Study on Polyvinyl Alcohol as Water-Based Drilling Mud Additive for Wellbore Isolation Strengthening and Reservoir Protection

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Study on Polyvinyl Alcohol as Water-Based Drilling Mud Additive for Wellbore Isolation Strengthening and Reservoir Protection

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ABSTRACT

The research aimed to enhance drilling fluid additives to strengthen wellbores, prevent circulation loss and mitigate drilling fluid-induced formation damage. Conventional industry tests, like High Temperature High Pressure (HTHP fluid loss tests, offered insights into critical aspects, including wellbore strengthening and formation protection. Consequently, novel mud balance methodologies were devised and assessed, including Polymer Integration in drilling mud formulation. These tests provided new insights into designing drilling fluids and additives to improve wellbore integrity and protect reservoirs.

The primary findings indicated that applying Polyvinyl Alcohol to Water-Based Drilling mud significantly eases mechanical wear while influencing the mud's relative effectiveness. Enhanced water-based fluids resulted in adequate internal wellbore isolation, previously challenged by temperature.

Introducing Polyvinyl Alcohol, studies on particle degradation revealed rapid deterioration under higher temperature conditions. Combining Cationic Polyvinyl Alcohol and Non-ionic Polyvinyl Alcohol proved effective in forming low-permeability filter cakes and preventing formation damage.

This thesis focuses on one crucial mud function: the first well isolation system. Considering the hydrostatic pressure is slightly higher than the formation pressure, the well isolation system by drilling mud depends on two active factors: the phase segregation mechanism (mud filtration) and mud cake resistivity.

CHAPTER 1
BACKGROUND

1-1. Introduction

The history of drilling mud evolution in the drilling industry consists of progressive scientific development driven by the need to surmount increasingly complex drilling challenges that the industry has faced [1]. Drilling mud, also called drilling fluid, consists of a liquid solution (base fluid), whether water, oil, or synthetic-based, mixed with swelling clays. The incorporation of swelling clays as primary constituents, regardless of the base fluid selection, creates a gelatinous fluid with the dual role of clearing out the well of cuttings and providing wellbore structural integrity by applying pressure control in wellbores while drilling. It is early understood that the mud's rheological and physiochemical characteristics enabling it to perform its functions are intricate with a swelling degree of the mud. Monitoring the effectiveness of the mud, therefore, always leaned on its swelling control. From the early 20th century, drilling mud was tailored with additives such as viscosifiers, weighting agents, lubricants, and sometimes solid materials according to the specificities of a particular formation [2][3]. From the second half of the 20th century into the 21st century, improved oil-based and synthetic drilling fluids became prominent as they fit the unique configurations of deeper, higher contaminated, and new challenging geological formations [4][5]. Research on mud swelling control kept rising with the advances in drilling practices, unveiling new challenges such as high-temperature reservoir settings and higher-pressure conditions. Therefore, the base fluid and chemical additions in the drilling mud composition are consciously selected to confer the predicted mud rheological and physiochemical characteristics that depend on the strata's lithological composition and the existing environmental

statutes [6][7]. Mud balance is, therefore, one of the basic parameters that are checked and assessed during the development of mud before and during drilling.

Academic works focusing on polymers have considered Polyvinyl Alcohol as a new form of swelling mud supplements. This paper delves into the influence of PVOH on mud swelling in a water medium [8][12].

1-2. Background

1.2.1 Mud Circulation System

Proceeding to drilling operations in any industry requires several appropriate pieces of equipment [13]. The pieces are assembled to push and direct active drilling equipment (drill bit and drilling pipe) and deeper drilling mud into the formation. Drilling mud stands out from other equipment as the only non-metallic (viscous, non-Newtonian fluid) [14][16]. More importantly, unlike other equipment, drilling mud's sole purpose is to ensure the fluidity of drilling proceeds at the bottom hole and provide well control [17]. Drilling mud points of action are a well's bottom hole and wellbore; therefore, the mud is suggested as the close loop circulation system, as shown in **Figure 1** below.

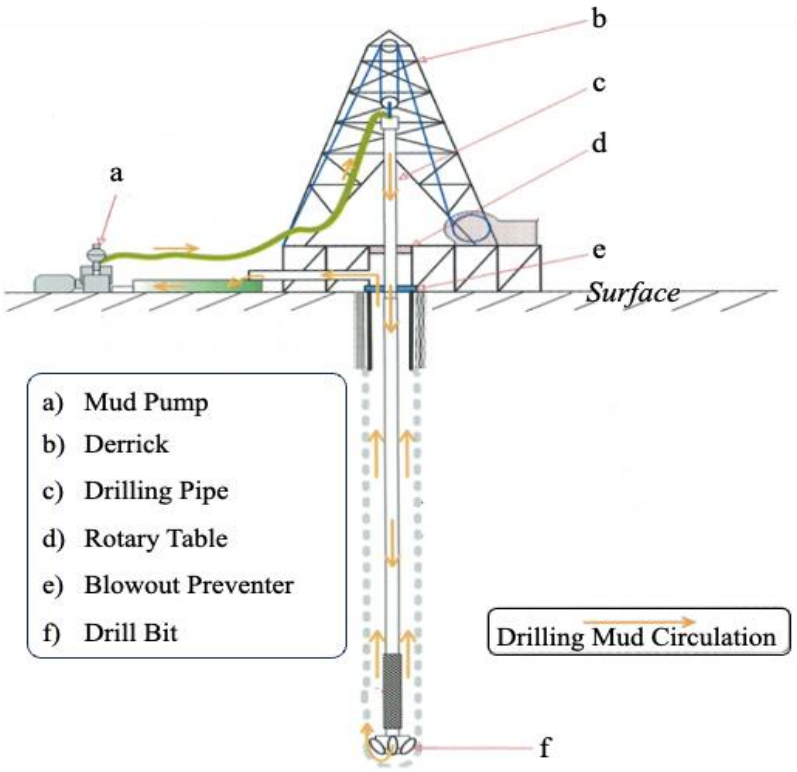


Figure 1. *Drilling Mud Circulation*

The drilling mud circulation system starts after mud preparation. Drilling mud is propelled by mud pumps that have enough force to climb the top of the derrick. From there, the drilling mud commences its descent into the well through a drilling pipe until it reaches the drill bit. The initial propelling force from mud pumps, plus gravity and mud viscosity, all influence the yield point of the mud required for it to flow upward through the annulus (space between drilling pipe and wellbore) to the surface [18][19]. Once at the surface, the mud is trapped between two safety equipment (Rotary table and BOP) before being directed to mud cleaning equipment (shale shakers, desander, desalter, centrifuges) to remove cuttings and impurities collected from the bottom hole. After solid removal, the mud is recycled in mixing equipment, where it is added to weighting agents before being stored in mud tanks and pushed back into drill pits by mud pumps.

1.2.2 Type of Drilling Muds

- *Oil-based or Synthetic-Based Drilling Muds*

Oil-based drilling fluids are primarily inverted emulsion systems, where water or brine is sheared into a base oil in the presence of an emulsifier. By applying high shear rates, the water, or the internal phase, is broken up into small droplets carried by the oil, the external phase. Further, organophilic clay is mixed to provide viscosity [20][23]. For the clays to work in the oil-based fluid, they have been chemically treated with oil-wetting agents to ensure the particles are dispersed. The clays that are made organophilic are typically either bentonite, which is plate-shaped and contributes to both viscosity and filtration control, or it may be sepiolite or attapulgite, which are spike- or rod-like clays and only regulate the viscosity [20]. The oil-to-water ratio may be adjusted to adjust the fluid's viscosity and density. A lower oil-to-water ratio typically increases viscosity over the whole shear rate range, resulting in higher yield stress.

Synthetic-based fluids are designed to replicate the functional advantages of oil-based fluids to obtain lower toxicity. In such fluids, the external or continuous phase is a synthetic organic material, whereas the internal phase is typically a brine. Oil- or synthetic-based drilling fluids have inherent benefits relative to water-based drilling fluid systems [24]. Shale and clay formations will swell in a simple water-based system, and salt formations will start to dissolve. The continuous phase of an oil- or synthetic-based fluid typically does not react with either the shale or the salts, so only the salinity of the internal brine phase needs to be regulated to limit the interaction with the formation being drilled. Also, this helps prevent drilled solids from breaking up into fine particles, which are difficult for the solids control systems to remove. Oil-based systems naturally have good fluid loss characteristics, temperature stability, good lubricity, and corrosion resistance. All these elements provide a stable fluid system performance and promote effective drilling and a high penetration rate (ROP). The main technical disadvantage of an oil-based system is related to

health, safety, and environmental (HSE) factors. This has led to a drive for lower-toxicity base fluids and more advanced water-based drilling fluids.

- *Water-based Drilling Muds*

Water-based drilling fluids are generally engineered for the formations being drilled. Spud mud is used to drill the simple fluids for the shallow top-hole sections. A typical spud mud may be composed of bentonite, flocculated with lime if used onshore, while either guar gum or salt gel is used offshore to create sufficient viscosity. As drilling progresses, it reaches a formation at a further depth, which increases technical complexity and hence calls for more advanced fluid composition. Water-based fluids are traditionally classified as:

Dispersed systems: Drilling mud dispersed systems are drilling fluids in which dispersed solid particles are stably suspended in a liquid phase. Uniform dispersants are added to deflocculated clay particles to control the fluid's viscosity and form a homogenous mixture with the liquid phase. They are, hence, commonly applied in various drilling operations to achieve, for instance, borehole stability, lubrication, and carrying drill cuttings to the surface. Typical examples of dispersed systems are water-based muds with clays and polymers as additives to suspend the solids. They allow higher fluid densities by weighting agents; they increase the tolerance of drilled solids. Lignosulphonates and lignitic chemicals are usually employed as dispersants. A pH range of 10 to 11 is generally needed and created to maintain the system's performance by adding chemicals such as NaOH (Caustic Soda).

Non-dispersed systems: Drilling mud non-dispersed systems, commonly called non-aqueous drilling fluids, when the solid particles remain suspended in the liquid phase but are not in a stable dispersion. In these systems, the solid particles typically are heavier than the liquid phase and, thus, settle out when the fluid is not in motion. Non-dispersed systems are used in many drilling

operations where water-based fluids cannot be used because of geometric formations or specific drilling conditions. They provide such advantages as higher thermal stability, low permeability formations, and a smaller possibility of formation damage. They are mainly used for drilling shallower sections.

Brine-based systems: Brine-based systems are the term used to describe drilling fluids whose principal liquid phase is a solution of water and salts, most often sodium chloride (NaCl) or potassium chloride (KCI). These fluids have many uses in drilling and are applied mainly when water-based muds cannot be used due to the conditions in the formation being drilled or when the drilling objectives cannot be fulfilled. All these are the benefits of brine-based systems, where density is high to control formation pressures, avoid well blowouts, and inhibit clay swelling, leading to more stable wellbores. Besides, it is also good at reducing formation damage and maintaining the characteristics of the fluid at extreme temperature conditions. They may be customized with various other tailored additives to meet the desired requirements while drilling.

Polymer-based systems describe drilling fluids in which polymers (natural or synthetic large molecules of repeating subunits or monomers) are used as the main constituent in the fluid system. Polymer-based systems have been dispensed mainly to improve the brine-based fluids' inhibitive characteristics in drilling shale-bearing formations. Polymer-based systems are commonly applied to increase viscosity, enhance fluid loss control, reduce shale swelling, and provide lubricity. They bring flexibility and variety in solving different drilling problems and are most favorable in many oil and gas operations. Thus, glycols or amines, besides salts, are primarily found in such systems. The most common salt in polymer-based fluids is potassium chloride, KCl, which, as mentioned before, has been an excellent shale inhibitor. The major drawback of these factors is that they are

incompatible with bentonite as a viscosity agent, and particular polymers must be added to control the viscosity and filtration characteristics.

1.2.3 Mud Functions

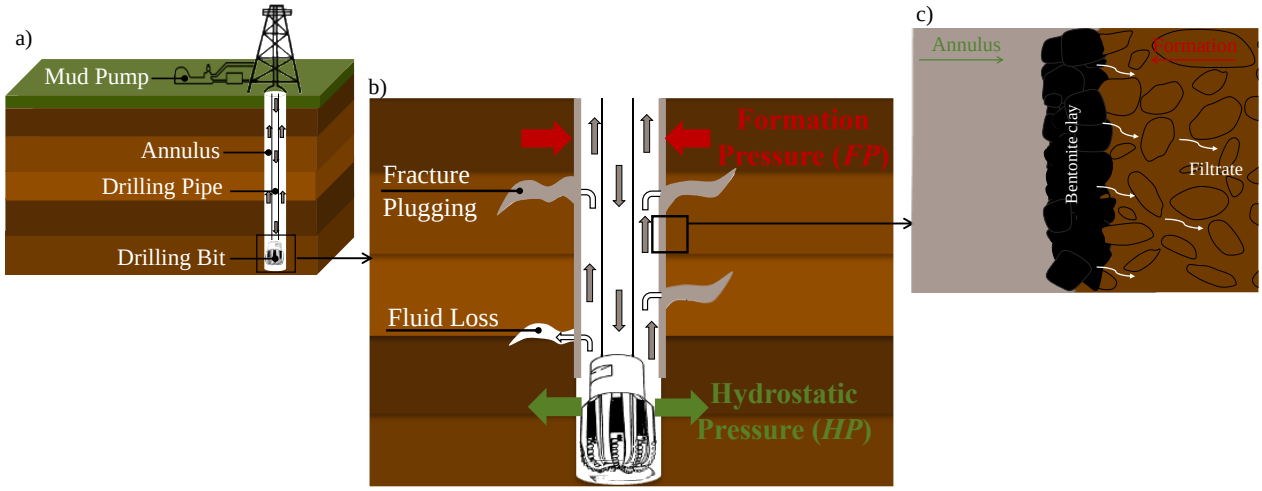


Figure 2.*a) Drilling Circulation, b) Mud Practicality, c) Cake Filtration*

The drilling process's fluidity (rate of penetration) and well isolation are often broken down into subfunctions, which are listed in **Table 1** below:

Table 1: *Mud Functions*

Drilling mud functions	
Drilling Fluidity	• Cuttings Removal from drilling bit • Cooling and lubrication of overheated drilling tools • Provide buoyancy to drilling tools • Carrying bottom hole cuttings to the surface
Well Control	• Hydraulic pressure control • Cake filtration • Wellbore Isolation

- *Cuttings Removal from drilling bit*

While the drill bit cuts through the rock or sedimentary layers, it makes small rock or sediment pieces called cuttings. Drilling mud ejecting pressure sweeps the cuttings away from the bit, preventing them from settling and clogging around drill bit teeth, thus allowing good penetration into the formation.

- *Cooling and Lubrication*

Drilling is associated with high temperatures resulting from friction between the drill bit and the drilled formation. Drilling mud cools and lubricates the drill bit and string to decrease frictional heating and wear on drilling equipment. This cools and lubricates to avoid overheating the drilling tools, thus providing longevity.

- *Hydraulic Pressure Control*

Drilling mud provides hydrostatic pressure against the wellbore walls, preventing a potential blowout or controlling formation pressures encountered while drilling. The drilling mud balances the weight created by the fluids existing within the formation and helps maintain the stability and integrity of the wellbore walls.

- *Provide Buoyancy*

Drilling mud buoyancy is the upward force the drilling mud provides against the bit while operating at the bottom of the wellbore. This buoyant force results from the pressure and density of the drilling mud column in the well. It stabilizes the drill bit by counterbalancing the downward gravitational forces and helps to maintain the bit in contact with the formation.*arrying Cutting to the surface*

The drilling mud carries cuttings from the wellbore bottom to the surface, separating them from the mud. Efficient cutting removal helps visualize the drilling process better. Moreover, drilling mud identifies the nature of the formation being drilled by bringing rock cuttings and formation fluids, such as oil, gas, and water, to the surface and allowing them to be analyzed for properties like porosity, permeability, and hydrocarbon content. Geologists and engineers use such information to infer the well's potential productivity and to make informed decisions about the drilling strategy.

- *Wellbore Isolation*

Drilling mud forms a thin streak of filter cake on the wellbore walls, a barrier against fluid invasion into the formation. This thin cake seals off the formation and minimizes damage to the porous and permeable formations. Therefore, drilling mud plays a vital role in well control and safety regarding people and equipment during drilling. It will help prevent kicks and blowouts by balancing formation pressures and responding instantly to any change in downhole conditions.

Drilling process fluidity and well control are fundamental and codependent purposes of drilling mud. If unattended, failing in one or both functions present substantial financial risks to shareholders, increasing drilling operation time and capital cost, low oil production, and equipment damage. They also represent security liabilities for equipment and staff, as failing to balance differential pressure increases risks of kicks, influxes, and blowouts.

- *Cake Filtration*

Drilling mud cake filtration is the naturally occurring phase separation during which drilling mud pushed against a wellbore under hydrostatic pressure forms a filter cake on the wellbore during operations while the base fluid (filtrate) penetrates the formation and the pore. This filtration offers fluid loss control, protection from formations, and stability and efficiency to the drilling process.

1-3. Filtration Control

1.3.1 Mud Balance on Cake Filtration

Mud balance is used to determine the density of the drilling fluid (mud). It is an essential procedure that occurs during drilling to form cakes. The main reason, as seen in **Figure 3a**, is that a less compact, low-permeable filter cake is obtained with low mud density. It is because the differential pressure is low; therefore, the number of parts of the particles being compressed against the wellbore walls is low. Low-density mud is built by a more porous cake [25]. Often, it is characteristically permeable. As a result, fluid loss is equally usually high for the instances related to low-density mud. This will make the formation more porous and may further damage the formation from the drilling fluid invasion. Generally, filter cakes formed by low-density mud are weak and may be scraped off easily. In other words, they may not offer significant wellbore stability, especially in unconsolidated formations. It reduces the risk of fracturing the formation. Still, it may result in excessive fluid loss and allow insufficient sealing, which will cause problems from the drilling standpoint and increase non-productive time. At high mud density, it has the potency to produce a relatively compact thick filter cake on the wellbore wall. This is so as the density of the mud will result in an increase in pressure difference across the filter cake, yielding a favorable increase in settlement of the solid particles and, consequently, cake compactness improvement . The filter cake is likely to exhibit low permeability and is compactly formed by high-density mud. Thus, the fluid loss to the formation is reduced, which is a critical point in the

stability of the wellbore. The filtration rate would decrease if filter cake were more poorly permeable with high-density mud. These properties, as such, will help retain well control and minimize differential sticking. Usually, the filter cake formed with high-density mud is generally more potent and more cohesive. Though it would be advantageous in earthen stability, a high density of mud might also disadvantage effective removal processes of swabbing or running out of a hole. Although high-density mud provides an excellent sealing-off effect for fluid losses, at the same time, it may cause excessive fracture induction within a formation, especially in weaker zones. This balance must be managed to ensure that there is no outcome of instability of the earth.

