



Universitetet
i Stavanger

FACULTY OF SCIENCE AND TECHNOLOGY

BACHELOR'S THESIS

Study program/specialization: Energy and Petroleum Engineering Drilling and well engineering	Spring semester 2022 Open access
Author: Sondre Hjelm	_____ (Author's signature)
Faculty Supervisor: Dr. Mahmoud Khalifeh	
Title of bachelor's thesis: “Revealing the Effect of Superplasticizers on Viscosity and Yield Stress of Geopolymers”	
Credits: (ECTS): 20	
Keywords: <ul style="list-style-type: none">• Geopolymer• Superplasticizer• Yield stress• Electrostatic repulsion• Zeta potential	Number of pages: 51 + attachments/other: 0 Stavanger, 29th of May 2022

Revealing the Effect of Superplasticizers on Viscosity and Yield Stress of Geopolymers

By

Sondre Hjelm

Bachelor's Thesis

Presented to the Faculty of Science and Technology

University of Stavanger

May 2022

Acknowledgement

I would like to thank my supervisor Associate Prof. Mahmoud Khalifeh who motivated me throughout my research and provided me with a lot of invaluable help. I would also like to thank him for giving me the possibility to join his team of researchers and giving me with a lot of hands-on experimental expertise on how to conduct research and experiments with the use of advance machines and technology.

Also, I would like to show my gratitude towards my friends and co-workers in the lab, Mohamed Omran, Dr. Paulo Moreira and Dr. Mohammadreza Kamali together with the geopolymer research team at the University of Stavanger for always reaching out a hand providing me with a lot of help and expertise when facing adversity in my project.

Finally, I am profoundly grateful to my girlfriend, Tina Hammervold Aslesen, together with my friends and family for always staying by my side, cheering me on in my journey to higher education as an engineer.

My final appreciation would go to my beloved dog, Tinka. Although no longer with us, accompanied me through most of my youth, always greeting me with a smile.

I also would like to acknowledge the Department of Energy and Petroleum Eng. for the opportunity through the research work conducted as part of SafeRock KPN project.

Sondre Hjelm
Stavanger, 2022

Abstract

Ordinary Portland cement has for a long time been the prime material used in well cementing, zonal isolation and permanent well abandonment. Cement is considered a necessity in the oil and gas industry for providing zonal isolation and ensuring long-term integrity through the life cycle of a well. Cement manufacturing is highly energy demanding and emission intensive because of the extreme heat required to produce clinker. A shift from the traditional oil and gas industry to an energy sufficient and greener alternative, sparked the interest of new environmentally friendly materials and products. To reduce the high carbon footprint coming from the cement industry, the concept of geopolymers was introduced. Geopolymers aim to replace Portland cement and to provide cleaner alternative to zonal isolation and permanent abandonment of wells.

In this research, the rheological properties and optimum concentration of admixtures on a rock-based geopolymer have been studied. The intention behind this research is to better understand early development in rheological properties and viscosity profiles occurring shortly after mixing. Using a viscometer, viscosity of the slurry was measured according to the API standard “*RP 10B-2:2013*.” The rheology data was unit converted and plotted in graphs with concentrations increments of 0.25% from 0 to 1.0% by weight of geopolymer (bwog). Additional measurements were performed with 0.10% concentration bwog with intention to investigate the initial impact of a superplasticizer (SP) at low concentrations. Both shear stress (SS) and viscosity profiles were observed to behave similarly, but with varying degree of magnitude. Difference in both concentration and SP revealed both an increase and decrease in the rheological properties. The theory of electrostatic and intermolecular forces was applied to the study and revealed the effective use of the zeta potential in geopolymers. Theory and interpretation of intermolecular forces made it possible to discuss how and where a potential optimum concentration could exist. Electrostatic repulsion has previously been focused mainly on ordinary Portland cement in this research been re-introduced to the study and development of geopolymers. Observations from the conducted experiments were written down, and results were plotted together with their rheology properties and viscosity profiles. Having graphs overlap each other made it possible to observe how changes in the zeta potential could affect the rheological properties of a geopolymer. One may assume an optimum concentration based on this research, but results should only be considered as indicators. Following the obtained results, it would be recommended for further research to conduct both quantitatively and qualitatively experiments on geopolymers ranging around the observed optimum concentration to ensure a more consistent conclusion.

Acronyms

BWOG	By weight of geopolymer
GGBFS	Ground-granulated blast-furnace slag
GHG	Greenhouse gases
NS	Naphtalenesulfonic acid formaldehyde condensate
Pa	Pascal
SP(s)	Superplasticizer(s)
SR	Shear Rate
SS	Shear stress
UCS	Uniaxial compressive strength
δ	Partial charge of a molecule

Table of Content

Acknowledgement	3
Abstract	4
Acronyms	5
Table of Content	6
List of Figures	7
1. Introduction	8
2. Literature review section	10
3. Test setup and experimental methodology	18
3.1 Geopolymer design and preparation	18
3.2 Viscosity and Shear stress.....	20
3.3 Zeta potential	21
3.4 Intermolecular forces and electrostatic repulsion	22
3.5 Impact on strength development	24
4. Results and Discussions	26
4.1 Viscosity, yield stress and shear stress.....	26
4.1.1 Superplasticizer 1.....	26
4.1.2 Superplasticizer 2.....	28
4.1.3 Superplasticizer 3.....	30
4.1.4 Superplasticizer 4.....	32
4.1.5 Superplasticizer 5.....	34
4.1.6 Comparison of performance of the superplasticizers.	36
4.1.7 pH measurements.....	38
4.1.8 Zeta potential measurements.....	38
4.1.9 UCS measurements.....	39
4.2 Optimum concentration of SP using zeta potential	40
4.2.1 Optimum concentration of SP1	41
4.2.2 Optimum concentration of SP2	42
4.2.3 Optimum concentration of SP3	43
4.2.4 Optimum concentration of SP4	45
4.2.5 Optimum concentration of SP5	46
5. Conclusion.....	48
6. References	49

List of Figures

Figure 1: Commercial blender setup with ingredients from left to right; Precursor, Retarder, Superplasticizer and Activator	18
Figure 2: Ofite Model 60 Atmospheric Consistometer	19
Figure 3: Ofite Model 900 Viscometer, stopwatch and measuring cup	20
Figure 4: inoLab pH 7110 used for pH measurements	20
Figure 5: Settled particles in distilled water due to sedimentation on an older sample (left). Colloidal system with particles still dispersed in distilled water (right)	21
Figure 6: Zetasizer together with a sample, sterile syringe and DTS1070 container	22
Figure 7: Repeating unit of the Polymer molecule structure present in SP1 – SP4	23
Figure 8: Structure of the molecule in SP5. (monomer)	23
Figure 9: MTS Criterion C45.105 Load frame used to test the uniaxial compressive strengths	24
Figure 10: Geopolymer sample of SP1 after 14 days of curing, getting prepared for UCS test.	25
Figure 11: Average shear stress from SP1	26
Figure 12: Maximum impact comparison on SP1	26
Figure 13: Average viscosity on SP1	27
Figure 14: Average shear stress from SP2	28
Figure 15: Maximum impact comparison on SP2	29
Figure 16: Average viscosity on SP2	29
Figure 17: Average shear stress from SP3	30
Figure 18: Maximum impact comparison on SP3	30
Figure 19: Average viscosity on SP3	31
Figure 20: Average shear stress from SP4	32
Figure 21: Maximum impact comparison on SP4	32
Figure 22: Average viscosity on SP4	33
Figure 23: Average shear stress from SP5	34
Figure 24: Maximum impact comparison on SP5	35
Figure 25: Average viscosity on SP5	35
Figure 26: Average shear stress in 0.10% concentration of superplasticizer	36
Figure 27: Average shear stress in 0.25% concentration of superplasticizer	36
Figure 28: Average shear stress in 0.50% concentration of superplasticizer	37
Figure 29: Average shear stress in 0.75% concentration of superplasticizer	37
Figure 30: Average shear stress in 1.0% concentration of superplasticizer	38
Figure 31: Uniaxial compressive strength with different % concentration after 14 days.	39
Figure 32: Optimum concentration based on zeta potential on SP1	42
Figure 33: Optimum concentration based on zeta potential on SP2	43
Figure 34: Optimum concentration based on zeta potential on SP3	44
Figure 35: Optimum concentration based on zeta potential on SP4	45
Figure 36: Optimum concentration based on zeta potential on SP5	47

1. Introduction

Research analysis has revealed that a relatively large portion of Greenhouse gases (GHG) are originating from the cement industry. For every tonne cement produced, 900 kg of CO₂ is emitted to the atmosphere. In fact, about 5 – 7% of global CO₂ emissions are caused by the cement plants alone (Benhelal et al., 2013).

Scientists and researchers have for a prolonged time studied the trend and effects of global warming and GHG coming from not only the industry, but from all our global activities. Observations show that the proliferation of products and process of manufacturing pose a heavy threat in the balance of our eco system. Realizing the gravity and effects of global warming and GHG emission was the first step for us to realize the urgent need for new and more environmentally friendly technology. Ignoring our global carbon footprint may result in catastrophic consequences for the future of both the environment as well as the economical part of our society (Benhelal et al., 2013; Zhang et al., 2012).

Narrowing the scope of GHG emissions coming from the oil and gas industry, reveal several links that show potential to be replaced by a more environmentally friendly solution. A recent milestone and good example on this, worth pointing out, is the replacement of fossil-driven power supply, with renewable electricity and electrification of the oil rigs. Considering other areas of GHG emissions, one may point their interest towards cement and cement operations. The concept and usage of cement in the Oil and Gas industry is an important key feature. Following a drilling operation, when the desired depth of a well is reached, a casing string would be run into the borehole to prepare for primary cementing. The purpose of primary cementation is to provide good zonal isolation and to establish a good source of well integrity. The use of cement enables the drilling engineer to further continue a drilling operation, reaching new depths and counter the effects from unstable formations and pressure differences.

Considering the overall efficiency and performance of cement in both zonal isolation and plugging operations, will prove it a challenging product to replace. Following an increased focus of stopping the global average temperature from rising, and expectations around renewable research, have together with the Paris agreement, pushed scientists and research teams to attempt to come up with new alternative products. The alternative cement, compared to ordinary Portland cement, would need to perform similar or preferably better in either one, or both the rheological and mechanical properties. In addition to the properties, the alternative cement would have to perform other specific and similar characterisations as the ordinary Portland cement does, to have a chance at being recognised in the field.

Through the study of inorganic polymers, which are considered as inorganic a polymer, is a concept introduced by Joseph Davidovits in 1975. The study between inorganic chemistry and ongoing geopolymerization reactions was observed to have a relation. Through research and optimizing with the mix design, observing the behaviour on different compositions and concentration of products, would potentially lead to an alternative product to Portland cement.

Following the research and development of this alternative cement, had researchers come up with the idea of geopolymer (Davidovits, 1991).

Geopolymers introduce new ways of utilizing industrial by-products to develop a new product. Geopolymers are observed to have the almost similar functionalities and properties as ordinary Portland cement while at the same time drastically reduce the initial production of GHG emissions. Polymers is observed to start developing through geopolymerization reactions happening at low temperatures, thus replacing the process needed for creating clinker. The ability to replace such an energy consuming process, requiring temperatures up to around 1400 °C, would reflect a drastic decrease to the initial GHG emissions in the cement industry (Barbosa et al., 2000; Ludwig & Zhang, 2015).

Considering the challenges happening during a cement operation, both onshore and offshore, give an idea of what to expect from the alternative cement. Corrosive environment, variation in thermal load and drilling fluid contamination are just some of many unwanted parameters that a cement could potentially occur. All incidents are parameters which could the impact the system of our cement resulting in poor cementation, loss of fluids, or in worst case, a blowout. Rheology and mechanical properties together with the viscosity profiles are properties that can be tailored to fit each specific operation. By introducing different concentrations of admixtures to the system, an operator could tailor the properties of the geopolymers to suit his desired requirements for that specific operation. As of today, there are a few theories and research being conducted on the rheological properties and viscosity profile of a geopolymer. The purpose of the research is to observe the different behaviours of the slurry in early phases of the mix design. Further on to develop a better understanding to what may cause an increase or decrease in the viscosity, as well as what may seem to be the optimum concentration of a specific admixture. Research and results have the potential to provide the industry with a broader understanding to how the concept of rheology work on geopolymers. Finding the optimum concentration of an admixture may also benefit the industry in terms of economy. Utilizing the observed optimum concentration will have the contractor portion less of a product, if not deemed necessary. An optimum concentration could help prevent the abundance of unnecessary components, thus ensuring less waste of resources, and potential savings in their budget. The purpose of geopolymer research and development is to first ensure an alternative to a greener cement, but to also provide the industry with the knowledge of what to expected from the geopolymers. In terms of different properties, behaviour as well as characteristics in details over several different geopolymer mix designs.

2. Literature review section

Concrete is a complex system produced using a combination of cement, aggregates, admixtures, and water. The theory behind cement originates from the society of ancient Greece and Rome, where the term *cement* derives from the Latin word “*caementum*” meaning stone or stone chippings. The science on cement continues developing until a key feature in cement and concrete technology is introduced, Portland Cement.

Portland cement, patented by Josef Aspdin in 1824, introduced a revolutionary way of extracting and providing cement. The production of clinker was observed to be a way more efficient solution compared to the earlier methods of creating cement. Portland cement is produced from a synthetic mixture of limestone and clay in solid form. When the solid form is mixed with water, the cement will set to a hard mass known as concrete. When introducing aggregates into the cement mixture, we form what is known as concrete or mortar (HANZLÍČEK et al.).

Following the modern application of cement, research and observation have revealed that by adding different admixtures to a cement have proved signs of enhancement on several different properties, depending on which admixture was added. Properties such as acceleration, retardation, air entrainment, water reduction, plasticity and dispersion are a few out of all the possible properties able to alternate the reaction and structure of the slurry and finished product (Ramachandran, 1996).

The application of cement is commonly used when constructing buildings and houses, civil engineering construction as well as the focus of my field of study, well construction. The concept of cement and concrete is being used globally every single day.

Cement has become one of the most widely used and produced products in construction globally. Portland cement is very user friendly and easy to use in addition to providing good results in the matter of mechanical strength. Portland cement also gets its popularity from being easily accessible to a cheap penny compared to other alternatives. Even though cement is cheap and easy to produce, does not make it the most environmentally friendly. According to Summerbell, the cement industry through its energy consuming process of production, is responsible for up to about 5% of the total anthropogenic CO₂ emissions and is also responsible for about 12-15% of the global energy consumption obtained from the industrial sector. (Summerbell et al., 2016; Usón et al., 2012).

The amount of pollution and greenhouse gases originating from the production of cement have for a long time been of global concern. As the modern age continues to develop new city infrastructure, large industry areas, as well as in daily life of the every-day man, cement does not seem to show any decrease in its popularity, rather the opposite.

New technology, science and methodology have guided the production of new and more environmentally friendly alternatives to Portland cement. The alternative cementitious product has many names but will for the sake of simplicity be referred to as “Geopolymer” (Davidovits, 1991).

Geopolymers are made up of a network of inorganic molecules which are dependent on thermally activated natural materials. Some examples may be fly ash or slag to provide the system containing either molecules of silicone or aluminum. When combining the industrial by-products with an alkaline activator, will cause an internal geopolymerization. The geopolymerization results in a cementitious slurry having similar characteristics and mechanical properties like Portland Cement (Aleem & Arumairaj, 2012; Majidi, 2009).

Applying new research to already working strategies out in the field may be a challenging process. Through quantitative and qualitative research done on rock-based geopolymer as seen in several different published papers have been starting to show off interesting results when looking into the relationship of the geopolymer system when applying different concentrations of several different admixtures and salts. Running tests and comparing the results obtained on both the enhanced geopolymer as well as the neat recipe of the geopolymer together with Class-G cement have given a lot of new values to use when considering further interest in geopolymer research and development (Chamssine et al., 2021; Khalifeh, et al., 2018a; Khalifeh, et al., 2018b).

With the petroleum industry being a major consumer for cement, these results, if successful, may yield great news for the industry and the global reduction of greenhouse gasses. Continuing further with the concept and theory of what a geopolymers are made up of, reveal a whole more in-depth science and chemistry theory. From the difference in main ingredients involved in the precursor, such as, fly-ash, mine tailings, metallurgical- or GGBFS (ground granulated blast furnace slag), to the fundamental role in the hydration of binders depending on the alkaline activator. Further reactions and properties may be affected depending on the introducing of admixtures to the system. Different concentrations of admixtures will affect the properties differently, thus making it possible to seek specific property and tailor the properties of the slurry and cement to meet the specific applications of interest (Duxson et al., 2007; Xie et al., 2019).

