

**DEVELOPMENT OF GEOPOLYMER SYSTEMS FOR OIL
AND GAS WELL CEMENTING**

BY

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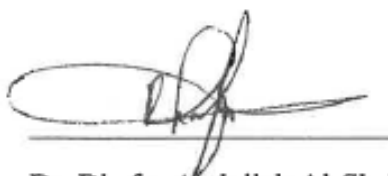
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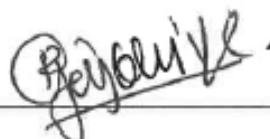


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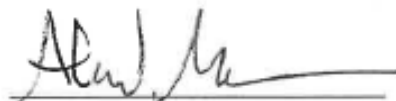
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To my parents, family, and friends

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LIST OF ABBREVIATIONS

API	:	American Petroleum Institute
Bc	:	Bearden units of consistency
BHCT	:	Bottomhole Circulating Temperature
BHST	:	Bottomhole Static Temperature
BWOB	:	By Weight of Binder
BWOC	:	By Weight of Cement
CCS	:	Carbon Capture and Storage
CT	:	Computed Tomography
DV	:	Density Variation
FA	:	Fly Ash
FFA	:	Class F Fly Ash
FTIR	:	Fourier- Transform Infrared Spectroscopy
GGBFS	:	Ground Granulated Blast Furnace Slag
GHG	:	Greenhouse Gas
GS	:	Gel Strength
HPHT	:	High Pressure High Temperature

NMR	:	Nuclear Magnetic Resonance
OBM	:	Oil-Based Mud
OPC	:	Ordinary Portland Cement
P&A	:	Plug and Abandonment
PNS	:	Poly-naphthalene Sulfonate
PR	:	Poisson's Ratio
PSD	:	Particle Size Distribution
PV	:	Plastic Viscosity
SEM	:	Scanning Electron Microscope
TGA	:	Thermogravimetric Analysis
UCS	:	Unconfined Compressive Strength
WBM	:	Water-Based Mud
XRD	:	X-ray Diffraction
XRF	:	X-ray Fluorescence
YM	:	Young's Modulus
YP	:	Yield Point

ABSTRACT

Full Name : [Ahmed Elsayed Ahmed Ibrahim Abdelaal]

Thesis Title : [Development of Geopolymer Systems for Oil and Gas Well Cementing]

Major Field : [Petroleum Engineering]

Date of Degree : [December 2023]

In the petroleum industry, ordinary Portland cement (OPC) is utilized for different applications including primary cementing, plug and abandonment (P&A), loss of circulation control, zonal isolation, and remedial activities. Yet, there are some technical and environmental issues for the usage of OPC in well-cementing. These technical concerns include gas invasion while setting, instability at corrosive environments, thermal instability at high temperatures, hydrostatic pressure loss (unloading) after placement, cement sheath failure while perforation and hydraulic fracturing, and strength retrogression. Additionally, OPC presents some environmental issues such as significant carbon dioxide (CO₂) emissions and massive energy consumption during cement production. These concerns persuaded the researchers to search for alternative materials to overcome the technical challenges and to provide more eco-friendly cement systems.

Geopolymer technology has a wide range of uses, particularly in the building industry. However, full-scale deployment in petroleum industry has yet to be seen. Researchers in the field of cementing are currently examining the characteristics of several geopolymer formulations under wellbore conditions. The reaction of aluminosilicate substances with alkali hydroxides and/or soluble silicates produces Geopolymer, an inorganic polymeric cementitious binder. In comparison to OPC, the geopolymer production process is cleaner,

and the source materials do not consume as much energy. Geopolymer uses some industrial and agro-wastes like fly ash (FA), ground granulated blast furnace slag (GGBFS), silica fume, coconut ash, rice husk that makes geopolymer eco-friendly in terms of low CO₂ manufacturing emissions and using industrial by-products as a source of aluminosilicate materials. Moreover, clays like metakaolin or some rocks like aplite can be used to form certain types of geopolymer. Consequently, geopolymers not only turns waste into treasure but are eco-friendly as well.

A review study was conducted to determine the extent of research on the application of geopolymer in well cementing applications. The study showed that geopolymer systems exhibit superior performance to conventional cement systems. Nevertheless, there are significant questions about their usage that have yet to be resolved, like managing pumpability while optimizing waiting time on setting.

Very few research was conducted to develop high density geopolymer systems using the available weighting agents used with OPC. The goal of this work is to develop high density geopolymer systems using different weighting agents like hematite and Micromax in addition to different source materials, especially industrial waste substances like FA and natural waste materials such as volcanic tephra to be utilized at high pressure and high temperature (HPHT) conditions. To evaluate the usability of high density geopolymers for cementing, this study investigates the properties of high density geopolymers and basic well cement as a reference. These properties include rheological properties, pumpability, fluid loss, mechanical properties, and temperature effects. The effect of different weighting materials and different source materials will be compared. The slurries will be designed and tested at a bottomhole circulating temperature (BHCT) of 150 to 194 °F, a bottomhole

static temperature (BHST) of 200 to 300 °F, and a bottomhole pressure equivalent to 15 to 18 ppg. This work introduced new high-density fly ash-based geopolymer formulations. A new mixture of additives was proposed to prolong the thickening time and address the pumpability issue of these formulations at downhole conditions. Three solutions were introduced to solve the sedimentation issues associated with hematite-based geopolymer cement systems. Moreover, a new moderate weight volcanic tephra-based geopolymer cement system was developed after activating the volcanic by a sodium hydroxide solution. This research promotes the circular carbon economy principles in addition to tackling some technical and environmental challenges of Portland cement.

ملخص الرسالة

الاسم الكامل: أحمد السيد أحمد إبراهيم عبدالعال

عنوان الرسالة: تطوير أنظمة الجيوبوليمر الأسمنتية لآبار النفط والغاز

التخصص: هندسة البترول

تاريخ الدرجة العلمية: ديسمبر ٢٠٢٣

في صناعة البترول، يُستخدم الإسمنت البورتلاندي العادي في تطبيقات متنوعة بما في ذلك عمليات الإسمنت الأساسية، وإغلاق الآبار، والتحكم في فقدان السوائل، وعزل المناطق، وعمليات الإسمنت التصحيحية. ومع ذلك، فإن هناك بعض المشكلات التقنية والبيئية لاستخدام الإسمنت البورتلاندي في إسمنت الآبار. تشمل هذه المشاكل التقنية غزو الغاز أثناء التصلب، وعدم الاستقرار في بعض البيئات القاسية، وعدم الاستقرار الحراري عند درجات حرارة عالية، وفقدان الضغط الهيدروستاتيكي أثناء عملية التصلب، وفشل غلاف الإسمنت أثناء عمليات التخريم والتكسير الهيدروليكي، وتناقص القوة. بالإضافة إلى ذلك، يتسبب الإسمنت البورتلاندي في بعض المشكلات البيئية مثل انبعاث ثاني أكسيد الكربون بشكل كبير واستهلاك كبير للطاقة خلال عملية إنتاج الإسمنت. هذه المشكلات دفعت الباحثين إلى البحث عن مواد بديلة للتغلب على التحديات التقنية وتوفير أنظمة إسمنتية صديقة للبيئة.

تحتل تكنولوجيا الجيوبوليمر مجموعة واسعة من الاستخدامات، خاصة في صناعة البناء. ومع ذلك، لم يتم رؤية النشر على نطاق واسع في صناعة البترول حتى الآن. يقوم الباحثون في مجال الإسمنت حاليًا بفحص خصائص عدة تركيبات جيوبوليمر تحت ظروف الآبار. تفاعل المواد الألومنيوسيليكات مع هيدروكسيدات القلويات و/أو السيليكات القابلة للذوبان ينتج عنه الجيوبوليمر، وهو عازل معدني عضوي. بالمقارنة مع الإسمنت البورتلاندي، تعد عملية إنتاج الجيوبوليمر أكثر نظافة، ولا تستهلك الكثير من الطاقة. يستخدم الجيوبوليمر بعض النفايات الصناعية والزراعية مثل رماد الفحم، وخبث الحديد، ورماد جوز الهند، وقش الأرز، مما يجعله صديق للبيئة من حيث انبعاثات ثاني أكسيد الكربون المنخفضة واستخدام النفايات الصناعية كمصدر لمواد الألومنيوسيليكات. وبالإضافة إلى ذلك، يمكن استخدام الطين مثل الميكاكولين أو بعض الصخور مثل الأبلت لتشكيل أنواع معينة من الجيوبوليمر. وبالتالي، لا يقوم الجيوبوليمر فقط بتحويل النفايات إلى كنز ولكنه صديق للبيئة أيضًا.

تم إجراء دراسة استعراضية لتحديد مدى البحث حول تطبيق الجيوبوليمر في تطبيقات إسمنت الآبار. أظهرت الدراسة أن أنظمة الجيوبوليمر تظهر أداءً متفوقاً على أنظمة الإسمنت التقليدية. ومع ذلك، هناك أسئلة كبيرة حول استخدامها لم تُحل بعد، مثل التحكم في قابلية الضخ. تم إجراء القليل من البحوث لتطوير أنظمة جيوبوليمر عالية الكثافة باستخدام مواد الوزن عالية الكثافة المتاحة المستخدمة مع الإسمنت البورتلاندي. هدف هذه الرسالة هو تطوير أنظمة جيوبوليمر عالية الكثافة باستخدام مواد الوزن عالية الكثافة مثل الهيماتيت والميكروماكس بالإضافة إلى مواد مصدر مختلفة، خاصة مخلفات المواد الصناعية مثل رماد الفحم والمواد الطبيعية مثل الرماد البركاني لاستخدامها في ظروف الضغط العالي والحرارة العالية. لتقييم إمكانية استخدام الجيوبوليمر عالي الكثافة في عملية الإسمنت، تقوم هذه الدراسة بفحص خصائص الجيوبوليمر عالي الكثافة واستخدام الإسمنت البورتلاندي البشري كمرجع. تشمل هذه الخصائص الخصائص الريولوجية، وقابلية الضخ، وفقدان السوائل، والخصائص الميكانيكية، وتأثير درجة الحرارة. سيتم مقارنة تأثير مواد الوزن المختلفة ومصادر المواد المختلفة. سيتم تصميم واختبار الخلطات عند درجة حرارة القاع الدورانية من ١٥٠ إلى ١٩٤ درجة فهرنهايت، ودرجة حرارة القاع الساكنة من ٢٠٠ إلى ٣٠٠ درجة فهرنهايت، وضغط القاع المعادل لـ ١٥ إلى ١٨ رطل لكل جالون.

قدم هذا العمل تركيبات جديدة للجيوبوليمر عالية الكثافة بناءً على رماد الفحم. تم اقتراح خليط جديد من المواد المضافة لتمديد وقت التصلب ومعالجة قضية قابلية الضخ لهذه التركيبات تحت ظروف الآبار. تم تقديم ثلاث حلول لحل مشكلات الترسيب المرتبطة بأنظمة الجيوبوليمر الإسمنتية المبنية على الهيماتيت. علاوة على ذلك، تم تطوير نظام جيوبوليمر إسمنتي جديد بوزن معتدل باستخدام رماد البراكين بعد تنشيط البراكين باستخدام محلول هيدروكسيد الصوديوم. يعزز هذا البحث مبادئ الاقتصاد الدائري للكربون بالإضافة إلى التعامل مع بعض التحديات التقنية والبيئية للإسمنت البورتلاندي.

CHAPTER 1

INTRODUCTION

1.1 Background

Well integrity can be defined as “application of technical, operational, and organizational solutions, to reduce the risk of uncontrolled release of formation fluids throughout the life cycle of a well”. Cement is used for different applications including primary cementing, P&A, loss of circulation control, zonal isolation, and remedial activity. The cement sheath plays an important role in well integrity. Primary cementing is performed to support the casing, prevent gas migration, protect the casing against corrosion, and provide zonal isolation (Ladva et al., 2005; Vrålstad et al., 2019; Xu et al., 2019). Zonal isolation loss may cause serious operational and environmental problems in addition to high remedial cost. In 2010, the Gulf of Mexico witnessed one of the worst blowouts in petroleum industry that resulted in a huge oil spill in which the failure of the cement job was a major reason (Santos and Ribeiro, 2017). Cement slurry design includes various additives that serve different purposes to provide a cement job with a high integrity. A proper laboratory procedure is required to investigate and optimize cement formulations used for different conditions and purposes to enhance the cement properties.

Although OPC is the most extensively used substance for well cementing, it has some technical issues, especially in deep formations, and environmental concerns. The technical issues include gas invasion while setting, instability at corrosive environments, thermal

instability at high temperatures, permeability issues, hydrostatic pressure loss (unloading) after placement, cement failure while perforation and fracturing due to high stiffness and brittleness, and strength reduction at temperatures above 230°F (Khalifeh et al., 2017; Y. Yan et al., 2020). OPC-based systems are susceptible to acid attack (Bakharev et al., 2003; Nasvi et al., 2013a). Another major issue that confronts cement operation is mud contamination. Cement contamination with mud may alter the slurry properties, which in turn negatively impacts the cementing operations. When mud contacts cement slurry, the compressive strength of OPC is significantly affected (Aughenbaugh et al., 2014; EI-Sayed, 1995). Additionally, mud has adverse effects on OPC rheological properties as it increases cement slurry viscosity that affects mud pumpability (Liu et al., 2016).

Moreover, OPC introduces some environmental challenges such as high greenhouse gas (GHG) emissions because OPC production process was considered one of the major sources of GHG. OPC production takes place through a reaction of calcium carbonate (lime) and silicon dioxide to produce calcium silicates and CO₂. Additionally, massive energy consumption is required during cement production. These challenges persuaded the researchers to search for alternative materials to overcome the technical challenges and to provide more eco-friendly cement systems. Lately, different researchers investigated the impact of various substances on cement properties like olive waste, nano clay, cellulose nanofibers, granite sludge, polypropylene fibers, metakaolin, rice husk ash, silicon carbide, iron ore tailings and sugarcane biomass waste. On the other hand, some researchers tried to totally replace the OPC through exploring new materials that can form cementitious binders such as geopolymers.

Geopolymer technology has a wide range of uses, particularly in the building industry (Sambucci et al., 2021). However, full-scale deployment in well cementing has yet to be seen. Researchers in the field of cementing are currently examining the characteristics of several geopolymers under wellbore conditions (Adjei et al., 2022b). The reaction of aluminosilicate substances with alkali hydroxides and/or soluble silicates produces Geopolymer, an inorganic polymeric cementitious binder (Davidovits, 1991a). In comparison to OPC, the geopolymer production process is cleaner, and the source materials do not consume as much energy (Davidovits, 2010; Patel and Shah, 2018; Singh et al., 2018; Worrell et al., 2003). Geopolymer uses some industrial and agro-wastes such as FA, GGBFS, silica fume, coconut ash, rice husk that makes geopolymer eco-friendly in terms of low CO₂ manufacturing emissions and using industrial by-products as a source of aluminosilicate materials. Moreover, clays like metakaolin or some rocks like aplite can be used to form certain types of geopolymer. The geopolymer systems exhibit superior performance to conventional cement systems. Low shrinkage, low permeability, low Young modulus, strength development, stability at high temperature, tolerance to oil-based mud (OBM) contamination, chemical corrosion resistance, and long-term durability make geopolymer systems a viable option to OPC in well cementing applications (Cong and Cheng, 2021; Nasvi et al., 2013a).

For the petroleum industry, HPHT wells drilling represents a new frontier. The exploration and production industry is looking for new resources to meet the rising demand of energy across the world and some of these resources are buried deeper in the earth's crust. Over half of known petroleum reserves in the US are located below 14,000 feet subsea. HPHT conditions will be encountered as we dig further into the strata. Drilling operations in such

HPHT conditions may be extremely difficult. As a result, businesses are obligated to fulfill or exceed a wide range of technical constraints as well as environmental, health, and safety regulations (Shadravan and Amani, 2012).

Special challenges are associated with cementing operation in HPHT wells owing to the physical and chemical changes under high pressure and temperature. These harsh conditions can introduce challenges not only while placement but also after cement setting (Moe et al., 2003; Wray et al., 2009). The challenges facing HPHT cementing can be summarized in Table 1 after (Proehl and Sabins, 2006).

High-density cement slurry with a density of 17 ppg or more should be utilized in deep wells or across high-pressure zones (Magarini et al., 2009). Decreasing water content is the cheapest approach to increase the density (Michaux et al., 1990). However, the American petroleum institute (API) advises a water-to-cement ratio of 44% for primary cementing (API, 2019), producing a 16.5 ppg slurry (Mahmoud et al., 2019). The main drawback of reducing the water content is the challenge of instantaneously attaining sufficient control of fluid loss, good rheological properties, and no settling of the solid particles. Uncontrollable fluid loss leads to slurry bridging. Settling of solid particles causes nonuniform compressive strength and bonding along the length of cement column (Nelson and Guillot, 2006). Therefore, using weighting materials is required to achieve higher density. These substances are commonly utilized in mud to overbalance high formation pressure formations. It is necessary to use weighting agents like hematite, barite, Micromax and ilmenite in cementing operations as deep wells are characterized by high pore pressures (Ahmed et al., 2019).

1.2 Problem Statement

In HPHT wells, the technical challenges such as OPC mechanical properties alteration, strength retrogression, and low thickening times are expected due to the unfavorable impact of temperature on the hydrated cement and slurries (Caritey and Brady, 2013; Costa et al., 2017; Karim et al., 2018). Moreover, OPC introduces some environmental challenges such as high greenhouse gas (GHG) emissions and consumes massive energy during its production. High temperatures are encountered in deep, geothermal, and steam injection wells (Szela, 2018; Alvarez and Han, 2013).

The progress of technology in the cementing operation is critical to increase the possibilities of isolating the targeted zones. Traditional cementing methods would not always be adequate to meet the additional problems posed by the deeper formations drilled. As a result, one method to get over this stumbling block is to develop a specific cement with unique properties for cementing deep wells with high temperature. It is obvious from the literature that some researchers flew in the direction of adding new materials to OPC to enhance its properties and to investigate their effects at elevated pressure and temperature such as rheological and mechanical properties. Other researchers tried to find new alternatives to OPC which can be more eco-friendly and can overcome the technical drawbacks of OPC such as geopolymers. Geopolymer technology is still evolving in the petroleum industry, and it has not seen a full-scale deployment in well cementing. Providing moderate to high density geopolymer cement systems using various weighting materials is rarely investigated in the literature.

Weighting agents can impact the rheology of mud and cement slurry (Basfar et al., 2019; Abdou et al., 2018) (Saasen and Log, 1996). Also, they can impact the fluid loss characteristics and gas migration occurrence due to sedimentation issues (Al-Yami et al., 2009). Weighting agents may adversely impact the slurry homogeneity by creating a cement column with different densities vertically because of segregation. Segregation may result in cement properties change like porosity, permeability, and strength. The high density of the weighting agents may lead to solid particles segregation, particularly when slurries contain large particle size components (Malyshev et al., 2013), and this issue produces varying characteristics vertically along the cement column, particularly density, porosity, and k . As a result, there is a dire need to propose new geopolymer cement systems to replace the OPC at HPHT wells. Additionally, the effects of adding different weighting materials to the geopolymer systems should be properly investigated and compared to the OPC as a reference.

1.3 Research Gap and Objectives

1.3.1 Research Gap

It is clear from the literature of using geopolymer systems in the petroleum industry that rare research work was conducted to develop moderate to high density geopolymer cement systems for HPHT wells. Additionally, the usage of different weighting materials in developing geopolymers was rarely investigated.

1.3.2 Research Objectives

There are three main objectives of this dissertation:

- The first objective is to develop an environmentally friendly and cost-effective moderate to high density geopolymer cement systems to replace OPC in cementing operations in a broad range of temperatures using aluminosilicate materials such as waste materials (fly ash) and natural materials (volcanic tephra).
- The second objective is to study the impact of various weighting agents such as hematite and Micromax on various geopolymer properties under HPHT conditions.
- The third objective is to introduce different solutions for pumpability, and sedimentation issues associated with hematite-based geopolymer cement systems.

1.4 Thesis Organization

The dissertation has 9 chapters. The objective of the dissertation is to develop new geopolymer cement formulations for oil and gas well cementing. Each chapter is an independent experimental study either introducing a new system or addressing an issue associated with these systems. The objectives of the different chapters are presented below.

Chapter 2

This chapter introduces an overview of geopolymer technology. This part summarizes the research results of the previous studies for different well applications highlighting advantages, disadvantages, and limitations of this technology.

Chapter 3

This chapter introduces the first hematite-based Class F fly ash geopolymer formulation for oil and gas well cementing. Unlike the other studies in the literature, this work used 4 M NaOH solution only as an activator that can reduce the overall cost. This work used fly ash (waste material) as aluminosilicate source which reduces the cementing cost, cement carbon emissions, and massive energy consumption and tackles the environmental issue related to fly ash disposal. Various properties of the designed slurry and hardened samples were evaluated using recommended practices with some modifications.

Chapter 4

This part addresses the problem of low thickening times and pumpability issues encountered while using high-density hematite based FFA geopolymers. This study introduced a solution to thickening time challenges at high temperatures using a mixture of a modified lignosulfonate retarder and a PNS superplasticizer. The effects of this mixture on thickening time, rheological and mechanical properties were evaluated.

Chapter 5

This chapter compares two high density geopolymer cement systems using hematite alone and a mixture of hematite and Micromax. The assessment included rheology (PV, YP, and GS), filtrate loss, strength, and elastic properties. This study showed the sedimentation problem associated with hematite as a weighting agent and introduced adding Micromax as a solution to mitigate this problem in geopolymers.

Chapter 6

This chapter shows the effectiveness of perlite in addressing sedimentation and stability issues in high-density hematite-based geopolymer systems was investigated. Overall, the results highlighted the significant benefits of incorporating perlite in geopolymer cement formulations, particularly in mitigating sedimentation and stability issues, improving compressive strength, and maintaining desirable rheological properties. These findings contribute to the advancement of geopolymer technology in the oil and gas industry, offering potential solutions for cementing challenges in various wellbore conditions.

Chapter 7

This part demonstrates the effectiveness of incorporating laponite in hematite-based geopolymer samples to address sedimentation and stability issues. Overall, incorporating laponite in hematite-based geopolymer systems offered a promising solution to address sedimentation and stability challenges, while improving key properties such as density uniformity, compressive strength, and flexibility.

Chapter 8

Chapter 8 shows the successful production of a new category of geopolymers using volcanic tephra as a source aluminosilicate material after activation by NaOH solution. Unlike the most developed geopolymer cement systems in the literature that used high concentrated NaOH solutions (8 to 14 M) in a combination with sodium silicates, this study used only 4 M NaOH solution as an activation solution in a step towards reducing the costs and the environmental impact of the geopolymer technology. Volcanic tephra-based geopolymer is considered a green approach to make extensive use of volcanic tephra and

tackle the challenges associated with Portland cement manufacturing and volcanic tephra accumulations at the same time.

Chapter 9

In the last chapter, a summary of the studies is presented and the recommendations for future work are provided.

CHAPTER 2

LITERATURE REVIEW

Currently, a new cost-effective and ecofriendly substance has emerged that has qualities comparable to OPC; this substance is termed as geopolymer. Their raw materials are of geological origin and geopolymer formation continues via inorganic polymerization and condensation, so they are also called geological polymers (Davidovits, 1994). Prof. J. Davidovits coined the term geopolymer in 1978, describing it as a green cementitious substance that is free of cement. As it contains a 3D structure of cross-linked polysialate chains, these were previously regarded a particular case of soil cement and referred to as geocements (Davidovits, 1991b).

Geopolymers can be formed by natural substances and/or waste materials as source materials activated by alkali or acids (Ahdaya and Imqam, 2019a). Resistance to fire and chemical corrosion, long-term durability, and excellent mechanical strength are some advantages of geopolymer technology (Aiken et al., 2018; Aliques-Granero et al., 2019; Lahoti et al., 2019; Y. Liu et al., 2020; Shill et al., 2020; Vafaei et al., 2018). Geopolymer is produced by the geopolymerization of aluminosilicate substances dissolved in the alkali solutions at room or high temperature, forming an amorphous to semicrystalline 3D silicoaluminate network structure (Palomo et al., 1999; Ren et al., 2017; Silva et al., 2007). Geopolymerization refers to geosynthesis, i.e., synthesis of chemically integrated minerals (Amritphale et al., 2019). The geopolymerization reaction forms viscous cementitious slurry that after hardening creates strong, durable, and compact geopolymeric substance

(Phair and Van Deventer, 2001). Despite researchers have various thoughts about the reaction mechanism taking place while this process, most agreed that the geopolymerization shall go through three main steps: dissolution, the transfer, solidification, and polycondensation (Duxson et al., 2006; Provis and van Deventer, 2007; Ren et al., 2017; Silva et al., 2007). The Si and Al in the aluminosilicate substances dissolve after contacting the alkali solutions to form monomers and oligomers going through polycondensation to form a 3D structure, called, polysialate \, polysialte-siloxo, and polysialate-disiloxo (Amritphale et al., 2019; Vrålstad et al., 2019).

2.1 Geopolymers for Various Well Applications

There is no such thing as an all-purpose cement. Cement slurry is designed depending on the existing wellbore conditions of pressure and temperature and cement job type. Most research has been conducted on not just searching for an alternative to OPC due to its environmental concerns during production but most significantly on confirming if the drawbacks of OPC can be mitigated by geopolymers. Four main research topics were investigated in the literature: applications in harsh environments, application in P&A, compatibility with mud, and temperature effects (Adjei et al., 2022b).

2.1.1 Harsh Environments

Harsh environments like acidic and high saline foster degradation that causes the ultimate loss of well integrity. Both depleted and active petroleum reservoirs are potential storage spaces for CO₂ in underground formations. CO₂ sequestration in subsurface formations is a proven way to reduce the CO₂ emissions by about 20% (Jenkins et al., 2012). OPC-based cement system in CO₂ environments exhibit deterioration due to carbonation and

detrimental precipitations causing corrosion and leakage (Brandvoll et al., 2009; Faqir et al., 2017; Laudet et al., 2011; Mahmoud and Elkatatny, 2020a; Nasvi et al., 2014a). **Figure 2.1** presents the degradation produced by CaCO_3 precipitates due to the reaction of H_2CO_3 and hydrated cement products.

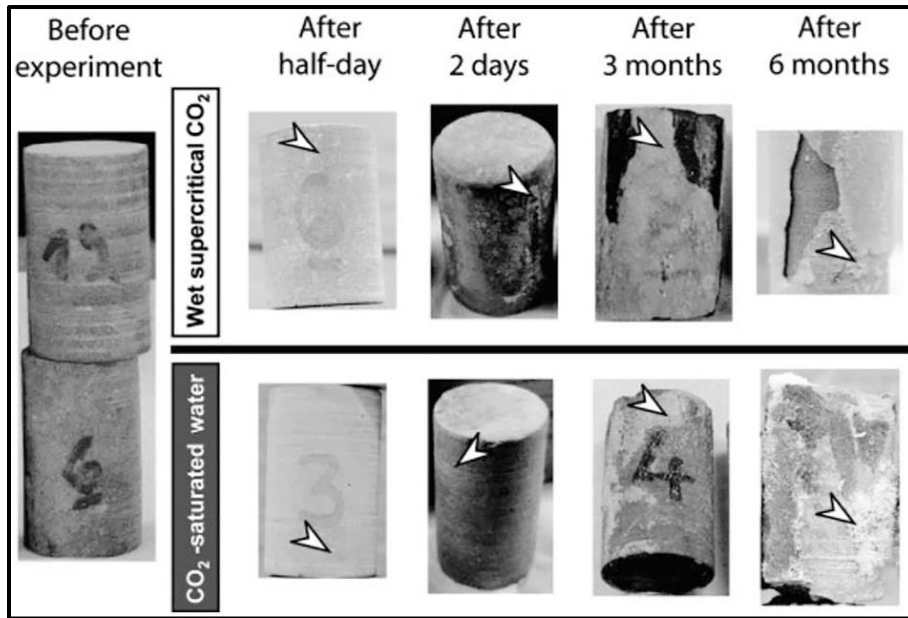


Figure 2.1 Degradation of OPC-based cement in two carbon dioxide environments. White arrow indicates CaCO_3 precipitates at the surface of the cement core samples (Rimmelé et al., 2008).

(Nasvi et al., 2013a) studied the permeability of FA-based geopolymers to be used for CO_2 sequestration. The developed geopolymer showed a very low CO_2 permeability that is less than the conventional systems permeability (10^{-20} to 10^{-11} m^2). These results proved that the tested geopolymer could serve as an excellent cementitious material for CO_2 storage. (Nasvi et al., 2013b) conducted an experimental work to compare the apparent CO_2 permeability of FA geopolymer of subcritical and supercritical CO_2 . The results showed that the pore pressure increase reduced the geopolymer permeability due to Klingenberg slip flow. Additionally, the CO_2 permeability reduced because of pore volume shrinkage

produced by increasing confining pressure. This conclusion showed the importance of super-critical CO₂ for effective and leak-free CO₂ storage in deep subsurface formations.

(Nasvi et al., 2014b) conducted an experimental work to compare the effects of three different geopolymer recipes (100% FA, 8% slag by weight with FA and 15% slag with FA) and class G cement on apparent CO₂ k for sub- and super-critical CO₂. The geopolymer k was 2 to 3 orders less than that of cement based on mix composition. The 15% GGBFS addition reduced the permeability by around 10 times and 1000 times compared to FA geopolymer and class G cement, respectively. (Barlet-Gouedard et al., 2010) investigated the metakaolin geopolymer durability in CO₂ environments. The sample curing lasted for 72 hours and put in a CO₂ container at 90 °C and 4,000 psi for 15 days. The system showed excellent mechanical properties and no remarkable degradation in the microstructural analysis.

The geopolymer mechanical integrity was investigated in CO₂ environment under downhole conditions and compared to a control geopolymer that was not exposed to CO₂ (Nasvi et al., 2016). The test was run at 3 MPa psi for up to 6 months. There was only about 2 % change in the compressive strength. The Scanning electron microscopy (SEM) did not show any significant variation in geopolymer microstructure after 6 months. The work demonstrated that the FA geopolymer can be a good substitute to OPC since it has high durability and strength. (Jani and Imqam, 2021) compared the mechanical degradation of OPC and class C FA geopolymer in HPHT CO₂ environments. The authors concluded that class C FA geopolymer possessed higher resistance to CO₂. FA geopolymers had higher compressive strength than Class G system (Dinesh et al., 2018).

(Lee and van Deventer, 2002) studied the effect of different inorganic salts on the strength of FA-kaolin geopolymers. It was observed that chloride salts like KCl, CaCl_2 and MgCl_2 were harmful to geopolymers. They reduced the durability by gradually resulting in precipitation and crystallization in the aluminosilicate gel. Contrarily, carbonate salts such as K_2CO_3 and CaCO_3 were useful by decreasing the dissolved water content and preventing hydrolytic attack on the gel.

(Nasvi et al., 2014d) studied the geopolymer mechanical properties of samples cured in water and brine solution. There was a general strength decrease, nevertheless, the decline was less in larger brine concentrations. According to the researchers, increasing brine concentration increased the interaction between the brine and the geopolymer, which slows leaching and strength reduction. Another work was conducted by (Giasuddin et al., 2013a, 2013b). The researchers mentioned that the geopolymers cured in saline water had better strength compared to the normal water. Microstructure studies showed pores and unreacted grains in the samples cured in normal water while saline water cured samples were more homogeneous.

(Ridha and Yerikania, 2015) simulated the behavior of geopolymer and OPC system under acidic environments (using a mixture of HCl and HF acids with the ratio of 12% to 3%). The geopolymer system was prepared by FA and silica fume which was cured at 120 °C and 4,000 psi for one day. Then, the systems were put into acidic solution at 65 °C for one day. The authors concluded that geopolymers had a greater resistance to acid attacks, understood from the less strength decrease (1.76%) compared to the OPC system (28% loss). The authors attributed the larger strength decrease of the OPC systems to the adverse interactions between the acid and $\text{Ca}(\text{OH})_2$ produced by OPC hydration. (Sugumaran,

2015) investigated the durability of FA-based geopolymers for low (2%) and high (10%) H_2SO_4 concentrations. The authors confirmed that the FA systems were more resistant at low acid concentrations.

(Khalifeh et al., 2016) studied the effects of harsh environments on rock-based geopolymers cured for one week at atmospheric conditions. Then, the samples were put in crude oil, brine, and hydrogen sulfide in brine at 100 °C and high pressure for 3, 6 and 12 months. There was a turning point after 6 months where the compressive and tensile strengths commenced to increase for crude oil and brine, while the samples that were in H_2S showed some degradation. The low geopolymer k was observed for the crude oil and brine samples while the geopolymer placed in H_2S system was changed to the extent that the k could not be estimated.

2.1.2 P&A

P&A takes place when the well economic limit is reached, and the abandonment may be permanent or temporary. OPC is the most widely used substance for this job, though, it has some drawbacks, for example, carbonation, which causes the formation of a high k matrix. A good barrier should stop leaks, as shown in **Figure 2.2**. Additional substances utilized in P&A are geopolymers, bentonite, gels, shales, and metals (Vrålstad et al., 2019).

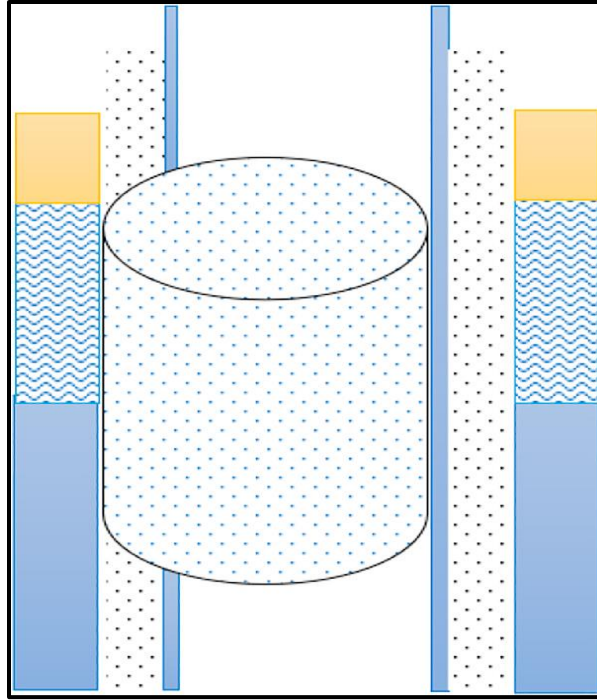


Figure 2.2 A graph of a plugged hole (Adjei et al., 2022b; Vrålstad et al., 2019).

(Khalifeh et al., 2014) conducted an experimental work to study the temperature effects and NaOH concentration on class C FA geopolymers activated by a combination of NaOH and Na₂SiO₃ for P&A. The specimens were cured at 188 °F and 257 °F and 5000 psi. For 188 °F, the strength was improved with raising sodium hydroxide concentration for 1–7 days. For 257 °F, the strength of the 8 and 10 M specimen was only larger than the 6 M sample after the first day, but the 6 M sample showed a strength greater than the other samples after 7 days. (Khalifeh et al., 2015) studied the usage of aplite rock to produce geopolymers for P&A jobs. The aplite was mixed with micro silica and GGBFA. Sodium and potassium-based hydroxides and silicates were tested in various mixtures to form twelve geopolymer recipes. The samples were cured at 87 °C and atmospheric pressure/1000 psi for various periods. The substances showed good mechanical properties and low k that are favorable for P&A application.

Gas migration in OPC system may take place due to cement shrinkage. Shrinkage in the cementing systems generates micro-annulus or induces a gap that may allow fluids migration; so, the system integrity system may be lost. Shrinkage is mostly resulted from the cement volume reduction as the hydrated cement products takes water while hardening, on the other hand, the geopolymer hardening process is different. (Salehi et al., 2017a) studied the usage of Class F FA geopolymer activated by NaOH/ Na₂SiO₃ for P&A and compared it to Class H cement. The authors mentioned that the geopolymer systems exhibited less shrinkage than OPC system. Additionally, the geopolymer systems exhibited a larger shear bond and compressive strengths. **Figure 2.3** presents that the Class H system exhibited more shrinkage over the investigation time (at 150 °F and 200 °F).

(Rahman et al., 2020) performed an experimental study to compare the linear expansion of geopolymers with the Class G cement for low density (13.7 ppg) and moderate density (15 ppg) at 60 °C for different curing times. The authors concluded that geopolymers had a self-expansive property in water without adding any expandable material. The geopolymer expansion after 1 and 18 days was 0.05% and 0.15%, respectively, and 0.02% and 0.06% for OPC system, **Figure 2.4**. The geopolymer sample expanded almost 2.5 times larger than the class G sample almost at all curing times. The authors added a commercial expandable material to both systems to study the effects of admixture on accelerating the expansion. The MgO based expandable material assisted in early expansion development, but it did not help to enhance the overall expansion at the end of curing. The elastomer-based substance enhanced overall and early expansion. Such findings revealed that geopolymers have a higher expansion capacity than class G OPC, which would be a benefit of geopolymer cement in terms of application (Cohen and Mobasher, 1988).

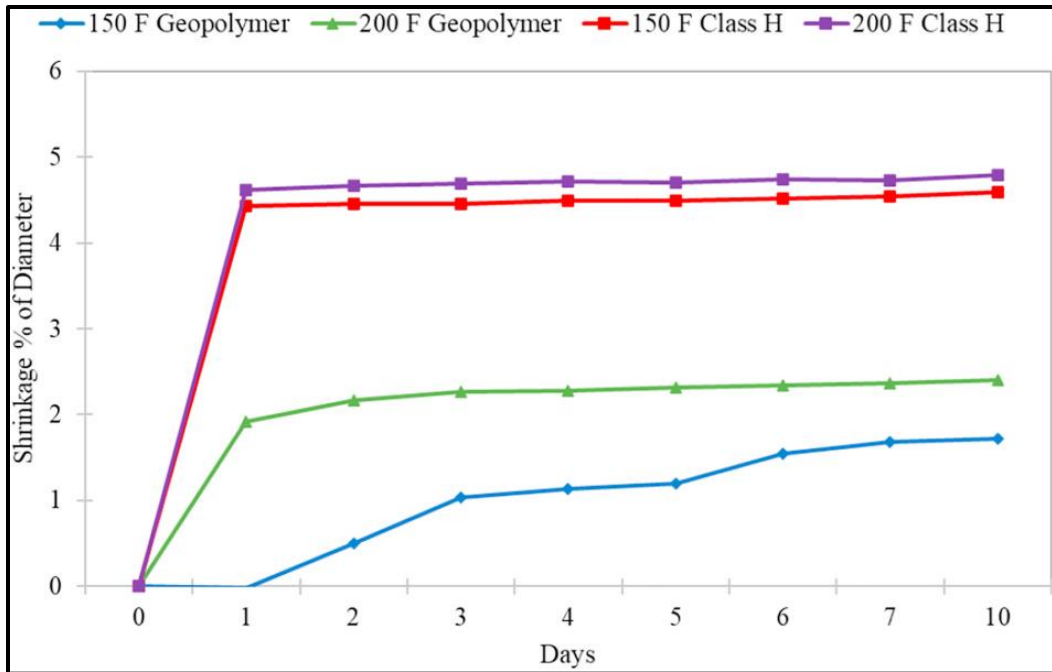


Figure 2.3 Shrinkage test (Salehi et al., 2017a).

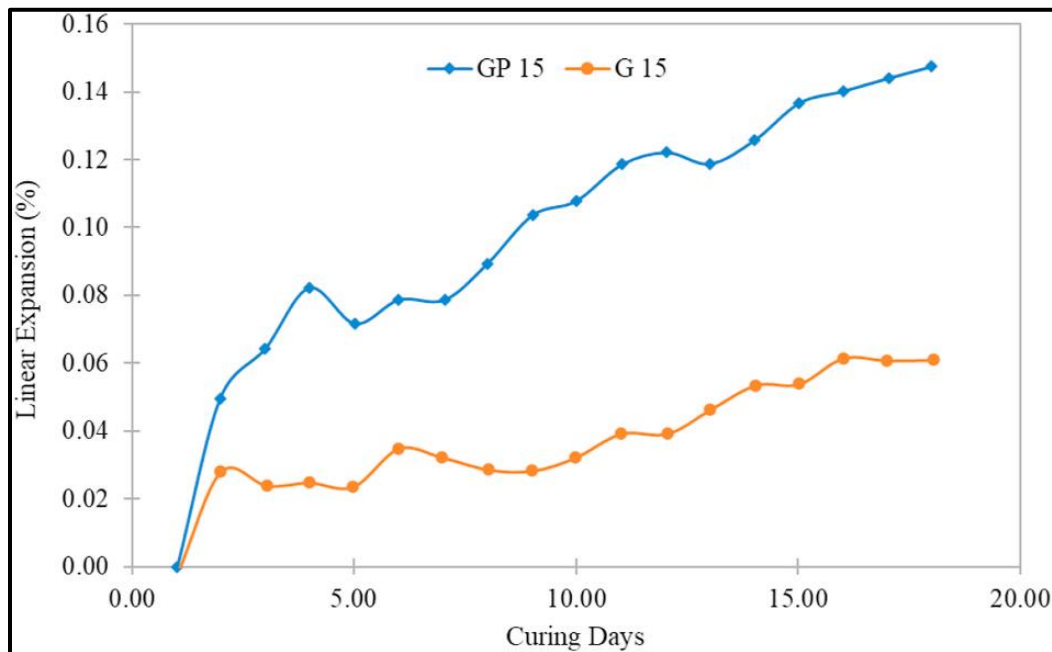


Figure 2.4 Shrinkage of geopolymer and Class H (Cohen and Mobasher, 1988).

2.1.3 Compatibility/ Combination with Mud

Mud is used to control the formation pressure, transport cuttings, cool and lubricate the bit and drill string and stabilize the hole (Rabia, 2002). A major problem takes place when the

OPC slurry is contaminated with mud that may result in cement integrity loss due to its incompatibility with mud (Aughenbaugh et al., 2014). The literature has shown that the geopolymer resistance to drilling fluid contamination is greater than that of OPC system. Furthermore, drilling fluid can be intentionally included in geopolymer recipe to get a system with good fluid and mechanical characteristics for hydraulic isolation and controlling the loss of circulation (Liu et al., 2019, 2017a). This also offers a sustainable method for mud disposal, particularly for non-aqueous drilling muds.

(Salehi et al., 2016) studied the geopolymer compatibility with drilling fluids by examining different oil-based mud (OBM) percentages addition into OPC and geopolymer systems. The OPC system exhibits a remarkable strength reduction. For example, the OPC showed about 88% strength decrease whereas the geopolymer exhibited 25% reduction for 10% OBM. (Liu et al., 2016) found that the geopolymer strength reduced by 30% while that of OPC reduced by 70% when mixed with 10% SBM. Even with 40% SBM, the geopolymer still possessed reasonable strength. In a relevant work, (Liu et al., 2017b) examined a FA geopolymer/mud-based system and studied the properties as a plug substance, particularly the self-healing ability. The geopolymer showed the capability to get back the strength.

(Ahdaya and Imqam, 2019b) also conducted an experimental investigation and concluded that geopolymer contaminated with drilling fluids outperformed the OPC systems. These outstanding characteristics in the performance included lower reduction in strength and improvement in the viscosity and fluid loss. (Olvera et al., 2019) investigated the chemical shrinkage of FA geopolymers consisting of 10% and 20% SBM. The authors mentioned that the geopolymer/mud composite exhibited shrinkage increase compared to geopolymer without mud (FA) at 23 °C, and 50 °C, with the effect more pronounced at 50°C, (**Figure**

2.5 - top). However, the shrinkage in the geopolymer/mud system was less than that of OPC/ mud system at 23 °C (**Figure 2.5** - bottom). A high shrinkage was noticed in the geopolymer system at 50°C and 20% mud concentration (**Figure 2.5**). (Bu et al., 2020) observed that a MK geopolymer/mud composite could possess a compressive strength of about 1160 psi. The authors found that the shear and hydraulic bond strength of the geopolymer were high for all the systems.

(X. Liu et al., 2020) mentioned that the geopolymer rheology can be improved when mixed with non-aqueous muds in amounts as much as 40% by volume. (Eid et al., 2021) investigated the effects of OBM and WBM on neat cement and geopolymers. The outcomes showed that geopolymer contaminated with OBM (5 – 20%) had less strength decrease and exhibited remarkable strength development and high flexibility with time. On the other hand, the geopolymers were more susceptible to WBM. However, the geopolymers in both cases outperformed the OPC systems.