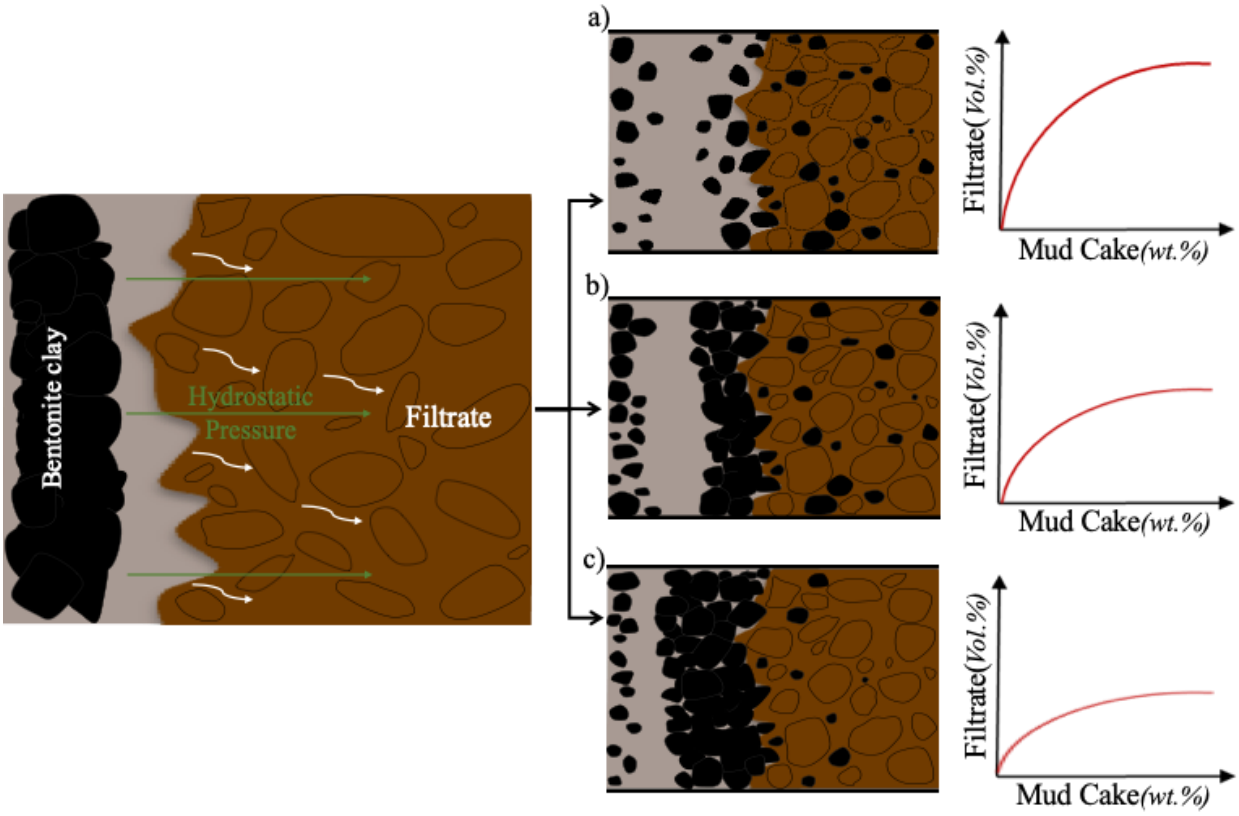


Figure 3.*Mud Balance on Filtration Control*

Filtration control materials reduce excessive fluid filtrate penetration into the formation, thus reducing the loss of drilling fluid. Water-based drilling fluid may be composed in diverse ways and use different filtration control materials [27][28].

1.3.2 Weighting Materials

The two most common groups of materials are bentonite and polymers. Bentonite is used to both create viscosity and control fluid loss. In earlier stages of filtration control, fluid loss was controlled by primarily balancing the bentonite-base fluid ratio in the mud (**Figure 3)** by monitoring the added concentration of Bentonite in the mud [29]–[32]. The amount of bentonite clays in the mud would increase the rate of pore formation plugging. However, as bentonite is known to cause permanent permeability damage, it is not used in reservoir drilling fluids [33].

1.3.3 Lost circulation and lost circulation materials

While filtration control materials are targeted to seal highly permeable formations, lost circulation materials (LMC) aim to prevent or stop circulation loss to the formation in formations of higher permeabilities or those with natural or induced fractures. LMCs help control the wellbore's pressure and avoid incidents like blowouts, wellbore collapse, differential sticking, or permeability change in any producing or injecting well of the formation. Therefore, LMC is chosen based on the fluid loss rate, as shown in **Table 2**.

Table 2: *Categorization of drilling fluid loss*

Category	Loss rate (m^3/hr)	Loss rate (bbl/hr)
Minor Loss	0-15	0-10
Partial loss	1.5-10	10-60
Sever Loss	>10	>60

The fluid loss rate is relative to the formation porosity as much as the drilling fluid's circulation rate. Defining a loss condition to differentiate between static and dynamic losses where the drilling fluid is circulated at some circulation rate is helpful. In the case of drilling mud circulation, a higher circulation rate typically increases pressures and giant bosses [34].

Particle-based systems are efficient and workable for deploying lost circulation materials. Sound isolation of wellbore to formation fluids in exceedingly high or total loss scenarios is possible with

gels or solidifying materials. Most particulate systems have carriers based on some carbonate or mineral carrier with calcium carbonate or mica, mineral wools, natural- or synthetic graphite, plastics, and by-products from organic material production, for example, sawdust, nutshells, or other cellulose-based products processed for some end-use. Particles should be usually chosen to avoid fallout during the solids control stage of preventative treatment; typical particle size distributions will thus go up to 100–250 μm. Typically, the standard concentration of preventative LCMs can be 14-114 kg (about 251.33 lb/m^3. Usually, preventative treatments are adequate to control fluid losses unless the formation drilled is pre-fractured, loose sand, or regular. An adequately designed preventative LCM treatment would prevent any seepage losses or some partial losses. With partial or severe losses, specially mixed LCM-pill mixtures can seal high-permeability formations or fractures. Such applications almost invariably include time-setting or temperature-setting mixtures that can be pumped to a loss site and, upon setting, form more rigid structures.

CHAPTER 2
LITERATURE REVIEW

2-1. Bentonite

Bentonite is very popular for viscosities in water-based drilling fluids non-inhibitive. It is an old clay mineral developed through volcanic ash weathering. Its name was taken from Fort Benton, Wyoming, while the most famous resource of montmorillonite clay was found in France. The basic structure of this material is that it contains a rich composition of montmorillonite or smectite minerals with multiple negatively charged lamination with exchangeable cations in the interlayer locations (Na^{+}, Ca^{2+}, K^{+}, Mg^{2+}) [35]. Bentonite Clays swell very quickly once hydrated, which allows water penetration through the osmotic process in the interlayer spaces. Water molecules interact with the functional groups at the bentonite surface and the interlayer cations to bring out the layer formation with an increased interlayer distance, hence an increase in particle size of bentonite. The increase in the culmination of dispersed swelling clays within the water-clay system leads to gelatinous and viscous formation at specific concentrations, forming a shear-thinning/pseudoplastic or thixotropic fluid. The gelling properties of bentonite heavily influence the weighting agent, cuttings suspension, and mud mobility, which are quantitatively assessed in weight-related properties, such as viscosity, yield point, and gel strength. The present chapter emphasizes the interrelationship of the mud swelling index with rheological characteristics.

Bentonite is divided into sodium bentonite and calcium bentonite as the main ingredients. Due to several reasons that best serve the drilling operation's needs, sodium bentonite often finds a place over calcium bentonite in drilling muds. Sodium bentonite showcases superior swelling capabilities and exceptional colloidal attributes. It has a higher exchange capacity, wherein the sodium ions may be easily exchanged with other cations in the drilling mud environment. This

property of Na^+ bentonite holds indications for higher stability with salinity-based or brine-based drilling fluids [10][36]. The swelling capacity of Na+ bentonite provides better wellbore stability as the filter cake formed on the wellbore walls with sodium bentonite is more impermeable and efficient than when calcium bentonite is used. This is vital in averting lost circulation into porous formations and fostering efficient drilling operations.

However, the rising complexity of reserves and targeted formations challenges the limitations of Sodium Bentonite. This highlights the need for additives and supplements to optimize drilling mud-up requirements.

2-2. Mud Optimization Using Polymers

2.2.1 Xanthan Gum (XG)

Xanthan gum is a biopolymer commonly used to drill mud in the oil and gas industry. It is added to the mud primarily to control viscosity. It helps maintain the viscosity of the drilling mud at various temperatures and pressures encountered during drilling operations [37]. As it has been, it is also a flow control agent, helping reduce the fluid lost to the drilled formation. In case of low drilling fluid flow, Xanthan Gum improves the mud gel strength as the mix shows better hold of the formation cuttings and trapping cuttings in suspension This property is essential for maintaining wellbore stability and preventing formation damage.

Xanthan Gum fluid loss control conducted by Navarrete et al. (2000) prepared xanthan fluid in a recirculating 40-gallon tank by first dispersing the xanthan gum into 20 gals of tap water. Based on the results, they argue that fines from the same formation, in combination with xanthan gum, provide the best fluid loss control and significantly reduce formation damage [38].

Gautam et al. (2020) on the XG effect on filtration reported a permeability reduction from clay-free mud containing 0.85.7g XG with 500 cm3 water (0.1290) to an aqueous XC solution

containing 5 XG with 500 cm3 water (0.00416) [39][40]. Another experiment conducted by Shafeeg et al. (2013) shows a constant increase of 1 gram of XG polymer addition in a 350ml water-based drilling mud reduces the mud's mobility by increasing the rheological properties. Moreover, the permeability is reduced until the mud becomes almost immobile at 2-gram XG polymer[41][42]. The drawbacks of Xanthan Gum include poor workability and surface area and a slow dissolution rate that can reduce the potential uses of XG.

2.2.2 Polyanionic Cellulose (PAC) Polymer

Another confirmed filtration control polymer is poly-anionic cellulose (PAC) [34]. These come in different varieties and are often mixed to achieve a specific fluid loss and viscosity level. PAC is usually considered to have better thermal stability and salt resistance than starch, whereas some starches provide effective fluid loss control with a lower viscosity impact than PAC [43]Starches are made from varied materials, such as potatoes and corn. Some starches are chemically modified or cross-linked to achieve specific characteristics, such as enhanced temperature stability or filtration control. The starches used for drilling fluids typically have a temperature stability of up to 90-120°C. For oil-based fluids, varied materials generally improve filtration control.

Another advantage of PAC is its enabling influence on shale swelling inhibition and dispersion, considerably preventing wellbore instability issues. Pac has been proven compatible with other additives, making it versatile under various drilling conditions.

However, PAC can be reactive to surrounding contaminants, affecting the mud's rheological performance. PAC also seems to require high concentration in order to improve a drilling mud, as it is reported by Eleman et al. (2014), investigating the impact of Polyanionic Cellulose Polymer on drilling fluids, it requires at least 25% PAC-LV of bulk volume for drilling fluids to reach API

specifications for viscometer dial reading at 600 rpm [44][45]. Therefore, PAC is relatively costly compared to the additives in drilling fluid, influencing its usage in budget-sensitive projects.

2.2.3 Polyvinyl Alcohol

PVOH is one promising synthetic polymer additive for drilling mud due to the polymerization process of vinyl acetate and its partial hydrolysis. Because it is low-cost, this hydrophilic polymer is widely applicable in various industries. It is of immense interest in drilling operations in the oil and gas industry. PVOH has proved to be a fine viscosity in drilling fluids, thus controlling and stabilizing the viscosity of the mud; this feature is handy when it is essential to have uniform viscosity for proper drilling operations. Otherwise, besides such typical use, it might be added to drilling muds to serve as a fluid loss control additive, which lowers the filtration rate into the formation of the drilling fluids. Therefore, wellbore stability will be improved, and the formation damage will be minimized. Other studies found that polyvinyl alcohol can act and inhibit shale hydration and dispersion under some drilling environments. In case shale does not swell and disintegrate, wellbore integrity shall be maintained; hence, stuck pipe incidents will not result. Polyvinyl alcohol generally has broad compatibility with various drilling fluid additive chemicals; therefore, it is versatile in its formulation. This can be of great benefit on the environmental front compared to the usage of other water-soluble and biodegradable drilling mud additives. Normally, the addition of PVOH into the drilling fluid system is made in small concentrations, usually ranging between 0.1wt% to 0.5wt% by weight. At the same time, this depends on the requirements of specific drilling operations in accordance with the properties of mud in use a customer desires to attain or maintain. It can be added to various mud types, including water-based, oil-based, and synthetic-based, to achieve the desired performance objectives. In the case of PVOH, the maximum benefits were realized through viscosity control and fluid loss reduction. However,

optimum performance requires adding factors into the drilling fluid, such as temperature and pH conditions, and other chemicals in optimum concentration. Proper testing and evaluation were conducted to determine the optimum concentration of PVOH addition and application of PVOH in the drilling mud for specific conditions of drilling and formations.

2-3. Objectif of the Research and Research Plan

2.2.4 Challenges

Changes in cake filtration happen swiftly, depending on the mud formulation and the formation conditions. It is reported that several properties, including formation permeability, can alter the filtration performance of a typical drilling mud. Because it is impossible to alter the conditions of a formation, it is, therefore, important for the mud to be selectively formulated, closely monitored, and tested several times a day during drilling operations. Drilling fluids are designed to handle the physical and chemical interaction with the formation, consuming the additives in the drilling fluid and influence the mud properties. Moreover, wrong mud design or failure to maintain required mud properties can lead to several costly complications and complex good control issues, putting personnel and the environment at risk [46]. To date, Water Based Drilling mud still has many disadvantages reported, including formation damage, low cake properties, and high fluid loss [30].

Several polymers (Xanthan Gum, PAC POLYMER, and carboxymethyl Cellulose) have been adopted and developed for drilling mud enhancement over the years. Their use has positively influenced filtration control, physiochemical properties, weighing agents, and saturated formations. However, these methods can use more exploring on the topic because the currently used polymers have display limitations such as Thermal sensitivity, chemical sensitivity, poor abrasion resilience, environmental implication and cost [47][48]. There is always need for other additives to control properties that were affected by weighting agents which at the end increase the operating cost. Not

to mention Bentonite and barite are also getting more expensive due to increase in demand. Polyvinyl Alcohol has been previously used in other industries like cosmetics and alimentation. It's harmless nature, accessibility and swelling ability already proved by previous related research, makes it a good potential filtration control additive.

2.2.5 Purpose and objectives of the research

The thesis objectives are subdivided into three sections and explained following the experimental flow in **Figure 4** and detailed in **Table 3**.

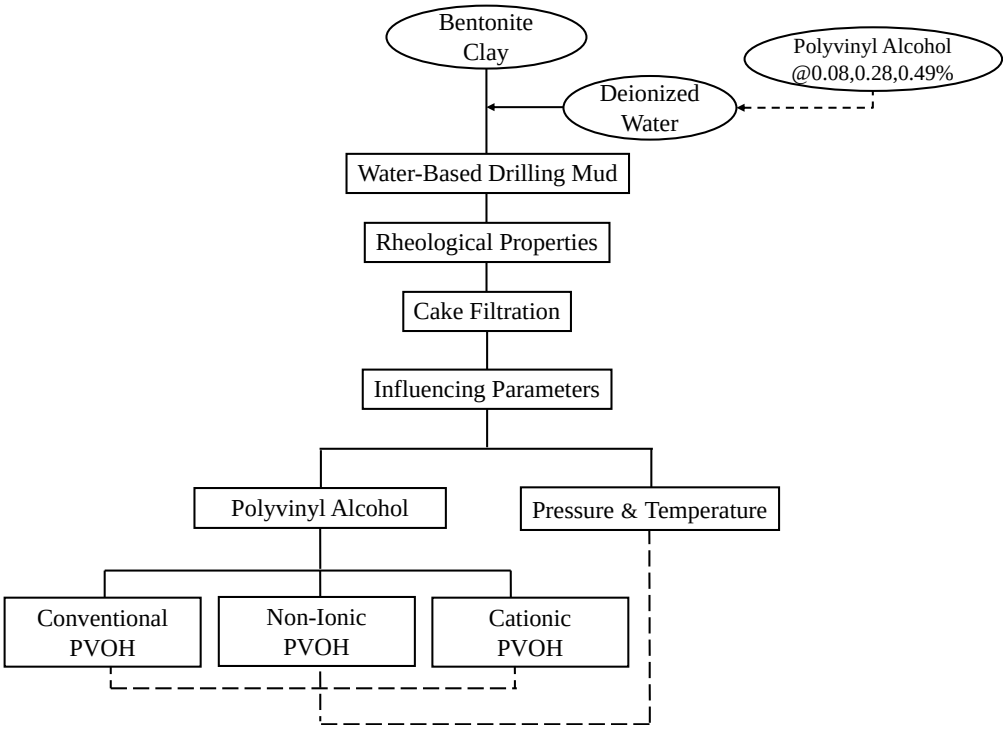


***Figure 4**.Experimental Flow*

- *Mud Balance influence on cake filtration*

The goal of the thesis is mud swelling optimization using Polyvinyl Alcohol (PVOH). The first step is to evaluate the PVOH effect on the drilling sample at a fixed concentration. The subject of comparison was the rheological properties measured, such as dynamic Viscosity, Specific gravity, and PH. The comparison was simultaneously based on the American Petroleum Institute API and

the PVOH with the sample without PVOH [49][50]. The following objective was then to analyze the sensitivity control of PVOH over drilling mud swelling magnitude. The variation in mud filtrations at different PVOH concentrations was studied and compared to related literature. The cake filtration change is a result of mud swelling.

- *PVOH adsorption*

To understand the mud swelling of samples, PVOH-Bentonite affinity and adsorption were measured using UV spectroscopy and analyzed through the Solid-Liquid Equilibrium Model after discussing the nature of the samples' adsorption and selecting the two best-controlling PVOHs for further testing. Understanding the Bentonite-PVOH affinity allows us to distinguish the most suitable polymer to use to control the rate of intermolecular bonding as well as the type of bonding prevalent in the muds; because controlling the bonding types and rates are immediately influencing control in our mud swelling index.

