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# **Controlling Pumpability of Geopolymers for Downhole Placement**

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MASTER'S THESIS

University of Stavanger, Norway

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**Aida Bayati**

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## ABSTRACT

Ordinary Portland cement (OPC) is the prime material used to manufacture concrete and as a barrier material in well construction. Cement has its own advantages such as pumpability, setting, bonding to steel and formation, etc. On the other hand, it has some drawbacks including but not limited to flexibility, long-term durability, permeability, etc. Geopolymer binders are potential alternative materials to Portland cement. They have not been field tested yet but obtained laboratory results have shown their potential as alternative barrier materials.

The objective of this study is to control the setting time of certain geopolymers by adding different dosages of retarders, at different wellbore conditions. The BHCT selected for this study is 50, 60, and 70°C, which is relevant to the North Sea area. As the temperature increases from 50, 60 and 70°C, the slurry sets quicker and retarders can postpone the setting time. UCA (Ultrasonic cement analyzer) results showed the effect of temperature and static conditions on setting time and sonic strength development.

# NOMENCLATURE

<b>Al</b>	Aluminum
<b>Al<sup>3+</sup></b>	Aluminum ion
<b>Al<sub>2</sub>O<sub>3</sub></b>	Aluminum oxide (alumina)
<b>API</b>	American Petroleum institute
<b>ASTM</b>	America society for testing and materials
<b>BWOC</b>	By weight of cement
<b>BHCT</b>	Bottom hole circulating temperature
<b>C</b>	Carbon
<b>Ca</b>	Calcium
<b>Ca<sup>+</sup></b>	Calcium ion
<b>CaO</b>	Calcium oxide
<b>CO<sub>2</sub></b>	Carbon dioxide
<b>DMA</b>	Dynamic Mechanical Analysis
<b>FA</b>	Fly ash
<b>Fe</b>	Iron
<b>Fe<sub>2</sub>O<sub>3</sub></b>	Iron (III) Oxide
<b>GGBFS</b>	Ground granulated blast furnace slag
<b>H<sub>2</sub>O</b>	Water
<b>H<sub>2</sub>S</b>	Hydrogen Sulfide
<b>K<sup>+</sup></b>	Potassium ion
<b>K<sub>2</sub>CO<sub>3</sub></b>	Potassium carbonate
<b>K<sub>2</sub>O</b>	Potassium oxide
<b>KOH</b>	Potassium hydroxide
<b>K<sub>2</sub>SO<sub>4</sub></b>	Potassium sulfate
<b>K<sub>2</sub>SiO<sub>3</sub></b>	Potassium silicate
<b>MPa</b>	Mega pascal
<b>Na<sup>+</sup></b>	Sodium ion
<b>OH<sup>-</sup></b>	Hydroxide ion
<b>OPC</b>	Ordinary Portland cement
<b>P&amp;A</b>	Plug and abandonment

<b>PSS</b>	Potassium silicate solution
<b>Si</b>	Silicon
<b>Si<sup>4+</sup></b>	Silicon ion
<b>SiO<sub>2</sub></b>	Silicon dioxide (silica)
<b>SO<sub>3</sub></b>	Sulfur trioxide
<b>Si(OH)<sub>4</sub></b>	Silicon hydroxide
<b>UCA</b>	Ultrasonic cement analyzer

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# 1 INTRODUCTION

## *1.1 Literature Review*

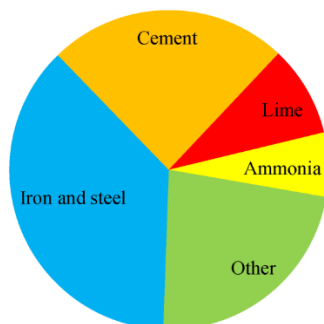
Portland cement is one of the most popular materials used for sealing the annular space between casing and formations for zonal isolation or placement of long plugs in wells. By permanent abandonment of the well, the production life of the hydrocarbon well ends. Permanent abandonment is the development to plug the well or part of it meanwhile there is no purpose to re-enter. There are regulatory elements connected with the plug and abandonment (P&A) work to make sure that formations, especially groundwater and freshwater aquifers are adequately isolated. Therefore, Portland cement is considered the most popular material to seal the annular space and isolate a particular zone or long plugs in wells (Khalifeh et al., 2014).

Generally, a barrier material should be non-shrinking and impermeable and provide long term integrity. In addition, the barrier material should be able to resist mechanical loads and different chemicals (e.g. H<sub>2</sub>S, CO<sub>2</sub>, and hydrocarbons) and it should provide bonding to steel and no harm to the integrity of steel tubular (Norsok, 2013).

When considering well construction or plug and abandonment of wells, a set of cement barriers are placed in the wellbore. Also, a set of tests are conducted at each stage to prove the hydraulic isolation of the barrier. Portland cement provides the basic criteria of a barrier as it develops strength and holds its position. On the other hand, the use of Ordinary Portland Cement (OPC) for downhole cementing has encountered difficulties such as mechanical failure, loss of durability, chemical attacks, sustained casing pressure and leakage. Such issues can lead to the loss of zonal isolation and affect the life span of the wellbore. Also, OPC experiences a decrease in strength with time when exposed to high temperature and pressure (Salehi et al., 2017a).

In recent years, due to the production of cement, the amount of CO<sub>2</sub> emissions has been massive and environmental problems have been the main concern. According to Naik (2008), by 2020, the production of cement will result in an increase up to 100% in the level of CO<sub>2</sub> emissions. This demonstrates the impacts of cement production on global warming (Naik, 2008). Another disadvantage of using Portland cement is the disposal of large volumes of waste materials such as ash from coal-fired power stations and slags from metal production (Gencel et al., 2012). Apart from these two issues, the cement industry produces SO<sub>3</sub> and NO<sub>x</sub> that cause the acid rain and greenhouse gases (Anand et al., 2006; Hendriks, 1999). **Figure 1.1** shows CO<sub>2</sub> proportion from industrial processes in 2012.

## CO<sub>2</sub> Emissions from Industrial Processes US, 2012



**Figure 1.1** The proportion of CO<sub>2</sub> emission in oil industry (after Goldstein (2015)).

Therefore, other sources of cementitious materials which are much cleaner than Portland cement are preferred in the oil and gas industry as they have the potential to reduce the environmental impact (Malhotra, 2002).

Also, the different challenges of Portland cement necessitate the look for alternative materials for zonal isolation and P&A operations (Barclay et al., 2004; Calvert and Smith, 1994; Khalifeh et al., 2013). One type of these alternative materials are geopolymers.

Davidovits introduced the term ‘geopolymer’ in 1979 to show the inorganic polymers proceed from geochemistry. Geopolymers are like other polymers and are macromolecules with certain molecular weight and size (Davidovits, 1989). Kriven et al. (2003) measured a molecular weight of 60,000-850,000 MW and a particulate dimension of 5-15 nm for geopolymers.

Davidovits also specified the polymerization number of K-poly type geopolymer (-Si-O-Al-O-Si-)n, when the aluminosilicate polymer is synthesized from alkaline activators mixed with metakaolin, fly ash or blast-furnace slag (Davidovits, 2008).

In a simple way, it can be said that geopolymers are aluminosilicate materials that react in an alkaline environment. Chemical reaction of aluminosilicate minerals with an alkaline solution would give several tiny molecules identified as oligomers. These molecules join into a covalently bonded network and result in polymeric chains, and original unit compositions which are three-dimensional macromolecular structures (Davidovits, 2013; Duxson et al., 2007; Škvára, 2007). This process is called “‘geopolymerization’” and results in a cementitious material with high mechanical strength and fire and acid resistance (Khalifeh et al., 2014). Geopolymerization is a complicated process which has not yet been completely realized and is still vague. Basically, the chemical combination of source materials and the alkaline activators would influence the final products of geopolymerization

(Duxson et al., 2007; Khalifeh et al., 2014; Yip et al., 2008).

The geopolymerization process depends on many parameters such as:

- Particle size distribution
- Chemical and mineralogical composition
- Surface area
- Type of alkali solution
- Curing temperature and pressure
- Alkaline activator to solid ratio
- Si/Al ratio of the raw material
- The types of additives (Diaz et al., 2010; Kong and Sanjayan, 2008; Kong et al., 2008; Ravikumar et al., 2010).

Various researchers confirmed that geopolymers provide better resistance to acid attack which undermines the use of Portland cement in the construction industry. Other research works show that after setting, geopolymers have excellent mechanical properties and show resistance to fire and corrosion (Eduok, 2016; Lizcano et al., 2012). As an example, Ground Granulated Blast Furnace Slag (GGBFS) which is an industrial by-product of steel or iron manufacturing, has been used in the production of a geopolymer concrete and resulted in improved mechanical properties (Aydın and Baradan, 2012; Islam et al., 2014).