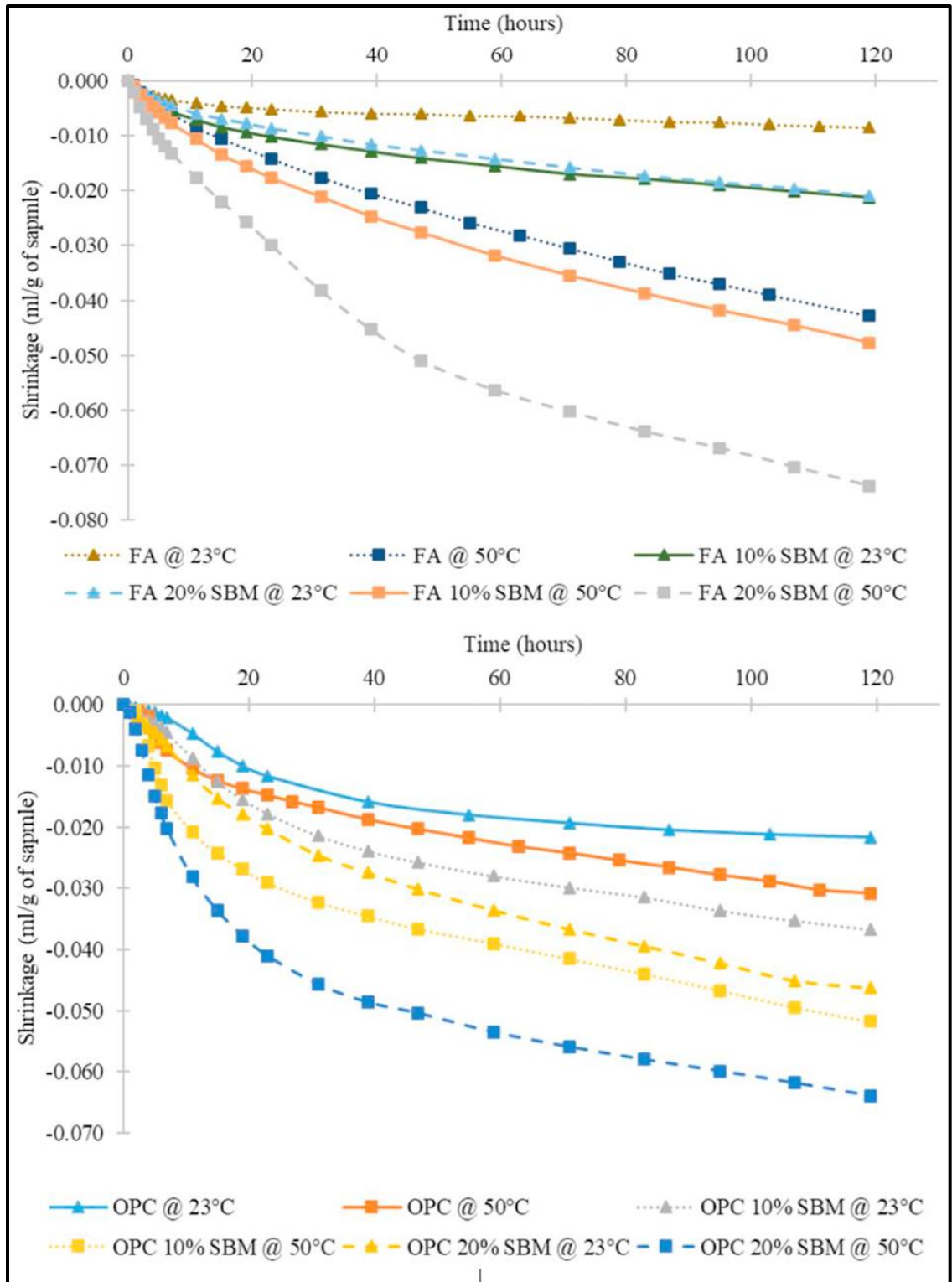


Figure 2.5 Shrinkage of the geopolymers (top) and OPC (bottom) systems (Olvera et al., 2019).

2.1.4 Temperature Effects

Hole conditions such as temperature impact the cement performance at different stages starting from displacement, placement to hardening after setting. For instance, the casing experiences thermal expansions that exert more forces on the cement during thermal operations such as steam injection that may cause radial cracking (Dean and Torres, 2002). Geopolymer systems have the potential for high-temperature applications (van Oort et al., 2019). The dissolution of the alumina and silica and polycondensation are enhanced at high temperature (Salehi et al., 2019). (Nasvi et al., 2012a) concluded that the optimum temperature for FA geopolymers for optimum performance was 140 °F. The authors found that strength increase is minor after this temperature and they agreed that factors such as the source of FA, curing way, and mix formulation may impact the strength. (Nasvi et al., 2012b) compared the temperature effects on the strength of FA geopolymer and Class G cement. The geopolymers showed less strength when cured at atmospheric conditions but got larger strength with raising temperature. The optimum geopolymer strength was in range of 50 to 60°C. The researchers attributed the poor geopolymer strength development at atmospheric conditions to the slow geopolymerization rate at low temperature. It was claimed that geopolymer is not a good choice in areas with a temperature less than 86 °F. (Nasvi et al., 2014c) evaluated the influence of temperature on the FA geopolymer permeability. The curing temperatures were in range of 73 °F to 158 °F. The outcomes confirmed that k increased with temperature. However, this k (0.04 μ D) was still much less than that advised by API. (Paiva et al., 2018) investigated the properties of MK geopolymer system at 49 °C. The geopolymer recipe without modifiers got a compressive strength of 2,524 psi that was only approximately 4% less than that of the OPC. (Salehi et al., 2019)

investigated the effect of temperature on the thickening time of FA geopolymer system at 150 °F, 175 °F, 200 °F, and 250 °F. They noticed a quick gelation in the test simulated at 250 °F. The researchers recommended using superplasticizer and retarder for geopolymers above 175 °F. (Suppiah et al., 2020) studied the geopolymer strength at 140 °F and 194 °F. They found that the specimens cured at higher temperatures possessed better strength after one day due to enhanced geopolymerization activity at high temperatures.

2.2 Major Findings

Scholars in well cementing have investigated the usage of geopolymer technology for different cement applications. The most important findings can be summarized in terms of advantages and drawbacks that require more research as follows:

2.2.1 Advantages

1. Geopolymers possess more resistance in acidic environment and therefore can be used in CO₂ sequestration.
2. Geopolymers possessed less permeability compared to OPC.
3. Geopolymers performed well in high saline environments because of reduction of alkali leaching.
4. Geopolymers showed less shrinkage and good shear bond strength which suggests them to be good candidates for zonal isolation and P&A.
5. In comparison to OPC systems, geopolymers are more compatible with mud, particularly the OBM.
6. The geopolymer strength increases with temperature owing to the increased polymerization rate and may be workable in steam injection.

7. The excellent mechanical properties promote their usage in the wells subjected to hydraulic fracturing jobs.

2.2.2 Limitations

1. Geopolymers are more susceptible to WBM.
2. The geopolymer strength is small below 86 °F owing to the slow geopolymerization rate.
3. Conventional geopolymers showed high brittleness.
4. Geopolymer systems have rapid gelation at high temperatures, hence more research is required to investigate their usage in HPHT wells.

CHAPTER 3

DEVELOPMENT OF HEAVY-WEIGHT HEMATITE-BASED GEOPOLYMER FOR OIL AND GAS WELL CEMENTING

3.1 Introduction

3.1.1 OPC Challenges

Although OPC is the most extensively used substance for well cementing, it has some technical issues, especially in deep formations, and environmental concerns. The technical issues include gas invasion while setting, instability at corrosive environments, thermal instability at high temperatures, cement failure while perforation and fracturing due to high stiffness and brittleness, and strength reduction at temperatures above 230°F (Khalifeh et al., 2017; Y. Yan et al., 2020). OPC-based systems are vulnerable to acid attacks (Bakharev et al., 2003; Nasvi et al., 2013a). When mud contacts cement slurry, the compressive strength of OPC is significantly affected (Aughenbaugh et al., 2014; EI-Sayed, 1995). Additionally, mud has adverse effects on OPC rheological properties as it increases cement slurry viscosity that affects mud pumpability (Liu et al., 2016). Moreover, OPC introduces some environmental challenges such as high greenhouse gas (GHG) emissions as OPC production process is considered one of the major sources of GHG. OPC production takes

place through a reaction of calcium carbonate (lime) and silicon dioxide to produce calcium silicates and CO₂. Additionally, massive energy consumption is required during cement production. These challenges persuaded the researchers to search for alternative materials to overcome the technical challenges and to provide more eco-friendly cement systems. Lately, different researchers investigated the effects of various materials on cement properties such as olive waste, nano clay, granite sludge, polypropylene fibers, perlite and metakaolin (Adjei et al., 2022a; Ahmed et al., 2020, 2018; Bageri et al., 2021; Mahmoud et al., 2019; Mahmoud and Elkatatny, 2020b, 2020c). On the other hand, some researchers tried to totally replace OPC through exploring new materials that can form cementitious binders such as geopolymers (Adjei et al., 2022b; Salehi et al., 2019, 2018).

3.1.2 Geopolymers

Geopolymer technology has a wide range of uses, particularly in construction industry (Sambucci et al., 2021). However, full-scale deployment in well cementing has yet to be seen. Researchers in the field of cementing are currently examining the characteristics of several geopolymers under wellbore conditions (Adjei et al., 2022b). Geopolymers are produced by the geopolymerization of aluminosilicate substances dissolved in alkali hydroxides and/or soluble silicates at room or high temperature, forming an amorphous to semicrystalline 3D silicoaluminate network structure (Palomo et al., 1999; Ren et al., 2017; Silva et al., 2007). Geopolymerization refers to geosynthesis, i.e., synthesis of chemically integrated minerals (Amritphale et al., 2019). The geopolymerization reaction forms viscous cementitious slurry that after hardening creates strong, durable, and compact geopolymeric substance (Phair and Van Deventer, 2001).

In comparison to OPC, the geopolymer production process is cleaner, and the source materials do not consume that much energy (Davidovits, 2010; Patel and Shah, 2018; Singh et al., 2018; Worrell et al., 2003). Geopolymer uses some industrial and agro-wastes like FA, slag, silica fume, coconut ash, rice husk that makes geopolymer eco-friendly in terms of low CO₂ manufacturing emissions and using industrial by-products as a source of aluminosilicate materials. Moreover, clays like metakaolin or some rocks like aplite can be used to form certain types of geopolymer. The geopolymer systems exhibit superior performance to conventional cement systems. Low shrinkage, low permeability, low Young's modulus (YM), strength development, stability at high temperature, tolerance to oil-based mud contamination, chemical corrosion resistance, and long-term durability make geopolymer systems a viable option to OPC in well cementing applications (Cong and Cheng, 2021; Nasvi et al., 2013a).

3.1.3 High Density Cement

Cement slurry is designed depending on the existing wellbore conditions of pressure and temperature and cement job type. High-density cement slurry with a density of 17 ppg or more should be utilized in deep wells or across high-pressure zones (Magarini et al., 2009). Decreasing water content is the cheapest approach to increase the density (Michaux et al., 1990). However, American petroleum institute (API) advises a water-to-cement ratio of 44% for primary cementing (API, 2019). The main drawback of reducing the water content is the challenge of instantaneously attaining sufficient control of fluid loss, good rheological properties, and no settling of the solid particles (Ahmed et al., 2022). Slurry bridging occurs because of uncontrollable fluid losses. Solid particle settling results in nonuniform compressive strength and bonding along the length of cemented section (Erik

B. Nelson and Guillot, 2006). Therefore, using weighting materials is required to achieve a higher density. These substances are commonly utilized in mud to overbalance high formation pressure formations. It is necessary to use weighting agents such as hematite, Micromax and ilmenite in cementing operations as deep wells are characterized by high pore pressures (Ahmed et al., 2019).

Limited research was conducted for using only barite in geopolymer area that included compressive strength and thickening time experiments. Kanesan et al. (Kanesan et al., 2018) estimated the thickening time of barite-based fly ash geopolymer at 140 °F and 2,000 psi. The authors used a combination of 8 M NaOH solution and Na_2SiO_3 . They concluded that retarders effect was significant in low and medium density slurries, but it slightly affected the high-density slurry thickening time. They mentioned that barite affected the retarder ability to form a layer around the reacting precursor particles. Salehi et al. (Salehi et al., 2017b) studied the effect of adding barite (15% BWOC) on compressive strength of the FA based geopolymer. Barite improved strength within the first 7 days of curing. However, barite could not improve the strength after 7 days. It is clear from the literature that rare experiments were conducted using only barite as a weighting material with geopolymers for oil well cementing.

3.1.4 Fly Ash

Fly ash is an industrial by-product generated from coal burning. According to ASTM C618, FA can be classified into 2 classes (F & C) based on CaO content. Class F ash is distinguished by its low CaO content and produced by burning bituminous coal. Conversely, class C fly ash is characterized by its high calcium content and resulted from lignite and sub-bituminous coal burning. FA is a widely available by-product that is often

used in the preparation of geopolymers. FA has been used since the early twentieth century, and it is typically used as a major component in concrete (Scrivener et al., 2018). Using **FA instead of PC** minimizes GHG emissions and lowers construction expenses. FFA has the advantages of being inexpensive, readily available, having a spherical structure, being rich in high activity alumina and amorphous silicate (Cong and Cheng, 2021).

This work evaluates the possibility of using hematite and fly ash to develop a new heavy weight geopolymer formulation for oil and gas well cementing. The biggest challenge in this work was developing a flowable heavy weight geopolymer formulation with good rheological properties and sufficient thickening time. Different properties such as rheology, filtrate loss, compressive and tensile strength, petrophysical properties, and elastic properties (Poisson's ratio (PR), and Young's modulus (YM)) were assessed for the high-density hematite-based geopolymer system. This work used only 4 M NaOH as an alkaline activator while most of the work in the literature used a combination of a high molarity NaOH and Na_2SiO_3 to form geopolymers.

3.2 Materials and Methodology

3.2.1 Materials

The materials used in this study were FFA as aluminosilicate material, hematite as a weighting agent, NaOH solution as an activator besides other chemical additives used to enhance geopolymer characteristics and facilitate using geopolymers in a wide range of wellbore conditions. The additives included retarders, deformers, and superplasticizers. The specific gravities (SG) of the FFA and hematite were 2.25 and 5.05, respectively. The

particle size distributions (PSD) of the FFA and hematite were obtained using the laser diffraction particle size analyzer as shown in **Figure 3.1**. The results showed that 50% of FFA and hematite particles had size below 19.35 and 21.54 μm , respectively.

Figure 3.2 shows the elemental composition of the hematite which was obtained by the Bruker M4 Tornado X-ray fluorescence (XRF). XRF results confirm that hematite has a high iron amount (around 95%) and X-ray diffraction (XRD) showed that it contained 100% hematite. XRF also showed that FFA has considerable amounts of silica (SiO_2) and alumina (Al_2O_3), as shown in **Table 3.1**, which play a vital role in geopolymer formation. The SEM images, as shown in **Figure 3.3**, confirm that the FFA particles have spherical shape while the hematite particles have irregular shape.

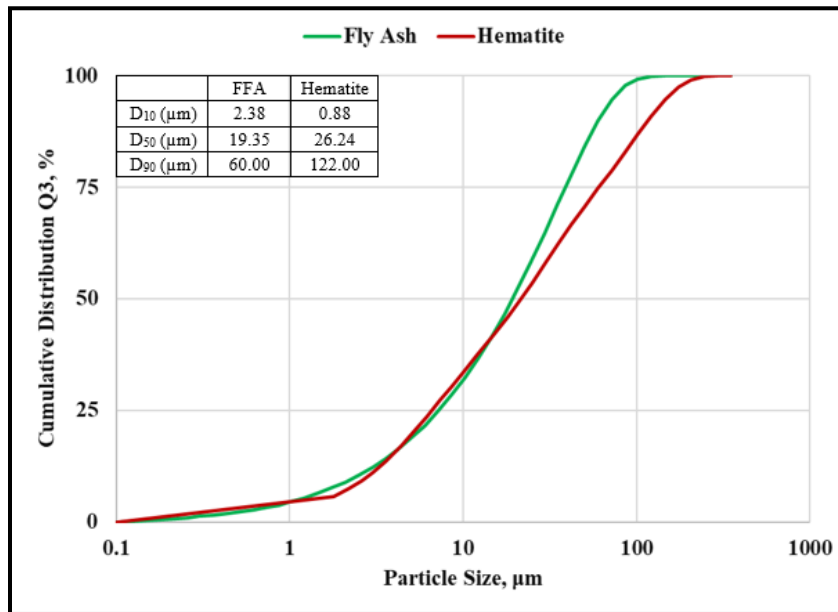


Figure 3.1 PSD results of FFA and hematite.

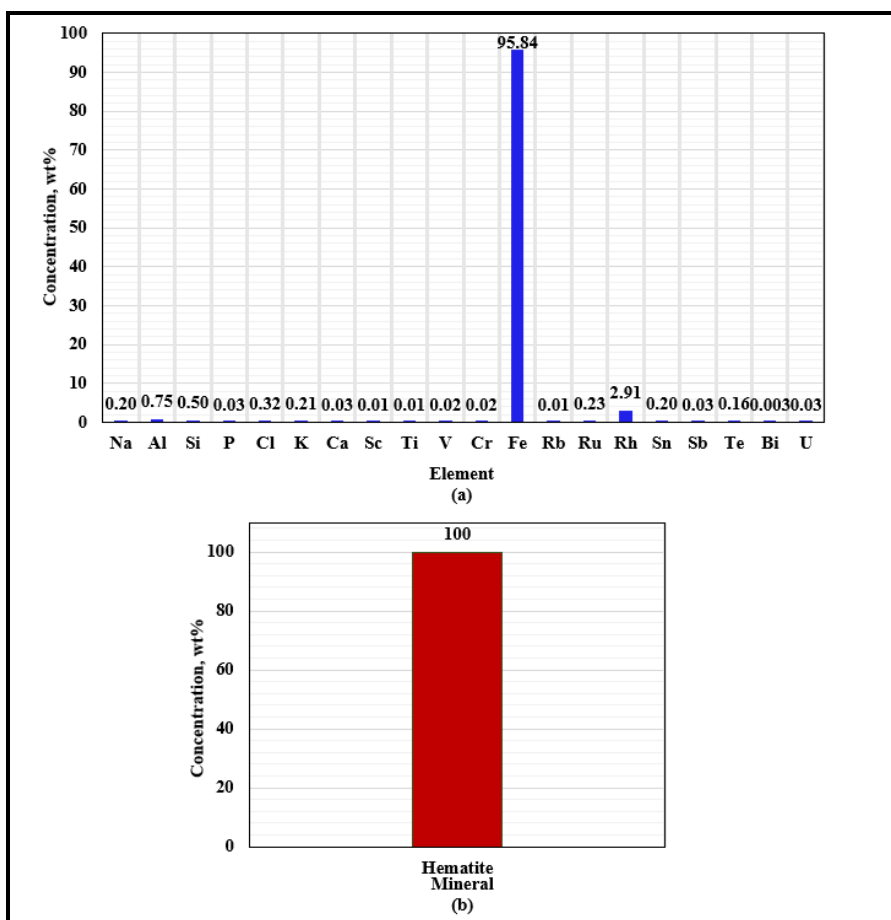


Figure 3.2 XRF elemental composition of hematite (a) and The XRD of the sample (b).

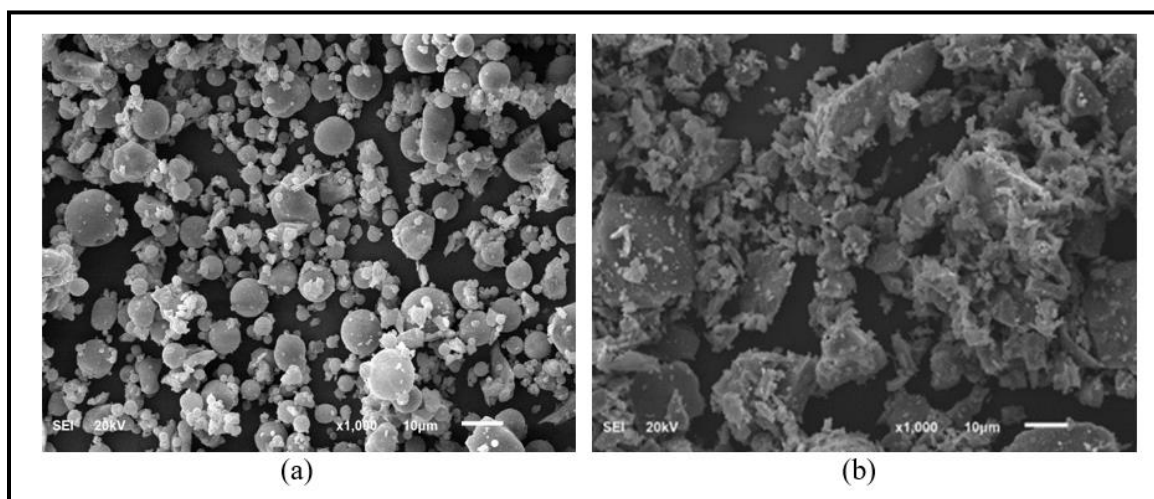


Figure 3.3 SEM images for FFA (a) and Hematite (b).

Table 3.1 The XRF of FFA used in this study.

Oxide	Percentage, %
SiO ₂	55.92
Al ₂ O ₃	29.54
CaO	5.49
Fe ₂ O ₃	4.93
TiO ₂	1.91
K ₂ O	1.66
SO ₃	0.39
MnO	0.04
Others	0.13

3.2.2 Methodology

This section discusses the methodology followed to conduct this study. It started with collection, characterization, and preparation of materials. Then, the mix design was determined based on mixability, pumpability and rheology. After that, the cured samples were tested for mechanical and elastic properties. **Figure 3.4** presents a summary of the methodology followed in this work.

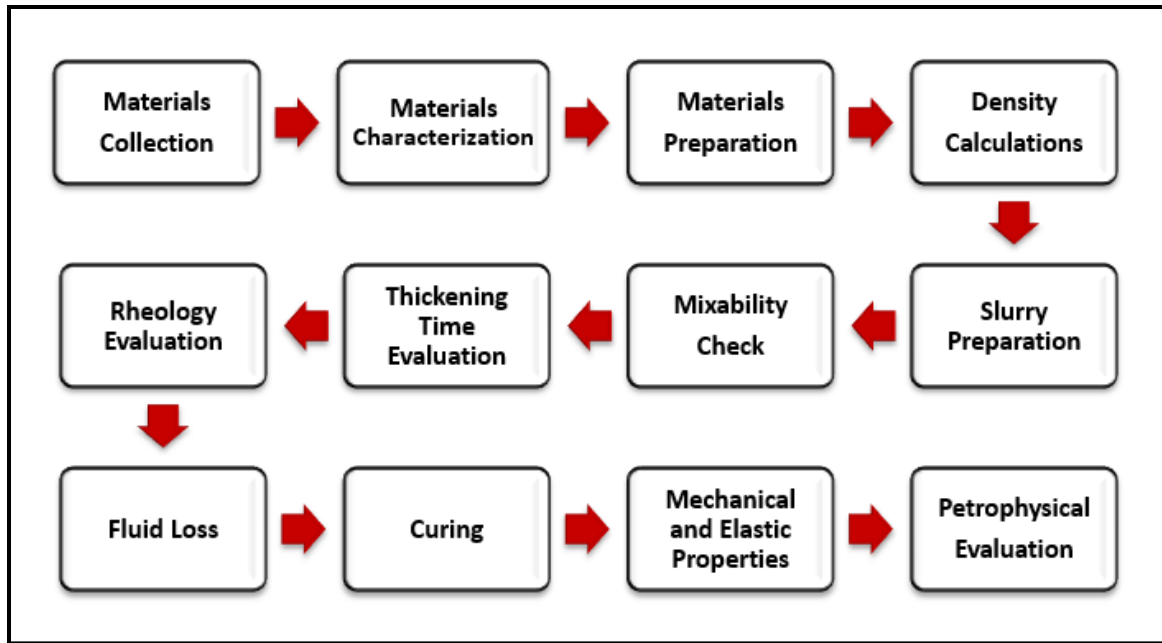


Figure 3.4 The Summary of the methodology in this work.

Materials Preparation

NaOH solution was prepared by dissolving NaOH pellets in distilled water using a magnetic stirrer. NaOH solution was allowed to cool down to room temperature at least for one day before experiment. The specific gravity of the used powders was measured to estimate the required amounts to reach the target density (17.5 ppg). The FFA was sieved to ensure particles' size was lower than 100 μm and then was confirmed by the PSD results. Two different processes (wet and dry) can be used to prepare geopolymer slurries (Salehi et al., 2017b). In wet process, A superplasticizer and/or retarder are mixed with activation solution for 2 min at high shear rate (12,000 RPM) using OFITE constant speed mixer. A binder such as FFA was then added and mixed with premixed solution at high shear rate for another 2 min.

Slurry Design

Several trials were conducted to get an initial flowable slurry formulation that can be easily mixed. Different parameters were tested such as NaOH molarity (4, 6, 8 and 10 M), liquid to binder ratio (0.5 to 0.8), and weighting agent percentage. Moreover, several additives with different concentrations were tested such as retarders, and superplasticizers to enhance the slurry workability. The mix design started with testing mixability, rheology and thickening time. Then, the testing went through strength, elastic and petrophysical properties evaluation.

Rheology, Fluid Loss, and Thickening Time

After mixing, a Grace atmospheric consistometer is used for conditioning the geopolymer slurries at 195°F and 150 RPM for 30 min. The OFITE 900 viscometer was used to conduct rheology evaluation at an average temperature of 195°F and atmospheric pressure. The OFITE HPHT filter press apparatus was used to measure the fluid loss. The thickening time test was conducted at 195°F and atmospheric pressure using an atmospheric consistometer to estimate how long slurry would be pumpable. The rheology and thickening time measurements were run at least 3 times using different devices to ensure reliability and reproducibility of the results.

Mechanical and Petrophysical Properties

Mechanical properties evaluation included unconfined compressive strength (UCS), tensile strength, dynamic elastic properties (YM and PR) while evaluated petrophysical properties were porosity and permeability. After conditioning, the slurry was poured into cubic (2 in. in length) and cylindrical (1.5 in. in diameter and 4 in. in length) molds and then were placed in an HPHT curing chamber at 292 °F and 3,000 psi for two periods (1 and 7 days).

The Brazilian test procedure was followed to estimate the tensile strength. The UCS was measured using two techniques: compression testing machine and scratch test. In compression testing, cubes of hardened geopolymer are crushed. The UCS is determined by the highest stress applied to a specimen that causes it to fracture.

The scratch test is designed to regulate and monitor the continual shearing action caused by the movement of a diamond cutter on a sample surface. The force operating on the cutter generates a continuous profile of rock strength along the sample. The YM and PR were then determined by getting the sonic velocities (i.e., compressional and shear waves). The ultrasonic test determines how long it takes a pressure wave to travel between two probes. The MATEST compression and flexural machine was used for compressive and tensile strength analysis, while EPSLOG scratch testing machine with sonic mode was used for elastic properties and UCS.

For porosity measurement, helium gas was used, and Boyle's law was used in measuring porosity as discussed by Peters (Peters, 2012). For permeability measurement, nitrogen gas was used for measuring gas permeability at room temperature and a confining pressure of 1,000 psi. The gas permeability was measured at different pressures and a plot was constructed between gas permeability versus $1/p_{\text{mean}}$. Then, a straight line was extrapolated to get the intercept value which corresponds to liquid permeability.

3.3 Results and Discussion

3.3.1 Mix Design

In the early stage, the FFA, hematite and NaOH solution were mixed without any chemical additives. Different parameters were changed such as NaOH molarity, hematite percentage and liquid to binder ratio. Initially, the mixing of the tested geopolymer slurries was difficult and the mixed slurries were thick and cannot be taken out of mixer. By adding hematite, the slurry became thicker until reaching non-flowable state at high density. Then, different superplasticizers and retarders were tested to enhance the workability and flowability of the geopolymer slurries. High NaOH molarity solutions (6, 8 and 10 M) developed mixable and flowable slurries, but the challenge was thickening time and cost optimization. As a result, a 4 M NaOH solution was used as an activator solution for next stage. The liquid to binder ratio was changed until getting good results around 0.56. The mix design used in this study is shown in **Table 3.2** and expressed as by weight of binder (BWOB).

Table 3.2 The mix design used in this study.

Component	BWOB (%)	Weight (g)	SG
FFA	100	400	2.25
Hematite	80	320	5.05
Defoamer	0.0164	0.0656	1.1
Superplasticizer	5	20.00	1.28
Retarder	5	20.00	1.22
4 M NaOH Solution	56	224	1.15
Overall Density (ppg)	17.5		

3.3.2 Thickening Time

The effect of hematite on thickening time was studied by increasing the hematite percentage from 25% to 75% BWOB at 195 °F without using any chemical additives. It is found that increasing the hematite percentage significantly decreased the thickening time as shown in **Figure 3.5**. Decreasing the hematite percentage from 75% to 25% increased the thickening time by almost 6 times. Then, different retarders and superplasticizers were tested to solve the thickening time challenge when increasing the hematite percentage in geopolymer slurries to achieve the required density. By doing so, a new mixture of a superplasticizer and a retarder succeeded in increasing the thickening time (100 BC) from 50 min to 392 min at BHCT of 195°F as shown in **Figure 3.6**. The addition of only superplasticizer (5% BWOB) slightly increased the thickening time and the same for the retarder. When both were added together (5% BWOB each) to the mix design, the thickening time was greatly improved.

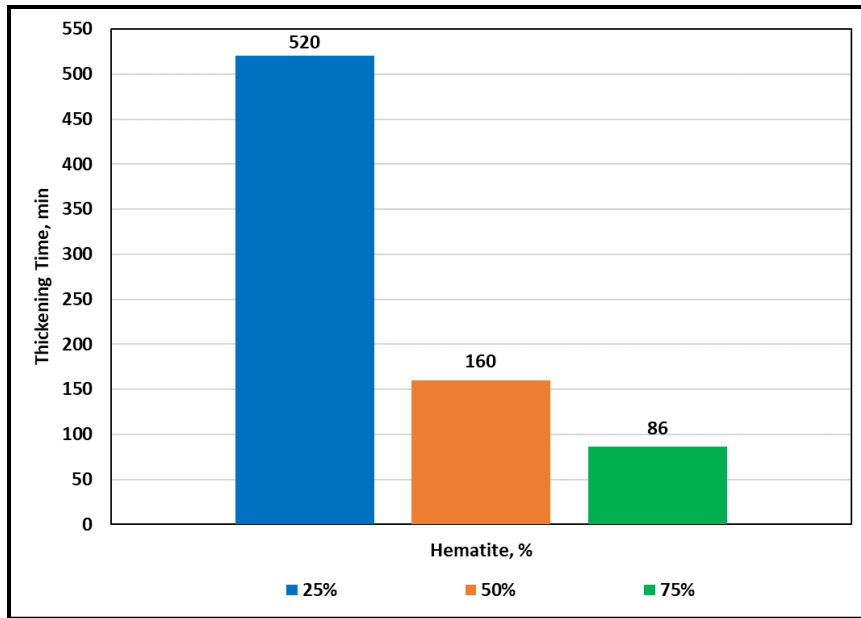


Figure 3.5 The effect of hematite without any additives on thickening time at 195°F.

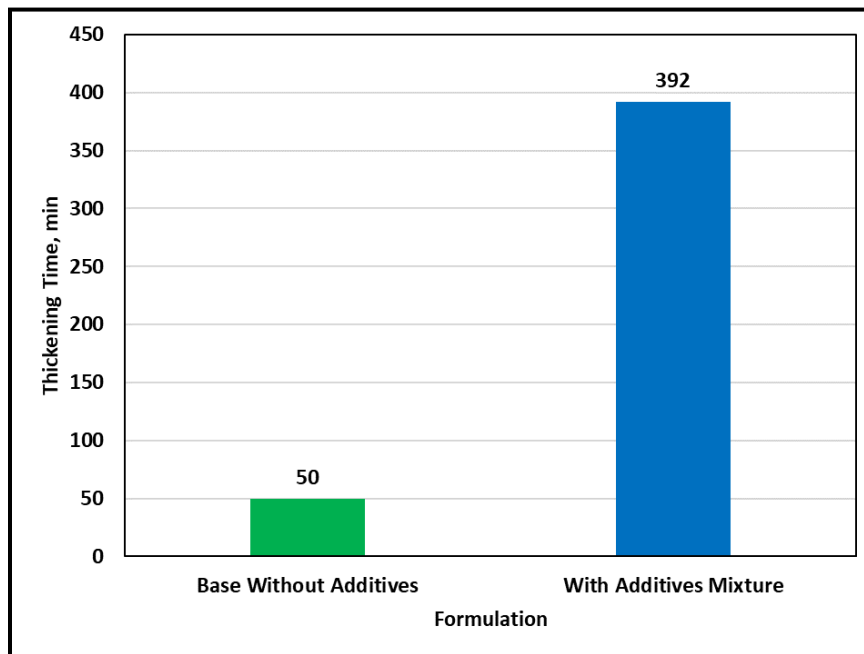


Figure 3.6 The effect of the developed mixture of additives on thickening time at 195°F.

3.3.3 Rheology Evaluation

Rheology evaluation of cement slurries is significant because it influences slurry mixing, pumping requirements, and drilling fluids displacement. The geopolymer rheology was evaluated at atmospheric (82.7°F) and downhole temperatures (186.6°F). The shear stress and viscosity versus shear rate are presented in **Figure 3.7** and **Figure 3.8**, respectively. The Bingham Plastic flow model provided the best fit for the rheology evaluated at 186.6°F with R^2 of 0.999. The plastic viscosity and the yield point were 192.49 cP and 10.45 lb/100ft², respectively. For atmospheric temperature, the flow curve did not follow the Bingham plastic model but the power law model with R^2 of 0.90. The consistency index (K) and power law index (n) were 7.79 lbf.sⁿ/100 ft², and 0.57, respectively. The power law index is lower than 1 indicating shear thinning behaviour and this can be confirmed by **Figure 3.8** in which the viscosity reduces with increasing shear rate. The gel strength of the developed geopolymer was also investigated at 10 sec and 10 min. The gel strength determines the slurries carrying ability in static condition and its growth helps resist gas invasion. The developed slurry acted more like a power law fluid at low temperatures and more like a Bingham plastic fluid at high temperatures. The summary of the rheological properties of the developed geopolymer slurry is presented in **Table 3.3**.

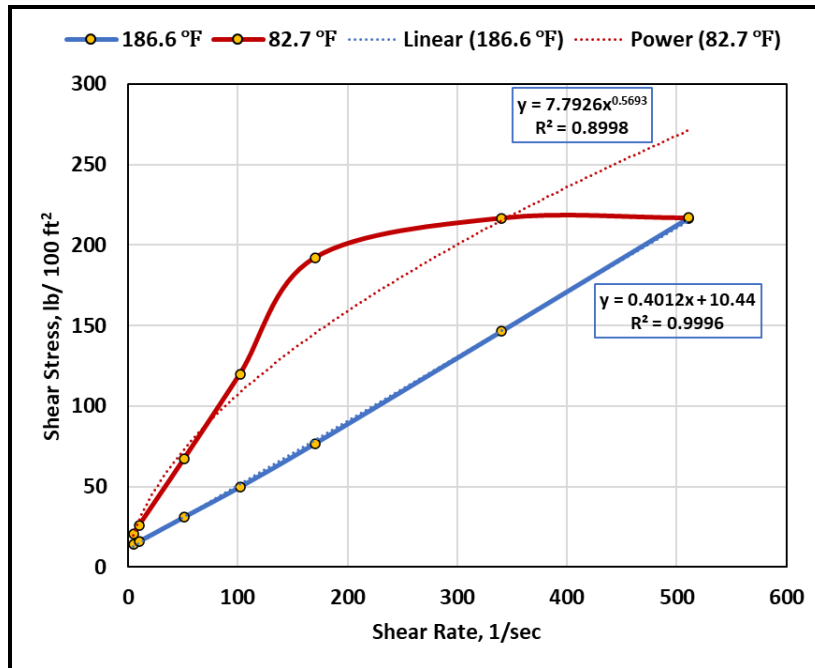


Figure 3.7 The shear stress vs. shear rate of the developed geopolymer slurry.

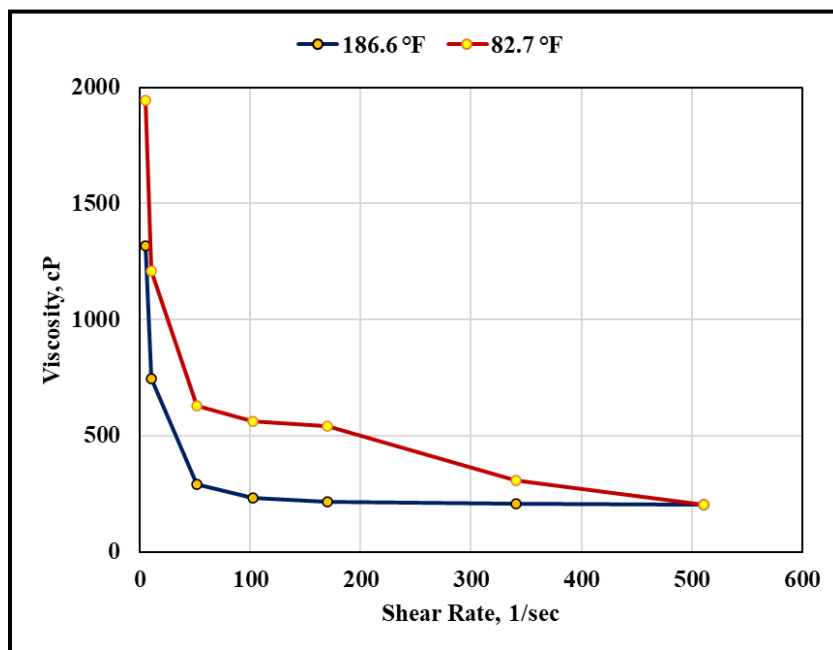


Figure 3.8 The viscosity vs. shear rate of the developed geopolymer slurry.

Table 3.3 The rheological properties of the developed slurry.

Property	Unit	186.6°F	82.7°F
PV	cP	192.49	-
YP	lb/100ft ²	10.45	-
n	dimensionless	-	0.56
K	lbf.s ⁿ /100 ft ²	-	7.79
10 s Gel	lb/100ft ²	16.00	23
10 min Gel	lb/100ft ²	171.00	204

3.3.4 Filtration

Water naturally leaks into subterranean formations from cement slurries. Fluid loss additives reduce loss by preventing cement slurry dehydration. If excessive fluid loss happens, a dry filter cake is formed. The filter cake may serve as a pathway for gas migration, impacting the whole zonal isolation. It also takes up space along the borehole wall, narrowing the annular gap, limiting the flow area, and raising the pressure required to pump the slurries. The estimated fluid loss indicates the slurries impedance to gas migration, where a high filtrate loss refers to a high gas migration possibility (Gefei. Liu, 2021). For high-performance slurries, the slurry should have a fluid loss of less than 50 mL/30 min as specified by API standards. The developed geopolymer slurry had a fluid loss of 38 mL/30 min as shown in **Figure 3.9**. It is worth mentioning that the developed formulation fell within the acceptable fluid loss ranges for different cementing applications as shown in **Table 3.4** (Gefei. Liu, 2021). The developed geopolymer formulation provided this fluid loss behavior without adding any fluid loss control additive.

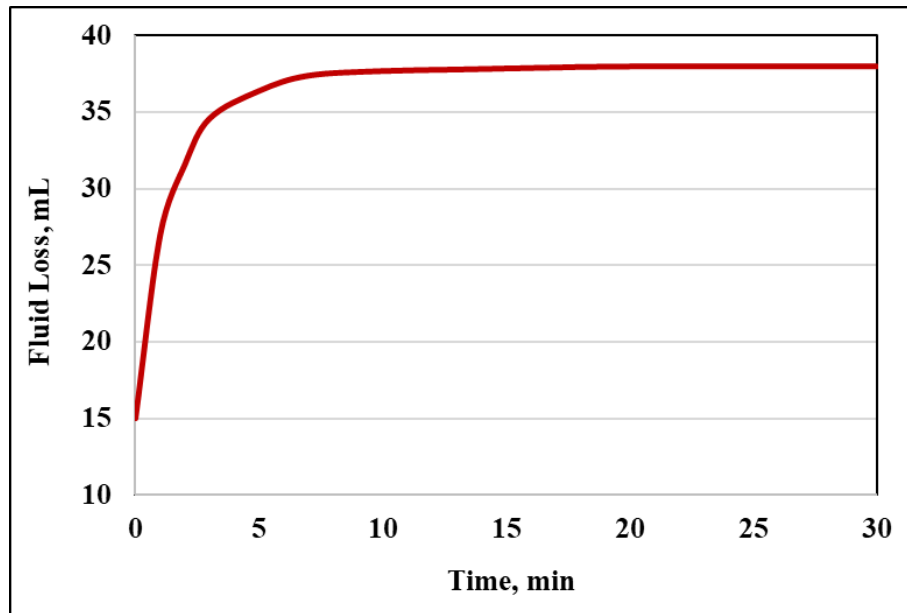


Figure 3.9 The effect of hematite on fluid loss for 30 min at 195 °F.

Table 3.4 Fluid loss ranges for different cementing applications (G. Liu, 2021).

Application	Fluid Loss
Horizontal well	< 50mL/ 30min
Risk of gas migration	30–50mL/ 30min
Casing cementing	100–300mL/ 30min
Low water content slurry (e.g., high-density slurry)	< 50 mL/ 30 min
Liner cementing	< 50mL/ 30min

3.3.5 Mechanical and Petrophysical Properties

Mechanical properties of the set geopolymers are considered an important part in well design. Two techniques were used to evaluate the compressive strength of the developed geopolymer hardened samples. Three cubes were crushed for each curing period (1 and 7 days), and the average was reported as the crush strength. For scratch test, cylindrical samples were used for scratch strength evaluation. The compressive strength values are

presented in **Figure 3.10** for both techniques. The compressive strength increased by 49% as calculated by the average values of both techniques for 1 and 7 days. The tensile strength was enhanced by 27.4% as the curing time increased from 1 to 7 days as shown in **Figure 3.11**. The improvement in both compressive and tensile strength with curing time indicated that the geopolymerization reaction continued for extended time but with smaller rate. When the slurry gets 50 psi compressive strength, it can serve as a barrier to fluid and gas flow. At 500 psi compressive strength, it is strong enough to be drilled or tagged. Although it is possible to drill cement with less than 500 psi, the industry utilizes this as a rule of thumb (G. Liu, 2021). The developed slurry got a 24 h compressive strength of at least 1,842 psi which is larger than some reported values in high density cementing programs in the Middle East.

Cement sheath flexibility is important in wells where cement is subjected to large stresses, e.g., steam injection, geothermal, and hydraulic fracturing. Long-term well integrity is provided by more flexible cements with lower YM and higher PR. Set cements should have a YM that is smaller than that of the surrounding formations. Smaller YM set cements may be preferable for unconsolidated strata than higher YM set cements (G. Liu, 2021). The developed geopolymer YM increased from 5.18 to 8.2 GPa and the PR decreased from 0.26 to 0.20 as curing time increased from 1 to 7 days, as shown in **Figure 3.12** and **Figure 3.13**. The developed geopolymer is more flexible than class G cement as presented in **Table 3.5**. Moreover, it possessed a YM that is lower than shale and consolidated formations and thus can be used adjacent to these formations as stated earlier by G. Liu, (2021). Generally, more flexible cements, those with lower YM and higher tensile strength, with enough compressive strength, tend to perform well when simulating sheath stresses.

The geopolymer YM increased with increasing strength that proved an agreement between strength results and the dynamic elastic properties of the developed system in this study. Petrophysical measurements such as porosity and permeability were conducted for the developed geopolymer system after drying the samples at 221°F for 24 hrs in an oven. The geopolymer system had a permeability of 0.01 mD and a porosity of 0.38.

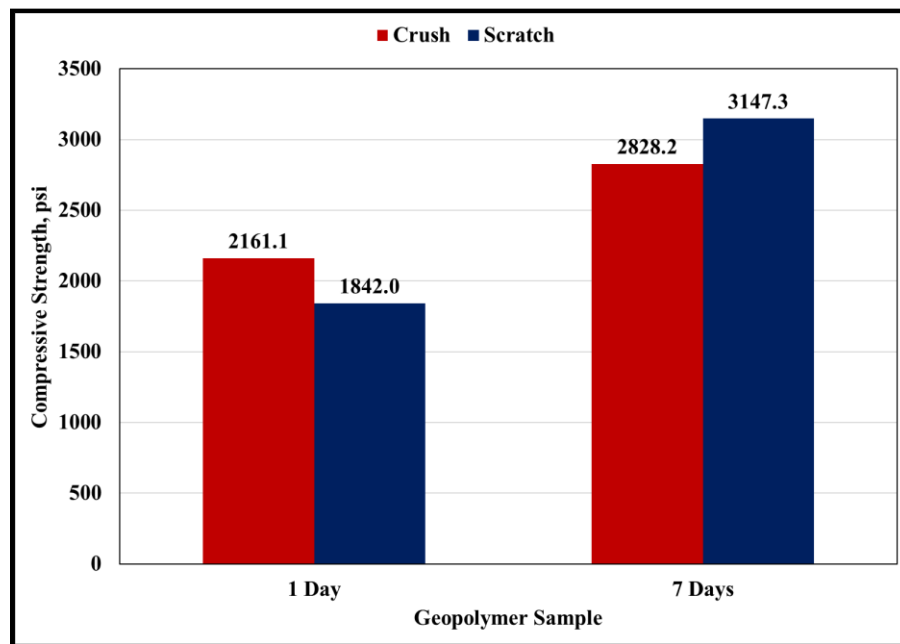


Figure 3.10 The compressive strength for different curing times at 292°F using scratch and crush tests.

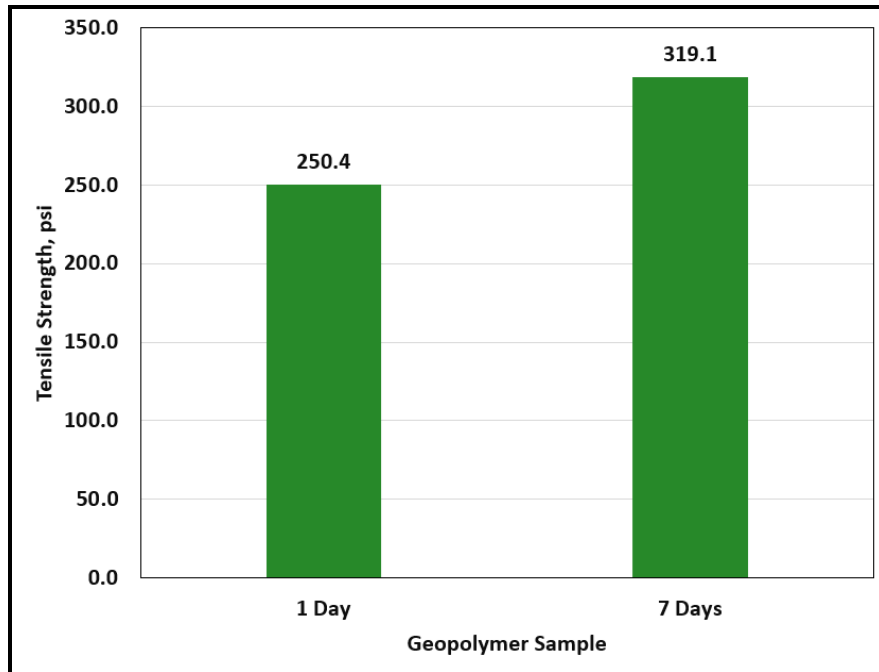


Figure 3.11 The tensile strength for different curing times at 292°F using the Brazilian test.