- *PVOH- enhanced drilling mud applicability*

Finally, the applicability of the polymer-enhanced drilling mud samples was tested by measuring the mud's thermal stability. The experimental process was conducted before atmospheric temperature and at conditioned setups (55^{o}C and 85^{o}C). The results were obtained and compared through literature, better assessing the mud's thermal resistivity.

Table 3: *Thesis Plan*

2021	**2022**	**2023**	**2024**
Stage1 Mud rheology and Cake Filtration		Stage2 Bentonite- PVOH Synergy	Stage 3 Thermal Stability
• Liquid-solid pressurized Phase Separation • Pressure Stability • Solids Deposition		• Polymer adsorption • Particle aggregation and pore sealing	• Temperature Control • Hydrostatic pressure prediction
Scientific Aspects to be Elucidated			

• Static filtration test • Pressure recording • Permeability	• UV Spectroscopy • Adsorption model selection • SEM analysis	• Oven • Thermogravimetry Analysis

CHAPTER 3
EXPERIMENTAL SETUP

3-1. Materials

The series of experiments were conducted on a lab scale at atmospheric temperature. The primary materials used were deionized water, sodium bentonite, and three types of Polyvinyl Alcohol.

3.1.1 Bentonite

The experiment series was conducted on a lab scale. Deionized water and sodium bentonite, provided by Nippon Synthetic Chemical Industry, were the primary materials used.

Table 4: *Chemical composition of Bentonite clay is used to prepare the different drilling muds.*

Chemical components	SiO_2	Al_2O_3	Fe_2O_3	Na_2O	MgO	CaO	TiO_2	K_2O
Percentage (%)	63.02	21.05	3.02	2.67	2.57	1.34	0.8	0.9

[a]XRF was performed by the supplier Nippon Synthetic Chemical Industry (Osaka, Japan).

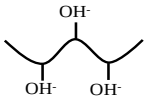
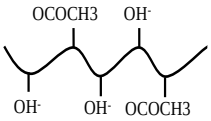
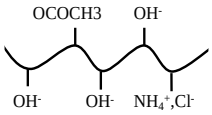
Table 4 shows the mineral composition obtained. X-ray fluorescent data show that bentonite consists of Na-Montmorillonite (67~73%), Ca-Montmorillonite (6~25%), Soda Feldspar (2~14%), and a negligible amount of Quartz (2~11%). X-Ray fluorescent spectroscopy revealed 63.02% of SiO_2, 21.05% of Al_2O_3, and 3.02% of Fe_2O_3. Also, the Atterberg limits are as follows: a liquid limit of 244.5%, a plasticity of 46.1%, and a plasticity index of 198.4%. It should be noted that bentonite was used as received.

3.1.2 Polyvinyl Alcohol

The polyvinyl Alcohol types used are Conventional PVOH-1, modified Non-Ionic PVOH-2, and modified Cationic PVOH-3. A sample with No PVOH was also prepared as a control sample.

The polymers were selected from preliminary screening after they physiochemical features fell into the acceptable range of optimal mud characteristics designed by the American Petroleum Institute (API) [51]. The samples have different chemical structures, as shown in **Table 5.**

Table 5: *Physicochemical properties of investigated PVOHs*

Polyvinyl Alcohol		Hydrolysis degree (%mol)
Conventional (PVOH-1)		85-89
Non-Ionic (PVOH-2)		86.5-89
Cationic (PVOH-3)		85.5-88.0

3-2. Equipment Setup

3.2.1 Mud Preparation

Mud samples were prepared under atmospheric conditions. Drilling mud samples were formulated using the following **Eq 1**.

Equation 1: Mud Sample Formulation**.**

$$Mud\ Sample = Bauid(Deionized\ Water + PVOH) + Bentonite$$

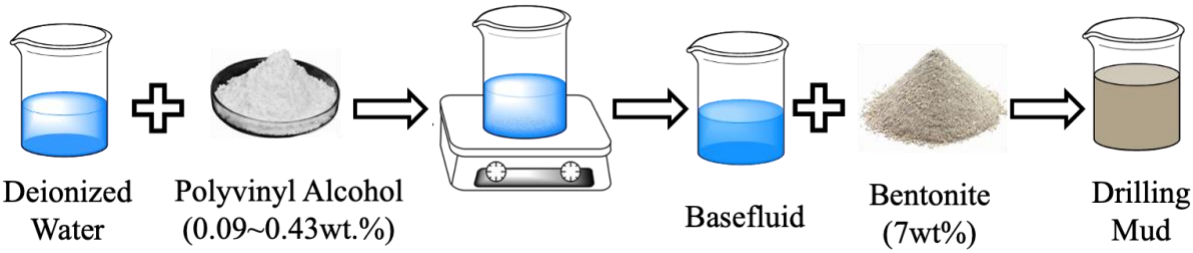


Figure 5. *Mud Sample Formulation*

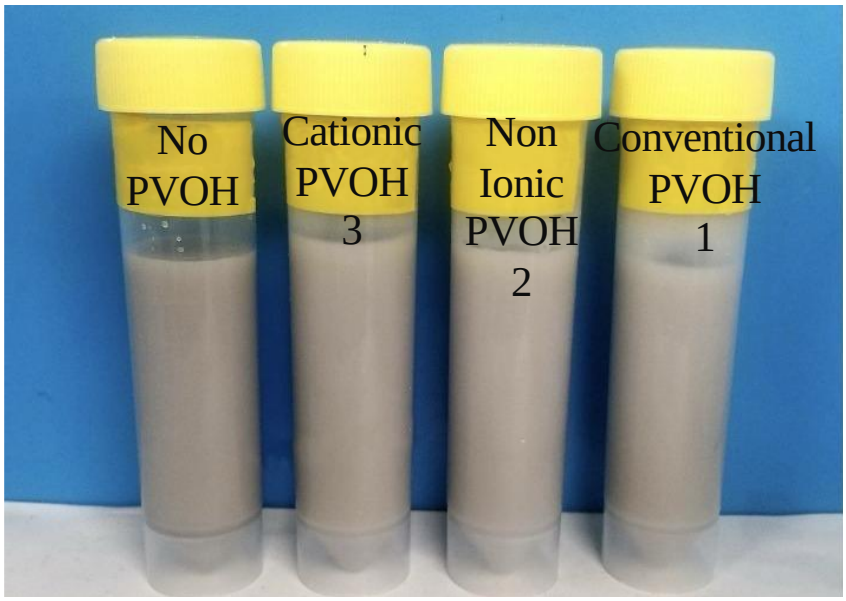


Figure 6. *Drilling Mud Samples*

A total of 10 samples were prepared using the above formula. The three lyophilized PVOH were individually added to 3 samples at the various concentrations in **Table 6**. An extensive two-hour mixing of deionized water and PVOH using a homogenizer (model AHG160A) resulted in homogeneous-based fluids. Bentonite was then added to the aqueous solution, and the mixture was stirred for another two hours to produce drilling mud samples. All samples were allowed to rest for at least 12 hours to complete mud swelling successfully.

Table 6: *Mud Formulation*

Sample Number	PVOH		Base fluid Composition		Na-Bentonite Concentration (wt.%)
			Concentration (wt.%)	Deionized Water (g)	
1	No PVOH		-	40	7
2	Conventional PVOH-1	a	0.08	350	7
3		b	0.28		
4		c	0.405		
5	Non-ionic PVOH-2	a	0.08	350	7
6		b	0.28		
7		c	0.405		
8	Cationic PVOH-3	a	0.08	350	7
9		b	0.28		
10		c	0.405		

After 12 settling hours in atmospheric temperature, the mud samples were tested for rheological properties, filtration, and spectrographic analysis of mud cakes. Subsequently, the mud permeability of the samples is determined using Darcy's law and the linear square method. Bentonite, a hydrophilic clay, is preferred for drilling mud formulation due to its significant swelling potential and cation exchange capacity. Procedures are described as follows.

3.2.2 Rheological tests

pH

The acidity tests were conducted using an ASONE AS800pH meter. Samples were placed in a tube from which the pH meter sensor would be dived. Inconsistent numbers are displayed on the screen of the pH meter for 45 seconds. The reading recorded is the last number on the reading panel of the pH meter.

Density

Specific gravity and Dynamic viscosity. The specific gravity of the samples was taken right after resting time using a mud balance supplied by West Japan Testing Machine Co., Limited aqua Horiba DS-72 from Osaka, Japan. Each sample (250ml) was placed in the cup. The mud samples were to fill the cup and spill out when the cup was closed with the lid. The mud balance was maintained by maintaining the gas bubble on the level glass centered. The weighting rider was moved back and forth on the balance arm until it found equilibrium. The density of the tested mud to be recorded is the number closest to the rider on the left side.

Viscosity

The samples' dynamic viscosity and gel strength were measured using a viscosity reader model Brookfield viscometer DV-I Prime with a connected thermal chamber (Thermosel) for a controlled temperature. The viscosity measurements started after prepping the viscometer and selecting a measuring bob of S 35 for all the samples. The viscosity readings were recorded at 5 to 100 rpm.

- *Cake Filtration Tests*

The static pressurized cake filtration tests at 25°C were conducted using 0.3 µm filter papers of 2ϕ porosity, a stainless-steel Millipore sigma filter holder 90 mm (about the length of the long edge of a credit card) model, and a 25ml (about 0.85 oz) gas holder, represented in **Figure 7**. The assemblage of equipment was the same for filtration tests at both temperatures. Ten (10) mL of Mud samples are placed on filter paper. The filter paper with mud sample was then positioned in the filtration area of the filter holder. Soon after the filter holder was hermetically closed, a Nitrogen (N_2) gas holder was attached to the filter holder. Each static pressurized filtration starts with Nitrogen's displacement to the filter holder's filtration area.

The gas was injected and maintained at a constant pressure of 1.28 MPa using valves and pressure indicators. The filtration tests lasted 5 hours for each sample, during which filtrate production and differential pressure were recorded.

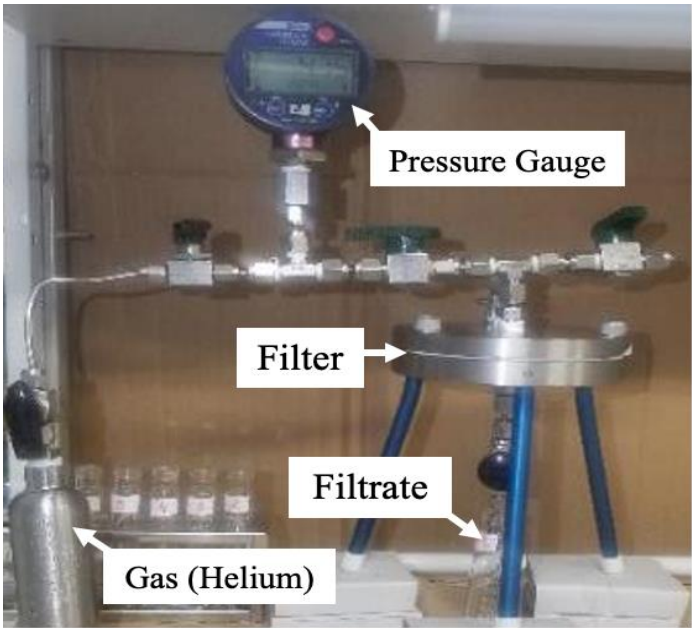


***Figure** 7. Cake filtration testing at 25°C*

CHAPTER 4
RESULTS AND DISCUSSION

4-1. Rheological Properties and Cake Filtration

4.1.1 Physio-Chemical Properties

- ***pH***

The results obtained for the de pH readings, shown in **Table 7**, show the change in acidity as PVOH is added to the mixtures. Based on Table 7, PVOH was able to maintain the PH between 8 and 10.b, which is the optimal PH control recorded by Ameru et al. (2017), controlling the acidity of the mud which plays vital roles in protecting equipment and ensuring the accuracy of formation analysis [42]. A Michigan State University journal dealing with soil pH indicates that the major factors affecting soil pH are calcium, magnesium, and potassium.

Table 7: *Physicochemical properties of formulated drilling mud specificities*

	Control	PVOH-1			PVOH-2			PVOH-3		
	No PVOH	a	b	c	a	b	c	a	b	c
pH	9.5	9.5	9.6	9.7	9.52	9.65	9.7	9.4	9.3	8.98

These elements maintain the pH on the alkaline side by themselves. Soil pH is related to how the soil attaches to these elements. Sand generally has a lower pH than clay because water moves through the sand faster than clay [37]. When added to drilling fluid, PVOH containing hydroxyl group OH- and OCOCH3 attach to the surface of the clay particles (SiO32, SiO) by hydrogen bonding[52]. However, with a charged moiety on the PVOH (NH4+), competitive adsorption between the different silicate ions (SiO32-, SiO44-) of the bentonite clay is prompted.

The oppositely charged ions are packed and held together by forces of electrical attraction, with each cation attracting all neighboring anions [52]. This same attraction also happened among other adjacent clay particles and their surrounding polymer extensions. They approached each other,

creating bridge flocculation, thicker and heavier mud [53]. In a similar work, Gamal et al. showed that increasing the pH from 9 to 10 increased the filtrated volume by 33%[54] . They argued that altering the pH of the aqueous solutions, within which the bentonite clay is mixed, impacts the mud's filtration properties. The mud, therefore, carries the ionic charge to the free leftover ions after saturations of bentonite particles. With the knowledge that WBDF performs better in a pH ranging between 8.0 and 10.5 [38], In the case of water-based drilling mud becoming acidic (< 7), precedes a boost of corrosion in drilling equipment, also polluting the environment.

- ***Dynamic Viscosity.***

Moreover, in comparing the different mud samples, one can highlight the extent to which the interactions between PVOH and clay particles are proportional to the former concentration [53]. An excess of PVOH concentration in mud formulation can alter the performance of mud, which is the case in **Table 7**.

Table 8: *Dynamic Viscosity @100RPM*

Nbr.	Polymers	Concentration	Dynamic Viscosity	Ref.
1	No PVOH	-	40	This Thesis
	Conventional PVOH	0.08wt%	60	
		0.28wt%	64	
		0.405wt%	78	
	Non-Ionic PVOH	0.08wt%	90	
		0.28wt%	120	
		0.405wt%	250	
	Cationic PVOH	0.08wt%	50	
		0.28wt%	52	
		0.405wt%	68	
2	Xanthan Gum	-	19	[55]
		0.14wt%	34	
		0.28wt%	56	
		0.428wt%	67	
3	PAC	2ppb	22	[56]

The water absorption occurring in all samples reduces the portion of the liquid phase of the mixture, which reduces the fluidity of the mud samples. As mentioned previously, more charged ions (PVOH) in the mixture enable more water absorption, and new clusters are formed among clay particles. Combined with lesser mobility due to intensified water reduction, these clusters display much more resistance against fluid flow [10].

This observation is consistent with the literature, which concluded that synthetic polymers are highly effective flocculants at small dosages but have poor shear stability [57] stating. According to this study, increasing the dynamic viscosity of the mud results in a remarkable rise in the number of clay particles and the intensification of bentonite flocculation as a result of PVOH addition, prompting more absorption. Much thicker filter cakes are expected to have mud flowing viscous rather than turbulent flow [58]. Another observation of those results is the disproportional rise of dynamic viscosity for mud with modified anionic PVOH. This sudden rise can be interpreted as modified anionic PVOH being highly reactive to bentonite particles in the presence of water. Making modified anionic PVOH a drastic but eligible possible weighing agent yet unstable.

4.1.2 Cake Filtration

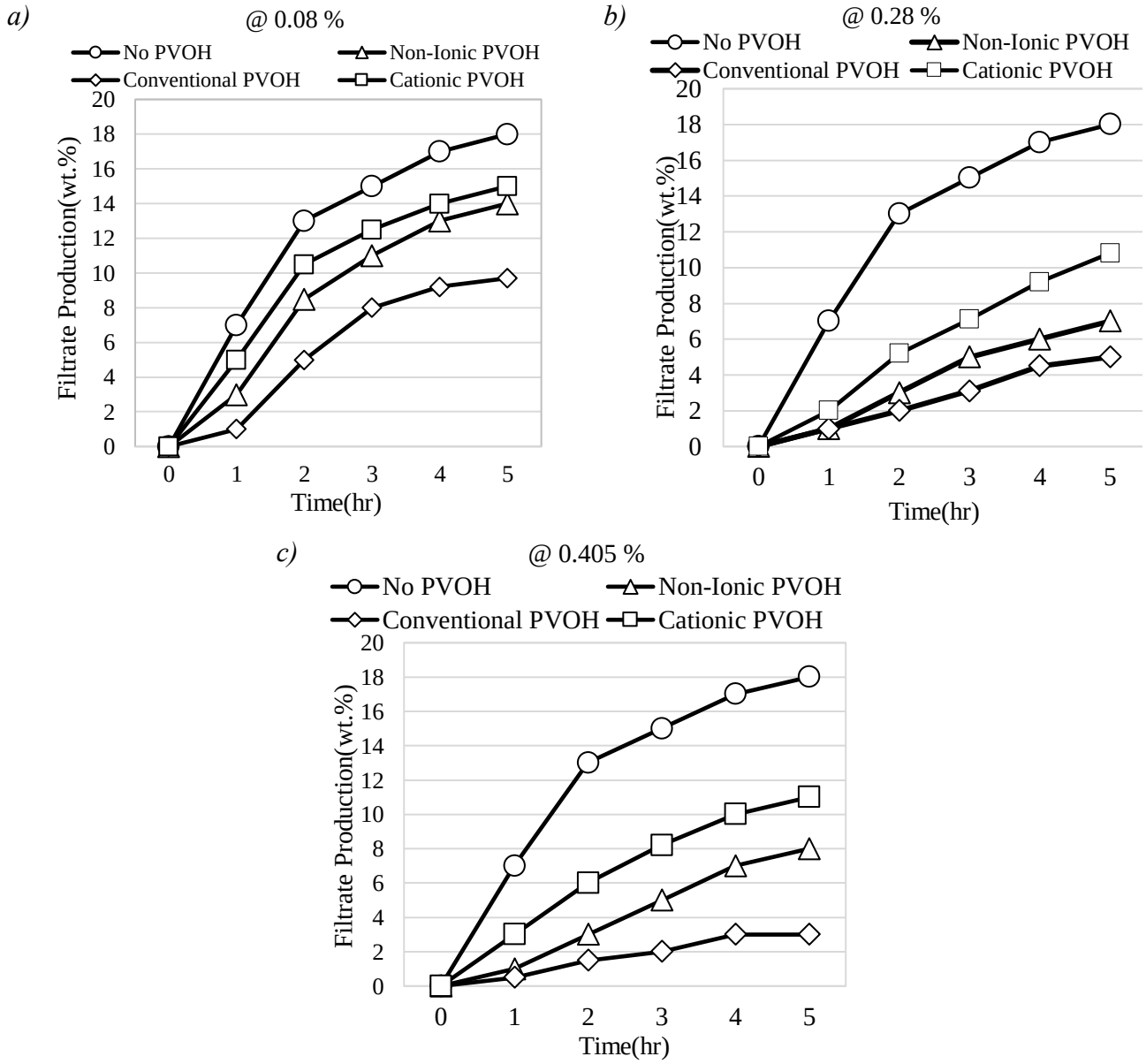


Figure 8. *Effluent Production*

The graph (**Figure 9**) represents a cumulative filtrate production of samples after the 5 hours. According to the data shown in here, filtrate recovery reduces with progressive increasing of any polyvinyl alcohol concentration.