Additional studies explain increased lifecycle expectancy and durability of geopolymers compared to Portland cement. For instance, according to Torgal et al. (2008), the fly ash particles contained in the geopolymer materials have resulted in improved consolidation and reduction in the permeability of these materials. This is because of the spherical shape of fly ash particles (Torgal et al., 2008).

Davidovits showed that when geopolymers were exposed to 5% of sulfuric and hydrochloric acid solutions, their consequent mass loss was lower than the OPC. Also, he indicated that with the exposure to acid solutions, geopolymers experienced a mass loss of 8% while the OPC was completely damaged (Davidovits, 1994). However, all the studies on geopolymers, carried out in lab scale and no field testing has been reported yet. Therefore, the main difficulty in the utilization of geopolymers in oil and gas wells is their verification procedures.

In a well, temperature and pressure changes can affect the cement; as the well gets deeper, the pressure and temperature increase. Since temperature is the most important variable which affects cement hydration, temperature differentials can make the slurry design difficult in different cementing operations. A static temperature at the upper part of the well may be substantially lower than the lower part of the wellbore. This situation may either result in

fast setting prior to placing the material at the right depth or delay the setting of the material. To reach the desired mix design for cement, some additives are added to the slurry which act as retarders or accelerators (MacEachern et al., 2003). Retarders prolong the pumpability, while accelerators expedite the setting. Also, adding such additives to the cementitious material results in the following:

- Improved workability
- Adjusted hardening time
- Increased mechanical strength (Hewlett, 1988)

## ***1.2 Aim of the thesis***

In this work, the pumpability of rock-based geopolymers is of interest. Some potential retarders are tested to see their effects on consistency of the geopolymer slurries. It is necessary to find the effect of increasing temperature on the pumpability of geopolymers and also, investigate the impact of two types of additives on setting time in order to increase the pumping time. Also, the compressive strength development of the geopolymer slurries is measured indirectly by the use of Ultrasonic Cement Analyzer (UCA) to study the setting time of geopolymers.

The main aim of this work is to focus on two different types of additives which are added to the liquid phase of the geopolymer slurries and evaluate the effect of their concentration on pumpability and setting time. In this way, it could be studied whether these additives work as retarders or accelerators.

## ***1.3 Outline of the thesis***

Chapter 2 considers the basic theories of geopolymers. In Chapter 3, all the experimental methods and works performed in this project are discussed. Chapter 4 presents the obtained results and finally Chapter 5 presents the concluding remarks.

## 2 THEORETICAL BACKGROUND

### 2.1 *Geopolymer*

Generally, natural polymers undergo polycondensation and set quickly at low temperatures. However, geopolymers are inorganic, ceramic and fire-resistant materials which can withstand temperatures as high as 1250°C (Davidovits, 2002).

Due to their different benefits, geopolymers have various applications. For instance, since geopolymers are heat-resistant, they can be used as coatings for fire protection of different materials. However, so far, geopolymers have been mainly used for construction purposes (Krivenko and Kovalchuk, 2007).

### 2.2 *Elements of the Geopolymers*

The geopolymer slurry consists of two phases:

- Solid phases (e.g. some natural rocks or by-product materials)
- Liquid phase (i.e. hardener).

Generally, in geopolymer slurries, modified potassium silicate solutions (PSS) are used as hardeners. Also, different additives which can act as retarders or accelerators can be used in the liquid phase of the geopolymer slurries.

According to Nath and Sarker (2014), the setting time of geopolymers can be modified by the following factors which are contained in the geopolymer slurries:

- The activator types
- The aluminosilicate materials
- The alkali contents
- The calcium content
- The water content (Nath and Sarker, 2014)

#### 2.2.1 *Hardener*

The potassium silicate solution which acts as a hardener, controls the initial mechanism of geopolymerization by absorbing the alumina and silica from the solid phase and dissolving them into the solution. Also, the hardener prompts the precipitation and crystallization of the aluminosilicate species present in the solution (Part et al., 2015). In the following section, an example of a hardener is explained.

#### 2.2.2 *Alkaline metal silicate solutions*

For more than 100 years, alkaline metal silicate solutions (commercially known as water-

glass) have been employed in wide range of industrial applications. For instance, they have been used as viscosifier, detergent, inorganic binder, waterproof coating, quicklime's retarder, etc. (Nordström et al., 2011; Skorina and Tikhomirova, 2012; Yang et al., 2008).

These days, alkaline metal silicate solutions are essential materials for many different industrial products and have numerous utilizations in inorganic polymers, coatings and consolidated silica products (Gualtieri et al., 2015; Kouassi et al., 2011). The most regularly used water-glass types are sodium silicate solution (i.e. sodium water-glass) and PSS (Yang and Zhang, 2016).

During the years, only few studies have been performed on the concept of PSS. For instance, Brady et al. (1953) studied the polymerization of aqueous PSS. Also, Hazel (1962) analyzed the lability of aqueous solutions of potassium silicate. Further, Knight et al. (1988) investigated the chemical exchange pathways in PSS.

### 2.2.3 *Geopolymeric precursors*

Geopolymer precursors are materials which can be used as solid phase in geopolymer slurries. Among these materials one can list: fly ash, GGBFS, red mud, silica fume, rice-husk ash rock, by-product materials and natural minerals like aplite. In order to select the appropriate source materials for geopolymerization, the following factors should be considered (Nawy, 2008):

- Type of application
- Economical aspect
- Availability
- Particular requirements of the users of the source material

Many researchers have studied the geopolymerization and the effect of various designs, industrial by-product materials and several natural minerals compounds in geopolymer slurry, and a variety of ways to promote the polymerization process examples (Dutta and Ghosh, 2014; Thakkar et al., 2014)).

### 2.2.4 *Retarders*

To reduce the rate of geopolymerization temporarily, chemical additives recognized as retarders may be used. Slowing down the geopolymerization increases the thickening time which is the time that geopolymer slurry remains pumpable in downhole conditions. The thickening time can be short or long depending on several parameters such as:

- Temperature
- Retarder type and concentration

- Reactivity of the precursors

The beginning of the strength buildup of some geopolymer slurries requires to be delayed. For this purpose, the effect of some retarders has been investigated by several researchers. For instance, Khalifeh et al. (2014) studied the effect of retarders as chemical additives to enhance the thickening time. Also, Huajun and XIAO (2013a) examined the impact of applying retarders to delay the geopolymer reaction and the thickening time. Thereby, they came up with a self-developed retarder made by the reaction of a dibasic organic acid and alkali metal salt. Further, they applied the retarder on a slag based geopolymer. Consequently, they discovered that by increasing the dosage of the retarder, the setting time of the geopolymer increased (Huajun and XIAO, 2013a).

The addition of retarders to geopolymers' source material with high calcium content leads to a decrease in the mechanical strength and consequently, increases the setting time (Huajun and XIAO, 2013a).

### ***2.3 Geopolymerization process***

Geopolymerization also known as polycondensation, is a complicated process which is responsible for the formation of geopolymers. For last decades, the mechanism of geopolymerization has been studied. However, it is still not completely understood (Provis and Van Deventer, 2009). Despite many research works on the concept of geopolymerization, a complete description of the structure and characteristics of geopolymers needs to be done.

Geopolymerization of aluminosilicate source materials leads to the formation of spatial structures which are amorphous or sub-crystalline and similar to zeolites (Koleżyński et al., 2018). The geopolymers contain polymeric structures of Si–O–Al. These structures include tetrahedra chains of  $AlO_4$  and  $SiO_4$  (Nguyen and Škvára, 2016). Each tetrahedra chain includes shared oxygen, bound water and metal cations such as sodium, potassium, lithium or calcium (Fletcher et al., 2005). As opposed to the structure of zeolites, the geopolymers have amorphous structures at ambient temperature. Thereby, geopolymers are complex to define since they have several structures, morphologies and compositions (Koleżyński et al., 2018).

