

**INVESTIGATION OF THE RHEOLOGY, FILTRATION LOSS AND H₂S
SCAVENGING PERFORMANCE OF ZEOLITIC-IMIDAZOLE
FRAMEWORK-67 (ZIF-67) AND LAYERED METAL HYDROXIDE (LTH)
NANOMATERIALS FOR OILFIELD DRILLING APPLICATIONS**

BY

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In Partial Fulfillment of the
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MASTER OF SCIENCE

In

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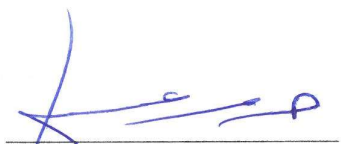
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This thesis is dedicated to my lovely mother, Mrs. Mariama Abdullah, and my late father, Mr. Iddrisu Yakubu, for their innumerable support and supplications rendered towards my development. |

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ABSTRACT

Full Name : Mustapha Iddrisu

Thesis Title : Investigation of the Rheology, Filtration Loss, and H₂S Scavenging Capacity of Zeolitic-Imidazole Framework-67 (ZIF-67) and Layered Triple Hydroxide Nanomaterials for Oilfield Drilling Applications.

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The rheological and fluid loss properties of drilling fluids are crucial to the success of any oilfield drilling operation. Among the additives that are used to control these properties, nanoparticles are showing great promise for use in drilling fluid formulations. Additionally, nanoparticles can be used to scavenge and mitigate the noxious effects of hydrogen sulfide (H₂S), which is usually encountered during oilfield drilling operations. In this regard, nano-additives with high affinity for H₂S are in increasing demand. In this work, zeolitic imidazolate framework-67 (ZIF-67), CuMgFe-layered triple hydroxide (LTH), and their nanocomposites were synthesized and utilized as nano-additives to formulate water-based drilling fluids (WBM). The crystallinity, functional groups, textural properties, and thermal stability of the synthesized pristine nanoparticles and their nanocomposites were characterized using XRD, FTIR, BET, and TGA techniques, respectively. Based on the results obtained, the inclusion of the nano-additives into the drilling fluids significantly boosted the H₂S scavenging performance when benchmarked with the base WBM formulation. The breakthrough and saturation times of the base drilling fluid were 34.5 and 325 min, respectively, corresponding to 52.3 and 294.6 mg H₂S/L mud. However, the amounts of H₂S scavenged by the drilling fluids containing ZIF-67, CuMgFe-LTH, and CuMgFe-LTH/ZIF-67 at the breakthrough time were 117.2, 216.3, and 140.8 mg/g,

respectively. At saturation, the amounts of H_2S scavenged by the above nano-WBMs reached 163.6, 268.0, and 184.8 mg/g, respectively. Additionally, the nano-additives improved the viscosity, yield points, and gel strengths of the base WBM. Interestingly, all the nano-WBMs exhibited acceptable filtration loss properties and desirable non-Newtonian behavior (i.e., pseudo-plasticity) as the base-WBM, which confirms that their addition to the formulation did not adversely affect the mud rheology. Further, rheological modelling revealed that the Herschel-Bulkley model best describes the rheology of all drilling fluids. The findings in this work demonstrate that the synthesized pristine nanomaterials and their nanocomposites are promising, effective, and suitable for the removal of H_2S and improving the rheology of aqueous drilling fluids. |

ملخص الرسالة

الاسم الكامل: مصطفى إدريسو

عنوان الرسالة: التحقيق في الريولوجيا، وفقدان الترشيح وأداء الكسح H₂S من المواد النانوية ZIF-67 و LTH لتطبيقات حفر حقول النفط

التخصص: ماجستير الهندسة الكيميائية

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تعتبر الخصائص الريولوجية وفقدان السوائل لسوائل الحفر حاسمة لنجاح أي عملية حفر في حقول النفط. من بين المواد المضافة المستخدمة للتحكم في هذه الخصائص ، تظهر الجسيمات النانوية وعدا كبيرا للاستخدام في تركيبات سوائل الحفر. بالإضافة إلى ذلك ، يمكن استخدام الجسيمات النانوية للبحث عن الآثار الضارة ل hydrogen sulfide (H₂S) والتخفيف من حدتها ، والتي تتم مواجهتها عادة أثناء عمليات حفر حقول النفط. في هذا الصدد ، يزداد الطلب على إضافات النانو ذات التقارب العالي ل H₂S. في هذا العمل ، تم تصنيع (ZIF-67) zeolitic-imidazole framework triple CuMgFe-layered hydroxide (LTH) ، ومركباتها النانوية واستخدامها كإضافات نانوية لصياغة WBMs. تم تمييز التبلور والمجموعات الوظيفية والخصائص التركيبية والاستقرار الحراري للجسيمات النانوية البكر المركبة ومركباتها النانوية باستخدام تقنيات XRD و FTIR و BET و TGA ، على التوالي. بناء على النتائج التي تم الحصول عليها ، فإن إدراج الإضافات النانوية في سوائل الحفر عزز بشكل كبير أداء كسح H₂S عند قياسه بتركيبه WBM الأساسية. كانت أوقات الاختراق والتشبع لسوائل الحفر الأساسي 34.5 و 325 min ، على التوالي ، المقابلة ل 52.3 و 294.6 mg H₂S / L. ومع ذلك ، فإن كميات H₂S التي تم كسبها بواسطة سوائل الحفر التي تحتوي على ZIF-67 و CuMgFe-LTH و CuMgFe-LTH / ZIF-67 في وقت الاختراق كانت 117.2 و 216.3 و 140.8 mg / g على التوالي. عند التشبع ، وصلت كميات H₂S التي تم كسبها بواسطة nano-WBMs المذكورة أعلاه إلى 163.6 و 268.0 و 184.8 mg / g على التوالي. بالإضافة إلى ذلك ، حسنت الإضافات النانوية للزوجة ونقاط الخضوع وقوة الهلام في قاعدة WBM. ومن المثير للاهتمام ، أن جميع nano-WBMs أظهرت خصائص فقدان ترشيح مقبولة وسلوك غير نيوتوني مرغوب فيه (أي اللدونة الزائفة) مثل قاعدة WBM ، مما يؤكد أن إضافتها إلى التركيب لم تؤثر سلبا على ريولوجيا الطين. علاوة على ذلك ، كشفت النمذجة الريولوجية أن نموذج Herschel-Bulkley يصف بشكل أفضل ريولوجيا جميع سوائل الحفر. توضح النتائج في هذا العمل أن المواد النانوية البكر المركبة ومركباتها النانوية واعدة وفعالة ومناسبة لإزالة H₂S وتحسين ريولوجيا سوائل الحفر المائية.

CHAPTER 1

INTRODUCTION

1.1 Background

Natural gas and crude oil have played pivotal roles in driving the progress of our civilization and fostering industrial advancement. Serving as the primary energy source and essential feedstock for petrochemical and related industries, these resources have been instrumental in catalyzing technological, social, and economic growth in numerous nations [1]. In the exploration and extraction of these valuable resources, a crucial and primary undertaking involves creating horizontal or vertical wellbores using specialized drilling equipment. This process is essential as it allows access from the surface to the subsurface hydrocarbon reservoirs, where these precious resources are confined and waiting to be tapped into [2,3]. To achieve this and ensure smooth and economical drilling operations, a special type of non-Newtonian fluid, known as drilling fluid or drilling mud, is always utilized [4]. Drilling fluids are a critical element and a basic requirement for the success of any hydrocarbon drilling operation. They are designed and optimized to ensure safety and perform an array of crucial functions. The drilling fluid employed ought to have suitable fluid properties for a productive drilling operation [5]. The fluid must be able to perform functions such as control subsurface pressures, transport, and prevent sagging of drill cuttings, enhance heat dissipation and lubrication of the drill string and bit, minimize formation damage, transmit hydraulic energy to downhole apparatuses, maintain wellbore integrity, seal permeable formations, and provide satisfactory data for formation evaluation[6–8].

Unfortunately, there have been some issues or challenges that hinder this process and the health and safety of drilling crew and infrastructure during oil and gas exploration. Most issues related to drilling fluids can be primarily traced back to the harmful consequences caused by the infiltration of certain contaminants into the mud system. One of the primary contaminants frequently encountered while drilling subterranean formations are acidic compounds particularly, gaseous hydrogen sulfide (H_2S) [9–11]. This gas infiltrates into drilling mud from different origins, such as hydrocarbon reservoirs and sulfide formations, along with H_2S produced by sulfate reducing bacteria (SRB) present in the fluid. Drilling into hydrocarbon formations that contain H_2S can cause significant corrosion of the drilling equipment, resulting in operational difficulties and substantive economic losses [12]. Likewise, when this gas mixes with the drilling fluid and reaches the surface, it poses severe health and safety risks to the working personnel. Unfortunately, the prevalence of H_2S in wells, particularly in older oil fields, is steadily escalating globally [13]. Consequently, it is becoming increasingly crucial to implement actions aimed at controlling and averting contamination to guarantee sustainable drilling operations.

H_2S is naturally found in a considerable number of hydrocarbon reservoirs and has generated there through a variety of biological and geological factors [14–16]. Notably, sulfur compounds make up approximately 1% of the dry weight of biological organisms. These sulfur compounds include amino acids such as cysteine and methionine, iron-sulfur clusters found in metalloproteins, coenzymes like coenzyme A, thiamine, and biotin, as well as bridging ligands such as cytochrome c oxidase [17,18]. Furthermore, Sulfur-bearing lipids such as Sulfoquinovosyl diacylglycerols contribute to the sulfur content present in cell wall and photosynthetic membranes. This indicates that during the

decomposition of biological biomasses, the process can generate some H_2S [17,18]. Additionally, the retrieval of sour gases containing as much as 94% H_2S suggests that a significant quantity of H_2S might have come from sulfate minerals, specifically within carbonate reservoirs [19].

The presence of H_2S causes sour corrosion, which poses the greatest threat to steel structures, leading to the formation of iron sulfide scales [20]. The resulting iron sulfide, which is also corrosive in nature, further attaches to steel surfaces as a hard layer and can cause pitting corrosion, reducing the equipment's lifespan. Additionally, the iron sulfide scales could potentially sag, causing the sticking of drill strings, and clogging of production pipelines [21,22].

Additionally, H_2S acts as a catalyst that triggers the generation of hydrogen ions. This, in turn, leads to the failure of metals through either hydrogen embrittlement or stress cracking [16]. The generated hydrogen ions become trapped and accumulate in gaps located along the grain boundaries of pipes, causing a buildup of pressure until it surpasses the tensile strength of the pipe. As a result, cracks begin to appear because of the pressure building over time [23,24]. A visual illustration of the corrosive effects of H_2S on metallic drilling pipes is depicted in Figure 1-1.

Besides, the transfer of H_2S to the drilling fluid triggers several effects on the mud, leading to decreased viscosity, increased fluid loss, and changes in fluid density [25]. These changes can lead to the problem of a well kick. Furthermore, the decrease in pH caused by H_2S makes the mud more corrosive to metal [26,27]. Also, it is important to note that when the pressure is low, typically around 350 to 400 psi, H_2S undergoes a transition from a gas to a liquid phase. Consequently, in the event of a kick involving H_2S , the H_2S remains in

its liquid phase until it nears the surface, at which point it rapidly converts into a gaseous phase, resulting in a significant and sudden expansion in volume [24,25]. This situation presents difficult well control challenge.

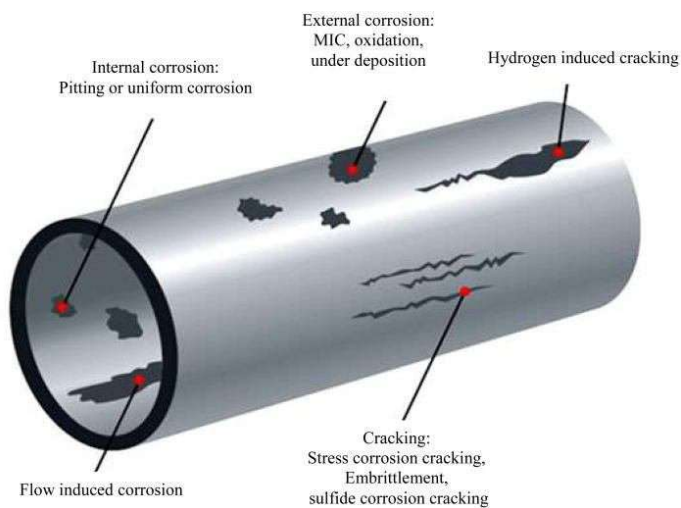


Figure 1-1: Effect of H₂S on steel structures [28].

H₂S is widely recognized as a cellular toxin, functioning as both an asphyxiant and an irritating agent. It interacts with *cytochrome c oxidase*, disrupting the metabolism and activity of the cellular mitochondrial and consequently resulting in dysfunction of the central nervous and respiratory systems [29]. Its health consequences vary depending on the exposed concentrations and duration of exposure. Table 1-1 highlights the effects of H₂S exposure at various levels. To abate the exposure of H₂S, strict regulations and guidelines have been prescribed. The Occupational Safety and Health Administration (OSHA) defines a maximum limit of 20 ppm of H₂S for short-term exposure, while the National Institute for Occupational Safety and Health (NIOSH) recommends an exposure threshold of 10 ppm for a duration of 10 min and classifies 100 ppm as immediately dangerous to life or health for workers. At higher concentrations, H₂S becomes lethal, with concentrations of 500 ppm leading to sudden death [30]. However, a concerning issue is that the odor associated with H₂S becomes undetectable at these higher concentrations. The

human nose can only detect or perceive this odor at small concentrations below one ppm [31]. In essence, exposure to higher concentrations of H₂S can be extremely detrimental, as it cannot be detected, necessitating the use of appropriate H₂S detectors. Undetected exposure to a concentration of 100 ppm can result in various severe health effects, including olfactory paralysis, loss of balance, memory impairment, unconsciousness, tremors, and convulsions [32,33]. Due to these harmful effects and detrimental consequences, H₂S is rightly considered a highly dangerous gas and its exposure must be effectively mitigated.

Table 1-1: Health effect of H₂S exposure [29,34].

H₂S Concentration (ppm)	Clinical effect of H₂S
0.13 – 0.15	Odour threshold
4.6 - 10	Fatigue, headache, nausea, eye irritation
100	Eye and throat irritation, dyspnea, olfactory paralysis
200-300	Olfactory paralysis, pulmonary edema, throat, and lung irritation
500-700	Cerebral edema, pulmonary edema, loss of consciousness, permanent loss of memory, death with few hours of exposure
1000-2000	Respiratory paralysis, asphyxia with cardiac arrest, sudden death

1.2 Significance of this research

The presence of H₂S is highly undesirable and poses significant challenges in the petroleum industry. It is corrosive to metallic infrastructure and detrimental to the health and safety of rig personnel. The hazardous nature of H₂S, along with its economic impact on drilling operations, makes it crucial to mitigate its exposure. Various techniques have been adopted to address these H₂S-related dilemmas. However, the approaches adopted have certain limitations, such as H₂S low reactivity and removal capacity, relatively expensive, and not entirely environmentally benign.

Despite the extensive research studies, there is a noticeable lack of published literature on the synthesis and application of layered triple hydroxides (LTH) and metal-organic frameworks (MOF), particularly zeolitic imidazole framework (ZIF-67), and their respective nanocomposites for H₂S scavenging. Therefore, this research aims to address this gap by focusing on the synthesis of ZIF-67, LTH, and their respective nanocomposites for the purpose of removing H₂S. Additionally, the present study will investigate the impact of these nanomaterials on the rheological and filtration properties to ascertain their potential for drilling fluid applications.

1.3 Research objectives

This research work seeks to investigate the H₂S scavenging performance, rheological and filtration properties of ZIF-67, LTH and their respective nanocomposites in an aqueous drilling fluid formulations. The specific objectives are as follows:

- i. Synthesize pristine and nanocomposites of ZIF-67 and LTH.
- ii. Characterize the synthesized nanomaterials using FT-IR, XRD, TGA, and N₂ adsorption/desorption isotherms.
- iii. Formulate and characterize the rheological parameters of water-based drilling fluids.
- iv. Evaluate the H₂S scavenging performance of the water-based drilling fluids comprising synthesized nanomaterials.
- v. Investigate the effects of the synthesized nanoparticles on rheological and fluid loss properties of the formulated drilling fluids.

| CHAPTER 2 |

| LITERATURE REVIEW

2.1 Background

This chapter provides an overview of drilling fluids, encompassing their distinct types and properties. Furthermore, it highlights on the rheological properties of these fluids, delving into their behavior and flow characteristics. Additionally, it explores the current literature on the techniques and nanomaterials that have been employed for effectively eliminating H₂S during oil and gas drilling operations and enhancing rheology.

2.2 Drilling fluid classifications and composition

In 1913, the utilization of drilling mud was first introduced as a means to manage subsurface pressures while drilling [35]. The process of extracting crude oil and natural gas from reservoirs typically entails the creation of either vertical or horizontal telescopic holes connecting the earth surface to the hydrocarbon reservoir, which may lie several kilometers below surface [36]. This is accomplished using a drilling bit attached to a lengthy string of drill pipe, which effectively crushes rocks into tiny pieces. To facilitate this operation, drilling fluid is circulated through the drill pipe from the surface to the bit face, where it carries the resulting rock fragments back up to the surface. On the surface, specialized machinery is employed to extract the cuttings from the drilling fluid. Afterwards, using strong pumps, the cleaned drilling fluid is reintroduced back into the wellbore for recirculation [3]. The schematic representation of this process is illustrated in Figure 2-1.

Besides the management of subsurface pressures, drilling fluids aids in stabilizing the exposed rock, guarding against the intrusion of unwanted substances into subsurface

formations and hydrocarbon fluids, providing buoyancy, inhibiting the dispersion of shale, and effectively cooling and lubricating the drill bits [4,37–39].

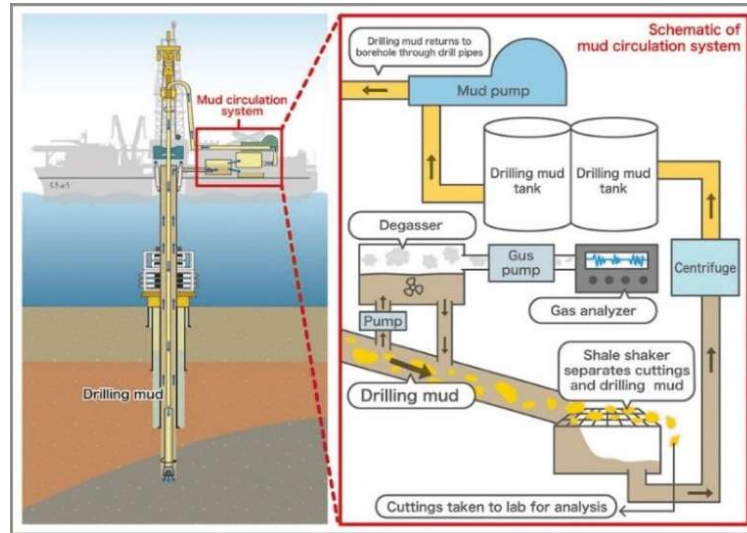


Figure 2-1: Schematic illustration of drilling fluid circulation system.

Consequently, it is essential to meticulously design these fluids to ensure optimal performance, even in challenging conditions. Additionally, it is imperative to guarantee that they do not cause any harm to the formations being drilled which could impede the drilling operations.

Drilling fluid is composed of a base fluid, to which various active and inactive chemical additives are introduced with the aim of attaining the preferred rheological characteristics [40]. The base fluid utilized determines the type of drilling fluids. The categorization of drilling fluids primarily consists of three (3) classes namely oil-based drilling fluids (OBM), water-based drilling fluids (WBM), and synthetic-based drilling fluids (SBM) [41]. Water-based fluids are highly prevalent and are viewed as more cost-effective compared to oil-based or synthetic-based alternatives [42]. They are employed in the drilling of around 80 – 90% of hydrocarbon formations and reservoirs. The base fluid used

in water-based drilling fluid can be seawater, saturated brine, fresh water, or a formate brine [43].

However, it is infrequent for oil-based and synthetic drilling fluids to be recommended for drilling operations due to environmental apprehensions. These fluids typically contain mineral oils, conventional diesel, or linear olefins and paraffins, which are toxic and extremely hazardous to the environment and more costly than the base fluids used in water-based drilling fluids [44,45]. Among the crucial stages in the life cycle of an oil field, drilling stands out as the most pivotal. A notable aspect of this process is the careful consideration of the drilling fluid, which falls within the purview of petroleum economics and risk management. For this study, a water-based mud using distilled water as the base fluid is employed.

Apart from the primary fluid, water-based drilling fluids also consist predominantly of clay, polymers, and weighting agents [41]. In addition to these materials, water-based mud may be made to incorporate various additional materials such as shale stabilizers, pH control agents, corrosion inhibitors, and acidic gas scavengers [46,47]. To maintain and enhance desirable drilling fluid properties, clays such as bentonite have traditionally served as a fundamental element in water-based drilling fluids formulations. Bentonite clay is used in about 80% of water-based drilling fluids [48]. This clay has the ability to expand when it encounters water, thanks to its associative and electrostatic interactions (i.e., edge-to-edge, face-to-face and edge-to-face) [49]. Moreover, the ability of its *c-axis* to accommodate and take up water in its layered structure enables it water uptake and expansion. This swelling characteristic of bentonite makes it an ideal choice to improve viscosity in drilling fluids and helps in the formation of thin and less permeable filter layers

thereby preventing formation damages [50]. Further, bentonite clay helps to prevent circulation losses and water seepage into permeable formations [51]. It should be emphasized, however, that an excessive amount of bentonite in drilling fluid can lead to negative consequences, including pipe sticking, reduced rate of penetration (ROP), and increased energy requirements for circulation. In contrast, insufficient bentonite fails to uphold the necessary rheological properties essential for efficient drilling, potentially causing sagging [49,51].

In addition to clays, polymers find applications for the enhancement of the rheological characteristics of drilling fluids. These polymers play a vital role in managing and augmenting the rheological properties, filtration efficiency, wellbore stability, and shale inhibition [52,53]. The interaction between water and shale results in the swelling of shale, which subsequently causes wellbore instability issues such as tight holes, shale dispersion, and bit balling [50]. Water-based drilling fluids use polymers to hinder shale swelling and fluid loss [54]. They achieve this by creating a protective coating around the shale through a thin layer of polymer, thereby preventing water from infiltrating the formation [50]. Also, polymers are used to boost the properties of simple systems such as clay-based muds and to avert bentonite flocculation [55]. These drilling fluids employ several types of polymers to effectively control rheological properties and to avoid loss of fluid into the formations. Several types of polymers are utilized in water-based drilling fluids, such as starch, polyacrylates, xanthan gum, amphoteric cellulose, hydrolyzed polyacrylamide, partially hydrolyzed polyacrylamide, polyacrylamide, polyanionic cellulose, and carboxymethyl cellulose [56,57]. This study focuses on enhancing the rheology of drilling fluid formulation through the inclusion of starch and xanthan gum. Starch is selected for its

capacity to improve temperature stability, moderately increase viscosity, and efficiently control fluid loss [58]. Moreover, starch offers the benefits of being readily available, cost-effective, and highly biodegradable [59,60]. Likewise, akin to starch, Xanthan gum is a high-molecular weight biopolymer that offers versatile control over the flow properties of substances. It is considered safe for use in environmentally sensitive areas and applications. The main purpose of xanthan gum is to increase the viscosity and flow resistance of cuttings, allowing for better transport and suspension [61]. It works effectively in a wide range of water-based drilling fluids, from those with low solids content to heavily weighted formulations. One of its advantages is providing an improved rheological profile, featuring elevated viscosity at low shear rates and significant shear-thinning characteristics with a low flow index [62]. This unique combination allows xanthan gum to maintain high effective viscosity, ensuring proper cleaning of the well and keeping cuttings suspended [63].

A primary objective of drilling mud is to manage the fluid pressure in the geological formation and safeguard the well stability. This can be effectively accomplished by introducing weighting agents into the mud, which raises its hydrostatic pressure above that of the formation pressure [64]. These weighting agents can be any substance denser than water, effectively increasing the drilling fluid density while leaving its essential properties unchanged. Besides factors like chemical inertness and specific gravity, the choice of a weighting agent is also influenced by considerations such as its availability in sufficient quantities. Various weighting agents are employed in the formulation of drilling fluids to enhance their density. These agents include barite, dolomite, micromax, ilmenite, calcite, and hematite [65,66]. This research employs calcite (CaCO_3) as a weighting agent, which

serves as both an acid-soluble bridging and weighting component to manage fluid loss and achieve the desired density [67,68]. It finds applicability in a wide range of drilling fluids, including conventional oil-based fluids. Moreover, acting as a bridging agent, calcite remains essentially inert and highly insoluble, thereby exerting minimal impact on fluid properties.

2.3 Rheology of water-based drilling fluids

Rheology is an aspect of physics that deals with the study of the flow of material (i.e., solids or fluids), their deformations, and the relationship between them [69]. All water-based drilling fluids display non-Newtonian characteristics; thus, they do not adhere to a straightforward relationship between the shear rate and the shear stress. As a result, different non-Newtonian models are employed to interpret the rheology of drilling fluids [70]. The Herschel-Bulkley and the Bingham plastic model are the two primary models extensively employed for elucidating the rheological characteristics of drilling fluids [71]. The rheological parameters that explain the non-Newtonian behavior of drilling fluids are the plastic viscosity, yield point, apparent viscosity, gel strength, and the dimensionless flow index [72,73]. The yield point signifies the minimal stress or force needed to initiate flow and is crucial in evaluating the drilling fluid cuttings transport and hole cleaning performance. The plastic viscosity characterizes the fluid resistance to flow during drilling, and a lower value indicates a smoother drilling process. Similarly, the apparent viscosity represents the effective viscosity during drilling, and a lower value usually signifies a smoother process. The gel strength, on the other hand, measures the strength of the 3D network structure that forms after circulation is interrupted. The flow behavior index provides information about the characteristics of drilling fluid. For instance, when $n=1$, the

fluid exhibits Newtonian behavior, while $n < 1$ indicates shear thinning or pseudoplasticity, and $n > 1$ signifies shear thickening or dilatant behavior. Understanding these model parameters offers valuable insights into the rheological properties, helps in selecting the appropriate drilling fluid, and gives an indication of the energy required for circulation [71]. In the case of water-based muds, properties like plastic viscosity, yield point, apparent viscosity, and gel strength hold significant importance for drilling fluids. The properties primarily depend on how the different drilling fluid particles associate and interact with each other. The shear rate-shear stress curve for typical rheological models is depicted in Figure 2-2.