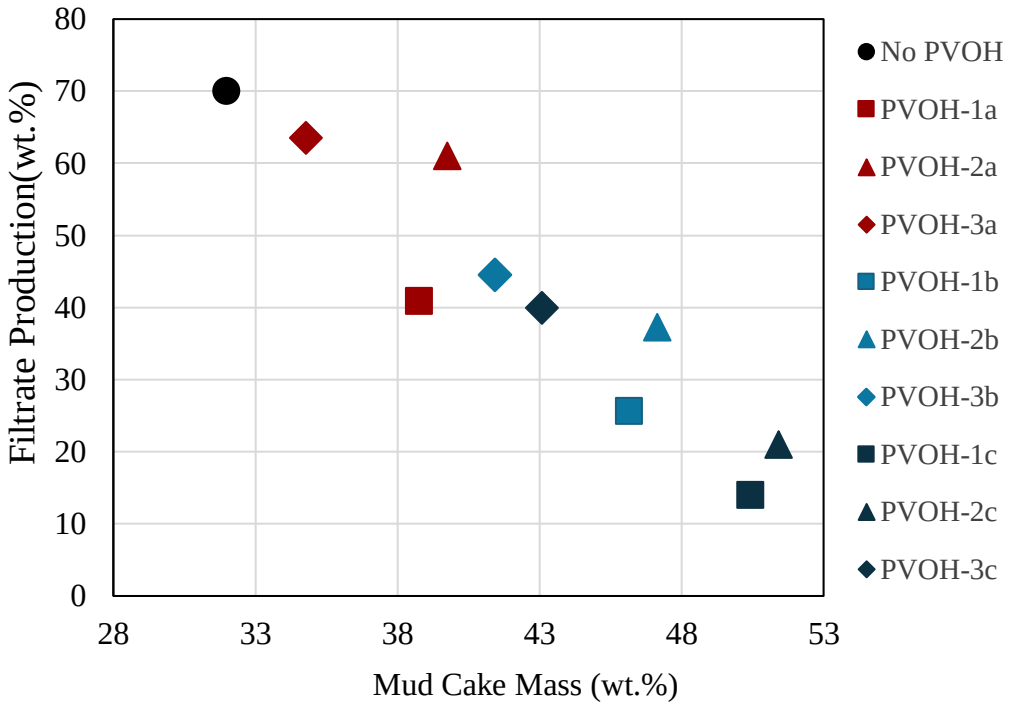


Figure 9. *Mud Cake vs Filtrate Volume*

The control sample seems to have the thinnest mud cake with higher effluent production. However, at any rise of PVOH concentration, mud cakes increase proportionally with a reduction of filtrate production. In reference to the control sample (no PVOH), the average decrease of filtrate recovery for samples containing Cationic PVOH-3, Non-Ionic PVOH-2, and Standard PVOH-1 was 21%,38%, and 43%, respectively, as their mud cakes increased in thickness and masses by 19%, 36%, and 48%. PVOH-3 has the highest water content, followed by PVOH-2 and PVOH-1. An hourly recording of the filtrate production (**Figure 8**) also showed that the control sample with no PVOH held the highest production yield, while the remaining samples obtained lower filtration rates with each PVOH increasing concentration. Considering the samples of the same base fluid volume, the differences in extracted filtrate suggest that the samples underwent different degrees

of mud dehydration before the filtration. Moreover, filtration curves stabilize before the test's termination, implying major fluid extraction in all samples around the 4th filtration hour. The effluent production capacity is the measuring feature of moisture level in the mud sample, with the control sample being the most hydrated; it is safe to say that PVOH is responsible for mud dehydration. Those results are in accordance with the previous hypothesis regarding the amplification of mud flocculation index due to PVOH addition.

It also shows inverse proportionality, respectively, represented by the mud cake thickness and mud effluent production. The control sample seems to have the thinnest mud cake with higher effluent production. However, at any rise in PVOH concentration, mud cakes increase proportionally with a reduction of filtrate production. The mud flocculation is due to the present Na+ bentonite particles in the mud absorbing more water. The inhibition between the bentonite particles and water with an increment of the adsorption degree results in a considerable increase in clay dehydration. Moreover, adding polymers in base fluids further reduces the mud hydration and enhances the absorption process of bentonite clays. When time for phase segregation, the remaining liquid not absorbed will be pushed out making lesser filtrate extraction. And the swallowed particles will form thicker cakes.

The effect of mud separation can better be appreciated by the mud cake formed after filtration. Mass is instead recorded instead of height for the sake of data accuracy. Leaving the solid particles with some remaining liquid trapped in a few pores' spaces make the mud cake. The flocculated particles to agglomerate together as the remain amount of refined grains can stick between them or within their open spaces, creating a compact mud cake on the borehole wall. The formation of mud filter cake in a drilling well does not proceed at a uniform and unbroken rate. Instead, the cake accumulation rate depends on the mud is being circulated. The present experimental study is

a static filtration conditions, which consists of the dead-end filtration in filter press and accumulation of suspended particles on the filter face. The fluid velocity at equilibrium cake thickness is dependent upon the thickness of the filter cake [59]. Muds having exceptionally high-water loss deposited thick filter cakes despite very high eroding velocities. The muds having good filtration characteristics deposited thin filter cakes at equilibrium circulating velocities well within the range of those used in a drilling well [58].

4.1.3 Solid Deposition and Permeability

Change in filtrate production is influenced by two factors: mud dehydration and cake thickening due to absorption and possible filter pore plugging **(Figure 10)**.

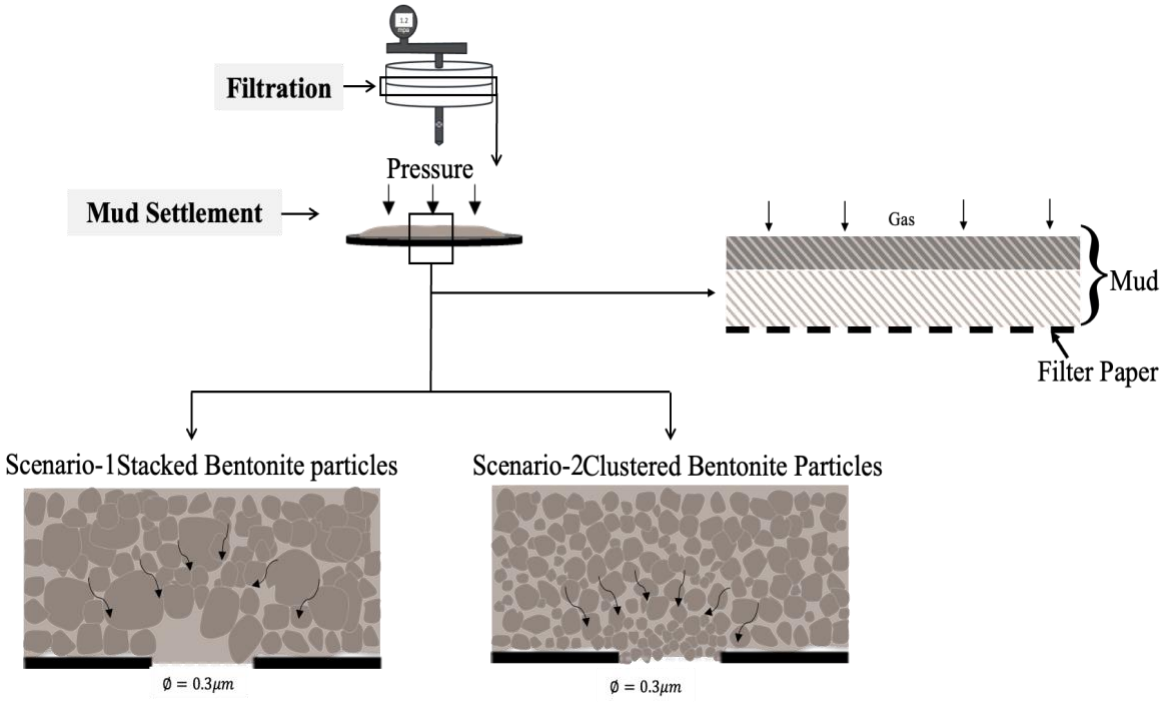


Figure 10. *Mud Deposition*

A filter plate of 0.3 micrometers was used to study the particle settlement and formation plugging. Aside from trapping the filtrate in between their open spaces, the filtrate extraction was interrupted by the bentonite particle stacking close to the pore, closing the exit. Also, finer particles would more likely be blocking the pore by clustering as their mud presents a more gelling texture,

narrowing the pore. That important phenomenon highly depends on the particle distribution of the cake samples as muds with less homogenous particle distribution will need more time for pore clogging. After plugging, it will have less permeability.

For a more controlled test, a metallic unipore filter plate of 0.3 micrometers was used to study the particle settlement and formation plugging. Aside trapping the filtrate in between their open spaces, the filtrate extraction was interrupted by the bentonite particle stacking close to the pore closing the exit. Also, finer particles would more likely be blocking pore by clustering as their mud present more gelling texture leading to the narrowing of the pore. That important phenomenon highly depends on particles distribution of the cake samples as muds with less homogenous particles distribution will need more time for pore plogging, and after plugging it will have a lesser permeability.

Gathered data from preliminary testing required to calculate mud permeability was done. Permeability was evaluated using:

Equation 2: Darcy's Law

$$k = \frac{q\mu L}{A\Delta p}$$

With:

q, Total Discharge (cm^3/s)

k, Permeability Darcy's

μ, Dynamic Viscosity (MPa.s)

A, Mud cake area (cm^2)

Δp, Filtration Pressure Difference (MPa)

L, Mud Thickness (cm)

Table 9: *Estimated Mud Filtration Parameters*

	NO PVOH	Conventional PVOH (wt.%)			Non-Ionic PVOH (wt.%)			Cationic PVOH (wt.%)		
		0.09	0.22	0.43	0.09	0.22	0.43	0.09	0.22	0.43
Filtrate Production *(ml/h)*	1.312	0.44	0.32	0.18	0.51	0.38	0.48	0.718	0.6	0.474
Flowrate *(cm^3/s)*	3.6.E-04	2.2.E-05	1.9.E-05	1.1.E-05	2.5.E-05	2.0.E-05	1.8.E-05	3.1.E-04	2.7.E-04	2.2.E-05
Area *(cm^2)*	50.24	55.389	55.389	55.389	72.345	75.391	78.5	58.058	60.790	63.585
Viscosity *(cp)*	40	60	64	78	90	120	250	50	52	68
Length *(cm)*	3.5	4.5	6	7.2	3.9	5	5.3	4	4.1	3.9
Permeability *(md)*	9.24.E-04	4.07.E-04	3.94.E-04	2.8.E-04	2.2.E-04	1.6.E-04	1.5.E-04	5.4.E-04	5.3.E-04	4.9.E-04

Drilling fluid contains a diverse range of solid particles with different sizes [60]. Theoretically, it is expected that the larger particles create the initial layers of the mud cake and then smaller particles are deposited over the formed cake [13]. The considerable difference in permeability between the control sample and the others is evidence on the PVOH enhancing the mud filtration. According to the result presented in **Table 9**, the permeability of the mud reduces as the mud cake mass increasing proportionally to PVOH concentration in the mud. A possible approach to explaining this result is that some of the tiny solid particles penetrate the porous media and cause permeability reduction [61]. Simultaneously, the deposited solid particles of mud cake got more compacted because of the drag force of the fluid that contains tiny particles while flowing within the cake [62]. Thus, porosity and permeability of the filter cake change during the particle deposition and these changes can affect the filtration behavior [63]. Gradually, more solid particles are deposited, and the cake got thickened. This process continues until the permeability of the porous media approaches to zero and then flow stops [64]. One necessity of a low permeable mud cake is it prevents the drilling fluids loss and, hence, reduces damage to the formation. It is also vital to monitor the mud cake thickness because a thicker mud cake can raise a few problems

during drilling operations. An ideal drilling mud will form a thin, impermeable mud cake, resulting in a limited fluid leak-off. Finally, the samples with conventional and non-ionic PVOH seem to approach the ideal mud cake features as they have; they are thicker and less permeable than the cationic PVOH.

4-2. PVOH-Bentonite Affinity

Polymer adsorption is evaluated through UV spectrometry of effluents and interpreted using adsorption models, including Langmuir and Freundlich isotherms. The solid-liquid equilibrium adsorption model is found to be the most suitable, revealing the intricate interactions between water, PVOH, and bentonite molecules.

4.2.1 U-V spectroscopy Reading

PVOH-Bentonite affinity evaluation was conducted by subjecting extracted filtrates to adsorption test using a UV-2450 spectrophotometer (Shimadzu, Japan). After setting the control sample (PVOH 0wt.%) sample as a baseline, PVOH adsorption was observed from the most negligible PVOH (0.08wt.%) to the highest PVOH (0.405 wt.%) concentration formulated in this experiment. The quantitative assessment of polymer adsorption was derived from U-V Spectrophotometry data of the sample filtrates, where most models produced an absorption peak at 450 nm.

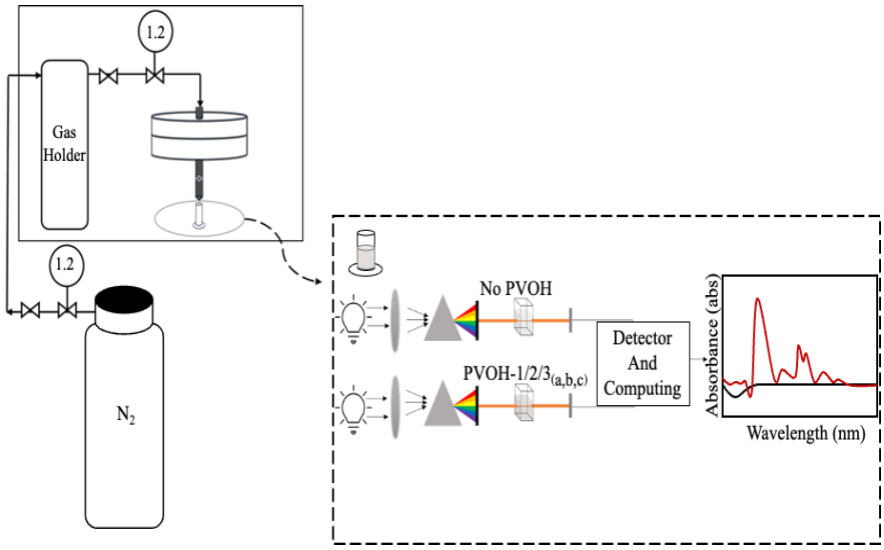


Figure 11. *PVOH-Bentonite Analysis*

4.2.2 Evaluation of Sorption Models

Isotherm describes the relationship between the equilibrium adsorbate concentrations in the liquid phase and the equilibrium adsorption amount on the solid phase at a constant temperature [24]. Isotherms models to evaluate the binding sites, providing a relationship between the amount binding experiments were carried out on solutions isotherms models are extensive irrespective of the assumption followed for the model development.

The experimental data were fitted to the isotherm models. The quantitative assessment of polymer adsorption q (mg/g) was calculated from U-V Spectrophotometry data of the sample filtrates, where most models produced an absorption peak at 450 nm. This study considered Freundlich, Langmuir, and Solid-Equilibrium (SLE) models shown in **Table 10**.

- *Freundlich Model*

Freundlich isotherm is the earliest known relationship describing the non-ideal and reversible adsorption, not restricted to monolayer formation [27]. It does not predict a saturation point and can describe adsorption over various concentrations. This empirical model can be applied to the non-uniform distribution of adsorption heat and affinities over the heterogeneous surface. Freundlich on linear form expressed in **Table 10** was used in this study, with constant n being the heterogeneity index.

- *Langmuir Model*

The Langmuir adsorption isotherm, originally developed to describe gas–solid-phase adsorption onto activated carbon, has traditionally been based on the assumptions that the reactive groups are homogeneously distributed over a particle's surface and that adsorbed molecules form an evenly distributed monolayer on the surface with no interactions between adjacent adsorbed molecules [65]–[69]. Moreover, Langmuir's theory has related the rapid decrease of the attractive intermolecular forces to the rise of distance. As a result of this, a dimensionless constant, commonly known as separation factor (RL), defined by Webber and Chakkravorti [70], can be represented as:

Equation 3: Separation Factor R_L

$$R_L = \frac{1}{1 + K_L Co}$$

In this context, a lower R_L value reflects that adsorption is more favorable. In a deeper explanation, R_L value indicates the adsorption nature to be either unfavorable ($R_L > 1$), linear ($R_L=1$), favorable ($0<R_L<1$) or irreversible ($R_L=0$). In a deeper explanation, R_L value indicates the adsorption nature to be either unfavorable ($R_L > 1$), linear (RL=1), favorable ($0<R_L<1$) or irreversible ($R_L=0$) [26].

Solid-Liquid Equilibrium

Solid−liquid equilibrium describes non-ideal adsorption. It is an ideal model for materials with heterogeneous binding site energies and typically with analytes with a high tendency to form multilayers. It also accounts for species' affinity for being in the adsorbed phase or the bulk phase and the degree to which molecules self-associate around the active sites of the adsorbent surface. The SLE model q_{SLE} used in this study is described in **Table 10**, where the constants ϕ and ε are respectively expressed as:

Equation 4: Solid Liquid Equilibrum Constants ϕ and ε

$$\phi = \frac{-1 + \sqrt{1 + 4K\varepsilon}}{2K}$$

$$\varepsilon = \frac{q_m * q}{q_m - q}$$

H is the measured Henry's law constant, an indicator of the absorbent's adsorption affinity (i.e., the strength of interactions for adsorption) onto a solid bentonite surface.