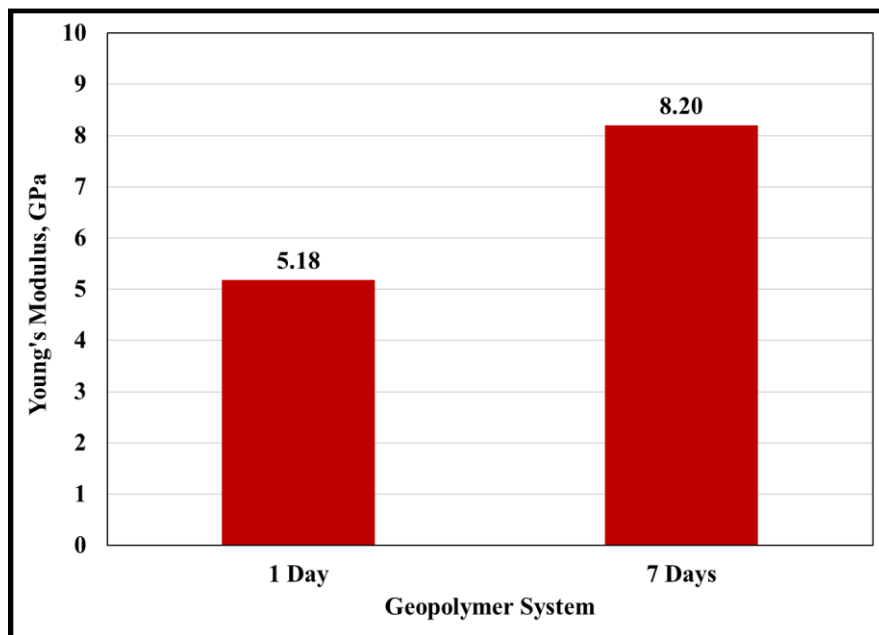


Figure 3.12 The effect of curing time on YM.

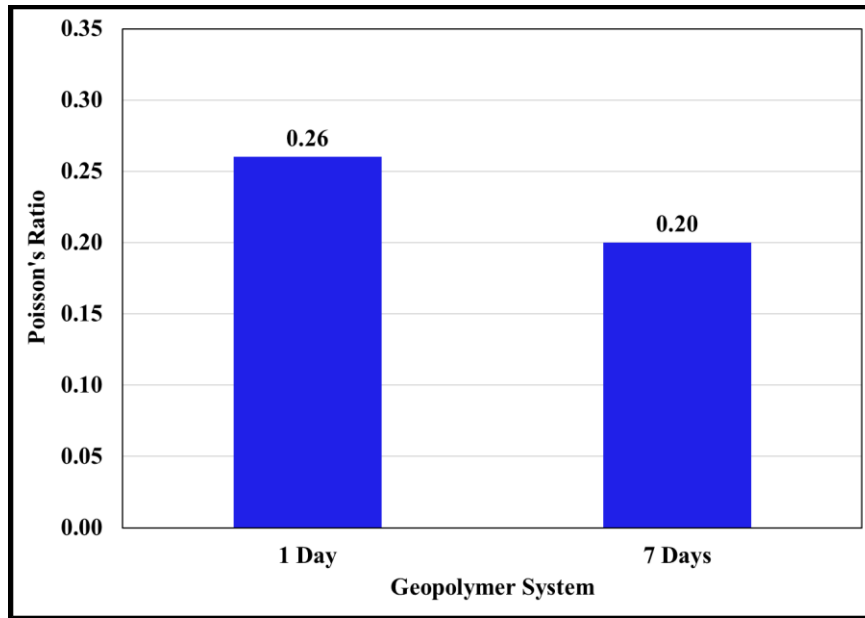


Figure 3.13 The effect of curing time on PR.

Table 3.5 Young's modulus and Poisson's ratio for some materials (G. Liu, 2021).

Material	YM (GPa)	PR
Shale	30.95	0.35
Consolidated sandstone	24.06	0.25
Unconsolidated sandstone	5.17	0.30
Class G cement	11.03	0.17
Extended cement systems	2.27	0.17
Flexible cement systems	1.99	0.22
The developed Geopolymer	5.18- 8.20	0.20- 0.26

3.4 Conclusions

This work introduced the first hematite-based class F fly ash geopolymer formulation for oil and gas well cementing. Unlike the other studies in the literature, this work used 4 M NaOH solution only as an activator that can reduce the overall cost. This work used fly ash (waste material) as aluminosilicate source which reduces the cementing cost, cement carbon emissions, and massive energy consumption and tackles the environmental issue related to fly ash disposal. Various properties of the designed slurry and hardened samples were evaluated using recommended practices with some modifications. The outcomes of this study can be summarized as follows:

- Increasing the hematite percentage significantly decreased the thickening time of geopolymers.
- A developed mixture of a retarder and a superplasticizer was introduced that enhanced the workability and prolonged the thickening time by 500%.
- The developed formulation achieved a low fluid loss without any fluid control additive (38 mL/30 min) that made it a good candidate for a wide range of cementing applications such as horizontal drilling, gas migration risk, and casing cementing that requires fluid loss <50 mL/30 min.
- The developed geopolymer slurry had a density of 17.5 ppg which can be used in high pressure well cementing and the developed slurry acted more like a power law fluid at low temperatures and more like a Bingham plastic fluid at high temperatures.

- The compressive and tensile strength were enhanced by increasing the curing time confirming the continuation of geopolymerization and the elastic properties of the developed geopolymer proved that it is more flexible than some cement systems.

CHAPTER 4

SYNERGY OF RETARDERS AND SUPERPLASTICIZERS FOR THICKENING TIME ENHANCEMENT OF HEMATITE BASED FLY ASH GEOPOLYMERS

4.1 Introduction

4.1.1 Geopolymers

Geopolymers are inorganic aluminosilicate forming long-range covalently bonded amorphous networks. Polymers are either organic such as carbon-based polymers or inorganic such as silicon-based polymers. Silicon-based polymers are mainly synthesized from rock-forming minerals of geological origin, thus the name: geopolymer. Moreover, some waste aluminosilicate materials such as fly ash and slag can produce geopolymers after activation by alkaline activators like sodium or potassium hydroxide and/or sodium or potassium silicates. After lime, used since ancient times, and OPC, used since the 19th century, geopolymers are generally regarded as a third-generation cement.

The synthesis of geopolymers offers considerable environmental and economic benefits, such as an 80 % or larger reduction in CO₂ emissions compared to OPC due to industrial wastes utilization and low energy consumption in geopolymers manufacturing. Technically, geopolymers possess high resistance to aggressive environments and high temperatures (Franzoni et al., 2021). Geopolymers is an evolving technology with different applications in the construction industry, but it is still in the research and development stage in the oil and gas industry. Various studies explored the use of different source materials, and activators and investigated their effects on the geopolymer properties for different well cementing applications (Adjei et al., 2022b, 2022a; Ahdaya and Imqam, 2019a; Eid et al., 2021; Paiva et al., 2018; Salehi et al., 2019, 2017b). It is obvious in the literature that developing high density geopolymer slurries for oil and gas well cementing requires more attention and work to fill this research gap.

4.1.2 High Density Cement

The cement slurry density should be high enough to balance the high-pressure formation fluids and prevent them from entering the wellbores, but not so high as to fracture weaker formations. It is necessary to increase cement slurry density while cementing high pore pressure formations. Reducing water content or/ and adding high specific-gravity solids are commonly used methods to increase slurry density. The common weighting agents used to increase slurry density include hematite and barite (Ahmed et al., 2022). Hematite is a reddish iron oxide ore (Fe₂O₃) having a specific gravity of approximately 5.02. The water requirement for barite (2.4 gal/100 lbm of barite) is relatively higher than that of hematite (0.36 gal/100 lbm hematite). The high-water content decreases the compressive strength of the cement and dilutes other chemical additives (Mitchell and Miska, 2011). High specific

gravity and lower water requirement of hematite make it a good weighting material for increasing cement slurry density. Weighting materials use in geopolymer cements is relatively new as few studies used only barite in small concentration to investigate its effect on compressive strength of fly ash geopolymers (Salehi et al., 2017b) . The authors concluded that barite improved compressive strength up to 7 days and did not show any improvement after this period. (Kanesan et al., 2018) studied the retarder effect on low, medium, and high-density barite based-fly ash geopolymers. The authors mentioned that retarders significantly affect the thickening times of low and medium slurries, but I slightly affected the high density geopolymer slurry.

4.1.3 Thickening Time

Thickening time is the period in which a cement slurry remains pumpable under wellbore conditions. Atmospheric or pressurized consistometers can be used to measure thickening time that can be defined as the elapsed time to reach 70 or 100 Bearden consistency unit (Bc). Some service companies consider 70 Bc as the pumpability limit (Rabia, 2002). As the slurry starts setting, the consistency then rises with an increasing slope until 100 Bc is reached. The point of departure is the point at which consistency starts to increase. The consistometer slurry cup design does not consider the fluid loss effect. Consequently, downhole thickening times may be decreased if a small or no fluid loss control is specified in slurry design (Erik B. Nelson and Guillot, 2006; Rabia, 2002). A right-angle set (RAS) cement is a slurry with a thickening time chart that rapidly transitions from pumpable (horizontal) to set (vertical), resembling the right-angle shape. The fast hydration that occurs in RAS slurries generates heat over a short period of time, which could develop micro-annuli (Rabia, 2002).

Understanding the cement slurry characteristics as it sets can be done using the thickening time chart. The curve indicates secondary, tertiary, or quaternary gelation as well as early gelation. When assessing early gelation and the development of compressive strength, static gel strength tests are helpful (G. Liu, 2021). The typical pumping period for cement slurries in deep wells is 3 to 4 h. The fluids circulated during drilling cool the formations, therefore most geothermal wells are not cemented under geothermal conditions, except for hot, dry rock completions with circulating temperatures as hot as 500°F (Carden et al., 1985). The design of cement systems with sufficient thickening time is often not an issue because the maximum circulation temperature during cement jobs rarely exceeds 240°F (E.B. Nelson and Guillot, 2006). Hematite has been found to have a minimal effect on the thickening time and compressive strength of cement at the concentrations that are typically used (Mitchell and Miska, 2011). On the other hand, the effect of hematite on the thickening time of geopolymers was never studied; thus, one of the aims in this work is to examine the effects of hematite on FFA based geopolymer cements.

4.1.4 Retarders and Superplasticizers

Retarders are the additives used to increase the thickening time of cement slurries. Some retarders are basically a mixture of different retarders that optimize the performance for extended temperature ranges. Temperature is one of the principal factors of the retardation reaction in cement slurries. In the hours following a cement job, a retarder is consumed, allowing the cement to set. Every retarder has a temperature range where it performs best. The most efficient retarder should be chosen for BHCT and bottom hole pressure conditions to which it will be subjected (G. Liu, 2021).

Adsorption, precipitation, nucleation, and complexation are the four main theories of retardation mechanisms. The main retarder types are lignosulfonates, hydroxycarboxylic acids, saccharide compounds, cellulose derivatives, organophosphonates and some inorganic compounds such as zinc oxide, lead oxide, some acids, and salts. The sodium and calcium salts of lignosulfonic acids are the retarders for well cements that are most often utilized. Due to their origin in wood pulp, lignosulfonates are polymers that are often not processed and include varying levels of saccharide components (E.B. Nelson and Guillot, 2006).

In order to improve the rheology of suspensions, such as in concrete applications, superplasticizers (SPs), often referred to as high range water reducers, are utilized in those situations where well-dispersed particle suspension is required. Their inclusion permits a decrease in the water to cement ratio without adversely affecting the mixture's workability. SPs have been increasingly used in the construction industry (Xu et al., 2000). Superplasticizers can generally be divided into four categories: sulfonated synthetic polymers, carboxylate synthetic polymers, and synthetic polymers with mixed functionality cementitious substances (Nkinamubanzi and Aïtcin, 2004). Other products based on polycarboxylic ethers are also available, but sulfonated naphthalene condensate or sulfonated melamine formaldehyde have traditionally been used to make SPs. Cross-linked melamine- or naphthalene-sulfonates, referred to as polymelamine sulfonate (PMS) and polynaphthalene sulfonate (PNS) are prepared by crosslinking of the sulfonated monomers using formaldehyde or by sulfonating the corresponding crosslinked polymer (Mollah et al., 2015).

The flocculated cement particles are dispersed by naphthalene and melamine sulfonate-based superplasticizers via an electrostatic repulsion mechanism. When the active ingredients are adsorbed onto cement particles, they give them a negative charge, which causes them to repel one another. Organic polymers include lignin, naphthalene, and melamine sulfonate superplasticizers. The cement particles are encircled by lengthy molecules, which give them a strong negative charge that makes them repel each other. In contrast to sulfonate-based superplasticizers, polycarboxylate ether superplasticizers (PCE) or simply polycarboxylate (PC) provide cement dispersion by steric stabilization. Polysulfonate-based and polycarboxylate-based superplasticizers have a good compatibility with high alkali and sulphate cements, while polysulfonate-based superplasticizers are poorly compatible with low alkali cements (Lu et al., 2019).

Weighting agents used in geopolymers are relatively a new area in oil and gas well cementing. The first objective of this study is to investigate the effect of hematite as a weighting agent on FFA geopolymer pumpability for oil and gas well cementing. The second objective is to find a solution to increase the thickening time of the high-density hematite based FFA geopolymers for possible use in well cementing. Then, the effect of the proposed mixture of additives on slurry rheology was evaluated to ensure good mixability and reasonable pumping requirements.

4.2 Materials and Methodology

4.2.1 Materials

The materials used in this study were FFA as aluminosilicate source material, hematite as a weighting material, sodium hydroxide as an activator, a PNS superplasticizer, a modified lignosulfonate-based retarder and a defoamer. The specific gravities (SG) of the FFA and hematite were 2.10 and 5.05, respectively. The particle size distributions (PSD) of FFA and hematite were evaluated using a laser diffraction particle size analyzer as shown in **Figure 4.1**. PSD results showed that x_{50} was 21.08 and 21.54 μm for FFA and hematite particles, respectively. **Figure 4.2** presents the oxide composition of FFA used in this study obtained by the Bruker M4 Tornado X-ray fluorescence (XRF). XRF confirms that FFA has substantial quantities of silica (SiO_2) and alumina (Al_2O_3), as shown in **Figure 4.2**, which play a key role in geopolymerization reaction. SEM, as depicted in **Figure 4.3**, demonstrates that FFA particles are spherical while hematite particles have irregular shapes.

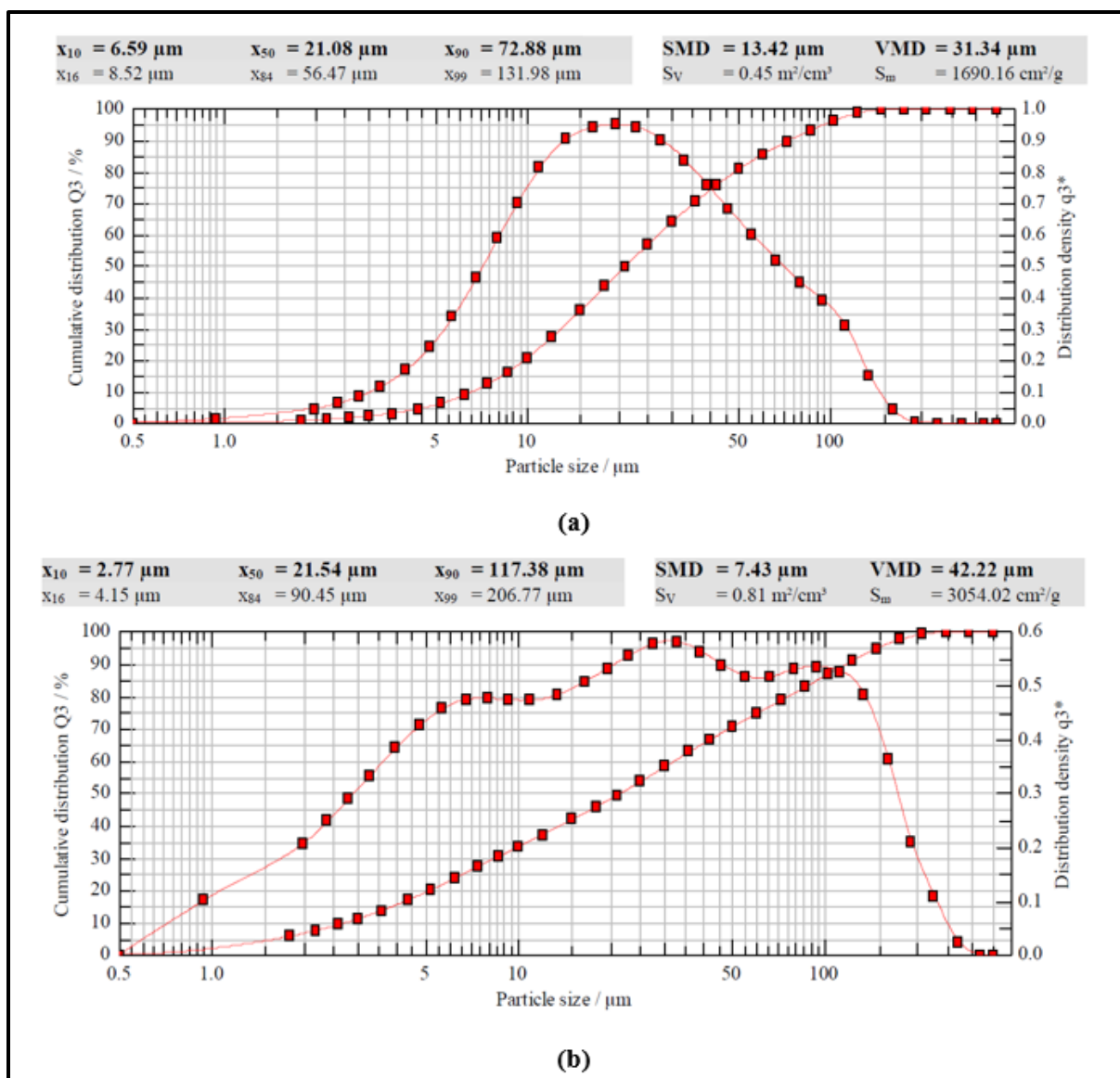


Figure 4.1 PSD of FFA (a) and hematite (b).

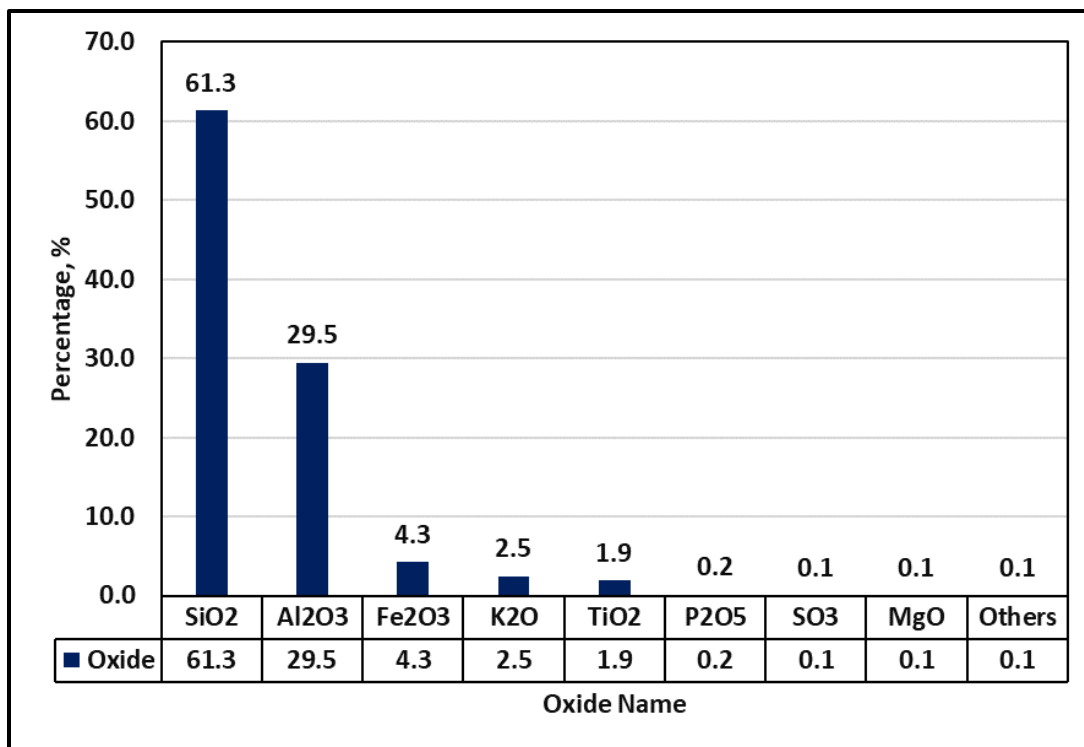


Figure 4.2 XRF of FFA used in this study.

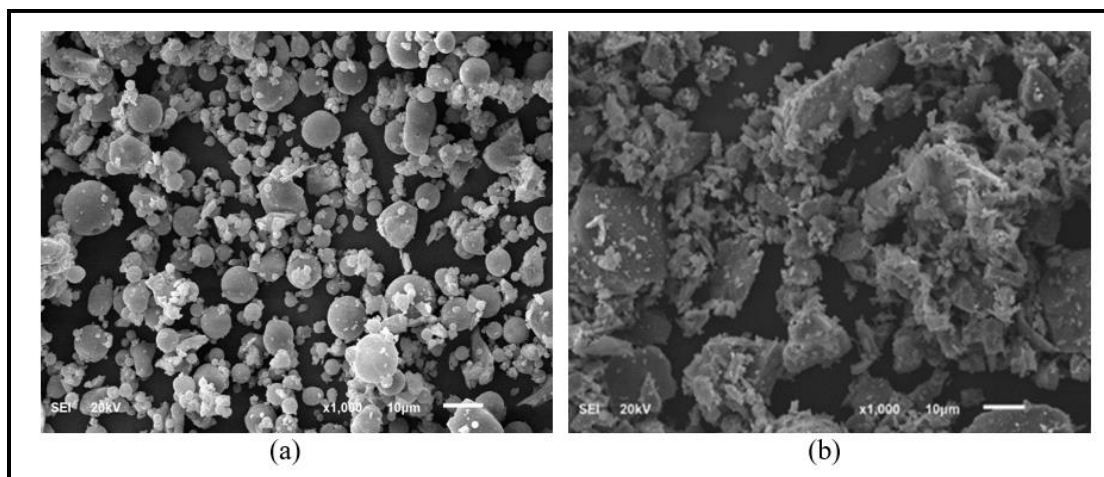


Figure 4.3 SEM images for FFA (a) and hematite (b).

4.2.2 Methodology

Slurry Preparation and Mix Design

NaOH solution was prepared by dissolving NaOH pellets in distilled water using a magnetic stirrer and then left to cool down at least for 24 h before experiments. FFA was sieved to ensure particles' size lower than 100 μm . Two different processes (wet and dry) can be used to prepare geopolymer slurries (Salehi et al., 2017b). In wet process, a superplasticizer and/or retarder are mixed with activation solution for 2 min at a high shear rate (12,000 RPM) using a constant speed mixer. A binder such as FFA was then added and mixed with premixed solution at a high shear rate for another 2 min. The wet process approach was followed to prepare the geopolymer slurries in this study. In the early stage, different types of retarders, superplasticizers, and combinations of both were tested until selecting the proposed mixture that gave the highest thickening time. The methodology went through mixability check, rheology evaluation and thickening time.

All the geopolymer formulations used in this study contained FFA (100% BWOB), 4 M NaOH solution (56% BWOB), and a defoamer (0.0164% BWOB). Firstly, hematite was added in three percentages (25, 50 and 75% BWOB) to study its effect on the thickening time. Then, the lignosulfonate-based retarder was added to the 75% hematite formulation in two concentrations (5% and 10% BWOB). The retarder effects on rheology and thickening time were assessed. After that, the PNS superplasticizer effects on thickening time and rheology were evaluated using two concentrations (5% and 10% BWOB). Finally, a mixture of a retarder and a superplasticizer (5% BWOB each) was tested.

Rheology and Thickening Time

The viscometer was used to evaluate rheology at atmospheric conditions. The readings were measured in ascending and descending orders and the average values were reported. Then, the observed data were checked to know which model provides the best fit for the data. The thickening time test was conducted at 195 °F to estimate how long the developed geopolymer would remain pumpable. The rheology and thickening time measurements were run at least three times using different devices to ensure reliability and reproducibility of the results.

Mechanical Properties

After mixing, an atmospheric consistometer was used for conditioning the geopolymer slurries at 170°F and 150 RPM for 30 min. The slurries were poured into cylindrical molds and placed in a water bath at 200°F for 24 h. Scratch test with sonic mode device was used to measure the unconfined compressive strength (UCS) and the dynamic elastic properties such as Poisson's ratio and young's modulus. The elastic properties were estimated using sonic waves (compressional and shear). The scratch or cutting test entails using a cutter to scratch a number of sequential grooves on the surface of a sample. The idea of the scratch test is to regulate and keep track of the continuous shearing action caused by the motion of a diamond cutter on the surface of core samples. The force acting on the cutter is used to calculate the continuous profile of rock strength (UCS) along the sample. The ultrasonic test calculates how long it takes a pressure wave to travel between two ultrasonic probes. The pressure wave velocities can be calculated from the travel times. The scratch test device with sonic mode is shown in **Figure 4.4**.

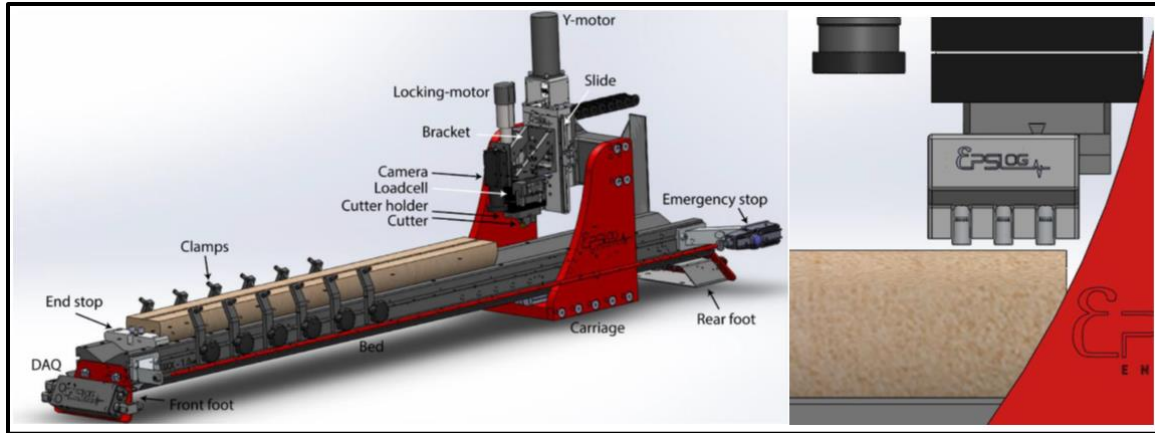


Figure 4.4 Scratch test device (left) and the sonic mode probes (right).

4.3 Results and Discussion

4.3.1 Thickening Time

Hematite Effect

It is obvious that increasing hematite percentage significantly reduced the thickening time at 195°F as shown in **Figure 4.5**. The thickening time decreased from 430 to 80 min with increasing hematite from 25 to 75 % BWOB. Moreover, the thickening time curve became more like right angle set by increasing the hematite percentage. The reduction in the thickening time can be attributed to the explanation given by Essaidi et al. (2014). The authors mentioned that Si-O-Al or Si-O-K bonds form faster in the consolidated material when kaolin is calcined, and iron oxide is present in the metakaolin based geopolymers (Essaidi et al., 2014).

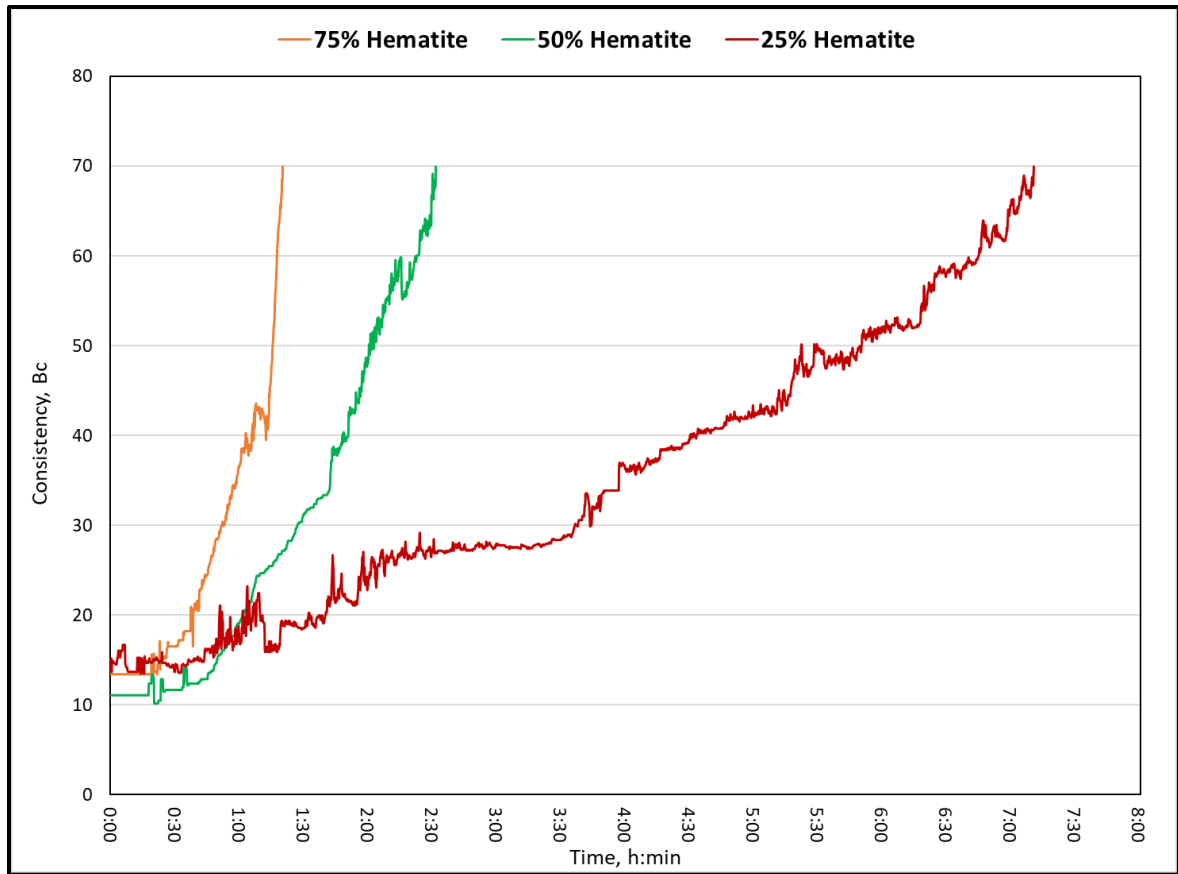


Figure 4.5 The effect of hematite on thickening time at 195°F.

Superplasticizer and Retarder Effects

Increasing the thickening time of the high-density hematite based FFA geopolymers is essential for well cementing. The effect of each additive on thickening time was individually investigated in 2 concentrations (5% and 10% BWOB). The modified lignosulfonate-based retarder increased the thickening time from 80 to 119 and 192 min for 5% and 10% retarder concentration, respectively as shown in **Figure 4.6**. The PNS superplasticizer increased the thickening time from 80 to 99 and 393 min for 5 % and 10% superplasticizer concentration, respectively as presented in **Figure 4.6**. It was found that a mixture of a PNS superplasticizer (5% BWOB) and modified lignosulfonate-based retarder (5 % BWOB) increased the thickening time from 80 to 580 min at 195°F. Adding PNS

superplasticizer alone decreased the viscosity in the beginning, and this can be confirmed by the low initial consistency as compared to other additives as shown in **Figure 4.6**. It is important to visually check the cement slurry and the consistometer pedal after the thickening time test as gelling around the pedal may result in misleading values. **Figure 4.7** shows the slurry at the end of the test and confirms that the slurry can be still pumped after the test.

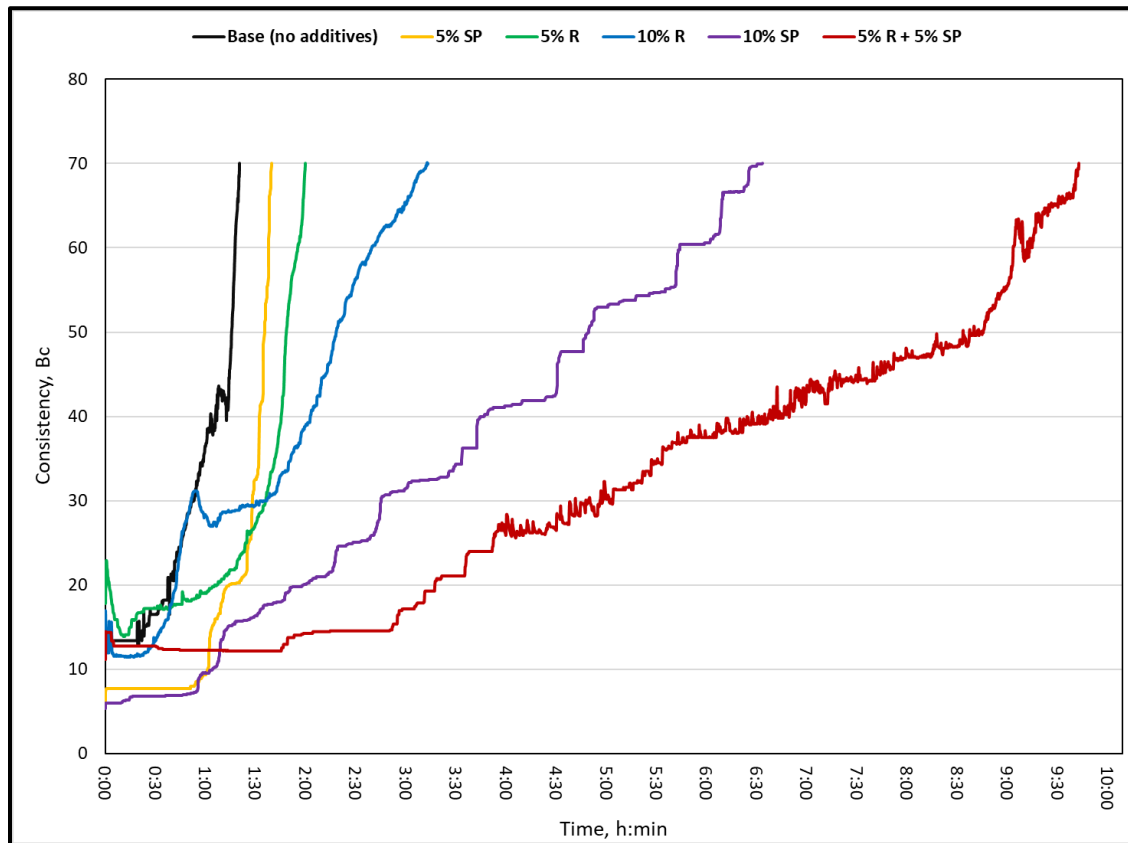


Figure 4.6 The effect of the proposed additives on thickening time at 195°F.

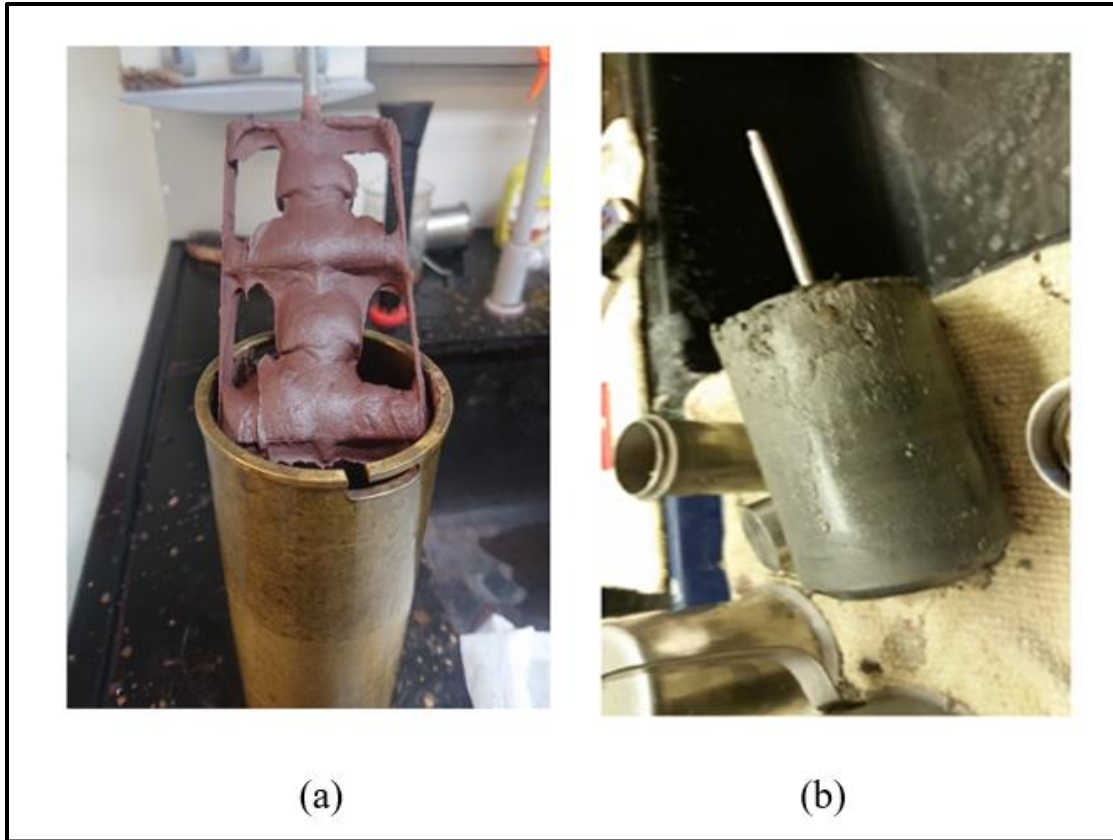


Figure 4.7 The geopolymer slurry at the end of the thickening time test in this study (a) and a gelling example (b) published by Salehi et al. (Salehi et al., 2018).

4.3.2 Rheological Properties

Although the primary objective of this study is to find a solution for thickening time challenge associated with high density hematite-based geopolymers, the effect of the proposed mixture on slurry rheology should be assessed. Rheological properties evaluation is required as it affects pumping requirements, mixing, and drilling fluids removal efficiency. The effect of the developed mixture of the PNS superplasticizer and the modified LS retarder on rheology was evaluated and compared to the performance of each additive (5% BWOB) when used on its own. The shear stress versus shear rate results of the three formulations are presented in **Figure 4.8**. The Bingham plastic model offered the

best fit for the measured data as indicated by a high coefficient of determination (R^2) of 0.999 as shown in **Figure 4.8**. All formulations had shear thinning behavior because viscosity decreases as shear rate increases as shown in **Figure 4.9**. The developed mixture produced a formulation with a plastic viscosity of 224.6 cP, which, as shown in **Figure 4.10**, falls between 159.4 cP and 344.6 cP for the superplasticizer and the retarder, respectively. Adding the PNS superplasticizer alone adversely affected the gel strength as the 10 min (8.1 lbf/100 ft²) value was lower than the 10 sec one (9.2 lbf/100 ft²) unlike other formulations. The 10 sec gel strength values for the 3 formulations were close. The developed mixture introduced a formulation with the highest 10 min gel strength value as shown by **Figure 4.11**. The yield point of the developed mixture formulation was 5.2 lbf/100 ft² that can be considered acceptable as mentioned by Rabia (Rabia, 2002). Rabia (Rabia, 2002) stated that horizontal sections cementing is generally more challenging than vertical sections and yield point for cement slurries used in horizontal sections should not be lower than 5 lbf/100 ft².

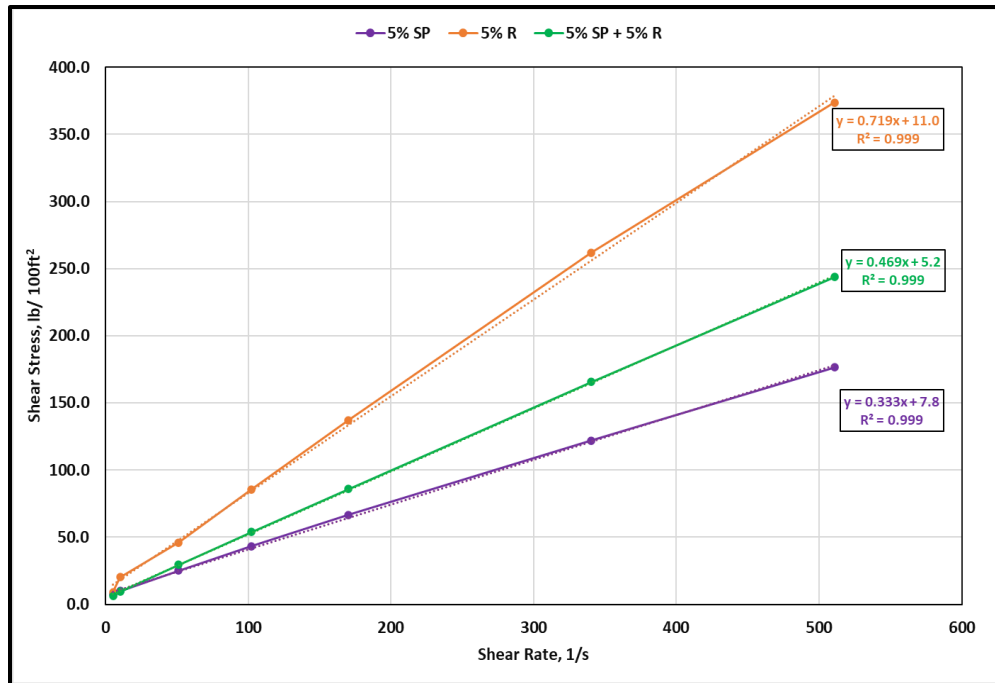


Figure 4.8 Shear stress vs. shear rate for the tested geopolymer slurries.

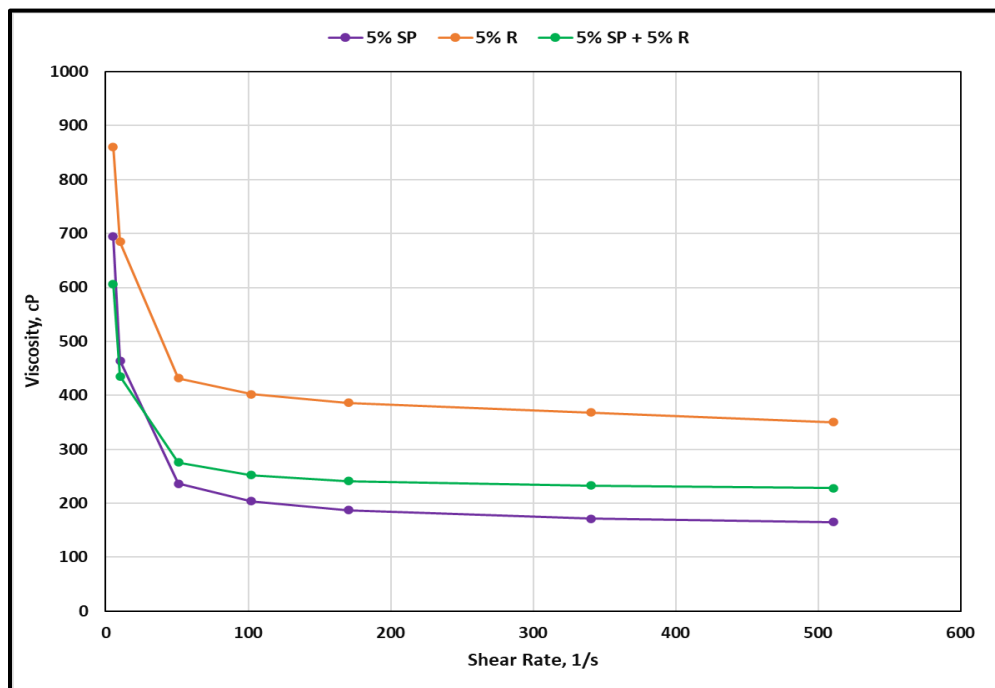


Figure 4.9 Apparent viscosity vs. shear rate for the tested geopolymer slurries.