Applying new technology and resources to the study of admixtures effect on geopolymers, have proven to generate a lot of interesting data and behaviour for further research. Different concentration of SPs, together with alternative recipes of geopolymers will all be observed to have different properties and max values, yet the characteristics should remain the same. Though comparing admixtures, deviations are to be expected. Each admixture may affect the geopolymer differently depending on the concentration. Admixtures may enhance the properties on one aspect, for then to have a negative effect on the others. Following results and conclusions of previously conducted experiments show observations that both an increase and decrease in the viscosity and rheological properties, as well as varying results on mechanical properties. Quantifying this research would help to provide the further progression of geopolymers as what to expect in terms of different properties (Alvi et al., 2020).

Research have shown situations where ordinary Portland cement, being the prime material used, did not meet the necessary requirements for the job, thus alternative barrier materials were suggested instead. When implementing geopolymers, one may recreate the similar downhole conditions to simulate the operation. Different measurements and tests could then be conducted to observe the behaviour of the geopolymer. A recipe may then be tailored and proposed to fit the necessary rheological, fluid, and mechanical requirements to be expected from the geopolymer as seen from previously done research. Thus, showing the importance of how geopolymer studies can be implemented to the field (Kamali et al., 2022).

Yield stress and viscosity are only two of many important property parameters to consider when researching and developing geopolymer. When looking into the rheological aspect of the slurry, different admixtures and concentrations may give different rheological properties and viscosity profiles. Looking into what may affect the yield stress and viscosity of the geopolymer, research define a huge variety of properties. In addition to admixtures added, solid to liquid content ratio, temperature, curing time, hardeners, retarders, SPs together with a possible ongoing chemical reaction will all influence the geopolymer and the ongoing geopolymerization reaction. Together with the different properties affecting the system, the ratio of solid phase, particle size and shape will also play an important part for the behaviour of the system. Further in-depth theory may be discussed considering internal energy in the slurry coming from either an altered temperature from either an external or internal source. Research have shown that temperature differences may cause acceleration or retardation to the ongoing geopolymerization reactions (Lu et al., 2017; Romagnoli et al., 2012).

The introduction of superplasticizers to cement has proved to be a milestone for the cement industry when it comes to the altering the rheological and mechanical profile of the cement. SPs are admixtures added to a cement mixture which depending on both the type and concentration used, will have significant effects on the workability, viscosity, and performance of the cement (Papayianni et al., 2005).

In general, plasticizers added to cement will allow the water contents to be reduced and to improve the separation of the particles to prevent the settling and clumping time. The name superplasticizer refers to an enhanced plasticizer having an enlarged or improved effect of impact on the cement, decreasing the yield stress drastically thus decreasing the viscosity drastically leaving the cement less viscous and easier to pump (Papayianni et al., 2005).

The concept and idea of SPs has also been applied to studies and research on geopolymers. Observations on the effects of a SP in geopolymers reveal a significant decrease in the rheological properties. Different SPs are observed to affect a geopolymer differently depending on the dominant compositions. A SP may cause varying effects on the system depending on when and how it is introduced during the initial mixing procedure. Results may also vary depending on which SP being studied, and to what type of alkaline activator was being used (Nematollahi & Sanjayan, 2014).

The molecular structure and length of a SP will impact the system differently depending on how the polymer act on the system. The differences may take place in the initial mixing, where the chemical reaction, geopolymerization or polycondensation are occurring.

Research done on the behaviour of molecules and their intermolecular interaction forces may help develop a better understanding of how early dispersion of particles take place and how this may affect the early rheology properties to a geopolymer design. Following the research of Anthony J. Stone, going in-depth with the idea and concept of intermolecular forces acting on atoms and molecules may help answering different behaviours when adding a SP. Depending on what the dominant particle is in the specific system, will yield different results following the electromagnetic interaction, repulsion, and dispersion of the particles. Unless the molecules both seem to be made up of ions having the same sign of charge, the interaction energy may be repulsive at all distances. This is where research may further help develop systems to identify, tailor and create geopolymer designs utilizing the potentials in these forces (Stone, 2013).

Continuing further in-depth on causes of rheological and mechanical properties, one reveal, as mentioned above, the intermolecular forces existing in a chemical reaction both during and after geopolymerization and polycondensation at both atomic and molecular scale.

All molecular and intermolecular forces are electrostatic in nature. For some pairs of molecules, in a relative orientation, the force of interaction energy may act repulsive at all distances, unless both molecules are made up of ions with the same sign of charge, there will always be orientation in which the interaction is attractive (Stone, 2013).

The theory behind intermolecular forces explains how molecules behave when experiencing either, or both repulsion and attraction to one another through forces known from electrostatic repulsion and internal kinetic energy in the form of steric effect. The charge of which the system have is dependent on the dominant composition of the materials in the system. Silicate phases such as SiO_2 , C-S-H (calcium silicate hydrate) and C_3S contain mainly negatively charged molecules. These molecules would provide the system with electrostatic repulsion forces and reveal the molecules' ability to repulse one another. On the other side of the force spectre, aluminate phases for example will do the opposite of electrostatic repulsion as these molecules would have a dominant positive charge. Steric effects and Van der Waals forces occurring from these positively charged molecules will affect the charged particles in the system, ultimately resulting in agglomeration of the cement grains (Larsson et al., 2012; Plank & Hirsch, 2007; Zhang et al., 2022).

The intermolecular forces may also experience deviations to how they behave when taking into consideration what the particle sizes are, as well as what shape these molecules have. Depending on these parameters in addition to the molecular geometry and structure of the molecules, intermolecular forces such as steric hindrance could affect the induction and dispersion

of the molecules, which could lead to a different behavior depending on how the molecules set (Davidovits, 1991; Stone, 2013).

When considering both the system's intramolecular and intermolecular characteristics, together with the potential electrostatic repulsion, it is important to classify what the type of products and materials are used in the research. The concept of what a geopolymer consists of are inorganic polymers created from a long chain of aluminosilicate materials formed by the process of geopolymerization. For a typical geopolymer, reactive alumina and silica-based materials are what is known as the precursor for the system and acts as the source material, although there are several alternatives i.e., Ground-granulated blast-furnace slag (GGBFS), silica fume and slag (Bouaissi et al., 2019).

When the precursor is mixed with a hardener, consisting of an alkali silicate solution, the chemical reaction of geopolymerization would be triggered

During the geopolymerization process, different mechanisms are taking place (Alvi et al., 2020; Aziz et al., 2016; Khalifeh et al., 2014):

1. Dissolution in alkaline solution
 - A process by which molecules of a solute are dissolved in a solvent.
2. Transportation
 - Dissolute ions move in the slurry
3. Reorganization
 - Diffusion of dissolved ions with formations of small, coagulated structures.
4. Nucleation and growth
 - Small nucleuses are formed from the liquid
5. Polycondensation
 - A chemical reaction converting the monomers and oligomers to geopolymers.

Kinetic energy has the tendency to keep the particles moving apart, while the attractive intermolecular forces between the particles tend to draw them together. Atoms within a molecule create covalent and ionic bonds with each other, but also participate in other interactions happening between the other molecules. The amount of force exerted by a molecule is depending on what kind of bond it has, while the amount of attraction between several molecules are depending on the orientation of the molecule. In addition to the molecule's orientation, ion-dipole and dipole-dipole molecules have particles with a dominant partially negative and partially positive charge, which would cause a difference to how other molecules is attracted.

Mentioned in the section above, there are 4 main categories of atom bonding: ion-ion, ion-dipole, dipole-dipole, and London dispersion (also known as van der Waals forces) ranged from strongest to weakest force of bonding, respectively. Depending on the molecule bonds that are

present in a system, will have a saying to how well the molecules will interact with each other when introduced to either more of the same, or other compositions.

With the presence of either ion-dipole or dipole-dipole molecules, the concept of partially charged particles take place. Using H₂O, which has also a hydrogen bond, the following concept of a partial charge may be illustrated as: H₂O molecules are polar because oxygen is more electronegative than hydrogen, therefore pulling the electrons in the bond towards itself. When combining these vectors of attraction exerted from the atoms, we see that water has an overall dipole, or in other words, a side where the molecule experiences some electron access - partially negative charge (referred to as δ^-) and some electron deficiency - partially positive charge (referred to as δ^+). Following these partially charged particles, dipole-dipole behavior is seen in water, where oxygen (δ^+) attracts the hydrogen (δ^-) and vice versa and the molecules bond together. It is the concept of a partial charge difference in an atom that show the importance of molecular geometry for whether a molecule is polar or nonpolar. Following the concepts of intermolecular electrostatic forces, one may essentially divide the type of forces acting around an atom or a molecule as either short-range or long-range electrostatic forces (Israelachvili, 2011).

The concept of short-range electrostatic forces and interactions is not the objective of this work but is worth mentioning. The intermolecular effects coming from the long-range electrostatic interactions will be discussed in the following section. Observations on the use of a partially charged atom, reveal the fundamental part of the electrostatic double layer theory. If a particle of a size greater than 1 nanometre is dispersed in water, there will be a reaction in the solid-liquid interface. Both parts in the solid and liquid interface carry different partial energy levels which lead to a tension at their interface once they get into close contact. It is this boundary that is referred to as the electrostatic double layer. The electrostatic double layer theory determines one of the basic macroscopic relations in electrochemistry and chemical reactions, which happen between the electrode charge and the potential capacitance (Schmickler, 2020).

Previous studies on the electrical double layer have been pointed out that differential effects in capacity is thermodynamically related to the interfacial tension, the surface charge density, and the concentration of each individual ion making up the double layer. Following the effect of polymer adsorption on the properties of the electrical double layer of colloids, one may point out the relevance for how the double layer theory may affects products, and the modern importance within many technological areas. Shifting the focus to the cationic part's ability to destabilizing colloidal systems, the concept of zeta potential emerges (Grahame, 1951).

The zeta potential is the scientific term given to the magnitude in force of repulsion measured in the electrostatic forces for a suspended, charged particles existing within a dispersed, colloidal system. The zeta potential can help measure and estimate the electrostatic potential exerted at the slipping plane of the electrostatic double layer. When the concept of zeta potential is considered, the focus is typically on the electronegative scope of the particle system in which it operates. Ensuring a relatively high, stable zeta potential reading will be beneficial in the

dispersion of particles. Previous research has observed a stable relation boundary between a stable and unstable suspension of particles. The stable boundary ranges from negative 30 to negative 40 mV (milli volt) to ensure good to strong interparticle repulsion. The more negative the zeta potential is, the stronger the interparticle repulsion will be. The more negative the zeta potential, the harder it will be for particles to form particle networks or gel structures. High zeta potential can be achieved by introducing long-chain surfactants to the initial design. This is where the concept of SPs is introduced, as they provide the system with negatively charged particles in the form of long-chain polymers. These polymers help generate weak agglomerated particles which easily can be broken apart into monodisperse particles due to the low steric effect and molecular geometry of the particles. With an increased amount of particle networks, following the decline in zeta potential, would lead to the particles coagulating and creating micro flocking. A further decrease in zeta potential would attract the micro flocking, no longer able to repulse each other, into the formation of macro flocking, ultimately resulting in sedimentation as the particles become too heavy. Continuing the research on the other side on the more positively charged field of electromagnetic forces, one may find the concepts of the steric effect and the Van der Waals forces. These are the forces used to explain the behavior of particles in the process of attraction and coagulation. Van der Waals forces explain the behavior of atoms, molecules, and surfaces through their formation of very weak dipole-dipole bonds. The weak bonds are created through attraction and repulsion forces exerted between particles and depends. In addition to the electromagnetic forces affecting the particles, correlations in the fluctuating polarization of the other nearby particles will remarkably disturb the bond. The steric effect on the other hand, refers to the impacts occurring in the kinetic and thermodynamical interactions in chemical reactions (Daimon & Roy, 1979; Huo et al., 2019; Larsson et al., 2012).

Looking into the concept of the steric effect quantitatively may be considered troublesome but forwarding the research in a qualitatively measure is relatively straight forward. It is possible to attach the concept of steric effect through observations on particles in the degree of substitution, and bulkiness of the particles involved. However, quantifying the magnitude of the steric effect in one reaction may seem rather difficult as steric effect rarely occur in the absence of other particularly effects (Coote, 2012).

The general idea of steric hindrance can be explained as an obstacle to reaction caused by the shielding of a reaction site by parts of the structure of a branched reactant (Ingold, 1957). Steric hindrance may be defined as the steric shielding of a particle as the process by which sterically demanding groups would limit the accessibility of its reactive center, thus making it harder for other particles to come break through or move around the reactive center (Pinter et al., 2012).

Bulky groups of particles do not only limit the accessibility to the reactive center of the molecule, but also provide the system with electrostatic repulsion forces if the bulk is large enough. To further understand the steric effect, one must consider radical stability between the molecules and atoms for when an unpaired electron enters the system as they merge. One may conclude that the steric effect has the best achieved stability when both the radical center and interacting

molecule are co-planar. However, with the presence of multiple bulky groups of substituents, the planar geometry of the molecule may become destabilized or even prevent the reaction from happening (Coote, 2012).

The internal stability of a molecule should increase when adding stabilizing substituents to the system. However, as discussed above, the total stability has several factors to how and when the molecules may exert attracting, or repulsive intermolecular forces. The total system of molecules may experience diminishing or enhanced effects depending on the different characterizations to the group of substituents introduced to the system. Therefore, in the name of geopolymer science, one may get an idea to what research of new substituents are taking into consideration, and what to keep in mind during the process of creating and evaluating new substituents and solutions.

Therefore, in this work, the impact of SPs on a rock-based geopolymer will be studied through viscosity measurements and zeta potential changes of the slurries. In addition, a methodology for optimization of the SP concentration is presented.

3. Test setup and experimental methodology

In this chapter, a general description of the equipment and instruments used to analyse the zeta potential are provided. The setup designed to accomplish the objective of this research will also be presented. The chapter will also cover the preparation and parameter conditions for the experiments.

3.1 Geopolymer design and preparation

The rock based geopolymer in this study was prepared by adding a solid phase (precursor) into a premade liquid phase (consisting of a hardener and a retarder) and lastly the addition of a superplasticizer (SP).



Figure 1: Commercial blender setup with ingredients from left to right; Precursor, Retarder, Superplasticizer and Activator

In advance of the mixing procedure, 4 containers, (see Figure 1) were prepared and brought to the mixer. The different containers, from left to right consisted of a precursor (solid phase), retarder (salt solution), SP (liquid phase) and a hardener (activator, liquid phase).

The machine used for the mixing was a Model 20 Constant Speed Blender provided from Ofite. The machine use a two-step Warner commercial blender configured at 4000 and 12.000 RPM following the guidelines stated within the API Specification 10.

The mixing design were as following.

1. Combine the hardener and retarder in the blender and mix at 4000 RPM for 10 seconds.
2. Start the API mixing procedure.
3. During step 2, for the first 15 second interval at 4000 RPM, pour the precursor into the mixer in intervals to ensure even mixing and to avoid spilling.
4. After the initial 15 seconds, step 2 is finished, and step 3 will continue automatically. The mixer continues mixing for additional 35 second at 12.000 RPM. During step 3, introduce the APof choice into the mixer.
5. Make sure to get all the precursor into the blending mix, as some may be clinging into the wall of the blender. The best way for me were to use a spatula.

To ensure a more consistent geopolymer slurry, the preparation continued with the use of a consistometer. The consistometer used in this experiment were the Model 60 Consistometer (see Figure 2) which follows the API specification 10 for conditioning cement slurries. The consistometer uses a designed blade to stimulate the ongoing geopolymerization reaction and to ensure an evenly mixed slurry. Additionally, the consistometer could provide the ability to track the solidifying process of the cement over a time interval at a set temperature.

For the sake of this research on the viscosity and yield stress, the consistometer were only used for prolonged mixing of the slurry and to ensure consistency in the measurements. Continuing with the preparation of the slurry after the initial mixing procedure, the geopolymer was poured into the consistometer cup and placed into the consistometer containing an oil bath to mix and cure at a pre-set room temperature (20 - 25 °C) for 20 minutes.



Figure 2: Ofite Model 60 Atmospheric Consistometer

3.2 Viscosity and Shear tress

After 20 minutes of conditioning at room temperature, the slurry was poured into a measuring cup and placed under the viscometer. The viscometer used in this research was the OFITE Model 900 Viscometer (see Figure 3). The viscometer operates on fluids exerting a viscous drag which then creates a torque force on the bob placed inside the measuring cup. The values are monitored by a transducer which measures the angular displacement of the bob and presents the shear stress (SS) value per given shear rate (SR). Following the API standard “*RP 10B-2:2013*”, measuring the interval from 0 to 300 RPM for ramp up as well as from 300 down to 0 RPM for the ramp down. Both measurements were then used to calculate and average. After performing the ramp up and down readings, a 10 second- and 10-minute gel tests were performed. In advance of the gel test the fluid were mixed at 300 RPM for 1 minute to ensure that the slurry did not have an initial gel structure and to provide more consistent measurements. After finishing all the measurements using the viscometer, the measurements data would be used for further calculating the viscosity on the slurry, as presented in the graphs in the next chapter.