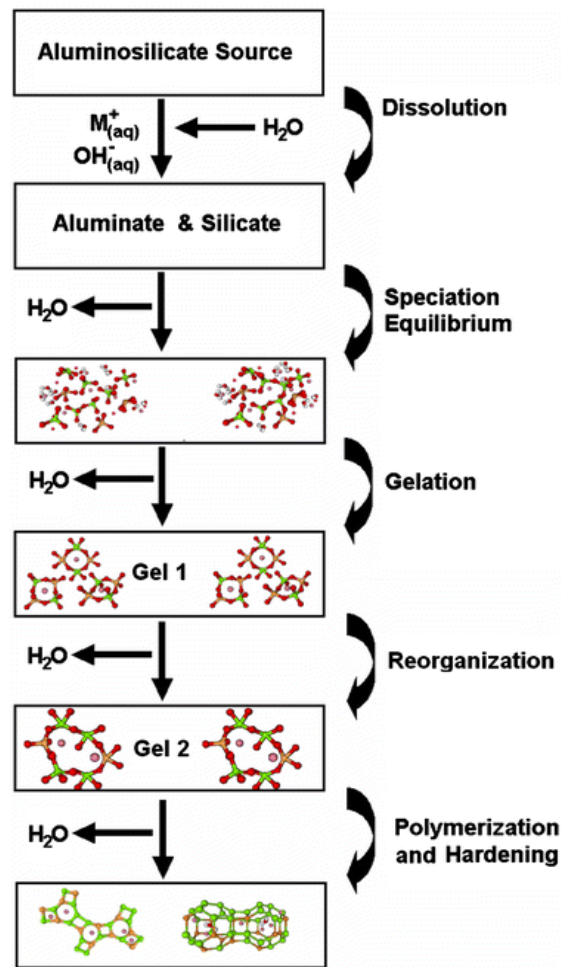
The geopolymerization process includes the following main stages:

1. Dissolution (deconstruction)
2. Oligomerization
3. Geopolymerization

**Figure 2.1** shows a conceptual model of the different stages of the geopolymerization



process. In the following sections, the three main stages of the process are explained.



**Figure 2.1** A conceptual model of different stages of the process of geopolymerization (after Duxson et al. (2007)).

### 2.3.1 Dissolution

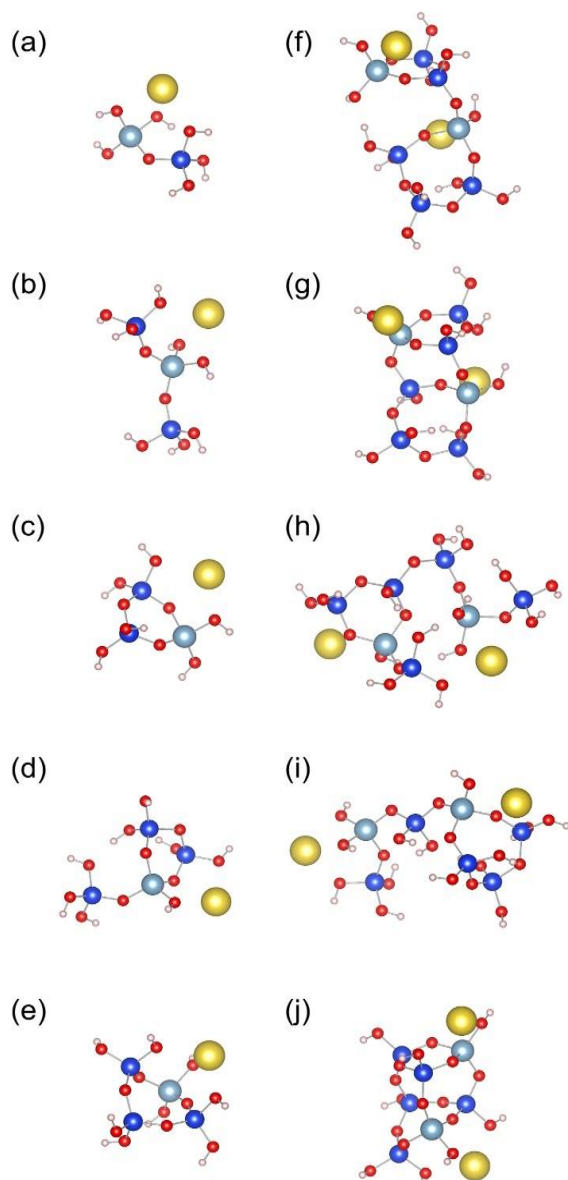
In the dissolution stage, the bonds of Si-O-Si, Al-O-Al and Al-O-Si break. These bonds exist in the solid aluminosilicate source material. This leads to the liberation of silicate and aluminate in the liquid phase (most probably in the form of monomers) (Duxson et al., 2007; Provis and Van Deventer, 2009).

### 2.3.2 Oligomerization

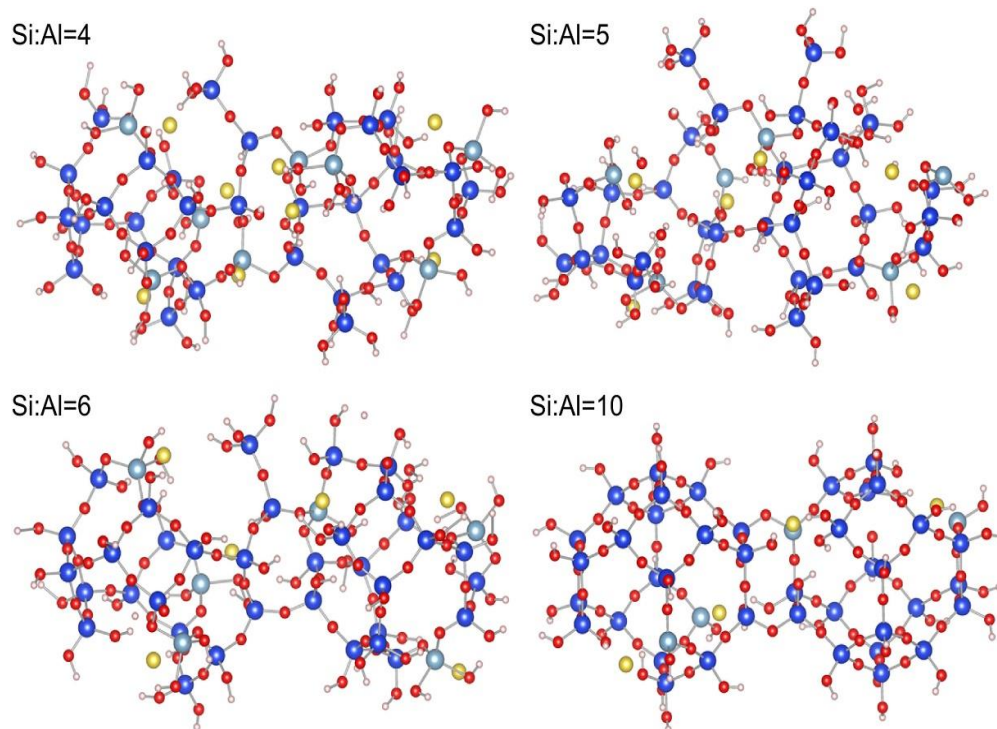
Generally, oligomers are small molecules which form 3D networks in the process of geopolymerization. In fact, oligomers are considered the main building units of geopolymers (Davidovits, 2008; Duxson et al., 2007). **Figure 2.2** and **Figure 2.3** show different structures of oligomers.

During the stage of oligomerization, polycondensation occurs in which the liberated

monomers of dissolution stage form coagulated structures (Duxson et al., 2007). These monomers react together in order to form different structures such as tetramers, dimers, trimers and higher molecules of the polymeric covalent bonding. These structures are referred to as oligomers. Poly(siloxane) Si-O-Si-O, Si-O-Al-O and poly(sialate-disiloxo) Si-O-Al-O-Si-O-Si-O are examples of oligomers (Provis and Van Deventer, 2009).



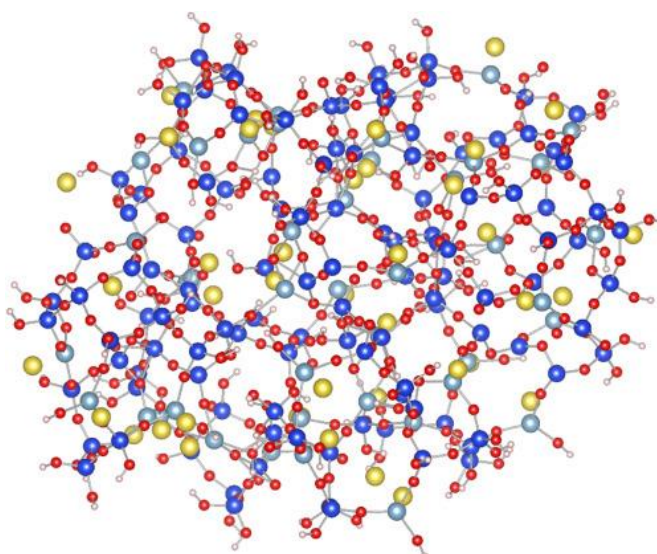
**Figure 2.2** The structures of five oligomers consisting of two basic oligomers (a–e), f): c + e, g): c + e connected by 2 oxygen bridges, h): b + d, i): b + e, j): c + e connected by 3 oxygen bridges. Si, Al, O, Na and H atoms are shown in blue, silver, red, yellow and beige colors, respectively (after Koleżyński et al. (2018)).