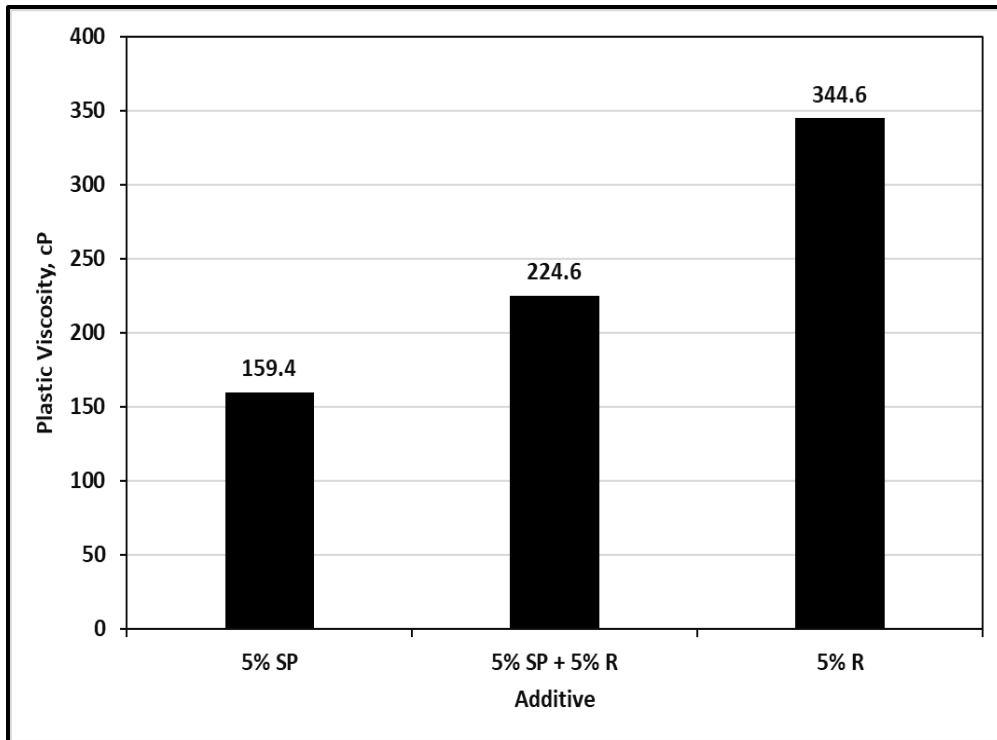


Figure 4.10 Plastic viscosity for the tested geopolymer slurries.

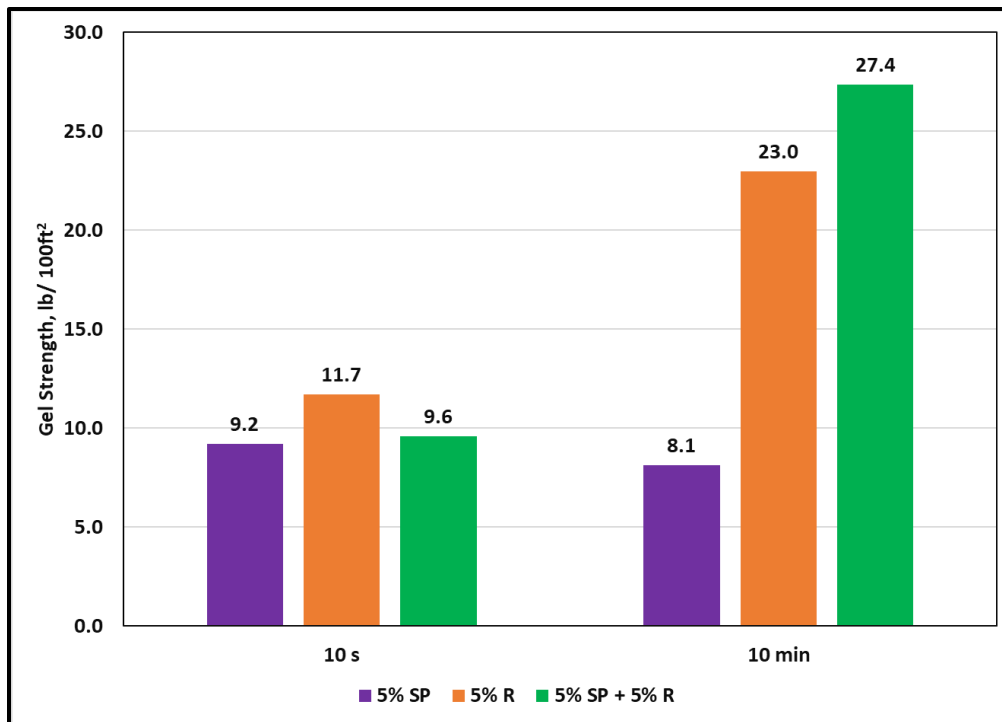


Figure 4.11: Gel strength for the tested geopolymer slurries.

4.3.3 Mechanical Properties

The effects of the developed mixture containing 5% BWOB of the PNS superplasticizer and 5% BWOB of the modified LS retarder on the geopolymer mechanical properties were investigated and compared to the individual effects of each additive (5% BWOB). The developed mixture formulation possessed the highest 24 h UCS (1,015 psi) as compared to the retarder formulation (928 psi) and the superplasticizer formulation (479 psi), as shown in **Figure 4.12**. Moreover, the developed mixture-based sample had a Poisson's ratio of 0.25 and a young's modulus of 4.66 GPa. **Figure 4.13** shows the results of the dynamic elastic properties (PR and YM) for different additives. All the samples had a PR that is higher than class G cement and a YM that is lower than class G cement as reported by Liu (G. Liu, 2021). These dynamic properties proved that the developed high-density FA geopolymer systems are more flexible than class G cement in terms of higher PR and lower YM. Although, using only superplasticizer provided the lowest YM, a good PR and reasonable rheological properties, it is not recommended to use it alone as it gave low UCS and short thickening time.

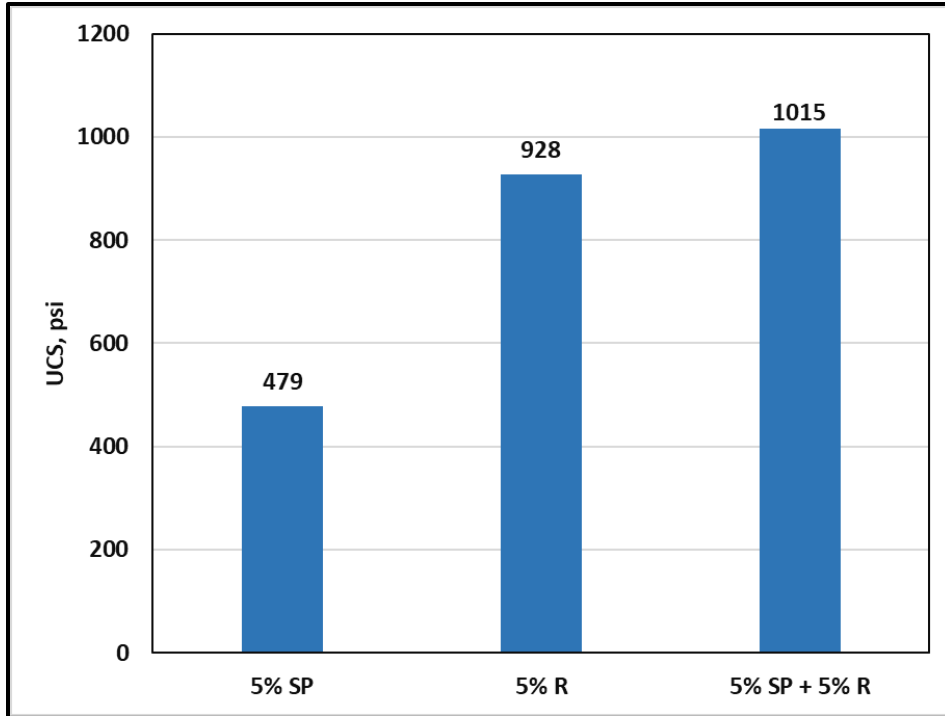


Figure 4.12: The 24 h UCS for the tested geopolymer slurries after curing at 200°F.

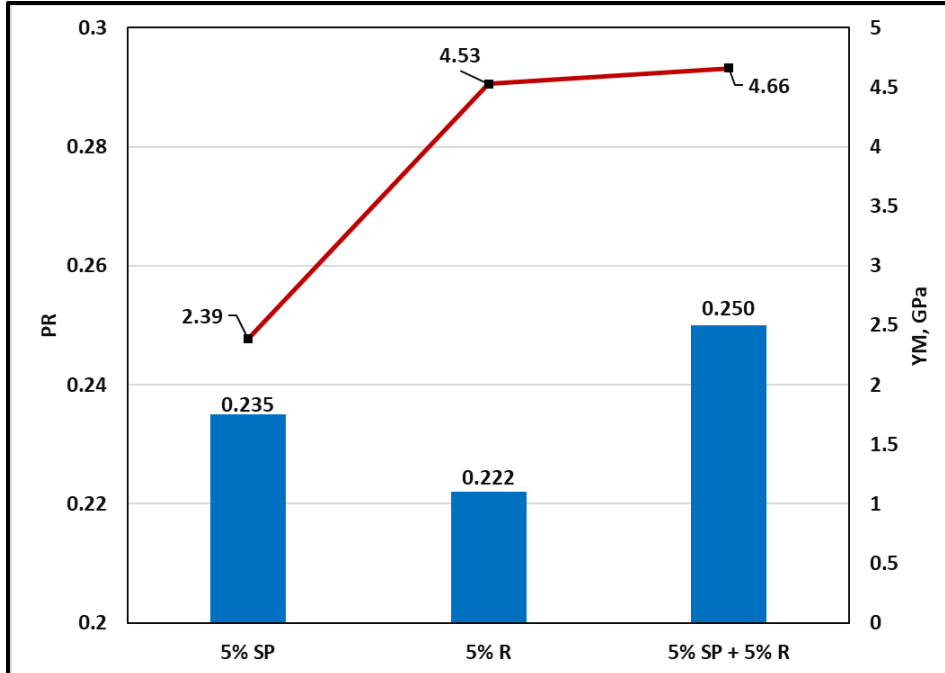


Figure 4.13 PR and YM for the tested geopolymer systems cured at 200°F.

4.4 Conclusions

This study addressed the problem of low thickening times and pumpability issues encountered while using high-density hematite based FFA geopolymers. This study introduced a solution to thickening time challenges at high temperatures using a mixture of a modified lignosulfonate retarder and a PNS superplasticizer. The effects of this mixture on thickening time, rheological and mechanical properties were evaluated. The outcomes of this work can be summarized as follows:

- The thickening time of the hematite based FFA geopolymer decreased by 81.4% with increasing hematite from 25 to 75% BWOB.
- The proposed mixture increased the thickening time from 80 to 580 min at 195°F for the 75 % hematite geopolymer.
- The proposed mixture developed a geopolymer with the highest UCS and PR as compared to other formulations using each additive individually.
- The mixture decreased the plastic viscosity of the high density geopolymer slurry by 29% which facilitates mixing and pumping.

CHAPTER 5

MIXED MICROMAX AND HEMATITE-BASED FLY

ASH GEOPOLYMER FOR HEAVY-WEIGHT WELL

CEMENTING

5.1 Introduction

OPC introduces some technical and environmental challenges such as high greenhouse gases (GHG) emissions and consumes massive energy during its production. These concerns persuaded the researchers to search for alternative materials to overcome the technical challenges and to provide eco-friendly cement systems. It is obvious from the literature that some researchers flew in the direction of adding new materials to OPC to enhance its properties (Adjei et al., 2022a; Ahmed et al., 2020, 2018; Bageri et al., 2021; Mahmoud et al., 2019; Mahmoud and Elkatatny, 2020b, 2020c). Other researchers tried to find new alternatives to OPC which can be more eco-friendly and can overcome the technical drawbacks of OPC such as geopolymers (Adjei et al., 2022b; Salehi et al., 2019, 2018).

Currently, a cost-effective and ecofriendly substance has emerged that has qualities comparable to OPC; this substance is termed as geopolymer. Their raw materials are of geological origin and geopolymer formation continues via inorganic polymerization and

condensation, so they are also called geological polymers (Davidovits, 1994). Prof. J. Davidovits coined the term geopolymer in 1978, describing it as a green cementitious substance that is free of cement. As it contains a 3D structure of cross-linked polysialate chains, these were previously regarded a particular case of soil cement and referred to as geocements (Davidovits, 1991b). Geopolymers can be formed by natural substances and/or waste materials as source materials activated by alkali or acids (Ahdaya and Imqam, 2019a). Geopolymer production is cleaner, and the source materials do not consume that much energy as compared to OPC (Davidovits, 2010; Patel and Shah, 2018; Singh et al., 2018; Worrell et al., 2003). The Si and Al in the aluminosilicate substances dissolve after contacting the alkali solutions to form monomers and oligomers going through polycondensation to form a 3D structure, called, polysialate, polysialte-siloxo, and polysialate-disiloxo (Amritphale et al., 2019; Vrålstad et al., 2019).

Cement slurry is designed depending on the existing wellbore conditions of pressure and temperature and cement job type. Most research has been conducted on not just searching for an alternative to OPC due to its environmental concerns during production but most significantly on confirming if the drawbacks of OPC can be mitigated by geopolymers. Four main research topics were investigated in the literature: applications in harsh environments, application in P&A, compatibility with mud, and temperature effects (Adjei et al., 2022b; Khalifeh et al., 2015; Liu et al., 2017b; Mahmoud et al., 2014; Rahman et al., 2020; Salehi et al., 2017a; Sugumaran, 2015).

In the petroleum industry, high pressure high temperature (HPHT) wells drilling represents a new frontier. The exploration and production industry looks for new resources to meet the rising demand of energy across the world and some of these resources are buried deeper

in the earth's crust. Over half of known petroleum reserves in the US are located below 14,000 feet subsea. HPHT conditions will be encountered as we dig further into the strata. As a result, businesses are obligated to fulfill or exceed a wide range of technical constraints as well as environmental, health, and safety regulations (Shadravan and Amani, 2012). Special challenges are associated with cementing operation in HPHT wells owing to the physical and chemical changes under high pressure and temperature. These harsh conditions can introduce challenges not only while placement but also after cement setting (Moe et al., 2003; Wray et al., 2009). Decreasing water content is the easiest way to increase the slurry density (Michaux et al., 1990). However, the American petroleum institute (API) advises a water-to-cement ratio of 44% for primary cementing (API, 2019). Water content reduction has challenges such as attaining sufficient fluid loss control, appropriate rheology, and no settling of the solid particles (Ahmed et al., 2022). Slurry bridging occurs due to uncontrollable fluid losses. Solid particle settling results in nonuniform compressive strength and bonding along the length of cemented section (Erik B. Nelson and Guillot, 2006).

Therefore, using weighting materials is required to achieve a higher density. Using weighting materials in geopolymers research area for oil and gas industry is relatively new. These attempts used only barite to study its effects on compressive strength and thickening time. (Kanesan et al., 2018) measured the thickening time of barite-based FA geopolymer at 140°F and 2,000 psi using a combination of 8 M NaOH solution and Na_2SiO_3 . The authors mentioned that retarder effect was major in low and medium density slurries, but it had a minor effect on high-density slurry thickening time. Salehi et al. (Salehi et al., 2017b) investigated the impact of adding 15% BWOC barite on compressive strength of

FA geopolymers. Barite improved strength up to 7 days of curing and could not enhance the strength after 7 days. It is clear from the literature that a few trials were performed using barite with geopolymers for well cementing applications. The big particles of weighting agents may cause particles sedimentation (Malyshev et al., 2013). The sedimentation problem in slurries creates a heterogenous cement column which is not favorable for strength and zonal isolation (Erik B. Nelson and Guillot, 2006).

Geopolymer technology is still evolving in the petroleum industry, and it has not seen a full-scale deployment in well cementing. Providing moderate to high density geopolymer cement systems using various weighting materials is rarely investigated in the literature. This study introduces the first usage of Micromax in geopolymer slurries for oil well cementing. The first goal in this work was generating flowable heavy weight geopolymer formulations with appropriate rheology and appropriate thickening time. The second goal was to solve the sedimentation issue associated with hematite based geopolymer by introducing a mixture of Micromax and hematite. The sedimentation of the weighting materials was investigated by the API method. In addition, various properties such as rheological properties, filtrate loss, strength (compressive and tensile), permeability, elastic properties were also evaluated for hematite based and mixed Micromax and hematite geopolymer systems.

5.2 Materials and Methods

5.2.1 Materials

The materials used in this work were Class F fly ash as a source material, hematite and Micromax as weighting materials, 4 M NaOH solution as an activator in addition to other additives utilized to enhance geopolymer characteristics and make it usable under wellbore conditions. The additives comprised retarder, retarder intensifier, deformer, and superplasticizer. The specific gravities (SG) of the used materials are listed in Table 1. The particle size distributions (PSD) were obtained using the laser diffraction particle size analyzer as shown in **Figure 5.1** and summarized in **Table 5.1**. The results showed that the median size of FFA, hematite and Micromax were 19.35, 21.54 and 1.98 μm respectively. **Figure 5.2** and **Figure 5.3** show the elemental composition of hematite and Micromax, respectively used in this work obtained by X-ray fluorescence (XRF). XRF results confirm that hematite has a high iron amount (around 95%) and X-ray diffraction (XRD) showed that it contained 100% hematite. XRF also showed that FFA had considerable amounts of silica (SiO_2) and alumina (Al_2O_3), as listed in **Table 5.2**, which play a vital role in geopolymer formation. The scanning electron microscope (SEM) results, as shown in **Figure 5.4**, show that FFA and Micromax particles are more like spheres and hematite particles possess irregular shapes.

Table 5.1 The SG and PSD results of FFA, hematite and Micromax.

	FFA	Hematite	Micromax
SG	2.25	5.05	4.68
D ₁₀ (μm)	2.38	2.77	0.55
D ₅₀ (μm)	19.35	21.54	1.98
D ₉₀ (μm)	60.00	117.38	6.05

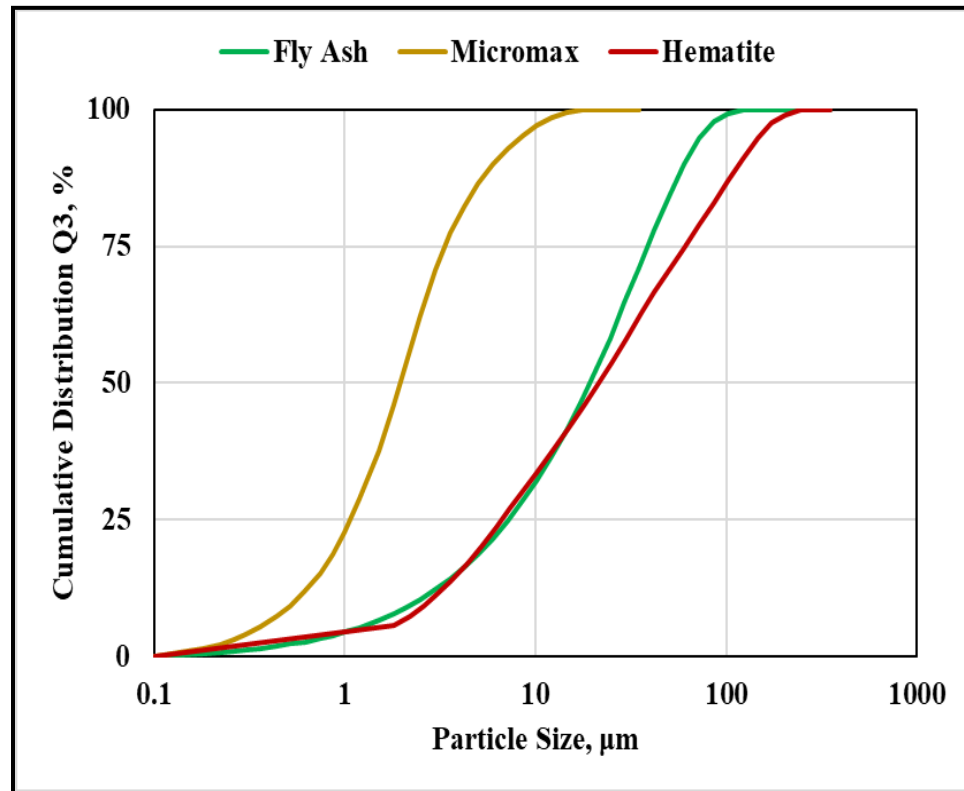


Figure 5.1 PSD results of the Class F FA, hematite and Micromax.

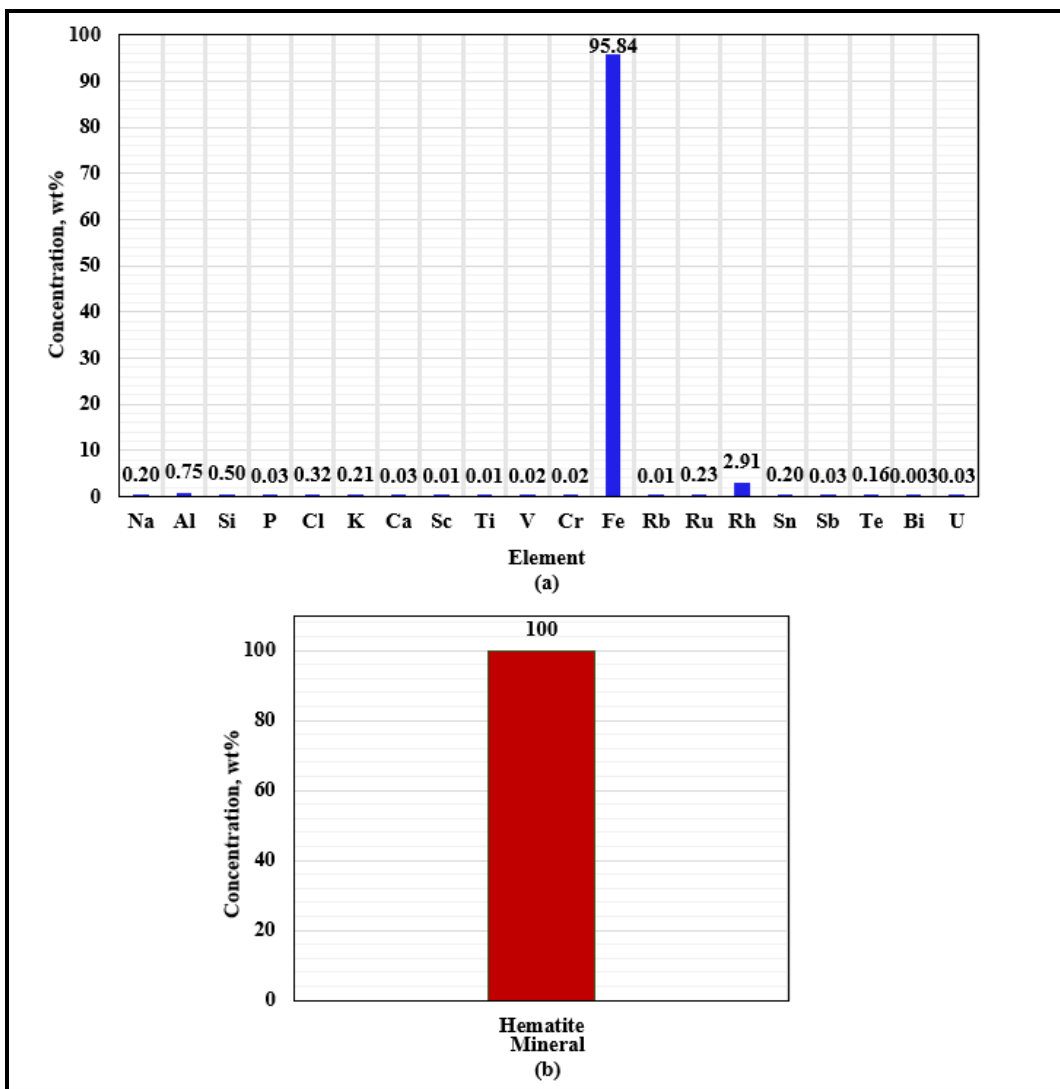


Figure 5.2 XRF elemental composition of hematite (a) and the XRD of the sample (b).

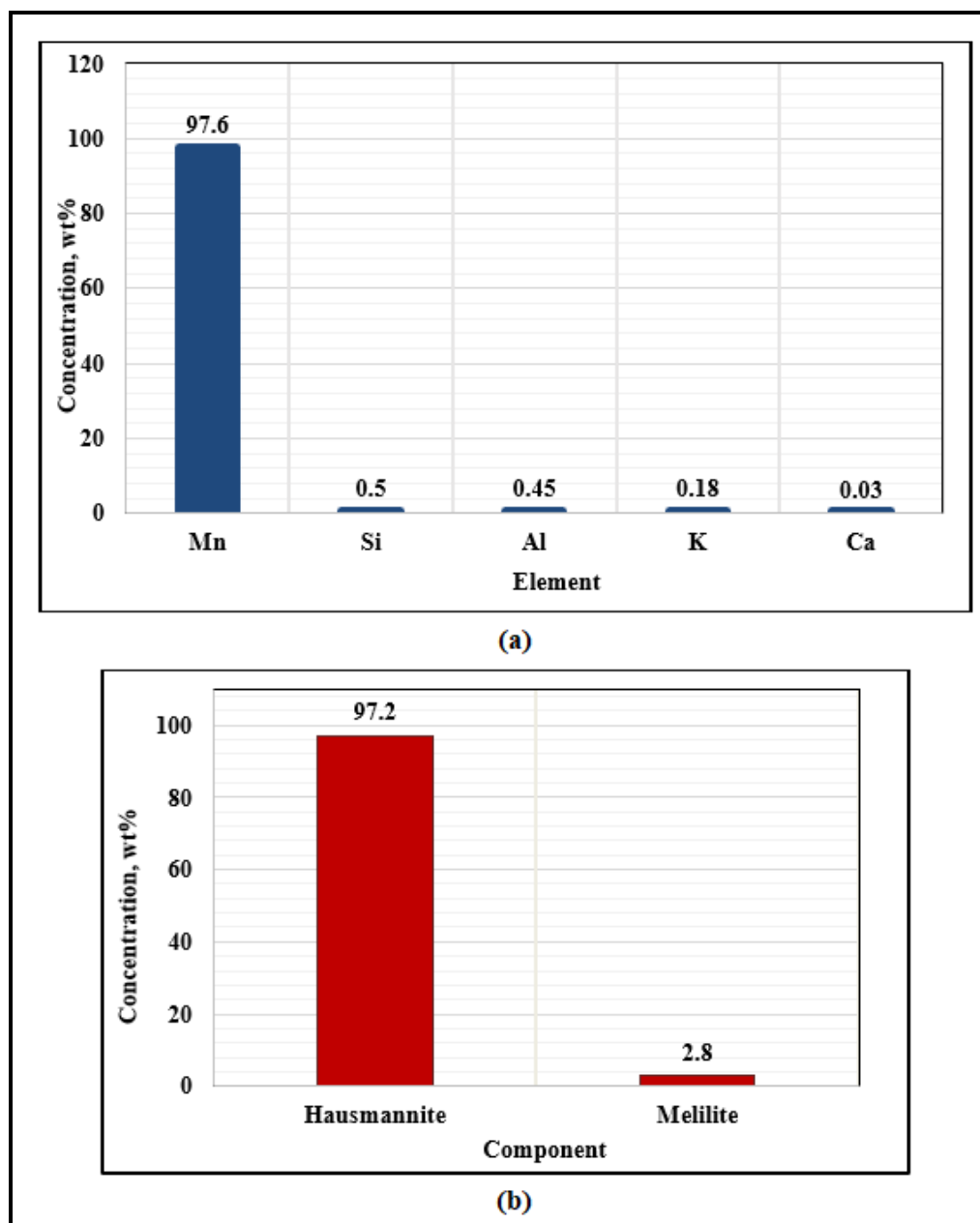


Figure 5.3 XRF elemental composition of Micromax (a) and the XRD of Micromax (b).

Table 5.2 XRF results of FFA used in this study.

Oxide	Percentage, %
SiO ₂	55.92
Al ₂ O ₃	29.54
CaO	5.49
Fe ₂ O ₃	4.93
TiO ₂	1.91
K ₂ O	1.66
SO ₃	0.39
Others	0.17

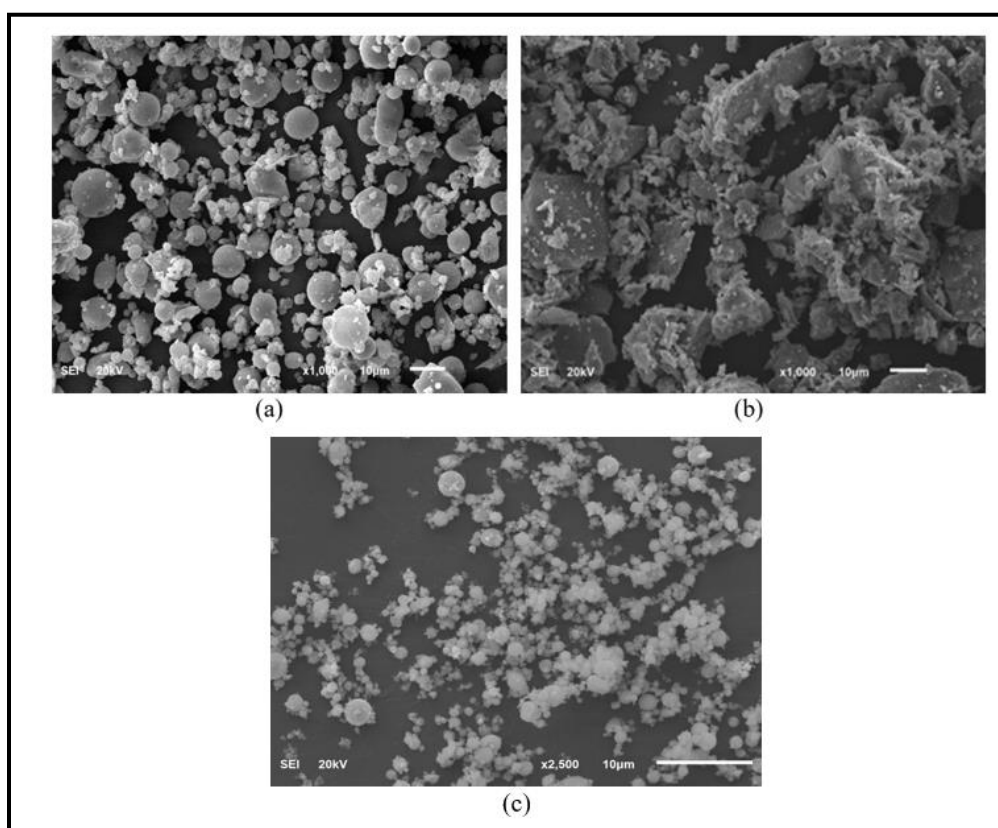


Figure 5.4 SEM images for FFA (a), hematite (b) and Micromax (c).

5.2.2 Methods

This part discusses the methods followed to perform this work. It began with collection, characterization, and preparation of materials. Then, the slurry ingredients were determined based on mixability, pumpability and rheology. Afterwards, the hardened geopolymer samples were evaluated for mechanical and elastic properties. **Figure 5.5** summarizes the methods followed in this study.

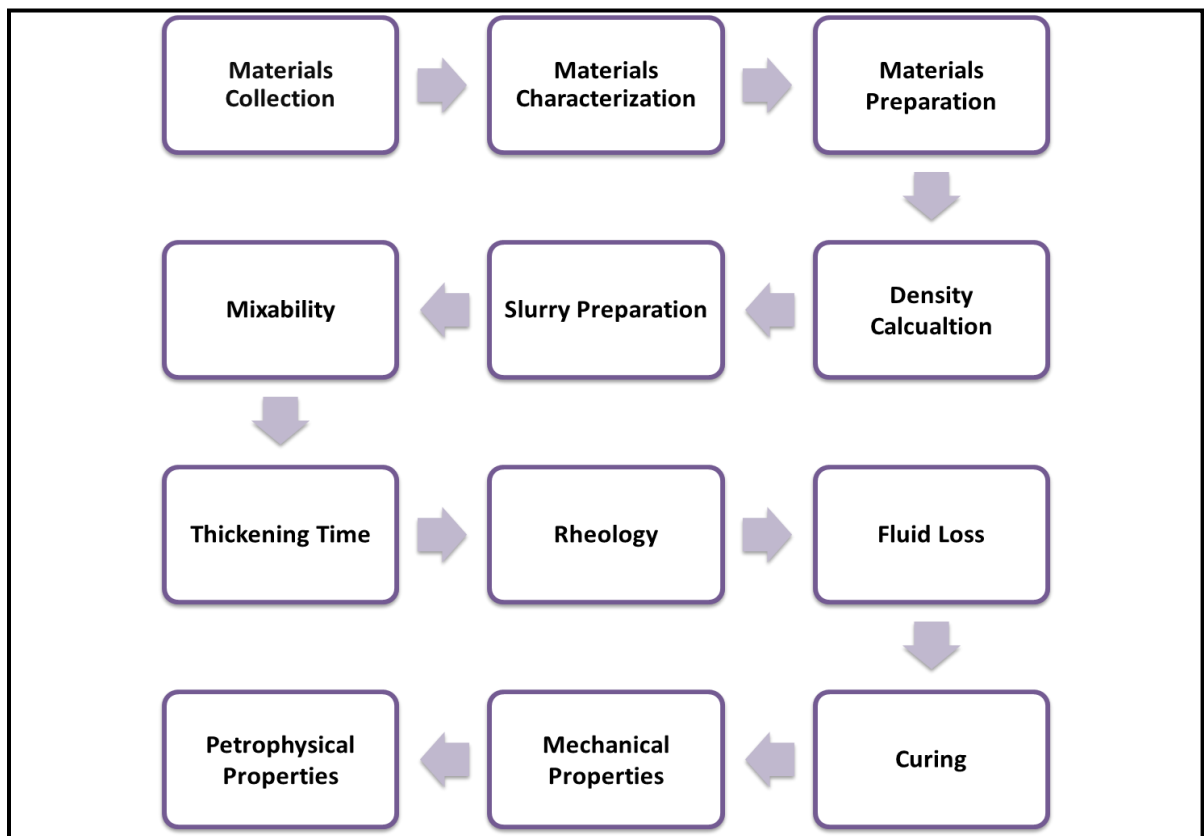


Figure 5.5 The Summary of methods in this study.

Materials Preparation

Sodium hydroxide solution was made by dissolving its pellets in distilled water using a magnetic stirrer. Then, it was left to cool down to atmospheric temperature at least for 24 h before experiment. The specific gravity of the powders was estimated to determine the

required amounts to reach the required density. The FFA was sieved below 104 μm and then was confirmed by PSD. Two different processes (wet and dry) can be followed to prepare geopolymer slurry (Salehi et al., 2017b). In wet process, a superplasticizer and/or retarder are mixed with activation solution for 2 min at high shear rate (12,000 RPM) using constant speed mixer. A binder such as FFA was then added and mixed with premixed solution at high shear rate for another 2 min.

Slurry Design

Different trials were performed to obtain an initial flowable slurry formulation that can be easily mixed. Different parameters were tested such as NaOH molarity (4, 6, 8 and 10 M), liquid to binder ratio (0.5 to 0.8), and weighting material amount. In addition, several additives with different concentrations were tested such as retarder, retarder intensifier and superplasticizer to enhance the slurry workability. The mix design started with testing mixability, thickening time and rheology. Then, testing went through strength, elastic and petrophysical properties and sedimentation evaluation.

Rheology, Fluid Loss, and Thickening Time

After mixing, an atmospheric consistometer is used for conditioning the geopolymer slurry at 195°F and 150 RPM for 30 min. The OFITE 900 viscometer was used to evaluate rheology at average temperature of 192°F and atmospheric pressure. The OFITE HPHT filter press was used to measure fluid loss. The thickening time was evaluated at 195°F and atmospheric pressure using an atmospheric consistometer to know how long slurry would remain pumpable.

Slurry Stability Testing

The geopolymer slurry is conditioned to simulate dynamic placement in wellbores and is then left static to determine if free fluid separates from the slurry. After curing, the cylindrical samples were cut into 3 sections (bottom, middle and top). Then, the sedimentation test procedure was followed by measuring the weight of each section in water and air. The density of each section was calculated by dividing the weight in air by the weight in water according to Archimedes Principal. The density difference of each section was calculated using Eq. 1. The amount of density difference that is acceptable will vary with the application.

$$\% \text{ Density Difference} = \frac{\text{Cement Segment Density} - \text{Cement Slurry Density}}{\text{Cement Slurry Density}} * 100 \quad (\text{Eq. 1})$$

Mechanical and Petrophysical Properties

Mechanical properties evaluation included unconfined compressive strength (UCS), tensile strength, dynamic elastic properties (Young's modulus (YM) and Poisson's ratio (PR)) and the evaluated petrophysical properties were porosity and permeability. After conditioning, the slurry was poured into cubic (2 in. in length) and cylindrical (1.5 in. in diameter and 4 in. in length) molds and then were placed in an HPHT curing chamber at 292°F and 3,000 psi for 24 h. The Brazilian test procedure was followed to measure the tensile strength. The UCS was measured using scratch test. The scratch test is designed to regulate and monitor the continual shearing action caused by the movement of a diamond cutter on a sample surface. The force operating on the cutter generates a continuous profile of rock strength along the sample. The YM and PR were then determined by getting sonic velocities. The

ultrasonic test measures how long it takes a pressure wave to travel between two probes. The compression and flexural machine was utilized for tensile strength analysis, while EPSLOG scratch testing machine with sonic mode was used for elastic properties and UCS. Nitrogen gas was used for measuring gas permeability at room temperature and a confining pressure of 1,000 psi. The gas permeability was measured at different pressures and a graph was constructed between gas permeability versus $1/p_{\text{mean}}$. Then, a straight line was extrapolated to obtain the intercept which refers to the liquid permeability.

5.3 Results and Discussion

5.3.1 Formulation Design

The hematite-based system mix design is listed in

Table 5.3. Although, this geopolymers system possessed acceptable properties, it showed density variation along the cylindrical samples due to hematite sedimentation. Replacing part of hematite with another weighting agent such as Micromax was investigated to tackle the sedimentation issue associated with hematite. The proposed mixture of retarder and superplasticizer that improved the thickening time of the hematite-based system did not have the same performance with the mixed system. As a result, different mixtures of additives were tested until obtaining a sufficient thickening time of around 5 h using a retarder intensifier with a retarder and a superplasticizer. The mix design was adjusted to replace 50% of hematite with Micromax. The proposed additives mixture allowed using only 0.5 liquid to binder ratio to have a flowable slurry with a reasonable rheology. The proposed formulations design for both systems are shown in

Table 5.3 and expressed as by weight of binder (BWOB).

Table 5.3 The mix design used in this work.

Component	SG	Hematite System (BWOB, %)	Mixed System (BWOB, %)
FFA	2.25	100	100
Hematite	5.05	80	30
Micromax	4.68	-	30
Defoamer	1.1	0.0164	0.0164
Superplasticizer	1.21	5	5
Retarder	1.22	5	3
Retarder Intensifier	1.76	-	2
4 M NaOH	1.15	56	50

5.3.2 Thickening Time

When the slurry was prepared by mixing FFA, hematite and NaOH solution, the thickening time at BHCT of 195°F was around 50 min. This thickening time was short to place the cement behind the casing. Different types and mixtures of retarders, dispersants, superplasticizers were tested to prolong the pumpability of geopolymer slurries. Using superplasticizer (5% BWOB) slightly increased the thickening time and the same for the retarder. When both were used together (5% BWOB each), the thickening time increased from 50 to 390 min. For the mixed Micromax-hematite system, the developed additives mixture increased thickening time to only 180 min. Consequently, different mixtures were

tested to increase the thickening time of the mixed system after adding Micromax. Another mixture of a retarder (5% BWOB), superplasticizer (3% BWOB) and a retarder intensifier (2% BWOB) increased the thickening time from 76 min to 300 min at BHCT of 195°F. The developed geopolymer slurries, as shown in **Figure 5.6** and **Figure 5.7**, did not have a right angle set unlike most of cement slurries. Thickening time charts for both systems are shown in **Figure 5.6** and **Figure 5.7**.

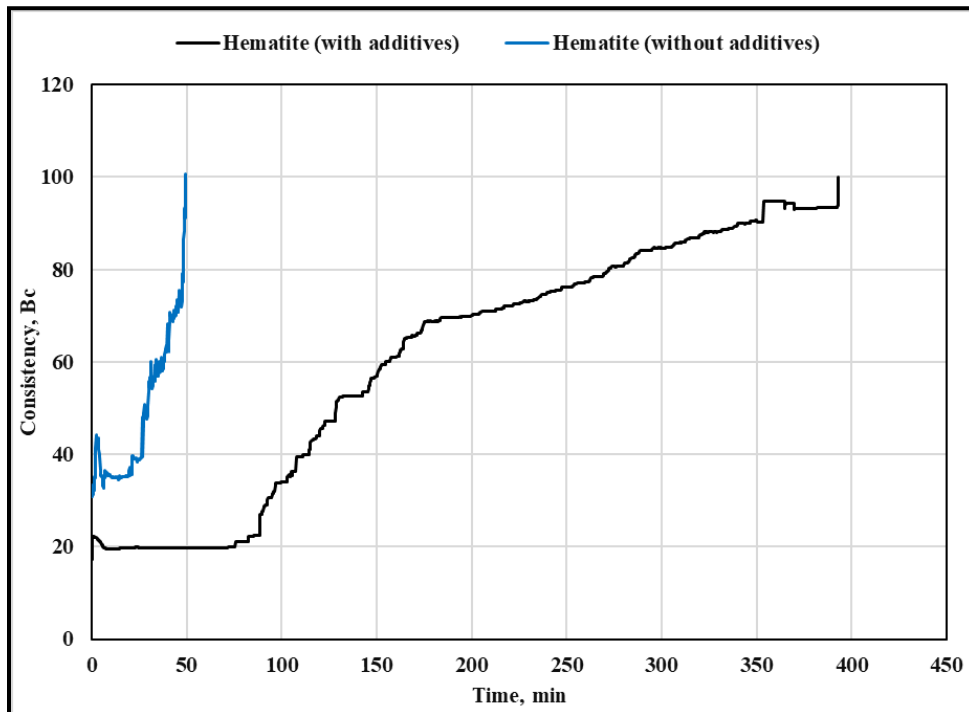


Figure 5.6 Thickening time chart for the hematite geopolymer system.

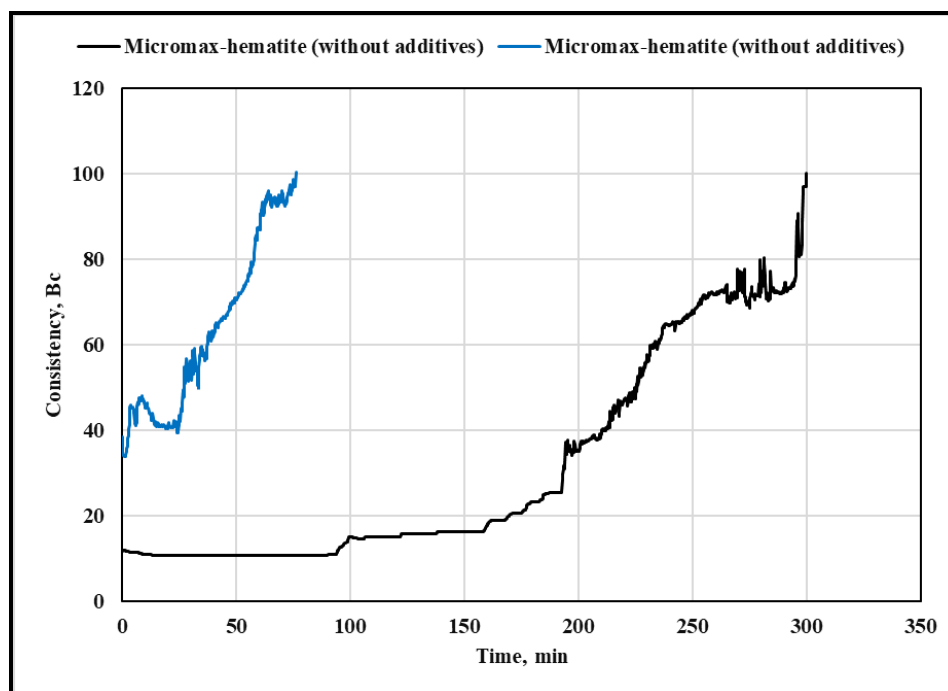


Figure 5.7 Thickening time chart for the mixed hematite-Micromax geopolymer system.

5.3.3 Rheological Properties

Evaluation of the rheology of cement slurries is important because it affects slurry mixing, pumping, and mud displacement. After conditioning for 30 min at 195°F, the rheology measurements were conducted using the OFITE 900 viscometer. The shear stress and viscosity against shear rate are shown in **Figure 5.8** and **Figure 5.9**, respectively. The Bingham Plastic model offered the best fit for the rheology of both systems with R^2 of 0.999. Adding Micromax to hematite decreased the plastic viscosity by 44.8%. Micromax particles are more like spheres, as shown in **Figure 5.4**, that minimize the friction of particles interaction and result in a low plastic viscosity. Yield point determines the force that should be overcome to initiate the flow and reflects the slurry carrying capacity under dynamic condition. Therefore, yield point should not be either that high or that low. The carrying capacity of slurry under static condition is determined by gel strength, and the

gel's growth aids in preventing gas migration. Both systems had a close performance in terms of yield point and the hematite-based system was more in terms of gel strength (GS) as presented in **Table 5.4**. Both systems had shear thinning behavior as the apparent viscosity reduced by increasing the shear rate as shown by **Figure 5.9**.

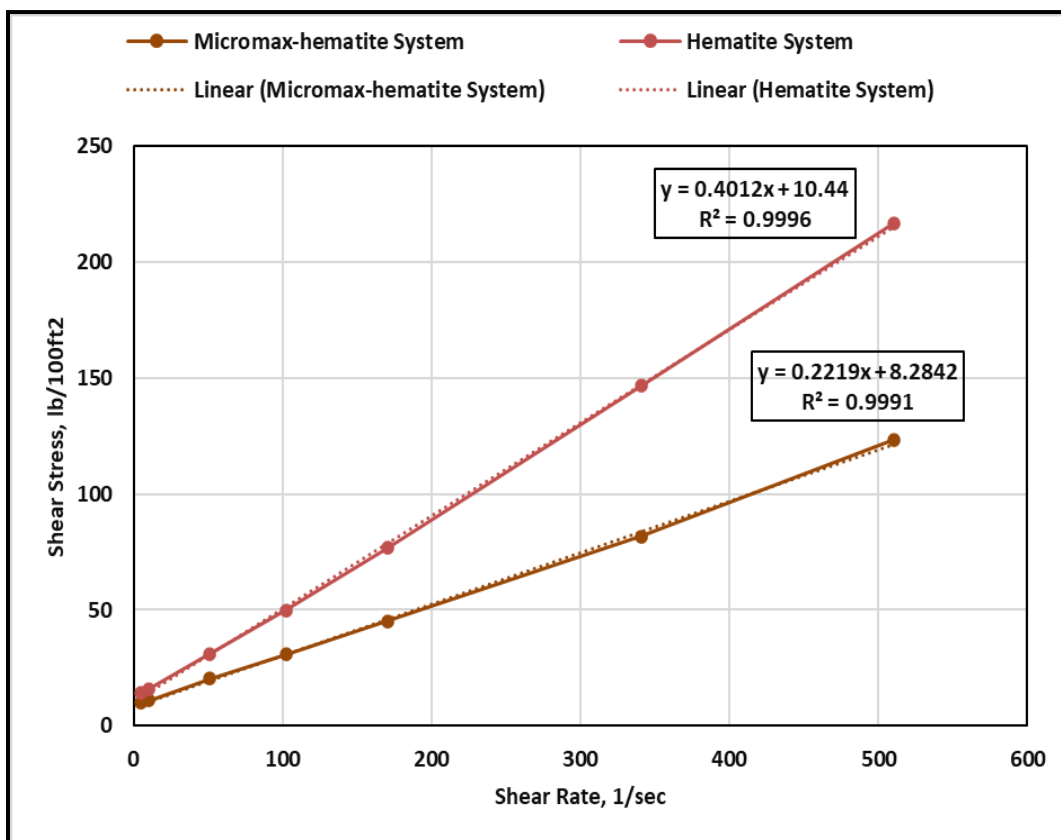


Figure 5.8 The shear stress vs. shear rate of the developed geopolymer slurries.