Figure 3: Ofite Model 900 Viscometer, stopwatch and measuring cup.



Figure 4: inoLab pH 7110 used for pH measurements

Following the research on the concept of zeta potential in geopolymers, reveal how highly sensitive the zeta potential is to changes in pH (Nägele, 1986).

Carefully measuring the pH is recommended for more consistent measurements in addition to observe if there are any ongoing chemical reactions or deviation affecting the system. Applying the zeta potential approach and importance of pH to geopolymers may help comparing results and find a correlation on the behaviour in rheology of a geopolymer. The pH was measured directly in contact with the slurry using inoLab pH7110 (see Figure 4). The pH on the slurry were measured both before and after conditioning.

3.3 Zeta potential

The zeta potential is the measurable parameter of a particle in a colloidal system. Zeta potentials help determining the magnitude of electrostatic repulsion forces acting between particles. The Zeta potential provide help in characterizing the optimal stability for dispersed particles in a colloidal system (Weiner et al., 1993).

The machine used to measure the zeta potential in this research was the Zetasizer Nano, provided by Malvern. The Zetasizer measures the magnitude of electrostatic forces exerted on the particles at a molecular level. The data collected from the measurements may help to further understand what causes the different properties in early hydration of cement and geopolymers.

For the purpose of consistency, all samples were measured under the same condition consisting of 0.10 gram of geopolymer slurry measured in a container for then to add 100.0 mL distilled water. After combining the two, a good shake is recommended for them to mix well. It is worth mentioning that there is a reason to why distilled water is used instead of de-ionized water or tap water. The de-ionized water could have a negative impact on the pH of the system, while the tap water could increase the ion content of a sample (Nägele, 1986).

It is, for the colloidal system, important to not let the sample remain stationary for too long. Particles will slowly lose their repulsion forces and quickly start to crystalize into tiny networks, creating micro, and ultimately macro flocking resulting in particles settling on the bottom of the container. (See Figure 5). Keeping the sample in dynamic motion, shaking often, would slow down the process of crystallisation. Though shaking the sample every now and then may seem effective, it is preferred for the sake of consistency, to measure the zeta potential of a sample as soon as possible for the most reliable measurements.

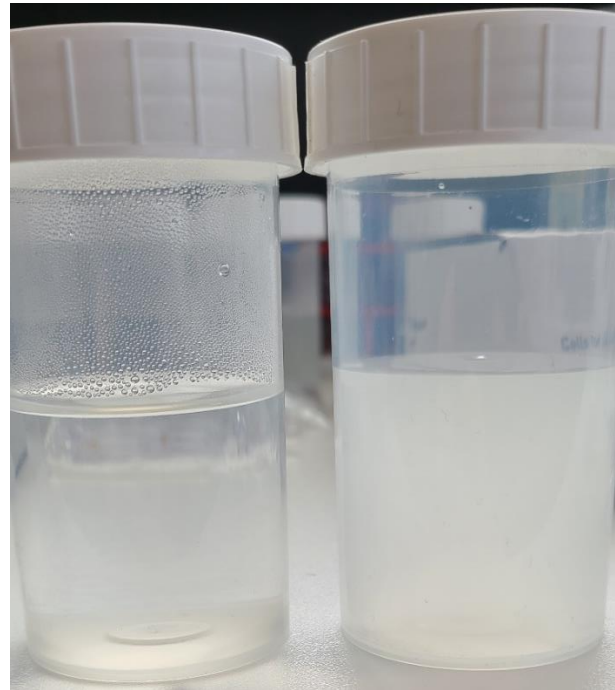


Figure 5: Settled particles in distilled water due to sedimentation on an older sample (left). Colloidal system with particles still dispersed in distilled water (right).

When preparing to measure a sample, one may use a Malvern produced container called DTS1070. The sample will be extracted from the container which hosts the sample, by using a sterile syringe. (See Figure 6) Next step would be to inject the sample into the DTS1070 container. It is recommended to follow Malvern's own recommendations for how to prepare a sample. According



Figure 6: Zetasizer together with a sample, sterile syringe and DTS1070 container

to Malvern, the container should be injected halfway, while being up-side-down to ensure that no air is left in the container which could lead to contamination. For then to continue filling the rest of the container holding it normally.

The Zetasizer uses an electrical current to measure the electrostatic forces acting on the particles suspended in a colloidal sample. If the particles had enough time to settle (as

seen in Figure 5), the measurements would become inconsistent and unusable. The reason behind why the sample become unstable is because after sedimentation, there are no particles to transport the current through.

3.4 Intermolecular forces and electrostatic repulsion

The theory of intermolecular forces was explained in greater details in the previous chapter, and briefly mentioned in the section above regarding the zeta potential. Even though the concepts have been discussed thoroughly, some key features are still worth pointing out for the following the research of SP use in geopolymers.

SP1 – SP4 are all based on commercially available SPs based of Sodium salts of Naphtalenesulfonic acid containing formaldehydes (NS) with different sizes of polymer chains. Since the SPs in these experiments were obtained commercially, have resulted in some information regarding the chemical composition of each SP being left unrevealed.

The SPs are based on the same main polymer being NS, with one of the only exceptions being in the different lengths on the polymer-chains. The polymer-chains therefore follow the same, continuously repeating unit of molecule seen in Figure 7. However, though having the same base molecular characteristic, the SPs are expected to have a difference in the formaldehyde, and sodium salts composition.

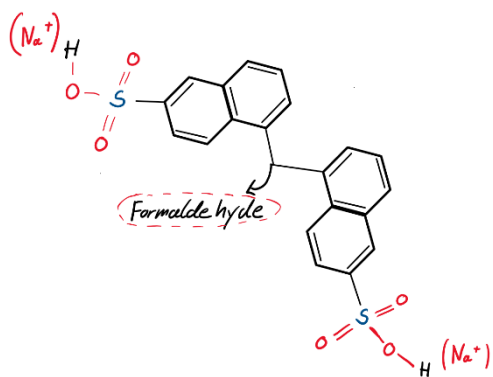


Figure 7: Repeating unit of the Polymer molecule structure present in SP1 – SP4.

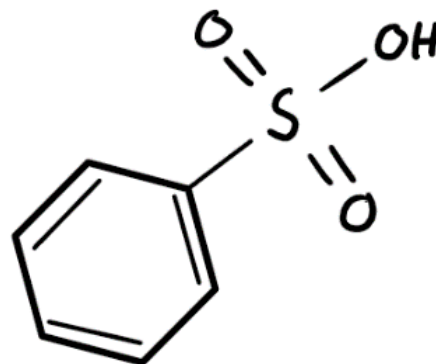


Figure 8: Structure of the molecule in SP5. (monomer)

On the other hand, SP5 is expected to have the lowest molecular weight among all the SPs. SP5 is based on the same Naphtalenesulfonic acid polymer chain but does not contain a formaldehyde group (see Figure 8). One could therefore, based on this information, have come up with the assumption that the measurement over SP5 could be observed to have different characteristics when compared to the other SPs. Looking into studies on what the polymerization effects of NS polymer are, one may reveal the following information:

NS is a surfactant with excellent rheological performance, as for why it is widely used in several different industries, including cement. NS has been an important anionic surfactant in the industry since its effective performance in dispersion is observed to closely related to its degree of polymerization. The differences in the molecular chain-length of polymer depend on the degree of polymerization (Yan-Min, 2019).

The following statement explain the how the degree of polymerization may be utilized, where n stands for the degree of polymerization.

- Low degree of polymerization ($n = 1 - 3$)
 - Mainly used for diffuser in textile printing and dying industry.
- Medium degree of polymerization ($n = 6 - 12$)
 - Mainly used as SPs for cement.
- High degree of polymerization ($n \geq 15$)
 - Can be used as additives for coal water slurry and extra-strong concrete.

The different degree of polymerization has been observed to greatly influence how a system responds, and to how it applies to the performance of the application. Improving the degree of polymerization may therefore improve the quality of a systems parameters and overall performance. When considering the use on cement, the optimum degree of polymerization should be between 6 – 12, according to previously conducted research.

As mentioned, the SPs were obtained commercially, therefore additionally research would have to be conducted to analyze the NS. Attempts to study the degree of polymerization have not

been conducted for this research, but following the research of Yan-Min, a list of methods has been proposed.

1. Analyzing the infrared spectra.
2. Analyzing the ultraviolet spectra.
3. Comparing the spectra in 1. and 2.
4. Spectroscopy.
5. Nuclear magnetic resonance.
6. Mass spectrometry.

(Yan-Min, 2019).

3.5 Impact on strength development

The purpose of cement and geopolymer research is to deliver an optimal and sufficient product to the market that also provide the desired strength and support of the product once it hardens. The idea behind the uniaxial compressive strength (UCS) is to crush a cured sample after a set number of days. The idea is to observe how different concentrations of a SP would impact the mechanical properties of the geopolymer after it have hardened. Good strength in mechanical properties is preferred to ensure that the integrity of the geopolymer is applicable to use in the field.

The machine used for the measurements was the “*MTS Criterion C45.105 Load frame*” (see Figure 9). The rate of applied pressure was following the API standard “API TR10TR7,2017” which applies pressure of 30kN/minute.

For this research, the following samples were cured for a total of 14 days before being crushed. The hardened sample (seen Figure 10) will at the final day of curing get prepared for the experiment by getting their top and bottom surfaces levelled. It is also important to write down the physical observed length of both the diameters and total length of the sample for further potential calculations.

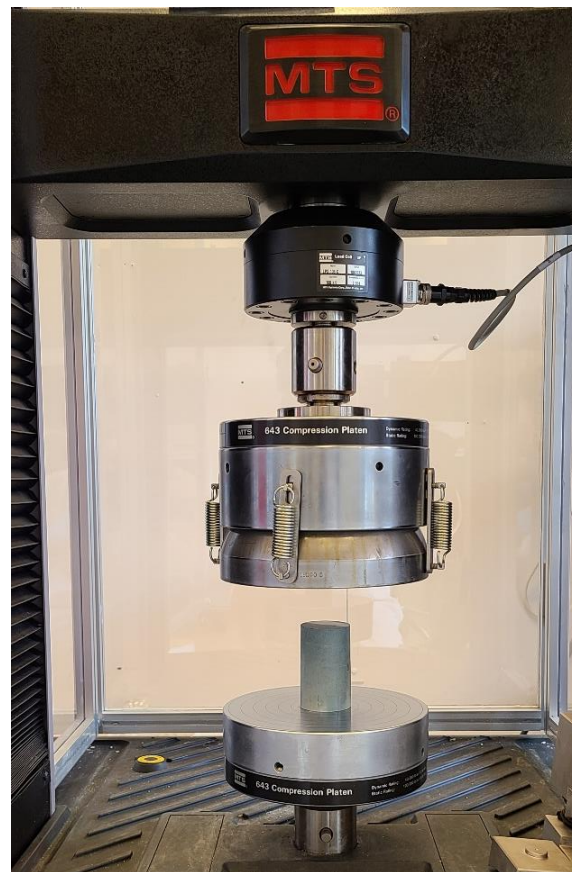


Figure 9: *MTS Criterion C45.105 Load frame used to test the uniaxial compressive strengths on a sample.*

When performing the UCS test, it is again important to reassure a smooth and levelled surface on both sides. Pressure applied from the machine rely on these smooth surfaces to have the pressure distributed evenly over the total area and volume of the sample. Ensuring a homogenous, smooth, and levelled surface will not only improve the measurements data, but also reduce a potential failure. Measuring an unlevelled surface may contaminate the results as pressure would be distribute unevenly over the surfaces, giving poorer results and in worst case cause experiment to fail.

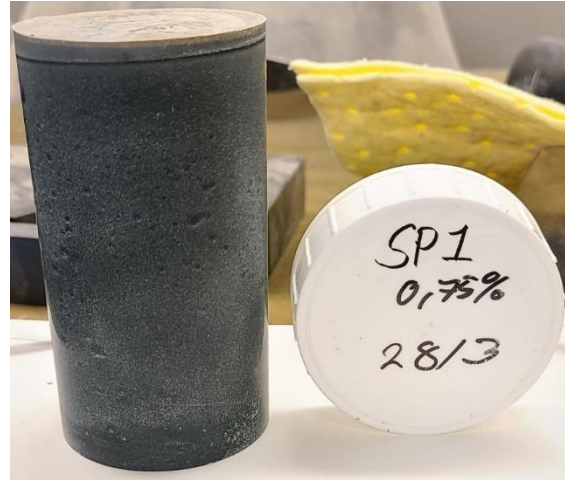


Figure 10: Geopolymer sample of SP1 after 14 days of curing, getting prepared for UCS test.

4. Results and Discussions

4.1 Viscosity, yield stress and shear stress

4.1.1 Superplasticizer 1

Impact of superplasticizer 1 (SP1) – The use of SP1 is based on previous work done by the research team at UiS.

When introducing SP1 to the neat geopolymer, the shear stress (SS) and viscosity was observed to decrease drastically. (See Figure 11) SS and viscosity on the neat geopolymer are presented in the graph as 0% by weight of geopolymer (bwog) and represents the rheological

properties of a geopolymer without any additional admixtures. 0% will act as the reference line when comparing the rheological effect of SPs on the geopolymer. The reference line will be present for all 5 SPs. Looking at the full picture, we observe that the geopolymer is acting in a shear thinning manner.

When adding 0.10% bwog of SP1 to the neat recipe, the geopolymer was observed to have a significant drop in the slurry's initial SS and viscosity. The significant drop in SS and viscosity

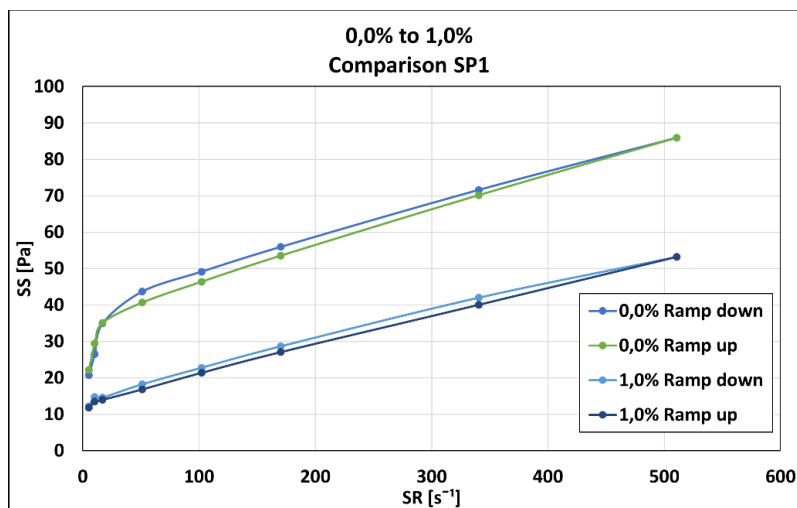


Figure 11: Average shear stress from SP1

Figure 12: Maximum impact comparison on SP1

may be directly connected to the effect of zeta potential, and how this increases the electrostatic repulsive forces acting in the geopolymer slurry. Increasing the concentration of SP1 from 0.10% to 0.25% bwog, are observed to create a further decrease in the SS. Upping the concentration further, from 0.25% to 0.50%, is observed to continue the decrease in SS. Assuming a similar trend

occurring, may assume that increasing the concentration will decrease the SS to a point where the measurements start overlapping. When the concentration was increased to both 0.75% and finally 1.0% bwog, measurements were observed to resulted in a further decrease from the initial SS happening throughout the different shear rates (SR) of the ramp up and ramp down measurements, yet with a more noticeable effect happening at the yield stress of the geopolymer. The yield stress represents the amount of force required to overcome the initial friction of the slurry (viscosity); thus, the observations of overlapping yield stress measurements may have revealed a critical concentration and a potential optimum for SP1 based on this assumption.

Comparing the results of maximum and minimum concentration of SP1 (as seen Figure 12), illustrate a difference in yield stress of almost 10 Pa. One may also notice an odd behaviour of the geopolymer slurry through the ramp up – ramp down measurement. The geopolymer slurry behave differently than what would have been expected for a Portland cement slurry, especially when considering previous research of cement. A normally expected behaviour of Portland cement slurry, in ramp up and ramp down measurements, would result in the ramp down trendline being under the ramp up. Geopolymer slurry on the other hand behave opposite, with a higher ramp down than ramp up. One of two theories may attempt to address why this happens. One theory could be because of an ongoing chemical reaction in the slurry design, where salts break down during the viscometer measurements, resulting in alternating values developing over time. The other theory could be that particles are already experiencing geopolymerization resulting in particle sedimentation.