**Figure 2.3** Structural models of approximately 200 atoms, with different Si:Al ratio: 10, 6, 5 and 4; atoms with various Si:Al ratio: 10, 6, 5 and 4; atoms shown in the same colors as in **Figure 2.2** (after Koleżyński et al. (2018)).

### 2.3.3 Geopolymerization

In this stage, the oligomers rearrange and bond together and result in the formation of three dimensional networks of aluminosilicate known as geopolymers (see **Figure 2.4**) (Duxson et al., 2007).



**Figure 2.4** An example of a geopolymer structural model which includes more than 800 atoms and a Si:Al ratio of 2.81 (after Koleżyński et al. (2018)).

## ***2.4 The effect of curing temperature on geopolymers***

Curing temperature is one of the vital factors in geopolymerization process. The curing temperature should be within the range of ambient temperature and 100°C (Davidovits, 2008; Zribi et al., 2019). Elevated curing temperatures speed up the processes of dissolution, polymerization and hardening in the geopolymerization reaction. The most favorable curing temperature of geopolymer is approximately 60°C. At this temperature, the geopolymer samples show the best mechanical properties. For instance, Mo et al. (2014) showed that metakaolin-based geopolymer samples achieved a good compressive strength after being cured for 7 days at 60°C. Also, Salehi et al. (2017b) tested sodium hydroxide and silicate-based geopolymer samples at temperatures of 25, 50, 60, 70, 80°C and curing time of 7 days. Their results showed that the highest compressive strength was obtained at 60°C (Salehi et al., 2017b).

## ***2.5 Retardation***

Retarders are used to postpone the setting time of geopolymers in a controlled manner. They are used in heated conditions to prevent the quick thickening of geopolymers due to high temperature. Also, the use of retarders provides enough time for mixing, moving and placing of the geopolymer slurries. The mechanism of retardation depends on the type of retarders and the geopolymer slurries mix design. The retarders have a temporary effect and after a predictable period, their effect disappears, and the geopolymerization process continues.

Generally, for Portland cement, there are four ways in which the retardation happens:

1. Adsorption: retarding admixture is adsorbed on the surface of the cement particles. A shielding skin around the cement particles is formed by The layer of retarding admixture . The shielding skin delays the reaction of water molecules with the cement particles. Consequently, the hydration of the cement is slowed down. This means that there are not a lot of hydration products to provide rigidity to the cement paste, so the cement remains plastic for a longer period (Young, 1972).
2. Nucleation: calcium and hydroxyl ions are liberated from the surface of particles when water is added to the cement. When the number of ions reach a certain value, the hydration products (such as  $C_2S$  and  $CS$ ) crystallize. Calcium hydroxide nuclei adsorbs a retarding admixtures which prevents calcium hydroxide nuclei from growing to some level of super-saturation (Young, 1972).
3. Complexation: through the first minutes, complexes with calcium ions are formed which

improve the solubility of the cement. In the presence of a retarding admixture an enhanced concentration of  $\text{OH}^-$ ,  $\text{Ca}^{2+}$ , Al, Si, and Fe will happen in the liquid phase during the hydration. Hydration is retarded when the mass of the calcium and hydroxyl ions prevent forming calcium hydroxide by limitation of the precipitation of those ions.

4. Precipitation: Precipitation of insoluble derivatives of retarder are produced by a reaction with the highly alkaline solution. So, after few minutes of the contact between water and cement, the pH of the slurry grows over 12 (Young, 1972).

Although the reaction mechanism involved in hardening of cement is hydration, the study of these mechanisms and inspiration of these mechanisms could be helpful to control the setting time of geopolymers by use of retarders. So, the next chapter will present the materials and analytical procedures used to investigate the retarder effects on setting time of geopolymers.

### 3 Experimental and Materials Description

#### 3.1 Overview

In this chapter, all the materials and their dosage used in the experimental study, are explained. Also, the mixing of materials and preparation of the slurries according to API 10B-2 standard are described in detail. Moreover, the devices applied for all measurements such as the consistency, setting time of geopolymer slurries and compressive strength are discussed.

#### 3.2 Materials

The materials used in this thesis are confidential and mainly consist of two phases, namely, solid phase and liquid phase. The solid phase includes rock or by-product materials and the liquid phase (i.e. hardener) includes potassium silicate solution. Further, in this study, two different types of additives are used as retarders. **Table 3.1** shows the weight percentage (Wt. %) of the solid components used in geopolymer samples for each test. Also, **Table 3.2** indicates the total amount of solids and hardeners as well as the type and percentage of the retarders used by weight of cement (BWOC %).

**Table 3.1** Wt. % of solid components used in the geopolymer samples

Tests	CaO	SiO <sub>2</sub>	MgO	Al <sub>2</sub> O <sub>3</sub>	TiO <sub>2</sub>	Mn <sub>2</sub> O <sub>3</sub>	S <sup>2-</sup>	SO <sub>3</sub>	Na <sub>2</sub> O	K <sub>2</sub> O	Fe <sub>2</sub> O <sub>3</sub>	P <sub>2</sub> O <sub>5</sub>	MnO	LOI	FeO
RW1	0.121	0.576	0.065	0.126	0.011	0.029	0.005	0.001	0.013	0.020	0.007	0.001	0.0003	0.0012	0.024
RW2-14	0.156	0.505	0.084	0.131	0.013	0.038	0.006	0.001	0.013	0.018	0.006	0.001	0.0002	0.0010	0.027
RW15-17	0.121	0.576	0.065	0.126	0.011	0.029	0.005	0.001	0.013	0.020	0.007	0.001	0.0003	0.0012	0.024
RW18-22	0.156	0.505	0.084	0.131	0.013	0.038	0.006	0.001	0.013	0.018	0.006	0.001	0.0002	0.0010	0.027

**Table 3.2** The total amount of solids, hardeners and retarders used in geopolymer samples

Tests	Solids (g)	Hardeners (g)		Retarders	BWOC %
		K <sub>2</sub> SiO <sub>3</sub>	H <sub>2</sub> O		
RW1	700	309	78	Type 1	0.2
RW2	700	313	78		
RW3	700	318	73		
RW4	700	318	73		
RW5	700	318	73	Type 1	0.2
RW6	700	308	83		
RW7	700	308	83		
RW8	700	308	83	Type 1	0.2
RW9	700	318	73	Type 1	0.2
RW10	700	318	73	Type 1	0.4
RW11	700	318	73	Type 1	0.6
RW12	700	308	83	Type 1	0.4
RW13	700	308	83	Type 1	0.6
RW14	700	308	83	Type 1	1
RW15	700	0	78	Type 1	0.2
RW16	700	0	78	Type 1	1
RW17	700	0	78	Type 2	1
RW18	700	318	73	Type 2	1
RW19	700	318	73	Type 2	2
RW20	700	318	73	Type 2	1
RW21	700	318	73	Type 2	2
RW22	700	318	73		

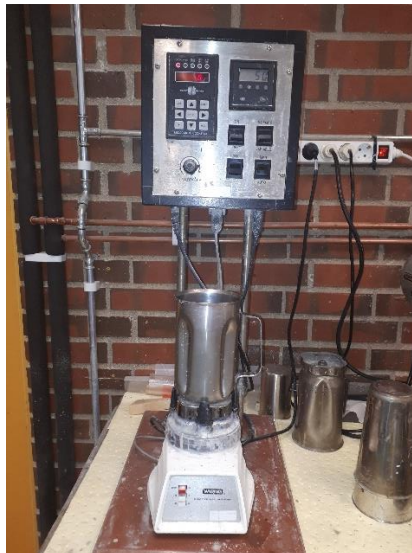
### 3.3 Experimental set-up

All the materials including solids, liquids and additives used for the tests were accurately measured using a Mettler Toledo scale (see **Figure 3.1**).



**Figure 3.1** The Mettler Toledo scale (with an accuracy of  $\pm 0.01$  g).

The mixing of the solid phase, the liquid phase and the additives was carried out using an OFITE Model 20 Constant Speed Blender which is used for oil well cement testing (see **Figure 3.2**).



**Figure 3.2** OFITE Model 20 Constant Speed Blender.

#### 3.3.1 Mixing process

Solids and liquids can be mixed in different ways. However, liquids are usually premixed before being mixed with solids. Nuruddin et al. (2011) and Rangan (2008) declared that premixing of liquids provides following advantages:

- Developed workability
- Excellent strength in the geopolymer samples

Also, Rangan (2008) pointed out that 3 minutes of wet mixing is adequate for preparing a homogeneous mixture.