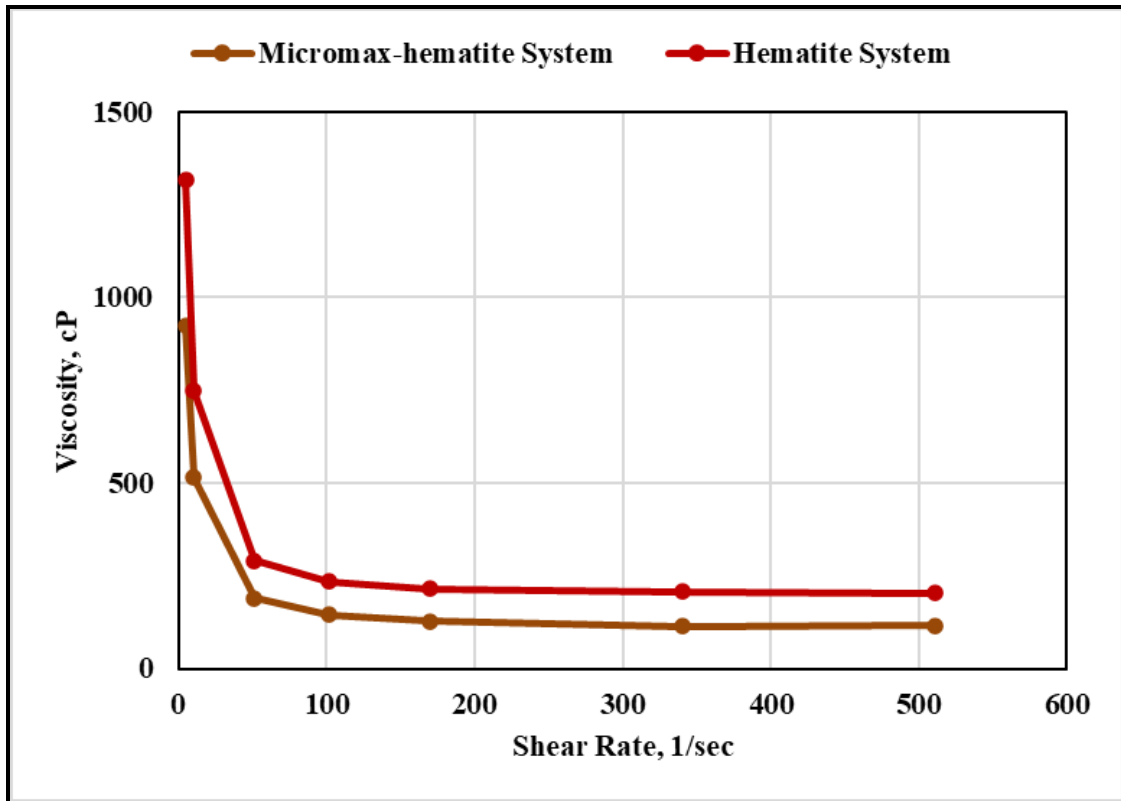


Figure 5.9 The viscosity vs. shear rate of the developed geopolymer slurries.

Table 5.4 The rheological properties of the developed slurries.

Property	Unit	Hematite System	Hematite- Micromax System
PV	cP	192.49	106.24
YP	lb/100 ft ²	10.5	8.3
10 s GS	lb/100 ft ²	16.0	11.3
10 min GS	lb/100 ft ²	171.0	130.0

5.3.4 Fluid Loss

It is advisable to minimize the slurry fluid loss into permeable zones to decrease hydration of water-sensitive shales and prevent increasing slurry viscosity during placement. Managed fluid loss also decreases annular bridges that can act like a packer and remove hydrostatic pressure holding back potentially over-pressure zones. In addition, it reduces cement dehydration during pumping into abandoned perforated interval allowing for plugging longer interval of perforations in a single job. Volume reduction occurs while cement makes transition from a liquid slurry to a solid. If fluid loss is high, much larger volume reductions are thought to be possible that may facilitate gas migration (Mitchell and Miska, 2011). The hematite-based slurry had a fluid loss of 38 mL/ 30 min while the mixed hematite and Micromax slurry had a fluid loss of 34 mL/ 30 min. The developed slurries fall within the acceptable fluid loss ranges as it should be up to 300 mL/ 30 min for casing cementing (G. Liu, 2021). Also, the developed geopolymers possessed a fluid loss below 50 mL/ 30 min which is recommended for special cementing applications such as horizontal wells, and liner cementing (G. Liu, 2021). The developed formulations provided this behavior without using a special fluid loss control additive.

5.3.5 Sedimentation

After curing at 292 °F and 3,000 psi for 24 h using an HPHT curing chamber. **Figure 5.10** and **Figure 5.11** show the density and density variation of different sections along the vertical orientation of the geopolymer samples. The sample heterogeneity can be expressed by the degree of density variation (DV) in such a way that the cement system becomes more homogeneous by decreasing the DV between the cement section and the slurry density. The particles sedimentation relies on size distribution, shape, density, and fluid

viscosity through which particles are moving. The results confirmed that the hematite system had a high sedimentation tendency with a density difference of 32.6% between the bottom and top sections while the Micromax system had only 0.95%. The hematite SG is larger than that of Micromax which boosts sedimentation. In addition, particle size distribution affects sedimentation tendency. The data, as shown in **Table 5.1** and **Figure 5.1**, confirmed that the D_{10} , D_{50} , and D_{90} for hematite were larger than those for Micromax. Generally, small particles have a higher surface area to mass ratio, so frictional drag slows their settling rate more than it does for larger particles. The harsh pressure and temperature conditions could affect the slurry viscosity resulting in a reduction in suspension capacity. Hematite has irregularly shaped particles, whereas Micromax particles are more approximately spherical in shape as shown by SEM in **Figure 5.4**. Round particles settle out more quickly than flat, angular, or irregularly shaped particles because friction reduces for rounded particles. The overall sedimentation behavior is controlled by the interaction of the abovementioned components that made SG and PSD prevailing factors and shape a minor element. The free fluid of the geopolymer slurries was almost zero (traces). For gas migration control, the slurry should have a fluid loss less than 50 mL/ 30 min and zero free fluid, and these requirements are fulfilled in the developed geopolymer slurries (G. Liu, 2021).

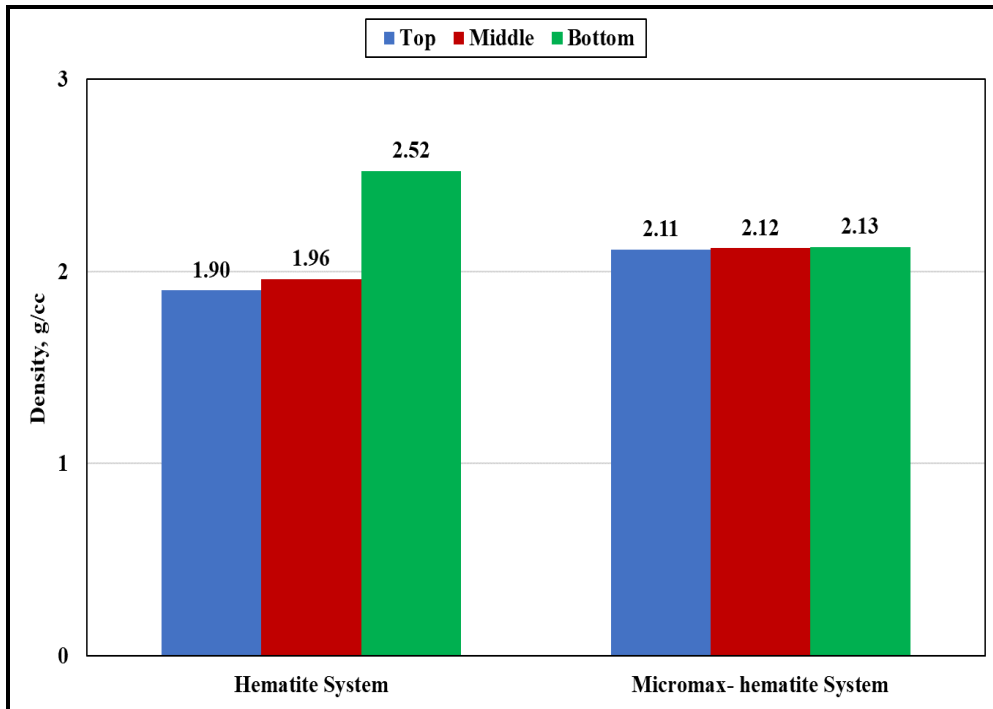


Figure 5.10 Effect of weighting agent on density of the cylindrical geopolimer samples.

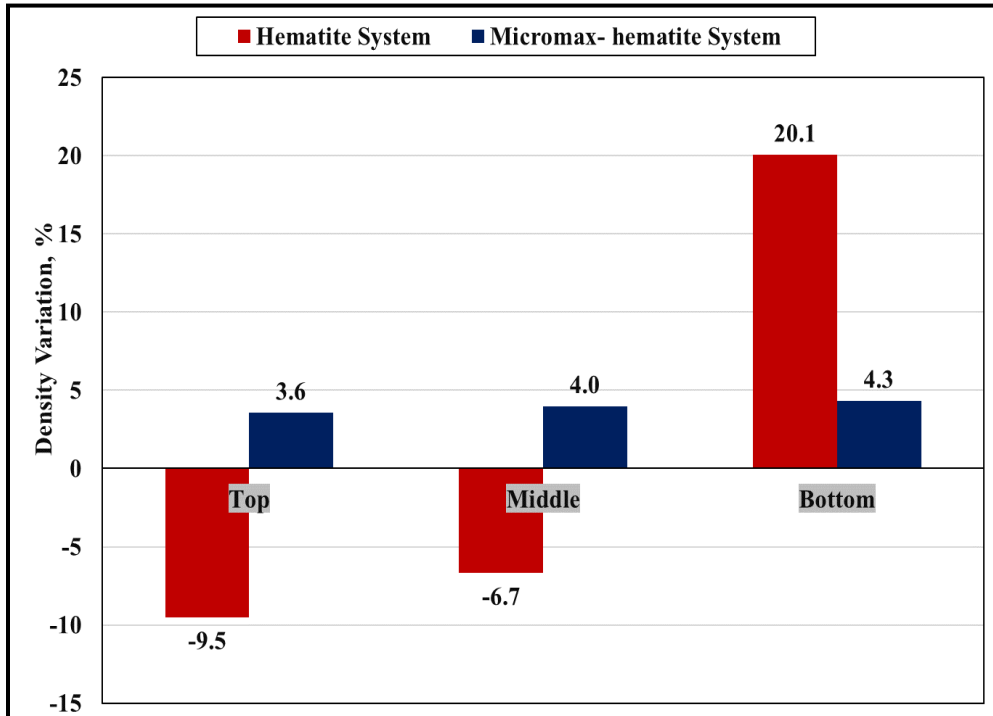


Figure 5.11 Density variation of the cylindrical geopolimer samples.

5.3.6 Strength

The hematite-based system 24 h-compressive strength is larger than that of the mixed system by 13.4% and its tensile strength is greater by 12.5 % as presented in **Figure 5.12** and **Figure 5.13**. However, the mixed based geopolymer possessed a 24 h-compressive strength of 1,624 psi which is more than three times the required value (500 psi) to resume drilling. Before resuming drilling or completion operations, the cement must harden and gain enough strength to support the casing and seal off fluid movement behind casing. It is difficult to pinpoint the precise compressive strength required before drilling through the casing shoe, however, a minimum of 500 psi is recommended in the field practice (Mitchell and Miska, 2011). Maximizing compressive strength has been a traditional approach in the past. The "more is better" philosophy may make this appear reasonable in the short term. However, in long term during well life, load conditions may take place where large strength may conflict with effective sealing and integrity support (Mitchell and Miska, 2011).

The developed geopolymer formulations possessed a 24 h-compressive strength of at least 1,624 psi and a tensile strength of at least 219 psi which are greater than the required values for different purposes in the literature and some reported values in high density cementing programs in the Middle East. Farris, (1946) experimentally showed that a tensile strength of only a few psi was adequate to support the casing weight under laboratory conditions; however, some considerations should be taken in case of dynamic loading imposed by drillstring rotation while subsequent drilling. Clark, (1953) investigated the required strength to stop major fluid movement behind casing. The author concluded that tensile strength as low as 40 psi is accepted, with maximum bonding reached at roughly 100 psi. Another work mentioned that 8 psi tensile strength, or around 100 psi compressive strength

is sufficient to support casing. There is a harmony between the compressive strength and tensile strength results in such a way that the higher in compressive strength is also higher in tensile strength. (Mitchell and Miska, 2011) mentioned that the ratio of compressive to tensile strength is approximately 8:1 to 12:1 for most cements and the study results (7.5:1) were so close to 8:1 ratio.

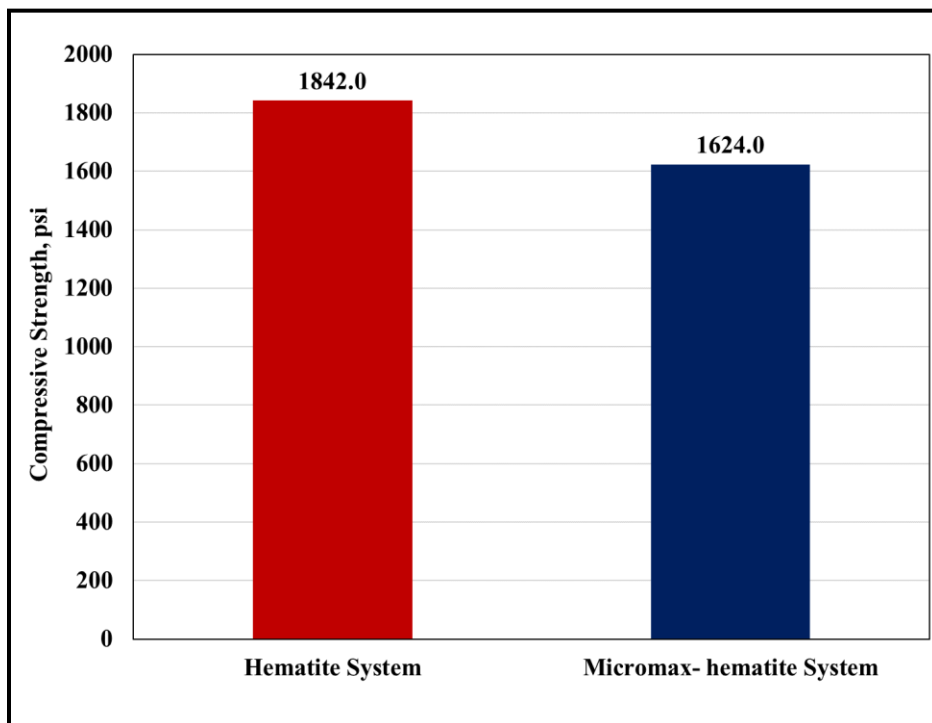


Figure 5.12 Compressive strength of both systems using scratch test.

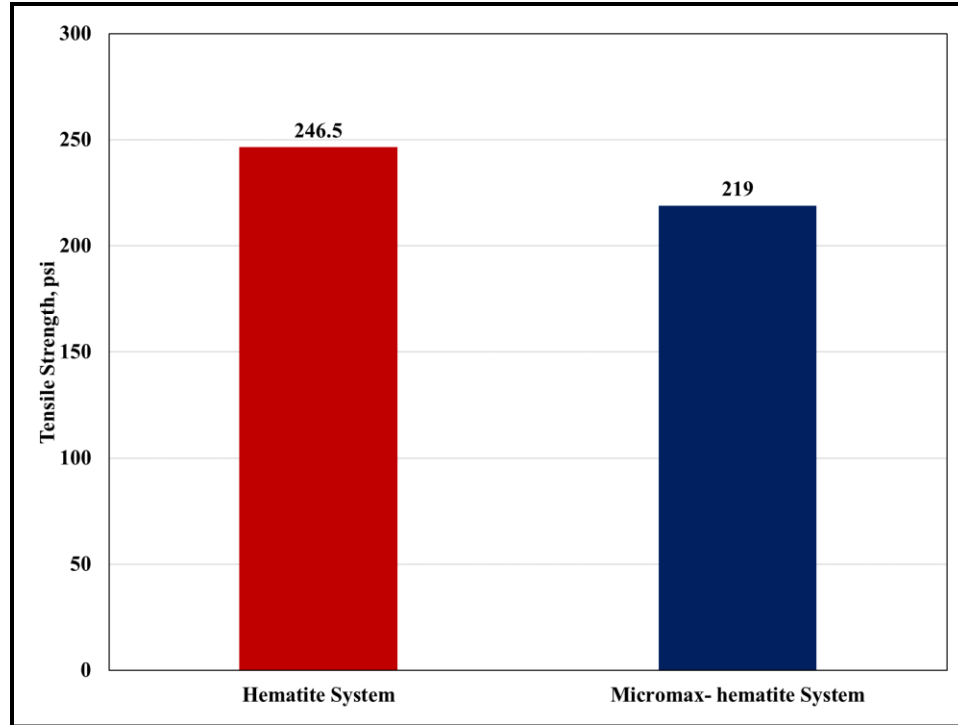


Figure 5.13 Tensile strength of both systems using the Brazilian Test.

5.3.7 Elastic Properties and Permeability

Cement sheath flexibility is significant where cement is under high stresses, e.g., steam injection, geothermal, and hydraulic fracturing. Flexible cements with a low Young's modulus and a high Poisson's ratio provide long-term well integrity. Set cement should have a lower YM than the surrounding formations. Small YM set cement may be preferable for unconsolidated strata than high YM set cement (G. Liu, 2021). The proposed geopolymer systems possessed YM of around 5.1 GPa and PR in the range of 0.22-0.26 as listed in **Table 5.5**. The developed geopolymers are more flexible than class G cement in terms of YM and PR as presented in **Table 5.5**. Moreover, they possessed lower YM than shale and consolidated formations and thus can be used adjacent to these formations as stated earlier by G. Liu, (2021). Normally, more flexible cement, this with smaller YM and larger tensile strength, with enough compressive strength, performs well while simulating

cement stresses. Permeability was measured for the two heavy weight geopolymer systems using Nitrogen. The liquid permeability was estimated by getting the y-axis intercept. The permeability was 0.015 and 0.009 md for the hematite and mixed geopolymer systems, respectively.

Table 5.5 YM and PR for some common materials against the developed geopolymers.

Material	YM (GPa)	PR (Dimensionless)
Hematite based geopolymer	5.18	0.26
Mixed based geopolymer	5.17	0.22
Extended cement systems	2.27	0.17
Flexible cement systems	1.99	0.22
Class G cement	11.03	0.17

5.4 Conclusions

Two high density geopolymer systems using hematite alone and a mixture of hematite and Micromax were introduced. The assessment included rheology (PV, YP, and GS), filtrate loss, strength, permeability, and elastic properties. This study showed the sedimentation problem associated with hematite as a weighting agent and introduced adding Micromax as a solution to mitigate this problem in geopolymers. The findings of this work can be summed up as follows:

- The Micromax-hematite weighted geopolymer is homogeneous with only 3.9% average density difference within the samples.
- A proposed mixture of a retarder, a retarder intensifier and a superplasticizer was introduced that increased the thickening time of the mixed system by 294%.

- The Mixed geopolymer had lower fluid loss without using any fluid loss control additive that made it a good candidate for cementing applications such as horizontal drilling, gas migration risk, and casing cementing that requires fluid loss less than 50 mL/30 min.
- At downhole temperatures, both systems followed Bingham plastic fluid model and the mixed system decreased the plastic viscosity by 44.8% and possessed a yield point close to the hematite-based system.
- The two formulations had close values in terms of strength, elastic properties, and permeability.

CHAPTER 6

PERLITE INCORPORATION FOR SEDIMENTATION

REDUCTION AND IMPROVED PROPERTIES OF

HIGH-DENSITY GEOPOLYMER CEMENT FOR OIL

WELL CEMENTING

6.1 Introduction

Portland Cement (PC) is used in well cementing for various applications such as casing support, zonal isolation, plug & abandonment, loss of circulation control, sidetracking and remedial activities. However, there are specific concerns associated with the properties of PC both before and after cement setting. These concerns include strength retrogression at high temperatures, cement failure due to low flexibility in terms of Poisson's ratio (PR) and Young's modulus, gas migration, and susceptibility to corrosive environments. The manufacturing process of PC requires significant quantities of natural resources and energy and emits substantial CO₂ emissions. The production of one ton of clinker, a key component of PC, requires approximately 3.2 GJ of energy and generates around 0.93 ton of CO₂ emissions (IEA, 2018; Xu et al., 2015).

Geopolymers have emerged as a promising alternative to traditional Portland cement in a range of applications, including oil well cementing. The term "geopolymer" was originally introduced and coined by Joseph Davidovits (Davidovits, 1991b). Geopolymers refer to a type of cement-like binder made by the reaction of aluminosilicate materials with alkali hydroxides and/or soluble silicates, resulting in an inorganic polymeric substance (Davidovits, 1991a; Xu and Van Deventer, 2000). More than 65 % of the crust of the earth consists of aluminosilicate materials (Xu and Van Deventer, 2000). Aluminosilicate materials encompass a wide range of substances, including both waste materials such as fly ash, red mud, and furnace slag, as well as certain clays like kaolinite and metakaolin.

In the literature, researchers have extensively explored the utilization of waste materials as sources of aluminosilicate materials for geopolymers production. Fly ash, a byproduct of coal combustion, has been widely investigated due to its high content of amorphous aluminosilicates (Abdelaal et al., 2023b; Abdelaal and Elkatatny, 2023a). These waste materials not only offer a sustainable alternative to traditional raw materials but also contribute to waste management and environmental sustainability. Additionally, certain clays, such as kaolinite and metakaolin, have been explored for their aluminosilicate content and suitability for geopolymers production (Adjei et al., 2022a). Further investigation and advancements in this area have the potential to contribute to the development of environmentally friendly and technologically advanced materials.

There is no universal cement formulation that can be used for all purposes. Cement slurries are tailored to meet the specific requirements of the downhole environment, considering factors such as temperature, pressure, and cement job type (Adjei et al., 2022b). Heavy-weight cement slurries can be formed either by reducing water to cement ratio or adding

weighting agents. Weighting materials are added to drilling fluids and cement slurries to increase their density, thereby enabling safe and effective drilling operations in high pressure oil and gas wells. Hematite, along with other weighting agents, helps control formation pressures, and enhance the performance and integrity of oil well cement. Weighting materials incorporation in geopolymers is a relatively new area in oil and gas well cement. High density hematite based geopolymers suffer from low thickening times and sedimentation issues (Abdelaal and Elkatatny, 2023b). Abdelaal et al. (Abdelaal et al., 2023a) introduced a hematite based FFA geopolymer system for oil well cement. Although the authors provided a mixture of additives to enhance the pumpability of the proposed geopolymer system, the sedimentation evaluation was not a part of their study. The occurrence of solid particles' settling introduces variations in the compressive strength and bonding across the cemented section. The sedimentation problem in slurries contributes to the formation of a non-uniform cement column, which adversely affects both the strength and zonal isolation.

Perlite is a natural amorphous glassy volcanic rock (Tekin et al., 2006), which owns a chemical composition equivalent to rhyolite (Bagdassarov et al., 1999). Chemically, perlite ore contains silica, alumina, and small amounts of several metal oxides (Maxim et al., 2014). It possesses a high silica content (around 70 wt %) and equilibrium water (2-5 wt %) (Bagdassarov et al., 1999). Perlite is neutral with a pH of 7.0-7.5 (Papadopoulos et al., 2008). Chemically, perlite is a durable substance capable of maintaining its stability over numerous years (Acuña et al., 2013); its stability remains relatively unaffected by acids or microorganisms. Recycling perlite presents no environmental concerns due to its inert nature. This rock is formed through the hydration of obsidian. It can be found in various

colors, ranging from transparent light gray to glossy black. When subjected to rapid heating at temperatures between 1,400 and 1,800°F, perlite exhibits a unique property known as expansion or "popping". This expansion process can increase the volume of perlite by a factor of 4 to 20, resulting in a product called expanded perlite (Maxim et al., 2014). Expanded perlite possesses several desirable physical properties, including low bulk density (Senff et al., 2011), good thermal insulation (Singh and Garg, 1991), high fire resistance (Singh and Garg, 1991), low sound transmission, high surface area (Senff et al., 2011), and chemical inertness (Papadopoulos et al., 2008). Both the original perlite rock and the expanded perlite product are commonly referred to as perlite (Maxim et al., 2014).

Perlite is considered a versatile and environmentally friendly mineral that is extracted and processed with minimal impact on the environment. Perlite can be used in different industrial applications such as sound insulation (sound-absorbing or blocking perlite-based products), high temperature insulation (chimneys, ovens, and foundry applications), filtration (perlite filter aids for food processing, pharmaceuticals, water treatment and fertilizers), construction (plaster and concrete), and horticultural (soilless growing mixes) (Perlite Institute, 2021). The different phases involved in producing expanded perlite yield various waste by-products that have the potential to be utilized in the construction sector, thereby promoting sustainability (El Mir and Nehme, 2017; Kotwica et al., 2017).

Managing waste expanded perlite is challenging due to its remarkably low bulk density, making handling and utilization problematic and contributing to dust formation. Kotwica et al. (Kotwica et al., 2017) mentioned that waste expanded perlite can be used as a supplementary cementitious material (either as a cement replacement or an additive). The

authors reported that perlite possesses pozzolanic activity by which it can react with calcium hydroxide and its incorporation enhanced strength.

In the petroleum industry, some researchers evaluated perlite for potential usage in drilling fluids and oil well cement (Adjei et al., 2021; Bageri et al., 2021; Basfar et al., 2022; Mohamed et al., 2020). Adjei et al. (Adjei et al., 2021) investigated the impact of perlite powder on heavy-weight barite cement. It was observed that increasing the concentration of perlite powder led to a decrease in plastic viscosity and an increase in yield point and gel strength. Perlite powder enhanced the 24 h compressive strength and reduced the settling tendency of barite. Basfar et al. (Basfar et al., 2022) investigated the usage of perlite as an additive in hematite water-based drilling fluids. The results indicated that the addition of perlite provided multiple benefits, including anti-sagging, improved rheological properties, enhanced filtration properties, and minimal changes in mud properties such as pH and density. These findings have implications for improved drilling operations, including better formation protection and reduced pipe sticking issues. Hence, there is a strong motivation to explore the feasibility of incorporating perlite into high-density geopolymer cement systems as well. The primary aim of this study is to assess the effectiveness of utilizing perlite particles in mitigating sedimentation problems within heavy weight geopolymer systems. The secondary objective is to assess the impact of perlite on the properties of Class F fly ash geopolymer cement.

6.2 Materials and Methodology

6.2.1 Materials

In this study, various materials were utilized to investigate their suitability for geopolymer applications under wellbore conditions. The aluminosilicate material used was FFA, while hematite served as a weighting agent. The activator employed was NaOH solution, and additional chemical additives such as retarders, deformers, and superplasticizers were included to improve the characteristics of geopolymers. The specific gravities (SG) of FFA and hematite were determined to be 2.25 and 5.05, respectively. Particle size distributions (PSD) were assessed using a laser diffraction particle size analyzer, as depicted in **Figure 6.1**. The findings revealed that 50% of FFA, hematite, and perlite particles had sizes below 19.35 μm , 21.54 μm , and 46.35 μm , respectively. X-ray fluorescence (XRF) analysis confirmed the high iron content (approximately 95%) of hematite, while X-ray diffraction (XRD) analysis confirmed its composition consisting solely of hematite. Furthermore, XRF analysis indicated that FFA contained significant amounts of silica (SiO_2) and alumina (Al_2O_3), as listed in **Table 6.1**. These components play a crucial role in the formation of geopolymers. Through comprehensive material characterization, this study provides valuable insights into the composition and properties of FFA, and hematite, and their potential applications in geopolymer formation.

The scanning electron microscopy (SEM) images, as shown in **Figure 6.2**, show that the FFA particles possess a spherical shape, the hematite particles have irregular shapes and perlite particles have a flake-like structure. In SEM analysis, perlite is observed to have a distinctive morphology characterized by its porous and lightweight structure. The SEM

images reveal an interlocking 3-dimensional structure with numerous interconnected voids and irregular-shaped particles, which contribute to its unique properties. The surface of perlite exhibits a rough texture with a high degree of porosity, allowing for enhanced water absorption and retention capabilities. This unique structure plays a role in minimizing shrinkage during the drying or curing process, thereby preserving the physical dimensions of the material in which they are incorporated. These SEM observations provide valuable insights into the microstructure and surface characteristics of perlite, which are important considerations in its various applications.

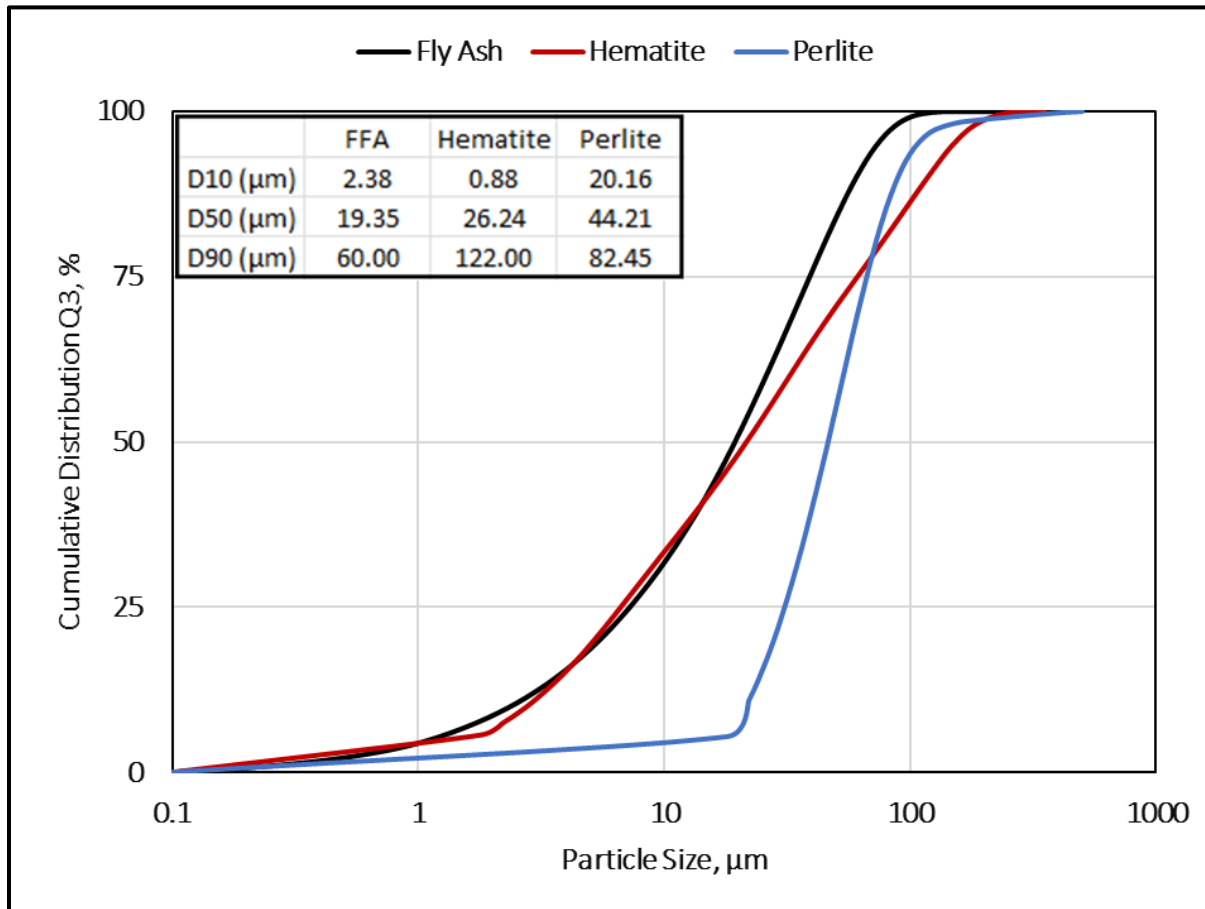


Figure 6.1 The PSD results of FFA, hematite and perlite.

Table 6.1 XRF of FFA used in this work.

Oxide	SiO ₂	Al ₂ O ₃	CaO	Fe ₂ O ₃	TiO ₂	K ₂ O	SO ₃	MnO	Others
FFA	55.92	29.54	5.49	4.93	1.91	1.66	0.39	0.04	0.13

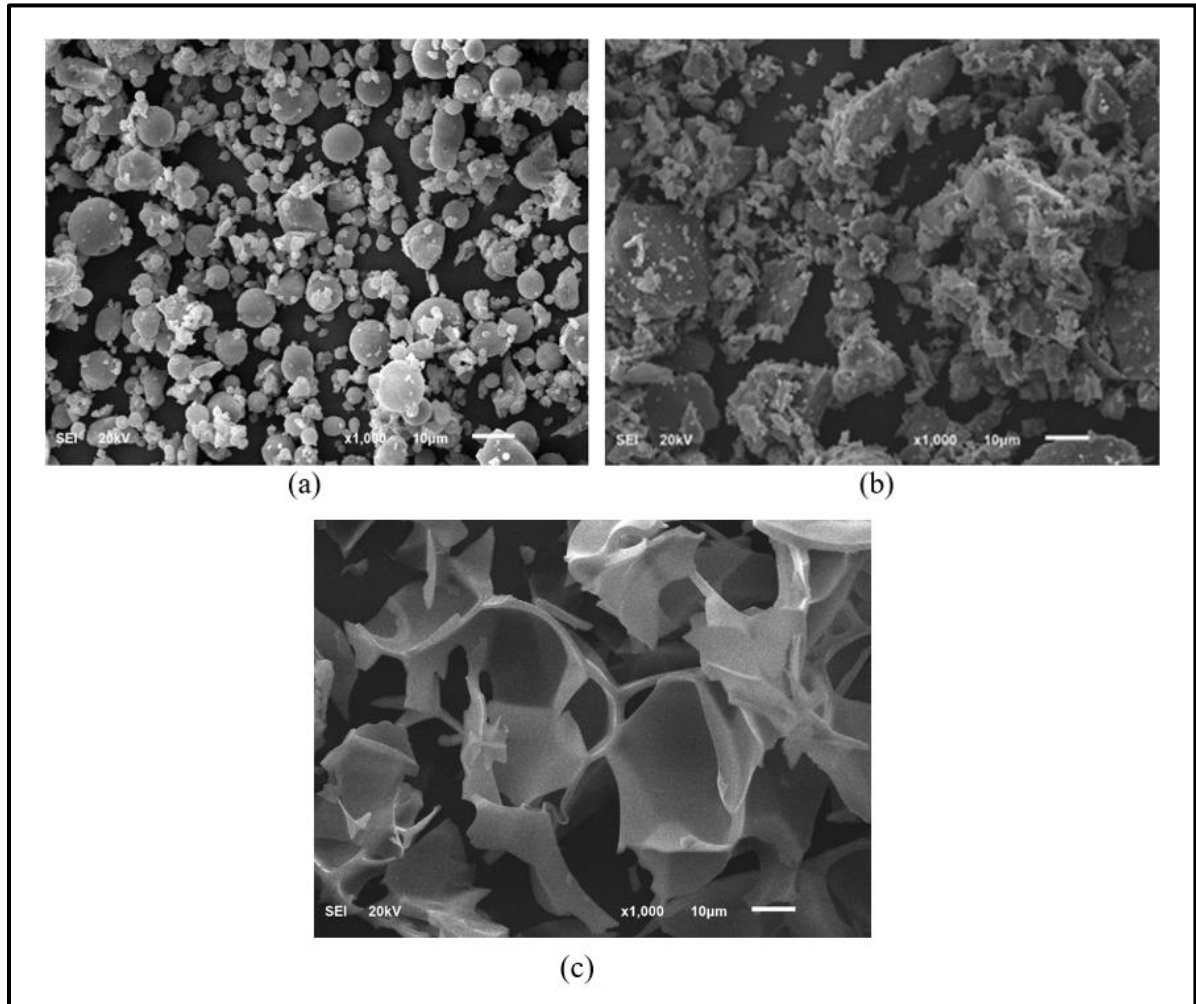


Figure 6.2: The SEM results for FFA (a), hematite (b) and perlite (c).

6.2.2 Methodology

This section presents an overview of the methodology employed in this work. The study commenced by gathering, analyzing, and preparing the necessary materials. Subsequently, slurries were prepared and checked for mixability and rheology tests. The sedimentation behavior was assessed through the application of three different techniques. Following this, the cured samples underwent mechanical and elastic properties evaluations. **Figure 6.3** shows an overview of the methods followed in this study.

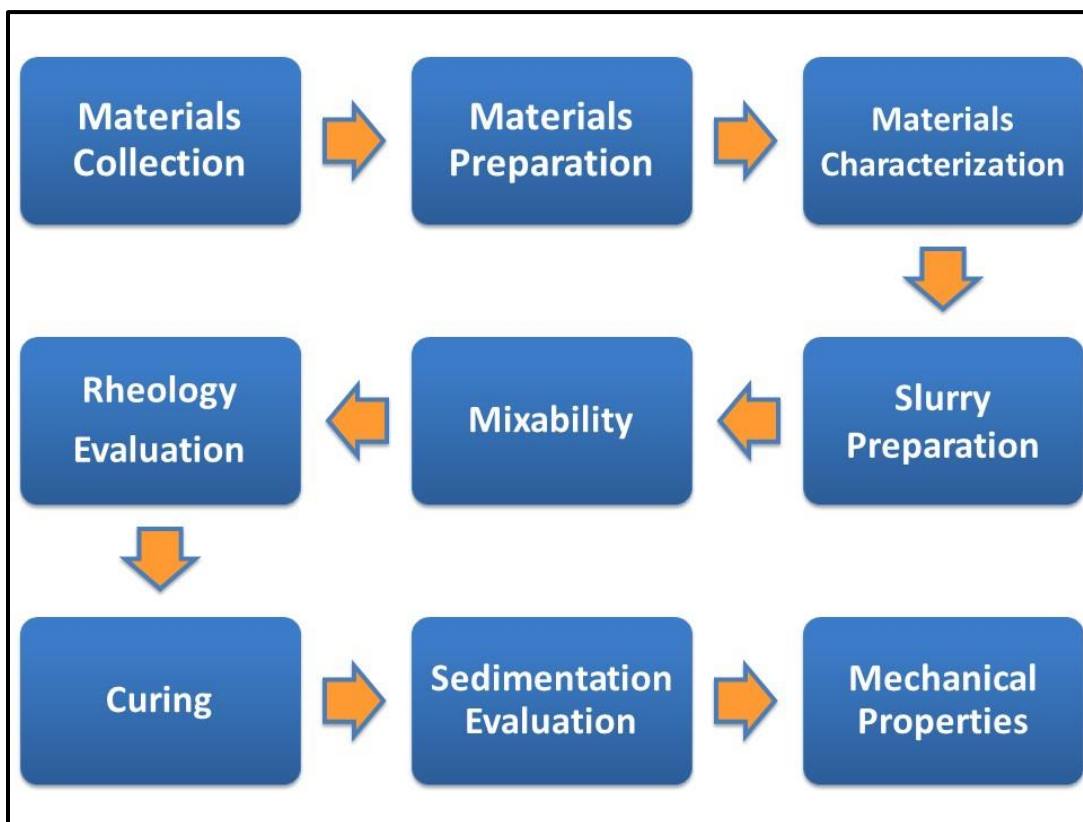


Figure 6.3: The overview of the methods followed in this work.

Materials and Samples Preparation

To prepare the sodium hydroxide (NaOH) solution, NaOH pellets were dissolved in distilled water using a magnetic stirrer to prepare a 4 M NaOH solution. The solution was left to cool at room temperature for a minimum of 24 h before starting the experiment. The

specific gravities of the powders were determined using a gas pycnometer. FFA underwent sieving to ensure that the particles' sizes were below 104 μm , which was confirmed by PSD. In the preparation of geopolymer slurries, two techniques, wet and dry, can be employed (Salehi et al., 2017b). For this study, the wet process technique was utilized. In the wet mixing, superplasticizers and/or retarders are mixed with activation solutions for 2 min at a high shear rate of 12,000 rpm using a mixer. The solid mixture is then added and further mixed with the pre-mixed solution for another 2 min. Three perlite concentrations (0, 1.5 and 3 %) were used to prepare the geopolymer slurries as increasing perlite percentage above 3 % resulted in a thick slurry with mixability difficulties. The liquid to binder ratio was fixed at 0.56 as used by Abdelaal et al (Abdelaal et al., 2023a). The mix design is listed in Table 2.

Table 6.2: The mix design of the prepared slurries.

Component	BWOB, %
FFA	100
Hematite	80
Defoamer	0.0164
Superplasticizer	5
Retarder	5
4 M NaOH	56
Perlite	0, 1.5 , 3

Sedimentation Evaluation

Sedimentation evaluation included using three techniques, namely API method, NMR and CT-scan. The cured geopolymer cement samples were cut into 3 sections (top, middle and bottom). The data obtained from the API method, NMR analysis, and CT scan imaging for each section of the geopolymer cement samples were analyzed. Comparative analysis among the sections provided insights into the variation of sedimentation behavior

throughout the sample height. The cured geopolymer sections were used to assess sedimentation using the API method. The weight of the geopolymer samples were measured in air and water using a balance. By applying the principle of Archimedes, the specific gravities of the cement sections were calculated by dividing the weights in air by the weights in water. The results are used to construct a density profile for the entire sample (API RP 10B-4, 2004).

NMR analysis was conducted to assess sedimentation in the geopolymer cement samples. The cured samples were prepared as cylindrical specimens and placed within the NMR apparatus with a low magnetic field. The NMR measurements were performed to capture the sedimentation behavior through showing the differences in NMR porosity among different cement sections. The resulting NMR data, such as relaxation times, were analyzed to quantify the sedimentation. CT-scan imaging was employed to visualize and analyze the sedimentation behavior of the geopolymer cement samples. The cured samples were scanned using a medical CT scanner, which captured cross-sectional images of the samples. The acquired CT images were processed and analyzed to determine the sedimentation patterns, including the distribution, and settling characteristics of the particles within the samples.

Rheological and Mechanical Properties

After mixing, the geopolymer slurries were conditioned using an atmospheric consistometer at a temperature of 195°F and a rotational speed of 150 rpm for a duration of 30 min. Rheology evaluation was performed using a viscometer at an average temperature of 195°F and atmospheric pressure. Rheological properties were evaluated using three different viscometers, and each measurement was repeated three times. The

average values obtained from these measurements were then reported. The assessment of mechanical properties included the determination of unconfined compressive strength (UCS) and dynamic elastic properties such as YM and PR. After conditioning, the slurry was poured into cylindrical molds which were 1.5 inches in diameter and 4 inches in length. Subsequently, the molds were placed in an HPHT curing chamber set at 292°F and 3,000 psi for a duration of 24 h. UCS was estimated using the scratch test method, which involves the continuous shearing action caused by a moving diamond cutter on the surface of the sample. The force exerted on the cutter creates a rock strength profile along the specimen. YM and PR were evaluated by measuring the sonic velocities, specifically the compressional and shear waves. The ultrasonic test measures the time it takes for a pressure wave to travel between two probes.

6.3 Results and Discussion

6.3.1 Sedimentation

Perlite was introduced to address sedimentation and stability issues accompanying the high-density hematite-based geopolymers. Then, its effects on different cement properties were evaluated. Three perlite percentages (0, 1.5 and 3% BWOB) were used in this study. Adding perlite (3% BWOB) to the system decreased the density variation between the top and bottom sections from 30.3% for 0% perlite to 3.73% for 3% perlite. **Figure 6.4** summarizes the densities of the three sections for each perlite concentration as obtained by the API method. NMR results show that increasing perlite percentage decreased the NMR porosity differences among the three sections of the geopolymer samples (top, middle and bottom) as presented in **Figure 6.5**. Adding perlite (3% BWOB) decreased the top section

porosity by 22.6% and increased the bottom section porosity by 74.3% as compared to 0% perlite. The expandable hollow microstructure of perlite particles, as confirmed by SEM, can accommodate FFA and hematite particles within it. Round and spherical particles exhibit faster settling rates in comparison to flat, angular, or irregularly shaped particles. This accelerated settling is a result of reduced friction associated with the smoother, rounded surfaces of the particles (Ahmed et al., 2022). The settling tendency of perlite particles with its content may be decreased due to their irregular shapes. **Figure 6.6** and **Figure 6.7** summarize the NMR porosities, density and porosity differences for different perlite concentrations used in this study.