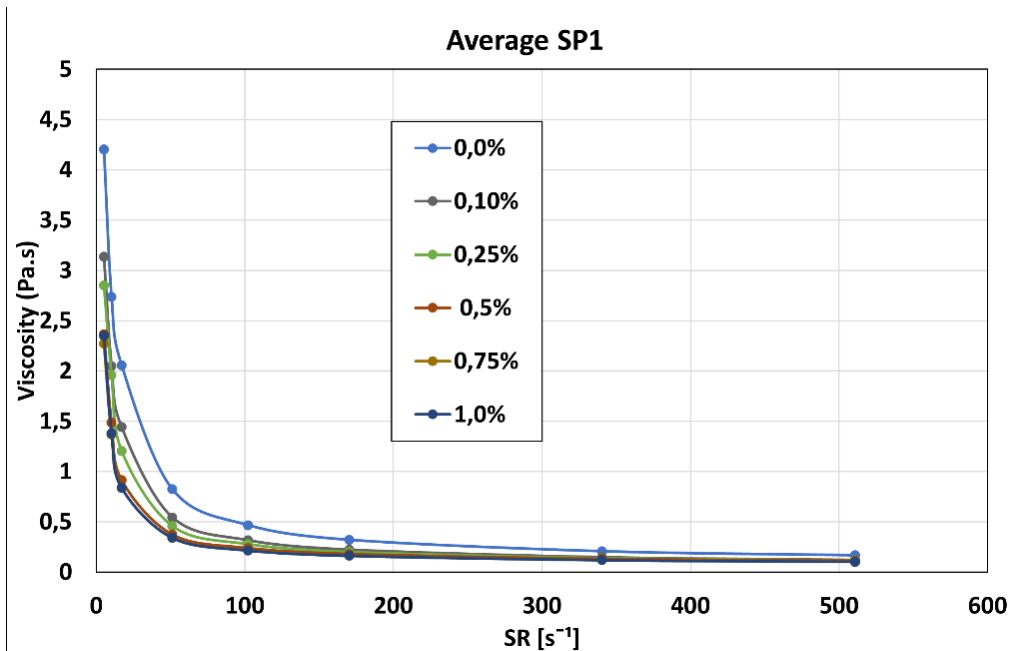


Figure 13: Average viscosity on SP1

Experiencing a decrease in SS when increasing the concentration of the SP does not necessarily mean that these are the optimal concentrations of this SP, nor is it commonly known about the consequences of having a higher concentration of SP in the geopolymer yet. To observe

this, further research using different amounts of concentrations would be considered beneficial. Some of the other parameters, like mechanical strength properties on a geopolymer will be discussed in a later chapter. Calculating and plotting the viscosity data of SP1, illustrates the viscosity profile on the geopolymer as seen above (see Figure 13). Interpreting the viscosity graph and comparing the results with the statements from the SS, could help reveal the different effects SP1 have on the rheological properties and viscosity on the geopolymer. When observing the behaviour on the viscosity and SS in the higher ranges of SR, we notice little to no difference in effect. Contrary, the slurry experiences a more noticeable difference in the lower SRs. The different effects provided by the SP, on viscosity in low SR as well as the yield stress, could be considered interesting for further discussion and research.

4.1.2 Superplasticizer 2

Impact of superplasticizer 2 (SP2) – The use of SP 2 was observed to have similar effects as compared to SP1. Measurements of SS and viscosity had been conducted the same way as in SP1 and plotted to make illustrate the graph seen in Figure 14.

SP2, though still experience a decrease in SS and viscosity, did not have the same drastic decrease seen for SP1. Comparing the two, one may

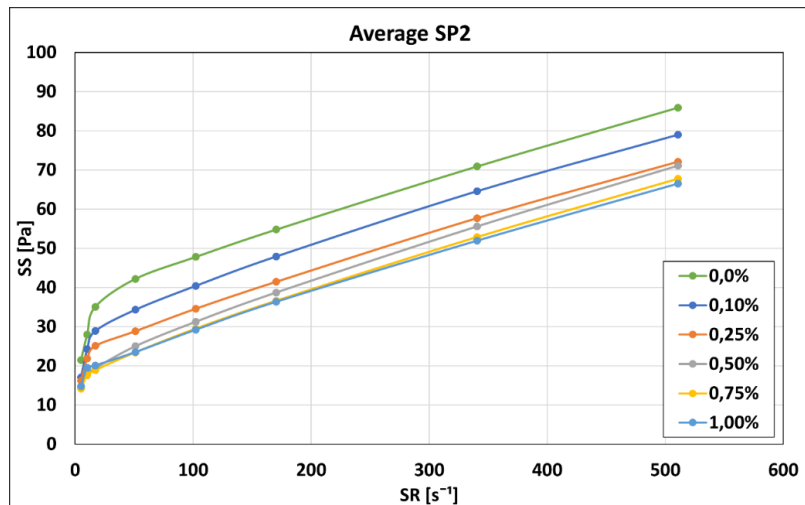


Figure 14: Average shear stress from SP2

point out the similar behaviour on the SS, but with a small difference in the yield stress. Following the increase in concentration of SP2, observations revealed that: The SS would experience an initial reduction in low concentrations compared to the neat geopolymer for both 0.10 and 0.25% bwog. Increasing the concentration further, to 0.50. 0.75 and 1.0% did not seem to cause a drastic effect, though showing signs of a lower SS in the higher range of the SR. The yield stress is observed to follow the same behaviour as for SP1, where the two lowest concentrations would cause a noticeable impact, while the concentrations from 0.50 to 1.0% would react a similar impact to one another. Observations may therefore conclude that there is a critical concentration existing somewhere around 0.50% bwog in SP2 with a potential optimum concentration.

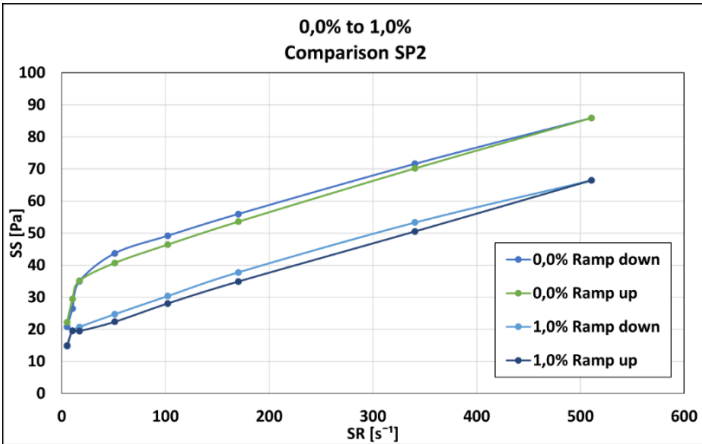


Figure 15: Maximum impact comparison on SP2

When comparing the ramp up and ramp down trends seen in Figure 15 we are provided with a new, yet similar result as seen for SP1. The difference is as mentioned above, a slight decrease in the magnitude which SP2 would affect the geopolymer.

Similar to SP1, the strange behaviour occurring in the ramp up and ramp down measurements of the geopolymer may be explained through

the two mentioned theories about either an ongoing reaction, or particle settlement. Continuing the observation on SP2's effect on viscosity as seen in Figure 16, following observations were noticed:

The initial introduction of SP2 to the geopolymer, in low concentrations, revealed a similar behaviour as observed in SP1, SP2 would still cause a drastic decrease in the initial viscosity in the two lowest concentrations but would noticeably overlap each other at concentrations ranging from 0.50 to 1.0%. When the viscosity overlaps each other, the assumption would once again seem reasonable to conclude a critical concentration of SP2. Observing when the viscosity and yield stress would stop deviating themselves from the rest, the conclusion would state that there could be an optimum concentration existing around the range of 0.50% bwog where the effects were highest.

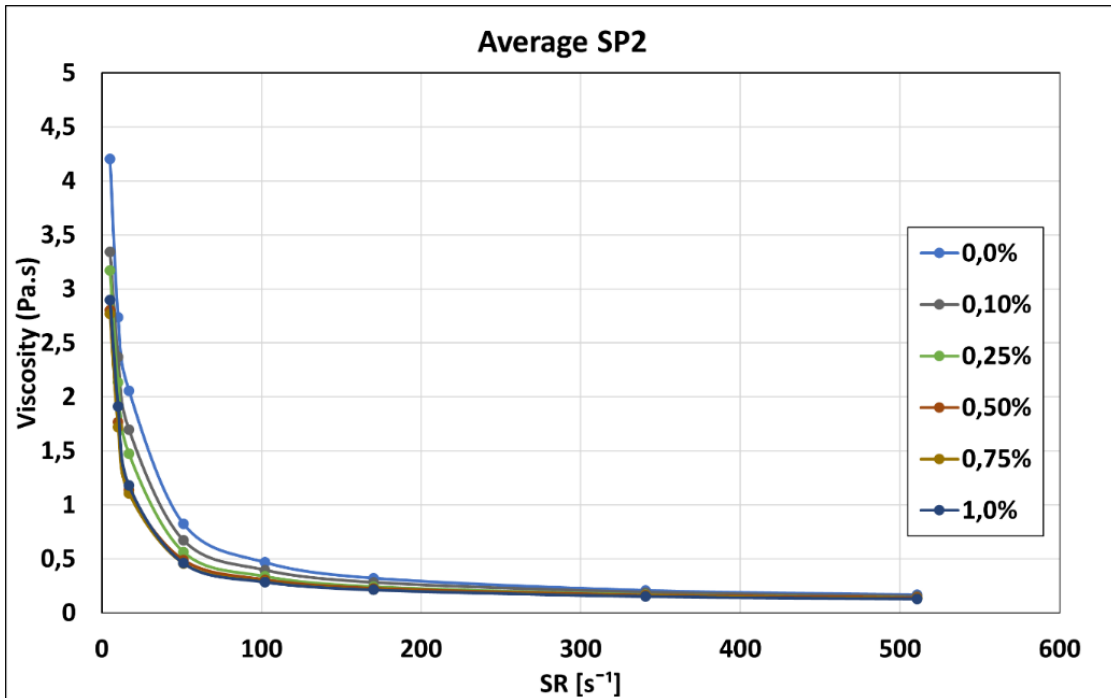


Figure 16: Average viscosity on SP2

4.1.3 Superplasticizer 3

Impact of superplasticizer 3 (SP3) – Observing the results obtained from measuring SP3 (seen in Figure 17), one may notice the similar characteristics seen in the previous two SPs. The difference observed in the graph is noticed through how the trendline behave. The SS is not observed to be as affected compared to the other two but does still provide an initial decrease in the SS and viscosity of the geopolymer.

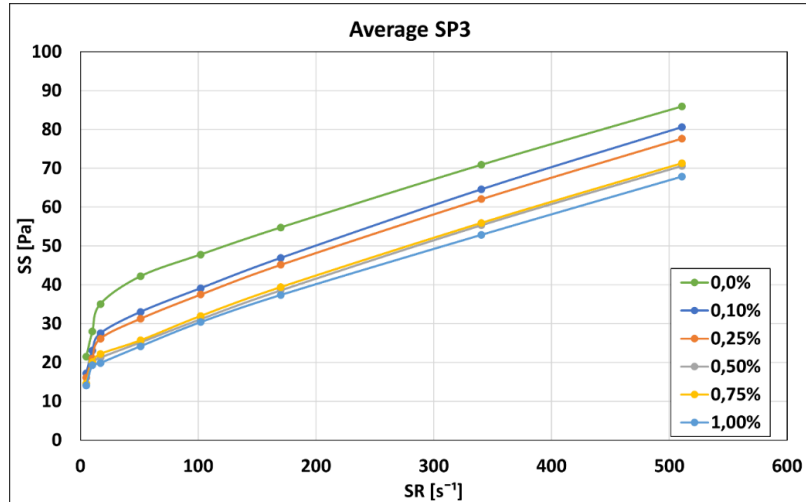


Figure 17: Average shear stress from SP3

Following the increase concentration of SP3, observations revealed that: The SS would experience an almost similar decrease in the two lowest concentrations compared to the neat geopolymer. Increasing the concentration to 0.50%, 0.75% and 1.0% would further the decrease, but would other than that become stable and not cause any noticeable changes to the SS. The yield stress is observed to have the similar behaviour for both two lower concentrations but would show similar characteristics in concentrations of 0.50% and up.

When comparing the results of the maximum vs minimum concentration of SP3 we get the following graph as seen in Figure 18 The graph show the same principle as it have on the previous

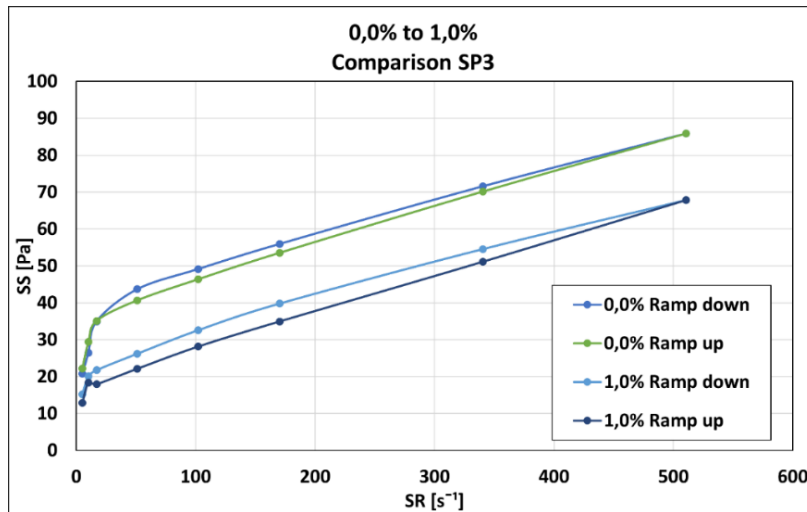


Figure 18: Maximum impact comparison on SP3

two SPs, but is observed to experience a slight deviation on the ramp down on the 1.0% measurement. The observed deviation may be from the two expected theories mentioned on the other two SPs but could also be a deviation caused by an inconsistency while performing the measurement.

Using the data obtained on the previous SPs, one may start to see the expected pattern of a SP. When adding a slam concentration, the SS would experience a slight decrease, yet have a similar trend line through the different SRs. Increasing the concentrations would cause the SS to decrease even further, until the point in where the measurements seem to overlap. For the yield stress, the critical concentration would be observed around 0.50% bwog.

After calculating and plotting the viscosity profile of SP3 seen in Figure 19, one may observe the similar behaviour when compared to two other SPs. A decrease in the initial viscosity is observed from the lower two concentrations, while increasing the concentration to 0.50% and up, show a steady decrease to the point in where it starts to overlap.

When the viscosity measurements start overlapping each other, the conclusion would once again be to estimate this as the potential critical concentration of SP3. Basing the assumption on both the yield stress and viscosity graph seem to point out the most optimum concentration being somewhere around the range of 0.50% bwog.

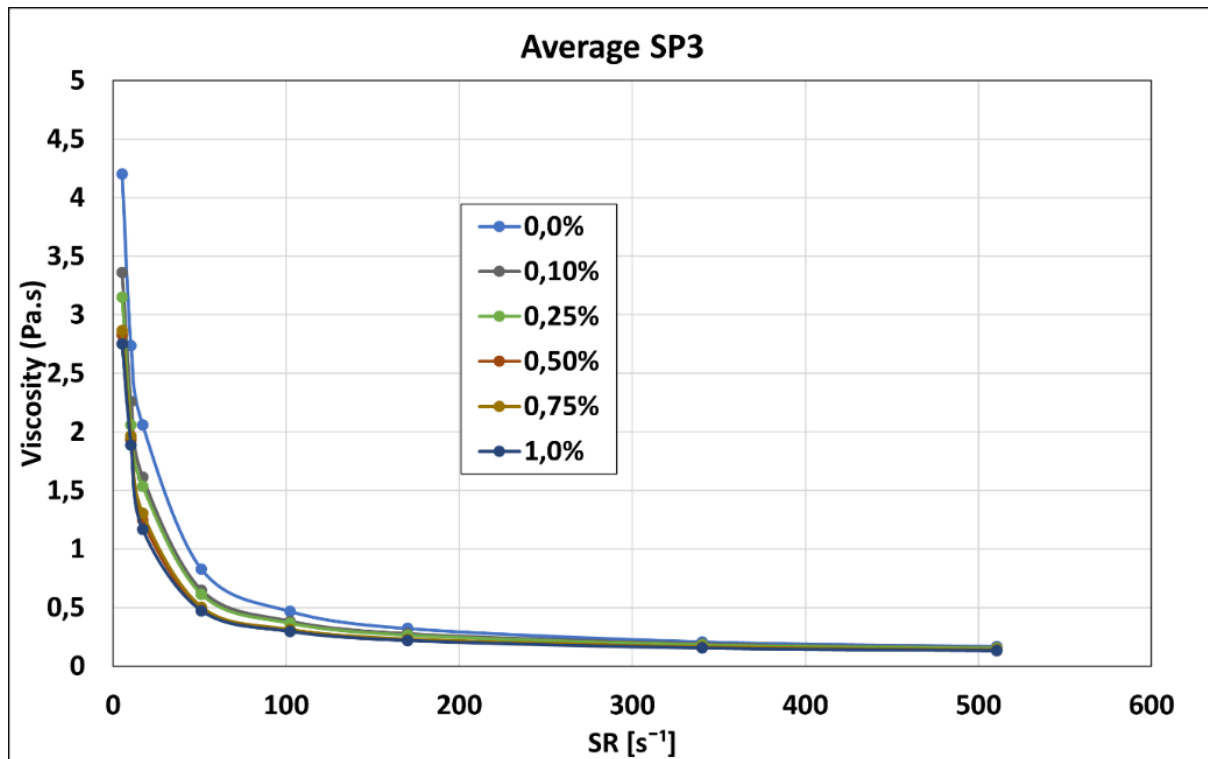


Figure 19: Average viscosity on SP3

4.1.4 Superplasticizer 4

Impact of superplasticizer 4 (SP4) – Continuing onto the next experiment, similar measurements have been conducted for SP4 in similar standard to as the other SPs and plotted in the graph as seen in Figure 20.