The lower the H value, the higher the affinity (i.e., the active sites are in locations easily accessible by the absorbate). K is constant and an indicator of rapid association of polymers once the primary sites are occupied.

Table 10: *Lists of Adsorption Isotherm Models*

Isotherm	Nonlinear Form	Linear Form	Plot	Ref
Langmuir	$q_L = \frac{q_{max} * K_L * C_e}{1 + K_L * C_e}$	$\frac{1}{q_e} = \frac{1}{q_{max}} + \frac{1}{K_L * q_{max} * C_e}$	$\frac{1}{q_e}$ Vs $\frac{1}{C_e}$	[71]
Freundlich	$q_e = K_F C_e^{1/n}$	$logq_e = logK_F + \frac{1}{n} logC_e$	$logq_e$ Vs $logC_e$	
Solid-Liquid Equilibrium	$q_{SLE} = \left(\frac{\phi * H}{(1 + K * \phi)} e^{\left(\frac{\phi}{q_{max}}\right)}\right)$	-	-	[72]

For each adsorption isotherm model used, the following common figures of merit are determined: The maximum adsorption capacity q_{max}(mg/g), K an indicator of rapid association of polymers once the primary sites are occupied. The accuracy of the models was determined by the correlation coefficients (R^2) and the root-mean-square error (RMS %) using the Microsoft Excel software package. It is crucial to ensure that the isotherm fitting parameters have consistent and comparable units of measurement.

4-3. Results and Discussion

Figure 12 presents the Freundlich, Langmuir, and SLE's nonlinear fit and the actual experimental data. In Langmuir modeling, the shape of the curve obtained for this study indicates an unfavorable isotherm, meaning the polymers require more energy to achieve economic adsorption.

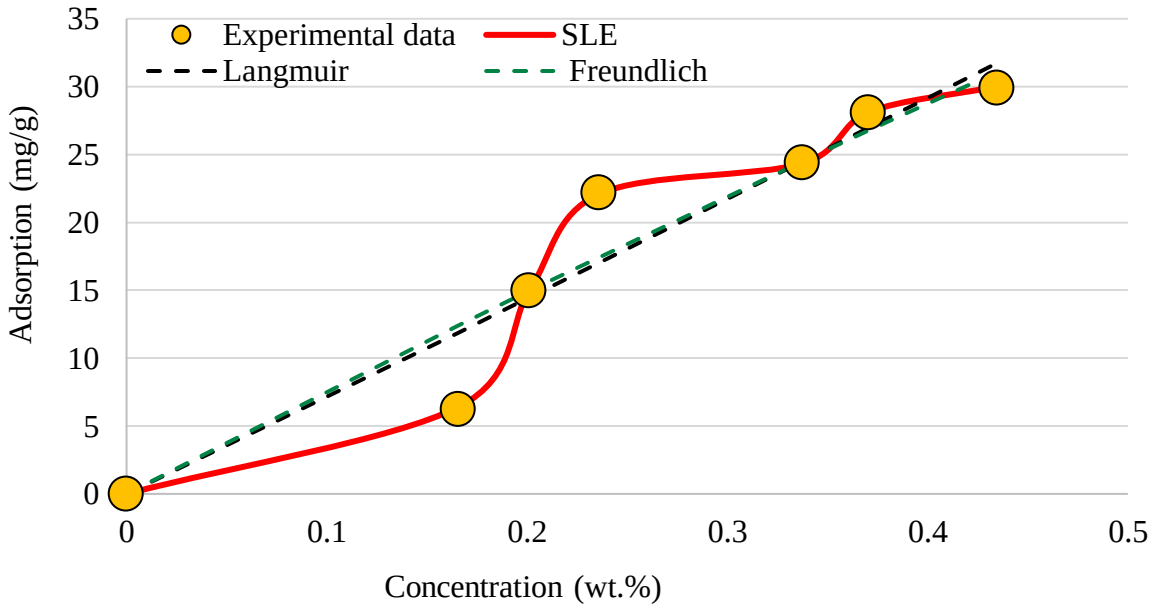
In Langmuir modelling, the shape of the curve obtained for this study indicates an unfavorable nature of the isotherm, meaning it requires more energy for the polymers to achieve economic adsorption. This interpretation is supported by the RL values obtained in **Table 11**. Moreover, the best fit of absorption data is commonly based on regression Coefficient (R^2). If R^2 is equal to 0.999 for Langmuir model, then the absorption is said to occur at a monolayer formation onto homogeneous surface [73].

Table 11: *Langmuir Isotherm Favorability*

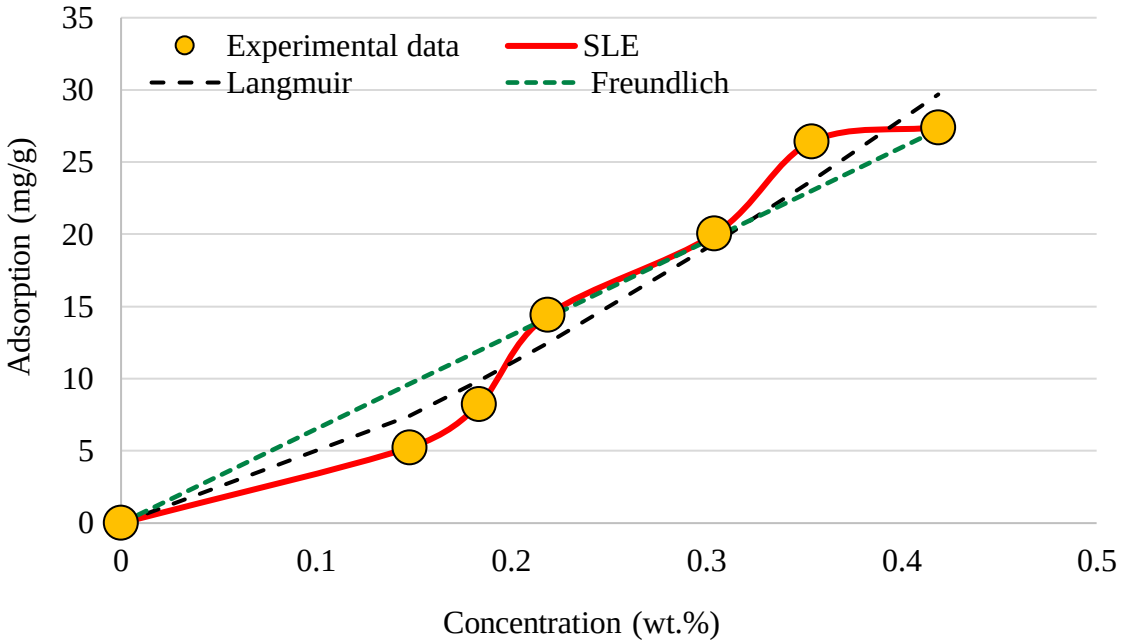
Polymers	R_L	Adsorption Type
Conventional PVOH-1	1.8	Unfavorable
Non-Ionic PVOH-2	2.3	Unfavorable
Cationic PVOH-3	2.7	Unfavorable

Solid-liquid Equilibrium was proposed as a suitable isotherm model, which was later revealed to be better fitting than the other model. This implies that the assumptions of the Langmuir model are invalid for the adsorption system being studied.

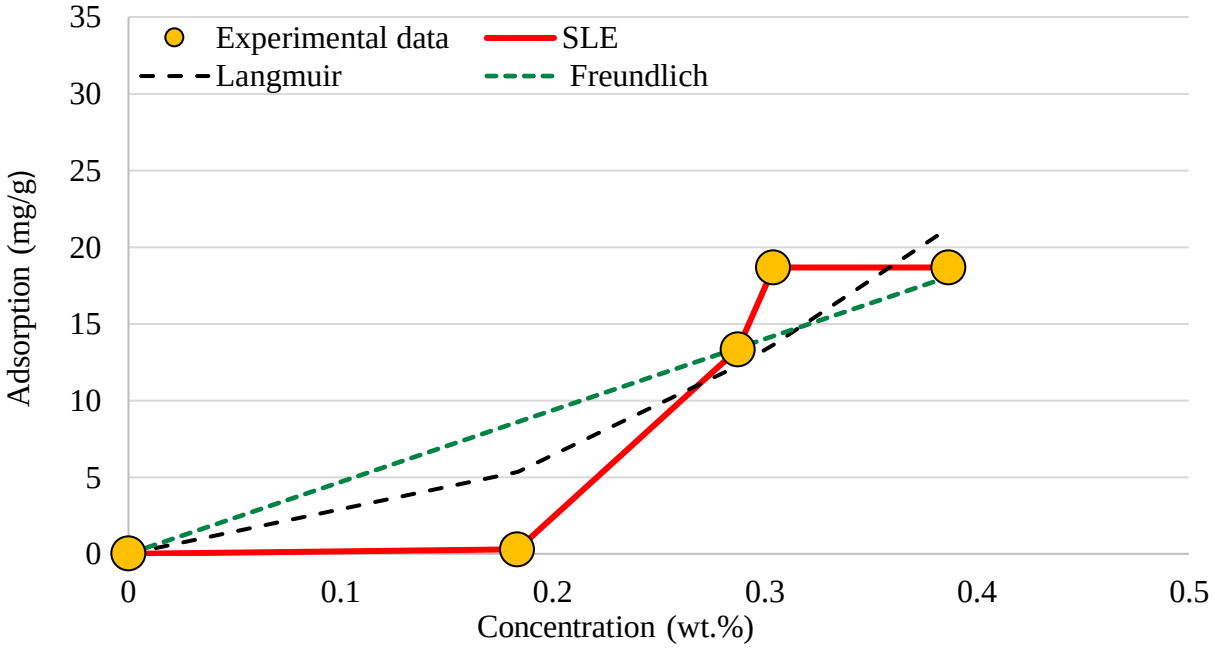
It is essential to consider alternative adsorption models or mechanisms that better represent the experimental data. Solid-liquid Equilibrium was proposed as a suitable isotherm model, which was later revealed to be better fitting than the other model.



a)Conventional PVOH-1



b) Non-Ionic PVOH-2



c) Cationic PVOH-3

Figure 12. *PVOH-Bentonite Adsorption Models*

Adding Polyvinyl Alcohol (PVOH) in base fluid increases the swelling mechanism of bentonite particles. As described in the base fluid formulation, the homogeneity of the base fluids was reached by extensive shaking of the PVOH-water solution, which eased the PVOH dissolution process. Depending on the PVOH chemical composition, the PVOH polymers were disrupted into free-charged molecules and ions such as hydroxyl group (OH-), ammonium (NH4+), or chlorine (Cl-), co-existing with water molecules in the base fluids. PVOH molecules penetrate the interlayer spaces of bentonite, causing intercalation. This can lead to an expansion of the clay layers and increased adsorption. Therefore, swelling mud intensification observed in samples containing PVOH results from an additional PVOH adsorption supporting the initial water adsorption in the control sample (No PVOH). PVOH adsorption is, therefore, a summation of chemical bonding between the PVOH-free charged ions and inversely charged unsaturated bentonite layers.

The use of Isotherms modelling is therefore to analyze the physical and chemical bounding's at the absorbent (bentonite) surface. Langmuir and Freundlich's isotherms are the most used models for homogeneous and heterogeneous adsorption studies, respectively.

Table 12: *Models fitting parameters.*

Models	PVOH	Adsorption parameters				Statistics	
		Adsorption affinity Constant K (mg/g)	Maximum Adsorption Capacity q_{max} (mg/g)	Self-Adsorption constant H (mg/g)	n	Root-mean Square RMS (%)	Square root R^2 (-)
Langmuir	PVOH-1	0.1787	430.8	-	-	30.12	0.903
	PVOH-2	0.0029	220.3			25.36	0.911
	PVOH-3	0.0104	147.9			38.86	0.540
Freundlich	PVOH-1	74.205	-	-	0.980	8.006	-
	PVOH-2	94.771			0.749	1.861	
	PVOH-3	122.92			0.541	3.439	
Solid-Liquid Equilibrium	PVOH-1	0.0115	118.8	1.065	-	3.688	0.993
	PVOH-2	0.0153	107.1	1.031		1.921	0.996
	PVOH-3	0.0166	84.51	1.018		0.753	0.992

SLE models recording the smallest error functions, the polymers PVOH-1, PVOH-2, and PVOH-3 maximum adsorption capacity (respectively 118.872 mg/g, 107.196 mg/g, and 84.5154 mg/g),

were found to be overestimated in Langmuir model (respectively 430.858mg/g, 220.3mg/g and 147.91mg/g). The factors enunciated above confirmed the applicability of the SLE model. SLE model results and analysis were divided into two sections, namely, (i) the Adsorption mechanism and (ii) the chemical structure of polymers affects the adsorption process. All SLE models show a type V (**Figure 12**)behavior according to the International Union of Pure and Applied Chemistry (IUPAC) classification [74]. Type V represents a combined monolayer (polymer-solid surface binding) and unrestricted multilayer formation (polymer-polymer binding) processes simultaneously. The latter process, being the lateral polymer interactions (self-association), is stronger in comparison to interactions between absorbent and absorbate.

The difference in affinity and self-association in PVOH-1, PVOH-2, and PVOH-3 is due to the difference in chemical composition. Hydrogen bonding is predominant because of the highly hydrophilic hydroxyl group (OH-) present in all PVOH's chemical structures. The difference in water dehydration in PVOH-1 and PVOH-2 despite both wearing hydroxy group leads to the conclusion that the acetoxy group is responsible for slowing water absorption in PVOH-2.

Similar to the present results, highlights by Shanjun Li, et al. also showed that the replacing of the hydroxy groups with acetoxy groups in the resin causes less water uptake but increases the infusibility of water in the resin[75]. The hydrophobic methyl group in acetoxy groups prevents water uptake, thus preventing PVOH adsorption. In addition to acetoxy group in PVOH-3, charged ions other than hydrogen such as NH4+ and Cl- prompt electrostatic reactions (ionic bonding).

This conflict in hydrogen-ionic bounds instead creates selective bonds and repulsion effect to same charged polymers [76]. The greater affinity in muds with Non-ionic modified PVOH as compared to the conventional is probably due to the extra acetoxy group present in the modified PVOH. However, the highest PVOH adsorption capacity recorded was that of muds with Cationic PVOH. Cationic modified PVOH containing ammonium chloride prompted another type of chemical bounding. Following the formulation procedure of the mud samples explained in chapter 3 (**Figure 5**), ammonium chloride in Cationic PVOH-3 was prior dissolved in water, and the mixture was shaken to ensure homogeneity. During the base fluid preparation, the cationic polymer got dissolved breaking bonds like ammonium chloride.

Equation 5: Ammonium Chloride Dissolution

$$NH_4Cl(sol) + H_2O = NH_4^+(aq) + Cl^-(aq)$$

The strength of the ionic bounding is largely influenced by the electronegativity values of the atoms involved in that ionic bond [77]. Electronegativity gives a measurement of the atoms' affinity for electrons. An atom with high electronegativity attracts electrons from an atom with lower electronegativity to form an ionic bond. Ammonium molecules with electronegative difference of 1.7 and Chlorine 3.16. when adding Sodium Bentonite, the hydrogen bonding previously engaging hydrogen atoms of OH and OCOCH3 is outdone by a competitive and selective ionic bounding taking place between Cl- and ammonium molecules with Silicate ions and water molecules [77]. This competitive ionic bonding is shown on the difference in polymer adsorption values of Non-Ionic, conventional PVOH and Cationic PVOH (**Figure 12**). It is safe to say that ammonium chloride addition in the mud prompted a type of ionic bonding stronger than that of the hydrogen bonding. The competitive reactions taking place led to quicker saturation of the bentonite particle and limiting the possibilities of water absorption by hydrogen bonding. A reduction of water absorption keeps the muds samples with Cationic PVOH more hydrated than the other samples [78]. Therefore, Muds with cationic PVOH have lesser mud dehydration and have the least reduction of filtration rate from the mud with no PVOH.

4.3.1 Mud cake filtration

The conditioned static cake filtration tests were captured in Figure 13 and conducted using the equipment.

Figure 13. *OFW-300V-R ETTAS*

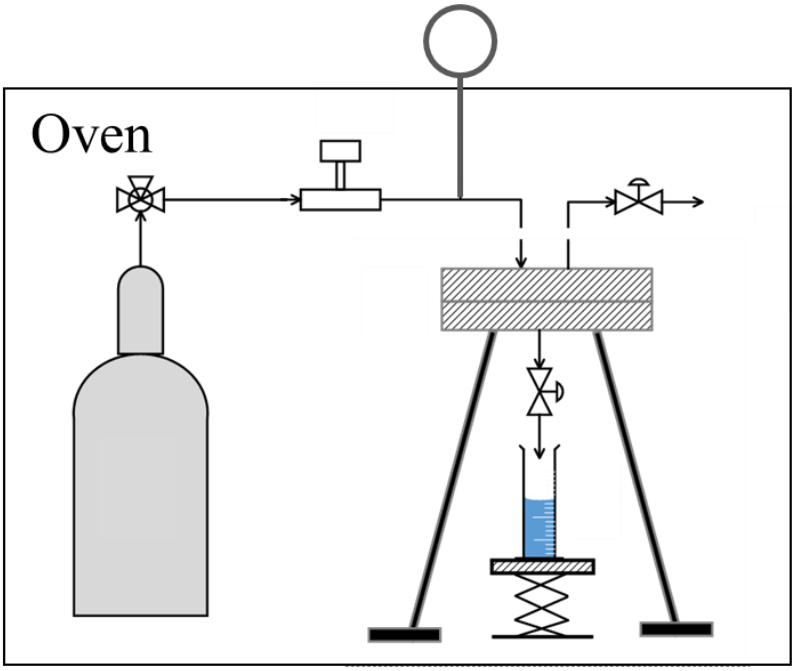


Figure 14. *Schematic Temperature Conditioned Static Filtration*

The amount of PVOHs tested was reduced to two; respectively Non-ionic PVOH-1 and Cationic PVOH-2. The reduction of samples was primarily a more concise experimental setup. Moreover, out of the three PVOHs, Non-ionic, and Cationic seemed to display more permeability control.