The coefficient of determination (R^2) between perlite concentration and the difference in density or NMR porosity was 0.99 and 0.98 as presented in **Figure 6.7**. There is an agreement between the density and NMR porosity data for different geopolymer cement sections as shown in **Figure 6.4** and **Figure 6.6**. CT-scan imaging confirmed the results obtained by NMR and API method as shown in **Figure 6.8**. There was a remarkable density variation among the slices in **Figure 6.8** (a) without perlite and this variation decreased by increasing perlite percentage (from left to right in **Figure 6.8**) until getting approximately the same color that indicated minimal density difference across different slices within the same sample as shown in **Figure 6.8** (c). The remarkable change in colors from blue (low density) to yellow (high density), as shown in **Figure 6.8** (a), may be attributed to the high settling rate and low suspension capacity in the absence of perlite. The color similarity among all slices, as shown in **Figure 6.8** (c), indicates homogenous density and porosity along the geopolymer sample from top to bottom after adding 3% BWOB perlite.

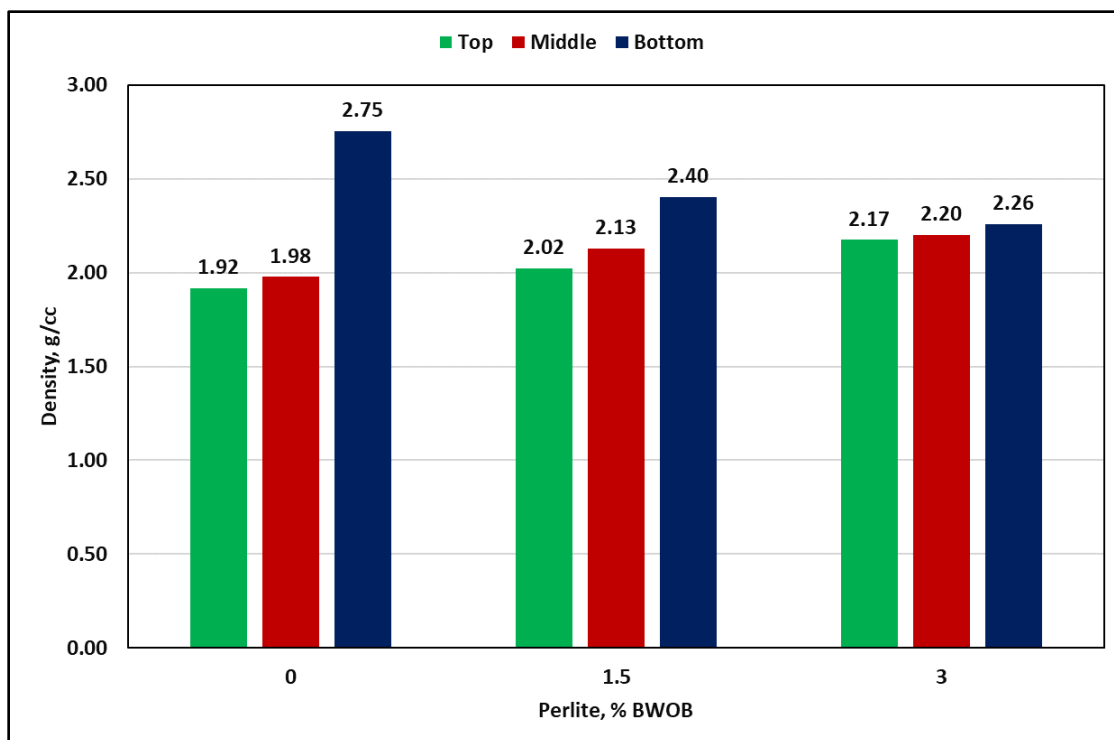


Figure 6.4: API method results for different perlite concentrations.

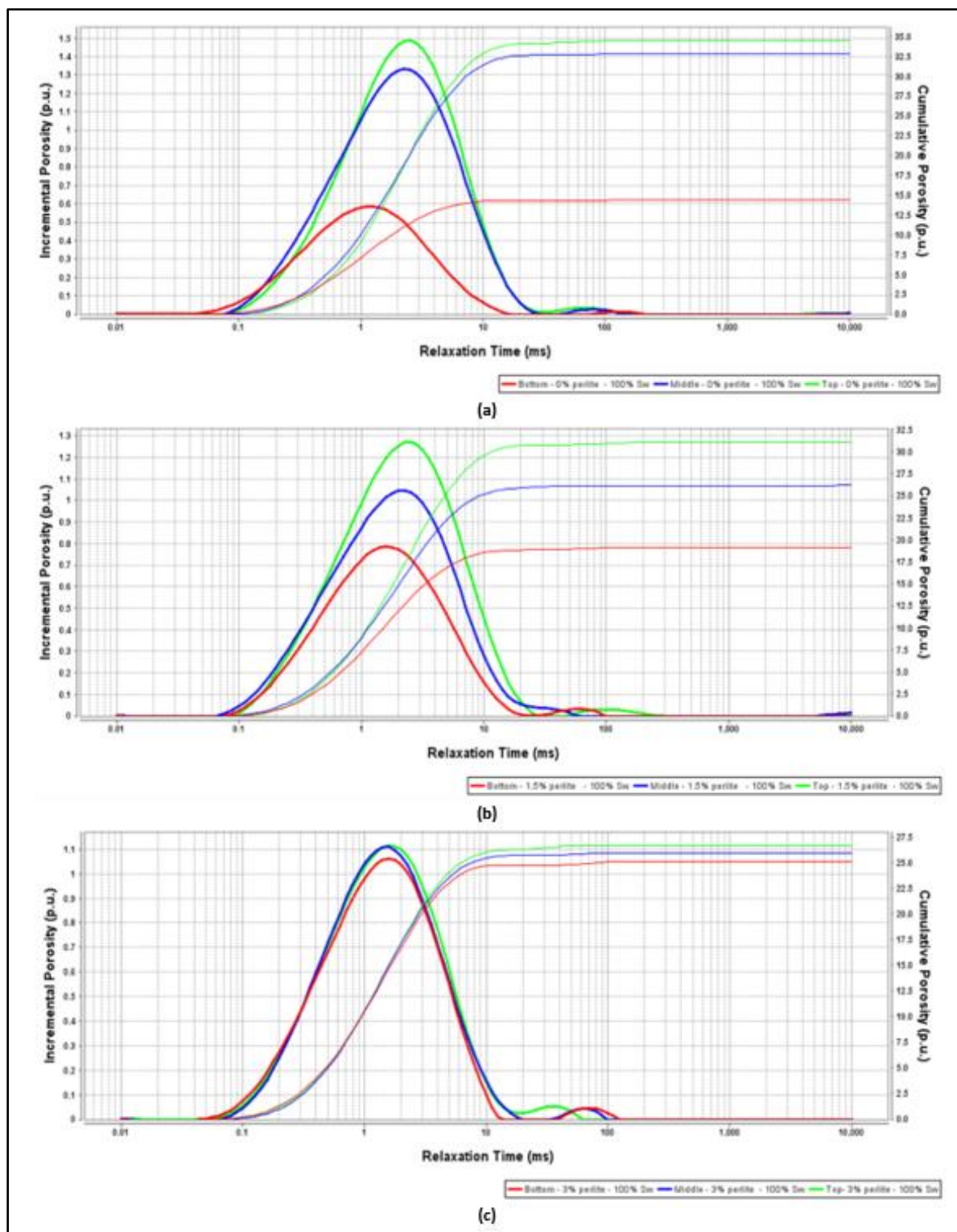


Figure 6.5: NMR results for the 3 perlite percentages used in this study (0 % (a), 1.5% (b) and 3 % (c)).

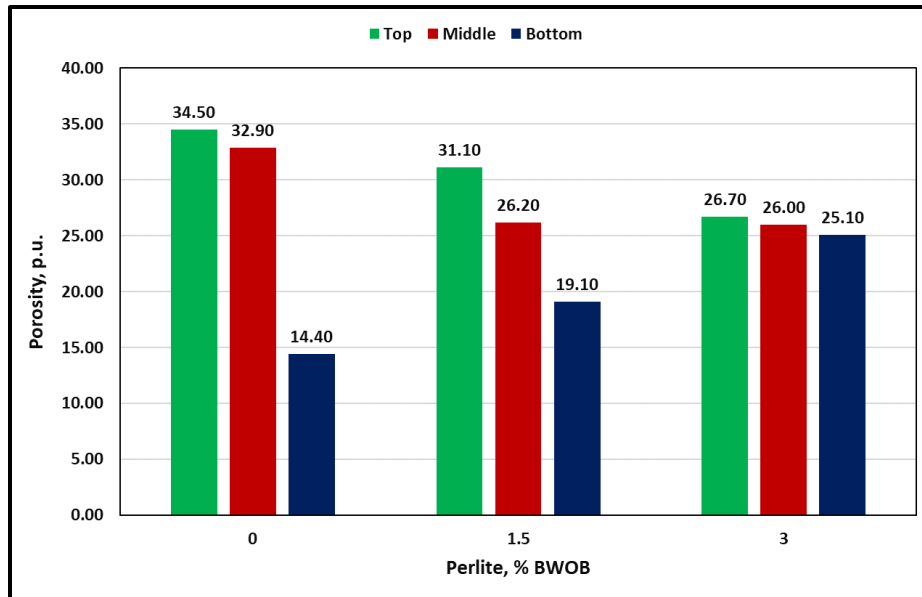


Figure 6.6: NMR porosities summary for different perlite concentrations.

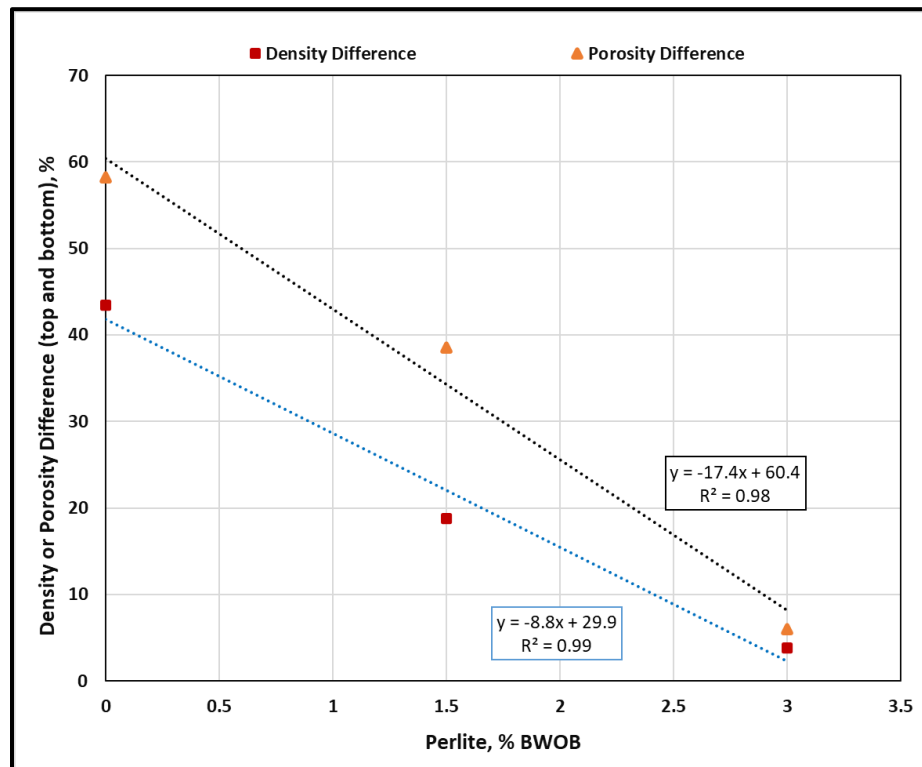


Figure 6.7: Density and porosity differences between top and bottom sections for different perlite concentrations.

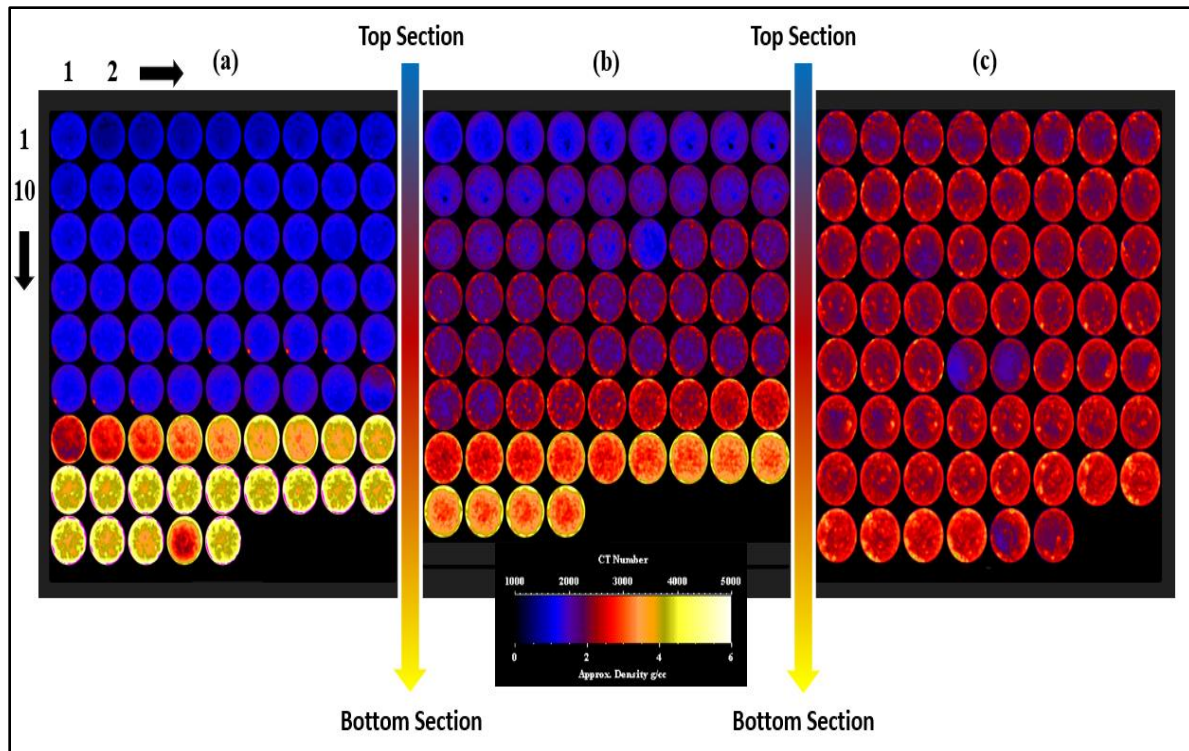


Figure 6.8: CT-scan results for different perlite concentrations (0 % (a), 1.5 % (b) and 3 % (c)).

6.3.2 Mechanical Properties

After ensuring that perlite can be used to address the sedimentation and stability issues, the effects of perlite on other geopolymer properties were assessed. The optimum perlite concentration increased the 24 h UCS of the developed geopolymer as compared to 0% perlite as presented in **Figure 6.9**. The increase in UCS may be attributed to the reduction in the overall porosity of the geopolymer cement samples. Determining the exact compressive strength needed prior to drilling through the casing shoe is challenging. Nonetheless, practical field recommendations suggest a minimum of 500 psi as a suitable guideline (Mitchell and Miska, 2011). The developed geopolymer formulations showcased a 24 h UCS of at least 1,842 psi, exceeding prescribed benchmarks found in literature and some reported values within heavy weight cementing programs.

The dynamic YM and PR showed little differences between the geopolymer samples with 0 and 3 % perlite concentrations, indicating that the presence of perlite has a minimal effect on the elasticity of the samples as presented by **Figure 6.10** and **Figure 6.11**. A cement with a smaller Young's modulus (YM) is often preferred for unconsolidated strata as it offers better performance compared to a cement with a higher YM (G. Liu, 2021). The proposed geopolymer systems possessed a YM in the range of 5.02 to 6.47 GPa and PR in the range of 0.25 to 0.26 as presented in **Figure 6.10** and **Figure 6.11**. The developed geopolymers exhibit greater flexibility in terms of YM and PR compared to class G cement. As previously mentioned by G. Liu (G. Liu, 2021), the developed geopolymers exhibit lower Young's modulus (YM) compared to shale and consolidated formations. This characteristic makes them suitable for use adjacent to these formations, offering advantages in terms of compatibility and performance. Flexible cement with small YM, large tensile strength, and adequate compressive strength tends to exhibit superior performance in simulating cement stresses. The combination of these properties enables the cement to withstand and adapt to different stress conditions effectively, leading to enhanced durability and overall performance.

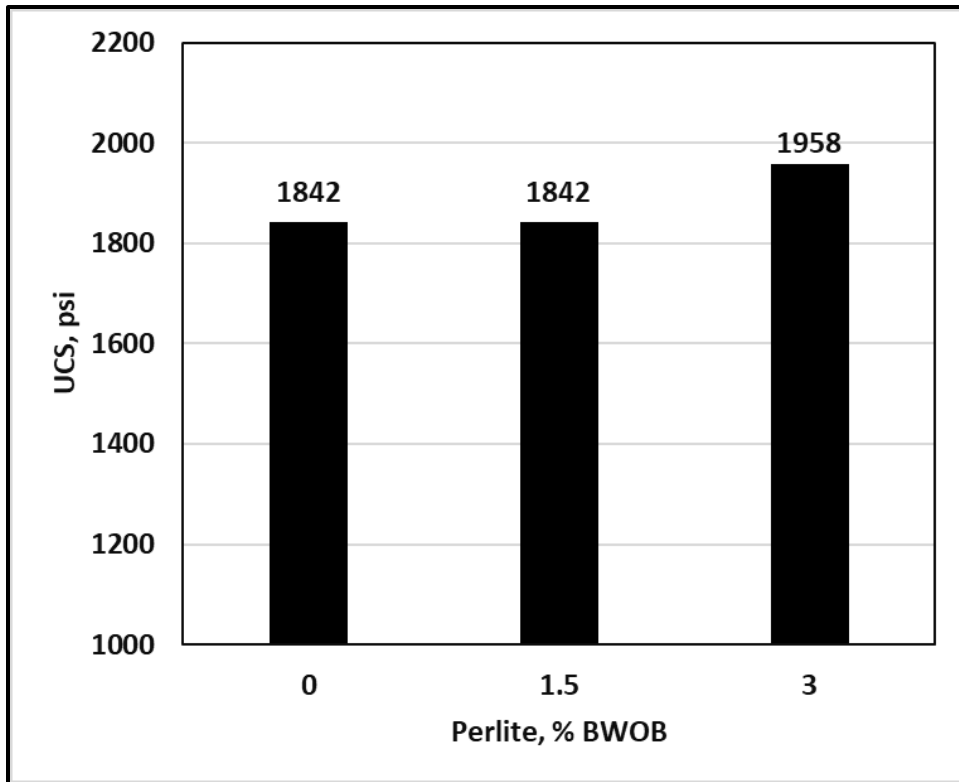


Figure 6.9: The effect of perlite on UCS.

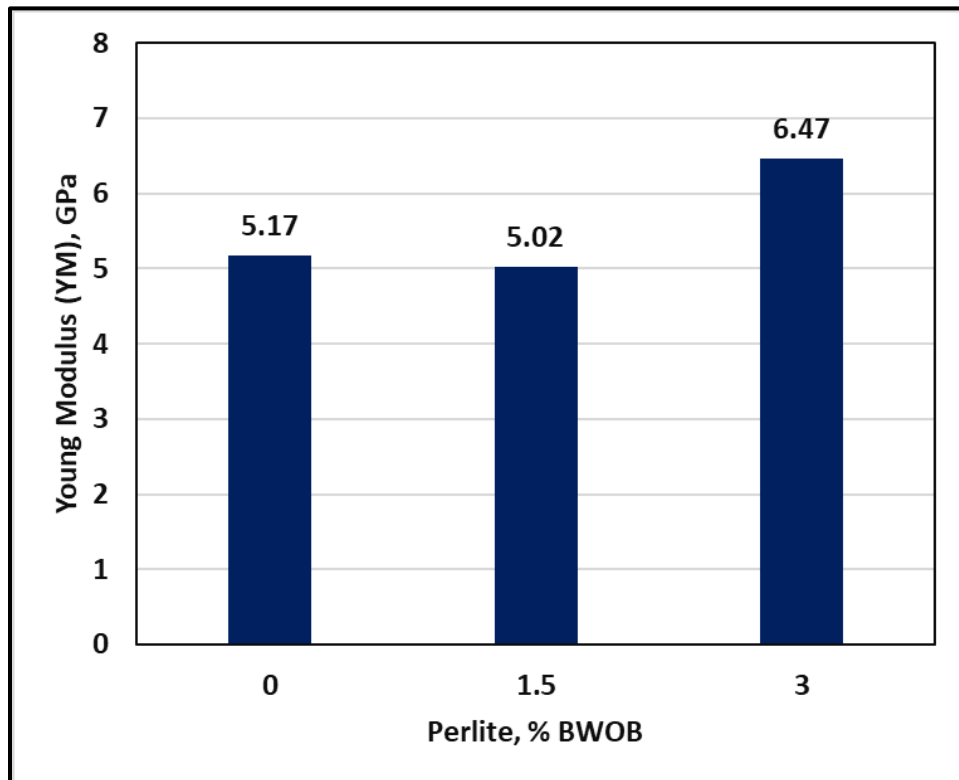


Figure 6.10: The effect of perlite on YM.

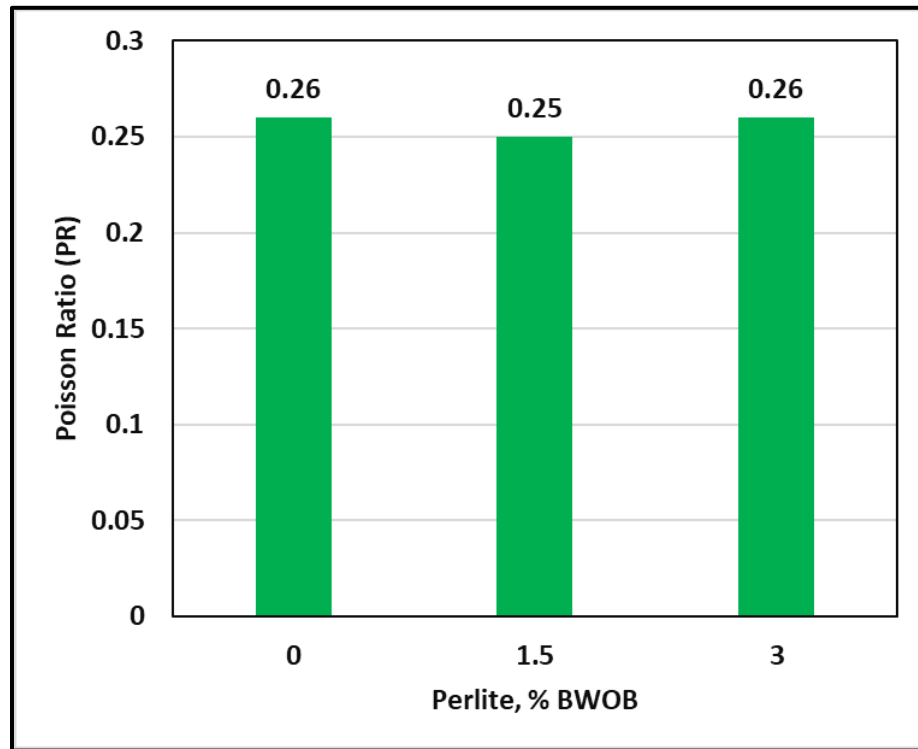


Figure 6.11: The effect of perlite on PR.

6.3.3 Rheological Properties

The evaluation of rheology in cement slurries is crucial due to its impact on various aspects such as slurry mixing, pumping requirements, and displacement of drilling mud. In this study, the rheology was assessed at an average downhole temperature of 195°F. The rheological analysis of the geopolymer slurries revealed that the Bingham Plastic flow model demonstrated the most accurate fit. This indicates a strong correlation between shear stress and shear rate, confirming the suitability of the Bingham Plastic model for describing the flow characteristics of the slurries. Increasing the perlite percentage increased the yield point by a factor of 1.8 but it adversely affects the plastic viscosity (PV) as it increased PV by 61.3 %, as presented in **Figure 6.12** and **Figure 6.13**. The study also examined the gel strength of the developed geopolymer at two-time intervals: 10 sec and 10 min. The gel

strength is a crucial factor that determines the ability of the slurries to maintain their carrying capacity under static conditions. Additionally, the growth of gel strength plays a significant role in resisting gas invasion. Adding perlite enhanced both 10 sec and 10 min gel strength. **Figure 6.12** and **Figure 6.13** provide an overview of the perlite effects on the rheological properties of the developed geopolymers slurries.

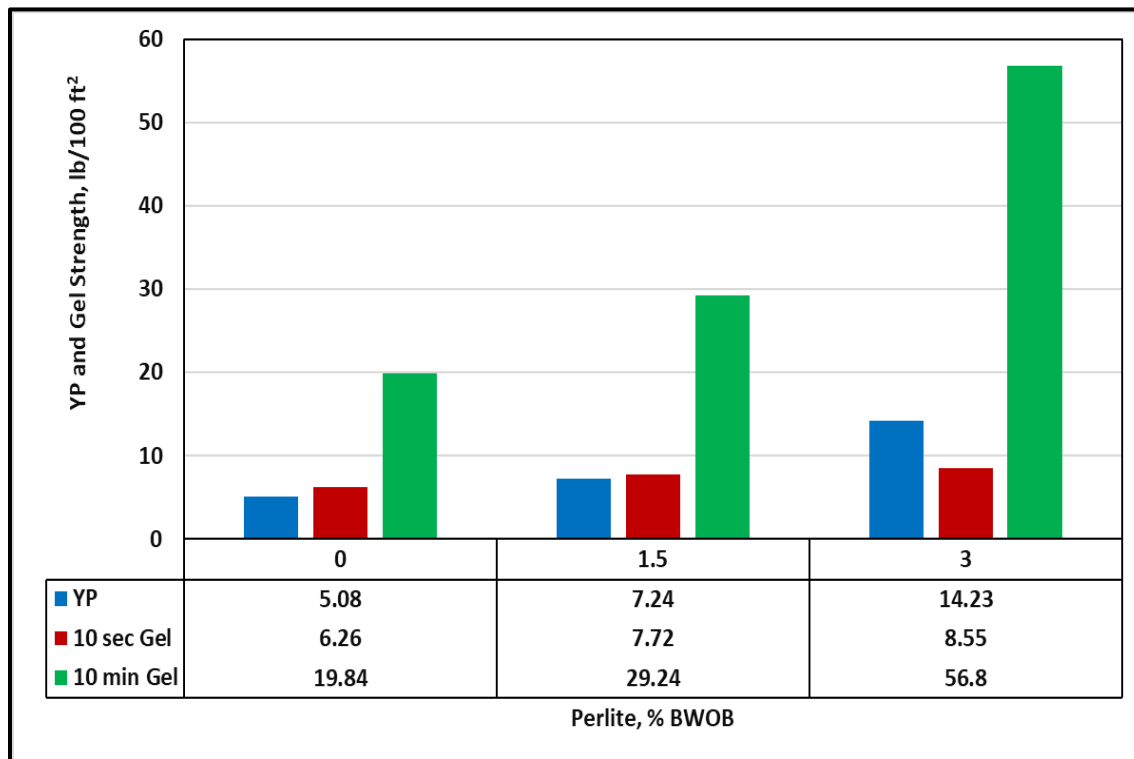


Figure 6.12: The effect of perlite on rheological parameters.

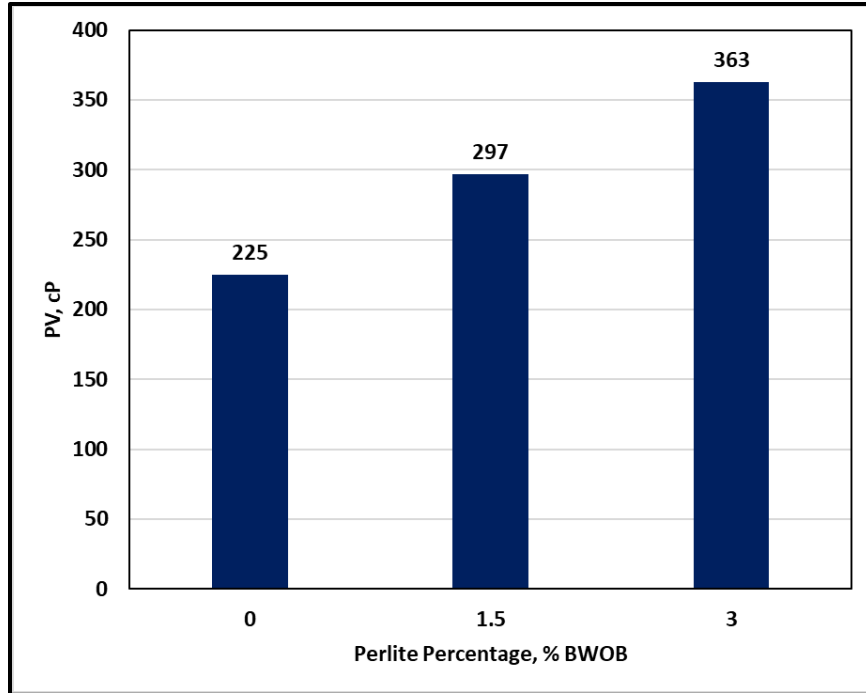


Figure 6.13: The effect of perlite on plastic viscosity (PV).

6.4 Conclusions

In this study, the effectiveness of perlite in addressing sedimentation and stability issues in high-density hematite-based geopolymer systems was investigated. Three different concentrations of perlite (0, 1.5, and 3% BWOB) were evaluated to assess their impact on various cement properties. Overall, the results highlight the significant benefits of incorporating perlite in geopolymer cement formulations, particularly in mitigating sedimentation and stability issues, improving compressive strength, and maintaining desirable rheological properties. These findings contribute to the advancement of geopolymer technology in the oil and gas industry, offering potential solutions for cementing challenges in various wellbore conditions. The study outcomes can be summarized as follows.

- The API method, NMR and CT-scan results demonstrated that the addition of 3% perlite significantly reduced the density and porosity variation between the top and bottom sections of the geopolymer samples.
- The addition of perlite had a positive effect on the compressive strength of the developed geopolymer, with the optimum perlite concentration leading to a 24-hour UCS of at least 1,952 psi, surpassing the minimum requirements for drilling applications.
- The Young's modulus and Poisson's ratio showed minimal differences between the geopolymer samples with 0 % and 3 % perlite concentrations, indicating that the presence of perlite had a negligible effect on the elasticity of the samples.
- Increasing the perlite percentage resulted in higher yield points but adversely affected the plastic viscosity.
- The gel strength of the geopolymer slurries was enhanced by the addition of perlite, both at 10 sec and 10 min.

CHAPTER 7

REVOLUTIONIZING HIGH-PRESSURE WELL CEMENTING: ENHANCING GEOPOLYMER CEMENT WITH LAPONITE FOR SUSTAINABLE AND SEDIMENTATION-FREE APPLICATIONS

7.1 Introduction

Although OPC is widely used in well cementing, it faces various technical challenges and environmental concerns. These include issues such as gas invasion, instability at high temperatures and in corrosive conditions, cement failure, and strength retrogression at elevated temperatures (Khalifeh et al., 2017; Y. Yan et al., 2020). OPC-based systems are also susceptible to acid attacks (Bakharev et al., 2003; Nasvi et al., 2013a) and experience a significant reduction in compressive strength when in contact with mud, which also adversely affects cement rheological properties and pumpability (Aughenbaugh et al., 2014; EI-Sayed, 1995; Liu et al., 2016). Furthermore, OPC production contributes to high greenhouse gases emissions and requires substantial energy consumption. To overcome these challenges and develop more sustainable cement systems, researchers have explored alternative materials. Recent studies have explored the effects of different materials on

cement properties (Adjei et al., 2022a; Ahmed et al., 2020, 2018; Bageri et al., 2021; Mahmoud et al., 2019; Mahmoud and Elkatatny, 2020b, 2020c). Additionally, some researchers have focused on exploring new materials, like geopolymers, as total replacement for OPC in cementitious binders (Adjei et al., 2022b; Salehi et al., 2019, 2018).

Geopolymer technology, widely utilized in the construction industry, is currently being explored for its potential in well cementing. Researchers investigate the behavior of various geopolymers under wellbore conditions to assess their suitability (Adjei et al., 2022b). Geopolymers are formed through the geopolymerization process, where aluminosilicate materials are dissolved in alkali hydroxides and/ or silicates, resulting in a compact geopolymeric substance (Palomo et al., 1999; Phair and Van Deventer, 2001; Ren et al., 2017; Silva et al., 2007). In contrast to OPC, geopolymers production is more environmentally friendly and requires less energy (Davidovits, 2010; Patel and Shah, 2018; Singh et al., 2018; Worrell et al., 2003). Geopolymers utilize industrial and agro-wastes such as fly ash, slag, silica fume, coconut ash, and rice husk, making them eco-friendly with lower CO₂ emissions (Abdelaal and Elkatatny, 2023c, 2023a). Additionally, clays such as metakaolin and certain rocks such as aplite can be employed to create specific types of geopolymers. Geopolymers demonstrate superior performance compared to traditional cement systems, exhibiting characteristics such as low shrinkage and permeability, strength development, high temperature stability, tolerance to mud contamination, and long-term durability, making them a promising alternative to OPC in oil well cementing (Cong and Cheng, 2021; Nasvi et al., 2013a).

The formulation of cement slurry is tailored to the specific conditions of the wellbore, including pressure, temperature, and the type of cement job. In deep wells or high-pressure zones, it is recommended to use heavy-weight cement slurries, typically with a density of 17 pounds per gallon (ppg) or higher (Magarini et al., 2009). One cost-effective method to increase density is by reducing water content in the slurry (Michaux et al., 1990). However, reducing water content poses challenges in terms of controlling fluid loss and maintaining desirable rheological properties (Ahmed et al., 2022). Reducing water content in the cement slurry may lead to a thicker slurry, resulting in higher pumping pressures. Additionally, the setting time of the slurry may be accelerated, reducing the time available for proper placement. These factors can potentially lead to complications and difficulties in achieving a successful cement job, making it necessary to employ weighting materials to attain the desired higher density. Weighting materials, such as hematite, are commonly employed in cementing activities, particularly in deep wells and across high pressure formations (Ahmed et al., 2019). Consequently, weighting agents are needed to get a higher density. Weighting materials are widely used in drilling fluids to balance high pressure formations. Limited research has been conducted on using weighting materials in the field of geopolymers technology for oil well cementing. These studies primarily involved experiments related to compressive strength and thickening time for barite-based geopolymers slurries (Kanesan et al., 2018; Salehi et al., 2017b). High density hematite-based geopolymers systems suffer from low thickening time and sedimentation issues (Abdelaal and Elkatatny, 2023b). Abdelaal et al., (2023) introduced a hematite based FFA geopolymers system for oil well cement. Although the authors provided a combination of a superplasticizer and a retarder to enhance the pumpability of the proposed geopolymers

system, the sedimentation evaluation was not a part of their study. Sedimentation may occur due to the presence of large particles of weighting materials (Malyshev et al., 2013). Sedimentation issues in slurries result in the formation of an uneven cement column, which is unfavorable for achieving optimal strength and effective zonal isolation. The settling of solid particles leads to an inconsistent distribution of compressive strength and bonding along cemented sections (Erik B. Nelson and Guillot, 2006). It is clear from the literature that weighting materials usage in geopolymer technology is a relatively new area in well cementing.

Fly ash is the by-product of coal combustion in industrial processes. It is categorized into two classes, namely Class F and Class C, based on the amount of CaO present, as per ASTM C618 (ASTM C618, 2023). Class F fly ash, generated from burning bituminous coal, has a low CaO content. On the other hand, Class C fly ash, resulting from burning lignite and sub-bituminous coal, contains a higher amount of calcium. Fly ash is widely available and commonly used in the production of geopolymers. Since the early 1900s, it has been widely utilized and frequently incorporated as an ingredient in concrete production (Scrivener et al., 2018). The use of fly ash instead of Portland cement offers several benefits, including the reduction of greenhouse gas (GHG) emissions and decreased construction costs. Fly ash possesses favorable characteristics such as cost-effectiveness, availability, a spherical structure, and a high content of active alumina and amorphous silica (Cong and Cheng, 2021).

Laponite, a synthetic clay mineral, is composed of lithium sodium magnesium silicate. This versatile material finds extensive use as a rheology modifier and reinforcement in various industries including mining, petroleum, pharmaceuticals, agrochemicals, and paint

polymers, among others (Jatav and Joshi, 2014). Laponite particles exhibit a disk-like morphology, characterized by a thickness of approximately 1 nm and a diameter ranging from 25 to 27 nm (Kroon et al., 1998). In its dry state, the electron-rich faces of laponite particles share their electrons with sodium atoms located in the interlayer space. However, when dispersed in an aqueous medium, the sodium ions dissociate, leading to a permanent negative charge on the faces of laponite particles (Jatav and Joshi, 2014). Laponite is used for different applications in oil and gas industry such as shale inhibition (Huang et al., 2018), barite anti-sagging in water-based muds (Mohamed et al., 2021), plugging and lubrication capabilities in water-based-drilling fluids (Huang et al., 2021).

These studies had consequences for improved drilling operations, so there is a strong motivation to explore the feasibility of incorporating laponite into high density fly ash geopolymer cement systems. This article introduced another application for laponite as a rheology modifier and an anti-sedimentation additive for hematite-based high-density geopolymers. The first objective of this study is to assess the effectiveness of using laponite particles in minimizing sedimentation problems within heavy weight geopolymer systems. The second objective is to evaluate the effect of laponite on the properties of Class F fly ash geopolymer cement.

7.2 Materials and Methodology

7.2.1 Materials

In this study, various materials were used to investigate their suitability for geopolymer applications under wellbore conditions. The aluminosilicate material used was FFA, while

hematite served as a weighting material. The activator was NaOH solution, and additional chemical additives like retarders, deformers, and superplasticizers were included to improve the properties of the geopolymers. The measured specific gravities (SG) for FFA and hematite were 2.25 and 5.05, respectively. Particle size distributions (PSD) were evaluated utilizing a laser diffraction particle size analyzer, as illustrated in **Figure 7.1**. The outcomes demonstrated that half of the FFA, hematite, and laponite particles exhibited sizes less than 19.35 μm , 21.54 μm , and 9.19 μm , respectively. X-ray fluorescence (XRF) analysis confirmed the high iron content (approximately 95%) of hematite, while X-ray diffraction (XRD) analysis confirmed its composition consisting of hematite only. In addition, XRF analysis indicated that FFA contained significant amounts of silica (SiO_2) and alumina (Al_2O_3), as listed in **Table 7.1**. These components are important in the production of geopolymers. The scanning electron microscopy (SEM) images, as presented in **Figure 7.2**, show that the particles of fly ash exhibit a spherical morphology, the hematite particles possess irregular shapes and laponite particles have a disk-shaped structure.

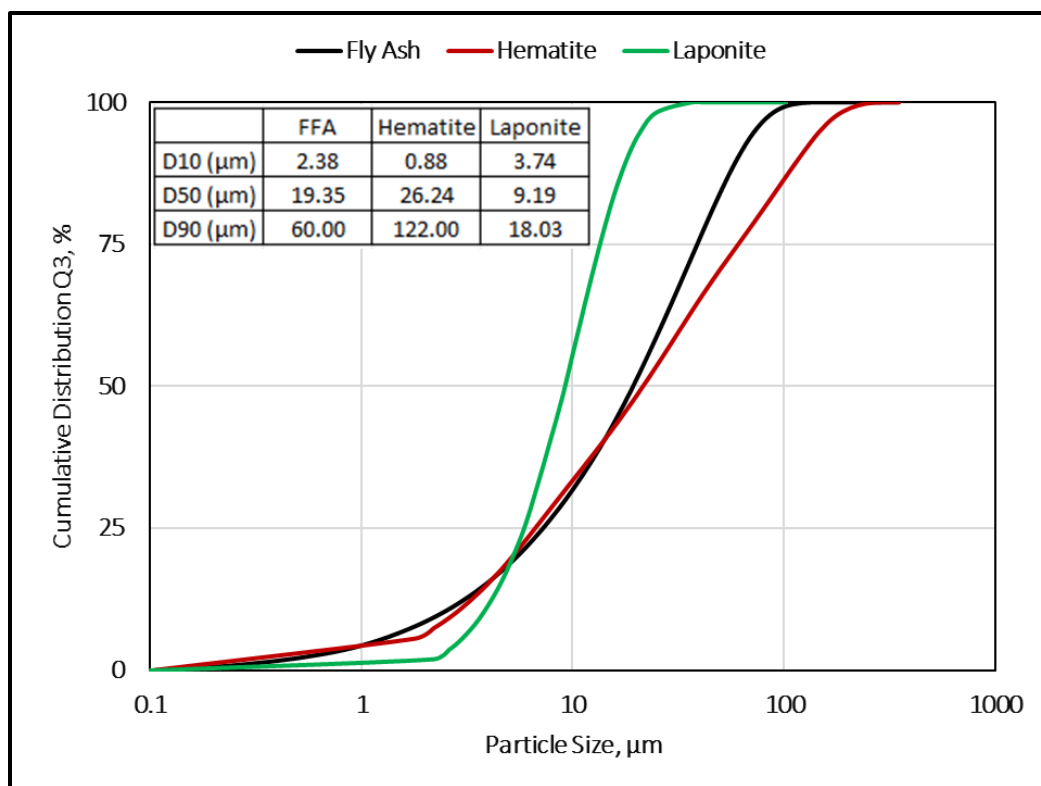


Figure 7.1 PSD of FFA, hematite and laponite.

Table 7.1 XRF of FFA and laponite in terms of wt %.

Oxide	SiO ₂	Al ₂ O ₃	MgO	CaO	Fe ₂ O ₃	TiO ₂	K ₂ O	Na ₂ O	SO ₃	MnO	Li ₂ O
FFA	55.92	29.54	-	5.49	4.93	1.91	1.66	-	0.39	0.04	-
Laponite	59.50	-	27.50	-	-	-	-	2.80	-	-	0.80

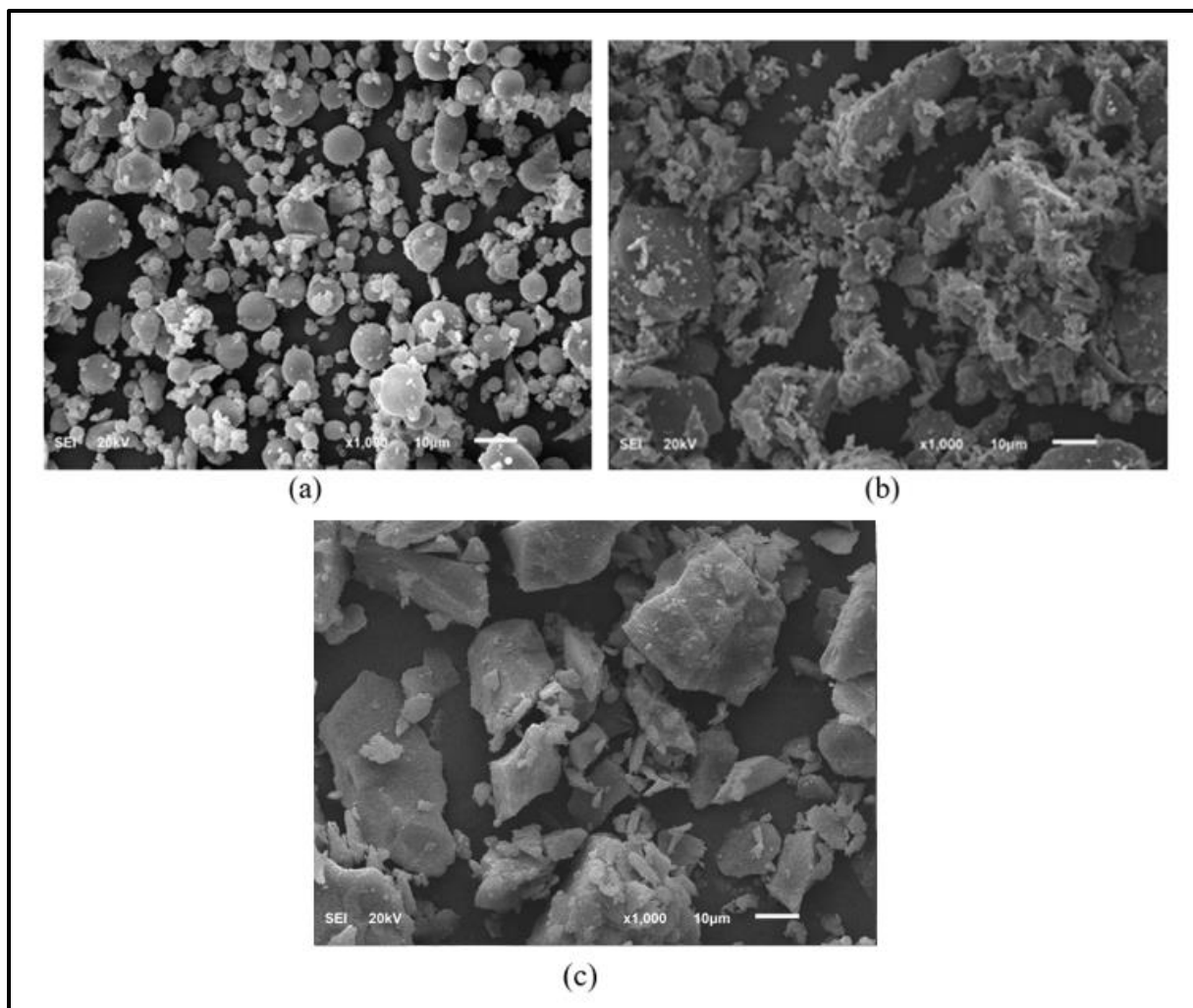


Figure 7.2 SEM of FFA (a), hematite (b) and laponite (c).

7.2.2 Methodology

This section presents an overview of the methods followed in this research. The study commenced by gathering, analyzing, and preparing the necessary materials. Subsequently, slurries were prepared and tested for mixability. The sedimentation was assessed through the application of three different techniques. Following this, the cured samples were evaluated in terms of mechanical and rheological properties. **Figure 7.3** provides a summary of the methods used in this study.