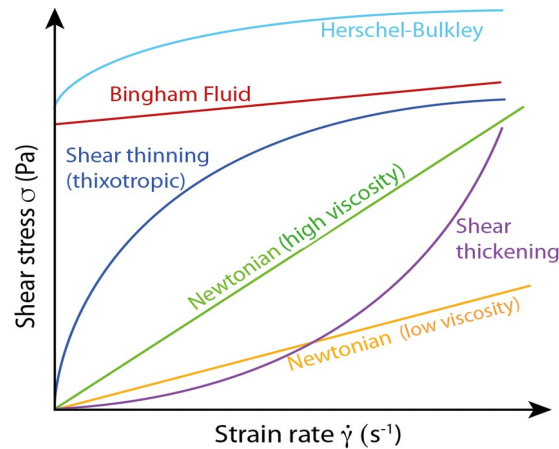


Figure 2-2: Shear rate-shear stress curve for typical rheological models [74].

The study of rheology is crucial for comprehending the effectiveness of water-based muds in drilling operations. To assess the suitability of experimental data, four widely recognized rheological models (Bingham, Power law, Herschel-Bulkley, and Sisko models) have been chosen [71]. This selection is necessary as no single rheological model can precisely and adequately describe or predict the relationship between the shear stress-shear rate data of all drilling fluids across all ranges of the shear rate. The Bingham model demonstrates that a certain minimum stress threshold is necessary to initiate flow, and once this stress is

reached and applied, materials behave like a Newtonian fluid. However, the model only fits experimental data best at low shear rates. The power law model establishes a power relationship between the shear rate and the shear stress. It offers better predictions for drilling fluids compared to the Bingham model, but it may deviate for low shear rates since it lacks consideration of the initial yield stress. In contrast, the Herschel-Buckley model can adequately describe both yield stress and non-Newtonian behavior of fluids across a wide range of shear rates. Consequently, it can more accurately predict the behavior of drilling fluids compared to other models as it combines the strengths of the Bingham and Power Law models while addressing the weaknesses of the latter. The Sisko model, involving three parameters, provides a generalized power-law relationship between shear stress and shear rate, encompassing Newtonian behavior as well. This model holds significant importance as it adequately describes non-Newtonian fluids, particularly in the crucial range of shear rates. Its appropriateness has been extended to explain the pseudoplastic behavior of non-Newtonian fluids [55,75].

2.4 Nanoparticles in drilling fluids

Nanoparticles (NPs) have recently made significant strides in the field of oil and drilling industries, particularly in drilling fluid technology. These nano-scale particles offer exceptional traits like high thermal conductivity and a wide surface area, which address various challenges encountered in drilling fluid applications. The benefits of integrating NPs into drilling fluids are manifold; they mitigate formation damage, reduce overall drilling fluid expenses, control fluid loss and mud cake formation, eliminate hazardous materials, enhance heat transfer and lubrication, and improve key rheological properties such as viscosity [76,77]. The use of nanoparticles in nano-based drilling fluids introduces

remarkable enhancements beyond their base materials. These enhancements may include bolstered stability against sagging, thanks to the superior attributes exhibited by these NPs. Nanotechnology has surged to the forefront of research and has already exerted a substantial impact on technological advancements across diverse industries. The exceptional physico-chemical characteristics of NPs, resulting from their minuscule size and extraordinarily high surface-to-volume ratio, set them apart from macro and micro-sized materials. It is these distinct properties that render NPs the most promising candidates for crafting intelligent drilling fluids. These fluids can be tailored to possess specific properties that align with the demanding conditions of upstream downhole environments.

2.4.1 Significance of nanoparticles in drilling fluids

In recent times, numerous research studies have been dedicated to incorporating different nanoparticles into water-based drilling fluids [3,60,70]. This integration aims to enhance the properties of these fluids. These improvements cover a range of aspects, including better rheological characteristics, improved thermal and electrical conductivity, and more effective control over fluid loss [42]. Traditional drilling muds often experience a decline in their rheological properties when exposed to elevated temperature and pressure conditions. This reduction leads to a decrease in drilling efficiency due to the loss of mud filtrate volume. To address this issue, nanoparticles like metal oxides, polymers and other nanomaterials are introduced. These nanoparticles contribute to improved heat transfer by enhancing thermal conductivity and filling pore formations to reduce the volume of mud filtrate [68,78].

Moreover, nanoparticles often offer enhancements to the physiochemical, electrical, and thermal properties of drilling fluids, thereby further improving their rheology. It is

important to note that altering the size distribution and concentrations of nanoparticles plays a crucial role in modifying these rheological properties [79]. In comparison to bulk phase materials, nanoparticles bring about significant improvements in various drilling fluid properties. These enhancements encompass rheology, fluid loss control, wellbore stability, wellbore strengthening, suspension of cuttings, and thermal characteristics. The improved rheological properties of nanoparticles are achieved through factors such as their concentration, inherent properties, and the continuous phase of the drilling fluid. Nanoparticles also find application in ensuring the stability of the wellbore when facing challenges like sloughing, swelling, and formations with abnormal pressure. By entering shale pores, nanoparticles function as bridging and wellbore strengthening agents [80].

Furthermore, the inclusion of nanoparticles enhances the heat conductivity and dissipation within drilling fluids. The substantial heat generated during the drilling process, combined with friction between the bit and rock surfaces, tends to degrade the performance of drilling fluids. To combat this, metal oxide nanoparticles, known for their high thermal conductivity, are introduced. These nanoparticles facilitate efficient heat transfer and cooling. Their unique random Brownian motion at the nano-scale further boosts thermal conductivity. Notably, elevated temperatures amplify thermal conductivity in drilling fluids enriched with nanoparticles, resulting in faster cooling when the fluid moves upward. The concentration of nanoparticles is directly proportional to the enhancement of thermal properties. Notably, nanoparticles in the nano-sized range surpass their micro-sized counterparts in terms of enhancing thermal conductivity. Additionally, nanoparticles increase the annular viscosity of drilling muds, thereby enhancing the lifting capacity by intensifying the drag force on drilled cuttings [81].

2.4.2 Effect of nanoparticles on rheology

Managing the rheological properties of drilling fluid is of utmost importance for upstream and deep subterranean operations particularly under high-pressure and high-temperature conditions. These properties play a critical role in evaluating both the hydraulics of the wellbore and the effectiveness of the mud system [4,82]. Key rheological characteristics of drilling mud, such as apparent viscosity, plastic viscosity, yield point, and gel strength, hold significant relevance in this context. Recent studies underscore the potential of incorporating different nanoparticles into the drilling mud as a means to alter and augment these rheological properties. This addition has a notable impact on improving the plastic and apparent viscosity, all the while maintaining the integrity of the yield point and gel strength. For example, Ismail et al. [41], conducted a study to examine and compare how nano and micro-sized materials impact the rheological properties of water-based drilling fluids. They investigated the suitability of nano-silica, multi-walled carbon nanotubes (MWCNT), as well as two distinct size distributions of glass beads (90-150 μm and 250-425 μm). The results indicated that the nanomaterials, specifically MWCNT and silica, displayed a superior coefficient of friction (COF) compared to the larger micro-sized glass beads. Moreover, both nano-silica and MWCNT demonstrated better control over viscosity, even though they exhibited a similar trend of the yield point when compared to the micro-sized glass beads [41].

In another study conducted by Bayat et al. [83], the influence of SiO_2 and TiO_2 nanoparticles on the rheological and filtration characteristics of a water-based polymeric drilling fluid was investigated at three distinct temperatures (25, 50, and 75 $^{\circ}\text{C}$). Initially, there was a noticeable decline in performance within the range of 0-0.1 wt.% nanoparticle

concentrations for both types of nanoparticles at the three temperatures. This decline was attributed to the reduction in mechanical friction between the components of the drilling mud in the presence of nanoparticles at lower concentrations. Subsequently, as the nanoparticle concentration increased from 0.1 to 0.5 wt.%, there was a notable increase in the PV of the base mud. Furthermore, the results obtained from yield point measurements indicated that muds containing nanoparticles displayed greater resistance to temperature variations when compared to the base mud. This enhanced performance was attributed to the higher thermal conductivity of the nanoparticles, which improved heat dissipation. As a consequence of the enhanced thermal properties of the nano-mud, the effect of temperature fluctuations on the gel strength was mitigated. At each of the tested temperatures, the gel strength exhibited improvement in the presence of nanoparticles [83].

Perween et al. [84] introduced BiFeO₃ NPs as an additive to water-based mud, in conjunction with bentonite and other polymeric additives. This incorporation of BiFeO₃ resulted in notable improvements in key properties, including apparent viscosity, plastic viscosity, yield point, and even the API fluid loss. The results further revealed that as the concentration of BiFeO₃ increased from 0 - 0.30 w/v%, a substantial 25% increase in AV, PV, and YP, respectively was observed. Moreover, they observed a significant 35% reduction in API filtrate loss at a temperature of 20 °C, prior to hot rolling. Interestingly, even after subjecting the BiFeO₃-mud to hot rolling at 110 °C, these properties remained relatively stable which demonstrated the enduring efficacy of the NPs in preserving the desired drilling fluid characteristics. Generally, the combination of NPs with bentonite platelets conferred enhanced thermal stability to the drilling fluid. Oseh et al.[85], introduced a novel surfactant-modified nanohydroxyapatite (Nano-HAp) as an additive to

enhance the rheological properties and salt resistance of water-based drilling fluids. The nano-HAp simultaneously improved fluid rheology and bolstered the base mud resistance to salt cation contamination. At 298 K, the nano-HAp increased viscosity by 78.6%, and at 353 K, it achieved a remarkable 79.2% increase in the viscosity. These results suggest that the inclusion of nano-HAp in the drilling fluid not only enhances viscosity but also has a positive impact on the thermal conductivity of the drilling fluid since the vast change in temperature did not have any appreciable effect on the viscosity.

Some researchers have also studied the effect of nanocomposites on the properties of drilling fluids. For example, Kalhori et al. [86], investigated the effect of $\text{CeVO}_4/\text{Al}_2\text{O}_3/\text{rGO}$ nanocomposite on rheological properties and thermal conductivity of water-based drilling fluid. A three and two-fold increase in the PV is observed with the incorporation of $\text{CeVO}_4/\text{Al}_2\text{O}_3$ and $\text{CeVO}_4/\text{Al}_2\text{O}_3/\text{rGO}$ nanocomposite respectively within the concentration range of 0.1 to 0.5wt%. In all drilling fluid formulation prepared, the shear thinning behavior was exhibited even with the nano-mud, which also exhibited good thermal conductivities. A summary of various nanomaterials incorporated into drilling fluids is presented in Table 2-1.

2.4.3 Effects of nanoparticles on filtration loss

Effective control of filtration is a crucial factor in enhancing the performance of drilling mud [56,87]. This is especially vital when dealing with demanding reservoirs, which could potentially result in significant loss of mud and intrusion of fluids. One innovative approach to tackle this challenge involves the incorporation of nanoparticles into the mud. By doing so, the loss of fluid is ceased, and thin filtration cake forms which improves drilling operation and prevent sticking of drill strings [59,88]. The formation of thin filter

layers is pivotal in preventing the invasion of fluids into the formation pores (see Figure 2-3). However, it is important to note that the concentration of nanoparticles must be managed with precision to prevent agglomeration which increases the permeability and porosity of the filter layer. A careful control is necessary to avert filtration problems stemming from the clumping of nanoparticles.

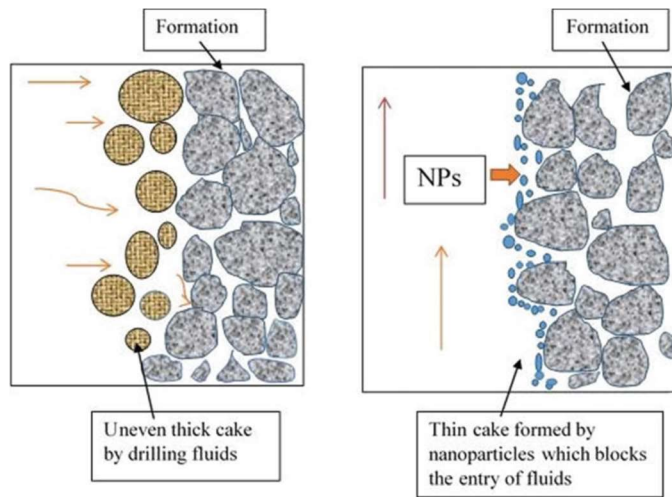


Figure 2-3: Filtration loss prevention by NPs and bulk materials [81].

Incorporation of NPs has been pivotal towards the mitigating and control of filtration loss and general fluid properties. For instance, Ahasan et al. [89], explored the impact of ZnO NPs on fluid loss in water-based drilling fluid under API low-pressure low-temperature (LPLT) conditions. They found that the addition of NPs did not significantly affect the volume of lost fluid. However, as the concentration of NPs increased, the thickness of the mud cake steadily decreased. At a 1.0wt% concentration of ZnO NPs, the mud cake reached its lowest thickness of 0.9/32 inch, representing a 55% reduction compared to the base mud. These reductions provide convincing evidence of a well-established connection between nanoparticles and drilling fluid additives within the mud cake, effectively sealing the pores of the filter cake (see Figure 2-4).

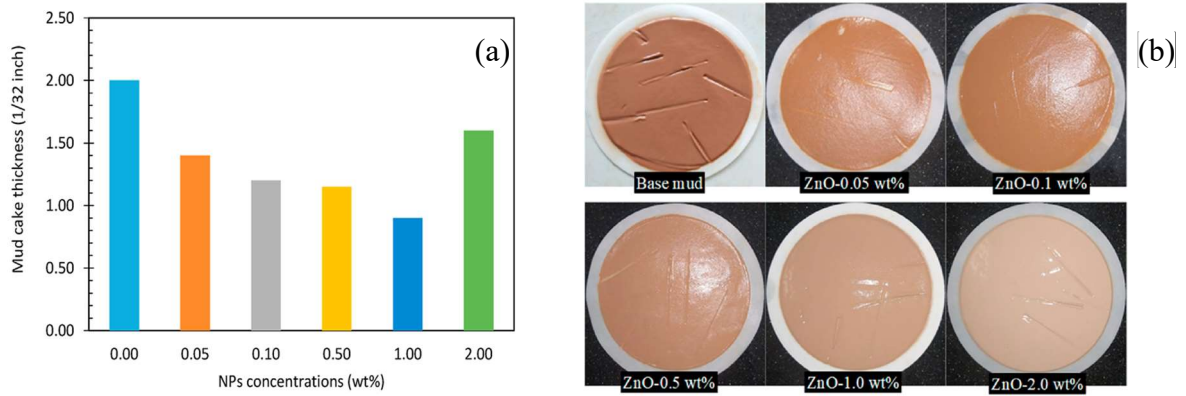


Figure 2-4: (a) Effect of ZnO NPs on the filter cake thickness and (b) formed cakes at different ZnO NPs concentration after 30 min LTLP API filter test [89].

The thickness of the mud cake is linked to how much fluid infiltrates the formation while drilling. When the mud cake on the wellbore wall is thick, it indicates that a significant amount of liquid and solid particles has infiltrated the formation near the wellbore. This thick mud cake creates a pressure difference between the mud column and the formation, leading to differential pipe sticking [78,90]. Therefore, it is preferable to have a thin and slippery mud cake during drilling operations. As shown in Figure 2-4, the thickness of the developed mud cakes clearly shows that incorporating NPs into the drilling fluid reduced the mud cake thickness across all NPs concentrations which is preferable for well development.

Also, Alam et al. [91], conducted a study to investigate the impact of Fe_2O_3 NPs on the filtration and rheological properties of low-solid non-dispersed drilling mud (LSND), both in field and laboratory-LSND. When the NPs were introduced into the laboratory-LSND mud, an improvement in fluid loss across all concentrations of NPs was observed. Specifically, at 0.5 wt.% NPs concentration, the filtrate volume significantly decreased by 23.75% relative to the base laboratory-LSND. However, at 1.0 and 3.0 wt.% NPs

concentration, the filtrate volume increased. Conversely, at 0.1 wt.% NPs concentration, a 40% reduction in the fluid loss was obtained in the field-LSND relative to the base mud. This suggests a substantial influence of NPs on fluid loss control, particularly at relatively lower concentrations. In essence, the active plugging of nanopores seems to occur due to the adequate dispersion of NPs at lower concentrations. At higher concentrations, on the other hand, agglomerated NPs deposit below the primary filter layers, forming a permeable layer, leading to increased fluid loss. Additionally, the presence of NPs in the drilling fluid resulted in a reduction in filter cake layer thickness at all NPs concentrations. The thinnest filter cake thickness for the laboratory-LSND mud was 0.75/32 inch at 0.5 wt.% NPs concentration, which is a significant 70 % reduction in thickness compared to the base mud filter layer. At NPs concentration of 0.1 wt.%, thickness of the field-LSND mud was found to have decreased by 47 % (0.80/32 inch) when compared to the base mud (see Figure 2-5). A summary of various nanomaterials incorporated into drilling fluids is presented in Table 2-1.

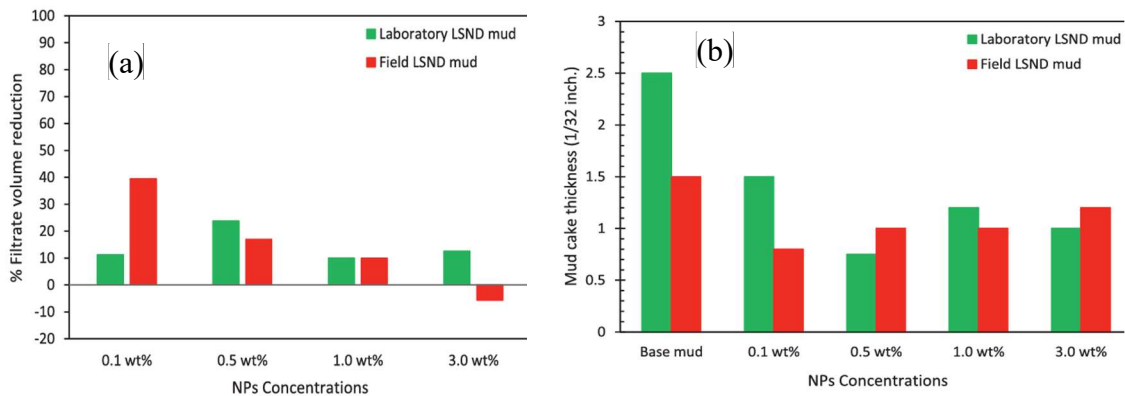


Figure 2-5: (a) Impact of NPs on filtration volume reduction and (b) filter cake thickness for under API LPLT test [91].

Table 2-1: Summary of various nanomaterials utilized to enhance the rheological, filtration, thermal and electrical properties of drilling fluids.

Type of Nanoparticle	Fluid type	Properties Tested	Experimental conditions	Findings	Ref.
MWCNT Nanosilica Glass beads	WBM	PV, AV, YP, GS Filtration Properties	LPLT	- NPs generally enhanced the rheological properties of the base fluid. - GB increased the FC thickness, whereas the MWCNT and NS showed negligible effects on the FC thickness. - MWCNT exhibited better control of FL than the other NPs and the base fluid.	[41]
SiO ₂ TiO ₂	Polymeric - WBM	PV, AV, YP, GS Filtration Properties	LPLT	- NPs exhibited appreciable control on the rheological properties. - SiO₂ and TiO₂ NPs enhanced the filtration loss and reduced the fluid loss volume in the polymeric WBM at all applied temperatures. - NPs-WBMs exhibited greater resistance to temperature variations.	[83]
Nanohydroxyapatite (Nano-HAp)	WBM	Rheology Filtration Properties Salt tolerance	LPLT HPHT	Nano-Hap enhanced the rheological, filtration, and resistance to salt (Ca²⁺ and Na⁺) contamination.	[85]
CeVO ₄ /Al ₂ O ₃ /rGO	Bentonite-WBM	Rheological properties Filtration properties Thermal conductivity	LPLT	- CeVO₄/Al₂O₃/rGO significantly decreased fluid loss and filter cake thickness in water-based drilling fluid. - The NPs improve the rheological properties of water-based drilling fluid. - CeVO₄/Al₂O₃/rGO slightly enhanced the thermal conductivity at 80 °C.	[86]
Fe ₂ O ₃	Low solid non-dispersed water base mud (LSND)	Rheological properties Filtration properties	LPLT	- The addition of NPs significantly enhanced the filtration properties and reduced the FL and FCT for both lab and field LSND. - NPs had a greater effect on the GS of the field-LSND than the lab-LSND. - At 0.1 wt.%, NPs reduced the filtrate volume and cake thickness of the filed-LSND by 40% and 47%, respectively. - The NPs generally enhanced the rheological parameters of the LSND muds.	[91]

Type of Nanoparticle	Fluid type	Properties Tested	Experimental conditions	Findings	Ref.
Mn ₃ O ₄	WBDM	PV, AV, YP, GS Filtration Properties H ₂ S Removal Corrosion Resistance	LPLT	- Mn₃O₄ enhanced the H₂S scavenging efficacy of the base mud (BM) by a remarkable 706.6%, surpassing the performance of triazine and Sourscav commercial scavengers by four to five-fold. - Mn₃O₄ reduced fluid loss volume, suggesting accelerated plugging and reduced formation damage. - Mn₃O₄ exhibited noncorrosive properties and an almost negligible corrosion rate.	[92]
ZnO KMnO ₄ Cu(NO ₃) ₂ ·3H ₂ O	WBDM	PV, AV, YP, GS Filtration Properties H ₂ S Removal	LPLT	- At saturation, ZnO removed 35.1 mg/g H₂S, Cu(NO₃)₂·3H₂O removed 146.8 mg/g H₂S, and KMnO₄ removed 307.5 mg/g H₂S. - KMnO₄ resulted in a 20% increase in AV, a 33% increase in PV, and a 10% increase in YP. - Both ZnO and Cu(NO₃)₂·3H₂O exhibited nearly identical rheological characteristics to the base mud, with no significant impact on the base mud's properties.	[12]
Hydrophobic Zn NPs	Invert Emulsion Diesel-Based Drilling Mud (IEDBM)	Plastic viscosity (PV) H ₂ S Removal Rheological model	LPLT	- At saturation, the NPs-IEDBM demonstrated a noteworthy capacity for scavenging H₂S, with a capacity as high as 4465 mg H₂S per liter of mud. - Additionally, the IEDBM-NPs demonstrated favorable characteristics of shear thinning, and this behavior aligns well with the Casson and Herschel-Bulkley models.	[93]
Steel-waste NPs	WBDM	PV, AV, YP, GS Filtration Properties H ₂ S Removal	LPLT	- SW-NPs significantly improved the H₂S scavenging capacity by almost 503% at 3.0 g SW compared to the BM. - Addition of SW-NPs improved the rheological parameters. - At 1 g, the steel waste reduced the FL by 32%.	[11]
Waste-Steel NPs	WBDM	PV, YP, GS Filtration Properties H ₂ S Removal Corrosion test	LPLT	- WS-NPs enhanced the H₂S scavenging capacity more than BM by 61%. - WS-NPs led to an increase of 16% in PV, a 9% increase in YP, and about a 15% improvement in the GS. - WS-NPs led to a 25% reduction in the volume of filtrate. - WS-NPs improved the corrosive resistance of the WBDM and did not exhibit any corrosive effects.	[94]

Type of Nanoparticle	Fluid type	Properties Tested	Experimental conditions	Findings	Ref.
SiO ₂ /Kcl/xanthan NC	WBDF	PV, AV, YP, GS Filtration Properties Shale Swelling	LPLT HPHT	- Rheological properties improved with the addition of SiO₂/Kcl/xanthan NC. - At 4000 ppm NC, the fluid loss volume was reduced by 90.13% and 90.71% under LTLP and HPHT conditions, respectively. - Shale swelling also decreased by 41 and 52.2% under LTLP and HPHT conditions, respectively.	[95]
Polymer grafted silica	WBDF	PV, AV, YP, GS Filtration Loss	LPLT HPHT	Incorporation of NCs led to enhancements in rheological characteristics and the reduction in FL volume was observed under both LPLT and HPHT conditions.	[96]
ZnO TiO ₂ Functionalized-MWCNT	Bentonite-WBDM	PV, AV, YP, GS Filtration Loss	LPLT HPHT	- NPs led to enhancements in the rheological characteristics of the water-based drilling fluid. - f-MWCNTs yielded superior rheological performance and the most substantial decrease in the filtrate volume of the drilling fluid.	[97]
ZrO ₂	Non-Damaging Drilling Fluid (NDDF)	PV, AV, YP, GS Filtration Loss	LPLT HPHT	- The rheological properties were improved by ZrO₂ NPs. - At 100 psi and 200 psi differential pressures, ZrO₂ NPs reduced the FL volume.	[98]
MnO	WBDF	PV, AV, YP, GS Filtration Loss Electrical Conductivity	LPLT	- NPs improved the rheological properties of WBDF before and after hot rolling at 100°C. - NPs effectively reduce both LPLT and HPHT filtrate loss of drilling fluid before and after hot rolling at 100°C. - NPs-WBDF increased the electrical conductivity to a small extent under LPLT and HPHT conditions.	[99]
Fe ₃ O ₄	Bentonite-WBM	PV, AV, YP, GS Filtration Loss Cuttings Carrying Efficiency	LPLT	- Fe₃O₄ NPs gave better rheology and filtration performance under non-saline conditions than under saline conditions. - Fe₃O₄ NPs. showed a higher cutting capacity index than that of conventional drilling fluids, which suggests that it could be used to improve the transport of cutting particles.	[100]