In this project, the solid components were mixed together at dry conditions before being added to the liquid phase. Also, the liquid components were mixed together for a few seconds using the blender (**Figure 3.2**) with a rotational speed of 4000 rpm. Further, the liquid phase and the additives were mixed together for 15 seconds in the blender. Then, the mixed solid phase was gradually added to the liquid phase for 15 seconds at 4000 rpm and the mixing continued for another 35 seconds at 12000 rpm in accordance with the API 10B-2 standard (API, 2005).

Deionized water was used in the liquid phase in all the experiments for the following purposes:

- Preparation the medium for the dissolution of aluminosilicates
- Transferring various ions
- Performing the hydrolysis of  $\text{Si}^{4+}$  and  $\text{Al}^{3+}$  compounds
- Conducting the polycondensation of different silicate and aluminate silicate hydroxyl species (Eduok, 2016)

The mixture was immediately poured into an atmospheric consistometer (**Figure 3.3**) for pumpability measurements.

### 3.3.2 Atmospheric consistometer

An atmospheric consistometer, OFITE model 60, was used for atmospheric consistency measurements and conditioning of the slurries. Atmospheric consistometers are designed for low temperature systems but have found an application in the conditioning of geopolymer slurries before testing. The main purpose of using an atmospheric consistometer for geopolymer slurries at this stage is to obtain proper homogenous mixtures. The atmospheric consistometer used in the experiments of this project, is shown in **Figure 3.3**. All the mixtures used in the experiments were placed and kept at the atmospheric consistometer until their consistency values reached 100 BC. This was in accordance with the API 10B-2 standard (API, 2005). The bottom hole circulating temperatures (BHCT) were selected to be 50, 60 and 70°C with a ramp-up rate of 1°C/min.





**Figure 3.3** Atmospheric consistometer OFITE model 60.

### 3.3.3 UCA

For the geopolymer to be used in oil well cementing, it requires to tolerate the forces located in the formation to protect the steel casing. Also, the geopolymer needs to support the weight of the casing and have enough resistance during perforating, fracturing and stimulation operations. In addition, the geopolymer has to develop sufficient compressive strength to meet these requirements.

Geopolymer's compressive strength demonstrates the capability of hardened geopolymer to resist forces. Several methods used in the laboratories to measure the compressive strength development of geopolymers. The most useful and effective method to accurately estimate the compressive strength is Ultrasonic Cement Analyzer (UCA) test. A picture of the UCA is shown in **Figure 3.4**. The UCA provides elevated pressure and temperature to simulate downhole conditions. It is also capable of distinguishing the start of the strength buildup in geopolymer samples. By performing measurements of the transit time of an acoustic signal, the UCA creates a constant profile of compressive strength as a function of time. By the use of empirical correlations, the measured transit times are converted to compressive strength (Khalifeh et al., 2014).

In this study, the UCA tests were performed to investigate the immediate strength improvement of the geopolymer slurries. For this purpose, three geopolymer samples were prepared and placed in the atmospheric consistometer where their temperatures reached 50, 60 and 70°C, respectively. The samples were kept at these temperatures for 20 minutes. Then, they were transferred to the UCA where their temperatures were increased and kept constant at 70, 80 and 90°C, respectively for a week. The curing pressure of the samples in

the UCA was selected to be 2000 psi.



**Figure 3.4** Ultrasonic cement analyzers.

## 4 RESULTS AND DISCUSSIONS

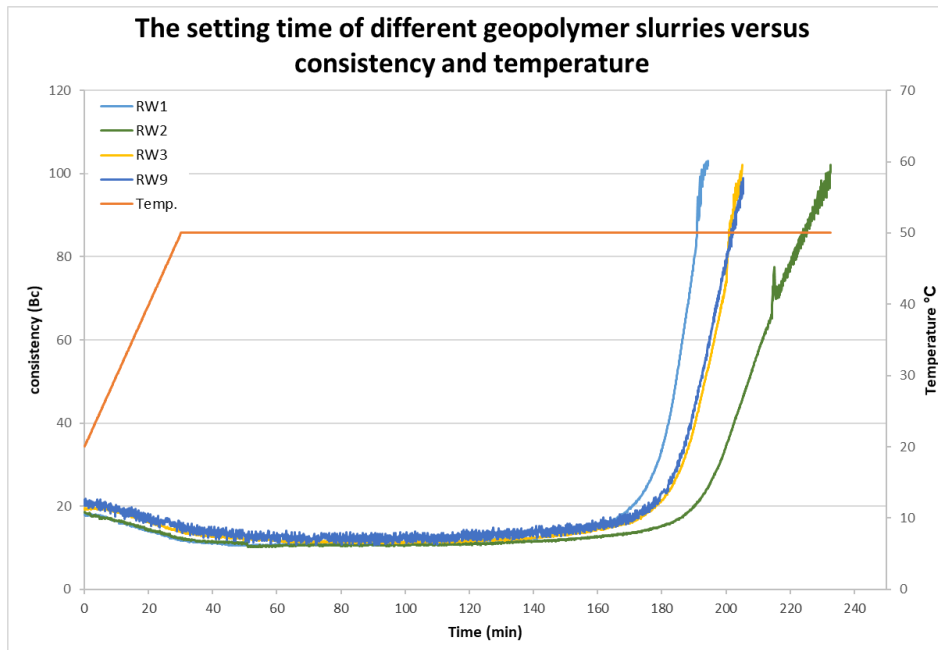
### 4.1 *The Effect of retarders on pumpability*

The pumpability is an important factor for the geopolymers to ensure a successful cementing operation. In this study, the effect of the retarders (i.e. the two additives) on the thickening time of geopolymer mixtures was investigated through several experiments. After the addition of retarders, the setting time of the geopolymers prolonged significantly. This demonstrated that the additives could retard the geopolymerization process. Also, the impact of increasing temperature on the pumpability of geopolymers was investigated. For this purpose, the temperature of the geopolymer samples was increased by 10°C (from 50 to 60°C). This temperature increase expedited the geopolymerization process depending on the specific geopolymer recipe. This was in agreement with the results obtained by Salehi et al. (2019) which showed that increase in temperature led to the decrease in the pumpability of geopolymers. Therefore, it is necessary to consider the variability of downhole temperatures during the geopolymer mixture designs.

The captured data from the atmospheric consistometer showed that pumpability of the geopolymer slurry was not significantly influenced by pressure.

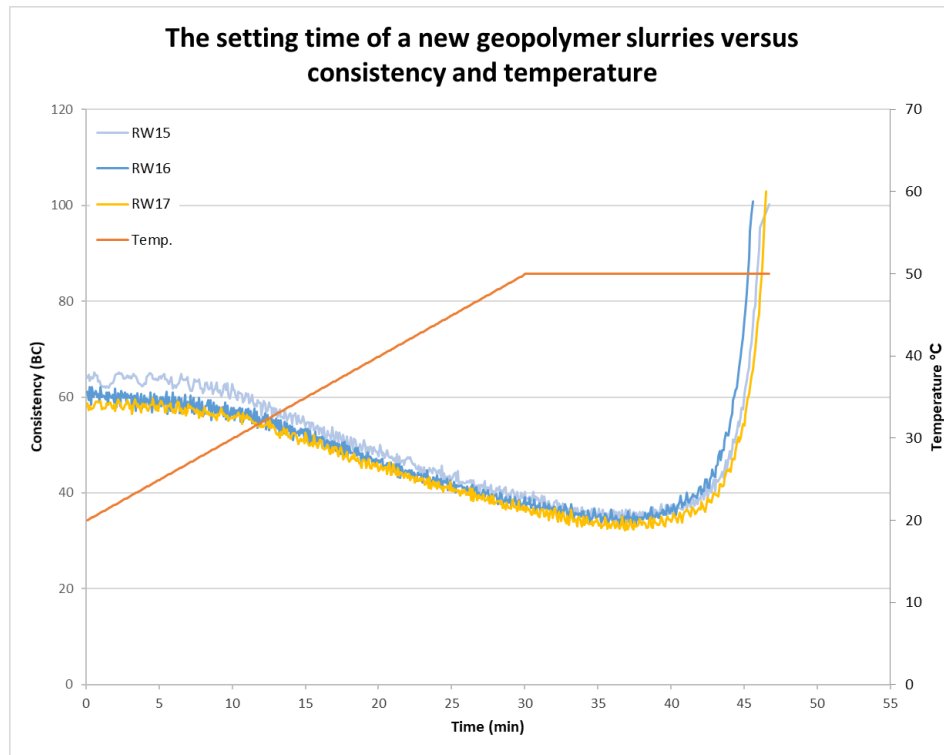
In this study, to determine the setting time of the geopolymer slurries prepared with different recipes, several tests have been performed. During these tests, the different geopolymer slurries were placed in the atmospheric consistometer and the temperature was increased from ambient to 50°C and kept constant. The setting times of the geopolymer slurries were then measured and plotted versus consistency and temperature as shown in **Figure 4.1**.