A volume of 10 mL of WBM was measured and placed on pre-weighed filter paper (pore size of 0.3 μm) priory positioned in the filter holder. With the filter holder closed, nitrogen gas could flow through at a constant pressure of 1.28 MPa. Samples underwent the same static filtration process as described earlier using OFW-300V-R ETTAS oven set at 55°C and 85°C, as illustrated **in Figure 14** below, for the entire duration of the filtration test. For each sample, the filtration test was conducted for five hours, during which the filtrate production and differential pressure across the filter holder were recorded. Although the standard filtration practice is usually 30 minutes, many reasons led to extending the filtration time to five hours (5 hours). The first reason was to achieve complete drainage of the mud cake, which was not obtained even after an hour. Another was to test the limit of the mud cake resistivity, as the filtration test was monitored through a pressure recorder. Finally, 5 hours was the chosen time limit because the mud cake serves as primal wellbore isolation until cementation, which is usually completed within 24 hours (6 to 12 hours) after drilling.

At the end of the test, the filter paper was retrieved from the holder, and its weight was recorded. The mud cake weight was the difference between the weight of the filter paper before and after the test. The surface morphology of the cake was further investigated using a low-vacuum-sensitivity scanning electron microscope (Model SU 3500). Scanning Electron Microscopy (SEM) photographs were taken using a low-vacuum observation and further processed with an image processor (Image J).

4.3.2 Polymer adsorption and modelling

Polymer adsorption was determined from filtrates centrifuged at 16,000 RPM using a centrifuge (As One, AS 165W). At the end of the centrifugation, the supernatant was analyzed for its polymer concentration using the UV-vis spectrophotometer (Shimadzu, UV- 2450). A calibration curve of UV-vis absorbance at ~450 nm versus the solutions with known concentrations was used to determine the polymer concentration.

The filtrate was obtained from control mud (WBM without PVOH). Polymer adsorption was then computed as;

Equation 6: Polymer Adsorption

$$q = \frac{C_i - C_f}{m_B}$$

where q is polymer adsorption (mg/g-rock), C_i is the initial polymer concentration (in mg/g), C_f is the polymer concentration in the supernatant filtrate (in mg/g), and m_B is the initial mass of bentonite used (g).

The present study selected Langmuir Isotherm and Solid-Liquid Equilibrium (SLE) isotherm models to describe the adsorption models. A detailed summary of the mathematical derivations and the thermodynamics behind each model are beyond the scope of the thesis.

4.3.3 Thermogravimetric Analysis (TGA)

The TGA analysis was conducted on PVOH solutions presented in **Table 13** below and their registered initial weights. The TGA-DTA8122 Rigaku was used to measure the weight changes of the polyvinyl alcohol (PVOH) isothermally as a function of time. An atmosphere of nitrogen was used at a 10ml/min gas flow rate. The temperature ranges from ambient to 85°C.

Table 13: *PVOHs baseline Initial Weight(mg)*

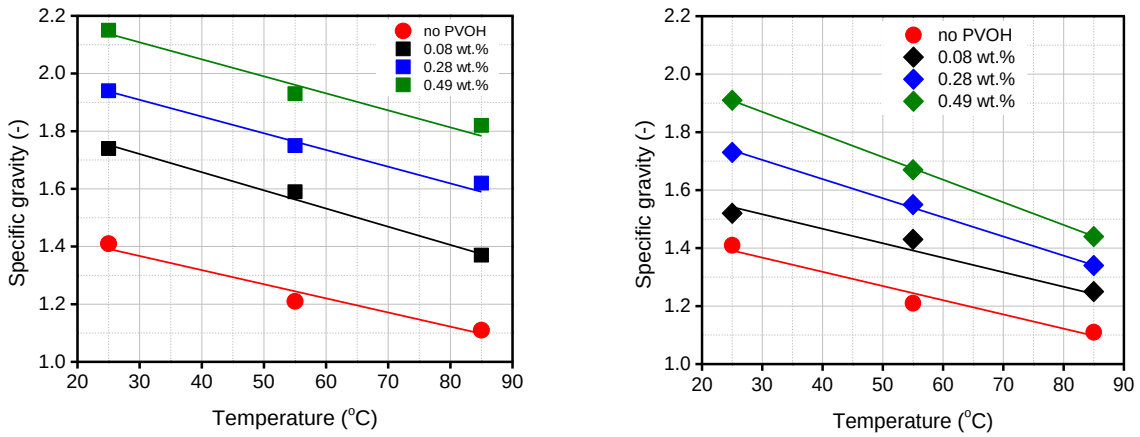
	Water	Non-Ionic PVOH			Cationic PVOH		
		0.08%	0.28%	0.49%	0.08%	0.28%	0.49%
Weight(mg)	67.12	65.826	65.751	69.211	67.47	67.795	67.899

Table 13 displays PVOH's ability to mitigate the thermal degradation of mud systems' density. The muds prepared with higher non-ionic PVOH-1 seem to have the most negligible weight reduction than those made with cationic PVOH-2, which are even higher than in the control sample. This shows higher thermal stability in samples with Non-ionic PVOH-2.

4-4. RESULTS AND DISCUSSION

4.4.1 Effect of PVOH Addition to Mud-Specific Gravity

Figure 15 shows the alteration of the specific gravity of prepared WBMs at different temperatures.



(a) PVOH-1 (b) PVOH-2

Figure 15. *Alteration of specific gravity of WBMs by PVOHs at different temperatures and concentrations*

The general trend shows that the specific gravity monotonically decreases with the temperature and the concentration in PVOHs. Raising the temperature from 25 to 55°C and later to 85°C decreases the specific gravity of the control WBM from 1.41 to 1.21 and 1.11, respectively. The reduction of specific gravity at every temperature rise suggests that mud's density heavily depends on the thermal conditions.

At ambient temperature, mud samples with PVOHs showed higher density values and maintained higher values than those of the control sample at equivalent temperatures. The hydrophilic nature of PVOH can explain this observation. Adding PVOHs to mud provides extra colloidal solids to the system, which competes with intermolecular reactions related to thermal change[79].

The increase in water density to control density at room temperature is owed to the expansion of hydrophilic clays that expand by absorbing water. This phenomenon occurs when water molecules are attracted and bound by hydrogen bonding (H-bonding), pushing the silicate layers apart and thus increasing the interlayer distance (d-space) [80].

Table 14: *Specific gravity reduction from reference (25°C) to investigated temperatures (55 and 85°C); all the values are given in percentage*

$T-T_{ref}$	**No**	**PVOH-1**			**PVOH-2**		
	PVOH	0.08 %	0.28 %	0.49 %	0.08 %	0.28 %	0.49 %
25-55°C	14.18	8.62	9.79	10.23	5.92	10.40	12.57
25-85 °C	21.28	21.26	16.49	15.35	17.76	22.54	24.61

[a] Specific gravity (*Sp.gr.)* reduction is computed per the equation

4.4.2 Effect of PVOH Addition to Mud Rheology

Figure 16 shows the alteration of apparent mud viscosity of WBMs at PVOH concentration.

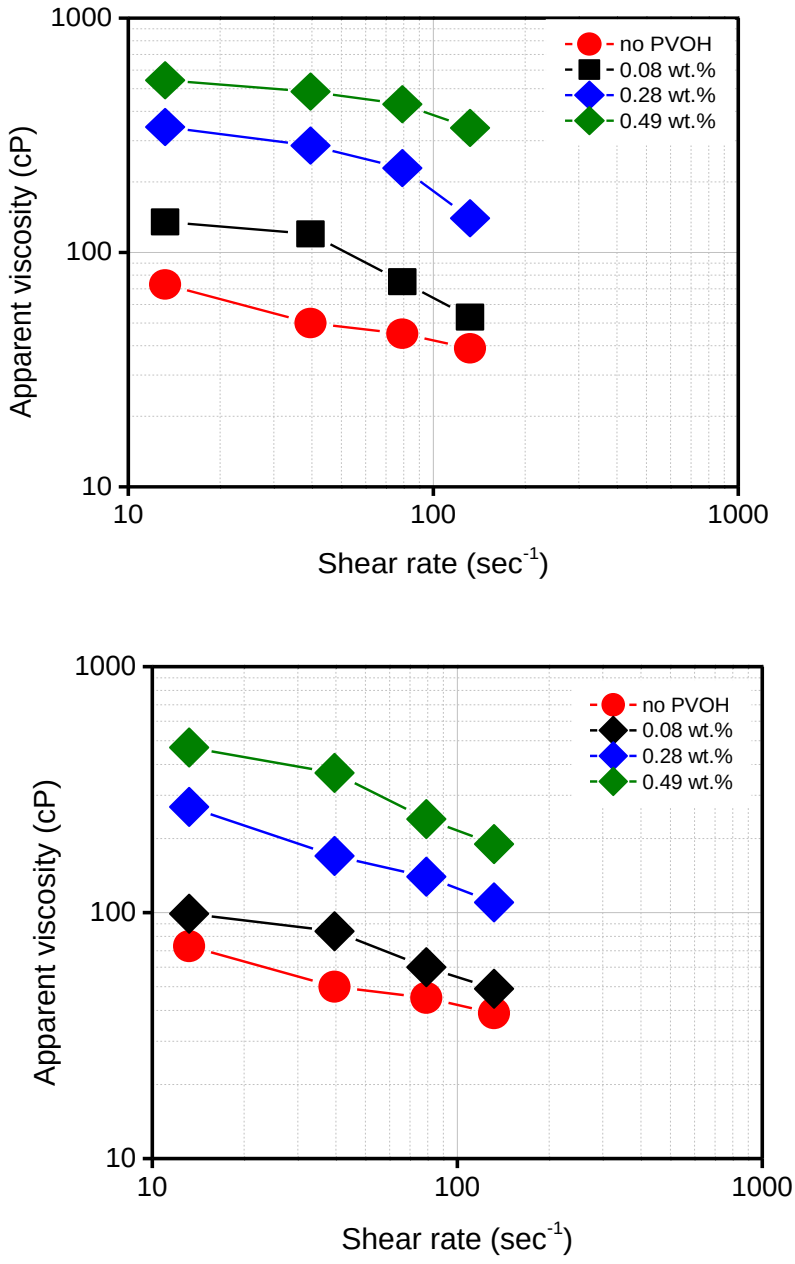


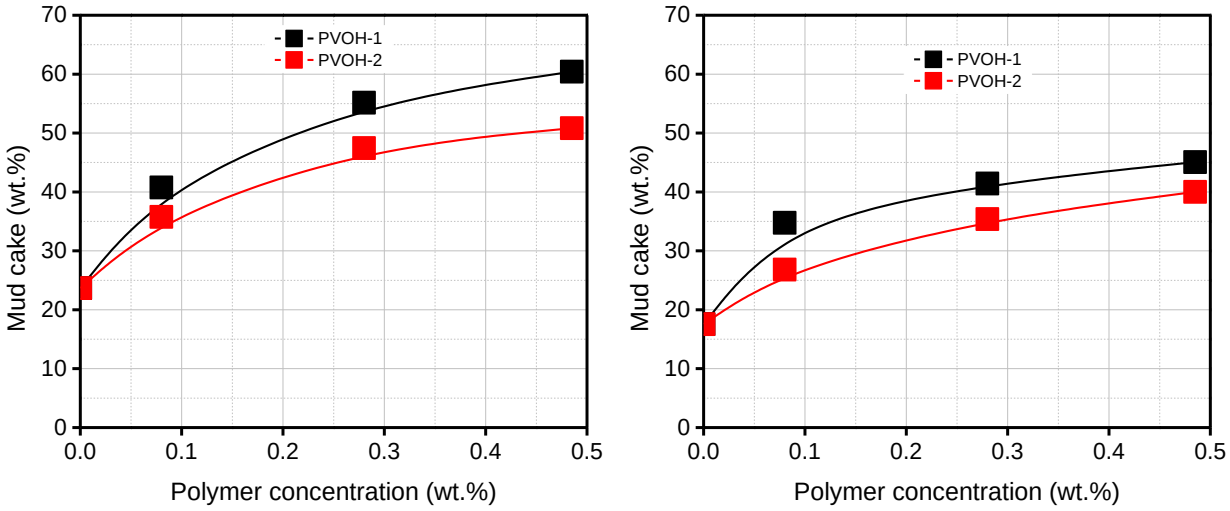
Figure 16. *Apparent Viscosity for a) PVOH-1, b) PVOH-2*

Increasing the concentration in the polymer increases the mud viscosity. However, the viscosity decreases with the temperature for the same concentration in polymer. Samples with PVOHs yielded higher viscosity values, as observed in **Figure 16**. Raising the temperature from 25 to 55°C,

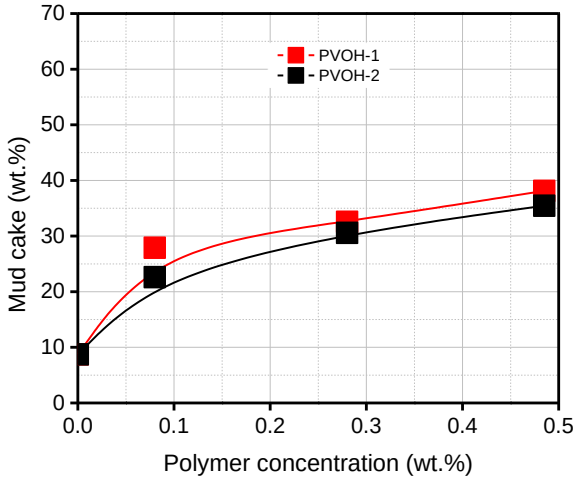
mud samples with PVOH-1 showed no viscosity reduction for samples with 0.08 and 0.028wt.% PVOH-1.

4.4.3 Polyvinyl Alcohol Addition Altering Cake Filtration

The results from filtration studies are shown in **Figure 17.**



(a) 25°C (b) 55°C



(c) 85°C

Figure 17. *Mud cake mass at (a) 25°C, (b) 55°C and (c) 85°C*

The reference sample (No PVOH) produced the least amount of cake (23.7 wt.%) of all the investigated WBMs at room temperature (**Figure 17a**). This value decreased by 17.6 and 8.7 wt.% when the filtration was performed at 55 and 85°C. Considering that the increase in temperature was inversely proportional to the apparent viscosity (**Table 14**), it is safe to say that the mud cake results in **Figure 17** pertain to a change in the solid phase ratio in the mud.

Adding PVOHs increases the mud weight, translating to larger mud cake values. The mud cake mass of samples with PVOH- 1 decreases from 40.8 (25°C) to 34.8 wt.% (55°C) and 27.9 wt.% (85°C). A similar analysis for PVOH-2 shows a decrease from 35.8 wt.% (25°C) to 26.81 wt.% (55°C) and 22.6 wt.% (85°C). PVOHs mitigate mud thermal degradation by providing extra mud weight through the solid phase. These observations were more pronounced with the increase in polymer concentration.

PVOH is a hydrophilic synthetic material; however, its negligible concentrations (0.08 ~0.28wt.%) in muds brought significant weight increase and mud masses. Their mud weight being higher than control sample suggests that mud samples with PVOHs host higher adsorption rates in their mixtures. The mud cake mass reduction at more elevated temperatures indicates a low water adsorption mechanism, which lessens the swelling index of the mud.

In addition, the apparent nuances of mud cake mass between samples with PVOH-1 and PVOH- 2 suggest that samples with PVOH-1 (non-ionic) might host a higher adsorption rate than that of PVOH-2 (cationic). The mud containing Cationic PVOHs showing lesser mud cake masses also seem to have experienced more cake mass reduction at rising temperatures than samples with PVOH-1.

Looking at the filtrate production, the control sample recorded the highest, at 75.4 wt.%, at 25°C (**Table 15**).

Table 15: *Effluent production increase under temperature change; the values are given in ml.*

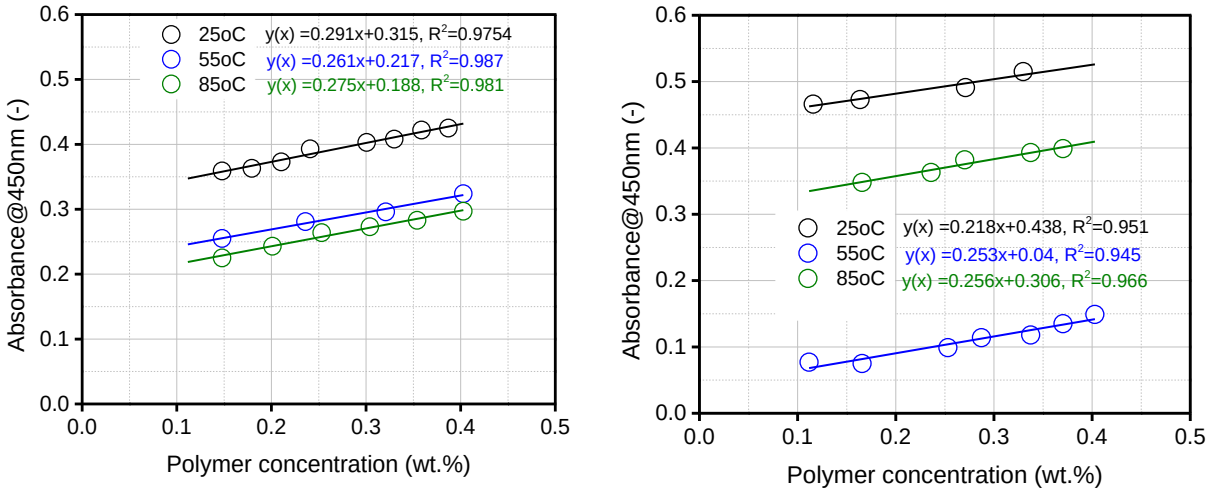
Temperature	No PVOH	PVOH-1			PVOH-2		
		0.08 %	0.28 %	0.49%	0.08 %	0.28 %	0.49%
25°C	7.54	5.46	4.19	3.86	6.32	5.17	4.71
55°C	8.08	6.44	5.75	5.36	7.11	6.37	5.81
85°C	8.92	7.11	6.54	5.99	7.63	6.86	5.33

Interestingly, samples with PVOH-1 and PVOH-2 yielded less filtrate at 25°C. The filtrates from the same samples increase with the increase in temperature. There seems to be a connection between mud cake mass and thermal resistivity, revealing that the higher the swelling index of mud, the more thermally stable it becomes.

4.4.4 Understanding Mud Swelling Control by PVOH Addition

- ***UV Calibration curves***

Figure 18 shows the calibration curves of investigated polymers at different temperatures. The plots were obtained by measuring the absorbance of aqueous polymers with known concentrations at ~450 nm using the UV-vis spectrophotometer (Shimadzu, UV-2450).