Type of Nanoparticle	Fluid type	Properties Tested	Experimental conditions	Findings	Ref.
Glucopyranose modified graphene. (Glu-Gr)	WBDF	PV, AV, YP, GS Filtration Loss Shale Dispersion Linear Swelling Test	LPLT	- Glu-Gr NPs showed improved rheological properties, even after hot rolling, and a high degree of thermal stability. - Glu-Gr NPs showed a lower loss of fluid and had a high recovery rate of the dispersion in comparison with the conventional drilling fluid. - At 0.85 wt.%, the Glu-Gr remarkably improved the shale recovery by up to 90%. - The swelling test substantiates better welling control by Glu-Gr as compared to Kcl.	[101]
GO-ZnO	WBDM	PV, AV, YP, GS Filtration Loss H ₂ S Removal	LPLT HPHT	- GO-ZnO significantly enhanced the rheological properties of the base mud. - Filtration rate was reduced by 57% at 0.3 wt.% GO-ZnO concentration. - GO-ZnO removed 100% H₂S (800 ppm) in 15 min and exhibited a better H₂S removal rate than bulk-ZnO, which removed only 2.02% H₂S after 60 min.	[102]
TiO ₂	WBDM	PV, AV, YP, GS Filtration Loss	HPHT	- TiO₂ NPs improved the filtration loss characteristics, thermal stability and rheological properties of mud systems were improved. - TiO₂ NPs imparted resistance to the thermal degradation of the rheological properties and the filtration properties of drilling fluids.	[103]
Fe ₂ O ₃ SiO ₂	WBDF	PV, AV, YP, GS Filtration Loss Rheological Modelling	LPLT	- Fe₂O₃ improved the fluid loss property of the drilling fluid compared to the base mud. Adding SiO₂ led to an increase in the filtrate volume and filter cake thickness. - At 0.5 wt.%, Fe₂O₃ reduces the filter cake permeability by 76.4%. - Herschel-Bulkley model best described the behavior of both Fe₂O₃ and SiO₂ drilling fluids. - Fe₂O₃ improved the rheological characteristics of drilling fluids whereas SiO₂ NPs have a negative impact on the rheology.	[104]

Type of Nanoparticle	Fluid type	Properties Tested	Experimental conditions	Findings	Ref.
TiO ₂ Al ₂ O ₃ SiO ₂	WBDF	PV, AV, YP, GS Filtration Loss	LPLT	- NPs significantly improved the rheological and hydraulic properties of the water-based muds at relatively lower concentrations within the range of 0.1 to 0.3 wt.%. - SiO₂ and TiO₂ NPs reduced the filtrate volume and thickness of the filter cakes whereas the addition of Al₂O₃ did not show any positive effect on the filtration loss.	[105]
MgO TiO ₂ GO	WBM	PV, AV, YP, GS Filtration Loss Clay Yield Rheological Modelling	LPLT	- MgO was found to be the best material to improve filtration, followed by graphene and TiO₂. The behavior of all the NPs-WBM and the base mud follows the Herschel-Bulkley Model. - Cake thickness is increased when nanomaterials are added at different concentrations.	[106]
Al ₂ O ₃ CuO Copper (Cu)	WBDNF	PV, AV, YP, GS Specific Heat Capacity Thermal Conductivity Filtration Loss	LPLT HPHT	- Cu produced the least filtrate volume, followed by CuO, Al₂O₃, and base fluid. Filtrate volume decreased with the increasing concentration of NPs. - At 0.9 wt.%, Cu NPs enhanced the heat capacity and thermal conductivity by 15.6% and 12%, respectively. - NPs significantly enhanced the rheological properties of nanofluids compared to the base drilling fluid. The addition of NPs resulted in reduced fluid loss and formation damage.	[107]
SiO ₂ CNT ZnO CNT-SiO ₂ hybrid	WBDF	Thermal Conductivity PV, AV, YP, GS	LPLT HPHT	- At 2 wt.% NPs concentration, SiO₂, CNT, and ZnO improved the thermal conductivity of the base fluid by 16.9, 12.5, and 22%, respectively. - NPs generally improved the rheological properties of the base fluid; however, the highest improvement was obtained from silica NPs.	[79]
ZnO-Am ¹	WBM	PV, AV, YP, GS Filtration Loss Shale Swelling	LPLT	- ZnO-Am improved the filtration and rheological properties of the drilling fluid under both HPHT and LPLT conditions. - ZnO-Am displayed minimal effect on the prevention of shale swelling.	[108]

¹ Acrylamide

Type of Nanoparticle	Fluid type	Properties Tested	Experimental conditions	Findings	Ref.
Micro fibrillated cellulose (MFC) Cellulose nanocrystals (CNC)	Bentonite-WBM	PV, AV, YP, GS Filtration Loss	LPLT HPHT	- MFC and CNCs increased the rheological properties of BT-WDFs. - CNC polymer films remarkably reduced the fluid loss volume and the thickness of the filter cake better than the MFC.	[109]
Fe ₃ O ₄ /PSSS ²	Bentonite WBM	Salt Tolerance PV, AV, YP, GS Filtration Loss Rheological Model	HPHT LPLT	- Fe₃O₄/PSSS can effectively improve Kcl tolerance. - At 0.1 wt.%, Fe₃O₄/PSSS exhibited superior filtration properties yielding less filtration loss and a substantially thinner filter cake. - The Bingham and Herschel-Bulkley models performed the best in predicting the rheological properties of Fe₃O₄/PSSS-WBDF.	[110]
BiFeO ₃	WBM	PV, AV, YP, GS Filtration Loss	LPLT	- BiFeO₃ enhances the rheological parameters of water-based mud. - NWBM demonstrates thermal stability, with no significant mud characteristic reduction after hot rolling at 110 °C. - BiFeO₃ reduces filtration loss both before and after hot rolling.	[84]
ZnTiO ₃	WBM	PV, AV, YP, GS Filtration Loss Kcl Inhibition	LPLT	- ZnTiO₃ improved the general rheological properties of the drilling fluid even with the addition of salt (Kcl). - At 1 wt.%, ZnTiO₃ NPs reduced fluid loss volume by approximately 7.7%.	[111]

²poly (sodium p-styrene sulfonate)

2.5 Methods of H₂S removal from drilling fluid

Sulphur compounds exhibit potent toxicity and corrosive properties, significantly impacting the well-being of workers, the environment, productivity, and the longevity of drilling equipment. The oil and gas industry commonly faces sulphury pollutants like hydrogen sulfide (H₂S), thiophenes, mercaptans, and polysulphides, which are the most frequently encountered [112]. H₂S exhibits a colorless appearance and possesses toxic, corrosive properties. It is recognized as a major environmental pollutant, emitting a foul odor reminiscent of rotten eggs. Additionally, it readily dissolves in various substances such as oil, water, alcohol, and most solvents [113]. Inhaling H₂S gas can lead to a range of health problems, including respiratory failure, lung collapse, unconsciousness, and potentially fatal consequences [114]. The presence of H₂S is critical in the upstream production of oil and gas, where it can naturally form on-site from reservoir biomass and sulfate-containing minerals through processes like microbial sulfate reduction (MSR) and thermochemical sulfate reduction (TSR) catalyzed by anhydrites. Additionally, the utilization of various technologies in the extraction of oil and gas, particularly from unconventional sources, plays a crucial role in either promoting or delaying the formation of hydrogen sulfide (H₂S). Notably, three methods that is; steam-assisted gravity drainage (SAGD), waterflooding for enhanced oil recovery, and hydraulic fracturing utilized in oil sands and shale oil or gas extraction, hold the capability to transform the sulfur content inherent in petroleum into H₂S or introduce an excess of H₂S as a byproduct of the production process [19,115].

H₂S exhibits different chemical forms depending on the pH of its surroundings. These forms are hydrogen sulfide (H₂S), bisulfide (HS⁻), and sulfide (S²⁻) [116]. The prevalence

of each form changes with the pH of the medium. Figure 2-6 provides a visual representation of this relationship. When the pH is below 7, the covalent H_2S form is dominant. As the pH rises within the range of 7 to 12, the bisulfide (HS^-) form becomes more prevalent. Further, the sulfide (S^{2-}) form predominates above pH of 12. This phenomenon shows how the chemical behavior of H_2S is highly influenced by the acidity or alkalinity of its surroundings.

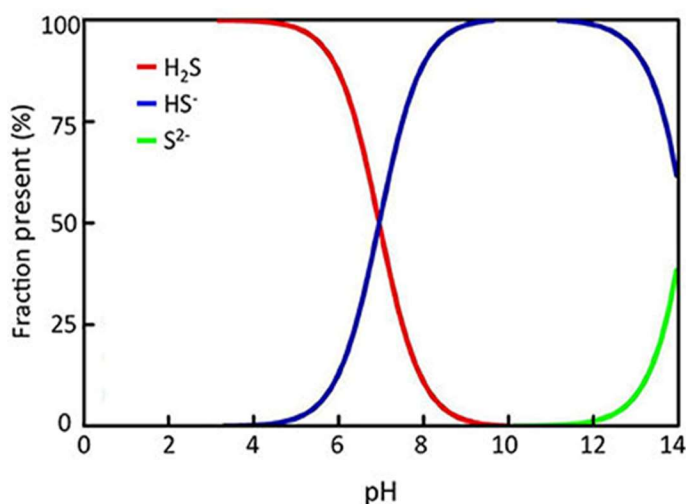


Figure 2-6: Effect of pH on the species distribution of hydrogen sulfide in aqueous solution [117].

The existence of hydrogen sulfide (H_2S) within oil and gas reservoirs poses significant risks to both drilling equipment and the well-being of personnel involved. Consequently, it becomes paramount to address the presence of H_2S directly at the source by implementing in-situ removal techniques from the drilling fluids. By doing so, not only can the integrity of the drilling equipment be preserved, but the well-being of personnel can also be safeguarded, creating a safer and more efficient drilling operation [9,25].

A widely suggested technique for eliminating H_2S involves raising the pH of the drilling fluid to consistently remain above 10 in a sour environment [118]. By doing so, a significant portion of the sulfide transforms into ionic sulfide form instead of covalent H_2S form. This shift from covalent to ionic sulfide reduces the vapor pressure of the gas, effectively controlling its release and mitigating potential issues. Moreover, it is essential to consistently keep the pH level above 10 in order to maintain the drilling fluid alkalinity during drilling operations. This is crucial to counteract the corrosive impact of H_2S and other acidic gases that may be encountered while drilling hydrocarbon reservoirs. This approach is vital for reducing the corrosion of drilling equipment. However, it is important to note that failure to sustain the pH through ongoing treatments or encountering a substantial influx of H_2S can lead to a decrease in pH, triggering a reversible reaction and the regeneration of H_2S . Besides this phenomenon, temperature fluctuations may also cause reversibility of H_2S . Although raising the pH level is advised to mitigate issues caused by H_2S , it is ineffective to be adopted as the sole approach to abate these effects of H_2S [119].

Recently, in oil and gas drilling operations, highly active chemical compounds or nanomaterials have been used as additives in the formulation of drilling fluid specifically to react with H_2S and abate the harsh effects of this corrosive gas. These compounds could either be in the liquid or solid phase, possess suitable chemical properties and high reactivity that improve the H_2S removal performance when added into drilling fluid formulations [12]. Generally, liquid scavengers occupy less space and weigh less compared to solid scavengers. Nevertheless, their ability to eliminate H_2S from the gas stream is notably diminished. In contrast, solid scavengers excel in efficiently extracting H_2S from gas streams, minimizing its presence to trace amounts [120]. More precisely, nano-scale

solid scavengers exhibit a higher surface area, which results in an increased number of sites available for H₂S removal. Moreover, nanomaterials serve as excellent H₂S adsorbents, and their smaller size also improves the rheology and fluid loss of drilling fluid [112]. The subsequent sections will present and discuss the different materials employed for the purpose of scavenging H₂S.

2.5.1 Application of metal-based scavengers

Metal-based scavengers, which encompasses metal salts, metal oxides, metal nitrates, metal carbonates, metal carboxylates, and organo-metallic compounds or chelates, are considered particularly advantageous for scavenging H₂S in drilling fluid due to their affordability, effectiveness, suitability for elevated temperature conditions, and safety. Moreover, when most metal-based scavengers react with H₂S, they form thermally stable and irreversible sulfide products, further enhancing their reliability for drilling fluid applications. Alkali metals like sodium (Na), lithium (Li), and potassium (K) on the other hand, provide defense against corrosion from H₂S by generating a shielding layer on the surfaces of the drill string, as opposed to solely eliminating the H₂S from the system [121]. Transition metals such as copper (Cu), zinc (Zn), and iron (Fe) compounds have been commonly employed for H₂S removal [11]. The reactions between copper compounds and H₂S are generally rapid, resulting in the formation of stable, insoluble solid sulfide products such as CuS or Cu₂S, which remains unaffected by pH fluctuations [122]. Nonetheless, an inherent drawback of copper compounds is their tendency to promote equipment corrosion due to the spontaneous electrodeposition of copper on to steel. Scavenger based on Zinc exhibit similar reactivity toward H₂S but do not induce any corrosive effects or damage, unlike copper compounds [123]. Zinc compounds possess amphoteric properties, meaning

they can function as either acids or bases based on the pH of the fluids. The major limitation of Zinc based scavengers is the likelihood to dissolve under highly alkaline conditions releasing free zinc ions which to some extent may augment H₂S removal performance. However, at pH levels exceeding 11, there is potential for the formation of zincate ions (Zn(OH)₄²⁻) which could adversely impact the rheological properties of the mud, potentially compromising drilling performance [25]. Scavengers based on iron have gained notable appeal due to the fact that iron is not considered an environmentally undesirable element, and it carries significantly lower toxicity compared to zinc. Besides, Fe based scavengers exhibit rapid reaction with H₂S and are remarkably effective at relative low pH. Generally, the utilization of soluble metal scavengers is unacceptable due to the formation gelatinous metal hydroxides because of the precipitation reaction of soluble metal at pH greater than 7 [124]. The use of insoluble metal scavenger is desirable for high performance toward H₂S removal. Despite that, additional variables like temperature, pH, the metal oxidation state, and the duration of the interaction with H₂S should be meticulously considered [122].

2.5.2 Application of oxidant-based scavengers

Oxidizing agents like potassium permanganate, potassium thiosulfate, hydrogen peroxide, and calcium hypochlorite have been employed for scavenging H₂S from drilling fluids. These agents convert or oxidize H₂S into less harmful sulfur compounds, such as sulfate ions or elemental sulfur. Potassium permanganate (KMnO₄) demonstrates its capability to oxidize hydrogen sulfide into harmless sulfur compounds. The combined action of KMnO₄ and the in-situ generated MnO₂ leads to a significant improvement in the H₂S scavenging ability of KMnO₄. The practical application of this scavenger in drilling fluids is

experimentally confirmed to have favorable rheological effects on the fluids [12]. Hydrogen peroxide (H_2O_2) finds application in eliminating H_2S to yield elemental sulfur. Nevertheless, its reactive properties render it unsuitable for drilling fluids applications. Being a non-selective reactant, hydrogen peroxide quickly dissipates as it reacts with other drilling fluid components. Consequently, achieving a controllable H_2S scavenging process becomes challenging [26,27].

2.5.3 Application of Amine-based scavengers

This category of materials finds extensive application in sour gas sweetening and drilling fluid formulations [125]. Specifically, alkanolamines such as monoethanolamine (MEA), diethanolamine (DEA), triethanolamine (TEA), diglycolamine (DGA), N-methyldiethanolamine (MDEA), diisopropylamine (DIPA), and 2-amino-2-methyl-1-propanol (AMP) are the widely employed amines [126,127]. Amine is characterized as being cost-effective, regenerative, and safe. Nevertheless, it tends to induce a rise in the fluid pH, leading to an increased risk of scale formation or corrosion. Furthermore, the reaction of H_2S with amine-based compounds may produce corrosive byproducts which might further impede the effectiveness of the scavenger. Additionally, amines are not thermally stable and may break down at elevated temperatures, usually above $150\text{ }^\circ\text{C}$, or when utilized continuously for extended periods in the circulation of drilling fluids in very deep formation.

2.5.4 Application of Triazine-based scavengers

Scavengers based on triazine exhibit high effectiveness, rapid reactivity with H_2S and are less expensive. The structures of triazine-based products exhibit diversity contingent upon their initial components. The interaction between triazine and H_2S produces byproducts

that are less harmful and readily biodegradable. Despite these advantages, the use of triazine faces certain challenges, such as scaling and fouling caused by the formation of insoluble and amorphous dithazine formation, as well as an increase in fluid pH that promotes corrosion. Moreover, the emergence of scales initiates the adhesion of drill strings, profoundly impacting circulation and possibly culminating in the costly replacement of drilling units. Also, triazine is non-thermally stable, making it unsuitable for upstream H₂S scavenging [128–130].

2.5.5 Application of other types of scavengers

The employment of aldehydes extends to the removal of sour gas in drilling operations and the processing of surface facilities, showing enhanced efficacy in surface cleaning and sweetening procedures. Nevertheless, their utilization is limited due to their expensive nature and involvement in intricate reactions, which give rise to health concerns. For example, formaldehyde, one of the aldehydes, is acknowledged as a carcinogenic substance. The most frequently used aldehydes include formaldehyde, acrolein, glyoxal, and glutaraldehyde. Both formaldehyde and acrolein are toxic [131,132].

2.5.6 Application of layered triple hydroxide (LTH)

Emerging advancements in materials science have led to the development of hierarchical nanomaterials with distinct and attractive properties. A prominent example of such materials is layered double or triple hydroxides (LDH and LTH), which are two-dimensional anionic clays represented by the formula $[M_{1-x}^{2+}M_x^{3+}(\text{OH})_2] (A^{n-})_{x/n} \cdot m\text{H}_2\text{O}$. Here, M^{2+} and M^{3+} refer to divalent and trivalent cations, respectively, A^{n-} stands for the interlayer anion, and x represents the molar ratio of $M^{3+}/(M^{2+} + M^{3+})$, falling between 0.2 and 0.33 [133,134].

Diverse LDHs can be easily synthesized by altering the chemical precursors and their proportions. By substituting M^{2+} with M^{3+} , the layers acquire a positive charge, which is balanced by interlayer anions. LDHs boast exceptional qualities such as substantial surface area, remarkable adsorption capacity, layered structure, and anion exchange capability [135]. Consequently, due to these outstanding attributes and their cost-effectiveness, LDHs find applications in various domains. They are widely used in energy storage systems like supercapacitors, act as catalysts, employed as additives in polymers to enhance mechanical and thermal properties, adsorbents, electrochemical sensors, and even serve as photocatalysts to combat environmental pollutants, among numerous other applications [135,136].

The structural integrity of LDHs is upheld by hydrogen bonding and electrostatic interactions between the layers [137]. Furthermore, LDH adaptability is augmented by their adjustable internal architecture, resistance to thermal changes, high structural positive charge density, and notable redox activity, endowing them with remarkable versatility [138]. The chemical structure of layered triple hydroxide is illustrated in Figure 2-7.

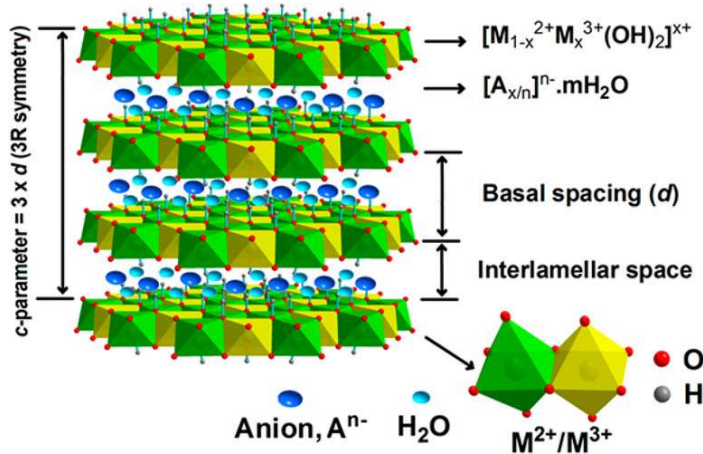


Figure 2-7: Chemical structure of layered triple hydroxides [139].

LDH appears to be a viable candidate based on its chemical and physical properties for the scavenging of H_2S in drilling fluids. Unfortunately, the H_2S removal capability of LTH has solely been examined in gaseous streams. For example, Zhao et al. [140] investigated the efficiency of Mg-Al-LDH in removing H_2S from a gas stream. The results indicated that Mg-Al-LDH shows great promise for H_2S removal, achieving a breakthrough time of 300 min [140]. Also, Lee et al.[141], conducted a dynamic breakthrough experiment to investigate the effectiveness of Co-Fe-LDH in removing H_2S from a high-humidity gas stream. The study examined different molar ratios of Co/Fe and observed a correlation between the crystallinity of the synthesized LTH and the performance of H_2S removal. Specifically, Co/Fe ratios of 1:1 to 1:3 exhibited lower crystallinity, while the crystallinity increased for the 2:1 and 3:1 ratio. Notably, the LTH sample with 3:1 ratio showed a more prominent presence of the 11.6° (003) phase (i.e., higher crystallinity) and demonstrated the highest yield and breakthrough capacity, indicating that a higher 003 phase may enhance H_2S uptake. The experiment achieved a maximum H_2S removal capacity of 0.209 g H_2S /g at a molar ratio of 3:1 and a pH of 10 at room temperature. Furthermore, the adsorption capacity of CoFe-LDH (0.209 g H_2S /g) was found to be 1.53 times greater than that of Co-hydroxide and 8.5 times greater than that of Fe-hydroxide. These results clearly indicate that the synergistic effect of Co-Fe double hydroxide significantly improves the adsorption capacity as depicted in Figure 2-8 [141].

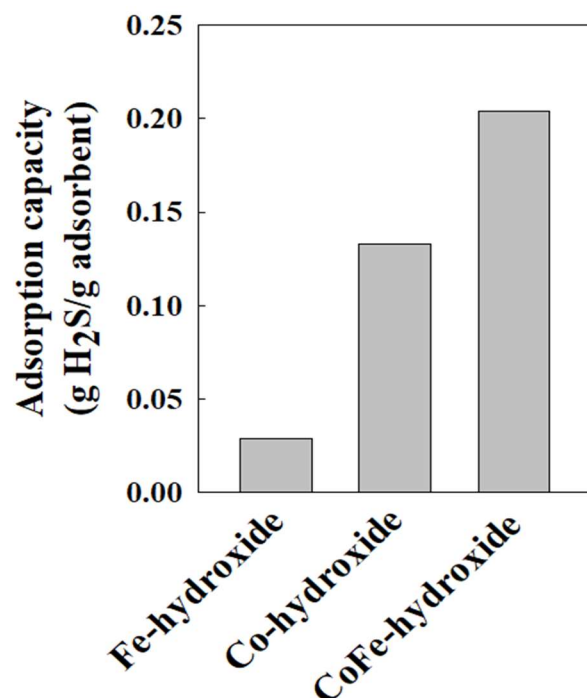


Figure 2-8: Comparison of H₂S removal capacity of Fe(OH)₃, Co(OH)₂, and CoFe-LDH at pH of 10, Co/Fe ratio of 3:1, 60 °C, gas flow rate of 0.3 L/min, and humidity level of 0% [141].

Another report by, Lee et al. [142], studied the removal of H₂S using ZnFe-LDH at room temperature. They found also that the formation of the bimetallic Zn-Fe-LDH synergistically improved the H₂S removal capacity compared to pristine Zn and Fe-hydroxides (see Figure 2-9). The synergy of zinc (Zn) and iron (Fe) led to an augmentation in the adsorption capability for H₂S, consequently exerting a favorable influence on both the physical morphology and surface composition of the resultant adsorbent material [142].

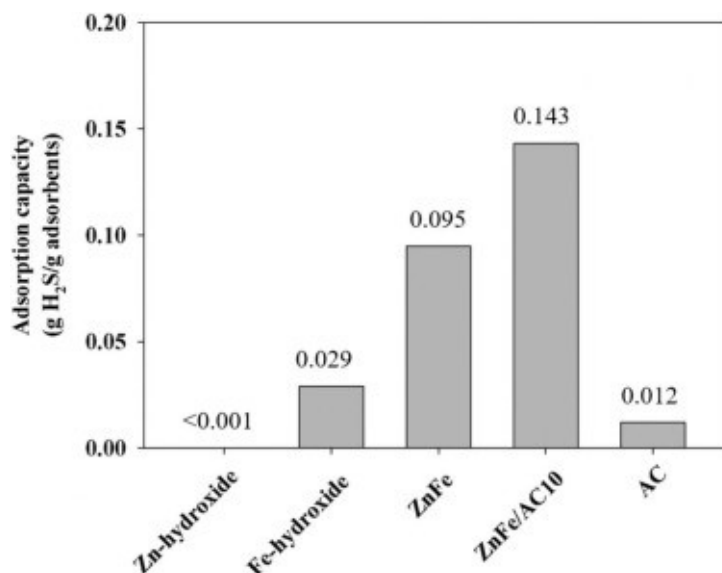


Figure 2-9: H₂S removal capacity at breakthrough of various adsorbents [142].

2.5.7 Application of Metal-Organic Framework (MOF)

MOFs encompass an extensive collection of crystalline substances with exceptionally high porosity, achieving levels of up to 90% in terms of unoccupied space, and featuring incredibly large inner surface areas that surpass 6,000 m²/g [143]. These exceptional attributes, along with the substantial diversity found in their organic and inorganic constituents, have generated significant recognition regarding the potential uses of MOFs. Among their notable traits is their varied and aesthetically pleasing architectures, frequently drawing inspiration from minerals found in nature such as zeolites [144].