Comparing the data and plot of SP4 with the other 3 SPs, show a more noticeable difference occurring. It is observed that SP4 no longer

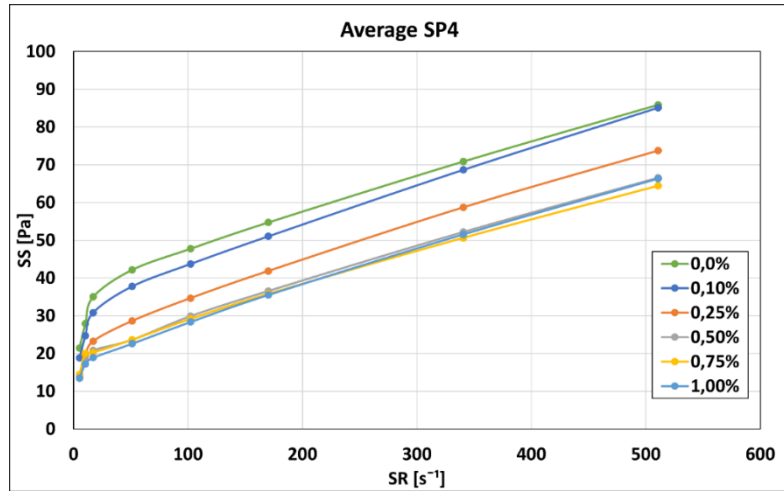


Figure 20: Average shear stress from SP4

cause as much of a decrease in the initial concentrations of 0.10% bwog, where also SS are observed to close in on the original value of the neat value to the geopolymers. Increasing the concentration to 0.25% bwog is observed to cause a larger drop in the initial SS. The behaviour

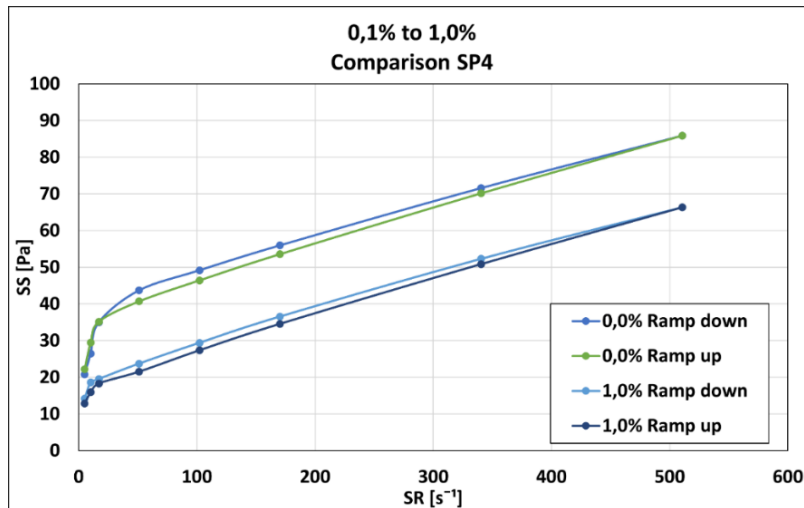


Figure 21: Maximum impact comparison on SP4

occurring in the lower concentrations when comparing with the other SPs, does seem a bit strange the way it is presented, thus a possible concluding could be because of a deviation occurring while performing the measurement. When comparing the minimum and maximum concentration seen in Figure 21, we observe the same characteristics as the other SPs. SP4 is also observed to behave in similar fashion with the other SPs, including the odd behaviour from where the ramp down values is higher than the values of ramp up.

Following the observations on the viscosity profile of SP4 seen in Figure 22, it is observed that: Similar characteristics are followed in the lower concentrations of SP4 as compared to the previously conducted viscosity observations. The initial viscosity experiences a slight drop following concentrations ranging from 0.25% and up. Further increasing the concentration will cause the viscosity measurements to overlap, thus making it possible to come up with a conclusion to where the critical concentration of SP4 may be. Comparing both the yield stress and viscosity of SP4, one may point out a possible optimum concentration to be somewhere around 0.50% bwog.

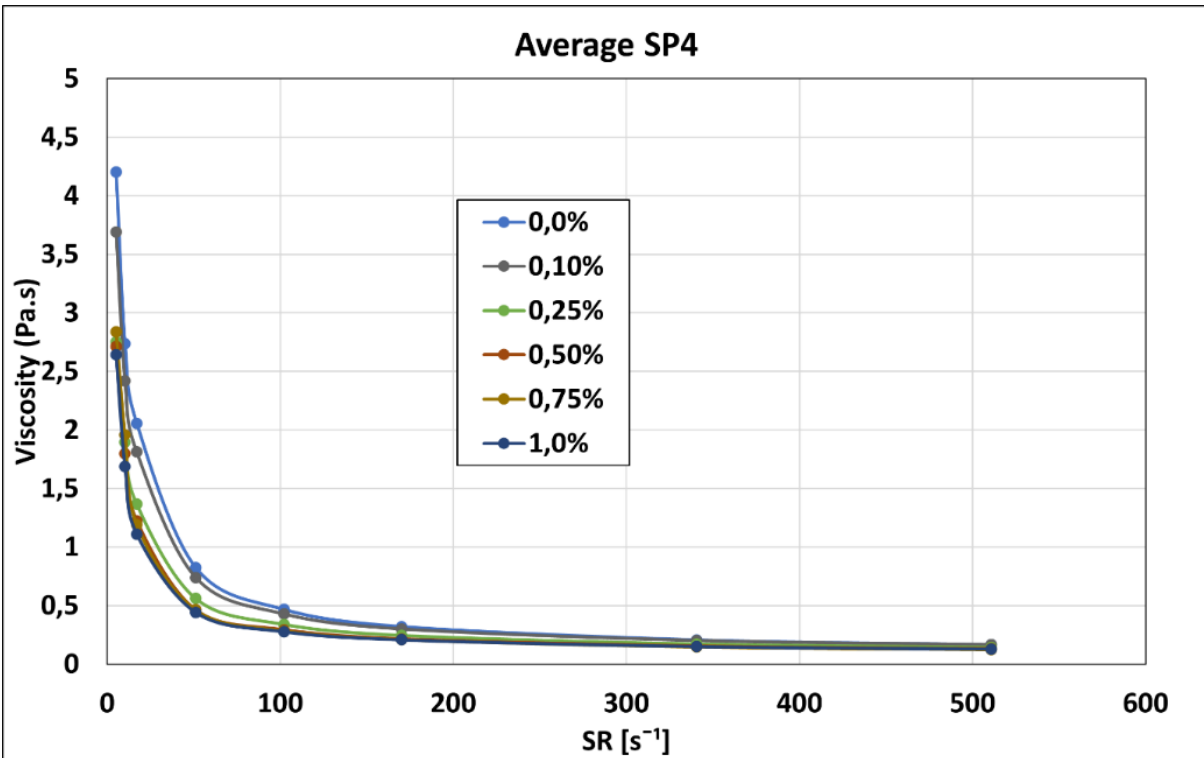


Figure 22: Average viscosity on SP4

4.1.5 Superplasticizer 5

Impact of superplasticizer 5 (SP5) – Wrapping up the experimental phase on viscosity and yield stress, provide the following data and observations occurring on a geopolymer with the use of SP5. A quick glance on the graph, seen in Figure 23, reveal a totally different behaviour on the SS of the geopolymer when introduced to SP5. Starting with the observation on lower

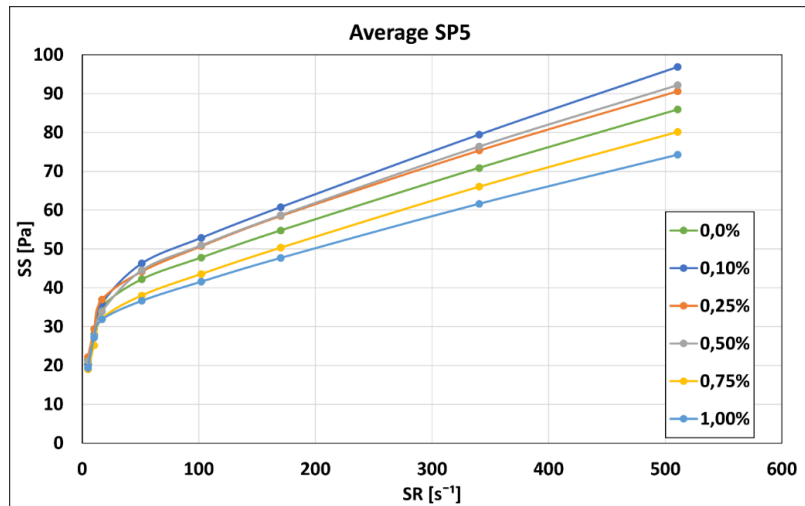


Figure 23: Average shear stress from SP5

concentrations, introducing 0.10% bwog of SP5 to the geopolymer seem to cause an increase in the initial SS of the geopolymer. The increase in SS is observed to increase more at an elevated SR rather than in the lower SRs. Similar behaviour, but with a smaller effect is observed to occur when further increasing the concentration from 0.10%, to both 0.25% and 0.50%. Continuing to increase the concentration of SP5 to 0.75% bwog have, despite the lower concentrations, been observed to have a decreasing effect on the initial SS. Following up with 1.0% concentration is observed to further the decrease SS on the geopolymer.

The behaviour of SP5 may be explained through the fact that SP5 is based on a single unit approach of the NS polymer without containing the formaldehyde group. Introducing the geopolymer to a lower concentration of SP5 may have been too low to provide the system with enough polymers to cause a reaction. Adding concentrations of SP5 ranging above 0.50% have been observed to cause a decrease in the initial SS. Considering the behaviour observed on the effect of SP5, one may conclude that the amount of SP5 added was too low for the polymer to cause a reaction. Even though adding SP5 in higher concentrations, decreasing the initial SS, was not observed to provide a sufficient reaction, thus pointing out that the possible critical concentration of SP5 may be at concentrations existing above the specified range. The result may seem interesting but may also mean that SP5 does not react well with the geopolymer mixture of the slurry.

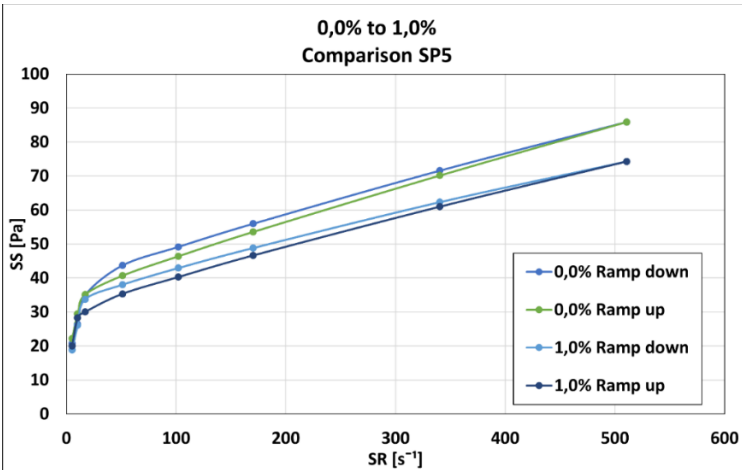


Figure 24: Maximum impact comparison on SP5

When comparing the minimum and maximum concentration for SP5 seen in Figure 24, we observe that the Ramp up and ramp down are still showing the odd behaviour together with the other SPs. This may point to a conclusion that the SPs do not cause any ongoing reaction, and that this behaviour could come from the slurry mixture itself.

Considering the viscosity of SP5, seen in Figure 25, observations pointed out the expected behaviour on the viscosity based on the different concentrations. The initial viscosity is higher for the 3 lowest concentrations, while the trend is observed to decrease as the concentration increases. Even though the rheology measurements from SP5 did not provide any good results on the geopolymer slurry, one could come with the conclusion that the optimum concentration of SP5 would be in the range of 1.0% (and above). The effect of SP5 would require further research to be able to come up with a better conclusion for this specific type of SP. Summarizing the observations, one could conclude that the size of the polymer chain could be of greater importance to a SP rather than the functional group.

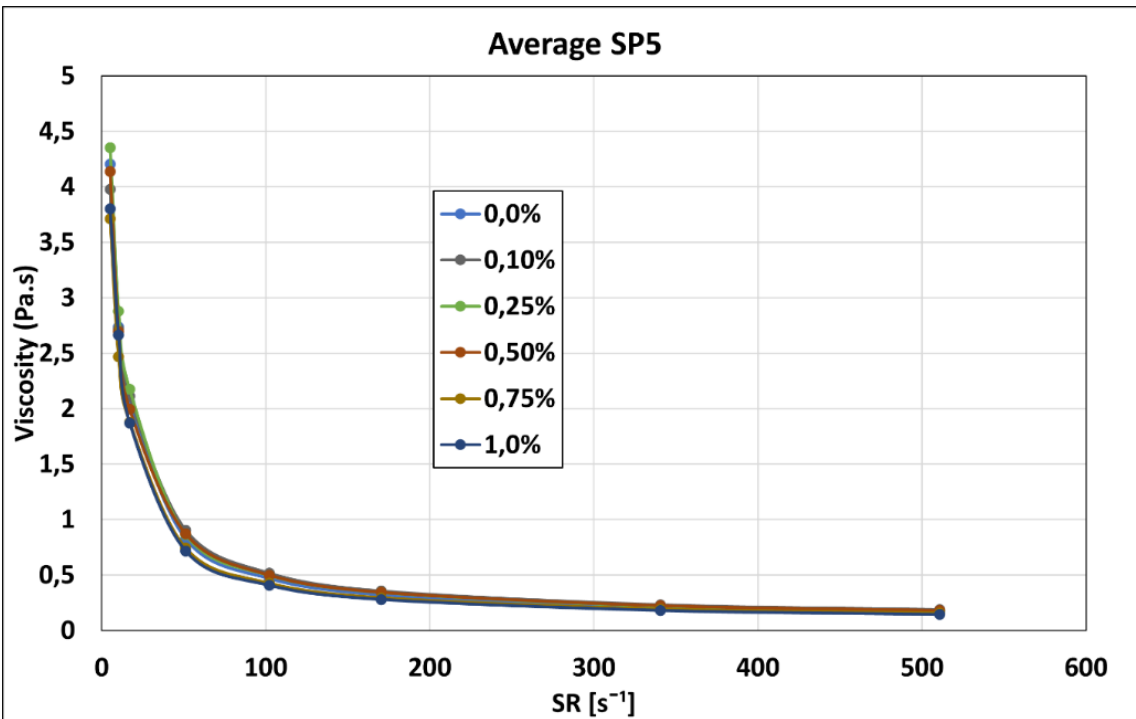


Figure 25: Average viscosity on SP5

4.1.6 Comparison of performance of the superplasticizers.

A brief showcase of the summary of the rheology measurements over the 5 different SPs compared to the neat geopolymer. Starting the comparison seen in Figure 26 reveals the 5 different trendlines from the SPs. In the low concentration of 0.10% bwog. One may conclude that the best rheology properties are observed in SP1, where SP5 on the other hand performed worst. At such low concentration one may also point out that the SPs barely influence the yield stress of the slurry.