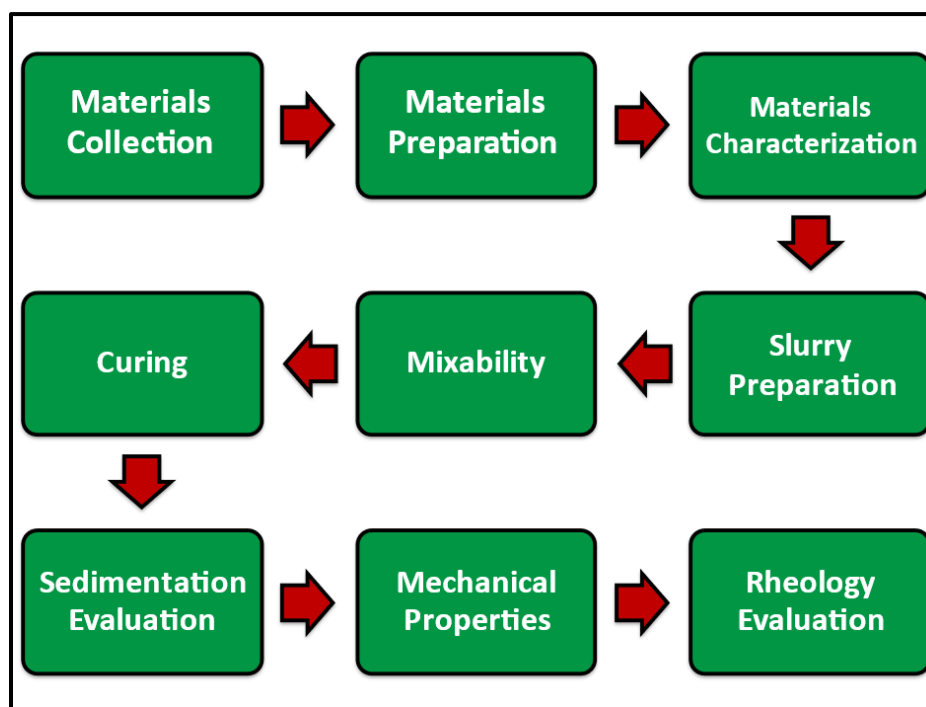


Figure 7.3 The overview of the methods followed in this study.

Materials and Samples Preparation

The specific gravities of the powders were determined using a gas pycnometer. FFA underwent sieving to verify that the particle sizes remained below 104 μm which was confirmed by PSD. To prepare the sodium hydroxide (NaOH) solution, NaOH pellets were dissolved in distilled water using a magnetic stirrer to prepare a 4 M NaOH solution. The

solution was left to cool at room temperature for a minimum of 24 h before starting the experiment. In the preparation of geopolymer slurries, two techniques, wet and dry, can be employed (Salehi et al., 2017b). For this study, the wet process technique was utilized. In the wet mixing, superplasticizers and/or retarders are mixed with activation solutions for 2 min at a high shear rate of 12,000 RPM using a mixer. The solid mixture is then added and further mixed with the pre-mixed solution for another 2 min. Nine Laponite concentrations (0, 0.3, 0.6, 0.9, 1.2, 1.5, 2, 2.5 and 3%) were used to prepare the geopolymer slurries as increasing laponite percentage above 3 % resulted in a thick slurry with mixability difficulties. The liquid to binder ratio was fixed at 0.56 as used by Abdelaal et al., (2023). The mix design is listed in **Table 7.2**.

Table 7.2 The mix design to prepared geopolymer slurries.

Component	BWOB, %
FFA	100
Hematite	80
Defoamer	0.0164
Superplasticizer	5
Retarder	5
4 M NaOH	56
Laponite	0 to 3 (9 concentrations)

Sedimentation Evaluation

Sedimentation evaluation included using three techniques, namely API method, NMR and CT-scan. The cured geopolymer samples were cut into 3 sections (top, middle and bottom). The data obtained from the API method, NMR analysis, and CT scan imaging for each section of the geopolymer cement samples were analyzed. Comparative analysis among the sections provided insights into the variation of sedimentation behavior throughout the sample height. To evaluate sedimentation using the API method, the cured geopolymer samples were cut into 3 sections (top, middle and bottom). The weight of the geopolymer samples were measured in air and water using a balance. By applying the principle of Archimedes, the specific gravity of the cement sections was determined by dividing the weight in air by the weight in water. The results are used to construct a density profile for the entire sample (API RP 10B-4, 2004).

NMR analysis was conducted to assess sedimentation in the geopolymer cement samples. The cured samples were prepared as cylindrical specimens and placed within the NMR apparatus with a low magnetic field. The NMR measurements were performed to capture the sedimentation behavior through showing the differences in NMR porosity among different cement sections. The resulting NMR data, such as relaxation times, were analyzed to quantify the sedimentation. CT-scan imaging was employed to visualize and analyze the sedimentation behavior of the geopolymer cement samples. The cured samples were scanned using a medical CT scanner, which captured cross-sectional images of the samples. The acquired CT images were processed and analyzed to determine the sedimentation patterns, including the distribution, and settling characteristics of the particles within the samples.

Mechanical and Rheological Properties

After mixing, the geopolymer slurries underwent conditioning in an atmospheric consistometer at a temperature of 195°F and a rotational speed of 150 rpm for 30 min. Rheology evaluation was performed using a viscometer at average temperatures of 82 and 195°F. The assessment of mechanical properties included UCS measurement and dynamic elastic properties such as YM and PR. Following conditioning, the slurry was poured into cylindrical molds measuring 1.5 inches in diameter and 4 inches in length. Subsequently, the molds were placed in an HPHT curing chamber set at 292°F and 3,000 psi for 24 h. UCS was measured using the scratch test method, which involves the continuous shearing action caused by a moving cutter on the sample surface. The applied force on the cutter produces a rock strength profile along the sample. YM and PR were estimated by measuring the sonic velocities, specifically the compressional and shear waves.

7.3 Results and Discussion

7.3.1 Sedimentation

Figure 7.4 shows the cured hematite-based geopolymer samples, which were prepared with varying concentrations of laponite. Laponite was incorporated to address challenges related to sedimentation and stability in the high-density hematite-based geopolymer systems. A total of nine laponite percentages were examined during the investigation. Adding 3% BWOB of laponite to the system decreased the density variation between the top and bottom sections from 39.38% when no laponite was present in the system to 0.58%. The densities of the three sections for each laponite concentration, determined using the API method, are summarized in **Figure 7.5**. NMR analysis revealed that increasing

laponite concentration led to a decrease in NMR porosity differences among the top, middle, and bottom sections of the geopolymer samples, as presented in **Figure 7.6**. **Figure 7.7** compares the NMR porosities for laponite concentrations of 0% and 3%, demonstrating notable porosity differences among the three sections at 0% and minor differences at 3%.

Figure 7.8 provides an overview of the density and NMR porosity differences for the various laponite concentrations investigated in this study. The coefficient of determination (R^2) between laponite concentration and the difference in density and NMR porosity was found to be 0.99 and 0.98, respectively, as displayed in **Figure 7.8**. The density and NMR porosity data for the various sections of the geopolymer cement are in agreement, as demonstrated in **Figure 7.5** and **Figure 7.6**. The results obtained through CT-scan imaging confirmed the findings obtained from the NMR and API methods, as illustrated in **Figure 7.9**. Notably, **Figure 7.9** (a) demonstrates significant density variation among the slices in the absence of laponite, whereas this variation decreased progressively by increasing the laponite concentration (from left to right in **Figure 7.9**), ultimately reaching a point where the slices displayed minimal density differences within the same sample, indicated by the approximately uniform color in **Figure 7.9** (c). Based on the outcomes derived from the three techniques, the optimal Laponite concentration was determined to be 3% BWOB.

These findings can be attributed to colloidal suspension stability, gel formation capability, thixotropic behavior, surface area and shape. Laponite is made up of plate-like particles that have a negative charge on their surface. When dispersed in a liquid, these particles repel each other due to electrostatic forces, preventing them from settling down quickly. This electrostatic repulsion creates a stable colloidal suspension, where the particles remain evenly dispersed throughout the solution. Laponite can form a gel-like structure when

dispersed in water or other liquids. This gel network traps water and other particles within its structure, preventing settling and sedimentation. This gel-like behavior contributes to the stability of the solution and reduces the tendency of suspended particles to settle over time. Laponite exhibits thixotropic behavior, which means that it becomes less viscous when agitated or sheared and returns to its more viscous state when left undisturbed. This property can help prevent sedimentation by allowing the solution to flow and mix easily during agitation, but then it quickly thickens again when agitation stops, helping to immobilize suspended particles and reduce settling. The flat plate-like structure of laponite particles and their relatively large surface area-to-volume ratio contribute to the particles' resistance to sedimentation. The particles tend to interact with the liquid and other components in a way that impedes settling.



Figure 7.4 Laponite-based geopolymer samples.

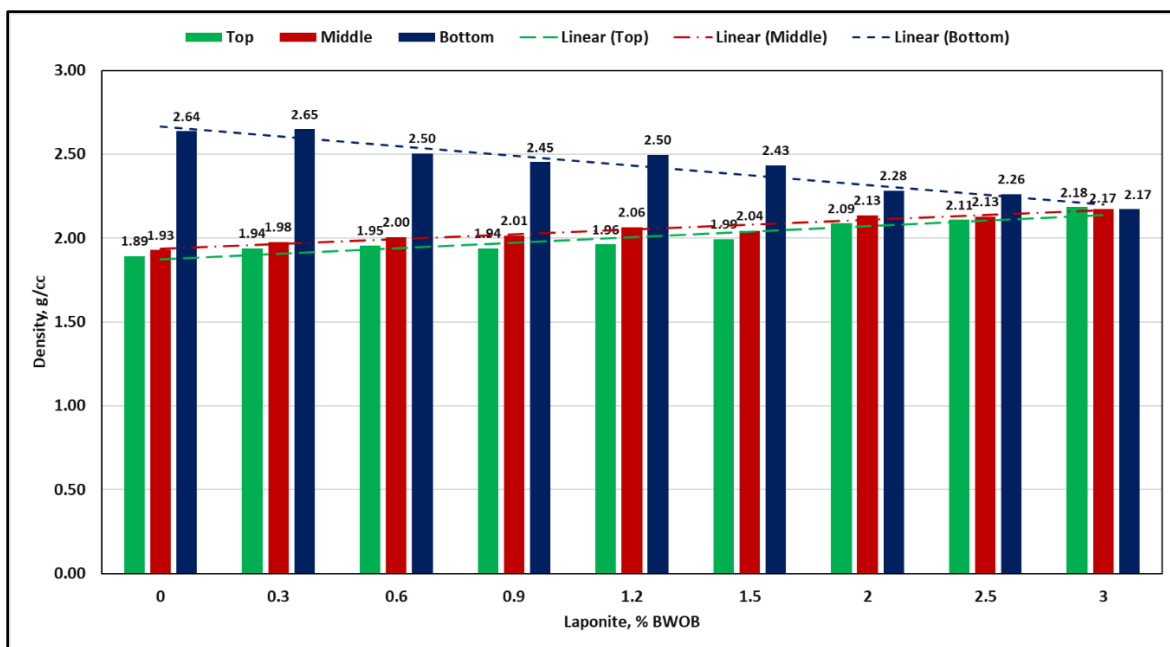


Figure 7.5 API method results for different laponite concentrations.

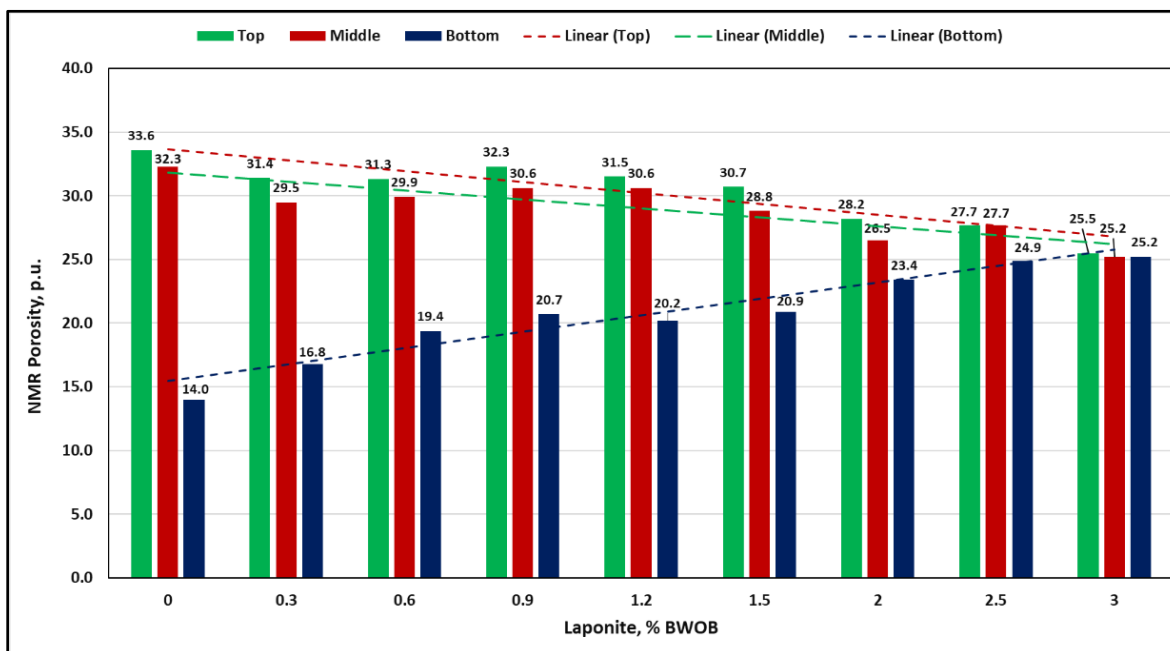


Figure 7.6 NMR porosities summary for different laponite concentrations.

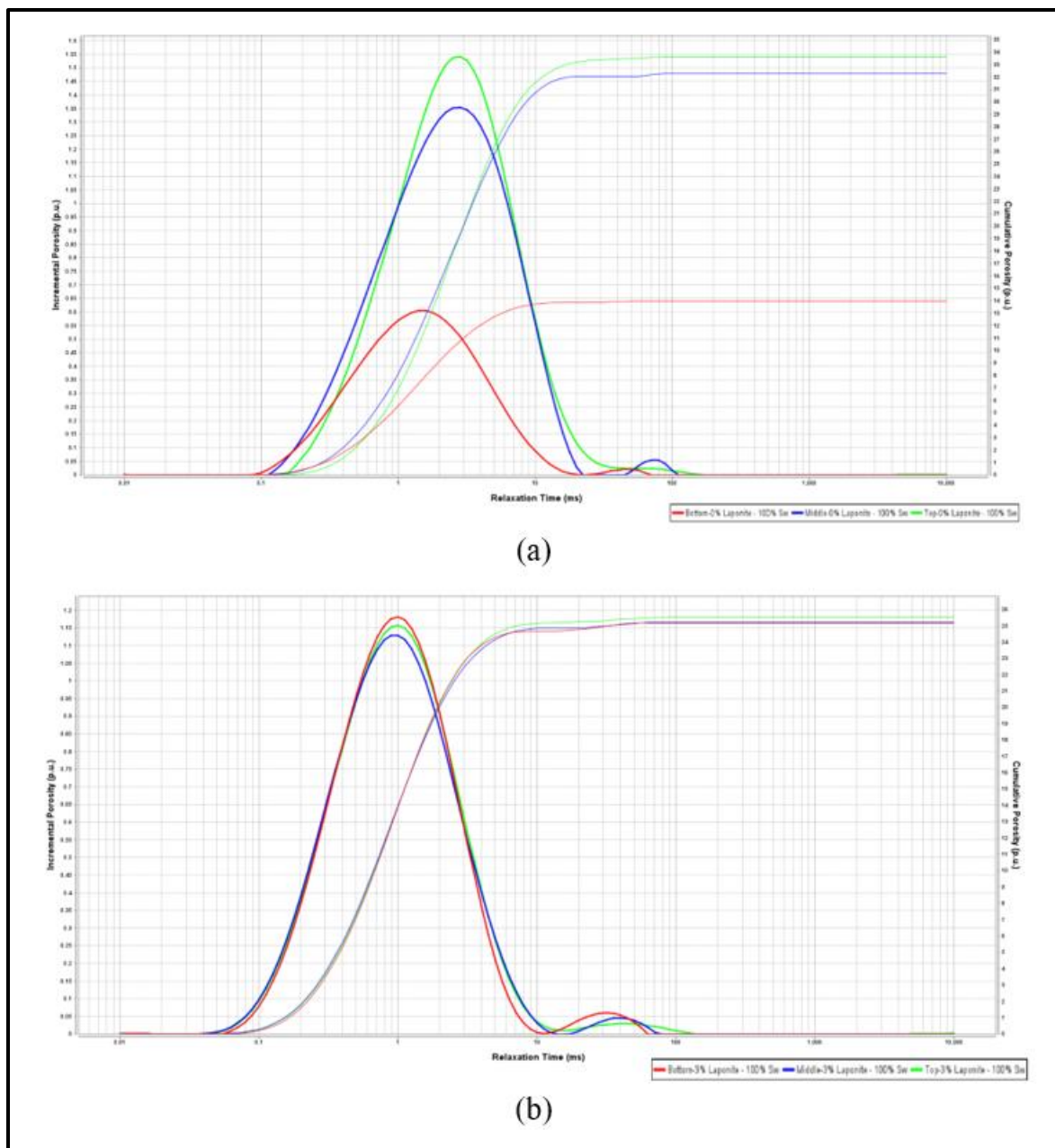


Figure 7.7 NMR results for 0% laponite (a), and 3% laponite (b) (red, blue, and green colors refer to bottom, middle and top sections respectively).

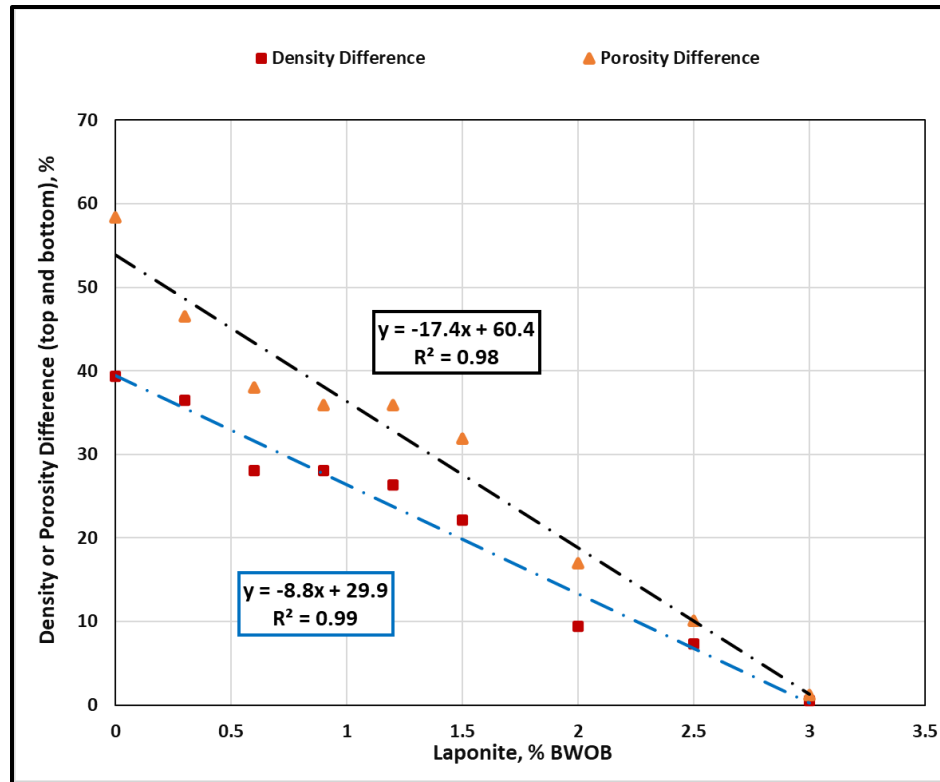


Figure 7.8 Density and porosity differences between top and bottom sections for different laponite concentrations.

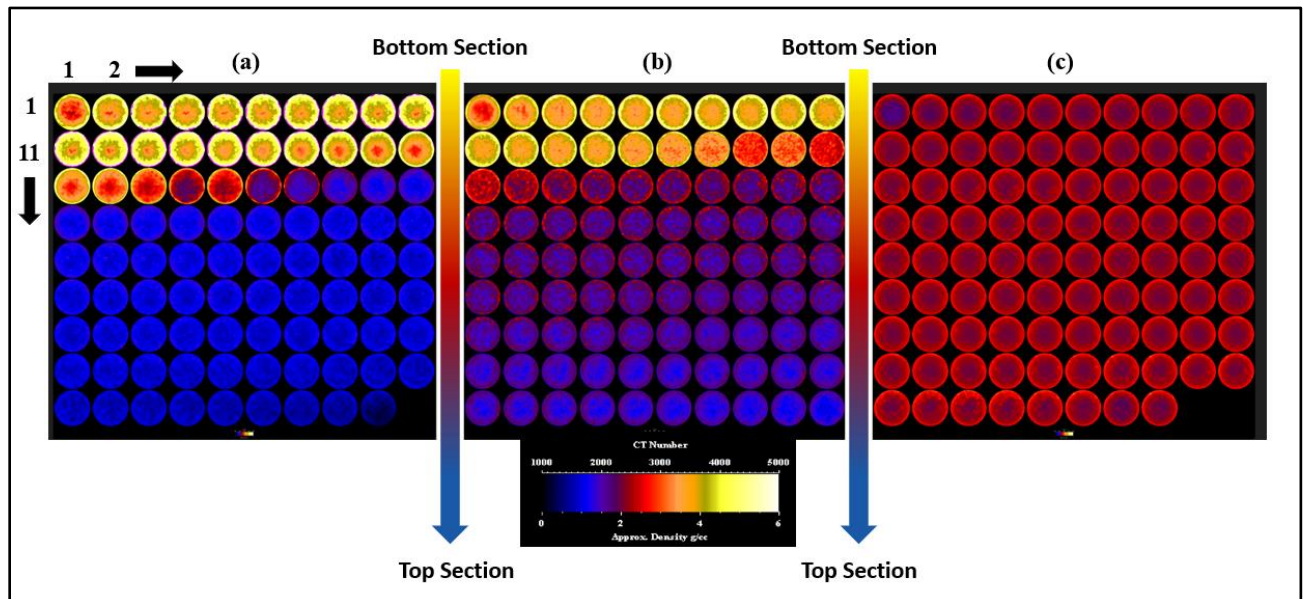


Figure 7.9 CT-scan results for different laponite concentrations (0% (a), 1.5% (b) and 3% (c)).

7.3.2 Mechanical Properties

After ensuring that laponite can be used to address the sedimentation and stability issues, the effects of laponite on other geopolymer properties were evaluated. The optimum laponite concentration increased the 24 h UCS of the developed geopolymer by 43.54% as compared to 0% laponite as shown in **Figure 7.10**. Laponite increased the UCS values linearly with a coefficient of determination (R^2) of 0.97 as depicted in **Figure 7.10**. Determining the exact required compressive strength prior to drilling through casing shoe can be challenging; nevertheless, field practice typically recommends a minimum of 500 psi. (Mitchell and Miska, 2011). The proposed geopolymers demonstrated a 24-h UCS of at least 1,798 psi, exceeding the minimum requirements stated in the literature for various applications and surpassing reported values in heavy-weight cementing programs. Despite the increase in laponite percentage from 0% to 3%, which led to an increase in Young's modulus (YM) from 4.9 to 6.9 GPa as shown in **Figure 7.11**, the YM values remained lower than those of Class G cement (G. Liu, 2021). Laponite had a positive effect on PR as it increased from 0.23 to 0.27 by increasing the percentage from 0 to 3%. Laponite demonstrated a linear enhancement in PR values, accompanied by an R^2 equal to 1, as depicted in **Figure 7.12**.

A cement with a smaller Young's modulus (YM) is often preferred for unconsolidated strata as it offers better performance compared to a cement with a higher YM (G. Liu, 2021). The developed geopolymers had a YM in the range of 4.8 to 6.9 GPa and PR in the range of 0.23 to 0.27 as presented in **Figure 7.11** and **Figure 7.12**. The developed geopolymers exhibit greater flexibility in terms of YM and PR compared to Class G cement. As previously mentioned by Liu (2021), the developed geopolymers exhibit lower Young's

modulus (YM) compared to shale and consolidated formations. This characteristic makes them suitable for use adjacent to these formations, offering advantages in terms of compatibility and performance. Flexible cement with small YM, large tensile strength, and adequate compressive strength tends to exhibit superior performance in simulating cement stresses. The combination of these properties enables the cement to withstand and adapt to different stress conditions effectively, leading to enhanced durability and overall performance.

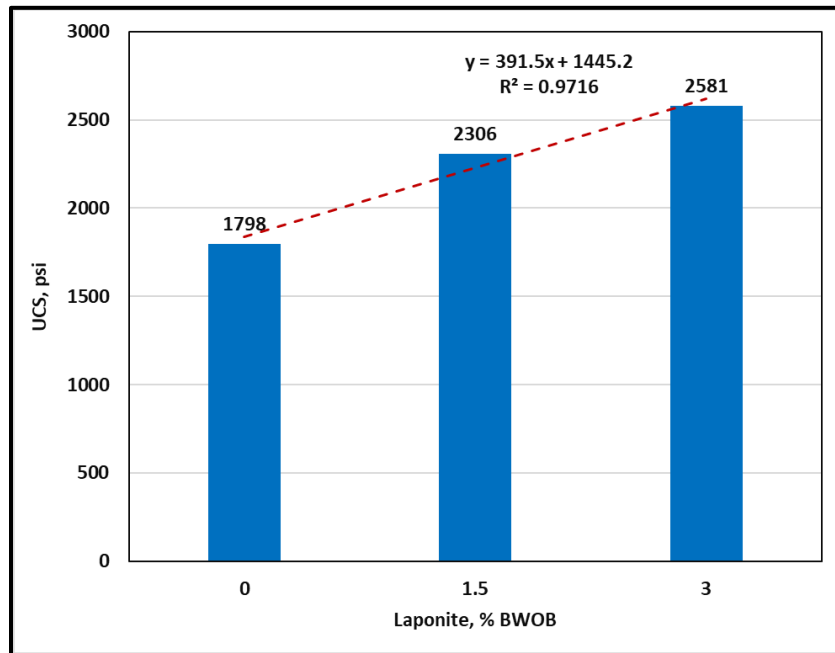


Figure 7.10 The effect of laponite on UCS.

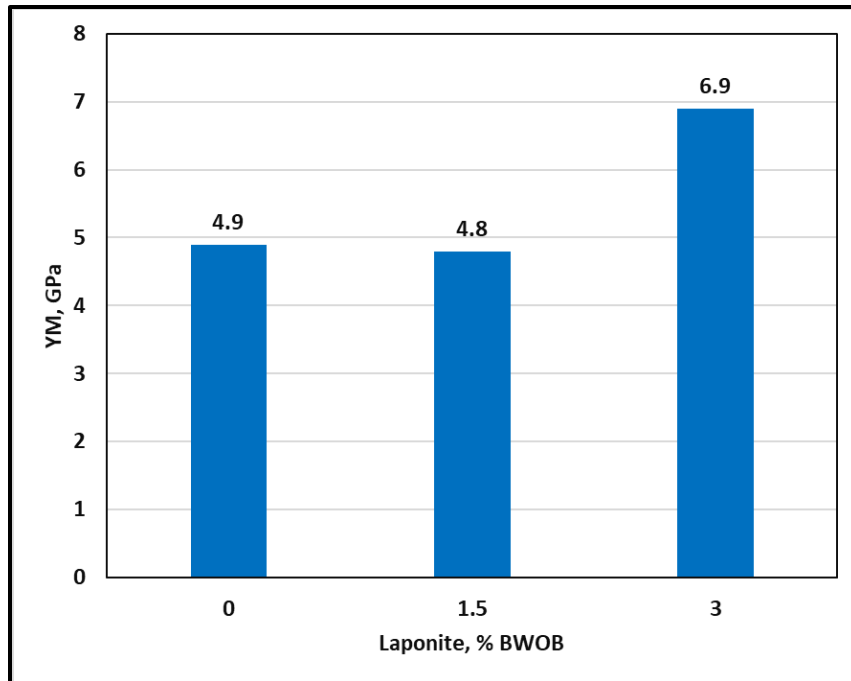


Figure 7.11 The effect of laponite on YM.

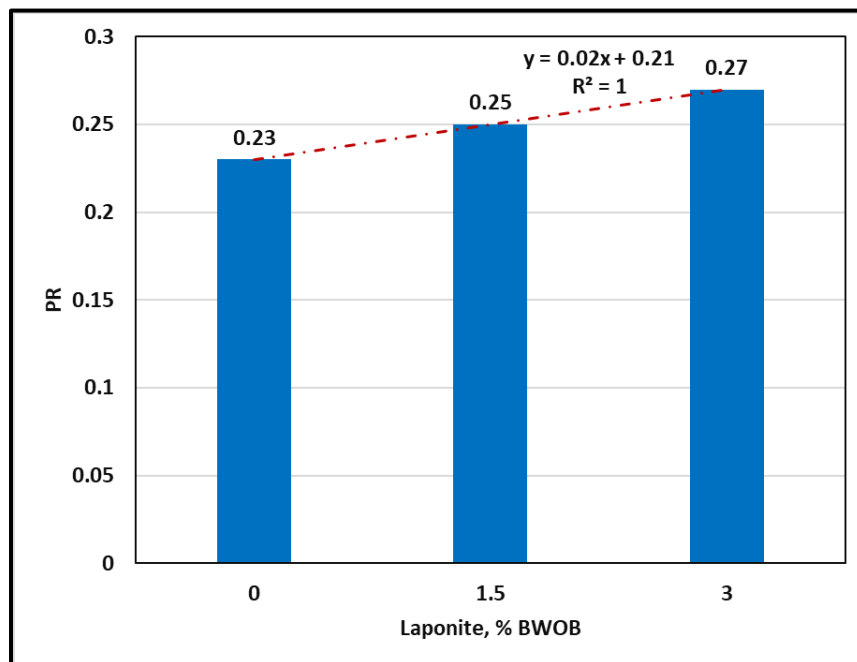


Figure 7.12 The effect of laponite on PR.

7.3.3 Rheological Properties

The rheology assessment of cement slurries is important owing to its effect on various aspects such as slurry mixing, pumping requirements, and displacement of drilling mud. In this work, the rheology of the geopolymer formulation with 3% laponite was assessed at an average surface and downhole temperatures (82 and 195°F, respectively). The rheological analysis of the geopolymer slurries revealed that the Bingham Plastic model demonstrated the best fit. **Table 7.3** and **Table 7.4** list the rheological parameters for 82 and 195°F, respectively. For yield point (YP), Laponite increased YP by 48.32 and 46.4% for 82 and 195°F, respectively. Increasing Laponite percentage adversely affected the plastic viscosity (PV) as PV increased by 56.65 and 24.17% for 82 and 195°F, respectively. The gel strength (GS) is a factor that determines the ability of the slurries to maintain their carrying capacity under static conditions. In addition, the growth of gel strength plays a significant role in resisting gas invasion. **Figure 7.13** provides an overview of the temperature effects on the rheology of the developed geopolymer slurry containing 3% laponite. It was found that increasing temperature had a positive effect on PV as it decreased by 65.74%. For YP and 10 sec GS, the values were close for both temperatures. The 10 min gel strength decreased by 74.25% by increasing temperature from 82 to 195°F.

Table 7.3 The effect of laponite on the rheological parameters at surface temperature (82°F).

Parameter	0 % Laponite	3 % Laponite
YP	8.96	13.29
PV	669	1048

Table 7.4 The effect of laponite on the rheological parameters at downhole temperature (195°F).

Parameter	0 % Laponite	3 % Laponite
YP	7.37	10.79
PV	289.1	359

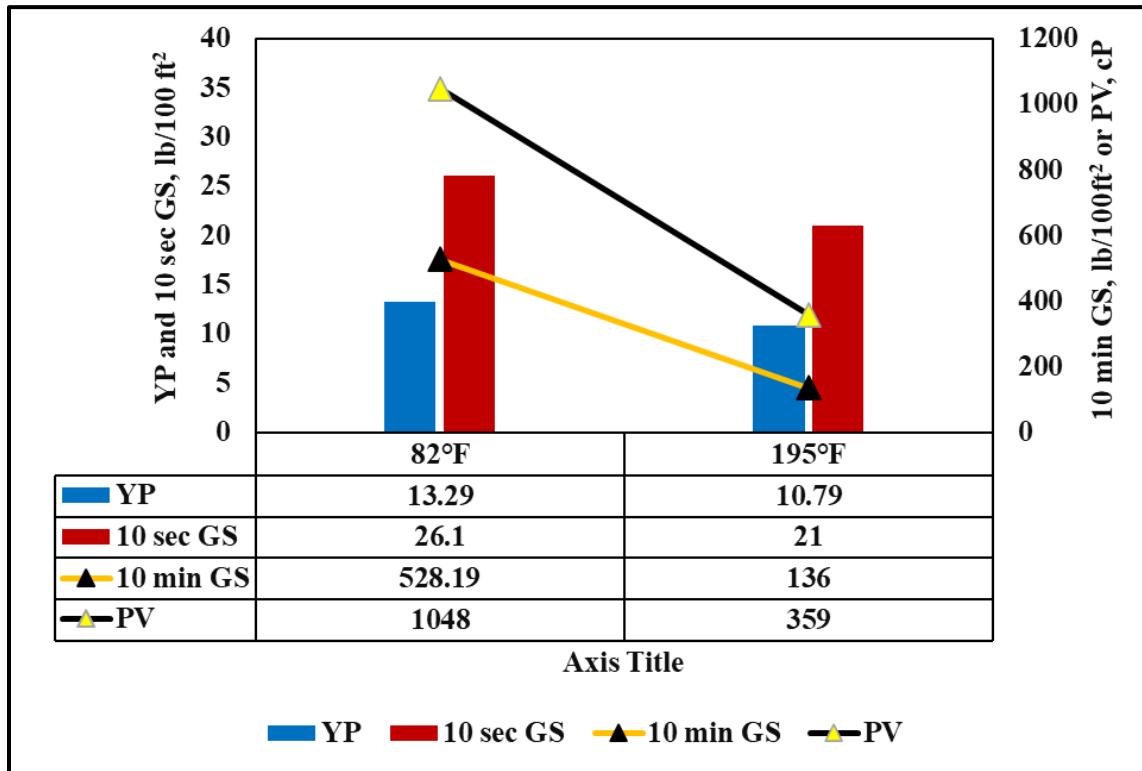


Figure 7.13 The temperature effect on the rheological properties of the 3% laponite formulation.

7.4 Conclusions

In summary, the research findings demonstrate the effectiveness of incorporating laponite in hematite-based geopolymer samples to address sedimentation and stability issues.

- The optimal laponite concentration was determined to be 3% BWOB for tackling sedimentation issues.
- Increasing Laponite concentration improved compressive strength, surpassing the minimum recommended values for field applications.
- YM remained lower than Class G cement, making the geopolymer suitable for unconsolidated strata and adjacent to shale and consolidated formations.
- Laponite addition increased PR and influenced the rheological properties of the geopolymer slurries, enhancing YP and GS.
- The temperature also influenced the rheological properties, with PV decreasing and YP and GS remaining relatively stable.

Overall, incorporating laponite in hematite-based geopolymer systems offers a promising solution to address sedimentation and stability challenges, while improving key properties such as density uniformity, compressive strength, and flexibility.

CHAPTER 8

A VOLCANIC TEPHRA-BASED NON-PORTLAND

CEMENT SYSTEM FOR WELL CEMENTING

SUSTAINABILITY

8.1 Introduction

Portland cement (PC) is widely employed in oil well cementing operations. Nonetheless, PC presents various technical difficulties, particularly in deep formations in addition to environmental concerns. Technical challenges associated with PC encompass concerns such as gas invasion, vulnerability to corrosive environments, instability at elevated temperatures, issues with permeability, susceptibility to cement failure during perforation and fracturing, and strength reduction when exposed to temperatures exceeding 230°F (Khalifeh et al., 2016; Yan Yan et al., 2020). In addition, the manufacture of PC has a substantial influence on the environment because of the high emissions of greenhouse gases and the use of large amounts of energy. To address the technical challenges, researchers are exploring alternative materials such as cellulose nanofibers, granite, polypropylene fibers, metakaolin, rice husk ash, olive waste, and perlite to improve cement properties (Ahmed et al., 2020; Bageri et al., 2021; Mahmoud and Elkatatny, 2020c, 2020d). Some researchers tried to find entirely new materials to replace OPC, such as

geopolymers. Geopolymer technology offers numerous possibilities for application, especially within the construction sector (Sambucci et al., 2021). However, its extensive adoption in the petroleum industry has not been observed thus far.

Currently, cementing researchers study the properties of various geopolymers under wellbore conditions (Abdelaal et al., 2023a; Abdelaal and Elkatatny, 2023c, 2023b; Adjei et al., 2022b; Khalifeh et al., 2014). Geopolymers are inorganic polymeric binders created by the reaction of aluminosilicate substances with alkaline activators and/or soluble silicates (Davidovits, 1991a). In comparison to traditional PC, the production of geopolymers is a cleaner process in terms of CO₂ emissions and requires less energy as compared to OPC (Davidovits, 2010; Patel and Shah, 2018). The production of geopolymers involves the activation of aluminosilicate substances with alkali solutions, leading to the creation of an amorphous to semicrystalline 3D silicoaluminate network (Palomo et al., 1999; Ren et al., 2017; Silva et al., 2007). This process of creating chemically integrated minerals is referred to as geopolymerization (Amritphale et al., 2019). The reaction generates viscous cementitious slurries which harden into a strong, compact geopolymeric material (Phair and Van Deventer, 2001). Although there is some debate among researchers on the exact reaction mechanism, the overall agreement is that it goes through main steps: dissolution, transfer, solidification, and polycondensation (Duxson et al., 2006; Provis and van Deventer, 2007; Silva et al., 2007).

Tephra is the term used to describe fragmented material resulting from a volcanic eruption, with no regard for its composition, the size of the fragments, or the method by which it is deposited. Tephra, in essence, consists of unconsolidated pyroclastic matter, encompassing particles spanning from fine ash (< 2 mm) and lapilli (2-64 mm) to blocks

measuring more than 64 mm in size (Arnalds, 2013). The chemical composition of volcanic products is affected by the nature of each volcanic system. Although silica content is conventionally utilized as the basis for classification, there are different approaches to further categorize igneous rocks. Through a prolonged effort undertaken by the Union of Geophysical Sciences, a classification system was developed, as depicted in **Figure 8.1** (Bas et al., 1986; Siebert et al., 2010). This classification relies on the silica and alkali content and is commonly referred to as the “TAS (total alkali–silica) classification”. While classification systems, including the TAS system, have limitations, the TAS system has shown notable suitability for igneous rocks. Basaltic eruptions, as indicated on the left in **Figure 8.1**, typically exhibit a nonexplosive character, referred to as effusive volcanism or a mixed where more lava is produced than volcanic ash. On the other hand, explosive eruptions leading to the production of tephra necessitate the fragmentation of the magma (Arnalds, 2013).

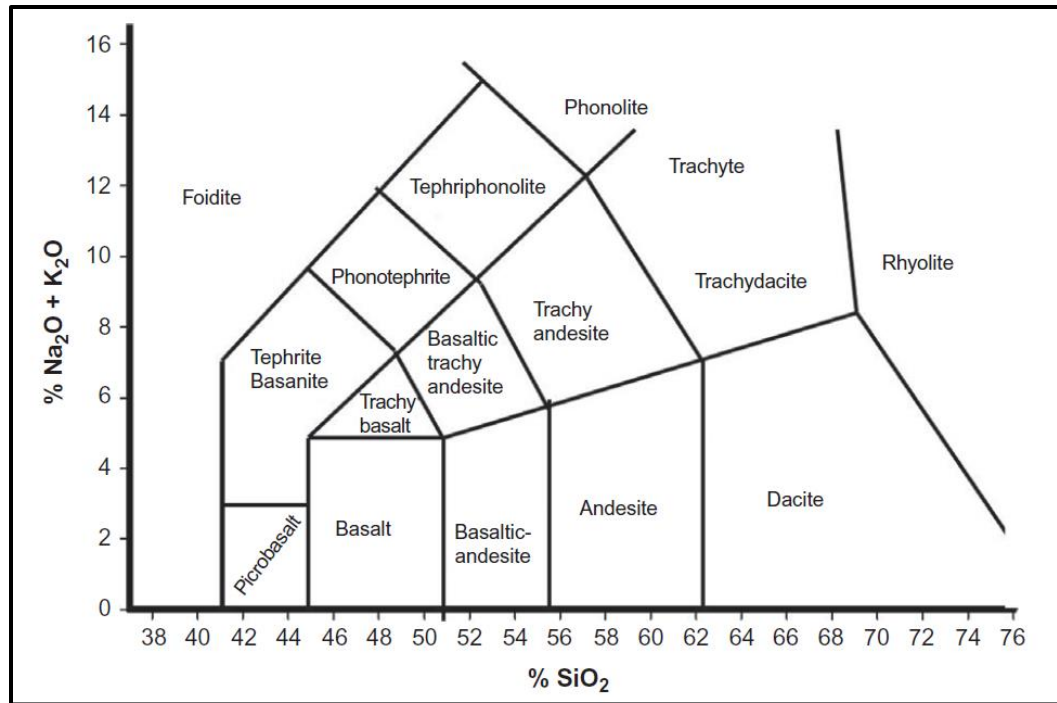


Figure 8.1 TAS (total alkali-silica) classification of rock types (Arnalds, 2013).

Volcanic eruptions impact a significant portion of Earth's ecosystems, spanning from subtle dust contributions to the deposition of thick layers near volcanic regions. Throughout geological time, these eruptions have adversely affected Earth's natural history by altering atmosphere composition, climate, and surface geochemistry (Arnalds, 2013). Volcanic eruptions release ash particles that, in some cases, can be extremely fine, posing health risks. High exposure to these particles can cause chest discomfort, coughing, eye irritation and skin irritation, particularly if the ash is acidic. Indirect effects are also significant, notably on infrastructure and communities. Ash affects roads, reducing visibility and creating slippery surfaces, potentially causing accidents. Ashfall can lead to power cuts, impacting health due to the lack of heating and reliance on electricity for infrastructure. Additionally, it affects water supplies, potentially contaminating them, inhibiting chlorination, and increasing water demand for cleanup. Sanitation systems may be temporarily disabled, potentially leading to increased disease in affected areas, and

there's a risk of roof collapse from ash accumulation, leading to fatal injuries. Animal health can also be jeopardized if grazing animals ingest ash-coated with hydrofluoric acid (Baxter et al., 1986; Hansell et al., 2006). Overall, volcanic ash not only poses direct health risks but also profoundly impacts infrastructure, water supplies, sanitation, and animal health. These consequences emphasize the severity of eruptions, affecting various aspects of human life and the environment.

However, volcanic tephra holds potential in various domains, including agriculture and construction sectors. The impact of volcanic ash on the environment is notably characterized by the formation of distinctive soils known as Andisols. These soils possess unique characteristics, featuring a carbon-rich mineral composition that imparts specific environmental attributes. These attributes, in turn, influence factors such as fertility and hydrology, showcasing the significant role volcanic ash plays in shaping soil properties (Shoji and Takahashi, 2002). Earlier research has explored the possible utilization of volcanic ash in various applications, including the production of ceramic goods, heat-insulating materials, filtering substances, and adsorbents (Lemougna et al., 2018). Volcanic ash meets the criteria outlined in ASTM C618 for pozzolanic materials. Its physical and chemical properties strongly suggest its potential suitability as a partial substitute for cement, paste, and mortar in construction applications (Siddique, 2012). It also can be used as aggregates in concrete production. In addition, different research studies used volcanic ash for geopolymer concrete production in construction sector (Baenla et al., 2019; Djobo et al., 2016; Lemougna et al., 2011). Volcanic ash possesses a range of distinctive physical and chemical characteristics, positioning it as a promising raw material for geopolymer production. Its porous structure and low density facilitate

easy extraction, contributing to a reduced environmental footprint compared to the conventional open-pit (quarrying) approach frequently employed for clay mining. The chemical composition, abundant in Si, Al, and other components, offers the essential elements required for the geopolymerization process (Zhou et al., 2021).

Given the substantial quantities of volcanic tephra generated by widespread volcanic activity and the consequential pollution of the atmosphere, soil, water, and plants with volcanic ash, there's a growing need for more sustainable approaches to upcycle volcanic ash in a greener way. Utilizing volcanic tephra in the production of geopolymers is considered a green and sustainable method, offering an eco-friendly approach to making extensive use of this abundant volcanic material. This approach not only addresses the challenge of volcanic ash disposal but also contributes to the development of environmentally conscious practices in materials utilization. The manufacturing process of Portland cement raises environmental concerns, as each ton of Portland cement results in approximately 0.95 tons of CO₂ emissions (Davidovits, 2013). Moreover, permitting the accumulation of volcanic waste following an eruption can give rise to diverse environmental challenges. Therefore, utilizing the potential of volcanic tephra as an alternative resource represents a sustainable approach to address carbon emissions and reuse some waste materials (Djobo et al., 2016). This approach will promote circular carbon economy principles. The motivation for conducting this study arises from the limited research on volcanic tephra, despite its considerable potential and the environmental challenges associated with both Portland cement and volcanic tephra accumulation. This paper investigates the possibility of using Saudi volcanic tephra to produce a non-Portland cement system for oil well cement.