In recent times, considerable attention has been directed towards metal-organic frameworks (MOFs) owing to their distinctive open crystalline arrangement, unique morphological attributes boasting substantial surface areas, precisely defined pores, and adaptable functionality [145,146]. These structures, which amalgamate inorganic and organic components into a three-dimensional matrix, are fashioned by linking metal ions with organic connectors. Among the diverse array of MOFs, the zeolite imidazolate

frameworks (ZIFs) have been the subject of extensive investigation [147,148], due to their versatile applications. These frameworks are fashioned through the combination of an imidazole-based ligand (Im) with transition metal cations such as Co, Zn, and Ni [149]. Inside the ZIFs, the transition metals are interlinked by an imidazole ligand, resulting in an M-Im-M angle of 145° , and their morphology closely resembles that of traditional zeolites mineral [150].

Over 150 ZIF structures have been reported thus far [151,152]. One standout among these is ZIF-67, which forms through the self-assembly of Co^{2+} ions and 2-methylimidazole (Hmim) organic linker. This results in a robust structure characterized by cubic crystal symmetry, with unit cell dimensions $a=b=c=16.9589\text{\AA}$ [153]. Notably, recent efforts have focused on synthesizing ZIF-67 and its derivatives with customizable porosity and morphology. Approaches such as the solvothermal, surfactant-assisted, sol-gel, microwave, and ultrasound-assisted methods have emerged for this purpose [154].

The remarkable physical and chemical characteristics of ZIF-67, along with its versatile synthesis methods, position it as an excellent candidate for H_2S removal. Notably, investigations into the H_2S removal capacity of metal-organic frameworks (MOFs) have been primarily focused on gaseous streams. In a groundbreaking contribution by Hamon et al. [155], the first instance of MOF application in H_2S capture was introduced. Specifically, their study featured MOF materials known as MIL-47 ($\text{M} = \text{V}^{\text{IV}}$) and MIL-53 ($\text{M} = \text{Al}^{3+}, \text{Cr}^{3+}, \text{Fe}^{3+}$), revealing their significant capability in H_2S removal [155].

In a subsequent work, Liu et al. [156] explored the selective separation of acidic gases, including H_2S and CO_2 , utilizing various MOF-based nanomaterials such as MOF-5, MOF-

74 (Mg, Zn), ZIF-8, UiO-66, UiO-66 (NH₂), MIL-101(Cr), M-BTC (Cu, Fe, Ce), and Cu-BDC (ted)0.5. The outcomes of their study unveiled that a majority of these MOF materials exhibited exceptional one-time high capacity and selectivity towards H₂S, as illustrated in Figure 2-10 [156].

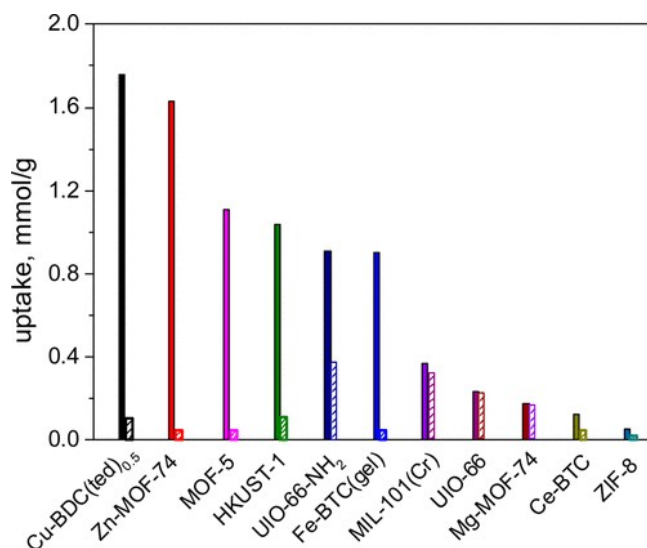


Figure 2-10: H₂S uptake capacity of various MOFs at ambient conditions. Solid column data shows absorption on original MOF adsorbents, and the stripe column shows absorption on regenerated adsorbents [156].

In a similar vein, the research conducted by Allan et al. [157] introduced a Ni(II)-based MOF known as Ni-CPO. This MOF was constructed using Ni(II)-oxygen octahedra connected by 2,5-dihydroxyterephthalic acid. Notably, the adsorption of H₂S was investigated, revealing remarkably high uptakes of H₂S (12 mmol/g at 298 K and 1 bar) [157]. Additionally, Gupta et al. [158] explored the efficacy of H₂S removal using different copper-based MOFs featuring various organic linkers. This investigation aimed to address H₂S gas removal at room temperature. Notably, column studies were employed to calculate the H₂S adsorption capacity of these MOFs, resulting in the following order: 105.6 mg/g

(CuBDC) > 27.1 mg/g (CuBTC) > 1.3 mg/g (CuBDC-N) under dry conditions as depicted in Figure 2-11 [158].

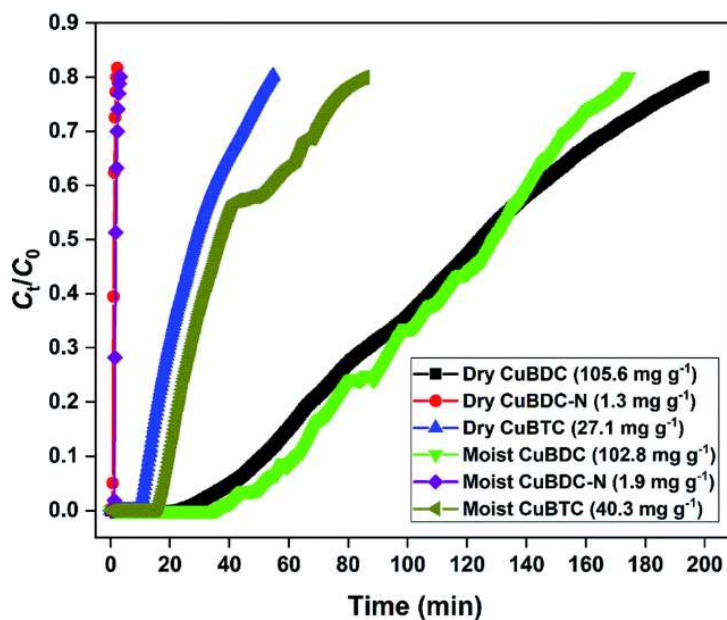


Figure 2-11: H₂S breakthrough curves of Cu-MOFs [158]

Table 2-2: Summary of H₂S scavenger used in drilling fluids.

Material	Dose	H ₂ S breakthrough capacity (mg/g)	H ₂ S saturation capacity (mg/g)	references
ZnO	0.1 wt. %	5.5	35.1	[12]
Cu(NO ₃) ₂ ·3H ₂ O		15.8	146.8	
KMnO ₄		125.3	307.5	
Triazine	1.0 g	-	217*	[25]
Mono ethylene amine (MEA)		-	270*	
Triazine	1.0 g	-	235.5*	[11]
Iron-gluconate		-	194.8*	
Steel waste		-	172.8*	

*(mg/L)

CHAPTER 3

MATERIALS AND METHODS

3.1 Background

This chapter provides an overview of the synthesis procedure for the scavenger nanoparticles. Additionally, the chapter presents the characterization techniques employed to thoroughly analyze the properties of the synthesized nanoparticles. A detailed description of the formulation steps for the drilling fluid, as well as the measurement of its rheological properties is provided. Furthermore, the chapter delves into the investigation of the H₂S scavenging capacities of the nanoparticles, offering a step-by-step account of the study.

3.2 Materials

All chemicals and additives used in water-based drilling fluid formulation and synthesis of the scavenger nanoparticles were analytical grade materials with high purity. Cobalt nitrate hexahydrate [Co(NO₃)₂.6H₂O, purity≥98%, MW=291.0347 g/mol, Sigma-Aldrich], Copper nitrate hexahydrate [Cu(NO₃)₂.6H₂O, purity≥98%, MW=241.6 g/mol, Sigma-Aldrich], Magnesium nitrate hexahydrate [Mg(NO₃)₂.6H₂O, purity≥99%, MW=256.4065 g/mol, Sigma-Aldrich], Iron(III) nitrate nonahydrate [Fe(NO₃)₃.9H₂O, MW= 404 g/mol, purity≥98%, Sigma-Aldrich], Sodium Hydroxide [NaOH, purity≥99%, MW= 39.99711 g/mol, Sigma-Aldrich], Sodium Carbonate [Na₂CO₃, purity≥99.5%, MW= 105.98844 g/mol, Sigma-Aldrich], Potassium Hydroxide [KOH, purity≥99.99%, MW=56.11g/mol, sigma-Aldrich], Calcium Carbonate [CaCO₃, purity≥98.5%, MW=100.09 g/mol, Sigma-Aldrich], Ammonium Hydroxide [NH₄(OH), 28-30% NH₃, MW= 78.002 g/mol, Sigma-

Aldrich], Starch $[(C_6H_{10}O_5)_n]$, Millipore], Bentonite [Sigma-Aldrich], and 2-methylimidazole $[C_4H_6N_2]$, purity $\geq$ 99%, MW= 82.10 g/mol, Sigma-Aldrich] were used. The materials and additives used for preparation of drilling fluids are listed in Table 3-1. All the chemicals and additives were used as received without any further purification.

Table 3-1: Composition of the 9 ppg WBM.

Steps	Mixing time (min)	Mixing rate (rpm)	Additives	Function	Quantities
1	-	-	Distilled water	Base fluid	350.0 mL
2	30	2400	Bentonite	viscofier	20.0 g
3	30	2400	Xanthan Gum	fluid-loss control	0.2/0.4 g
4	30	2400	Starch	fluid-loss control	6.0/10 g
5	10	2400	KOH	pH control	0.5 g
6	20	2400	CaCO ₃	weighting agent	30.0 g
7	20	1200	ZIF-67/LTH	H ₂ S scavenger	0-1wt. %

3.3 Methods

3.3.1 Synthesis of ZIF-67

ZIF-67 nanoparticles were synthesized according to the method reported previously by [159,160] with slight modifications. Briefly, 0.11 mols of $Co(NO_3)_2 \cdot 6H_2O$ was completely dissolved in 80 ml distilled water under magnetic stirring for 10 min. In another volumetric flask, 0.22 mols of 2-methylimidazole was completely dissolved in 200 ml of aqueous NH_4OH solution. The 2-methylimidazole solution is then quickly poured into the Cobalt nitrate solution and the resulting purple suspension is continuously stirred for 30 min. The purple suspension formed is centrifuged at 10000 rpm and washed with distilled water until a pH of supernatant of 7. The obtained ZIF-67 nanoparticles are dried overnight at 60 °C. Finally, ZIF-67 nanoparticles were sieved with a 450-micron mesh and stored for subsequent use.

3.3.2 Synthesis of CuMgFe-LTH

The CuMgFe-LTH was synthesized by co-precipitation followed by hydrothermal treatment at 150 °C. Briefly, a 150 mL metallic solution containing 12.70 mmol $\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 6.35 mmol $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, and 6.35 mmol $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, and a 150 mL alkali solution containing 50.78 mmol NaOH and 3.18 mmol Na_2CO_3 , were prepared in separate volumetric flasks. The molar ratios of $\text{Cu}^{2+}/\text{Mg}^{2+}$ and $(\text{Cu}^{2+}+\text{Mg}^{2+})/\text{Fe}^{3+}$ were maintained at 2/1 and 3/1, respectively. The two solutions were slowly added dropwise simultaneously into a beaker containing 100 mL distilled water, initially at a pH of 10, while continuously stirring with the aid of a magnetic stirrer. The pH of the mixture in the beaker was maintained between pH 9.5 - 11 during the addition of the metal and alkali solutions. After the complete addition of the above solutions, the reaction mixture was left to stir at room temperature for 30 min to aid in the formation of the triple hydroxide layers. The resulting product was transferred into an autoclave reactor for hydrothermal treatment at 150°C for 24 h. The product obtained after the hydrothermal treatment was centrifuged at 6000 rpm and washed seven times with distilled water to get rid of impurities and unwanted ions. Finally, the synthesized CuMgFe-LTH was dried in an oven at 80 °C.

3.3.3 Synthesis of LTH/ZIF-67 nanocomposite

Three (3) LTH/ZIF-67 nanocomposites with different weight ratios (i.e., 2/1, 1/1 and 1/2) were prepared as presented in Table 3-2. To prepare each nanocomposite, the desired mass of the LTH is first dispersed in an aqueous cobalt nitrate precursor solution of the required concentration by stirring for 10 min followed by ultra-sonication for 1 h (50% Amplitude, 30 sec on, 3 sec off). Then 2-methylimidazole and NH_4OH solution mixture of also the required concentration is poured into the LTH-Co solution and left to stir for 1 h. The obtained nanocomposite is then centrifuged at 6000 rpm, washed seven times with distilled

water to get rid of impurities, and dried at 80 °C. Finally, nanocomposite is ground, sieved with a 450-micron mesh, and stored for subsequent use.

Table 3-2: Weight ratio of ZIF-67 and LTH in the nanocomposites.

Nanocomposite	LZ1	LZ2	LZ3
Weight ratio (LTH: ZIF-67)	2:1	1:1	1:2

3.3.4 Aqueous drilling fluid formulation

The compositions, mixing sequence and mixing time of the water-based drilling fluid is illustrated in Table 3-1. The drilling mud formulations were prepared by adding various additives at required proportions to distilled water as the base fluid and mixed at 2400 rpm with the aid of a laboratory mixer. The additives were specifically used to control pH, viscosity, filtration loss, gel strength, and filter cake formation. Briefly, bentonite is first dispersed in the distilled water base fluid, then filtration loss agents (Xanthan Gum and Starch) are added. The pH control agent (KOH) is then added followed by weighting agent ($\text{Ca}(\text{CO}_3)$). Finally, the H_2S scavengers/synthesized nanoparticles were added at the specified concentrations.

3.3.5 Breakthrough H_2S study

The H_2S scavenging test were conducted based on previous report of [161] with slight modifications to determine the H_2S scavenging capacities of the drilling fluid formulations. The tests were carried out at room temperature and atmospheric pressure. The schematic illustration of the setup is depicted in Figure 3-1. In each H_2S scavenging test, 10.0 g each drilling fluid formulation of interest was placed in a bubble column. The inlet of the bubble column was connected to a cylinder that contained 100ppm of H_2S which served as a

continuous H₂S source. The outlet of the bubble column was connected to an H₂S detector with a 0.1 ppm detection limit. A flowmeter was mounted to control the inlet gas flowrate at 100mL/min throughout the experiment. The outlet concentration of the H₂S was continuously monitored and recorded until breakthrough and saturation time were reached for each drilling fluid sample. The amount of H₂S scavenged at breakthrough and saturation time were calculated using equations 3-1 and 3-2 respectively. The condition for the breakthrough experiment is shown in Table 3-3.

$$\text{Breakthrough Capacity (mg/L)} = \frac{Q_v \rho_{H_2S} \int_0^{t_b} (100 - C_{out}) dt}{V f} \quad (3-1)$$

$$\text{Saturation Capacity (mg/L)} = \frac{Q_v \rho_{H_2S} \int_0^{t_s} (100 - C_{out}) dt}{V f} \quad (3-2)$$

Where Q_v is the inlet volumetric gas flow rate (mL/min), ρ_{H_2S} is density of H₂S (1.391 mg/ml), t_b is the breakthrough time (min), t_s is the saturation time (min), V is the volume of scavenger (mL), f is conversion factor (10^6), and C_{out} is the outlet H₂S concentrations (ppmv), respectively.

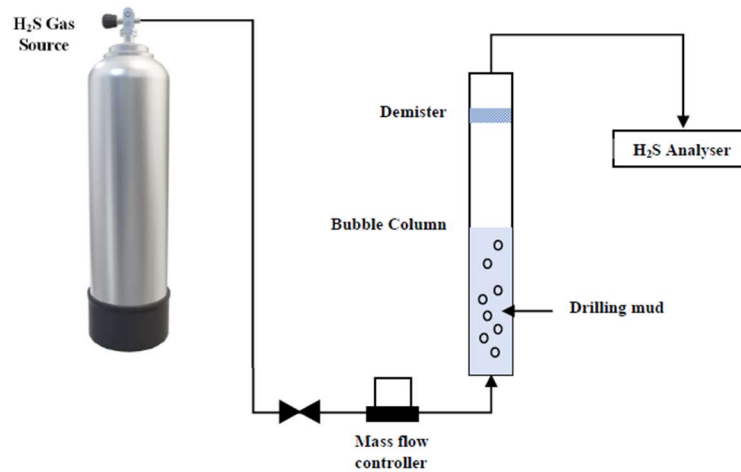


Figure 3-1: Illustration of the H₂S scavenging setup.

Table 3-3: Conditions for the H₂S breakthrough studies

Parameter	Value
Mass of WBM samples (g)	10
H ₂ S flowrate (mL/min)	100
H ₂ S breakthrough concentration (ppmv)	0.5
H ₂ S saturation concentration (ppmv)	100
Minimum H ₂ S detection limit (ppmv)	0.1
Maximum H ₂ S detection limit (ppmv)	100
Temperature (°C)	~ 25

3.3.6 Measurement of the rheological properties

The rheological parameters such as the plastic viscosity (PV), apparent viscosity (AV), yield point (YP), 10-s/10-min gel strength (GS), were determined according to the American Petroleum Institute (API) standard operating procedure with the aid of a FANN viscometer (Model M3600, Grace Instrument) at 120 °F and atmospheric pressure. The Bingham plastic model was adopted to calculate the rheological parameters such as PV, AV and YP based on the dial readings measured at 600 rpm and 300 rpm using the equations (3-3), (3-4), and (3-5) given below. The 10-s and 10-min gel strengths were measured at a low shear rate of 3 rpm after subjecting the mud to static periods of 10s and 10 min, respectively.

$$PV(cP) = \phi_{600rpm} - \phi_{300rpm} \quad (3-3)$$

$$YP\left(\frac{lb}{100ft^2}\right) = \phi_{300rpm} - PV \quad (3-4)$$

$$AV(cP) = \frac{\phi_{600rpm}}{2} \quad (3-5)$$

Where ϕ_{600rpm} and ϕ_{300rpm} are dial reading at 600 rpm and 300 rpm, respectively.

3.3.7 Measurement of API low temperature-low pressure filtration loss

The evaluation of the filtration loss volume and filter cake thickness for drilling fluid formulations was carried out using the API filter press under conditions of low temperature and low pressure. A schematic illustration of the API fluid loss set up is presented in Figure 3-2. To conduct the experiment, a filtration cell equipped with a mesh having a pore size of 10 μm was loaded with 350 mL of the respective drilling fluid formulation. Subsequently, an applied differential pressure of 100 psi was exerted on the sample at ambient temperature over a duration of 30 min. The resulting filtrate volume was collected and recorded using a graduated cylinder. Additionally, an assessment of the thickness of the resultant filter cake was performed as part of the analysis using a graduated ruler.

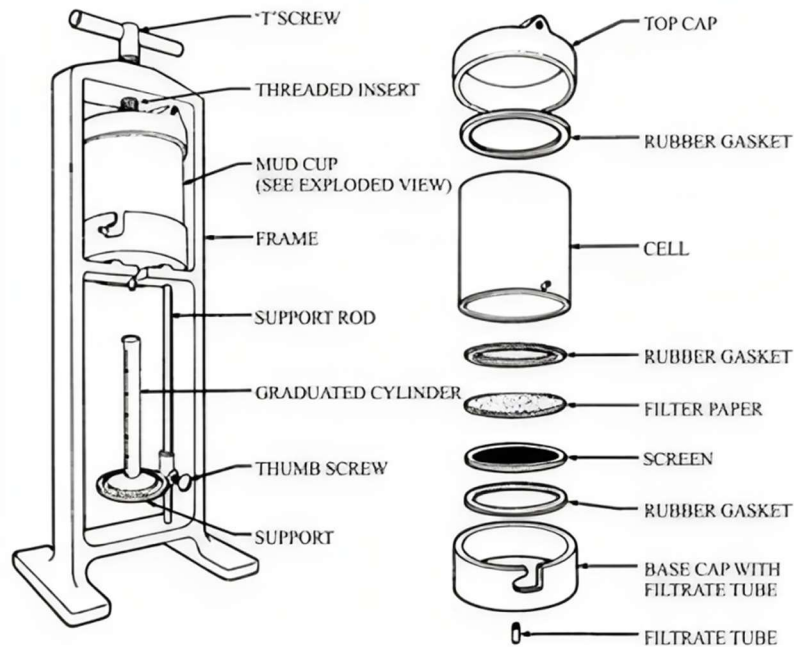


Figure 3-2: Schematic of the API filter press [162].

3.4 Characterization of materials

3.4.1 Powder X-Ray Diffraction Analysis (XRD)

The crystal structure and phases of the synthesized nanoparticles were characterized by X-ray diffraction (XRD). The XRD measurements were carried out using Cu K α radiation at 40 kV and 30 mA, scanning over a 2-theta range of 5–65°.

3.4.2 Fourier Transform Infrared Spectroscopy (FTIR)

Fourier transform infrared (FTIR) spectroscopy was carried out to confirm the presence of functional groups and verify the formation of synthesized nanoparticles. The FT-IR spectra were measured by performing 32 scans across the wavenumber range of 400 to 4000 cm⁻¹.

3.4.3 Thermogravimetric Analysis (TGA)

The TGA curves of the synthesized nanoparticles were measured to evaluate their thermal stability for drilling fluid application. This was carried out under inert nitrogen (N₂) atmosphere at a heating rate of 10 °C/min over the temperature range of 30 to 900 °C.

3.4.4 Nitrogen Adsorption-Desorption Isotherm

The nitrogen (N₂) adsorption/desorption isotherms of the synthesized nanoparticles were measured at a temperature of -196 °C, covering a partial pressure(P/P_o) range from 0 to 1. These isotherms were then analyzed using the Brunauer-Emmette-Teller (BET) equation. The purpose of this analysis is to determine the textural properties of the nanoparticles, including their specific surface area, pore volume, and pore size. By conducting the BET measurement, we aim to gain insights into the structural characteristics and porosity of the nanomaterials.

CHAPTER 4

H₂S SCAVENGING PERFORMANCE AND RHEOLOGICAL PROPERTIES OF ZIF-67 NANOPARTICLES IN WATER-BASED DRILLING FLUID

4.1 Introduction

Drilling fluids are multi-component systems that contain many additives carefully formulated to perform specific functions during drilling operations. Some of these functions include providing hydrostatic control, maintaining wellbore stability, minimizing the corrosion of handling equipment, controlling formation pressure, cooling, and lubricating the drilling bit, suspending, and circulating the drilling cuts, sealing the permeable well formations, and minimizing formation damage [163,164]. The choice and quantity of additives that make up drilling fluid are primarily vital to attain optimal rheological properties, fluid loss prevention, corrosion inhibition, and mitigation of sour gas exposure. There are three main types of drilling fluids that are currently being used, namely, water-based, oil-based, and synthetic-based muds [165,166]. Water based mud is generally preferred because it is relatively cheap, environmentally friendly, and has low toxicity [167,168]. Even though oil-based and synthetic-based muds might offer superior drilling performance, they are more expensive, difficult to handle, and environmentally unsafe due to the toxicity of the mineral oils and synthetic solvents used in their formulation [42,105].

In the drilling of subsurface formations, the presence of sulfhydryl compounds such as mercaptans, thiols, dithiol acids, etc., causes major operational issues [42]. Among the sulfhydryl compounds, H₂S is one of the most encountered. H₂S exists naturally in oil and gas reservoirs due to the biological decomposition of sulfate-containing organic matter or

minerals by the sulfate-reducing bacteria (SRB) under anaerobic conditions, and by the thermochemical reduction (TCR) of reservoir biomass or other sulfhydryl compounds catalysed by the presence of anhydrites [169,170]. In addition to drilling operations, technologies employed for enhancing oil and gas production and recovery, such as water flooding of low permeable reservoirs, also account for the generation of H₂S [15]. Under such instances, SRB or other microbes from the surface penetrate, breed, colonise the reservoir and subsequently induce the reduction of sulfate (SO₄²⁻) containing minerals and biomass thereby increasing H₂S content [171].

H₂S is a colourless, flammable, and highly toxic gas with a distinct odour of rotten egg only detectable at low concentrations (0.01-1.5 ppm) [9,30]. The exposure to H₂S poses substantial health and operational risks to drilling personnel, equipment, and the rheology of the drilling fluids. According to the Occupational Safety and Health Administration (OSHA) and the U.S. National Institute for Occupational Safety and Health (NIOSH), the maximum recommended or permissible H₂S exposure limits within a 10 min period should be 50 ppm and 10 ppm, respectively [30]. Prolonged exposure, even at low H₂S concentrations (<50 ppm), could cause serious adverse health effects such as respiratory disturbances, loss of consciousness, and eventually death. Also, the exposure of metallic structures to H₂S induces pitting corrosion as a result of the formation of ferrous sulfide scale and free hydrogen ions [20]. The free hydrogen ions penetrate metallic structures causing hydrogen embrittlement, which might lead to further equipment failures [115]. Moreover, the presence of H₂S in the drilling environment has significantly negative effects on the rheology of the utilized mud. The exposure of drilling mud to H₂S could potentially lead to a decrease in mud viscosity, reduction of gel strength, and compromise wellbore

stability. H₂S is both toxic and explosive, so protection measures must be taken to prevent its build-up [172]. Such H₂S build-up will result in serious health, safety, and economic penalties, requiring the proper mitigation of this life-threatening gas during drilling operations.

Several classes of materials have been studied and incorporated into drilling fluid formulations for H₂S scavenging. These classes of materials generally remove H₂S through chemical reactions or physical adsorptive mechanisms that capture H₂S from sour streams, eliminating the health and operational risks resulting from the exposure to this lethal gas [16,172]. Materials such as transition metals, oxidizing agents, amines, aldehydes, and triazine have been widely studied [118,172,173]. These scavengers are available either in solid or liquid form. One of the key technical requirements is that incorporating an H₂S scavenger into a drilling fluid should not adversely affect its rheological properties.