As shown in **Figure 4.1**, the test RW3 shows better setting behavior compared to the test RW2. This is because the RW3 curve (i.e. the yellow curve) ends up with a right angle. This means the geopolymer slurry used in RW3 has a better chance to set compared to the one used in the RW2. Also, the RW3 has more setting time in comparison to RW1. Therefore, the RW3 was chosen as the optimum geopolymer mixture on which further tests were performed to investigate the effect of retarders and increasing temperature.



**Figure 4.1** Different tests with various geopolymer recipes at 50°C.

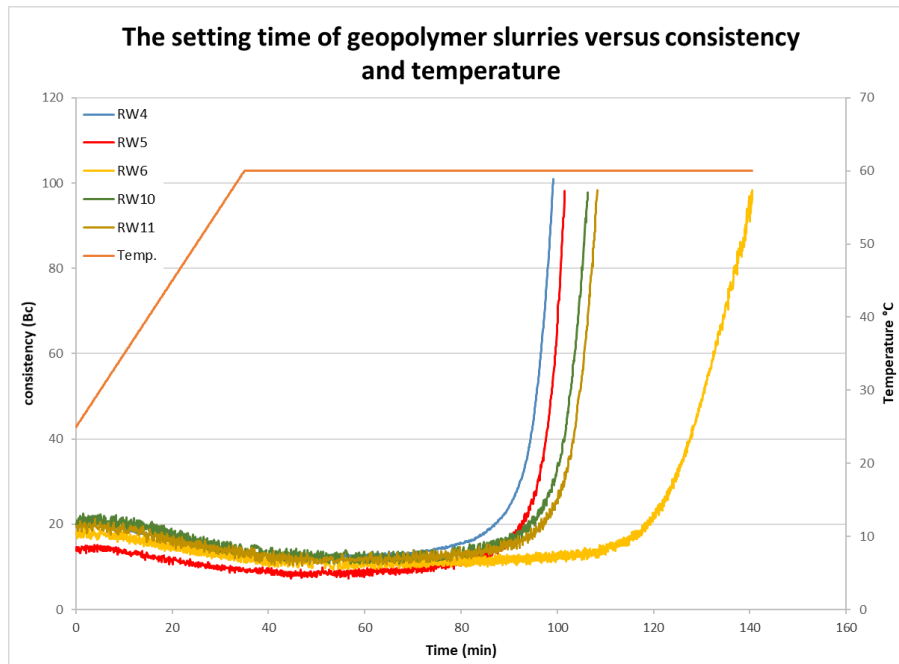
Also, for further investigation, it was decided to examine a new hardener and see the effect of two types of retarders on this new recipe. **Figure 4.2** shows a mixture design (i.e. RW15) with a liquid phase which consists of 0.2% BWOC of retarder type 1. The setting time for RW15 at the consistency of 40 BC was 42 minutes. Further, the amount of the same retarder was increased to 1% BWOC and resulted in RW16 for which the setting time at 40 BC did not change. The test was repeated with retarder type 2 for the same recipe. By adding 1% BWOC of the retarder type 2 to the initial recipe, the setting time at 40 BC was the same as RW15 and RW16. Therefore, this recipe was rejected to continue with for further tests.



**Figure 4.2** No changes in setting time by adding retarders to a new geopolymer recipe at 50°C.

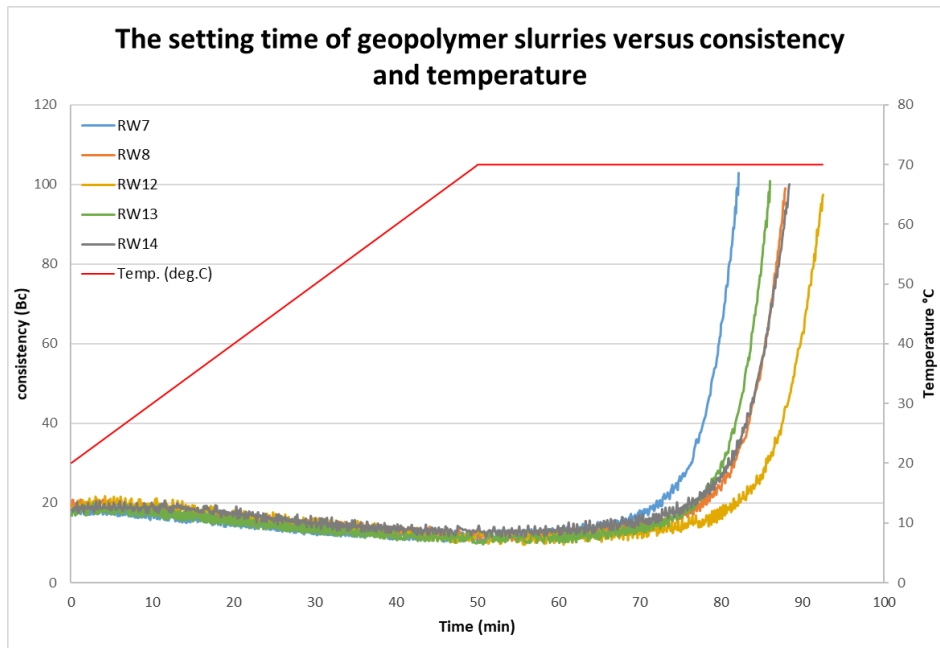
Further, a geopolymer mixture was prepared (i.e. RW4) with the same recipe as that of RW3. However, for RW4, the experimental condition changed by increasing the temperature up to 60°C. The setting time of RW3 at 40 BC was 189 minutes (**Figure 4.1**) whereas the setting time of RW4 at 40 BC was 94 minutes. This shows the significant effect of temperature on setting time which is reduced by an increase in temperature. Then, the retarder type 1 with different dosages was added to RW4 to observe its impact on the setting time. The results are shown in **Figure 4.3**. As the dosage of the retarder was increased to 0.2, 0.4 and 0.6% BWOC, the setting time was postponed slowly by 5 minutes. Consequently, the curves of RW5, RW10 and RW11 shifted to the right of RW4, respectively. Khalifeh et al. (2019) performed a study on the effect of retarders in which they had the same observations.

RW6 is a recipe which has more water in its initial mix design. Water does not contribute in the geopolymerization process but transports the ions among the slurry. The water level should be optimized to avoid any detrimental effect on the geopolymerization and final properties of the geopolymers. As shown in **Figure 4.3**, for RW6 which contains more water than RW4, the setting time increases dramatically. RW6 is chosen for further tests at 70°C since its consistency reaches 40 BC in 127 minutes. However, this might be due to the contamination of the geopolymer mixture by water.



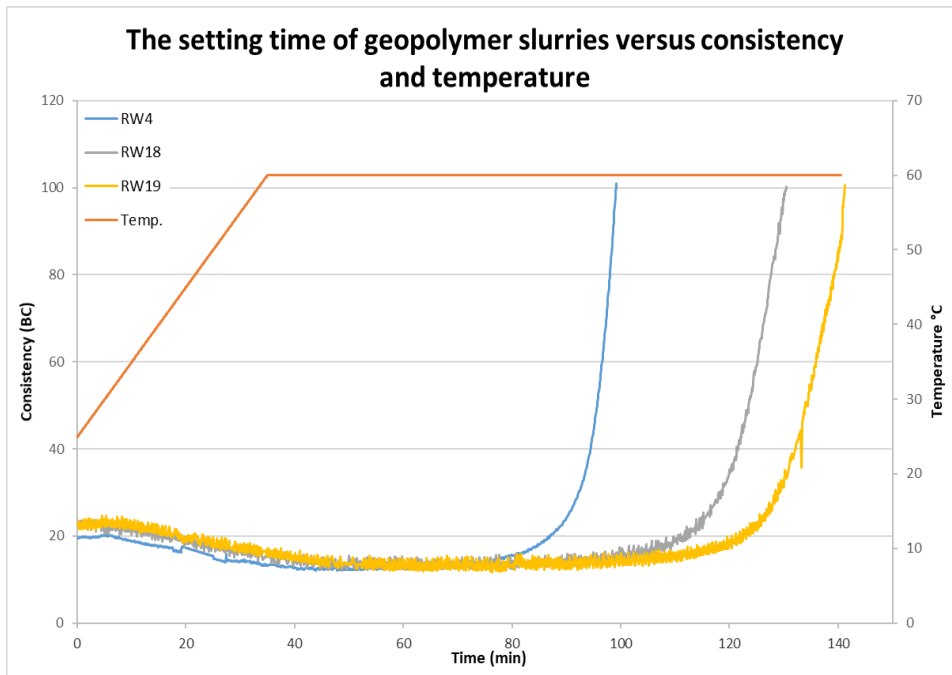
**Figure 4.3** The effect of retarder type 1 on the setting time at 60°C.