(**1**) Non-ionic and modified PVOH, PVOH-1 (**2**) Cationic and modified PVOH, PVOH-2

Figure 18. *Calibration curves of different polymers @450 nm*

Another decisive element in determining Langmuir isotherm applicability is the regression coefficient R^2. According to the Langmuir model, adsorptions are said to occur at monolayer formation onto the homogenous surface as R^2 is equal to 0.999.

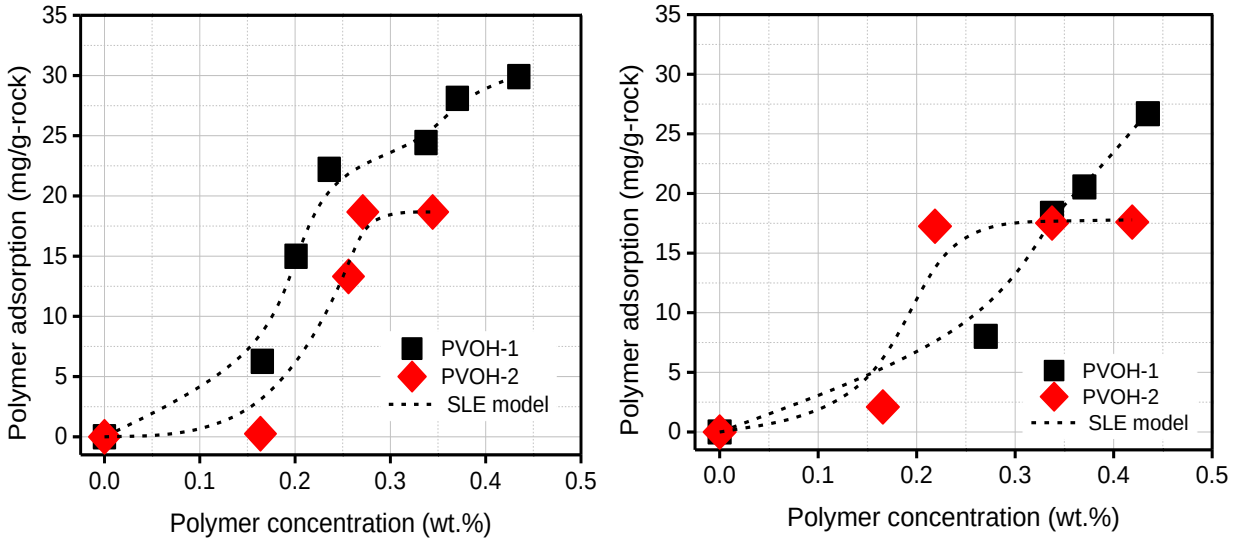
Table 16: *Langmuir Fitting Parameters of polymer samples @ 25°C*

Polymers	K_L (mg/g)	R_L (-)	R^2	q_{max} (mg/g-rock)
Non-Ionic PVOH-1	0.00295	2.3	0.91063	220.3
Cationic PVOH-2	0.01047	2.7	0.54036	147.91

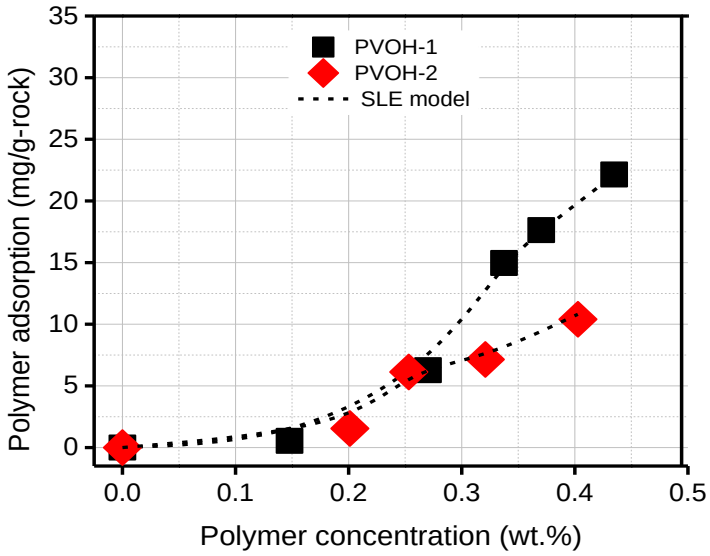
Therefore, the separation factor R_L displayed in Table S1 leads to the conclusion that Langmuir isotherm is unsuitable for Bentonite-PVOH modeling. Finally, the Langmuir regression coefficient R^2 value fails to confirm the homogeneity character of the bentonite-polymer adsorption.

- ***PVOH adsorption***

Figure 19 illustrates the results of PVOH adsorption at 25, 55 and 85°C.



(a) 25°C (b) 55°C



(c) 85°C

Figure 19. *Polymer adsorption was obtained from WBM filtrates.*

All adsorption data were fitted with SLE models and followed an adsorption type V. Per the literature, a type V is a combination of monolayer formations, which are PVOH-bentonite (interlayers cations) bindings represented in steep slopes, as well as unrestricted multilayer formation polymer-water and polymer-polymer (self-aggregation) bindings defined by shallow slopes [51][52].

The possibility of polymer chain bonding (adsorption) depends on its affinity with nearby bentonite, water molecules and adjacent polymers. Considering that bentonite and water compositions are the same for all samples, the rate of polymer bonding depends solely on the structural composition of the PVOH. Non-ionic PVOH made of highly hydrophilic hydroxyl groups (OH^-) provided the highest polymer adsorption values (Figure 19a-c, Table 17).

Table 17:Langmuir and SLE Adsorption models at 25°C

Langmuir Model [a]		**SLE Model [b]**	
PVOH-1	PVOH-2	PVOH-1	PVOH-2

q_m (mg/g)	220.3	147.9	q_m (mg/g)	118.9	84.52
***K_L* (mg/g)**	0.003	0.010	K_{SLE} (mg/g)	0.012	0.017
R_L	2.300	2.700	*H* (g/g)	1.055	1.068
R^2	0.911	0.540	R^2 (-)	0.999	0.999

[a] q_m: maximum adsorption capacity; K_L: Langmuir constant; R_L: separation factor

[b] q_m: maximum adsorption capacity; K_{SLE}: constant expression of the self-associative nature of the polymer; and *H*: constant expression of the affinity of PVOH towards bentonite.

The hydroxyl groups induce strong inter- and intramolecular hydrogen bonding, significantly inhibiting the solubility in water [83]. This observation directly correlates polymer adsorption in the base fluid and the solid-liquid balance in the mud. As the system's temperature increases, the mobility of the heated particles increases, resulting in a greater frequency of collisions.

Cationic polymer (PVOH-2) containing in its structural composition ammonium (NH_4^+) and chlorine (Cl^-) provides a higher quantity of bindable ions and molecules, which increase PVOH-bentonite affinity in the base fluid (**Figure 20**).

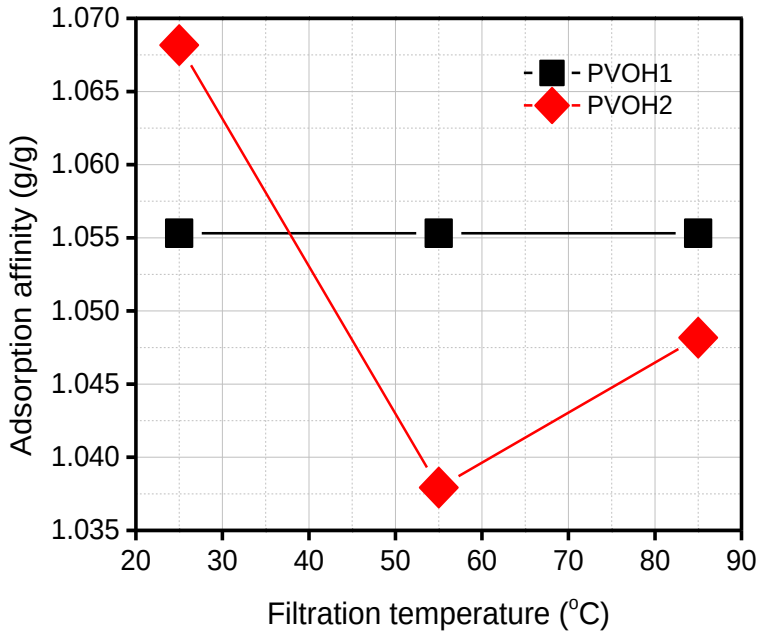


Figure 20. *Estimated polymer adsorption affinity vs. filtration temperature.*

However, the low q_{max} values insinuate that high affinity in a system does not automatically guarantee high adsorption of the adsorbate by the adsorbate. One cause of low adsorption capacity is that the simultaneous bonding types in base fluids are complementary but somewhat competitive. In dilute solutions where the polymer (mass) concentration lowers 5wt.%, the polymer chains typically behave as isolated hard spheres [51][52][54][56], making them highly mobile.

A specific ion or molecule's binding rate depends on its concentration in the mixture and electronegativity. The latest statement makes the bonding in PVOH-2 base fluids more selective, leading to a negligible ionic bonding frequency compared to hydrogen bonding. Another cause of Low q_{max} partially replaces the highly hydrophilic hydroxyl group (OH—) with highly hydrophobic acetoxy groups (-OCOCH3) in the cationic PVOH structural composition.

This replacement of OH^- by $-OCOCH_3$ on PVOH-2 binding sites considerably reduced the possibilities of such polymer binding with water molecules (H^-bonding) and adjacent polymers. The presence of the hydrophobic acetate groups also affects the conformation of polymer chains adsorbed on the particle surface. As the number of acetate groups increases, steric hindrance disturbs the intermolecular chains' arrangement and inhibits the formation of hydrogen bonds between the molecular chains [54]–[59].

To conclude, the higher q_{max} of Non-ionic PVOH-1 is the adsorption of a polymer solely made of (OH^-), while the lower q_{max} of Cationic PVOH-2 is the adsorption of a polymer where (OH^-) was partially replaced by NH_4^+, Cl^- and $-OCOCH_3$. Therefore, the polymer adsorption rate in a system depends on the amount of hydroxyl group (OH-) in a polymer composition, which determines the rate of hydrogen bonding in the system.

- ***Thermogravimetric analysis of PVOH***

The thermal stability of PVOHs was assessed by conducting thermogravimetric analysis on Basel fluids (I.e., deionized water and PVOHs). Based on **Figure 21**, compared to the sample with no PVOH(H_20), the weight change curves of PVOH samples seem to overlap. The curves suggest that the mass loss of the samples occurs as low as 30°C around the 5 to 10 minutes of combustion. This weight loss is attributed to the loss of volatile components such as moisture and monomers.

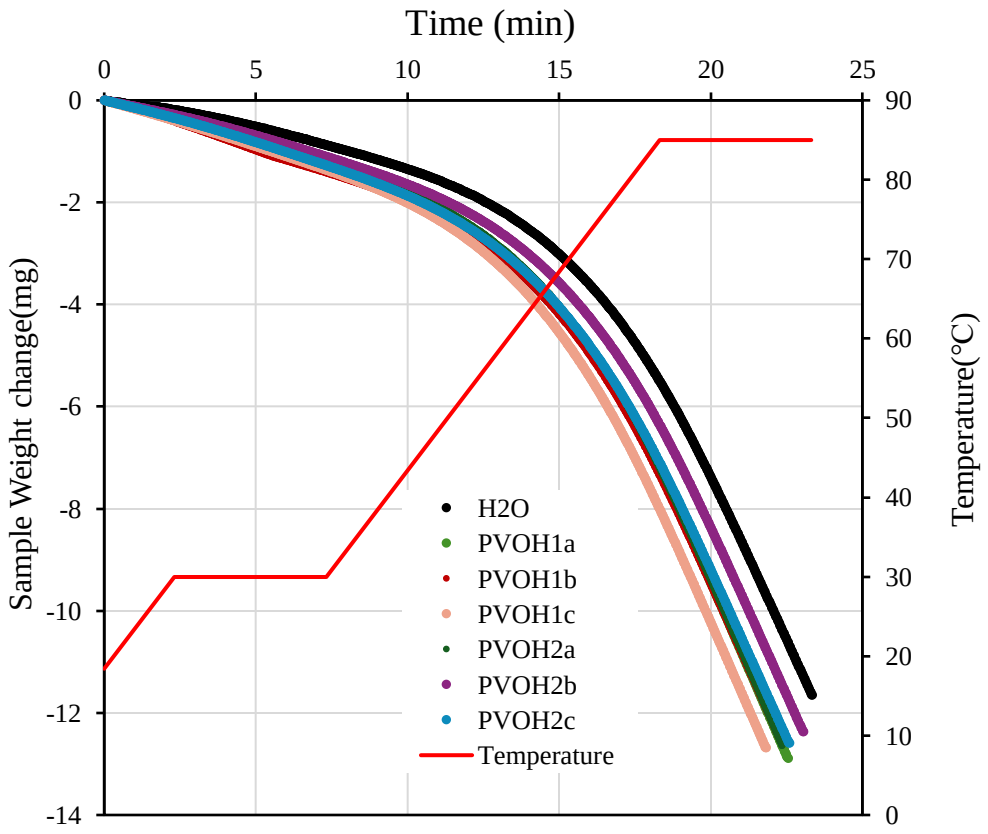


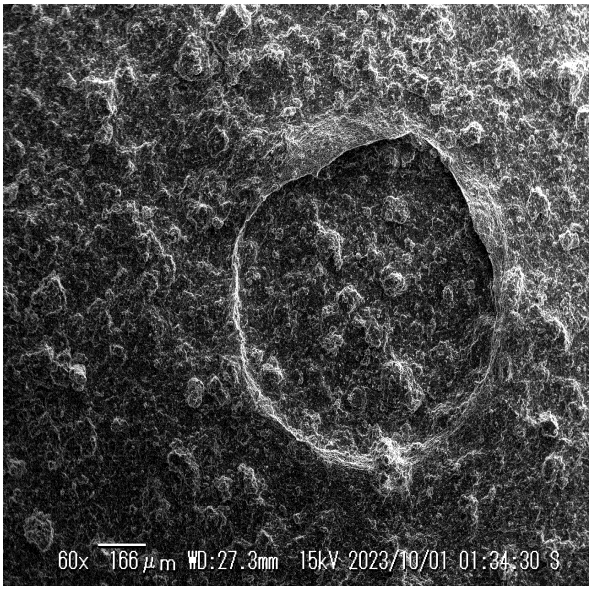
Figure 21. *Thermogravimetric analysis of PVOH solutions*

The onset temperature of all samples ranged from 68 to 74°C, followed by a significant drop in mass loss, which is indicative of the PVOHs' decomposition of the polymer. The overlapping of the TGA curves of both Non-Ionic and cationic PVOHs is anticipated as they confirmed their similarities in the chemical structure main component [-$CH_2CH(OH)$-] n. Despite the strong similarities, cationic PVOH shows greater thermal stability than non-ionic PVOH. The base fluid

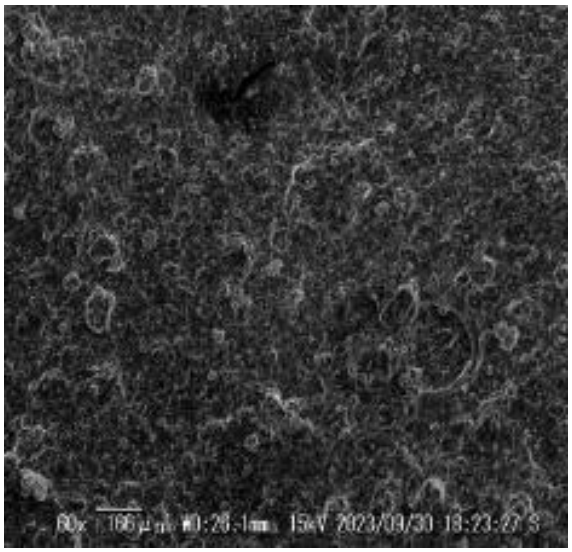
with 0.28wt%Cationic PVOH shows an onset decomposition 5°C degrees earlier than Deionized Water. Based on the observations, PVOH seems to provoke a significant downward shift in the thermal stability of the solutions compared to deionized water. Since water is made of stronger and stable bondings, the addition of PVOHs prompts the breakage of said bondings, weakening the solutions' stability. The increase in temperature complicates any H-bonding (hydrogel formation) from taking place as the ions increase in mobility. The weakening and breakage of bondings in the presence of PVOH engender higher amounts of free and bindable ions and monomers, increasing the possible reaction rate once adding bentonite particle clays, which dictates the swelling index of the bentonite particles.

- ***Surface morphology and mud swelling***

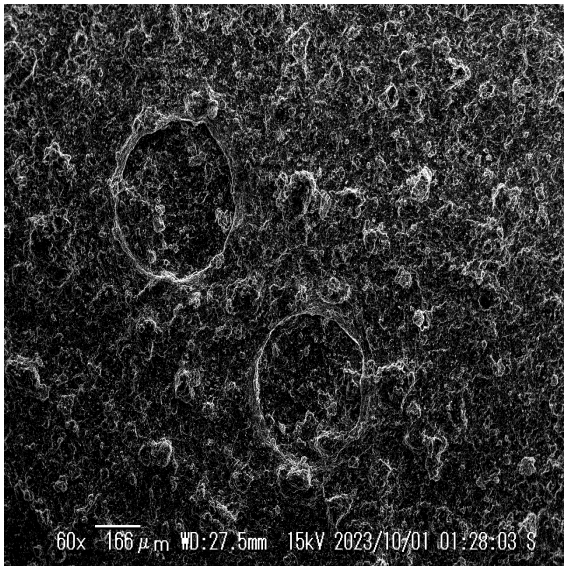
Figures 22, 23 and 24 show the SEM photographs of the mud cakes of WBMs prepared from non-ionic (PVOH-1) and cationic polymer (PVOH-2) at different temperatures.