Recently, metal organic frameworks (MOFs) have gained a great deal of interest for various applications in several fields, such as gas purification through the selective adsorption of impurities, separation processes, catalysis, chemical sensing, proton conduction, and drug delivery, among other emerging applications [174]. The interest in utilizing MOFs in these applications is fueled by the excellent properties these porous materials possess, such as large surface area, tunable pore size, surface functionalities, and good thermal stability [146,175]. MOFs are inorganic-organic hybrids with extremely high porosity and crystallinity. They are made up of networks of metal-ion anodes connected to polydentate organic ligands through coordinate bonds [149]. Although some MOFs have demonstrated superior performance towards the sorption of polar and non-polar gases under dry conditions, the structures of most MOFs tend to collapse in aqueous media due

to the weakening of their metal-organic ligand coordinate bonds [176]. This water-instability limits the applications of MOFs in operations where aqueous media (such as drilling operations) are utilized/encountered.

Recently, a new class of MOFs (i.e., zeolitic imidazolate frameworks (ZIFs)) has emerged as more water-stable materials with usually superior textural properties, tunability, and thermal/chemical stability, making them excellent candidates for many applications [147,148]. These ZIFs are composed of $\text{Co}^{2+}/\text{Zn}^{2+}$ and an imidazole ligand and shows a similar morphology as conventional zeolites, which gives them the first part of their name [150]. One of the most attractive ZIFs is ZIF-67, which possesses exceptional water stability, abundant coordinated open metal sites, ease of fabrication in aqueous media, high yield, and enormous potential for utilization in water phase applications [154].

One of the attractive ZIF-67 applications is its utilization in the formulation of drilling muds as an H_2S scavenger and, potentially, a rheological properties enhancer. However, there are no published studies in the literature on the inclusion of ZIF-67 or any other ZIF (or even any MOF) material in the formulation of any drilling fluid, to the best of our knowledge. Accordingly, the key aim of this study is to synthesize ZIF-67 NPs and include them in the formulation of water-based muds. After the synthesis of ZIF-67 NPs, they will undergo typical characterizations (i.e., X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), thermogravimetric analysis (TGA), and nitrogen adsorption/desorption measurements) to get insights into their crystallinity, thermal stability, and textural properties. Then, these ZIF-67 NPs will be incorporated into water-based drilling formulations. The H_2S scavenging performance of the prepared formulations will, then, be investigated. Additionally, the rheological properties (i.e., plastic viscosity,

apparent viscosity, yield point, gel strength, filtration loss) of the formulated water-based muds in the absence and the presence of different ZIF-67 contents will be thoroughly investigated. Furthermore, the obtained shear rate-shear stress data will be subjected to modelling in order to get numerical insights into the effect of the addition of ZIF-67 NPs into the water-based mud formulations on their flow behaviour. Finally, the drawn conclusions from this study and recommendations for future work will be provided.

4.2 Results and discussion

4.2.1 Characterization of ZIF-67

The FT-IR analysis was conducted to determine the surface functional groups on the synthesized ZIF-67 NPs. Figure 4-1 depicts the FT-IR spectra of the ZIF-67 NPs. The 2-methylimidazolate framework exhibited broad and strong absorption peaks between 1570 cm^{-1} – 683 cm^{-1} that could be linked to the vibration and bending of the imidazole ring [177,178]. The peak appearing at 3630 cm^{-1} could be assigned to the O-H stretching vibration of moisture in the KBr deliquescence or the analysed ZIF-67 sample [179]. The peak at 2978 cm^{-1} could be assigned to the aromatic and aliphatic C–H stretching vibration of the methyl group in the imidazole ring [180]. Further, the peak at 1576 cm^{-1} is attributed to the presence of C=N stretching vibration in the imidazole ring [181]. The stretching and bending vibrations of the C–N in the aromatic imidazole ring is characterized by the peaks at 1146 and 995 cm^{-1} , respectively [179]. The absorption peak located at 683 cm^{-1} is attributed to the aromatic sp^2 C–H bending vibration [180]. The peak at $455\text{--}422\text{ cm}^{-1}$ is assigned to the Co–N bond stretching vibration of the ZIF-67 nanocrystals, which is in good agreement with the previous reports [181,182]. Therefore, FT-IR results confirm the formation of ZIF-67.

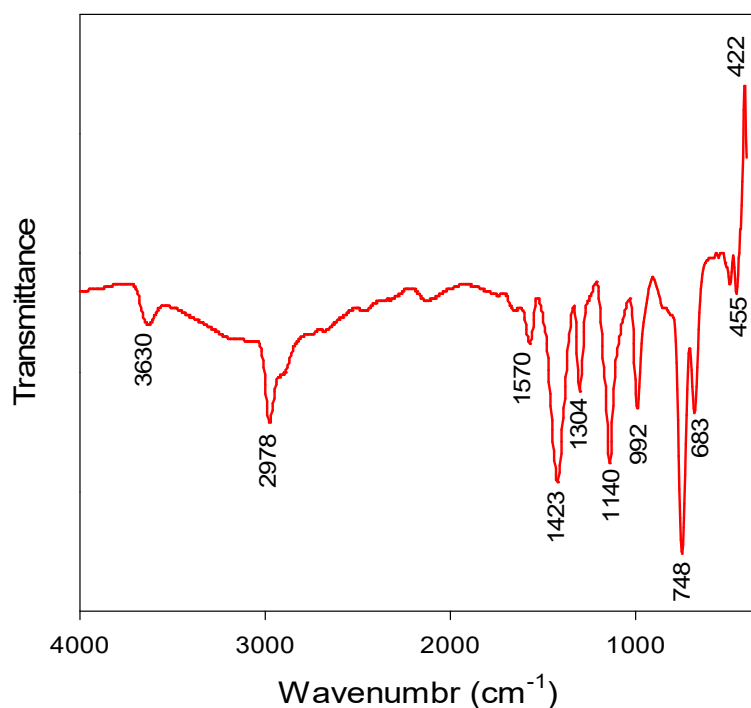


Figure 4-1: FT-IR spectra of the prepared ZIF-67.

The crystal structure and phase composition of the synthesized ZIF-67 NPs were examined by XRD. As illustrated in Figure 4-2, the XRD pattern exhibited well-defined peaks at 2θ of 7.41, 10.44, 12.78, 14.76, 16.53, 18.09, 22.17, 24.54, 25.65, 26.70, 29.70, 30.63, 31.56, and 32.49° which correspond to the (011), (002), (112), (022), (013), (222), (114), (233), (224), (134), (044), (334), (244), and (235) crystal planes, respectively. Notably, the intensities of the peaks at 2θ of 12.78 and 7.41 attributed to the (112) and (110) planes, respectively, are much stronger than other peaks, illustrating the favorable orientation of the (112) and (110) directions. Also, the sharp diffraction peaks indicate the high crystallinity and purity of the synthesized ZIF-67. Overall, the XRD pattern of ZIF-67 agrees with the crystallographic structure described in previous reports [181,183], indicating that ZIF-67 was synthesized successfully.

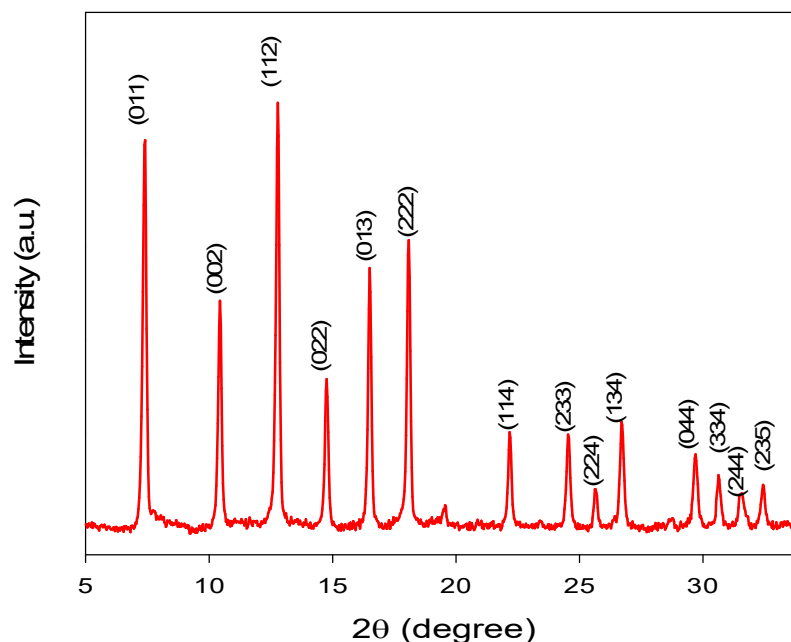


Figure 4-2: XRD patterns of the prepared ZIF-67 NPs.

The BET surface area, pore volume, and pore size of the synthesized ZIF-67 were analysed by the Nitrogen (N_2) adsorption-desorption isotherm at 77 K. Figure 4-3 illustrates the nitrogen adsorption-desorption isotherm of ZIF-67 NPs. The isotherm shows a characteristic Type I adsorption behaviour, which is typical for microporous materials primarily due to the steep increase in the N_2 adsorption on ZIF-67 at low relative pressure [184]. The BET surface area was calculated to be $1158 \text{ m}^2/\text{g}$. The average pore size, specific pore volume, and average particle size based on the adsorption/desorption isotherm were estimated to be 1.71 nm, $0.495 \text{ cm}^3/\text{g}$, and 20.7 nm, respectively.

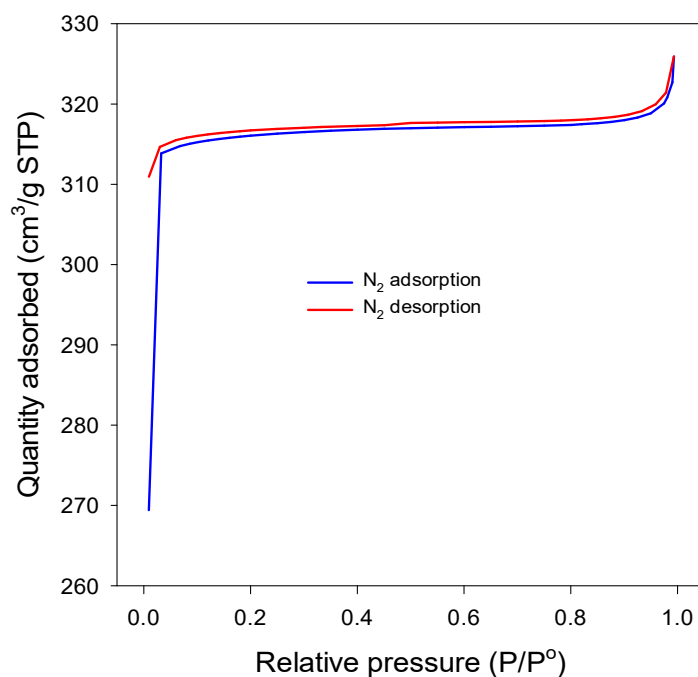


Figure 4-3: The N₂ adsorption/desorption isotherms on/from ZIF-67 NPs.

Further, the thermal stability of the prepared ZIF-67 NPs was investigated by thermogravimetric analysis, and the result is depicted in Figure 4-4. The synthesized ZIF-67 NPs show an initial weight loss of only ~20% up to a temperature of ~200 °C, which corresponds to the removal of bound water moisture and other guest molecules [185]. No further weight loss was observed upon increasing the temperature up to about 500 °C. Above 500 °C, the framework of ZIF-67 collapses and the organic linker (i.e., 2-methylimidazole) decomposes, resulting in about 34% weight loss. Nonetheless, the TGA result presented in Figure 4-4 indicates that the prepared ZIF-67 material is thermally stable up to ~500°C. This excellent thermal stability suggests its suitability for drilling applications and H₂S scavenging since the maximum temperature encountered during drilling operations is below 500 °C.

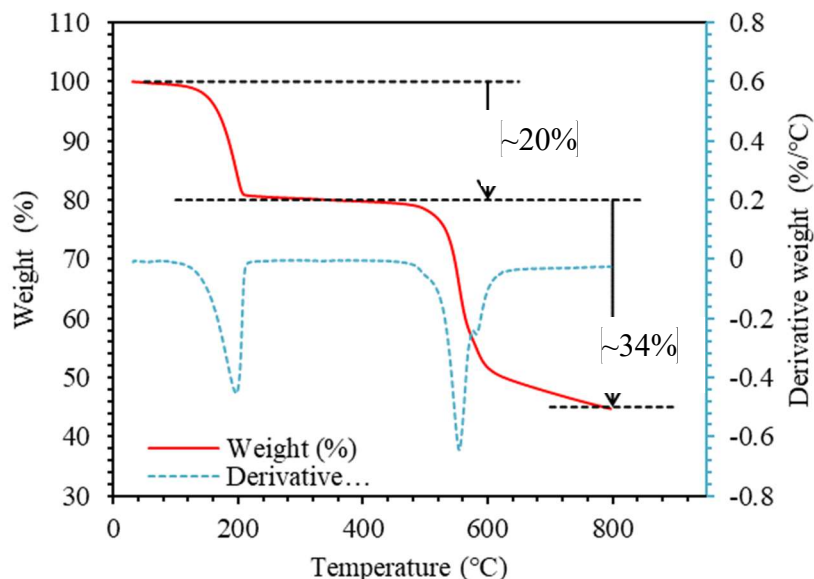


Figure 4-4: Stability of the prepared ZIF-67 NPs measured using TGA under N₂ gas environment.

4.2.2 Hydrogen sulfide removal

The H₂S scavenging performance of the base and the ZIF-67-containing drilling fluids were evaluated in a bubble column under continuous flow of the sour gas (100 ppmv H₂S in methane). The obtained H₂S breakthrough curves are depicted in Figure 4-5, and the corresponding calculated H₂S scavenging capacities are given in Table 4-1. The selected formulations for the H₂S scavenging test are the base mud without any scavenger, and the mud with 1 wt.% ZIF-67 NPs. The base drilling mud exhibited a very low scavenging capacity, whereas the ZIF-67-based mud showed a remarkable H₂S scavenging performance. The breakthrough time of the base mud was 34.5 min, corresponding to 52.3 mg H₂S/L scavenging capacity. At saturation, the total amount of H₂S scavenged by the base mud was 294.6 mg H₂S/L. The observed scavenging capacities of the base mud could be attributed to the presence of free metal ions and the solubility of H₂S in the fluid. As illustrated in Figure 4-5, the H₂S scavenging capacities of the ZIF-67-based mud are

several folds higher than those of the base mud. Specifically, the breakthrough time of 842 min, corresponding to 1259.8 mg H₂S /L was recorded in the presence of ZIF-67 NPs. The saturation time and the H₂S capacity scavenged at saturation were 1440 min and 1758.1 mg H₂S/L, respectively.

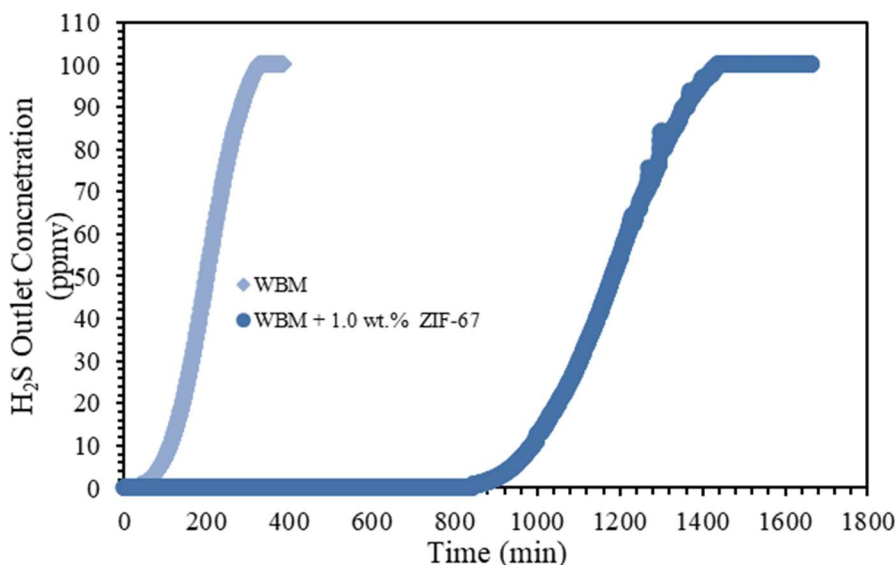


Figure 4-5: H₂S scavenging breakthrough curve using the base and ZIF-67 containing water-based drilling fluids.

Hydrogen sulfide under aqueous conditions can exist as either H₂S, HS⁻ or S²⁻ primarily depending on the pH of the medium [116,186]. The pH of the various drilling fluid formulations prepared was maintained within the range of 11-11.5. The dominant dissolved fraction of H₂S present in the drilling muds upon the bubbling of the sour gas are HS⁻ ($\geq 95\%$) and S²⁻ ($\leq 5\%$) [186]. The H₂S and this dissolved HS⁻ fraction is actively scavenged by the uncoordinated open metal (Co(II)) sites and basic sites originating from the N-H group on the imidazole ring as depicted in Figure 4-6 [187,188]. Although, the removal of H₂S from drilling fluid using some chemical additives has been reported in the published literature [9,12,16,25,122,123,173,189], there is a complete lack of studies on the

utilization of any ZIF or even any metal-organic framework (MOF) for this purpose, which highlights the novelty of the current study.

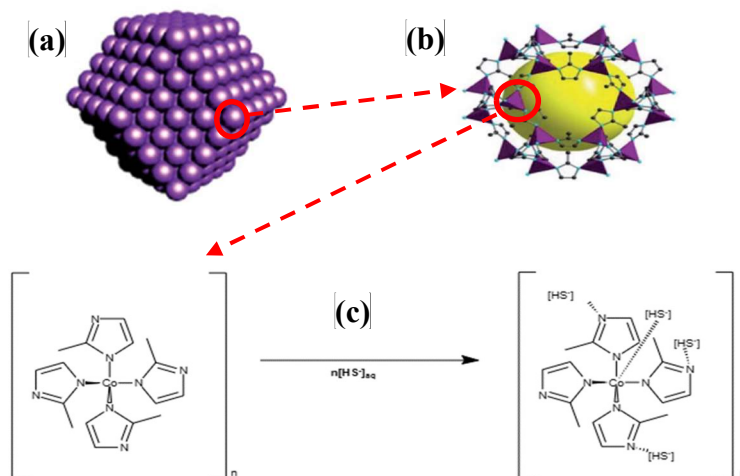


Figure 4-6: Schematic representation of the structural information of ZIF-67 NPs (a-b) [190], and (c) possible mechanism of H₂S Scavenging on ZIF-67 NPs.

Table 4-1: Breakthrough time, breakthrough capacity, saturation time, saturation capacity of drilling muds.

Parameters	WBM	WBM + 1 wt.% ZIF-67
Breakthrough time (min)	34.5	842
Saturation time (min)	325	1,440
Breakthrough capacity (mg/g)	-	117.19
Saturation capacity (mg/g)	-	163.55
Breakthrough capacity (mg/L)	52.3	1,259.8
Saturation capacity (mg/L)	294.6	1,758.1
Breakthrough capacity (g/barrel)	8.3	200.3
Saturation capacity (g/barrel)	46.8	279.5

As shown in Table 4-1 and Figure 4-5, the ZIF-67 NPs exhibited excellent H₂S scavenging performance. However, besides the H₂S scavenging performance, the addition of a scavenger should not compromise the mud flowability and rheology. To evaluate the

impact of the ZIF-67 NPs on the rheological properties of the mud, a series of mud formulations with varying amounts of ZIF-67 (0, 0.05, 0.25, 0.5, 0.75, and 1 wt.%) were prepared. All the key rheological parameters were measured, including PV, YP, AV, and gel strengths (10 s and 10 min). These rheological properties depend primarily on the physical properties of the additives, their interactions within the base fluid, and their concentration [191]. The result and discussion of the effect of the ZIF-67 on the rheological parameters is discussed in subsequent sections.

Table 4-2: Recommended rheological properties for WBM [42,192,193].

Rheological Parameters	Specifications
Plastic viscosity (cP)	8-35
Yield point (lb/100 ft ²)	5-50
10 s gel point (lb/100 ft ²)	<15
10 min gel point (lb/100 ft ²)	< 35
API fluid loss (mL)	< 15

4.2.3 Effect of ZIF-67 on the PV and AV

Plastic viscosity (PV) is one of the key rheological parameters for evaluating the viscosity of drilling mud systems at an infinite shear rate based on the Bingham model [191]. It quantifies the flow resistance of drilling muds caused by mechanical friction between solid particles in the mud [89]. Higher magnitudes of PV indicate a correspondingly higher resistance and particulate friction within the drilling mud, which is uneconomical, increases the power required for circulation and decreases the rate of penetration (ROP). Conversely, PV values below the specified ranges are deleterious to fluid loss, increase sagging of cuttings, and reduce hole cleaning efficiency. For successful and continuous recirculation of drilling mud, the PV should be maintained within the specified range to maintain the

hydrostatic pressure, reduce energy requirements for pumping, prevent settling of cuttings, maintain wellbore stability, and enhance the drilling rate [192,194]. Figure 5-8 depicts the PV and AV of the WBM with different ZIF-67 contents. As seen in Figure 4-7, the plastic viscosity increases with increasing NPs concentration in the mud. The base mud had a PV of 15.56 cP. The incorporation of the NPs resulted in an increase in solid content and a gradual increase in friction between the mud particles, causing the observed increase in plastic viscosity. However, at 0.05 wt.% ZIF-67, the plastic viscosity drops slightly by 1.29%. This slight reduction could be due to the initial disruption of the gel formation within the drilling mud [195]. Moreover, the ZIF-67 NPs at such a low concentration in the mud acts as a ball bearing between the larger particles present, thereby reducing inter-particulate friction [105]. The highest plastic viscosity of 19.47 cP is measured at 1 wt.% ZIF-67. However, even at this ZIF-67 content, PV is still far from the maximum recommended limit, as shown in Table 4-2.

The apparent viscosity (i.e., the ratio of shear strain to shear stress) is referred to as the effective viscosity of drilling mud when examined at a finite shear rate [194]. According to the Bingham model, it is one half of the dial reading at 600 rpm of shear strain. As depicted in Figure 4-7, the base mud had an apparent viscosity of 19.08 cP. Similarly, at 0.05 wt.% ZIF-67, the apparent viscosity reduced marginally by about 1.52%, which is likely due to the decrease in particulate friction, ball bearing effect, and gel disruption. Subsequent increase in the NPs resulted in a steady increase in the apparent viscosity up to a maximum value of 26.71 cP at 0.75 wt.% ZIF-67 NPs in the mud. A reduction of the apparent viscosity by about 4.0% was observed upon the further increase of the ZIF-67 NPs to 1 wt.%. Interestingly, the incorporation of the ZIF-67 NPs had no adverse effect on

the plastic and apparent viscosities of the drilling mud. All the measured viscosities for the ZIF-67 based muds are within the recommended range, as shown in Table 4-2. Moreover, the observed trends of the PV and AV agree with reports in the literature [89,191]. Usually, increasing the solid content would result in an increase in drilling mud viscosity, however, due to ionic and particulate interactions of the mud solids, and the physical properties of NPs such as particle size, density, and surface charge, this is not always the case as seen by the slight decrease of the AV at 1 wt.% NPs content [191].

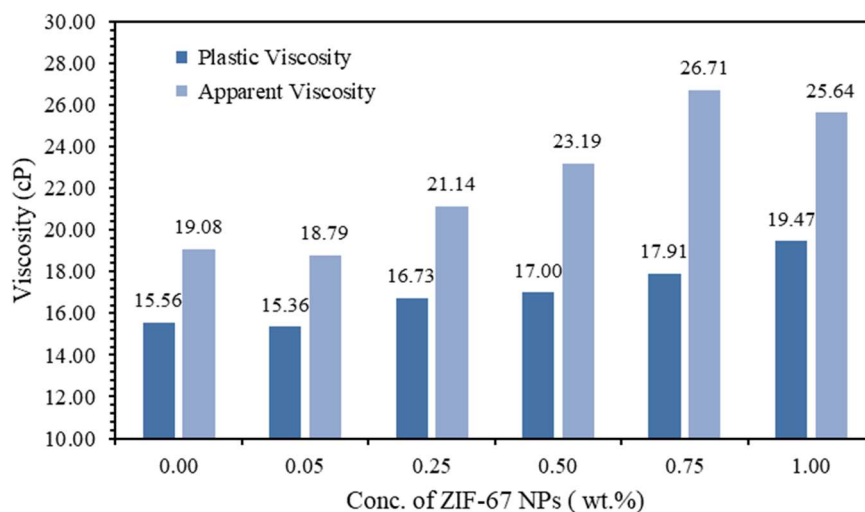


Figure 4-7: Influence of ZIF-67 NPs on viscosity of the formulated WBM.

4.2.4 Effect of ZIF-67 on the YP and Carrying Capacity

The yield point of a drilling mud is a measure of the initial resistance of the drilling fluid to flow due to electrochemical interactions [191]. The YP provides a useful indication of the carrying capacity of drill cuttings to the surface by a given mud [196]. The magnitude of the YP indicates the ability of mud to suspend and circulate cuttings [195]. As such, an optimal YP within the recommended range is desirable in drilling muds. Relatively lower YP values lead to the sagging of weighing agents and cuttings, whereas excessively high

YP increases the power requirement for circulation and affects the rate of penetration (ROP) [197].