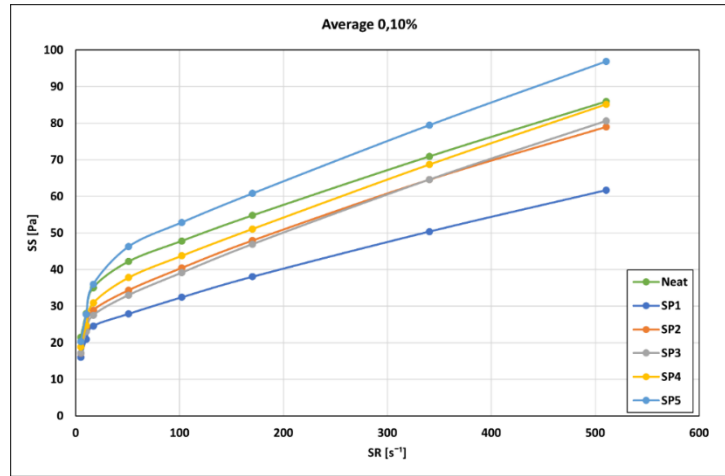


Figure 26: Average shear stress in 0.10% concentration of superplasticizer

By increasing the concentration to 0.25% bwog observations show similar yet different trendlines as seen in Figure 27. Through observations one may start to notice a smaller difference on SP1 – SP4 as they slowly seem to start having a decreased effect on their yield strength. SP5 in opposite to the rest of the SPs, remain at the yield stress like the one of the neat geopolymer, though the SS seems to increase above the neat geopolymer at higher SRs. One may conclude on the 0.25% averages that the best rheological properties are obtained from SP1 while the worst continue to be SP5.

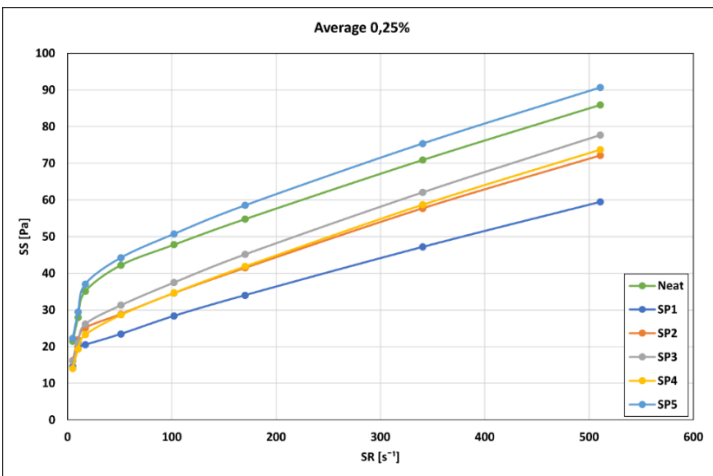


Figure 27: Average shear stress in 0.25% concentration of superplasticizer

Continuing further to the averages in 0.50% concentration bwog, the graph seen is Figure 28 is created. One may observe the gap being formed in between the different SPs. It is observed that SP1 – SP4 affect the initial SS resulting in a as well as a drop in the initial yield stress. SP5 is observed to still affect the geopolymer resulting in an increased SS, though having the same yield stress. when compared to the neat recipe.

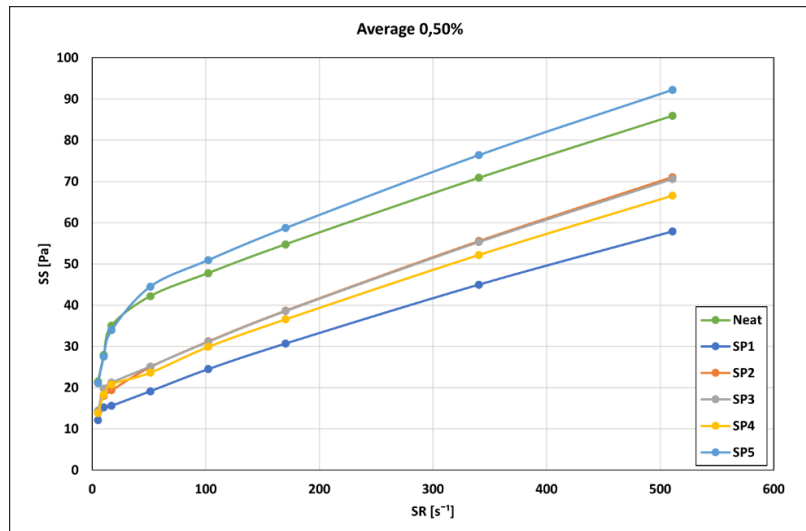


Figure 28: Average shear stress in 0.50% concentration of superplasticizer

One may conclude on the 0.50% averages that the best rheological properties are still obtained from SP1 while the worst continue to be SP5.

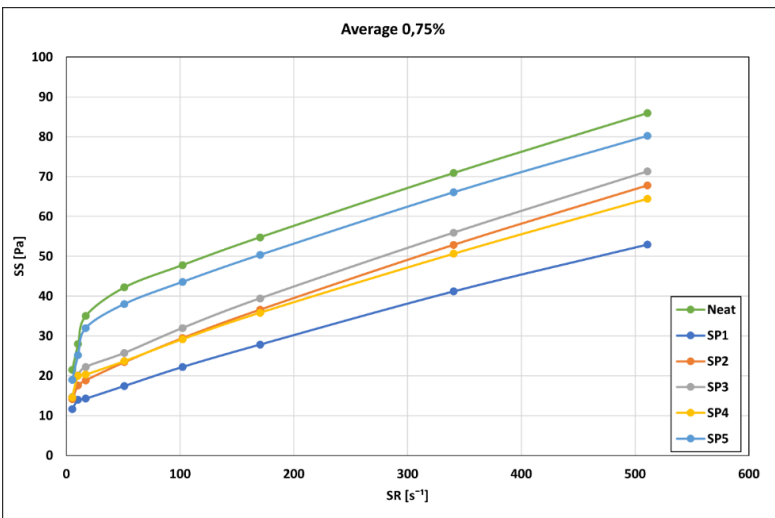


Figure 29: Average shear stress in 0.75% concentration of superplasticizer

Continuing further to the averages in 0.75% concentration bwog, the graph seen is Figure 29 is created. Observations may point out the difference occurring throughout every SP, as the results are now all below the initial SS of the geopolymer. One may therefore come up with another conclusion that through the 0.75% averages, the best rheological properties are obtained from SP1 while the worst continue to be SP5.

The final concentration of 1.0% bwog, seen in Figure 30, reveal the average results for the 5 different SPs. Observing what the graph is showing, may help understanding what the different SPs have in common, but also make the appear different to one another. Pointing out the best SP is observed to be the same as in all the other averages, SP1. SP1 have is proved to be the best match in term of rheology properties and viscosity profiles for this specific

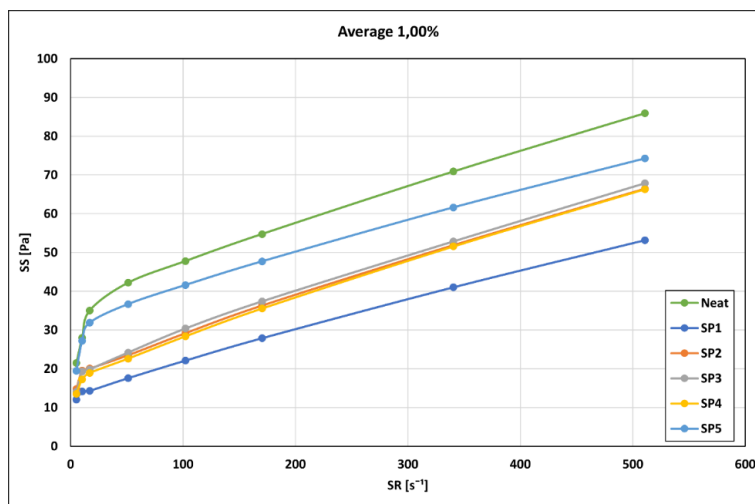


Figure 30: Average shear stress in 1.0% concentration of superplasticizer

geopolymer design. Not surprising, SP5 have been observed to be the least effective SP among the 5, thus being condemned as the worst match for this geopolymer design.

4.1.7 pH measurements

In advance of the viscosity experiments, the different SPs had been mixed with a portion of distilled water at a ratio of 3 g SP and 4 mL of distilled water. The reason for measuring the SPs outside of the geopolymer, is to observe what the different pH values are for each specific SP, as well as to address the expected pH value in which the SPs would become reactive enough to affect the geopolymer. Following the mixing procedure, every sample were measured individually, and at two separate occasions. Once after the initial mixing of the slurry and once after the 20 minutes conditioning. The reason for measuring twice were to observe and potentially filter a parameter out if the geopolymer slurry changed its initial pH. Tests previously done by the geopolymer team at UiS have observed and calculated the time it takes for the geopolymer to set. In the researched geopolymer design, setting time was observed to happen at around 42 minutes after the initial mixing. In conclusion, the pH level did not change in neither the initial mixing of the slurry, nor after the 20-minute conditioning. The pH measurements were all observed to stay in the range of 14 ± 0.2 on every measurement done over the total amount of samples.

4.1.8 Zeta potential measurements

Following the use of the Zetasizer nano machine, several parameters had to be set in advance of running the test. The parameters were to help correct for potential error margins while conducting the tests. Some of the parameters involved specifying the refractive index of the dominant component in the geopolymer, as well as defining the range and specifications of each run, per sample. The refraction value was set to correct for the dominant compound as well as defining the measures to conduct 3 measurements over the total span of 100 runs. Specifying 100 runs does not necessarily mean that each measurement may go through all 100 runs but will continue from the first run to a minimum of 10 before checking for deviations on the readings. If

the 10 first readings were observed to be within the specified margin of ± 1.5 mV, the measurement would continue to the next one, until a total of 3 zeta potential values were obtained. Following this procedure for the zeta potential resulted in a range of different values on each of the SPs. Values from the zeta potential measurements were observed to range from -29 to -42 mV. The reason for why the values range in the electronegative spectre, is because of the dominant components in the geopolymer. As for example different silicates which are all negatively charged molecules.

4.1.9 UCS measurements

As briefly mentioned in chapter 3 under, each sample were cured for 14 days each at room temperature. As this research is based more towards the rheology aspect of the geopolymer, these values may serve only as additional information to help see if the difference on the impact of rheology have any major effect on the compressive strength on the geopolymer. Each sample were crushed following a pre-set 30kN/minute API TR10TR7,2017 setup where the values obtained have been plotted in the graph below see Figure 31. What could be interesting to observe during a UCS test, are high compressive strength linked up with a low viscosity profile. Comparing the compressive strength results with the measurements done over the rheology of the could help aid the progress of what may be implemented in future studies and research. The UCS machine operates in kN, and for a better understanding of the forces in play, one may choose to present the graph in a more familiar terms, such as through pressure measured in Pascal (Pa), or Mega Pascal (MPa). Each SP has been colour coded to the same preference as for their rheology counterpart, to make it easier to compare the results.

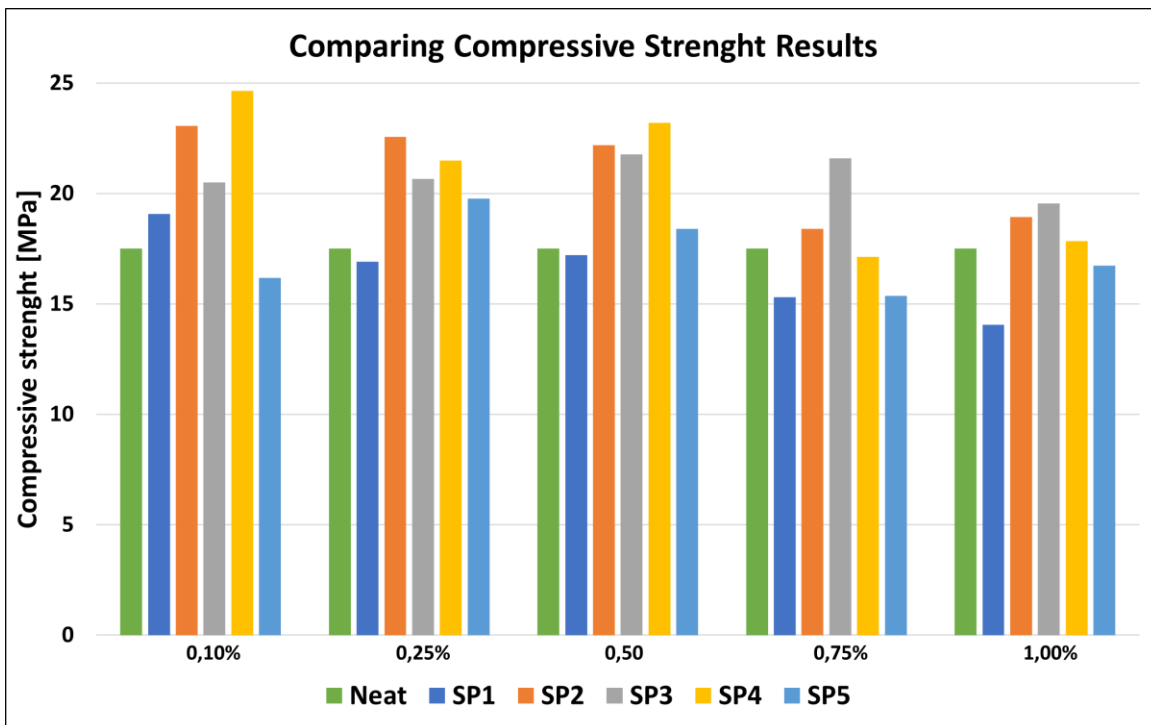


Figure 31: Uniaxial compressive strength with different % concentration compared with the neat recipe after 14 days.

Looking into the different values obtained through the UCS tests, provide a lot of different results. Every concentration has been compared to with the neat recipe illustrated as the green bar, to make it easier to see the overall impact compared to the reference line.

The expected compressive strength of the neat recipe for the geopolymer is supposedly around 18 MPa after the span of 14 days curing time. When comparing the 0.10% concentration bwog with the neat recipe, one may notice that SP4 is giving off the highest compressive strength readings for that specific concentration. As for the opposite, the lowest compressive strength is observed to come from SP5.

Looking into 0.25% concentration, observations may point out a small, overall decrease in the maximum compressive strength. Even SP5 have been observed to have gained some extra strength in this concentration. Each of the SPs are observed to have similar compressive strength value beside SP1 which is observed to have a decrease in its compressive strength.

0.50% concentration continue to provide higher compressive strength results for SP2 – SP4, while SP1 continue having a decrease in its compressive strength compared to the neat recipe.

At 0.75% one may notice the drop in total maximum values of each of the different SP as they all are observed to have dropped. The effect of SPs at 0.75% may therefore cause a decrease to the overall compressive strength of the geopolymer.

Lastly, observations could point out that the 1.0% concentration bwog reveal the poorest results in compressive strength on the geopolymer over all the SPs. The strength is observed to have been compromised and may no longer provide the support compared to the neat geopolymer. A noticeable change in strength, worth pointing out is on the measurements over SP1 which is observed to have the lowest strength reading out of all the concentrations and measurements done.

Further studies on different admixtures on geopolymer are required to help understand and correlate a broader and better understanding between the rheological and mechanical properties of the geopolymer. In conclusion, following the results represented seen in FIGURE 31. one may say that SP2 and SP4 is observed to improve the compressive strength of the geopolymer when the dosage of SP is between 0.10 – 0.50% bwog.

4.2 Optimum concentration of SP using zeta potential

Referring to the detailed description of electrostatic forces in chapter 2, regarding the theory of zeta potential. The focus in this section will be on trying to implement the concept of zeta potential to the geopolymer. The zeta potential will be introduced following a new methodology is presented using the different graphs in the following section. The graphs are based on the rheological properties obtained from the geopolymer slurries as well as the zeta potential averages from each sample. By implementing a new methodology and method for how to analyze the effect of admixtures in early hydration of geopolymers, future research may benefit from the idea.

Looking into where the most effective area of the rheological properties and viscosity took place, one may shift the focus on what effects are occurring during the time of 17 s^{-1} . Observations may conclude to this being the most affected area for each SP on the geopolymer. At this rate, changes in the viscosity were more noticeable. The 10 second- and 10-minute gel strength would also be measured accordingly, this to consider the viscosity effect, yield stress as well as the ability for the geopolymer slurry to develop a gel structure over time.

The obtained data from every experiment have been plotted into 5 different graphs depending on the SP. The purpose for presenting the data in such a way is to figure out a possibility to discuss the measurements in both terms of maximum and minimum concentration, as well to observe the different reactions occurring in the reaction of the geopolymer. Each graph illustrates every aspect of a sample rheology together with the structure of developing parameters as both the concentration and zeta potential increases.