(a) no PVOH

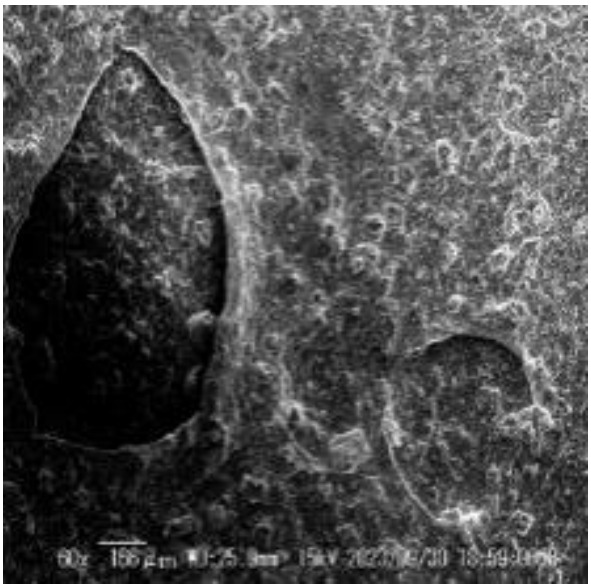


(b) PVOH-1

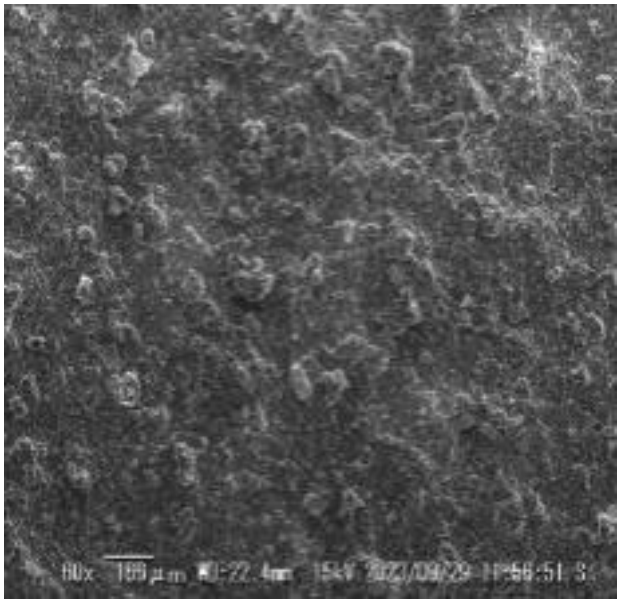


(c) PVOH-2

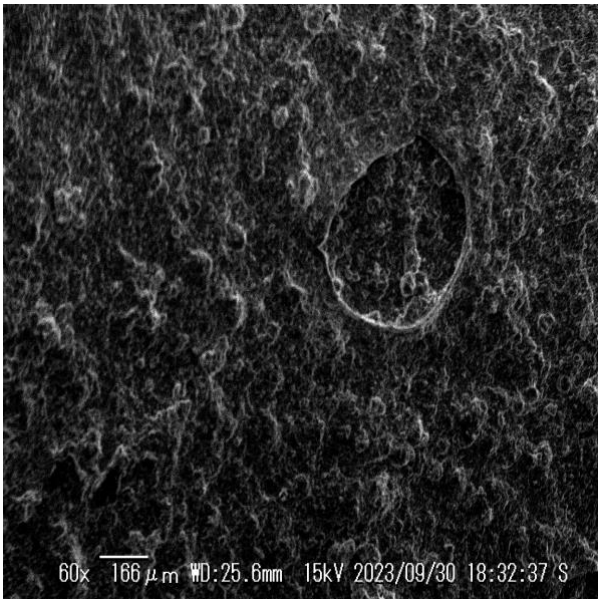
Figure 22. *SEM pictures of WBM mud cakes@25°C*



(a) no PVOH

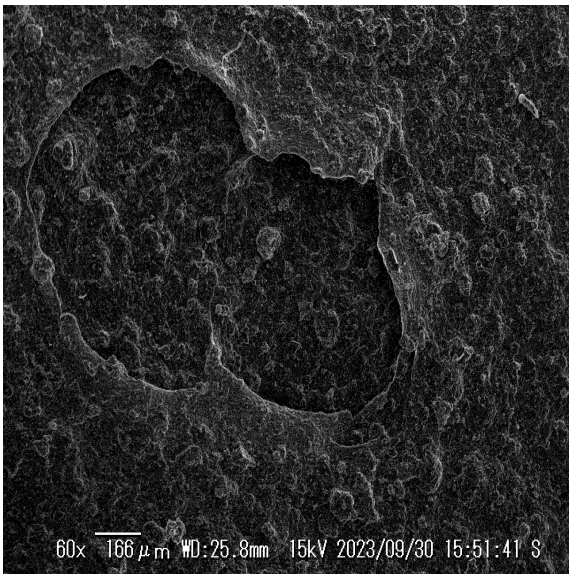


(b) PVOH-1

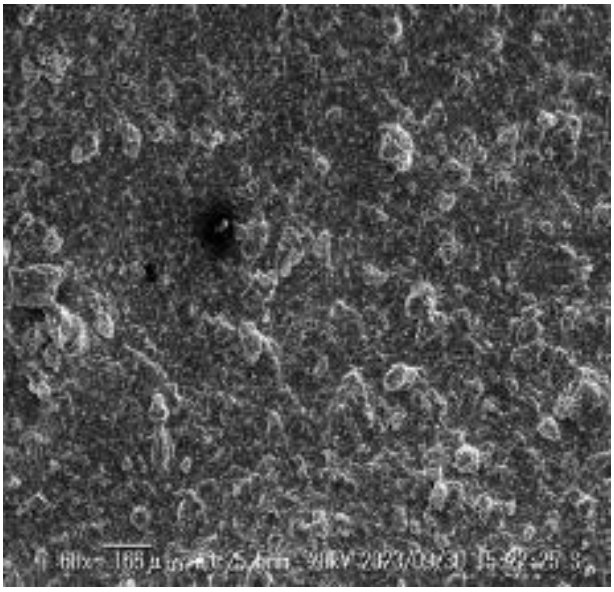


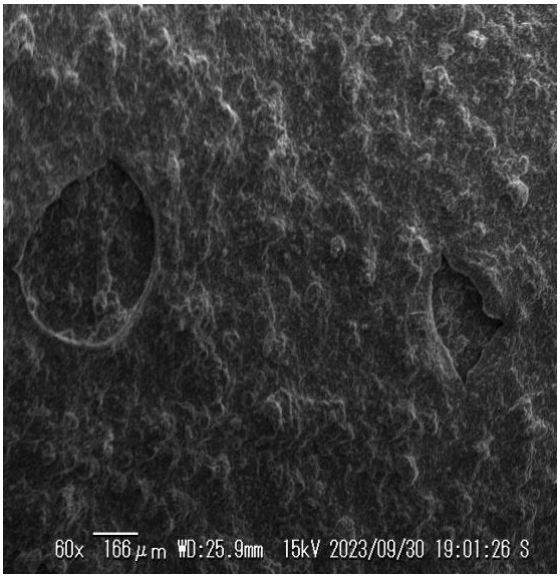
(c) PVOH-2

***Figure 23**. SEM pictures of WBM mud cakes@55°C*



(a) no PVOH





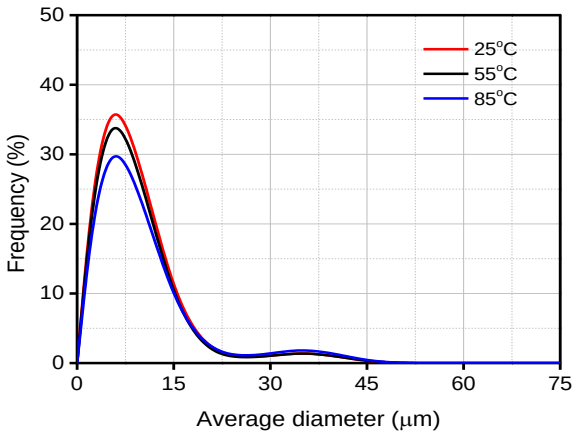
(b) PVOH-1 (c) PVOH-2

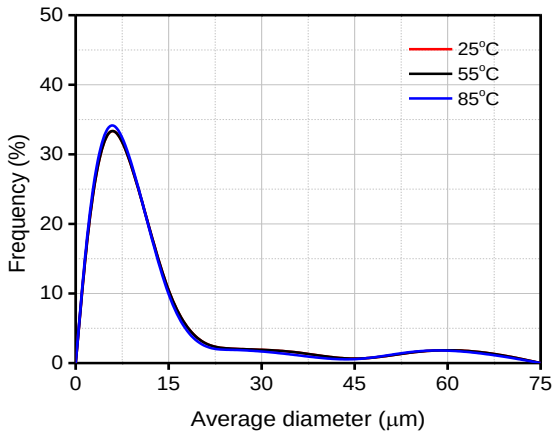
Figure 24. *SEM pictures of WBM mud cakes@80°C*

SEM photographs were then processed by an open-source image processing (Image J) to obtain the particle size distribution of different mud cakes**.**

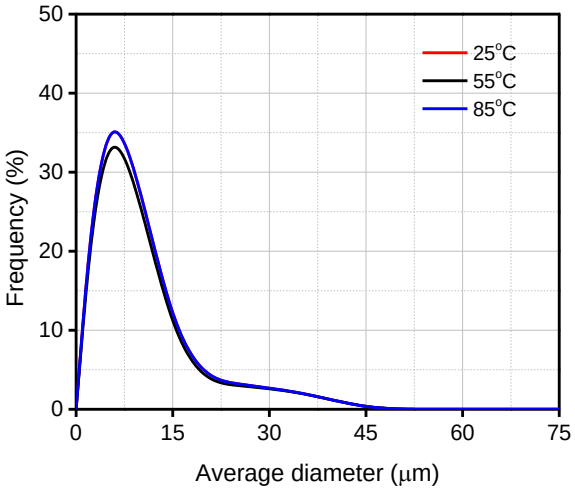
- ***Particle Size Analysis***

Figures 25 and **26** show the particle size results of the mud cakes after filtration at different temperatures.

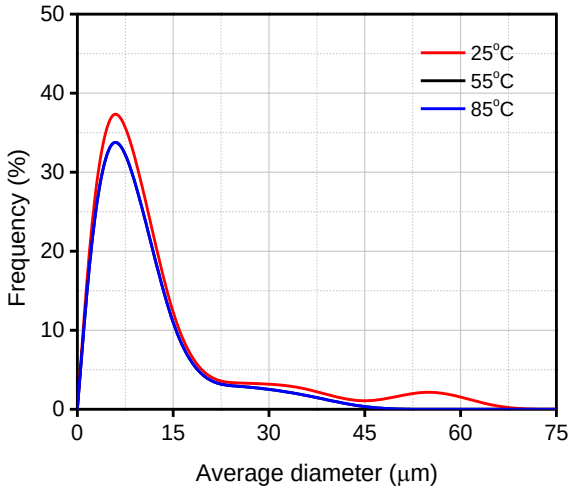




(a) No PVOH-1 added to the mud (b) PVOH-1, 0.08 wt.%

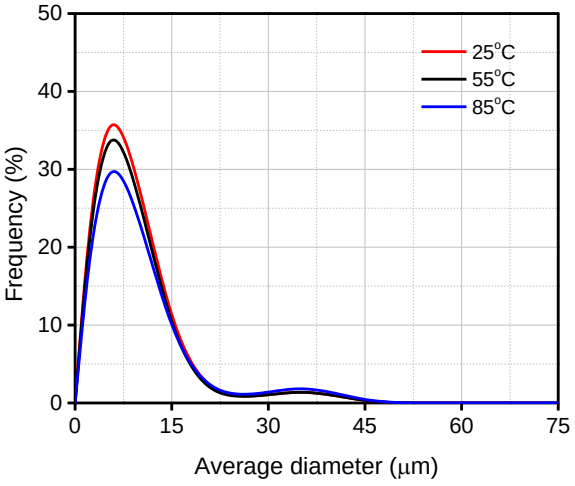


(c) PVOH-1, 0.28 wt.%

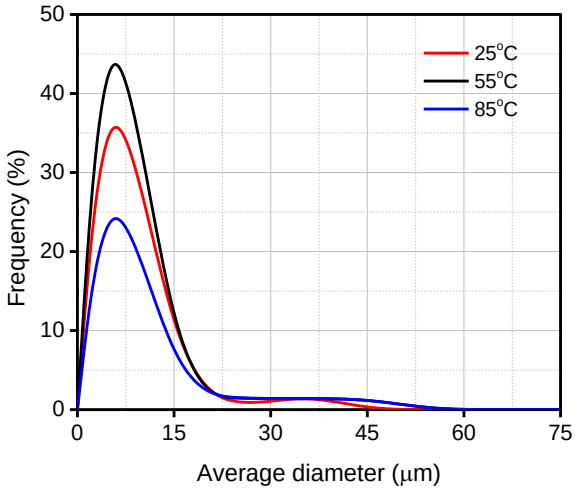


(d) PVOH-1, 0.49 wt.%

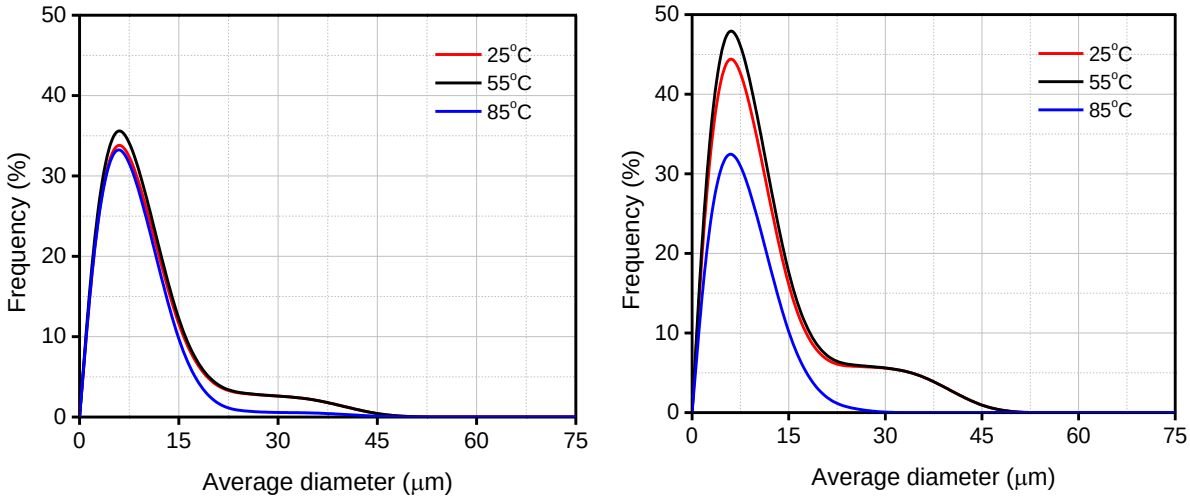
Figure 25. *Particle size distribution obtained from mud cake prepared using PVOH-1 at different temperatures.*



(a) No PVOH-2 added to the mud



(b) PVOH-2, 0. 08 wt.%



(c) PVOH-2, 0.28 wt.% (d) PVOH-2, 0.49 wt.%

Figure 26*. Particle size distribution obtained from mud cake prepared using PVOH-2 at different temperatures.*

The particle size and frequency obtained in **Figure 25a** at 25oC are identical to those recorded by Magzoub et al. (2019) when investigating the swelling magnitude of the Bentonite system using Particle analysis. The most prominent frequency (up to 64%) was obtained at an average particle size of 5 μm (**Figure 25-26**)[90]. The swelling of the mud is represented by the decline of the amount of particles at 5 μm and a rise of the curves at higher particle sizes. For instance, in this research, the samples formulated from PVOH-1 (Non-ionic polymer) displayed the most significant mud particle increase to <30-75μm>. The WBDs with cationic PVOH-2 exhibited lesser particle expansion <30-51μm>. The mud swelling was defined as:

Equation 7: Mud Swelling Computation

$$Swelling = 100 \times \left(1 - \frac{d_{avg_i}}{d_{avg_0}}\right)$$

where d_{avgi} is the average particle size of the mud cake at a given temperature and polymer (μm), d_{avg0} is the average particle size of the dry bentonite (d_{avg0} =2μm). The mud swelling change was computed therefrom (**Table 18**).

Table 18: *Influence of polymer concentration and temperature on mud swelling.*

Temperature	No PVOH	PVOH-1			PVOH-2		
		0.08 %	0.28 %	0.49 %	0.08 %	0.28 %	0.49 %
25℃	65.0	66.5	74.3	68.4	74.0	76.2	92.0
55℃	61.3	66.5	78.9	64.3	69.0	64.7	98.7
85℃	56.1	66.2	46.7	68.4	58.4	64.7	56.9

Table 18 shows that an increase in temperature decreases the mud swelling. These results are consistent with polymer adsorption (**Figure 19**) and mud balance (**Figure 17**). The mud swelling index seems to regress regardless of PVOH additions; this can be due to either the challenging higher temperature in the mud, the expansion saturation of the mud, or the combination of both phenomena. It is confirmed that PVOH enhances mud swelling by increasing solid mud expansion initially carried out by Bentonite clays. The swelling of clays is primarily attributed to the widening of the interlayer gap between the double layers. The unsaturated oxygen on the bentonite surface layers provides multiple binding sites for polymer chains to land and bond.

The electrical forces between negatively charged clay surfaces and positively charged ions attract the cations to the bentonite surface, further increasing the size of bentonite particles until saturation. Also, the muds with PVOHs showing higher swelling index seemed to have lower cake mass reduction than the control sample of similar temperature.

Abdou and El-Sayed Ahmed (2011) investigated the effect of bentonite's particle size on the physio-chemical Properties of WBMs. They observed that with a constant 7.5 w/v % bentonite concentration, the thixotropic nature of the mud decreases with an increase in the particle size[91]. Considering the drastic viscosity reduction observed in control WBM (**Figure 4**), these findings show that adding PVOHs mitigates temperature dehydration on mud swelling.

CHAPTER 5
CONCLUSION

This study investigated the contribution of polyvinyl alcohol (PVOH) addition on mud filtration of water-based drilling mud (WBM). Non-ionic and cationic polymers, formulated from sodium bentonite clay and deionized water, were added at 0.08, 0.28, and 0.49 wt.% to WBM. Specific gravity, mud rheology, and mud filtration were conducted at 25, 55 and 85^{o}C. The specific gravity and apparent viscosity monotonically decrease with the increase in temperature, irrespective of PVOH addition or concentration. However, increasing PVOH concentration within the base fluid gives a denser and heavier mud. On average, a rise in temperature of 30oC reduces the mud viscosity of WBM (without PVOH) by 23 % from its initial value. Adding only 0.1 wt.% of cationic and non-ionic polymer gives a viscosity reduction of 15 and 9 %. At the same filtration conditions, adding non-ionic polymer improves mud filtration by up to 52.12%; the value was more significant than adding cationic polymers by 44.68%. The difference is credited to the preferential adsorption of the former polymer onto bentonite clay. PVOH addition successfully helps to achieve better thermal stability by a) boosting the mud swelling index and b) establishing a stronger affinity with the bentonite clay through hydrogen bonding. However, the presence of charged groups on the PVOH backbone counterbalances the efficiency of the polymer.

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