based geopolymer slurry for hours. This is important when considering setting plugs for P&A in deep and ultra-deep wells.

Also, scholarly articles have shown that mixing sequence could greatly affect the overall mechanical property of CFA and FFA-based geopolymer. However, it is important to also observe similar effect with aplite-based geopolymer.

Furthermore, when plugs are set and complete zonal isolation is achieved, what is the pressure that can introduce micro channeling in the plug during well overpressure? Further research can also be focused on this area as well.

Since temperature plays a role in the formation of geopolymer, future work could be tailored to observe what the effect of elevated temperature will be on aplite-based geopolymer

# References

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