8.2 Materials and Methodology

Firstly, VT was collected from the western part of Saudi Arabia. After that, VT was ground, milled and sieved to make it in a fine powder form (below 104 μm) for geopolymer preparation. In this study, VT and NaOH pellets were utilized to prepare the geopolymer slurry. The specific gravity and particle size distribution are summarized in **Table 8.1**. The oxides composition of VT, as determined by XRF (X-ray fluorescence), is listed in **Table 8.2**. Experiments were carried out to find a flowable slurry formulation that could be easily blended. The formulation design involved examining the mixability, pumpability, and rheology. Then, the tests continued to assess the strength and sedimentation. The geopolymer slurries mixture was prepared to mimic its behavior in downhole conditions.

An atmospheric consistometer was used to estimate the thickening time of the proposed slurry at 170°F. The rheology assessment was conducted using the rotational viscometer. A water bath was used to cure the geopolymer samples at 200°F. After curing, three sections were cut from the cylindrical samples (bottom, middle, and top). The sedimentation evaluation included API method and NMR technique. The API-test was performed by weighing the sections in both water and air. The geopolymer section specific gravity was calculated by dividing its weight in air by its weight in water, as per Archimedes' principle. A scratch testing device with a sonic mode was employed to evaluate UCS and dynamic elastic properties.

Table 8.1 SG and PSD of VT.

Parameter	Volcanic Tephra (VT)
SG	2.85
D10 (μm)	1.40
D50 (μm)	10.57
D90 (μm)	43.23

Table 8.2 XRF results of VT.

Oxide	Volcanic Tephra (VT)
SiO ₂	42.52
Al ₂ O ₃	15.29
CaO	10.54
Fe ₂ O ₃	17.34
TiO ₂	2.76
K ₂ O	1.62
MgO	6.66
Na ₂ O	2.41
P ₂ O ₅	0.37
Others	0.48

8.3 Results and Discussion

This part presents the results of a new category of geopolymers produced by volcanic tephra as a source material after activation by sodium hydroxide solution. **Figure 8.2** shows a schematic of VT-based ingredients and the final product. **Figure 8.3** shows a VT-based geopolymer cement sample that does not contain any fraction of Portland cement. **Table 8.3** lists the mechanical properties of the developed VT-based geopolymers.

Upon achieving a compressive strength of 50 psi, the slurry demonstrates its capability to function as a barrier to fluid and gas flow. At a compressive strength of 500 psi, it attains the robustness necessary for drilling or tagging. While drilling with less than 500 psi is feasible, industry practice often adopts this threshold as a practical guideline (G. Liu, 2021). Notably, the developed sample exhibited a 24-hr compressive strength of 2,900 psi after undergoing curing at 200°F, surpassing some reported values in industry cementing programs.

In wells exposed to substantial stresses such as steam injection, geothermal operations, and hydraulic fracturing, the flexibility of the cement sheath is a critical consideration. Long-term well integrity is ensured by employing flexible cement systems characterized by lower Young's Modulus (YM) and higher Poisson's Ratio (PR). It is emphasized that the YM of set cements should be less than that of the adjacent strata, making smaller YM set cements potentially preferable for unconsolidated formations compared to those with higher YM (G. Liu, 2021). The proposed geopolymer system demonstrates enhanced flexibility compared to class G cement. Notably, its YM is less than that of shale and

consolidated strata, aligning with previous observations by Liu (2021). This characteristic allows for the geopolymer's use in proximity to these formations. Generally, cements with greater flexibility—characterized by low YM, high tensile strength, and sufficient compressive strength—tend to function well when subjected to simulated stresses.

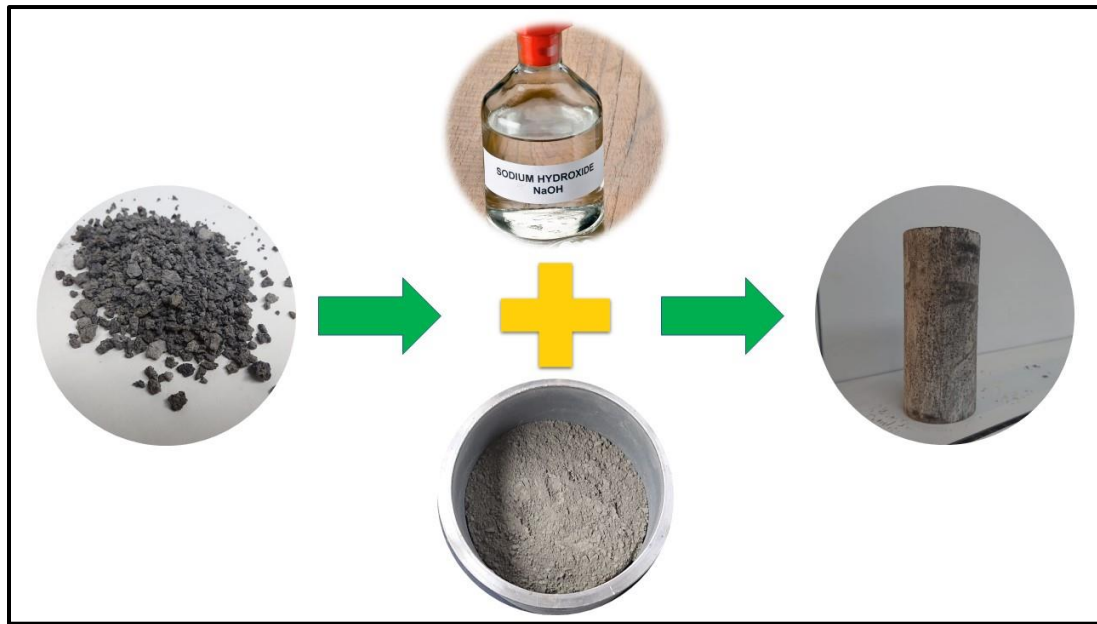


Figure 8.2 Schematic of the VT-based geopolymer ingredients.



Figure 8.3 VT-based geopolymer cured sample after 24 h at 200°F.

Table 8.3 The mechanical properties of the developed VT-based geopolymer system.

Property	Value	Unit
UCS	2,900	psi
PR	0.29	-
YM	7.69	GPa

The density difference between the top and bottom sections of the developed samples was only 1.07 % as presented in **Figure 8.4**. This result was confirmed by NMR results as shown in **Figure 8.5**, the NMR porosity difference between the top and bottom sections of the developed system was only 2.6 %. Based on the aforementioned results, the developed VT-based samples did not show any evidence of sedimentation. The assessment of rheological properties in cement slurries is crucial as it directly impacts processes such as slurry mixing, pumping requirements, and the displacement of drilling fluids. In the case of the geopolymer, rheological evaluation was conducted at a downhole temperature of 160°F. **Figure 8.6** and **Fig 8.7** illustrate shear stress and viscosity versus shear rate, respectively. Utilizing the Power Law flow model yielded the most accurate representation of the rheological data at 160°F, with an R^2 value of 0.9733. The power law index, indicating shear thinning behavior, was observed to be lower than 1. This characteristic is further substantiated by **Fig 8.7**, demonstrating a decrease in viscosity with an increase in shear rate. The examination of gel strength for the developed geopolymer included assessments at both 10 sec and 10 min. This gel strength measurement is essential for determining the slurry's capability to resist gas invasion. The 10 sec and 10 min gel strength were 54.92 and 99.83 lbf/ 100 ft², respectively. The thickening time of the VT-based geopolymer slurry was measured to determine how long

the slurry remains pumpable under downhole temperature without using any retarder. The thickening time in this study was determined when the slurry reaches 70 Bearden units of consistency (Bc) as widely applied by the industry. **Figure 8.8** presents the thickening time chart of the developed system indicating that the VT-based slurry can remain pumpable at 170°F for 3.5 h without using any retarder.

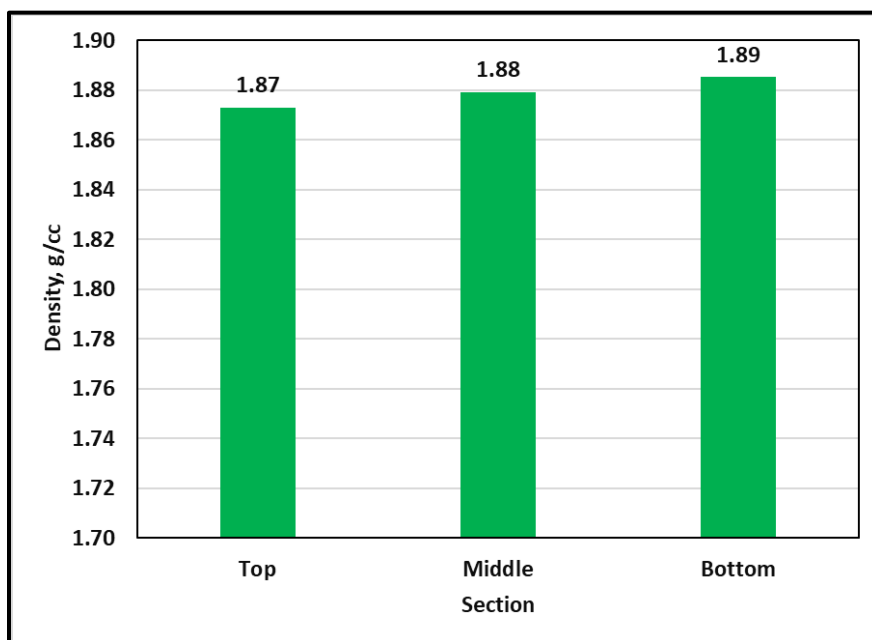


Figure 8.4 The effect of VT on sedimentation.

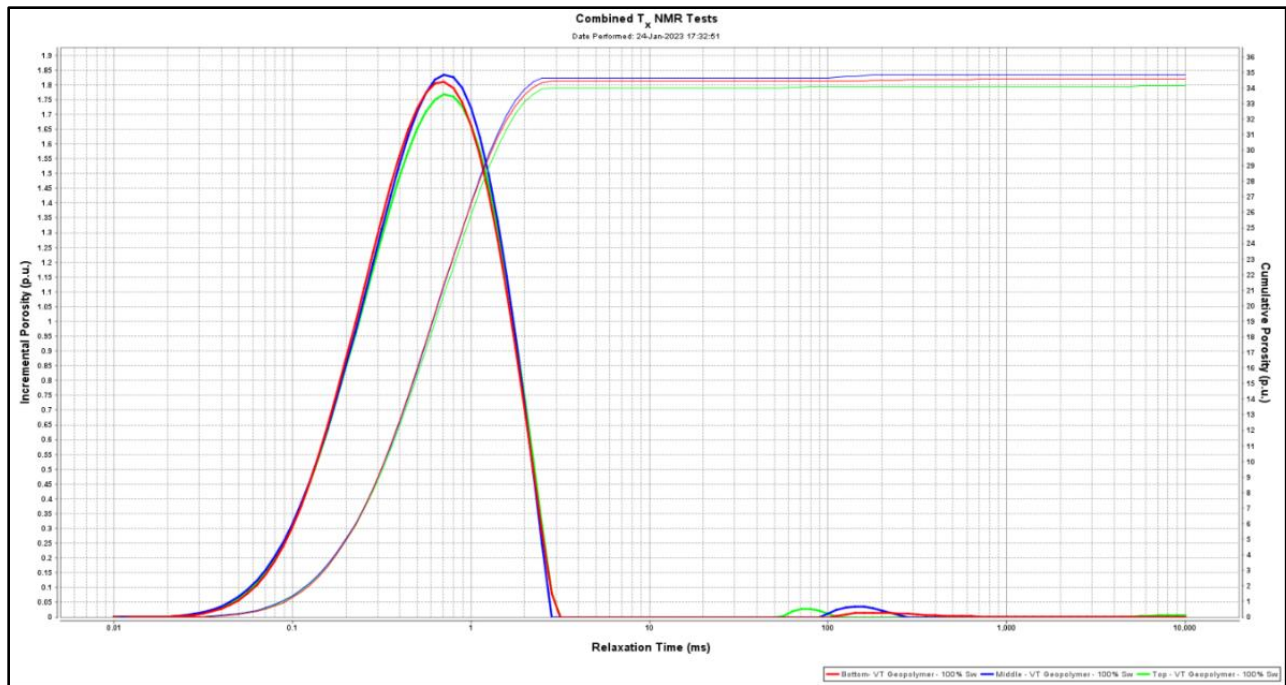


Figure 8.5 The NMR results for the bottom, middle and top sections of VT-based geopolymer.

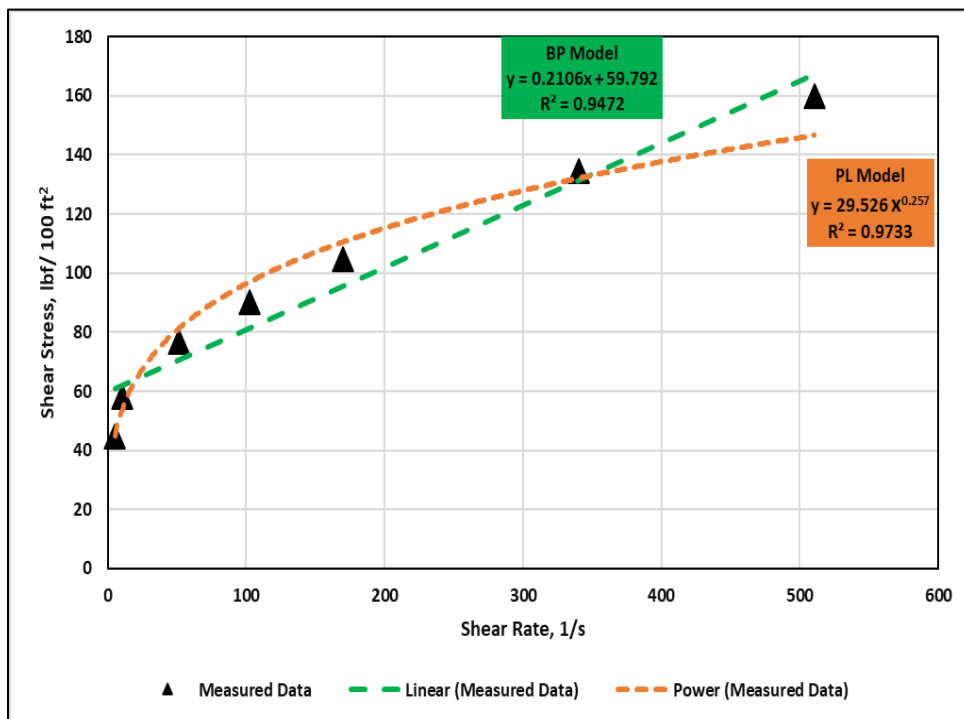


Figure 8.6 Shear stress vs. shear rate for the VT-based geopolymer slurry.

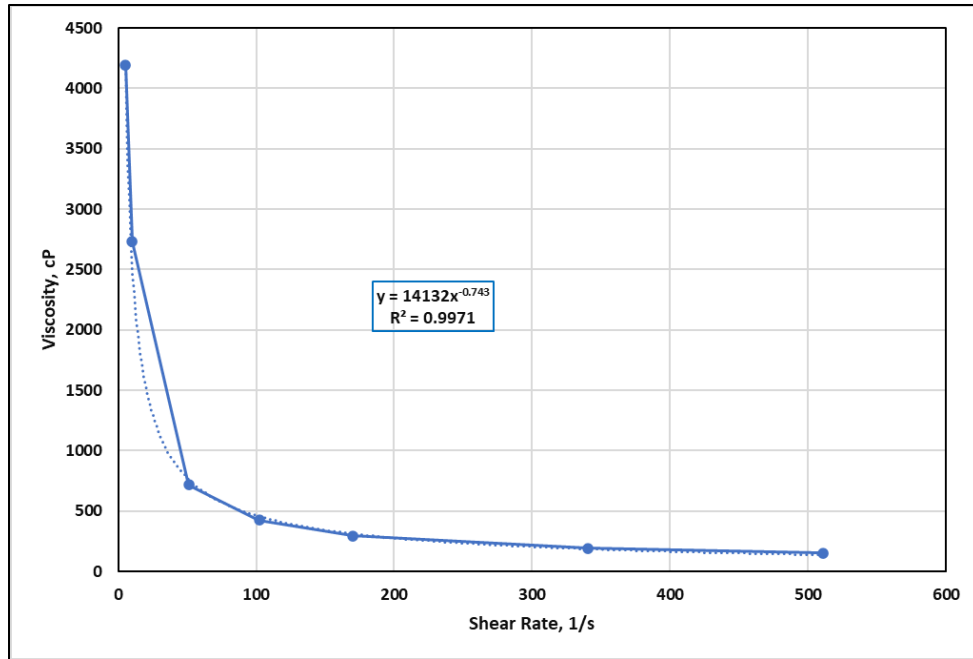


Fig 8.7 Viscosity vs. shear rate for the VT-based geopolymer slurry.

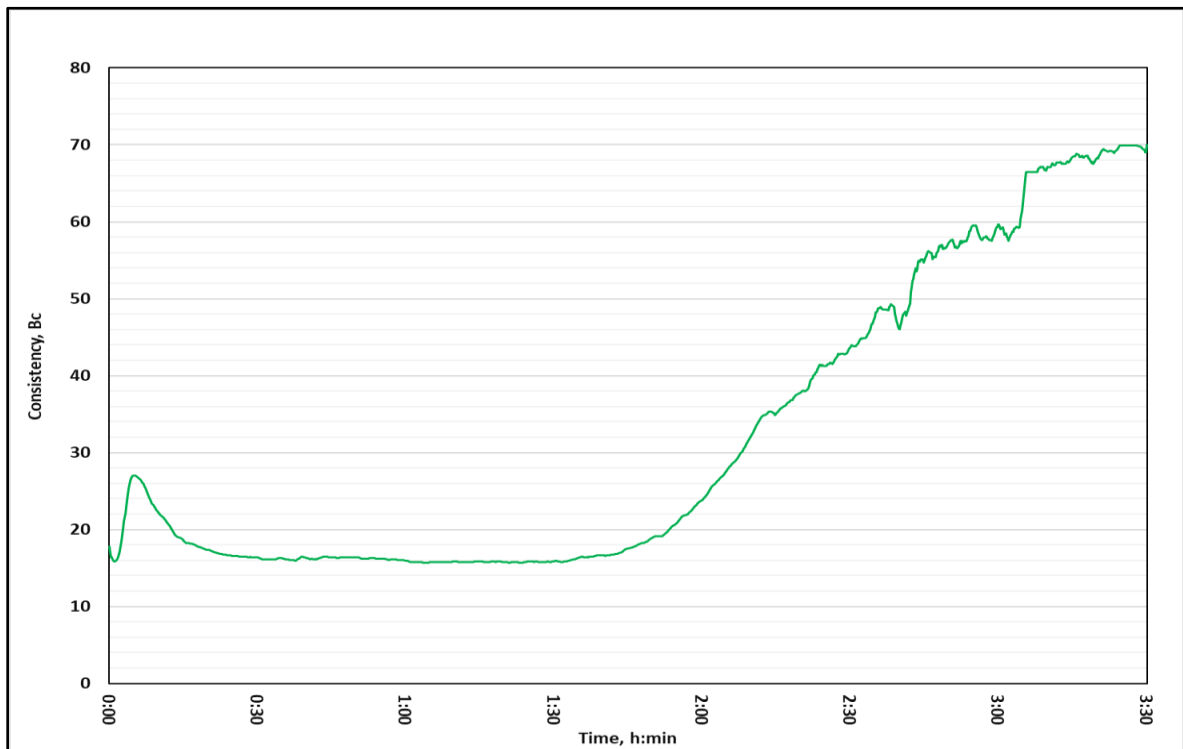


Figure 8.8 The thickening time chart of the developed VT-based geopolymer slurry at 170°F.

The VT-based geopolymer sample lost less than 10 % of its weight after heating it up to 1,100°C using TGA confirming its thermal stability at elevated temperatures as shown in **Figure 8.9**. The weight loss may be attributed to the loss of strong chemically bound water associated with the formation of gobbinsite as presented in XRD analysis in **Figure 8.10**. **Figure 8.11** shows the FTIR analysis of the raw VT and the VT-based geopolymer. In recent studies, various aluminosilicate minerals have undergone investigation using FTIR spectroscopy. Much attention has been given to the behavior of the (Si, Al-O) band, typically located in proximity to 1000 cm⁻¹. In the case of the VT-based specimen, the peak near 1000 cm⁻¹ exhibits lower intensity compared to the raw VT powder. This disparity suggests that silica in the raw VT powder underwent some degree of reaction to produce the geopolymer sample. The peak near 1000 cm⁻¹, most pronounced in the raw VT powder at 1043 cm⁻¹, is indicative of silicate stretching and it undergoes a shift. After the raw VT reacts with the activating solution, there is a restructuring of the structure where aluminum ions become part of the [SiO]⁻⁴ tetrahedra, establishing the Si-O-Al network. It's noteworthy that the extent of the peak shift has been previously observed to correlate with the amount of aluminum integrated into the silicate structure at fixed alkali content.

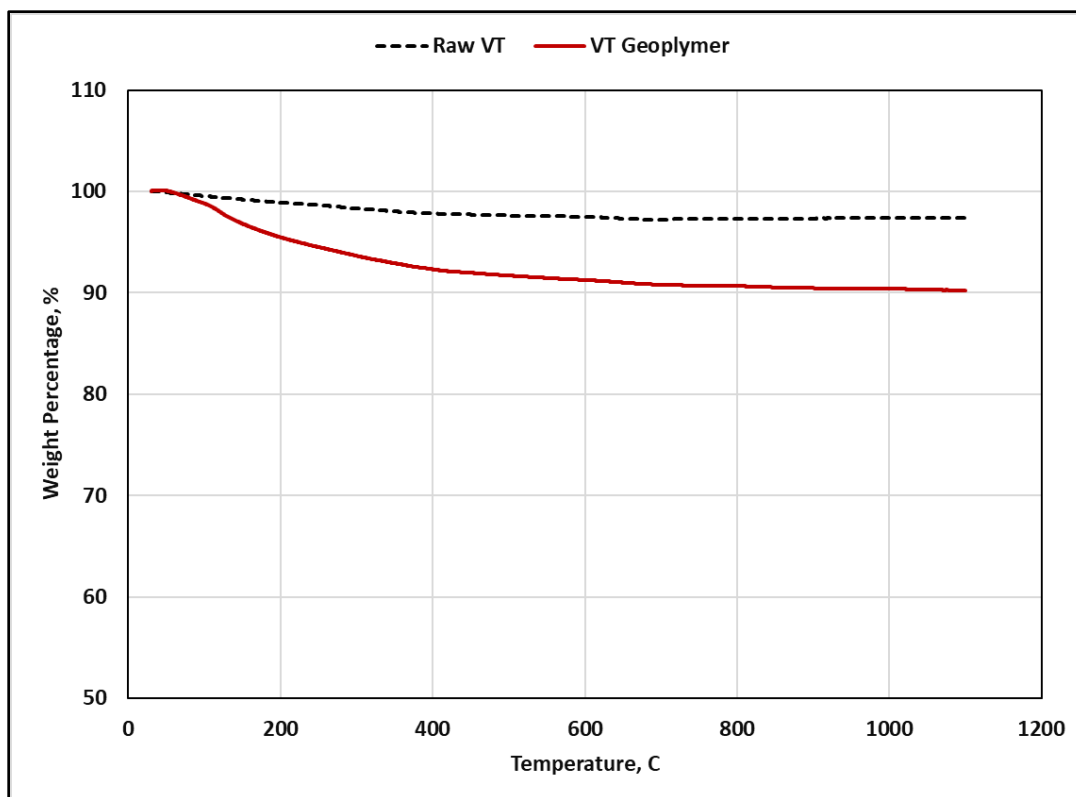


Figure 8.9 Thermogram of the raw VT and VT-based geopolymer as obtained by TGA.

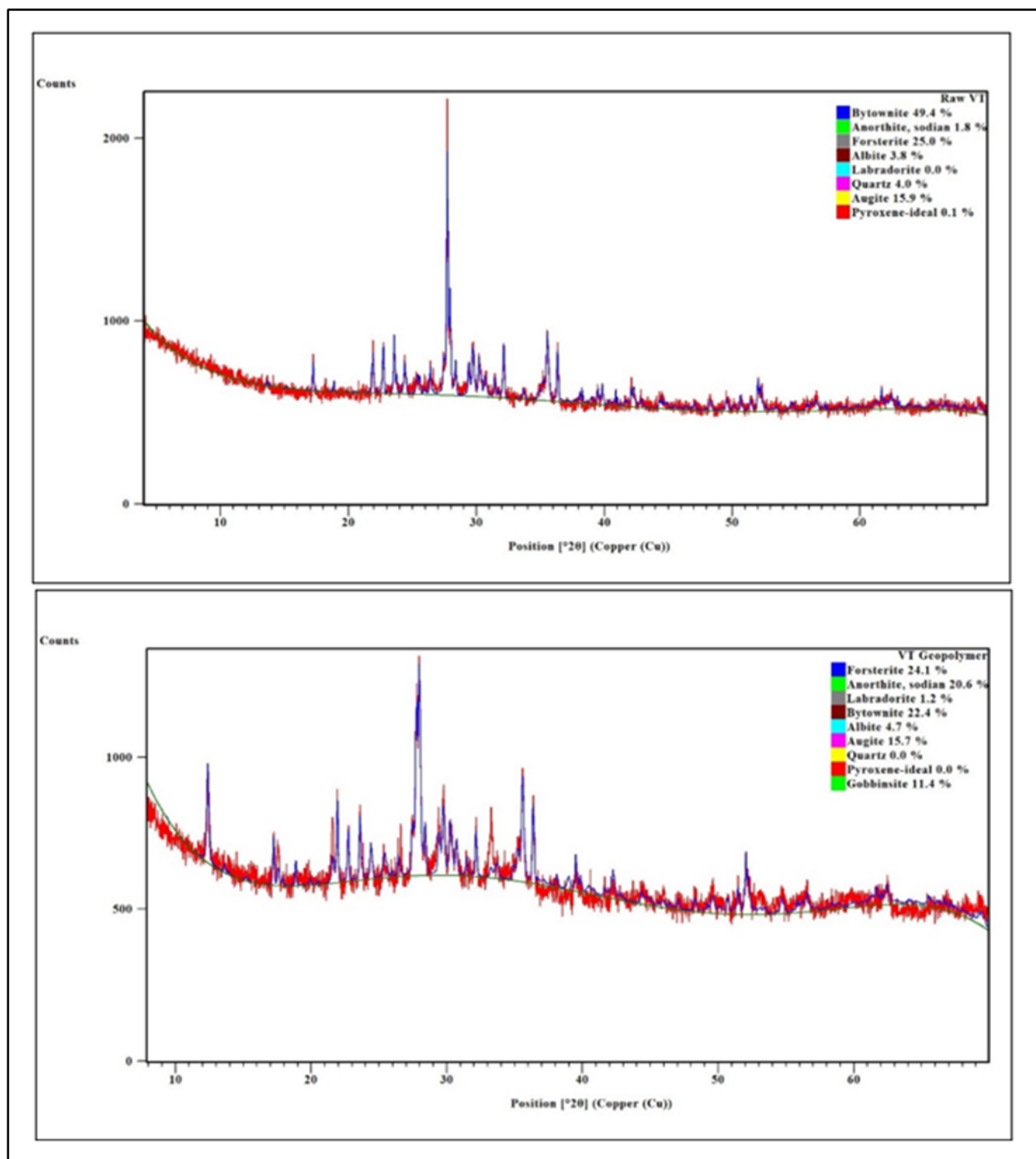


Figure 8.10 XRD of the raw VT and VT-based geopolymer sample.

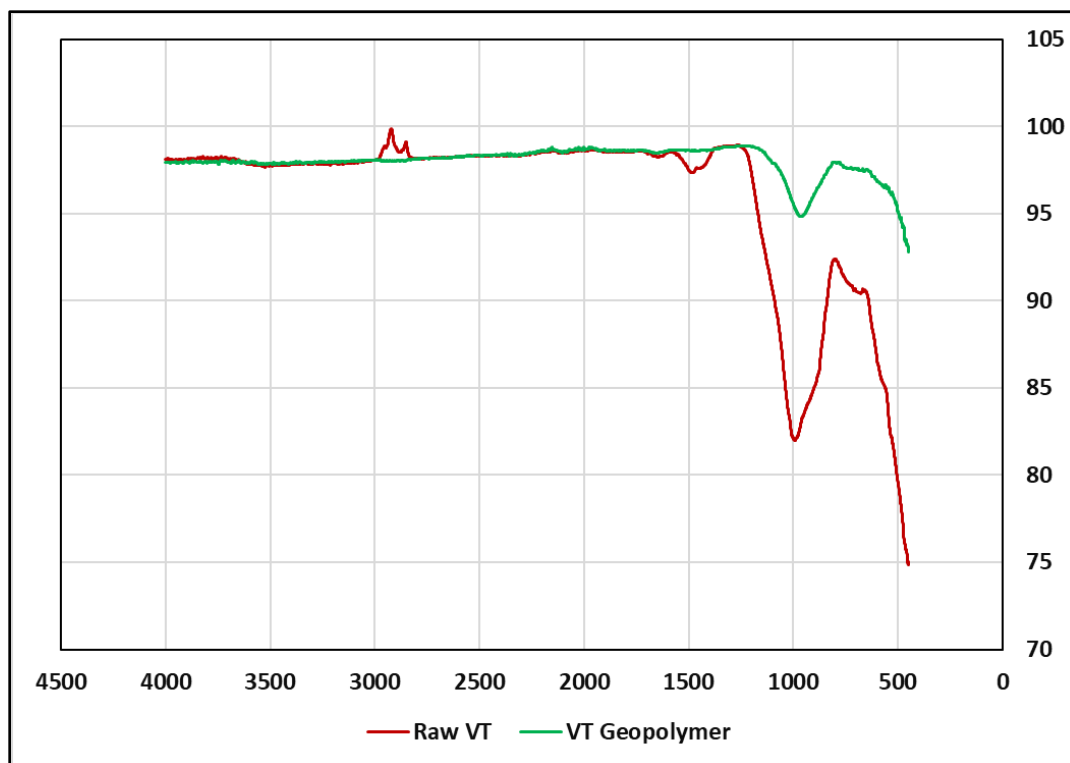


Figure 8.11 FTIR of the raw VT and VT-based geopolymer.

8.4 Conclusions

The outcomes of this work demonstrate the successful production of a new category of geopolymers using volcanic tephra as a source aluminosilicate material activated by NaOH solution. Unlike the most developed geopolymer cement systems in the literature that used high concentrated NaOH solutions (8 to 14 M) in a combination with sodium silicates, this study used only 4 M NaOH solution as an activation solution in a step towards reducing the costs and the environmental impact of the geopolymer technology. Volcanic tephra-based geopolymer is considered a green approach to make extensive use of volcanic tephra and tackle the challenges associated with Portland cement and volcanic tephra accumulations at the same time. The results of this work can be summarized as follows:

- The VT-based geopolymer slurry remains pumpable at 170°F for 3.5 h without using retarders.
- The developed geopolymer exhibited an accepted 24-h compressive strength and enhanced flexibility compared to Class G cement in terms of YM and PR.
- The density difference across the developed specimen is minimal, with only a 1.07% variation between the top and bottom sections, indicating no sedimentation.
- The power law model provided the best fit to model the rheology data of the developed geopolymer slurry.
- The developed geopolymer cement system showed high thermal stability after losing only 10 % of its weight after heating up to 1,100°C using TGA.

CHAPTER 9

CONCLUSIONS AND RECOMMENDATIONS

Scholars in cementing have investigated the usage of geopolymer technology for different cement applications. The most important findings can be summarized in terms of advantages and drawbacks that require more research as follows:

Advantages

1. Geopolymers possess more resistance in acidic environment and therefore can be used in CO₂ sequestration.
2. Geopolymers possessed less permeability compared to OPC.
3. Geopolymers performed well in high saline environments because of reduction of alkali leaching.
4. Geopolymers showed less shrinkage and good shear bond strength which suggests them to be good candidates for zonal isolation and P&A.
5. In comparison to OPC systems, geopolymers are more compatible with mud, particularly the OBM.
6. The geopolymer strength increases with temperature owing to the increased polymerization rate and may be workable in steam injection.
7. The excellent mechanical properties promote their usage in the wells subjected to hydraulic fracturing jobs.

Limitations

1. Geopolymers are more susceptible to WBM.

2. The geopolymer strength is small below 86 °F owing to the slow geopolymerization rate.
3. Conventional geopolymers showed high brittleness.
4. Geopolymer systems have rapid gelation at high temperatures, hence more research is required to investigate their usage in HPHT wells.

Chapter 3 introduced the first hematite-based class F fly ash geopolymer formulation for oil and gas well cementing. Unlike the other studies in the literature, this work used 4 M NaOH solution only as an activator that can reduce the overall cost. This work used fly ash (waste material) as aluminosilicate source which reduces the cementing cost, cement carbon emissions, and massive energy consumption and tackles the environmental issue related to fly ash disposal. Various properties of the designed slurry and hardened samples were evaluated using recommended practices with some modifications. The outcomes of this study can be summarized as follows:

- Increasing the hematite percentage significantly decreased the thickening time of geopolymers.
- A developed mixture of a retarder and a superplasticizer was introduced that enhanced the workability and prolonged the thickening time by 500%.
- The developed formulation achieved a low fluid loss without any fluid control additive (38 mL/ 30 min) that made it a good candidate for a wide range of cementing applications such as horizontal drilling, gas migration risk, and casing cementing that requires fluid loss <50 mL/ 30 min.
- The developed geopolymer slurry had a density of 17.5 ppg which can be used in high pressure well cementing and the developed slurry acted more like a power law

fluid at low temperatures and more like a Bingham plastic fluid at high temperatures.

- The compressive and tensile strength were enhanced by increasing the curing time confirming the continuation of geopolymerization and the elastic properties of the developed geopolymer proved that it is more flexible than some cement systems.

Chapter 4 addressed the problem of low thickening times and pumpability issues encountered while using high-density hematite based FFA geopolymers. This study introduced a solution to thickening time challenges at high temperatures using a mixture of a modified lignosulfonate retarder and a PNS superplasticizer. The effects of this mixture on thickening time, rheological and mechanical properties were evaluated. The outcomes of this work can be summarized as follows:

- The thickening time of the hematite based FFA geopolymer decreased by 81.4% with increasing hematite from 25 to 75% BWOB.
- The proposed mixture increased the thickening time from 80 to 580 min at 195°F for the 75% hematite geopolymer.
- The proposed mixture developed a geopolymer with the highest UCS and PR as compared to other formulations using each additive individually.
- The mixture decreased the plastic viscosity of the high density geopolymer slurry by 29% which facilitates mixing and pumping.

Chapter 5 introduced two high density geopolymer systems using hematite alone and a mixture of hematite and Micromax were introduced. The assessment included rheology (PV, YP, and GS), filtrate loss, strength, permeability, and elastic properties. This study

showed the sedimentation problem associated with hematite as a weighting agent and introduced adding Micromax as a solution to mitigate this problem in geopolymers. The findings of this work can be summed up as follows:

- The Micromax-hematite weighted geopolymer is homogeneous with only 3.9% average density difference within the samples.
- A proposed mixture of a retarder, a retarder intensifier and a superplasticizer was introduced that increased the thickening time of the mixed system by 294%.
- The Mixed geopolymer had lower fluid loss without using any fluid loss control additive that made it a good candidate for cementing applications such as horizontal drilling, gas migration risk, and casing cementing that requires fluid loss less than 50 mL/ 30 min.
- At downhole temperatures, both systems followed Bingham plastic fluid model and the mixed system decreased the plastic viscosity by 44.8% and possessed a yield point close to the hematite-based system.
- The two formulations had close values in terms of strength, elastic properties, and permeability.

Chapter 6 shows the effectiveness of perlite in addressing sedimentation and stability issues in high-density hematite-based geopolymer systems was investigated. Three different concentrations of perlite (0, 1.5, and 3% BWOB) were evaluated to assess their impact on various cement properties. Overall, the results highlight the significant benefits of incorporating perlite in geopolymer cement formulations, particularly in mitigating sedimentation and stability issues, improving compressive strength, and maintaining desirable rheological properties. These findings contribute to the advancement of

geopolymer technology in the oil and gas industry, offering potential solutions for cementing challenges in various wellbore conditions. The study outcomes can be summarized as follows.

- The API method, NMR and CT-scan results demonstrated that the addition of 3% perlite significantly reduced the density and porosity variation between the top and bottom sections of the geopolymer samples.
- The addition of perlite had a positive effect on the compressive strength of the developed geopolymer, with the optimum perlite concentration leading to a 24-hour UCS of at least 1,952 psi, surpassing the minimum requirements for drilling applications.
- The Young's modulus and Poisson's ratio showed minimal differences between the geopolymer samples with 0 % and 3 % perlite concentrations, indicating that the presence of perlite had a negligible effect on the elasticity of the samples.
- Increasing the perlite percentage resulted in higher yield points but adversely affected the plastic viscosity.
- The gel strength of the geopolymer slurries was enhanced by the addition of perlite, both at 10 sec and 10 min.

Chapter 7 shows the effectiveness of incorporating laponite in hematite-based geopolymer samples to address sedimentation and stability issues. The outcomes can be summarized as follows:

- The optimal laponite concentration was determined to be 3% BWOB for tackling sedimentation issues.

- Increasing Laponite concentration improved compressive strength, surpassing the minimum recommended values for field applications.
- YM remained lower than Class G cement, making the geopolymer suitable for unconsolidated strata and adjacent to shale and consolidated formations.
- Laponite addition increased PR and influenced the rheological properties of the geopolymer slurries, enhancing YP and GS.
- The temperature also influenced the rheological properties, with PV decreasing and YP and GS remaining relatively stable.

Overall, incorporating laponite in hematite-based geopolymer systems offers a promising solution to address sedimentation and stability challenges, while improving key properties such as density uniformity, compressive strength, and flexibility.

Chapter 8 demonstrates the successful production of a new category of geopolymers using volcanic tephra as a source aluminosilicate material activated by NaOH solution. Unlike the most developed geopolymer cement systems in the literature that used high concentrated NaOH solutions (8 to 14 M) in a combination with sodium silicates, this study used only 4 M NaOH solution as an activation solution in a step towards reducing the costs and the environmental impact of the geopolymer technology. Volcanic tephra-based geopolymer is considered a green approach to make extensive use of volcanic tephra and tackle the challenges associated with Portland cement and volcanic tephra accumulations at the same time. The results of this work can be summarized as follows:

- The VT-based geopolymer slurry remains pumpable at 170°F for 3.5 h without using retarders.
- The developed geopolymer exhibited an accepted 24-h compressive strength and enhanced flexibility compared to Class G cement in terms of YM and PR.
- The density difference across the developed specimen is minimal, with only a 1.07% variation between the top and bottom sections, indicating no sedimentation.
- The power law model provided the best fit to model the rheology data of the developed geopolymer slurry.
- The developed geopolymer cement system showed high thermal stability after losing only 10% of its weight after heating up to 1,100°C using TGA.

Recommendations

- Unlock the potential of the volcanic tephra for lightweight and high-density cement.
- Developing new fiberglass waste-based cement formulations.
- Exploring the potential of red mud in geopolymer applications.
- Testing the developed formulations for geothermal applications.
- Testing the durability of the developed formulations in harsh environments.
- Testing different techniques for geopolymers preparation.
- Diving deeper in Geopolymer chemistry.

Given the urgency of the challenge and the time taken historically for technology systems to evolve, a considerable push will be needed to get the next generation of low-carbon cements out of the lab and into the market.

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Publications

Peer-Reviewed Articles and Technical Reports

1. **Abdelaal, A., et al. (2023).** Mixed Micromax and hematite-based fly ash geopolymer for heavy-weight well cementing. **Scientific Reports.**
2. **Abdelaal, A., et al. (2023).** A Data-Driven Framework for Real-time Rheological Properties Prediction of Flat Rheology Synthetic Oil-based Drilling Fluids. **ACS OMEGA.**
3. **Abdelaal, A., et al. (2023).** Development of Heavy-Weight Hematite-Based Geopolymer for Oil and Gas Well Cementing. **ACS OMEGA.**
4. **Abdelaal, A., et al. (2023).** Synergy of Retarders and Superplasticizers for Thickening Time Enhancement of Hematite Based Fly Ash Geopolymers. **Geoenergy Science and Engineering.**
5. **Abdelaal, A., et al. (2023).** Improvement of supercritical carbon dioxide foam performance for EOR in sandstone reservoirs: An experimental and optimization study. **Gas Science and Engineering.**
6. Ahmed, A., **Abdelaal, A., et al. (2023).** Evaluation of Hematite and Micromax-Based Cement Systems for High- Density Well Cementing. **Journal of Petroleum Science and Engineering.**
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8. **Abdelaal, A., et al. (2022).** Real-time prediction of formation pressure gradient while drilling. **Scientific Reports.**
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11. **Abdelaal, A., et al. (2022).** Data-Driven Approach for Resistivity Prediction Using Artificial Intelligence. **Journal of Energy Resources Technology.**
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13. **Abdelaal, A., et al. (2021).** A review of foam-based fracturing fluids applications: From lab studies to field implementations. **Journal of Natural Gas Science and Engineering.**
14. **Abdelaal, A., et al. (2021).** Data-Driven Modeling Approach for Pore Pressure Gradient Prediction while Drilling from Drilling Parameters. **ACS Omega.**
15. Gamal, H., **Abdelaal, A., et al. (2021).** Machine Learning Models for Equivalent Circulating Density Prediction from Drilling Data. **ACS Omega.**
16. **Abdelaal, A., et al. (2020).** Mixed CO₂/N₂ Foam for EOR as a Novel Solution for Supercritical CO₂ Foam Challenges in Sandstone Reservoirs. **ACS Omega.**

Conference Proceedings

1. **Abdelaal, A., et al. (2023). A Non-Portland Cement System: A Step Forward Towards Sustainability of Oil Well Cementing. **SPE Annual Technical Conference.****
2. **Abdelaal, A., et al. (2023). The Path to Sustainable Cementing: Embracing a Non-Portland Cement Solution for Oil and Gas Wells. **Abu Dhabi International Petroleum Exhibition.****
3. **Abdelaal, A., et al. (2023). High Density Geopolymers: A Step Forward Towards Low Carbon Footprint Cementing Operations. **SPE Offshore Technology Conference.****
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6. **Abdelaal, A., et al. (2023). A Geopolymer System for High Pressure Oil and Gas Well Cementing. **Middle East Oil and Gas Show.****
7. **Abdelaal, A., et al. (2023). Viscometer Readings Prediction of Flat Rheology Drilling Fluids Using Adaptive Neuro-Fuzzy Inference System. **Middle East Oil and Gas Show.****
8. **Abdelaal, A., et al. (2022). Drilling Data-Based Approach for Pressure Gradient Estimation Using Random Forest. OnePetro. **International Geomechanics Symposium.****
9. **Abdelaal, A., et al. (2022). Formation Pressure Abnormality Identification Using Artificial Neural Networks: A Classification Model. OnePetro. **56th U.S. Rock Mechanics/Geomechanics.****
10. **Abdelaal, A., et al. (2022). Rheological Properties Prediction of Flat Rheology Drilling Fluids. OnePetro. **56th U.S. Rock Mechanics/Geomechanics.****
11. **Abdelaal, A., et al. (2021). Pore Pressure Estimation While Drilling Using Machine Learning | ARMA/DGS/SEG International Geomechanics Symposium | OnePetro. **ARMA/DGS/SEG 2nd International Geomechanics Symposium.****
12. **Gamal, H., Abdelaal, A., et al. (2021). Artificial Neural Network Model for Predicting the Equivalent Circulating Density from Drilling Parameters. OnePetro. **55th U.S. Rock Mechanics/Geomechanics Symposium.****
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Vitae

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Academic Background :Petroleum Engineering

Education

King Fahd University of Petroleum & Minerals (KFUPM) Dhahran, Saudi Arabia
Doctor of Philosophy in Petroleum Engineering - CGPA: **(4.0/4.0)** Dec. 2023

KFUPM Dhahran, Saudi Arabia
Master of Science in Petroleum Engineering - CGPA: **(3.93/4.0)** Dec. 2019

Suez University Suez, Egypt
Bachelor of Science in Petroleum Engineering – Grade: Excellent July 2014

Work Experience

Department of Petroleum Engineering, KFUPM Jan. 2018 – Present
Teaching & Research Assistant

Department of Petroleum Engineering, Suez University Jan. 2015 – Dec. 2017
Assistant Lecturer

Awards and Honors

Society of Petroleum Engineers (SPE)

SPE Paper Contest (SPC)

- **1st Place** in SPE **International** SPC - Ph.D. Division Oct. 2023
- **1st Place** in SPE **MENA** SPC - Ph.D. Division Mar. 2023

SPE KFUPM SC Excellence Award, KFUPM Sep. 2022

SPE International Presidential Award June 2022

- A key officer in the high board and was selected to receive the award in 2022
ATCE

Society of Petroleum Engineers, SPE Petrobowl Contest

- **2nd Place** in 2022 SPE MENA Petrobowl
- **1st Place** in 2021 SPE MENA Petrobowl
- **3rd Place** in 2019SPE MENA Petrobowl, Bahrain
- Qualified with KFUPM team to the international Petrobowl for 4 years in a row 2019-2022

Professional Affiliations / Service

Peer Reviewer 2021 – Present

- ACS OMEGA, ACS Publications
- Gas Science and Engineering, Elsevier
- Journal of Petroleum Exploration and Production Technology, Springer
- Journal of Energy Resources Technology (JERT), ASME
- Journal of Cleaner Production, Elsevier

IADC KFUPM SC Chairman April 2022 – Oct. 2023

- Cofounder of the first IADC SC in the Middle East

SPE KFUPM SC 2019 – June 2023

- Membership Chair (*April 2020 – June 2023*)
- SPE KFUPM PetroBowl Team Leader, (*Jan. 2019 – Present*)
 - 1- Team recruitment & mentor for the regional and international competitions
 - 2- Achieved first place 2 times, the second place once and third place once in MENA region and qualified to the international competition 4 times with KFUPM team
- Social media pages admin, (2020-Present)

SPE Suez University SC Oct. 2012 – May 2014

- SPE Active Member in academics and HR committees