In **Figure 4.4**, the initial mix design is RW7 which is the same as RW6. The temperature increased up to 70°C. The setting time of RW6 at 40 BC is 127 minutes whereas the setting time of RW7 at 40 BC is 77 minutes. This shows the significant effect of temperature on reducing the setting time. Then, 0.2 and 0.4% BWOC of retarder type 1 is added to the initial mix design. Consequently, the setting times of RW8 and RW12 were postponed, respectively. However, adding a higher dosage of the same retarder to the initial mixture did not give the same result as before. By adding 0.6% and 1% BWOC of retarder type1, the curves RW13 and RW14 were generated. As it can be observed from **Figure 4.4**, the addition of higher dosages of the retarder did not have a significant effect on the setting time. Therefore, the right dosage of additives should be chosen for the additives to act as retarders.



**Figure 4.4** The effect of retarder type 1 on the setting time at 70°C.

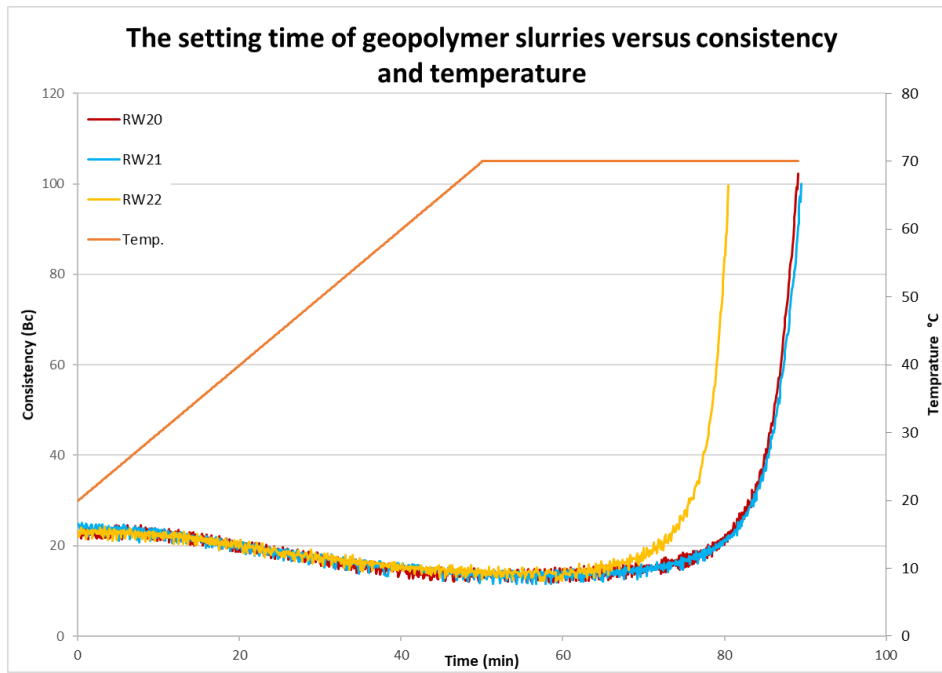
**Figure 4.5** shows the effect of the addition of retarder type 2 to RW4 on the setting time of geopolymer at 60°C. By adding 1 and 2% BWOC of the retarder to the liquid phase of initial recipe (i.e. RW4), the setting time was postponed significantly and the curves shifted to the right (RW18 and RW19, respectively). The setting time of RW18 at 40 BC is 121 minutes and the setting time of RW19 at 40 BC is 132 minutes. It shows by adding 1% more retarder the setting time postponed about 10 minutes. Therefore, with the addition of the retarder type 2 to the geopolymer mixture, the hydration of the geopolymer was delayed more significantly compared to the retarder type 1.



**Figure 4.5** the effect of retarder type 2 on the setting time at 60°C.

Further, the mixture RW22 was prepared with the same recipe as the RW4. However, for RW22, the experimental condition changed by increasing the temperature up to 70°C. The setting time of RW4 at 40 BC is 94 minutes (**Figure 4.3**) whereas the setting time of RW22 at 40 BC is 77 minutes (**Figure 4.6**). This shows that the setting time of RW22 at 70°C is significantly shorter than that of RW4 at 60°C. Therefore, at higher temperature, the geopolymer sets faster. By adding 1% BWOC of retarder type 2, as shown in **Figure 4.6**, the setting time is postponed about 10 minutes. However, adding 2% of the same retarder does not have a significant effect on the setting time. As it can be observed, both RW20 and RW21 reach 40 BC in 85 min.





**Figure 4.6** the effect of retarder type 2 on the setting time at 70°C.

**Table 4.1** shows the value of the setting times at 40 BC and 100 BC for each test.

**Table 4.1** Setting times at 40 BC and 100 BC

Tests	RW1	RW2	RW3	RW4	RW5	RW6	RW7	RW8	RW9	RW10	RW11	RW12	RW13	RW14	RW15	RW16	RW17	RW18	RW19	RW20	RW21	RW22
Time in 40 BC (min)	182	202	189	94	97	127	77	83	189	101	103	87	81	83	42	41	43	121	132	85	85	77
Time in 100 BC (min)	193	232	204	99	101	140	82	88	204	107	108	93	86	88	46	45	46	130	141	89	89	80
Temperature (°C)	50	50	50	60	60	60	70	70	50	60	60	70	70	70	50	50	50	60	60	70	70	70

## 4.2 Sonic strength

The measurement of the sonic strength development of the geopolymer mixtures at the simulated downhole situation was done by using a Chandler Ultrasonic Cement Analyzer (UCA) (see **Figure 3.4**).

The UCA has been designed to evaluate the sonic strength of OPC by estimating the transmit time of ultrasound and converting it to sonic strength by implementing a pre-defined algorithm. For any recently developed element, a new algorithm should be generated (Khalifeh et al., 2019). Consequently, a new algorithm was formed for the geopolymers and implemented in the custom algorithm option of the UCA.

Further, the mixtures RW1, RW11 and RW12 which were conditioned in the atmospheric consistomer for 20 minutes were placed in the UCA to investigate whether these geopolymer mixtures set properly.

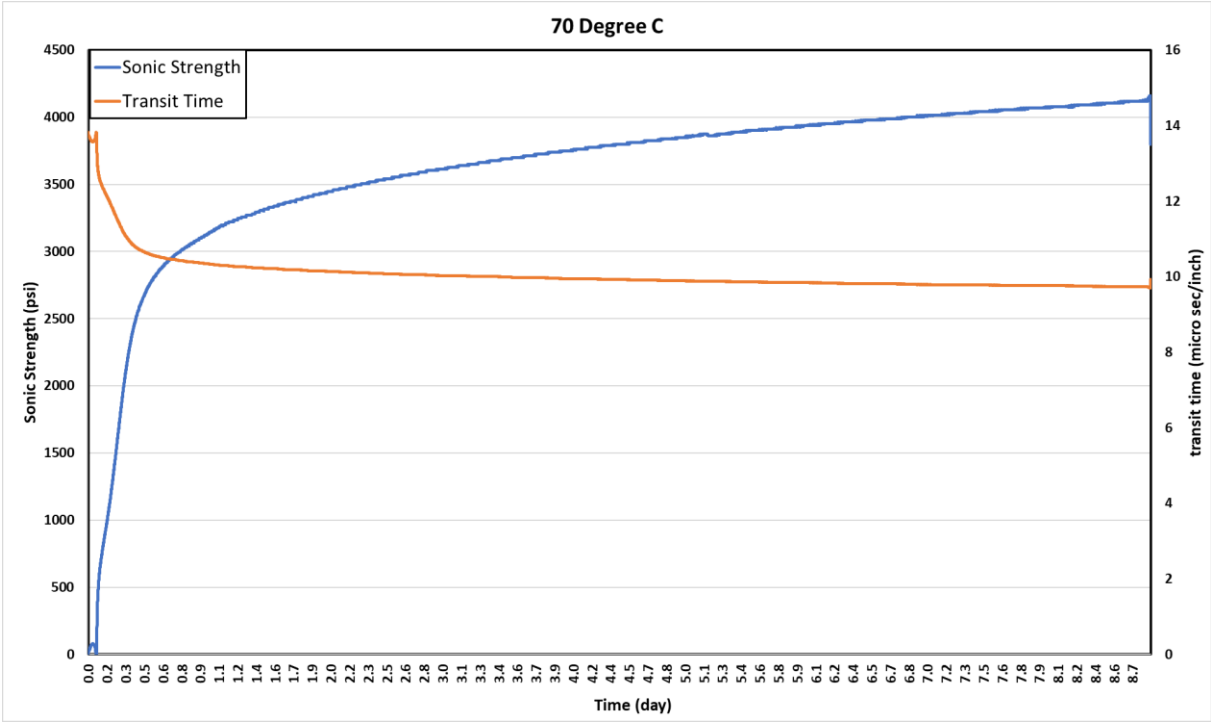
The sonic compressive strengths of the mixtures were calculated by using an empirical correlation. The empirical correlation was able to convert measured transit times to