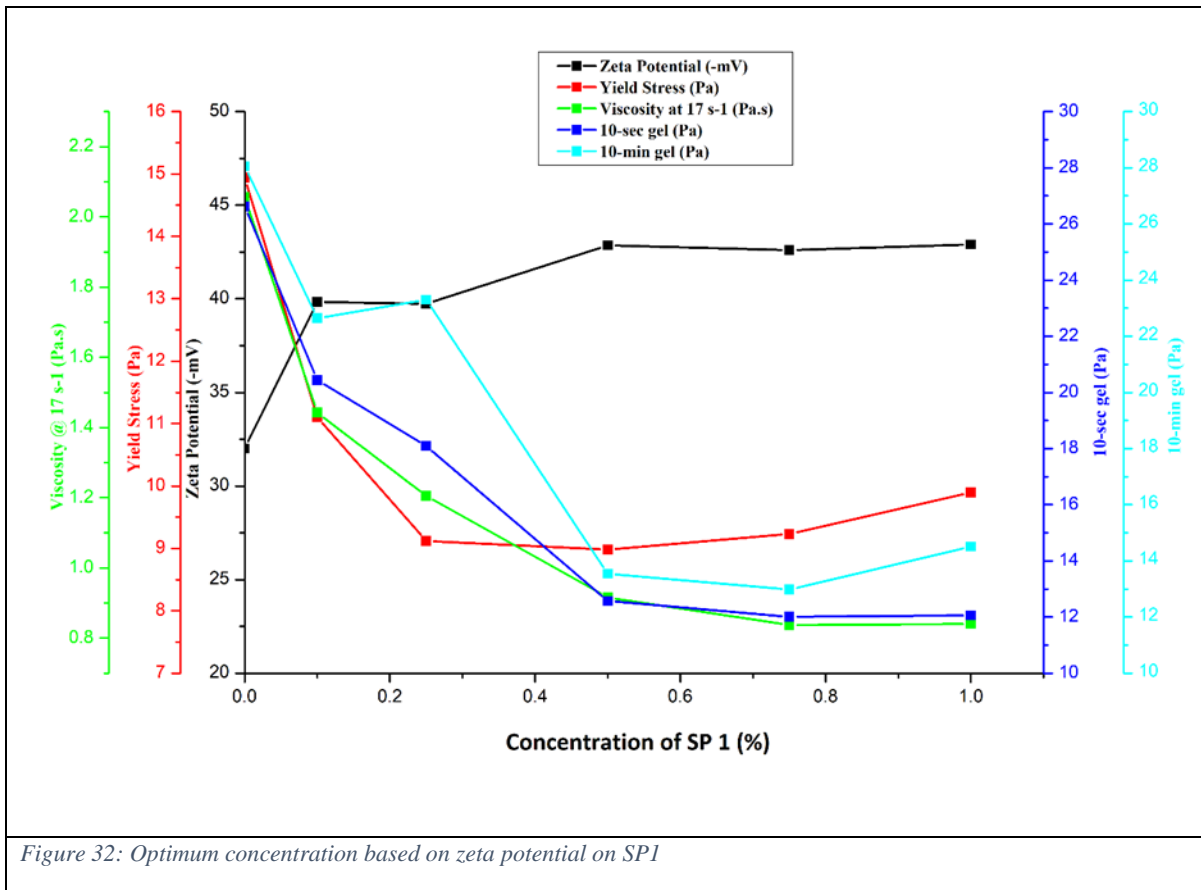
4.2.1 Optimum concentration of SP1

Starting off with the results obtained from measuring over SP1. seen in Figure 32 one may point out:

- The initial zeta potential of the geopolymer is observed to be of about -32 mV, increasing the concentration seem to make enhance the zeta potential up to about the mid -40 mV range in the lower concentrations. Further increasing the concentration is observed to enhance zeta potential to reach a stable value of about -43 mV for the concentration of 0.50% up until 1.0%.
- The yield stress is observed to decrease from the initial neat geopolymer, starting off at 15 Pa for then to decrease to about 9 Pa after adding 0.25% of SP1. With an increase in the concentration of SP1, the yield stress is observed to slowly have an increase in magnitude. However, keeping an eye on the range for yield stress, only reveal the slow increase to experience a 1 Pa increase.
- The viscosity values plotted are all using the values from the different concentration readings at 17 s^{-1} as this gave the impression to have the largest outcome based on the viscosity graphs discussed for SP1 earlier. The graph is observed to have a decreasing trend on the viscosity as the concentration of SP1 increases, which is expected based on the viscosity profile. The viscosity decreases until it becomes stable, at around 0.50% concentration bwog. Further increasing the SP up until 1.0% does not seem to have any major impact on the viscosity
- The gel strength both at 10 second- and 10-minute readings are observed to provide similar results, beside a few higher readings done on the 10-minute gel strength on 0.25% and 1.0% concentration respectively. Overall, the gel strength is observed to decrease from the initial magnitude of the neat geopolymer until about 0.50% concentration. From 0.50% and up, the gel structure is observed to have a stable relation of about 12 – 13 Pa. The effect of SP 1 is observed to cause a cut the ability of developing a strong gel structure to about half of the

initial magnitude. The decrease in the ability to create a gel structure mean that the geopolymer slurry will not be able to develop a gel structure as quickly and efficient as it would do in the occurrence of a stand-still than compared to the neat values of the geopolymer.

- Considering the conclusions previously mentioned, regarding the effects of SP1 on the rheological properties of a geopolymer, one may already have an estimated assumption of the optimum concentration. However, using the zeta potential and theory of intermolecular forces, one may come up with a stronger conclusion. As for the use of SP1, in the range of 0.50% concentration bwog, it is observed in addition to the zeta potential, to result in the most stable reactions, thus concluding that the optimum concentration of SP1 should be around 0.50%

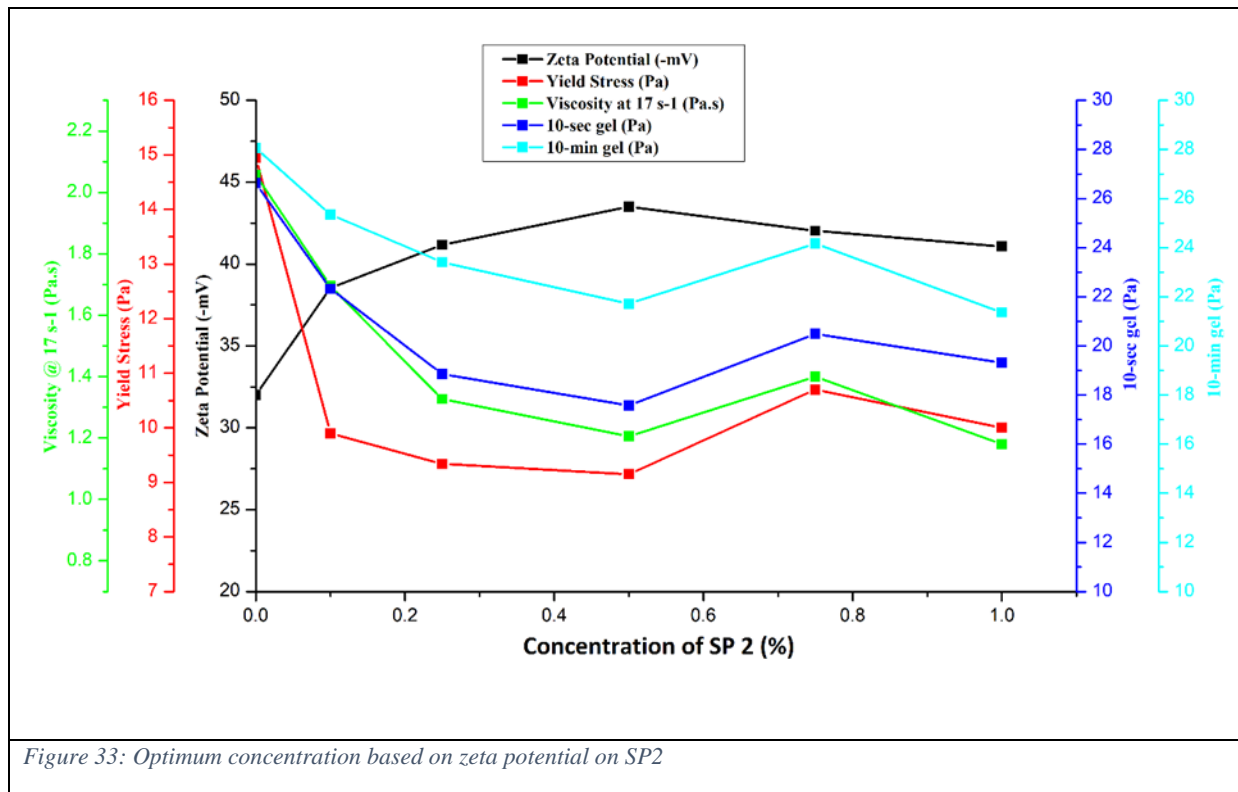


4.2.2 Optimum concentration of SP2

Continuing with the results obtained from measuring SP2, seen in Figure 33 one may point out:

- Observations on the zetapotential across the different concentration reveal a steady increase from the initial geopolymer up until about 0.50% concentration. The zeta potential at 0.50% was reaching the peak value of -43,5 mV which is a very good magnitude considering the dispersion of particles. Increasing the concentration is observed to cause a decrease in the zeta potential.

- The yield stress is observed to go through a quick decline from the initial yield stress of the neat geopolymer when introduced to SP2. Observing the yield stress in higher concentrations reveal a stable relation beside a slight increase occurring at around 0.75% followed by a smaller decrease at 1.0%.
- The viscosity following the trendline of yield stress at each concentration including the slight increase occurring at 0.75% before continuing in a downward trend again.
- The gel structure on the geopolymer slurry is observed to follow the same trend observed in both yield stress and viscosity through the different concentrations.
- Observing the increase in the zeta potential from the use of SP2, reveal a steady increase reaching the peak magnitude at around 0.50% concentration. Together with the other rheology properties reaching a noticeable stable relation at this concentration may point to the conclusion that 0.50% could be the optimum concentration of SP2 when considering the use of zeta potential to predicts the stable relation of the properties. The different behaviour occurring at 0.75% concentration could be from an internal reaction at this specific concentration, or a possible deviation to how the measurement had been conducted in the initial mixing of the geopolymer slurry.



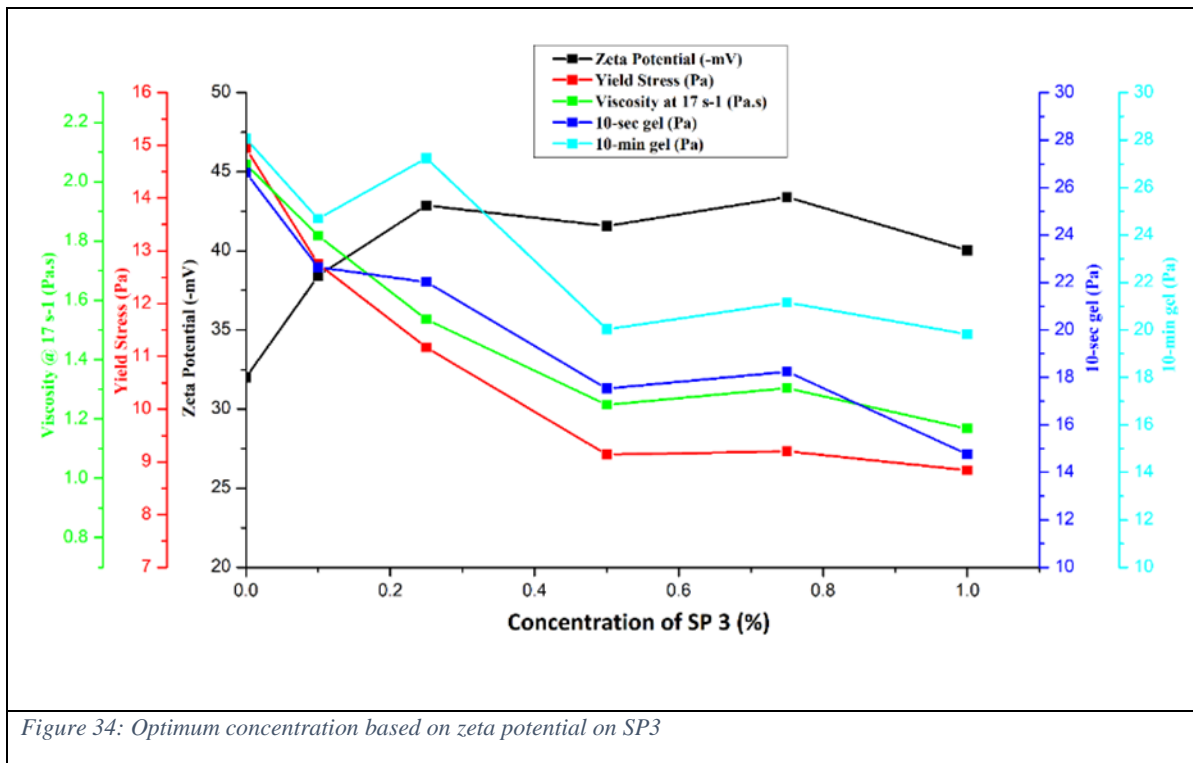
4.2.3 Optimum concentration of SP3

Continuing with the results obtained from measuring SP3, seen in Figure 34 one may point out:

- The zeta potential from the use of SP3 is observed to experience deviation in how one would expect the behaviour to be presented. At first the zeta potential is observed to

increase for the lower concentrations up to 0.25%, followed by a smaller decrease for the 0.50% concentration. However, the same behaviour is observed for both 0.75 and 1.0% as well, where the zeta potential is observed to again increase, followed by an immediate decrease.

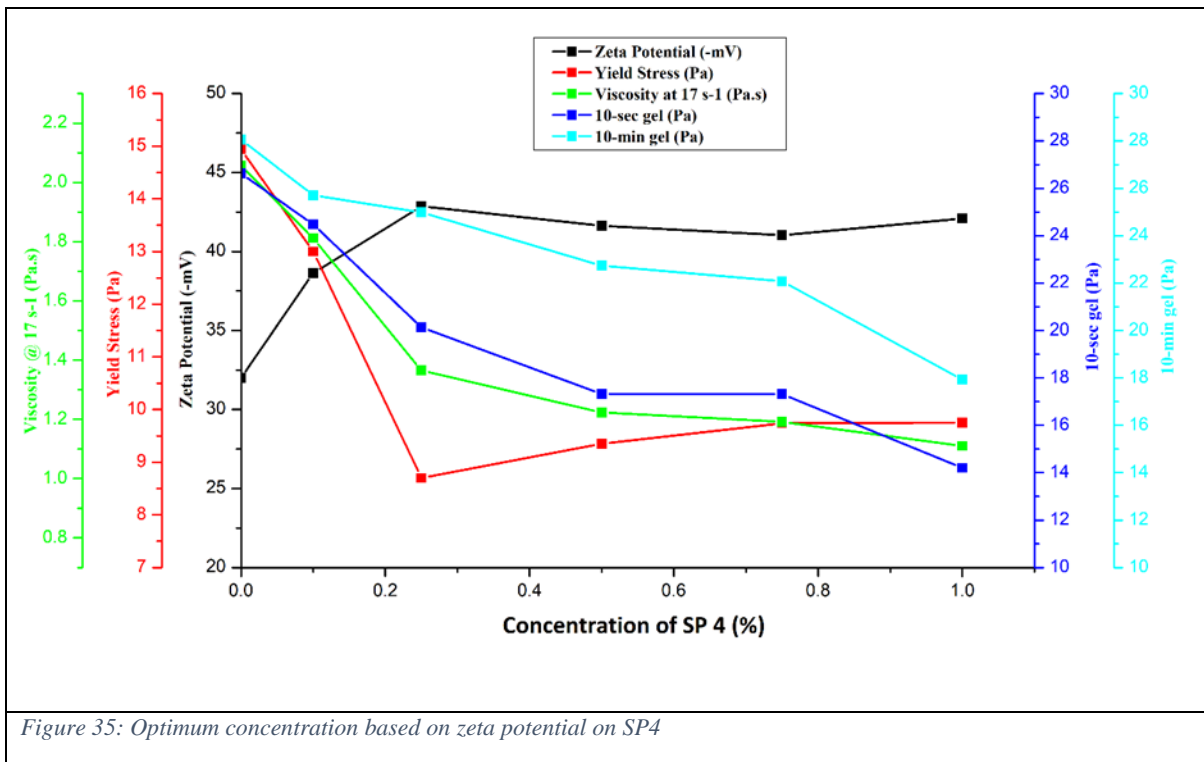
- The yield stress is observed to follow a consistent decrease following the increase in concentration. The drop from the initial yield stress of the neat geopolymer is observed to happen until about 0.50% concentration for then to become stable for higher concentrations.
- The viscosity is observed to have the same behaviour as the yield stress, with a steady decline and a stable relation occurring at around 0.50% concentration
- The gel strengths are observed to experience a varying range of magnitude depending on the concentration of SP3. The 10-minute gel strength is observed to have a slight increase at 0.25% concentration, while the 10-second gel strength is experiencing a slight decrease at 1.0% concentration.
- The zeta potential on the effect of SP3 is observed to reach a stable relationship between 0.25 and 0.75% concentration. One may argue to what would define the most optimum concentration of SP3, but worth pointing out is the stable relationship observed at both 0.50 and 0.75% concentration for the rest of the rheological properties. One conclusion to why the zeta potential is observed to decrease at 0.50% concentration may be due to a deviation happening while conducting the initial mixing procedure, as the expected value should range higher than what was measured.