The influence of ZIF-67 NPs on the yield point and carrying capacity is illustrated in Figure 4-8. The base mud possesses a YP of 7.05 Ib/100 ft² while the lowest and highest YP of 6.85 and 17.61 Ib/100 ft² were measured at 0.05 and 0.75 wt.% ZIF-67 NPs in the mud, respectively. The reduction in the YP of the base mud by 2.84% was observed with the addition of 0.05 wt.% ZIF-67 NPs to the base mud. The YP values increased progressively from 6.85 to 17.61 Ib/100 ft² after increasing the ZIF-67 NPs concentration from 0.05 to 0.75 wt.%. Subsequent increase in the ZIF-67 NPs concentration from 0.75 to 1 wt.% caused a reduction in YP by about 30% (it dropped to 12.33 Ib/100 ft²). The observed decrease in YP on addition of 1 wt.% ZIF-67 NPs can be attributed to the decrease in the total electrostatic potential of the drilling mud due to the agglomeration of ZIF-67 NPs [191]. However, the drop at 1 wt.% ZIF-67 NPs will not compromise the hole cleaning and wellbore stability of the ZIF-67-based mud since the result falls within the specified range shown in Table 4-2. Interestingly, the results have shown that ZIF-67 NPs can be utilized to improve the YP and enhance hole cleaning efficiency of water-based drilling fluids besides their primary role as H₂S scavenger.

Another important rheological property that is related to YP and PV, is the mud carrying capacity defined as the ratio of YP/PV. As depicted in Figure 4-8, the carrying capacity exhibited a similar trend as that observed for the yield point at various ZIF-67 NPs concentrations. This is usually the case since both parameters indicate the hole cleaning ability of drilling fluids. Interestingly, the addition of the ZIF-67 NPs resulted in an increase in the carrying capacity of the drilling fluid, which shows the multiple benefits of

incorporating ZIF-67 in drilling fluids (e.g., significant enhancement of H₂S scavenging, enhanced yield point, and improved carrying capacity).

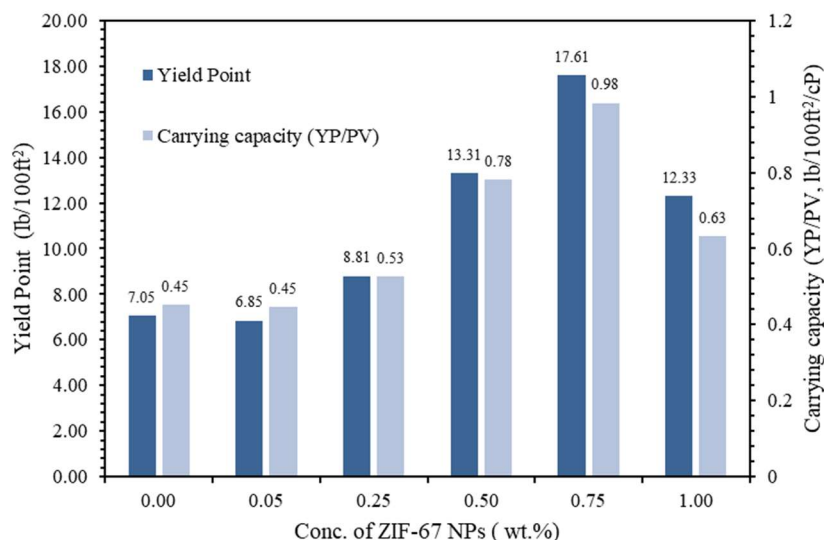


Figure 4-8: Influence of ZIF-67 NPs on yield point and carrying capacity of the formulated WBM.

4.2.5 Effect of ZIF-67 on the gel strength

The gel strength is another vital rheological parameter that is correlated to the mud ability to suspend drill cutting and the mud solids under static conditions when there is a cease of mud circulation [172]. It is a measure of intraparticle electrochemical interactions in the drilling fluid under non-flow conditions measured at 10 s and 10 min, respectively [192]. This rheological parameter is important because the drilling mud must be able to suspend drill cuttings and maintain a stable wellhole, while also transporting the cuttings to the surface. An optimal gel strength value is always required to minimize the usually excessive circulation pressure required to restart drilling mud flow and prevent sagging of drill cuttings. The influence of ZIF-67 NPs on 10 s and 10 min gel strengths is depicted in Figure 4-9. As illustrated in Figure 4-9, the gel strength increased upon the addition of ZIF-67

NPs to the base mud. The 10 min gel strength at all NPs concentrations is greater than the corresponding 10 s gel strength. The base mud had 10 s and 10 min gel strengths of 3.52 and 18.19 Ib/100ft², respectively. The 10 s and 10 min gel strength increased with increasing the ZIF-67 NPs concentration until they peaked at 0.75 wt.% ZIF-67 NPs concentration, with respective values of 13.50 and 41.87 Ib/100ft². The 10 s and 10 min gel strengths, however, reduced to 8.02 and 32.68 Ib/100ft² on the further increase of ZIF-67 NPs to 1 wt.%. This occurrence is due to agglomeration at 1 wt.% ZIF-67 NPs concentration as discussed earlier. Similar trends of the 10 s and 10 min gel strength have been reported in literature in the presence of other NPs [89,191]. Notably, the observed increase of the gel strength (10 s and 10 min) over the range of 0.05 to 0.75 wt.% ZIF-67 NPs concentration could be due to the strengthening of the gel structure and increase in electrostatic interactions within the mud upon addition of ZIF-67 NPs.

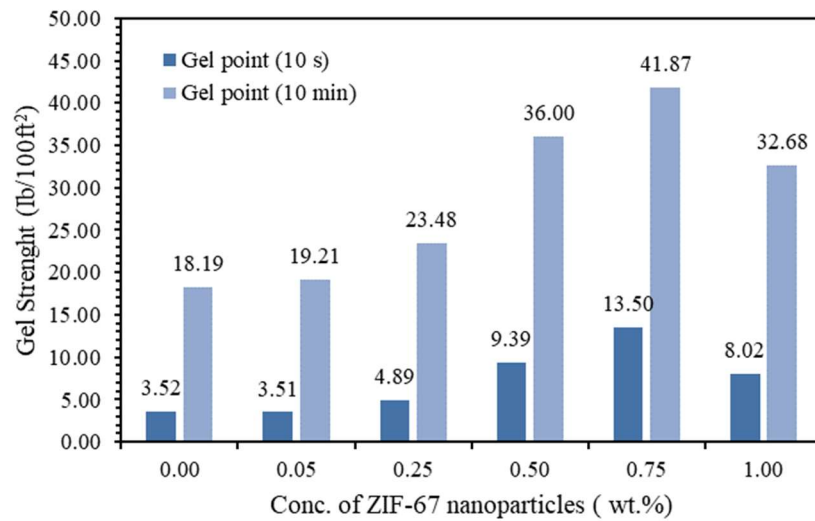


Figure 4-9: Influence of ZIF-67 NPs on the 10 s and 10 min gel strengths of the formulated WBM.

4.2.6 Effect of ZIF-67 on the on the API filtration properties

The filtration properties of drilling fluids, such as API fluid loss and API filter cake thickness, are vital parameters for the evaluation of wellbore stability of the utilized mud during drilling operations. The API fluid loss signifies the dischargeable filtrate volume of the drilling fluid when subjected to 100 psi pressure differential and ambient temperature conditions over a period of 30 min [198]. According to the API specifications, the fluid loss should not exceed the recommended value of 15 mL (Table 4-2). A high fluid loss volume will compromise the stability of drilling mud and cause excessive formation damage [42]. The filter cake is the deposited layer of the suspended drilling fluid solids during the API fluid loss test. The filter cake thickness measures the amount of solid deposited, which indicates the cake formation in the wellbore across permeable zones during drilling operations. To avoid formation instabilities, excessive fluid loss, and the sticking of drill string, an impermeable, strong, and thin filter cake is preferred [191,192,199]. The recommended thickness of filter cake is less than 3/32 inch. The 30 min API fluid loss for the base mud and the mud at 1 wt.% ZIF-67 NPs concentration is illustrated in Figure 4-10. The base mud had a fluid loss volume of 12.8 mL, whereas the maximum concentration of ZIF-67 NPs in the base mud had a fluid loss volume of 14.8 mL; the fluid loss in both cases is within the API recommended. Despite the slight increase in the fluid loss upon the addition of the maximum ZIF-67 content into the base drilling mud, the gained benefits from adding ZIF-67 in terms of the dramatic increase in the H₂S scavenging capacity and the improvement of some rheological properties much outweigh the insignificant fluid loss.

Although the API fluid loss volume of drilling fluid is usually expected to reduce in the presence of NPs due to the increase in solid content of the mud, this is not always the case since the NPs size also plays a primary role in the permeability of the deposited solids. Moreover, agglomeration at high NPs concentrations could create layers of permeable cake that will increase the fluid loss volume [89,200]. The possible increase in the inter-particle spacing of the fluid loss control agent due to the presence of ZIF-67 NPs might have slightly decreased the close packing needed to form an impermeable cake [105]. Nonetheless, the API fluid loss volume in the presence of the ZIF-67 NPs is not significantly higher than in the case of the base mud and is still within the recommended API specifications as mentioned above.

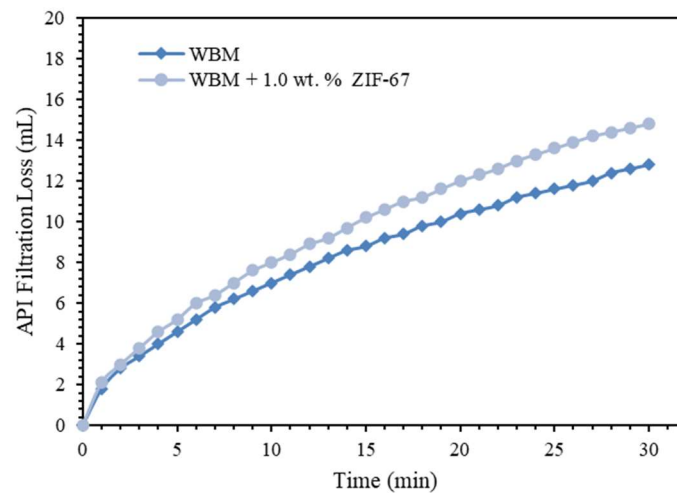


Figure 4-10: API fluid loss of the base and the 1 wt.% ZIF-67 mud formulations.

Table 4-3 and Figure 4-11 (a-b) illustrate the filter cake thickness and the images of the filter cakes obtained with the base mud and the ZIF-67-based mud, respectively. As shown in Table 4-3, the base mud had a filter cake thickness of 3/32 inch while the 1 wt.% ZIF-67-based mud had a filter cake thickness of 4/32 inch. The filter cake thickness increased with the addition of the ZIF-67 NPs. A similar result is also reported in the literature for

other nanomaterials. For instance, Mohanty et al. [191] reported on the application of zirconia-clay nanocomposite for improving the rheology of water-based mud. They found out that the addition of 0.3% of the nanocomposite resulted in a 11.39% (0.44 inch) increase in filter cake thickness when compared to that of the base mud (0.395 inch) without the zirconia-clay composite material [191]. In this study, the measured filter cake thickness corroborates the magnitudes of the fluid losses, respectively. This marginal increase in the filter cake thickness at the highest ZIF-67 dosage (i.e., 1 wt.%) used could be due to particle agglomeration. However, this increase in the filter cake is insignificant and did not adversely affect the fluid loss volume as discussed above. This is indicative that the ZIF-67 NPs would not compromise wellbore stability during drilling operations and could be successfully incorporated into drilling fluids.

Table 4-3: API filter cake thickness and lost volume.

Formulation	Cake Thickness		Lost volume (mL)
	1/32 inch	(mm)	
WBM	3	2.38	12.8
WBM + 1 wt.% ZIF-67	4	3.18	14.8

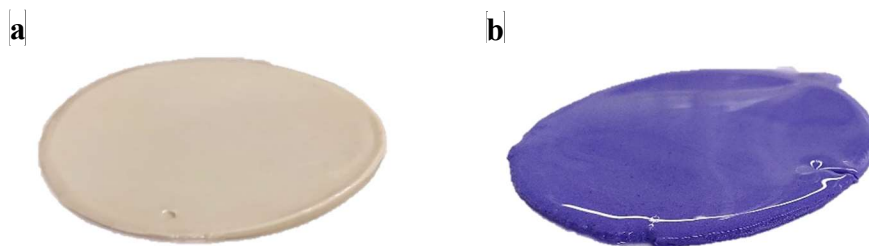


Figure 4-11: Filter cake obtained from the API filter press after 30 min (a) without ZIF-67 NPs and with (b) 1.0 wt.% ZIF-67 NPs.

4.3 Shear rate-shear stress curve and rheological modelling

The shear rate-shear stress curve demonstrates the correlation between the shear stress and shear rate of a drilling fluid. The shear stress describes the force per unit area that the fluid experiences due to its motion, while the shear rate defines the rate at which each layer of the drilling fluid moves relative to another layer. By examining this curve, the behavior of fluid viscosity exhibited and the general rheological behavior (i.e., Newtonian, or non-Newtonian) could be characterized. The shear rate-shear stress curve of the base mud and the scavenger containing mud at the various concentrations is illustrated in Figure 4-12.

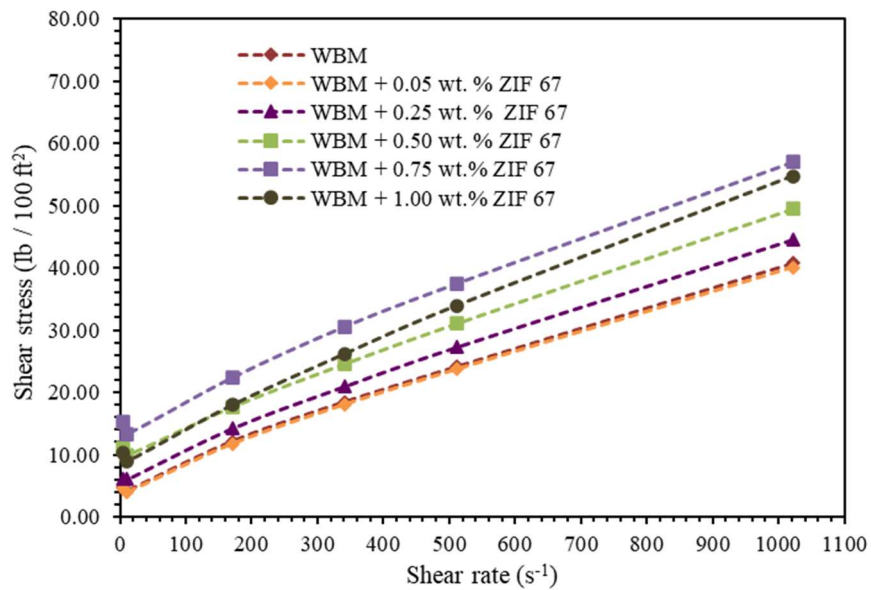


Figure 4-12: Shear stress-shear rate curves of the base and the ZIF-67 water-based mud formulations.

As depicted in Figure 4-12, the addition of ZIF-67 NPs resulted in a progressive increase in the shear stress of the drilling mud, which is primarily due to the increase in the solid content of the drilling mud. Interestingly, the drilling fluid formulation at all NPs concentrations, including the base mud, exhibited non-Newtonian shear thinning behavior, which is desired in drilling fluids [172]. This behavior enhances the mud flowability, reduces pressure or frictional losses during mud circulation, improves hole cleaning,

maintains wellbore stability, improves the rate of penetration (ROP), reduces differential sticking of drill string, and provides better drilling rates. The non-Newtonian shear thinning behavior has been also reported elsewhere for waxy crude oil [201] and crude oil nano emulsions [202–204].

Table 4-4 and Figure 4-13 shows the results obtained from the rheological modelling of the base mud formulation and those containing various ZIF-67 contents. The rheological modelling was conducted using the five most utilized models to identify the one that best describes the general behavior of the formulated water-based drilling fluid. These utilized rheological models are the Newtonian (Eqn. 4-1), Bingham Eqn. 4-2), Herschel Buckley (Eqn. 4-3), Ostwald Power Law (Eqn. 4-4), and Sisko Model (Eqn. 4-5) [71,205].

$$\tau = \mu_p \gamma \quad (4-1)$$

$$\tau = \tau_o + \mu_p \gamma \quad (4-2)$$

$$\tau = \tau_o + K_H \gamma^n \quad (4-3)$$

$$\tau = K_P \gamma^n \quad (4-4)$$

$$\tau = K_1 \gamma + K_2 \gamma^n \quad (4-5)$$

Where, τ , μ_p and γ are the shear stress, viscosity, and shear rate, respectively. K_1 is the coefficient of viscosity, K_2 , K_H and K_P are the consistency coefficients of the Sisko, Herschel Buckley, and Ostwald Power Law models, respectively. n is the flow index of the fluid (i.e., $n < 1$ represents a pseudoplastic (shear thinning) fluid, $n > 1$ represents a dilatant (shear thickening) fluid, and $n = 1$ corresponds to a Newtonian fluid).

As illustrated in Figure 4-13 (a), the fitting line of the Bingham model ($R^2=0.994$) is fairly close to the measured experimental values of the base mud. However, the rheological

models that best track the measured values of the base mud are the Herschel Buckley ($R^2=0.999$) and the Sisko model ($R^2=0.999$) since they exhibit a higher coefficient of determination (i.e., R^2) than the Bingham model. Similarly, the rheological models that best describe the various ZIF-67 mud formulations are the Herschel Buckley ($R^2 = 0.998-0.999$) and the Sisko model ($R^2 = 0.997-0.999$) since they showed a higher R^2 than the Bingham model, which had R^2 ranging from 0.994 up to 0.997 (See Table 4-4 and Figure 4-13(b-f)). Further, the flow index (n) values of the base mud according to the Herschel Buckley, Ostwald power law, and Sisko models were found to be less than 1, indicating a pseudoplastic behavior of the base drilling mud. On the other hand, the coefficient of viscosity (K_1), which describes an important property that determines the drilling fluid ability to efficiently remove cuttings from the drilled wells, suspend and transport them to the surface, and maintain wellbore stability. According to the Sisko model ($R^2=0.999$), the base mud had a coefficient of viscosity of 3.131 cP. Interestingly, the addition of ZIF-67 NPs resulted in an increase in the coefficient of viscosity of the drilling mud, which indicates that the incorporation of ZIF-67 NPs could be used to enhance the performance of drilling fluids. Similarly, the values of the consistency coefficients (K_2 , K_H and K_P), which measure the average viscosity of non-Newtonian fluid, increased with increasing ZIF-67 NPs concentration, indicating that the incorporation of ZIF-67 NPs improved the average viscosity of the mud [206]. The trends and rheological behavior of the base mud are closely similar to the observed trends of the various ZIF-67 mud formulations, which shows that the addition of ZIF-67 NPs did not adversely affect the rheology of the base mud but rather improved it in some instances, as previously discussed.

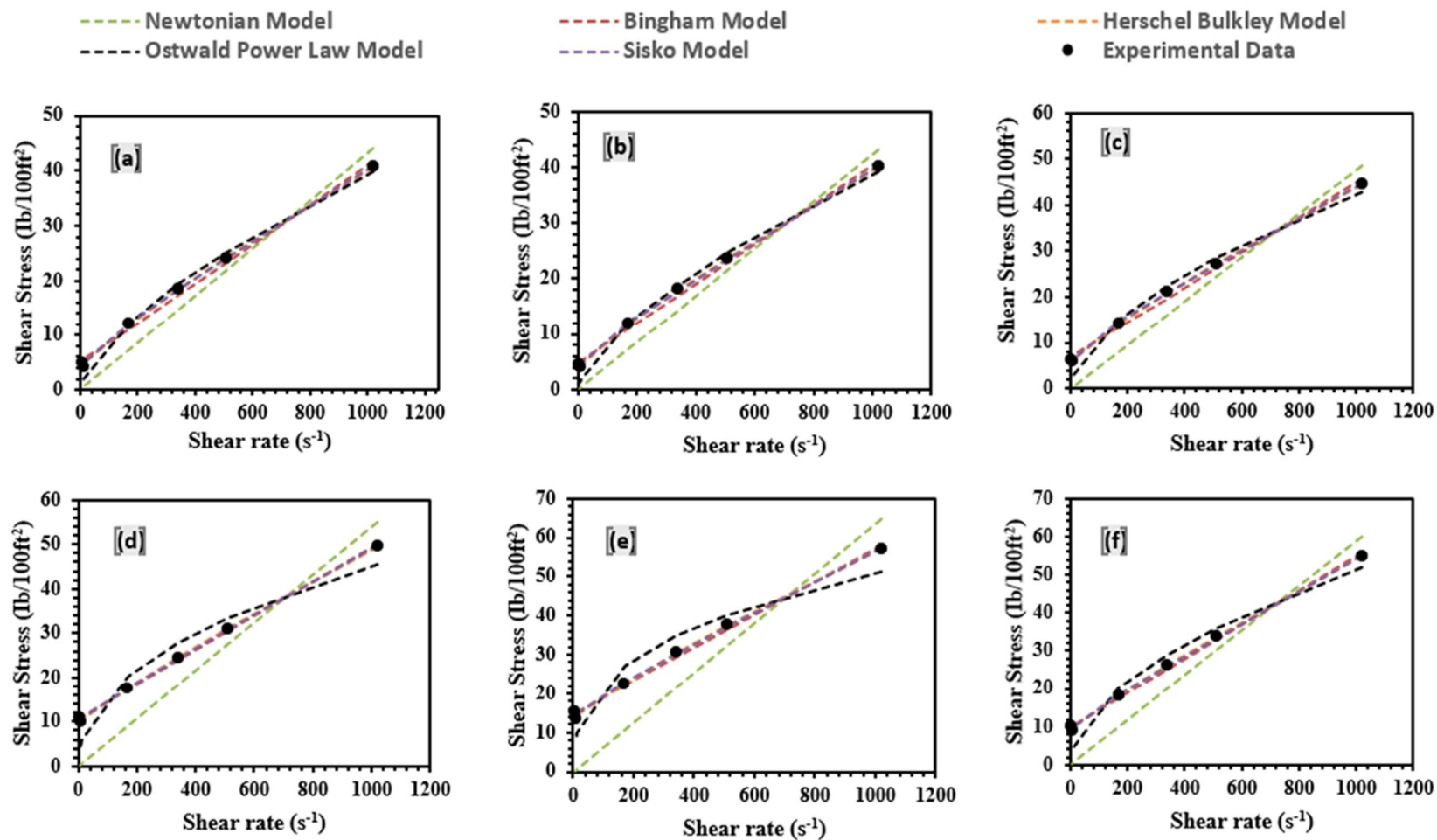


Figure 4-13: Rheological modelling of the (a) the base mud, and the ZIF-67 NPs containing mud at (b) 0.05 wt.%, (c) 0.25 wt.%, (d) 0.50 wt.%, (e) 0.75 wt.% and (f) 1.0 wt.% concentrations, respectively.

Table 4-4: Rheological parameters of water-based drilling fluids containing ZIF-67 NPs at different concentrations.

ZIF-67 (wt.%)	Newtonian model		Bingham model			Herschel Buckley model				Ostwald power law model				Sisko model		
	μ_p	R^2	μ_p	τ_o	R^2	τ_o	k_H	n	R^2	k_P	n	R^2	k_2	k_1	n	R^2
0.00	0.043	0.919	0.036	5.161	0.994	3.965	0.101	0.850	0.999	0.430	0.653	0.979	0.031	3.131	0.156	0.999
0.05	0.042	0.924	0.035	4.909	0.994	3.760	0.098	0.854	0.999	0.392	0.665	0.980	0.031	2.966	0.157	0.999
0.25	0.048	0.884	0.038	6.846	0.994	5.449	0.117	0.838	1.000	0.731	0.588	0.969	0.033	4.437	0.136	1.000
0.50	0.054	0.785	0.039	10.673	0.997	9.992	0.069	0.916	0.999	2.032	0.449	0.915	0.036	9.439	0.040	0.998
0.75	0.063	0.711	0.042	14.836	0.994	13.679	0.101	0.875	0.998	4.340	0.357	0.902	0.039	12.796	0.048	0.997
1.00	0.059	0.840	0.045	10.017	0.996	8.997	0.094	0.893	0.999	1.314	0.530	0.941	0.041	8.203	0.064	0.998

4.4 Summary

The current study represents a pioneering investigation into the application of ZIFs (and MOFs, in general) in oilfield industries. The use of these attractive materials for enhancing the H₂S scavenging performance of water-based (or even oil-based) fluids, or as a rheology modifier is still lacking in the published literature, to the best of our knowledge, highlighting the novelty of this study. The addition of ZIF-67 NPs to the WBM boosted the H₂S scavenging capacity by many folds, demonstrating the efficacy of this attractive material in managing the risk of encountering H₂S during drilling operations. In addition to the excellent H₂S scavenging performance, the inclusion of ZIF-67 into the WBM formulations also enhanced some key rheological properties such as plastic viscosity, yield point, and the carrying capacity of the drilling cuttings. The desirable shear-thinning behavior observed for all the ZIF-67 containing formulations further supports the favorable effect of ZIF-67 addition on the rheology of the formulated WBMs. The modelling exercise revealed that the Herschel Buckley and Sisko models best fit all the shear stress-shear rate data; this finding is in line with the observed shear-thinning behavior of the formulated WBMs. The minimal increase in the filtrate volume and the filter cake thickness at the highest ZIF-67 dosage in the WBM formulation do not compromise the beneficial effects of ZIF-67 addition. The findings reported in this study suggest the commercial potential of utilizing ZIF-67 for mitigating the encountered H₂S during oilfield operations and as NPs for enhancing the key rheological properties of drilling fluids.

CHAPTER 5

EFFECT OF CuMgFe-LAYERED TRIPLE HYDROXIDE ON RHEOLOGY, FILTRATION LOSS AND H₂S SCAVENGING PERFORMANCE

5.1 Introduction

Hydrogen sulfide (H₂S) is a known highly corrosive and toxic gaseous substance that is geologically generated in-situ in subterranean reservoirs [10,20]. The mechanism of subterranean H₂S formation is either through anaerobic microbial degradation or thermal reduction of sulfate-containing biomass, minerals, and hydrocarbons [169,170]. Additionally, other technologies, such as water flooding of reservoirs for enhanced oil recovery, also generate H₂S as a result of the proliferation of sulfate-reducing bacteria [15,171]. The presence of H₂S in subterranean formations is associated with serious safety concerns during drilling and well development stages in the oil and gas industry. The exposure of drilling fluids to H₂S during circulation leads to the release of this corrosive, toxic, and flammable gas to the surface, resulting in severe hazards to rig personnel and infrastructure [9,12].