compressive strengths. This correlation is shown in the following equation

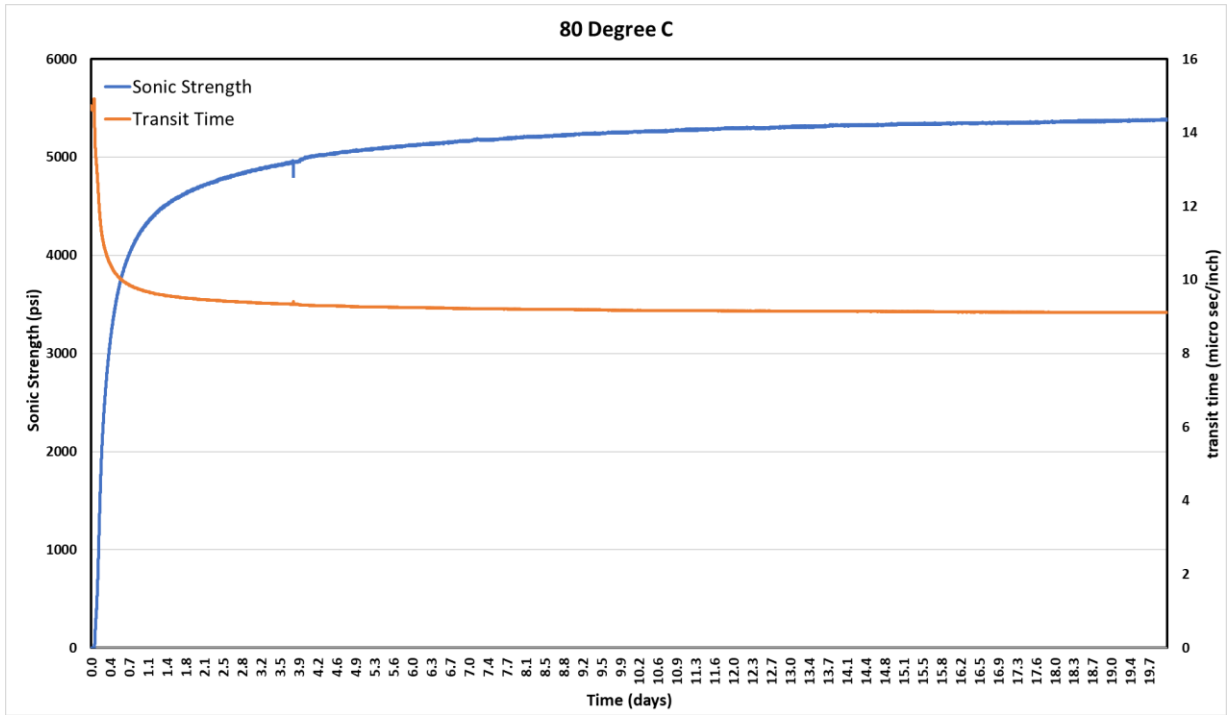
$$Y = +177x^2 - 5177x - 37652$$

As the pre-defined algorithms in the UCA program were not accurate to estimate the sonic strength, the custom algorithm option was applied. The generated sonic strength plots revealed a steady strength development over time (see **Figure 4.7**, **Figure 4.8** and **Figure 4.9**).

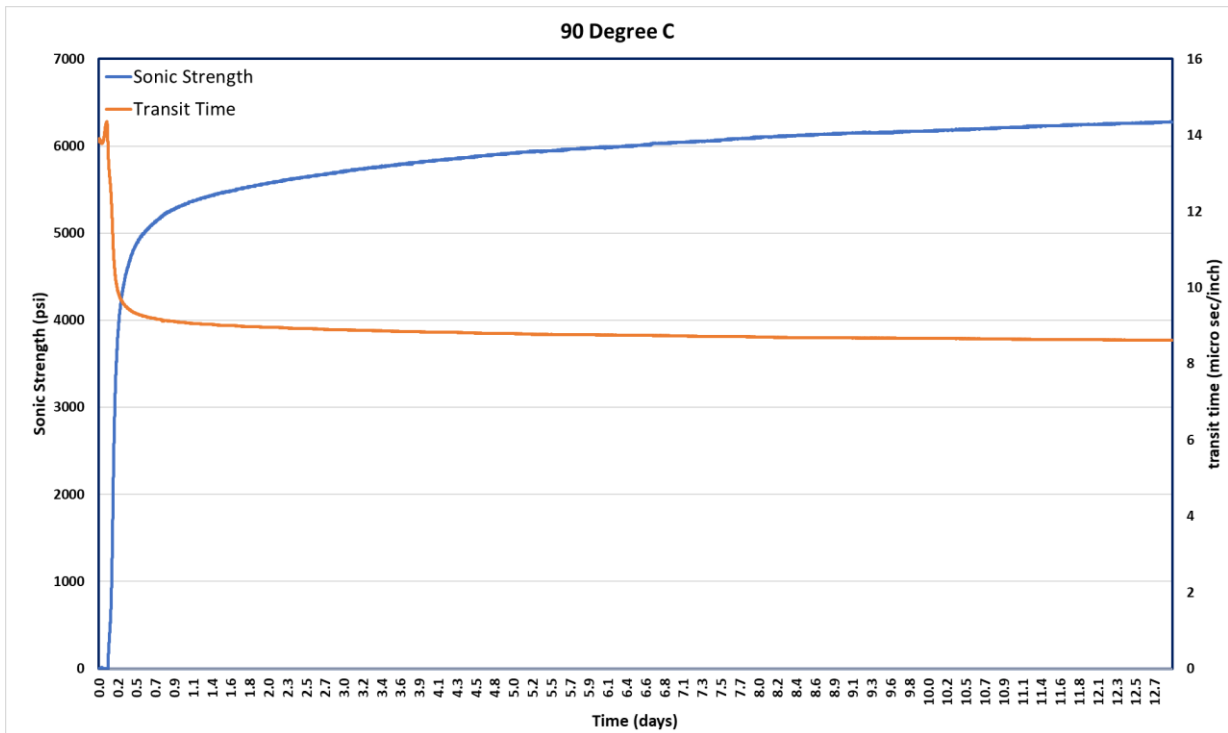
The obtained values of the sonic strength for the geopolymer at 90°C after 7 days of curing are higher in comparison to those for the geopolymer at 80°C (see **Figure 4.8** & **Figure 4.9**). Similarly, the obtained sonic strength values for the geopolymer at 80°C after 7 days of curing are higher compared those obtained for the geopolymer at 70°C (see **Figure 4.7** & **Figure 4.8**).



**Figure 4.7** Sonic strength development generated by applying the custom algorithm option in the UCA; at 70°C and 2000 psi.



**Figure 4.8** Sonic strength development generated by applying the custom algorithm option in the UCA; at 80°C and 2000 psi.



**Figure 4.9** Sonic strength development generated by applying the custom algorithm option in the UCA; at 90°C and 2000 psi.

Compression of the UCA and consistency data shows that geopolymerization at static condition occurs faster than dynamic condition. It could be due to agitation and subsequently, destruction of oligomers at dynamic condition.

The UCA data shows that the slurries set and retarders have no negative effect on setting

time but can increase the pumpability. Sonic strength measurements show that the rate of strength development is higher during the first 12-hr of placeability. But the reaction is not complete even after 8 days of curing.

## 5 CONCLUSION

- This study analytically analyzed the impacts of the addition of two types of retarders on the setting time of the geopolymer.
- After the addition of retarders, the hydration in geopolymer was delayed. This resulted in delaying the geopolymerization and prolonging the setting time. The addition of the two types of retarders postponed the setting time of the geopolymers. Hence, these retarders might make it possible for the geopolymers to be pumped through the well and back to the annulus.
- Based on the results obtained from the experiments with the atmospheric consistometer, the curves which ended with right angle showed that the geopolymer sets efficiently. However, the curves which did not have right angle at the end could be affected by retarders or water contamination.
- The results of the experiments indicated that the geopolymers experienced acceleration of geopolymerization at elevated temperatures. Also, the setting time of geopolymers at higher temperatures (i.e. 60 and 70°C) was significantly shorter than the setting time at 50°C. This shows that the increase in temperature has a strong influence on the thickening time and pumpability of geopolymer mixtures.
- The obtained results from the UCA showed that the sonic strengths of the geopolymers increased with increasing temperature.
- Totally, geopolymerization at static condition occurs faster than dynamic condition.

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