4.2.4 Optimum concentration of SP4

Continuing with the results obtained from measuring SP4, seen in Figure 35 one may point out:

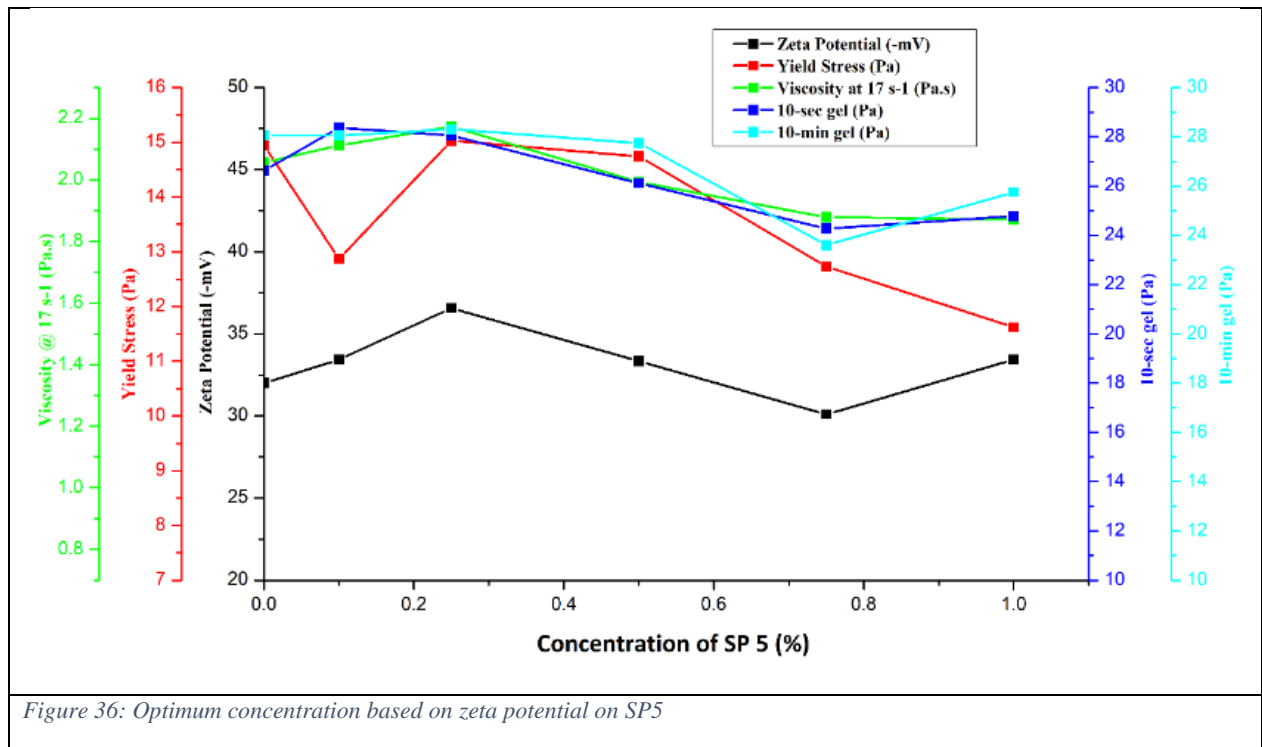
- The zeta potential is observed to quickly increase from the initial geopolymer and become stable at around 0.25% concentration.
- The yield stress is observed to experiences a larger drop from the initial yield stress to about 0.25% concentration. A further Increase in the concentration is observed to slowly effect yield stress causing it to increase and the concentration increases.
- The viscosity is observed decreasing from the initial magnitude at around 0.25% concentration for then to be observed becoming stable at 0.50%.
- The gel strength is observed to have a minor decrease throughout the increase of concentration, up to the point of 1.0%. At 1.0% the gel structure is observed to have a slight decrease.
- Even though the zeta potential became stable at the concentrations of 0.25%, the other rheology properties did not seem to follow the same behaviour. It was not until about 0.50% concentration was added that the rheological properties were observed to give stable readings. Following this statement, one may come up with the conclusion that the expected optimum concentration for SP4 is somewhere in between the 0.25 and 0.50% concentration.



4.2.5 Optimum concentration of SP5

Finishing the experimental process on SP5 have given the following graph see Figure 36:

- The zeta potential is observed to have a drastic difference compared to the other SPs and does not show any resemblance. The zeta potential observed to experience a minimal effect of the different concentrations but is observed to have the peak magnitude occurring at 0.25% and the lowest magnitude at 0.75%. Other than the mentioned deviation, the zeta potential does not observe to have a stable reaction in the range of these concentrations.
- The yield stress is observed to have a relatively high magnitude in the smaller concentrations of the SP whereas it is observed to gradually decrease in when introduced to a higher concentration of SP5. The yield stress is also observed to experience an initial drop on the yield stress, but this is not to be expected and is most likely a product of a deviation occurring in the initial mixing procedure.
- The different concentration of SP5 is not observed to have any significant effect on the viscosity of the geopolymer slurry. The viscosity is only observed to show smaller signs of effect in the higher concentrations of SP5.
- Observations on the gel structure also conclude to what is mentioned for the other properties, no significant changes to the rheological properties beside smaller deviations most likely occurring as an error margin.
- Observations done on the different concentrations of SP5 on the geopolymer does not seem to cause any major effect on the rheological properties of the geopolymer, nor does the zeta potential show an appealing magnitude. The decrease in magnitude of zeta potential could initially result in a poor electrostatic repulsion followed by less effective dispersion of particles. With a lower electronegative force exerted between the particles, sedimentation could occur, thus resulting in poor performance when introduced to the geopolymer. The conclusion may point out that SP5 does not really fit to this specific geopolymer recipe, or that the concentration of SP5 could have proven to be too low to be able to cause an effect at all.



5. Conclusion

The goal of this research was to analyse and study the different rheological effects a superplasticizer would cause when introduced to a rock-based geopolymer. Based on the results and discussion, it can be concluded that:

- For this specific geopolymer slurry, when zeta potential goes to negative values, the viscosity and yield stress will be reduced.
- The expected zeta potential should be lower than -42 mV to ensure an optimal electrostatic repulsion force and dispersion of the particles. However, when the zeta potential goes towards higher values, the effect of SPs is minimized or removed.
- Considering the length of the polymer chain and functional group of the SP, size of the polymer chain is observed to be the most critical factor, not only the presence of the functional group.
- Using a SP with too few degrees of polymer-chains could potentially aggravate the rheological properties of the geopolymer.
- The introduction of SPs to a geopolymer may result in particle sedimentation, but can be identified through logging ramp up, ramp down, 10-sec, and 10-min gel strength data.
- Through several comparisons between the 5 SPs have proven that SP1, for this specific geopolymer, have the most suitable chain length, functional group, and salts to provide the optimum performance.
- Using the optimum SP on this specific geopolymer, rheological properties such as the yield stress could experience a total decrease by up to about 39.9% compared to the initial value
- Following the use of SP1 – SP5 in the geopolymer did not significantly deteriorate the mechanical strength of the geopolymers. However, observation on measurements on SP2 and SP4 showed results that through low dosage of the SP up to 0.50% bwog could improve the development of additional strength to the geopolymer.
- It is possible to develop a new methods and methodology for analysing early geopolymer hydration and the optimal dispersion of particles by using the concept of electrostatic repulsion and zeta potential.

6. References

- Aleem, M. A., & Arumairaj, P. (2012). Geopolymer concrete—a review. *International journal of engineering sciences & emerging technologies*, 1(2), 118-122.
- Alvi, M. A. A., Khalifeh, M., & Agonafir, M. B. (2020). Effect of nanoparticles on properties of geopolymers designed for well cementing applications. *Journal of Petroleum Science and Engineering*, 191, 107128. <https://doi.org/https://doi.org/10.1016/j.petrol.2020.107128>
- Aziz, I. H., Abdullah, M. M. A. B., Yong, H. C., Ming, L. Y., Hussin, K., Kadir, A. A., & Azimi, E. A. (2016). Manufacturing of fire resistance geopolymer: A review. MATEC Web of Conferences,
- Barbosa, V. F. F., MacKenzie, K. J. D., & Thaumaturgo, C. (2000). Synthesis and characterisation of materials based on inorganic polymers of alumina and silica: sodium polysialate polymers. *International Journal of Inorganic Materials*, 2(4), 309-317. [https://doi.org/https://doi.org/10.1016/S1466-6049\(00\)00041-6](https://doi.org/https://doi.org/10.1016/S1466-6049(00)00041-6)
- Benhelal, E., Zahedi, G., Shamsaei, E., & Bahadori, A. (2013). Global strategies and potentials to curb CO2 emissions in cement industry. *Journal of Cleaner Production*, 51, 142-161. <https://doi.org/https://doi.org/10.1016/j.jclepro.2012.10.049>
- Bouaissi, A., Li, L.-y., Al Bakri Abdullah, M. M., & Bui, Q.-B. (2019). Mechanical properties and microstructure analysis of FA-GGBS-HMNS based geopolymer concrete. *Construction and Building Materials*, 210, 198-209. <https://doi.org/https://doi.org/10.1016/j.conbuildmat.2019.03.202>
- Chamssine, F., Khalifeh, M., Eid, E., Minde, M. W., & Saasen, A. (2021). Effects of Temperature and Chemical Admixtures on the Properties of Rock-Based Geopolymers Designed for Zonal Isolation and Well Abandonment. International Conference on Offshore Mechanics and Arctic Engineering,
- Coote, M. L. (2012). 3.03 - Radical Reactivity by Computation and Experiment. In K. Matyjaszewski & M. Möller (Eds.), *Polymer Science: A Comprehensive Reference* (pp. 39-58). Elsevier. <https://doi.org/https://doi.org/10.1016/B978-0-444-53349-4.00062-5>
- Daimon, M., & Roy, D. M. (1979). Rheological properties of cement mixes: II. Zeta potential and preliminary viscosity studies. *Cement and Concrete Research*, 9(1), 103-109. [https://doi.org/https://doi.org/10.1016/0008-8846\(79\)90100-5](https://doi.org/https://doi.org/10.1016/0008-8846(79)90100-5)
- Davidovits, J. (1991). Geopolymers: inorganic polymeric new materials. *Journal of Thermal Analysis and calorimetry*, 37(8), 1633-1656.
- Duxson, P., Fernández-Jiménez, A., Provis, J. L., Lukey, G. C., Palomo, A., & van Deventer, J. S. J. (2007). Geopolymer technology: the current state of the art. *Journal of Materials Science*, 42(9), 2917-2933. <https://doi.org/10.1007/s10853-006-0637-z>
- Grahame, D. C. (1951). The role of the cation in the electrical double layer. *Journal of The Electrochemical Society*, 98(9), 343.
- HANZLÍČEK, T., Perna, I., Ertl, Z., & Miller, S. M. Pre-Portland cements and geopolymers.

- Huo, W., Zhang, X., Gan, K., Chen, Y., Xu, J., & Yang, J. (2019). Effect of zeta potential on properties of foamed colloidal suspension. *Journal of the European Ceramic Society*, 39(2), 574-583. <https://doi.org/https://doi.org/10.1016/j.jeurceramsoc.2018.08.035>
- Ingold, C. (1957). Quantitative study of steric hindrance. *Quarterly Reviews, Chemical Society*, 11(1), 1-14.
- Israelachvili, J. N. (2011). *Intermolecular and surface forces*. Academic press.
- Kamali, M., Khalifeh, M., Saasen, A., Delabroy, L., & Godøy, R. (2022). Materials for Well Integrity– Rheological Behavior Study. SPE Norway Subsurface Conference,
- Khalifeh, M., Motra, H. B., Saasen, A., & Hodne, H. (2018b). Potential Utilization for a Rock-Based Geopolymer in Oil Well Cementing. International Conference on Offshore Mechanics and Arctic Engineering,
- Khalifeh, M., Saasen, A., Hodne, H., Godøy, R., & Vrålstad, T. (2018a). Geopolymers as an alternative for oil well cementing applications: A review of advantages and concerns. *Journal of Energy Resources Technology*, 140(9).
- Khalifeh, M., Saasen, A., Vralstad, T., & Hodne, H. (2014). Potential utilization of class C fly ash-based geopolymer in oil well cementing operations. *Cement and Concrete Composites*, 53, 10-17. <https://doi.org/https://doi.org/10.1016/j.cemconcomp.2014.06.014>
- Larsson, M., Hill, A., & Duffy, J. (2012). Suspension stability; why particle size, zeta potential and rheology are important. *Annual transactions of the Nordic rheology society*, 20(2012), 6.
- Lu, Z., Kong, X., Zhang, C., Xing, F., & Zhang, Y. (2017). Effect of colloidal polymers with different surface properties on the rheological property of fresh cement pastes. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 520, 154-165. <https://doi.org/https://doi.org/10.1016/j.colsurfa.2017.01.067>
- Ludwig, H.-M., & Zhang, W. (2015). Research review of cement clinker chemistry. *Cement and Concrete Research*, 78, 24-37. <https://doi.org/https://doi.org/10.1016/j.cemconres.2015.05.018>
- Majidi, B. (2009). Geopolymer technology, from fundamentals to advanced applications: a review. *Materials Technology*, 24(2), 79-87. <https://doi.org/10.1179/175355509X449355>
- Nematollahi, B., & Sanjayan, J. (2014). Effect of different superplasticizers and activator combinations on workability and strength of fly ash based geopolymer. *Materials & Design*, 57, 667-672. <https://doi.org/https://doi.org/10.1016/j.matdes.2014.01.064>
- Nägele, E. (1986). The Zeta-potential of cement: Part II: Effect of pH-value. *Cement and Concrete Research*, 16(6), 853-863.
- Papayianni, I., Tsohos, G., Oikonomou, N., & Mavria, P. (2005). Influence of superplasticizer type and mix design parameters on the performance of them in concrete mixtures. *Cement and Concrete Composites*, 27(2), 217-222. <https://doi.org/https://doi.org/10.1016/j.cemconcomp.2004.02.010>
- Pinter, B., Fievez, T., Bickelhaupt, F. M., Geerlings, P., & De Proft, F. (2012). On the origin of the steric effect. *Physical Chemistry Chemical Physics*, 14(28), 9846-9854.
- Plank, J., & Hirsch, C. (2007). Impact of zeta potential of early cement hydration phases on superplasticizer adsorption. *Cement and Concrete Research*, 37(4), 537-542. <https://doi.org/https://doi.org/10.1016/j.cemconres.2007.01.007>

- Ramachandran, V. S. (1996). *Concrete admixtures handbook: properties, science and technology*. William Andrew.
- Romagnoli, M., Leonelli, C., Kamse, E., & Lassinantti Gualtieri, M. (2012). Rheology of geopolimer by DOE approach. *Construction and Building Materials*, *36*, 251-258.
<https://doi.org/https://doi.org/10.1016/j.conbuildmat.2012.04.122>
- Schmickler, W. (2020). Double layer theory. *Journal of Solid State Electrochemistry*, *24*(9), 2175-2176.
<https://doi.org/10.1007/s10008-020-04597-z>
- Stone, A. (2013). *The theory of intermolecular forces*. oUP oxford.
- Summerbell, D. L., Barlow, C. Y., & Cullen, J. M. (2016). Potential reduction of carbon emissions by performance improvement: A cement industry case study. *Journal of Cleaner Production*, *135*, 1327-1339.
- Usón, A. A., Ferreira, G., López-Sabirón, A. M., Sastresa, E. L., & De Guinoa, A. S. (2012). Characterisation and environmental analysis of sewage sludge as secondary fuel for cement manufacturing. *Chemical Engineering Transactions*, *29*, 457-462.
- Weiner, B. B., Tscharnuter, W. W., & Fairhurst, D. (1993). Zeta potential: a new approach. Canadian Mineral Analysts Meeting,
- Xie, J., Wang, J., Rao, R., Wang, C., & Fang, C. (2019). Effects of combined usage of GGBS and fly ash on workability and mechanical properties of alkali activated geopolimer concrete with recycled aggregate. *Composites Part B: Engineering*, *164*, 179-190.
- Yan-Min, Z. (2019). Study on Naphthalene Sulfonic Acid Formaldehyde Condensate by Ultraviolet Absorption Spectrum. *Journal of Physics: Conference Series*,
- Zhang, C., Kong, X., Yu, J., Jansen, D., Pakusch, J., & Wang, S. (2022). Correlation between the adsorption behavior of colloidal polymer particles and the yield stress of fresh cement pastes. *Cement and Concrete Research*, *152*, 106668.
<https://doi.org/https://doi.org/10.1016/j.cemconres.2021.106668>
- Zhang, X. F., Zhang, S. Y., Hu, Z. Y., Yu, G., Pei, C. H., & Sa, R. N. (2012). Identification of connection units with high GHG emissions for low-carbon product structure design. *Journal of Cleaner Production*, *27*, 118-125. <https://doi.org/https://doi.org/10.1016/j.jclepro.2012.01.011>