The infiltration of H₂S into the drilling fluids causes a decline in their pH, rendering the fluids more corrosive, altering their density, and therefore affecting their viscosity and gel strength. As a result, the overall performance of the drilling fluid is significantly diminished. Further, the presence of H₂S poses significant risks to metallic drilling equipment, leading to detrimental consequences such as pitting corrosion, hydrogen embrittlement, and sulfide stress cracking. These corrosive effects not only compromise the structural integrity of the equipment but also result in substantial economic losses [115]. Equally concerning is the profound impact H₂S can have on human health, ranging from

loss of consciousness to respiratory disorders, and even fatalities [207]. To effectively control and minimize the harmful effects of this gas, the Occupational Safety and Health Administration (OSHA) and the U.S. National Institute for Occupational Safety and Health (NIOSH) have established rigorous safety regulations. These specify maximum exposure limits of 50 parts per million (ppm) and 10 ppm, respectively, within a 10-min timeframe [30]. Accordingly, it is imperative to implement effective measures in the formulation of drilling fluids to minimize any potential exposure and mitigate the adverse consequences H_2S may pose to oil and gas drilling operations.

One approach for controlling the release of H_2S during drilling operations is to keep the pH of the drilling fluid above 10. At this pH, H_2S is mostly present in ionic sulfide forms (i.e., HS^- and S^{2-}) instead of the covalent H_2S form. Converting H_2S into these soluble (i.e., ionic) forms might minimize the release of H_2S [119]. However, this approach is a double-sided sword since these ions will recombine to form H_2S at low pH. Thus, the sole elevation of the pH is not an effective method. Additionally, the solubility of HS^- and S^{2-} in the formulated mud is limited, making the eventual release of H_2S inevitable. Besides, due to the accumulation of soluble sulfide, a slight drop in pH will result in the release of uncontrollable and unpredictable amounts of H_2S [118]. Another approach, which involves the oxidation of sulfide ions to produce sulfur, has also been adopted to mitigate H_2S exposure in drilling fluids [20]. Nonetheless, this method is undesirable since the sulfur product generated is itself difficult to remove from the aqueous drilling fluid and further adversely affects the rheological behaviors of the fluid. Moreover, this method is ineffective as it is unable to remove all the H_2S completely and quickly in the drilling fluid [20].

Thus, a highly effective technique for scavenging H₂S involves incorporating additives that can swiftly convert it into stable, non-reversible, and safe chemical products. For instance, additives such as amines, aldehydes, and transition metal compounds, among others, have been utilized in drilling fluid formulations to effectively capture H₂S and mitigate its effects during drilling operations [16,118,122,173]. Soluble and insoluble metal-based scavengers are among the most commonly used because they are inexpensive, effective, and form stable insoluble metal sulfide upon reacting with H₂S [20,118].

The most widely used metals include alkali or transition metal carbonates, nitrates, oxides, and organic metal compounds, among others [16,119,208]. In recent years, layered double hydroxides (LDHs), alternatively referred to as hydrotalcites, have emerged as attractive materials for a wide range of applications due to their peculiar properties, such as low toxicity, lower cost, high chemical and thermal stability, and high sorption capacity [209,210]. For instance, LDHs have been utilized as drug carriers, flame retardants, catalysts, supercapacitors, and sorbents for various organic and inorganic pollutants [135,136]. They have the chemical formula of $[M^{2+}_{1-x}M^{3+}_x(OH)_2]^{x+}[A^{n-}_{x/n} \cdot yH_2O]^{x-}$, where M²⁺ (e.g., Mg²⁺, Ca²⁺, Cu²⁺, Fe²⁺, etc.) and M³⁺ (e.g., Fe³⁺, Cr³⁺, Ga³⁺, Al³⁺, etc.) are the divalent and trivalent metals, Aⁿ⁻ (e.g., CO₃²⁻, NO₃²⁻, OH⁻, etc.) is the intercalated anion, and x is the molar ratio of M³⁺/(M²⁺+M³⁺), which should be, preferably, within the range of 0.17 to 0.33 in order to obtain pure hydrotalcite phase [133,134]. The LDH structure consists of stacked, positively charged, brucite-like layers of divalent metal ions that are octahedrally coordinated to six hydroxyl groups, in which part of the divalent ions are replaced by trivalent ions [26]. The general crystallinity of LTH, and the intensity of the (003) crystal planes or facet has been reported to enhance the H₂S removal of LTH. Lee et

al.[141], conducted a dynamic breakthrough experiment to investigate the effectiveness of Co-Fe-LDH in removing H_2S from a high-humidity gas stream. The study examined different molar ratios of Co/Fe and observed a correlation between the crystallinity of the synthesized LDH and the performance of H_2S removal. Specifically, Co/Fe ratios of 1:1 to 1:3 exhibited lower crystallinity, while the crystallinity increased for the 2:1 and 3:1 ratio. Notably, the LDH sample with 3:1 ratio showed a more prominent presence of the 11.6° (003) phase (i.e., higher crystallinity) and demonstrated the highest breakthrough capacity, indicating that a higher intensity of 003 phase may enhance H_2S uptake. Furthermore, the adsorption capacity of CoFe-LDH (0.209 g H_2S /g) was found to be 1.53 times higher than that of Co-hydroxide and 8.5 times higher than that of Fe-hydroxide. These results clearly indicate that the synergistic effect of Co-Fe double hydroxide significantly improves the adsorption capacity [141].

Despite the attractive characteristics of LDHs, including their potential effectiveness in H_2S scavenging, their inclusion in drilling fluids has not been reported yet, to the best of our knowledge. Furthermore, the inclusion of a third metal in the LDH framework (forming a layered triple hydroxide) could result in a better-performing material.

Hence, we report herein the fabrication of a layered triple hydroxide (LTH) composed of copper, magnesium, and iron. The formed tri-metallic nanosheets were characterized using Fourier transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD), thermogravimetric analysis (TGA), and nitrogen adsorption isotherm in order to, respectively, evaluate its surface functionality, structure, thermal stability, and surface area. The synthesized CuMgFe-LTH was incorporated into an aqueous drilling fluid formulation to boost its H_2S scavenging performance, which was evaluated using a breakthrough

experiment. Additionally, the influence of the CuMgFe-LTH on the rheology and filtration loss of the drilling fluid was investigated and discussed.

5.2 Results and discussion

5.2.1 XRD analysis

The crystallographic structure of the CuMgFe-LTH is analyzed, and the pattern is depicted in Figure 5-1. It can be inferred that the synthesized CuMgFe-LTH is highly crystalline due to the existence of sharp, symmetric, and intense diffraction peaks. The XRD pattern exhibited diffraction peaks at $2\theta = 11.43, 23.02, 34.09, 35.54, 38.97, 46.32, 48.32, 60.84,$ and 61.50° which can be indexed to the (003), (006), (009), (012), (015), (018), (110), and (113) crystal planes, respectively. The measured peaks match very well with those observed for carbonate-containing LTHs, suggesting the successful formation of a multilayer brucite-like nanosheet structure [211]. The mean inter-brucite layer distances of the (d_{003}) reflection plane were calculated to be 0.782 nm, indicating the interlamination of CO_3^{2-} and H_2O molecules [212,213]. Also, the c parameter, which indicates the interlayer spacing of the sample, is calculated from the reflection at $2\theta = 11.43^\circ$ using this formula $c = 3(d_{003})$ and found to be 2.35 nm. The value of the c parameter strongly depends on the nature of the intercalating anion, which in this case indicates the presence of carbonate anions in the interlayer spaces [214,215]. The lattice parameter a , which indicates the average distance between the cations, is calculated from the diffraction peak originating at $2\theta = 60.82^\circ$ using $a = 2(d_{110})$ [215], and found to be 0.305 nm. The peak positions and lattice parameter values obtained confirm the formation of the CuMgFe-LTH.

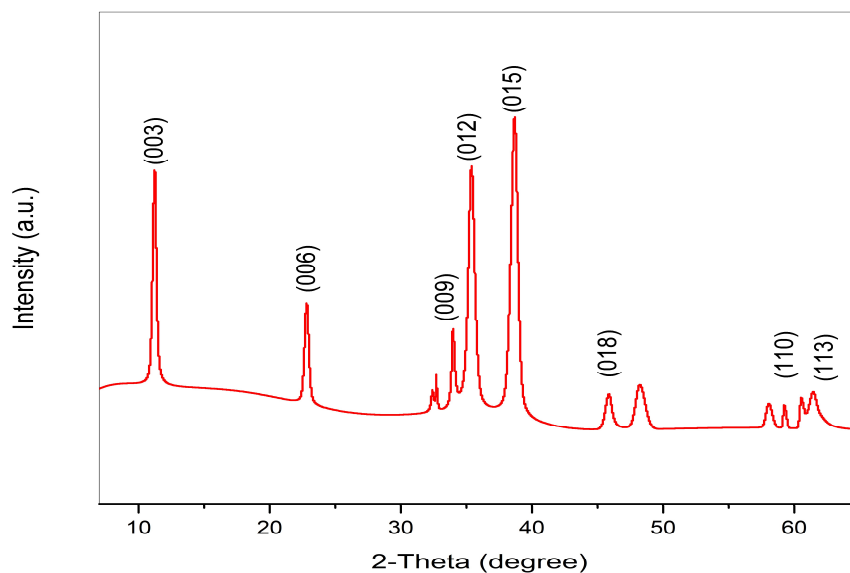


Figure 5-1: XRD pattern of the synthesized CuMgFe-LTH.

5.2.2 FT-IR analysis

The FT-IR spectra of the synthesized CuMgFe-LTH is presented in Figure 5-2. The spectra show the typical absorption bands associated with the LTH intercalated with CO_3^{2-} anions [216,217]. The wide absorption band around 3447 cm^{-1} could be attributed to the O-H vibrational stretch of the water molecules present in the brucite layer [218]. The band at 2982 cm^{-1} can be attributed to the strong O-H-O stretch of the hydrogen bonding in the interlayer space connected to the intercalated CO_3^{2-} anion or water molecules [219]. The peak at 1645 cm^{-1} corresponds to the O-H bending vibration of the water molecules intercalated in the interlayer space. The absorption band characterizing the asymmetric vibration of the CO_3^{2-} anion is located within the range of 1360 to 1072 cm^{-1} [220]. The bands in the region from 1000 to 500 cm^{-1} is related to the lattice vibrations of the condensed metal oxides M-O, M-O-M and O-M-O (M = Cu, Fe, and Mg) [221]. Overall,

the FT-IR spectra reveals the presence of CO_3^{2-} , O-H, and metal ions, confirming the formation of CuMgFe-LTH.

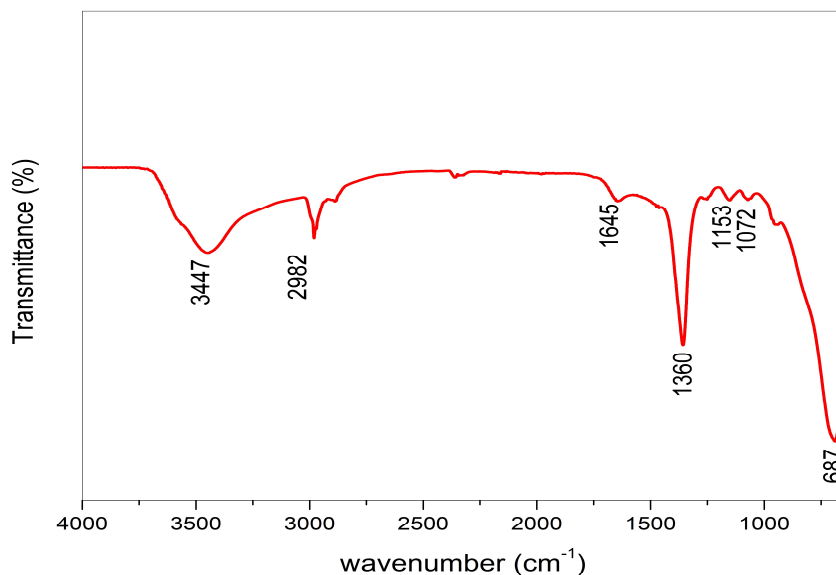


Figure 5-2: FT-IR spectra of the synthesized CuMgFe-LTH.

5.2.3 Thermogravimetric analysis

The thermal stability of the CuMgFe-LTH was investigated and the profiles obtained from the TGA are depicted in Figure 5-3, which shows several weight loss stages occurring between 33 and 902 °C. The first stage, ranging from 33 to 85 °C, is associated with the removal of physically bound water molecules from the external surface (0.5-1.5% weight loss). The second occurred between 105 and 195°C, this is primarily due to the loss of interlayer water molecules (1.75-6.34% weight loss). Between 207 and 500 °C, the removal of the intercalated CO_3^{2-} anions and the decomposition of the metal hydroxide layers take place, contributing to a weight loss of about 9%. Further, the weight loss of about 4.6% observed between 759 and 901 °C is as a result of the decomposition of any in-situ

generated or residual metal carbonate phases present [222]. Overall, the synthesized CuMgFe-LTH demonstrates excellent thermal stability across the entire temperature range from 33 to 902 °C making the material well suited for utilization in drilling fluid applications.

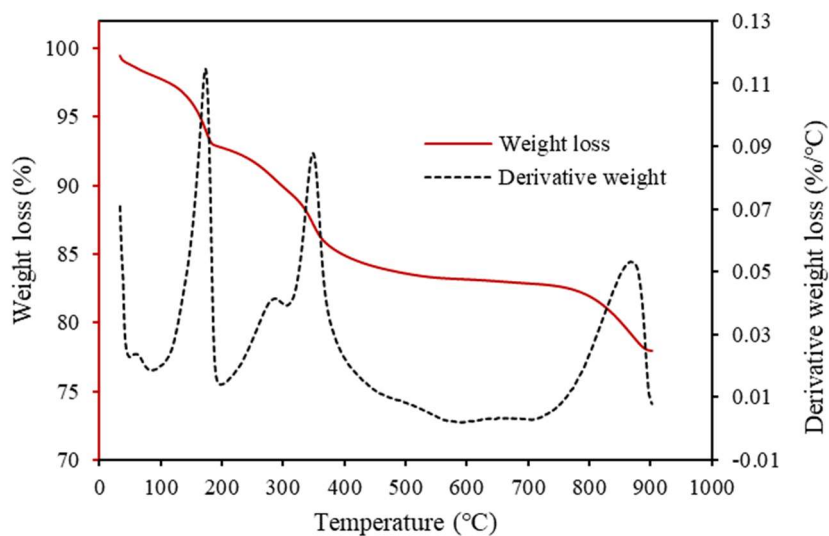


Figure 5-3: Thermogravimetric profile of the synthesized CuMgFe-LTH.

5.2.4 Textural properties

The textural properties of the synthesized CuMgFe-LTH were evaluated using the N₂ adsorption-desorption isotherms analysis conducted at −196 °C; the obtained isotherms are depicted in Figure 5-4 (a). The CuMgFe-LTH exhibited a type IV isotherm with a type-1 hysteresis loop according to the IUPAC classifications [223]. This indicates the existence of uniform mesopores with slight micropores. The specific surface area, pore volume, and average pore size were determined to be 56.64 m²/g, 0.36 cm³/g, and 12.46 nm, respectively. Interestingly, the results of the BET analysis indicate that the CuMgFe-LTH is mesoporous and, thus, potentially has a high H₂S scavenging capacity. Further, the pore

size distribution shown in Figure 5-4 (b) corroborates that most of the pores are within the mesoporous range (2-50 nm), with a narrow and monomodal distribution and an average pore size of 12.46 nm.

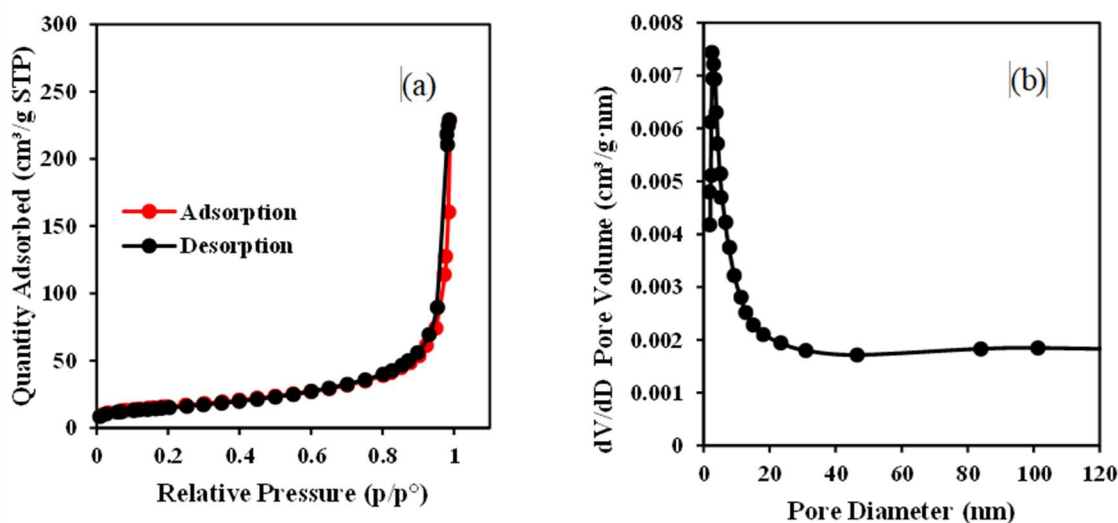
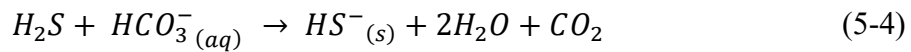
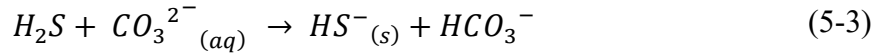
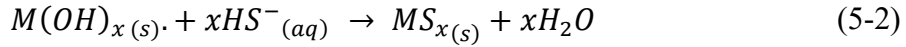
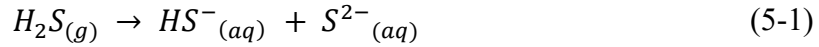


Figure 5-4: (a) N₂ adsorption-desorption isotherm, and (b) pore size distribution of the synthesized CuMgFe-LTH.

5.2.5 Hydrogen sulfide removal

Figure 5-5 depicts the H₂S scavenging performance of the CuMgFe-LTH. The breakthrough time obtained for the aqueous drilling fluid formulation containing 1.0 wt.% CuMgFe-LTH (abbreviated as LTH-BM, hereafter) was about 1554.5 min (i.e., 25.9 h) which corresponds to an H₂S removal capacity of 216.3 mg H₂S/g scavenger. Up until the breakthrough time, the LTH-BM was capable of continuously removing all the H₂S from the entering gas stream without any H₂S leaving with the outlet gas stream. Beyond the breakthrough time, the H₂S concentration in the gas effluent gradually increased up to the saturation time, at which the amount of H₂S in the outlet stream is the same as that in the inlet stream. At saturation, most of the H₂S scavenging sites on the CuMgFe-LTH are

utilized. The H₂S scavenging capacity of the LTH-BM at the saturation time of 2659.5 min (i.e., 44.3 h) reached 268.0 mg H₂S/g scavenger. Compared to the base mud without any scavenger (BM), which only reached breakthrough and saturation after 34.5 and 325 min, respectively, the LTH-BM exhibited a very remarkable H₂S scavenging capacity, as seen in Figure 5-5. The plausible mechanisms of H₂S removal by the LTH is either through anion exchange between the ionic sulfide species and the intercalated carbonate and hydroxyl groups within the LTH structure, or ionic reaction with metal hydroxide layers of the LTH. The reaction of the CuMgFe-LTH with H₂S in the ionic form to produce insoluble metal sulfide and water might have occurred according to the plausible reaction mechanism (equation 5-1, 5-2, 5-3, and 5-4) shown below:



H₂S gas in aqueous drilling fluid dissociates into ionic sulfide intermediates, HS⁻ and S²⁻. The dissociated HS⁻ immediately reacts with the divalent and trivalent metal hydroxides to produce metal sulfide (MS_x), and water. Further, HS⁻ and bicarbonate ion (HCO₃⁻) are formed via the reactions of H₂S with carbonate ion present in the LTH. The H₂S further reacts with the bicarbonate ion (HCO₃⁻) produced in the preceding reaction to form HS⁻, CO₂ and water. The generation of HS⁻ ion from the exchange reaction with carbonate further increases the removal performance of the metal hydroxide.

The LTH has exhibited better performance towards H₂S removal, even better than other scavengers that have been reported. For instance, Onaizi et al. [12] reported the H₂S scavenging performance of Cu(NO₃)₂·3H₂O in an aqueous drilling fluid formulation. This material exhibited an H₂S scavenging capacity of 15.8 and 146.8 mg/g at breakthrough and saturation, respectively [12]. Additionally, Wang et al. [224] prepared a series of porous Cu-based sorbents for H₂S removal in dynamic conditions at ambient temperature [224]. The highest H₂S scavenging capacity obtained was 147 mg/g. Accordingly, the LTH-containing drilling fluid formulated in this study has superior H₂S scavenging performance compared to previous literature.

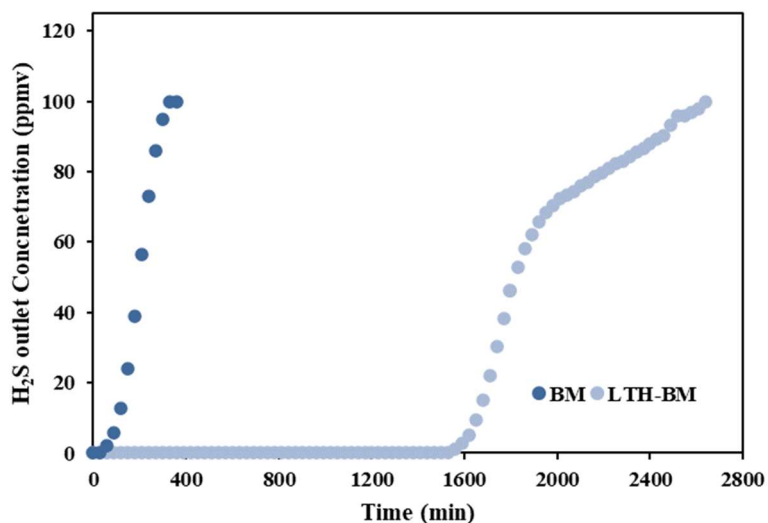


Figure 5-5: H₂S scavenging performance of the BM and LTH-BM in a continuous breakthrough experiment. The LTH-BM formulation contains 1 wt.% CuMgFe-LTH NPs.

5.2.6 Filtration properties

API filter press tests were performed to get insights into the amount of filtrate that will be lost, and the thickness of the mud cake layer formed. The fluid loss property is an essential aspect of drilling fluid behaviour and has significant implications for wellbore stability and

overall fluid performance [199,225]. Figure 5-6 depicts the API LPLT fluid loss volumes of the BM and LTH-BM. The filtrate volume of the BM is about 12.8 mL, whereas 14.2 mL was obtained for the LTH-containing formulation at 1.0 wt.%. The filtrate volume increased with the addition of the CuMgFe-LTH. Despite the increase, the obtained filtrate volume is still within the recommended range under LPLT conditions.

Preferably, the filtrate volume should decrease when nanoparticles (NPs) are introduced due to the increase in solid content. Nevertheless, the particle size and degree of dispersion of the NPs play a primary role in the permeability of the deposited filter cake layer and therefore the fluid loss volume [226]. Further, agglomeration can influence the fluid loss volume by creating layers of permeable cake that can increase the filtrate volume [89,200]. This might have accounted for the observed 10.9% increase in the filtrate volume for the LTH-BM formulation. Despite this increase, the CuMgFe-LTH demonstrates potential for effectively controlling fluid loss since the filtrate volume remains below the recommended limit of 15 mL, indicating its ability to mitigate fluid loss. Moreover, the LTH-BM formulation offers an additional advantage by enhancing H₂S scavenging performance. This makes CuMgFe-LTH an extremely favourable additive for drilling fluid applications.

Interestingly, comparable results have been reported by other researchers working with other NPs. For instance, Bayat et al. [227] investigated the impact of SiO₂, ZnO and TiO₂ NPs on the rheological properties of water-based drilling fluids. The inclusion of 0.05-0.50 wt.% SiO₂ in the drilling fluid was found to increase the fluid loss volume from 12.0 to 13.1 mL and from 15.5 to 16.3 mL at 25 and 50 °C, respectively. Also, Mahmoud et al. [228], studied the filtration properties of ferric oxide (Fe₂O₃) NPs and found that the filtration loss volume increased from 6.4 to 8.9 mL within the concentration range of 0.3-

1.0 wt.%. Compared to the based mud, which had a filtrate volume of 7.7 mL, the fluid loss at 1.0 wt.% increased by 15.6% [228].

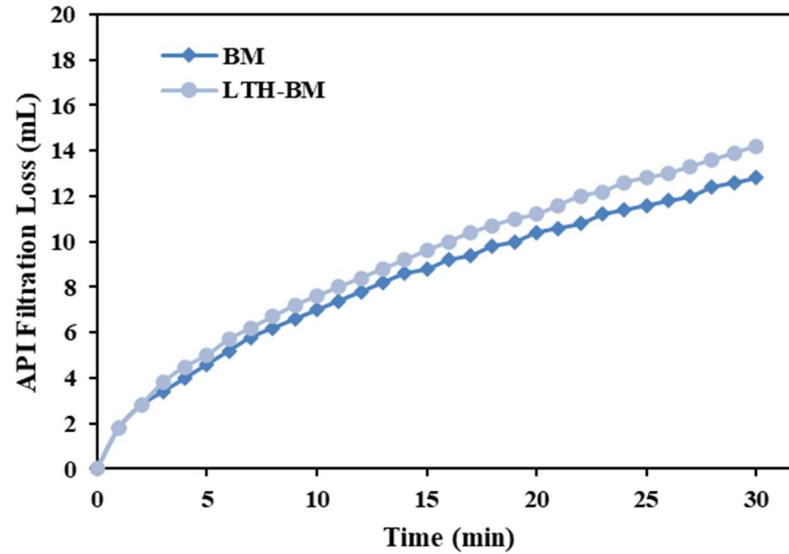


Figure 5-6: API LPLT filtrate loss of the BM and the LTH-BM formulations.

Another key fluid loss property, which is the thickness of the filter cakes was also measured. The filter cake layer acts as a barrier, restricting further filtrate loss into the formation and helping to maintain wellbore integrity [229]. The thickness of the filter cake can be influenced by factors such as the mud properties, operating conditions, and formation properties [230,231]. A properly controlled filter cake thickness is crucial as it improves cutting transport and controls well pressure [90]. The thickness of the BM and LTH-BM filter cake layers is presented in Table 4-3, and their photos are shown in Figure 5-7(a-b). The results obtained show that incorporation of the 1.0 wt.% CuMgFe-LTH in the BM formulation had no effect on the thickness of the filter cake layer. Additionally, physical inspection of the LTH-BM filter layer shows a smooth, thin, and lubricating

surface, as depicted in Figure 5-7; these textural characteristics are desirable in drilling operations [89].

Table 5-1: API LPLT filter cake thickness.

Formulation	Cake Thickness		FL (mL)
	1/32 inch	(mm)	
BM	3	2.38	12.8
LTH-BM	3	2.38	14.2

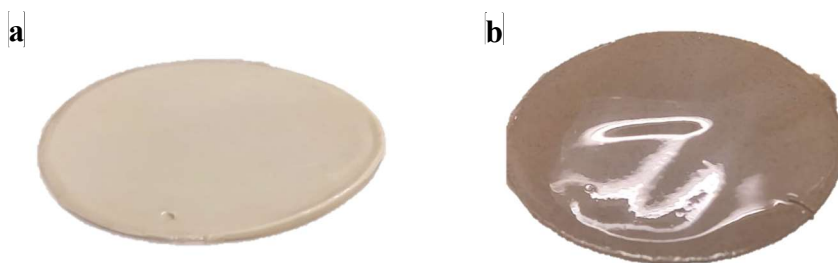


Figure 5-7: Photos of the API LPLT filter cake of (a) BM and (b) LTH-BM formulations.

5.2.7 Effect of CuMgFe-LTH on the rheological properties

Plastic viscosity (PV) is a key rheological property of drilling fluids that determines their resistance to flow due to mechanical friction measured at an infinite shear rate [78,191]. This property holds a significant importance as it directly impacts drilling fluid performance and wellbore stability. Further, it influences cutting transport by preventing sagging and maintaining effective hole cleaning [42,194]. Another important rheological property (i.e., the apparent viscosity (AV)) describes the resistance to flow when evaluated under a finite shear rate [194]. It differs from plastic viscosity in that it accounts for both internal friction and the effect of shear rate. In drilling fluid applications, the apparent viscosity of the drilling mud is crucial for assessing its flow behaviour, pumpability, and

overall performance. It also provides valuable information about the fluid ability to circulate, transport cuttings, and maintain the desired flow properties.

The changes of the PV and AV with increasing CuMgFe-LTH content is presented in Figure 5-8. As displayed in Figure 5-8, the values of the AV are greater than the PV for all the formulations prepared. Further, the AV increases gradually from 18.98 to 22.21 cP with the increase of CuMgFe-LTH content from 0.05 to 1.0 wt.%. Similarly, the PV increases from 14.94 to 17.12 cP within the range of 0.25 to 1.0 wt.%. This general increase in viscosity is as a result of the increase in solid content [232]. However, the PV is observed to reduce by about 2.5 and 3.8% at 0.05 and 0.25 wt.%, respectively, when compared to the base mud. Compared to the literature, similar trends have been observed with other NPs added to aqueous drilling fluid formulations. For instance, Bayat et al. [83] observed a declining trend of the PV upon the addition of up to 0.1 wt.% TiO₂ and SiO₂ NPs to the base mud at various temperatures [83]. Additionally, Smith et al. [76] reported a similar decreasing trend of both PV and AV with aluminum oxide and silica NPs within the range of 0 to 0.5 wt.% contents [76]. Dejtaradon et al. [232] investigated the impact of ZnO and CuO NPs on the rheological properties of water-based drilling fluids and observed an initial decreasing trend in both PV and AV upon the addition of CuO and ZnO NPs [232].

The primary reason for the observed reduction in PV and/or AV is the possible decrease in inter-particle friction resulting from charge compensation, which increases the repulsive forces between drilling fluid particles. The increase in repulsive forces leads to an increase in inter-particle distance, which in turn results in a reduction in the mud viscosity [105,233]. Further, the CuMgFe-LTH at such lower concentrations could serve as a ball-

bearing between the larger drilling fluid particles, thereby reducing the inter-particle friction, and hence the fluid viscosity [42].

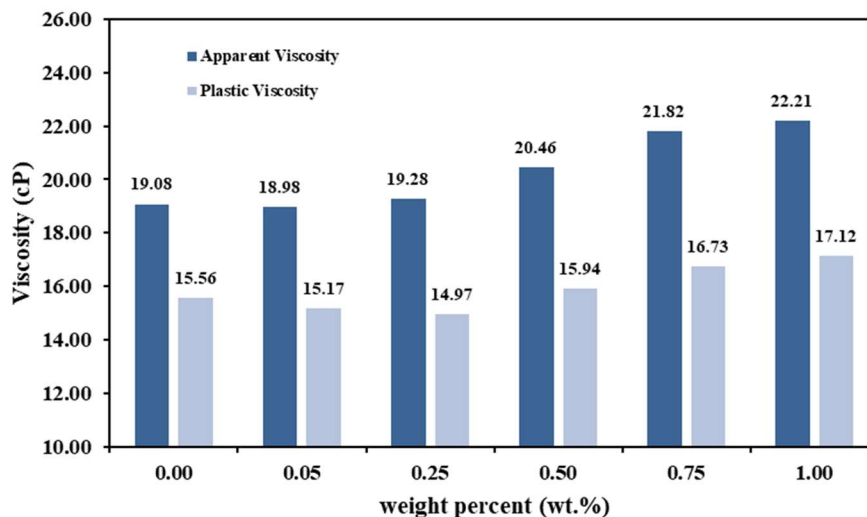


Figure 5-8: The effect of CuMgFe-LTH on PV and AV.

Figure 5-9 depicts the influence of CuMgFe-LTH on the yield point (YP) and carrying capacity. The YP of a water-based drilling fluid measures the minimum shear stress required to initiate flow [191]. It represents the ability of the fluid to resist initial flow under applied stress due to electrochemical interactions between the mud constituents [191]. In aqueous mud formulations, this property is primarily influenced by the presence of colloidal solids like bentonite and starch, which can form a three-dimensional network within the fluid and contribute to the internal strength and ability of the fluid to withstand shear stress. When the applied shear stress exceeds the yield point, the intermolecular forces holding the network together are overcome, and the fluid begins to flow [234]. The YP is a crucial parameter because it directly affects the ability of the drilling fluid to suspend cuttings [194]. Similarly, the carrying capacity, another important rheological

property, also measures the ability to effectively transport and suspend drilled cuttings from the bottom of the wellbore to the surface during the drilling process [235,236]. It is influenced by factors such as viscosity, yield stress, fluid density, and solid content [237]. A relatively high drilling fluid density can provide better buoyancy for the cuttings, facilitating their upward movement. Similarly, optimized fluid viscosity and yield stress are advantageous for better carrying capacity [237].

As presented in Figure 5-9, the YP and carrying capacity of the formulated water-based drilling muds increase upon the addition of the CuMgFe-LTH. However, unlike the initial drop observed for the drilling fluid viscosity, the YP and carrying capacity gradually increase with increasing CuMgFe-LTH content. The YP and carrying capacity increased by about 8.2 and 11.1%, respectively, with the addition of 0.05 wt.% CuMgFe-LTH. The CuMgFe-LTH was found to be good for increasing the yield point and carrying capacity and further exhibited better dispersion without any form of agglomeration. This increase in these rheological properties indicates that the CuMgFe-LTH can improve the hole cleaning performance of the drilling fluid. The observed trend could be attributed to the increase in electrostatic interaction between the drilling fluid particles [238]. Further, the increase in PV discussed earlier as a result of the increase in solid contents is likely to contribute to the increase in carrying capacity.

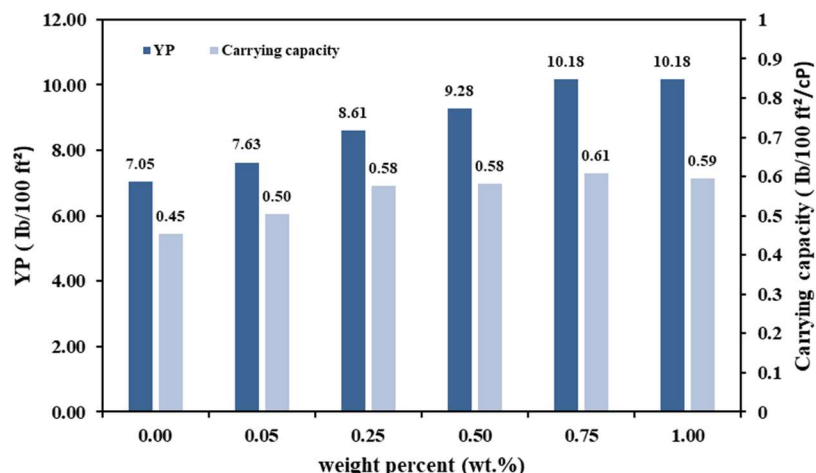


Figure 5-9: The effect of CuMgFe-LTH on YP and carrying capacity.

Another key rheological property of drilling fluids is their gel strength, which indicates the ability of the fluid to develop and maintain a gel-like structure when at rest or when subjected to completely static conditions [191]. This thixotropic property of drilling fluids helps in preventing the settling of cuttings when circulation is paused, ensuring their suspension, and preventing their accumulation at the bottom of the wellbore [37]. The gel strength of the drilling fluid also contributes to wellbore stability by providing support to the walls, minimizing fluid invasion into the formation, and reducing the risk of differential sticking [239,240].

Figure 5-10 presents the influence of the CuMgFe-LTH on the gel strength of the formulated water-based muds. The recommended range for the 10 s and 10 min gel strength (GS) should be less than 15 and 35 lb/100 ft², respectively [42]. As demonstrated in Figure 5-10, the base mud and LTH-containing formulations satisfied this requirement at all the added weight ratios. Further, the 10 s GS is smaller than the 10 min GS, indicating the influence of drilling fluid static periods on its rheological property. The 10 min GS is

measured after a 10 min static period within which the CuMgFe-LTH and other drilling fluid additives rearranged in such a manner that the free energy is minimized through electrostatic surface charge compensation [84]. This arrangement results in the formation of a stronger gel structure compared to the 10 s static time, thus giving a higher GS.

Additionally, increasing the CuMgFe-LTH concentration resulted in an increase in both 10 s and 10 min GS. Generally, nanoparticles in drilling fluids or other aqueous dispersions usually possess surface charges [238,241]. As the concentration of NPs in the fluid rises, both the zeta potential and surface charge of the particles increase [241]. This phenomenon leads to a higher abundance of colloidal and surface-charged particles in the fluid, thereby strengthening the gel strength. Hence, a major reason for the increase in the GS upon the addition of the CuMgFe-LTH could be attributed to the positively charged layers of the CuMgFe-LTH, which might have strengthened the gel structure and network of drilling fluid additives through electrostatic interactions [84]. Interestingly, similar findings have also been reported in the published literature using other NPs [242,243].

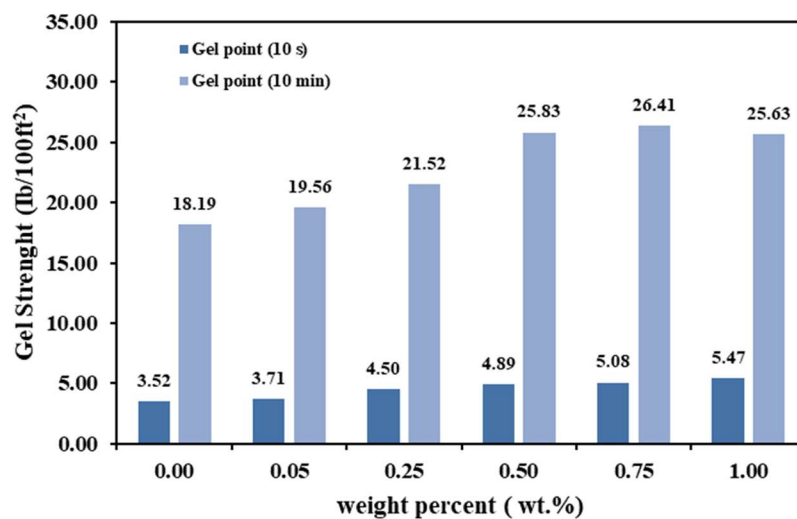


Figure 5-10: The effect of CuMgFe-LTH on the 10-s and 10-min gel strengths.

5.2.8 Rheological modelling of the WBM's

To identify the rheological model(s) that best describes the flow behavior of water-based drilling fluid formulations, rheological modelling was performed using the Newtonian, Bingham plastic, Herschel-Bulkley, Power-law, and Sisko model [82]. Table 4 depicts the predicted model parameters of the drilling fluid formulations. Based on the obtained value of the R^2 , the Herschel-Bulkley model is the most suitable one for describing the behavior of all the prepared formulations since its R^2 is the closest to unity. A typical shear rate-shear stress data fitting example is presented in Figure 5-11 for the BM and LTH-BM formulations. Additionally, the dimensionless flow index (n) obtained using the Herschel-Bulkley, Ostwald power law, and Sisko models for the base mud and CuMgFe-LTH formulations is less than 1, suggesting that they all behave like pseudoplastic or shear-thinning fluids. Further, the dimensionless flow index shows a decreasing trend with increasing CuMgFe-LTH content. This is in line with the findings reported in the literature using other NPs [88,244,245]. Certainly, this decreasing trend is desired since lower values of the dimensionless flow index is an indication of a proper hole cleaning [244]. Intriguingly, the introduction of CuMgFe-LTH resulted in an increase in the coefficient of viscosity of the drilling mud, indicating that CuMgFe-LTH may be employed to improve the capacity to remove cuttings from drilled wells, suspend and transport them to the surface, and preserve wellbore stability [246].

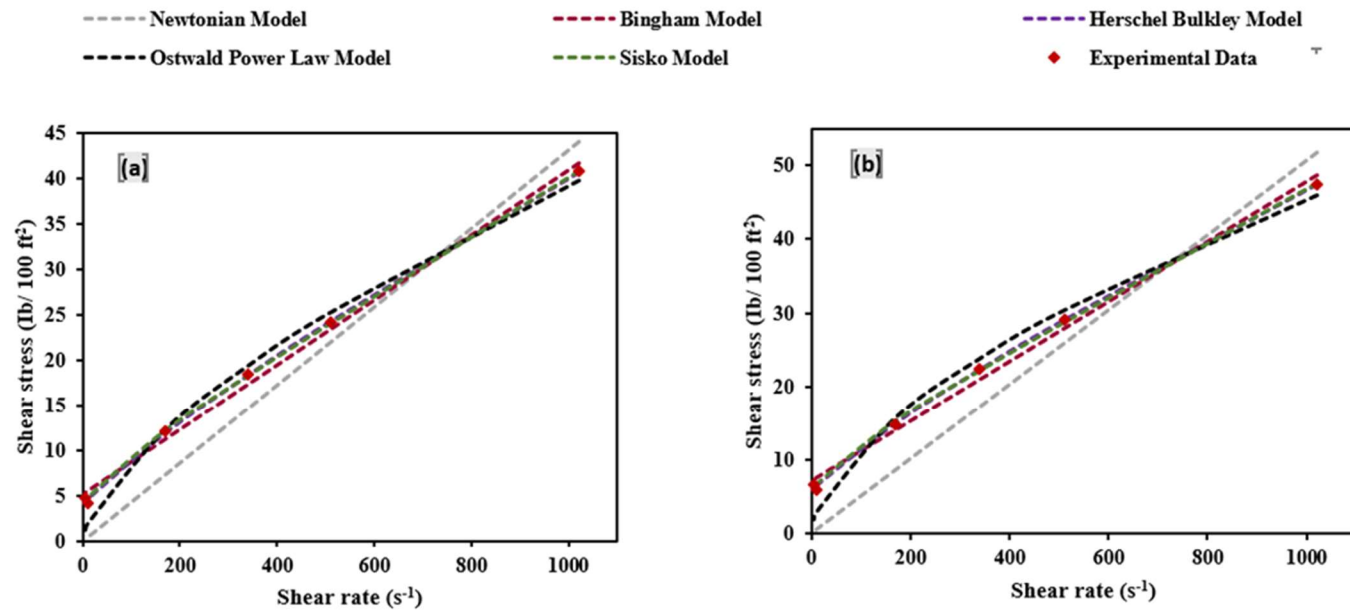


Figure 5-11: Shear rate-shear stress curve of the (a) BM and (b) LTH-BM and their regression using Newtonian, Bingham plastic, Herschel-Bulkley, Power-law, and Sisko model.

Table 5-2: Rheological parameters of the formulated BM and the LTH-containing samples.

LTH (wt.%)	Newtonian model		Bingham model			Herschel Buckley model				Ostwald power law model			Sisko model			
	μ_P	R^2	μ_P	τ_o	R^2	τ_o	k_H	n	R^2	k_P	n	R^2	k_2	k_1	n	R^2
BM	0.0430	0.9190	0.0357	5.1611	0.9942	3.9650	0.1013	0.8504	0.9994	0.4295	0.6533	0.9788	0.0309	3.1306	0.1561	0.9991
0.05	0.0431	0.9045	0.0351	5.6005	0.9935	4.3447	0.1057	0.8421	0.9994	0.5171	0.6253	0.9749	0.0302	3.4787	0.1489	0.9989
0.25	0.0439	0.8979	0.0355	5.9058	0.9933	4.5945	0.1102	0.8379	0.9996	0.5704	0.6134	0.9733	0.0305	3.7114	0.1454	0.9989
0.50	0.0486	0.8960	0.0392	6.5859	0.9928	5.0848	0.1261	0.8328	0.9995	0.6530	0.6082	0.9735	0.0334	4.0657	0.1508	0.9990
0.75	0.0500	0.8835	0.0398	7.1566	0.9920	5.5558	0.1344	0.8257	0.9993	0.7731	0.5867	0.9703	0.0337	4.4895	0.1459	0.9986
1.00	0.0508	0.8890	0.0407	7.1066	0.9926	5.5560	0.1302	0.8333	0.9994	0.7316	0.5975	0.9708	0.0348	4.5101	0.1424	0.9986

5.3 Summary

The application of CuMgFe-LTH as a drilling fluid additive has not been reported elsewhere, to the best of our knowledge, demonstrating the novel contribution of this study. CuMgFe-LTH has proved to be an attractive additive for significantly boosting the H₂S scavenging performance of WBM. The inclusion of this material into a water-based drilling mud formulation could provide several folds enhancement (exceeding nine (9) times) in the H₂S scavenging capacity of the base mud; further tuning and optimization could boost this performance further. Additionally, the incorporation of CuMgFe-LTH in water-based drilling muds could provide a useful means to enhance some of their rheological properties (i.e., apparent and plastic viscosities, yield point, gel strength, and overall carrying capacity). This material is extremely thermally stable, and, thus, it would not be affected by the elevated reservoir temperature. The pseudoplastic (i.e., shear thinning) behavior of the LTH-containing muds confirms that the addition of CuMgFe-LTH to the base mud provides/maintains a favorable fluid flow behaviour. The increase in the filtration loss in the presence of CuMgFe-LTH is insignificant and still within the recommended range. Overall, the application CuMgFe-LTH in drilling applications might carry multiple benefits, highlighting the commercial potential of this material in oilfield industries.

CHAPTER 6

EFFECT OF CuMgFe-LTH/ZIF-67 NANOCOMPOSITES ON H₂S SCAVENGING CAPACITY AND RHEOLOGICAL PROPERTIES

6.1 Introduction

Hydrogen sulfide (H₂S) is a highly corrosive and toxic gas that occurs in underground reservoirs through two processes: anaerobic microbial degradation and thermal reduction of biomass, minerals, and hydrocarbons containing sulfate [169,170]. Additionally, water flooding for enhanced oil recovery can also generate H₂S due to sulfate-reducing bacteria [15,171]. The presence of H₂S in underground formations raises significant safety concerns during drilling and well development within the oil and gas industry. Whenever drilling fluids encounter H₂S, it can be released to the surface, posing severe hazards to rig personnel and infrastructure [9,12].

The presence of H₂S in drilling fluids has several negative effects. Firstly, it reduces their pH, making them more corrosive and altering their density, viscosity, and gel strength. This overall decline in drilling fluid performance is a significant concern. Furthermore, H₂S poses notable risks to metallic drilling equipment, leading to issues such as pitting corrosion, hydrogen embrittlement, and sulfide stress cracking, which can result in substantial economic losses [115]. Beyond economic implications, exposure to H₂S also poses serious threats to human health. It can lead to respiratory disorders and even fatalities [207]. To safeguard against these hazards, regulatory bodies like OSHA and NIOSH have established maximum exposure limits for H₂S [30]. Consequently, implementing effective measures in the formulation of drilling fluids becomes crucial to minimize exposure and mitigate adverse consequences during oil and gas drilling operations.

Controlling the release of H₂S during drilling operations can be achieved through various methods. One approach involves maintaining the pH of the drilling fluid above 10, which converts H₂S into soluble ionic sulfide forms (HS⁻ and S²⁻), thus reducing its release [119]. However, this method has its limitations, as the ions can recombine to form H₂S again at low pH, and the solubility of HS⁻ and S²⁻ in the mud is limited, eventually leading to H₂S release [118]. Additionally, even a slight drop in pH can cause the uncontrolled release of unpredictable amounts of H₂S. Another method to mitigate H₂S exposure is the oxidation-reduction of sulfide ions, producing free sulfur and water. However, this approach is not ideal since removing the generated sulfur from the drilling fluid is challenging and negatively affects its rheological properties. Moreover, this method is not entirely effective in rapidly removing all H₂S from the drilling fluid [20].

One highly efficient method for removing H₂S involves the use of additives that can rapidly convert it into secure and irreversible chemical products. These additives, like amines, aldehydes, and transition metal compounds, have been successfully employed in drilling fluid formulations to capture H₂S effectively and minimize its impact during drilling operations [16,173]. Among the existing H₂S scavengers, triazines stand out as an economical choice with a swift reactivity towards H₂S. However, these scavengers generally have limited thermal stability and are usually not suitable for long-term downhole applications since they are only applicable at temperatures below 200°C [247]. Additionally, their use may lead to the undesired precipitation of dithazine as a byproduct and the formation of scales [92]. Also, oxidizing agents like hydrogen peroxide, chlorine dioxide, and perchlorates typically engage in rapid and irreversible interactions with soluble sulfide ions. Their high solubility allows for easy dispersion within drilling fluids.

Nonetheless, these oxidants tend to undergo uncontrolled reactions and may react with other additives in the drilling fluid, thereby restricting their effectiveness against H_2S . Additionally, they exhibit instability under high pH conditions and sometimes present corrosion issues [247]. Aldehydes can react with H_2S rapidly. Despite their significant scavenging potential, these substances are typically not advisable for use as scavengers because of concerns related to health hazards and usability. Also, aldehydes, including formaldehyde, acrolein, glyoxal, and glutaraldehyde, are expensive and tend to have very intricate reaction kinetics [123]. Metal-based compounds offer an attractive option owing to their cost-effectiveness, efficiency, and safety considerations [247]. When employed as scavengers, these compounds interact with dissolved H_2S in drilling mud, leading to the formation of insoluble metal sulfides. Notably, these metal sulfides exhibit better thermal stability and do not regenerate H_2S , offering a reliable means of removing H_2S , unlike alkanolamine, oxidants, and triazines. In recent years, layered double hydroxides (LDHs) and metal-organic frameworks (MOFs), especially ZIF-67, have emerged as attractive materials for a wide range of applications due to their unique properties. Further, these materials have exhibited satisfactory performance towards the removal of H_2S .

Hence, we report herein the fabrication of a nanocomposite of ZIF-67 and layered triple hydroxide (LTH) composed of copper, magnesium, and iron. Three (3) CuMgFe-LTH/ZIF-67 nanocomposites with different ratios (2:1, 1:1, and 1:2) were synthesized and referred to as LZ1, LZ2, and LZ3, respectively. The synthesized CuMgFe-LTH/ZIF-67 nanocomposites were incorporated into an aqueous drilling fluid formulation to investigate their H_2S scavenging performance, which was evaluated using a breakthrough experiment. Additionally, the influence of the CuMgFe-LTH/ZIF-67 nanocomposite with the best

performance toward H₂S removal on the rheology and filtration loss of the drilling fluid was investigated and discussed. The base fluid formulation utilized in this section of the work was similar to the previous formulation used however, the fluid loss agents that is the starch and XC polymer contents were increased to 10.0 and 0.4 g respectively to increase fluid retention in the drilling fluid. Interestingly, this increase of the FL agent showed a 4.6% fluid retention compared to the base fluid used in the previous sections. Notably, the additional FL agents incorporated neither improved the breakthrough nor saturation time of the mud and had no discernable influence on the H₂S removal performance. The rheological parameter, on the other hand, increased in the base mud.

6.2 Results and discussion

6.2.1 FT-IR analysis

Figure 6-1 depicts the FT-IR spectra of the synthesized CuMgFe-LTH/ZIF-67 nanocomposites. The spectra show the typical absorption bands associated with both ZIF-67 and LTH intercalated with CO₃²⁻ anions [216,217]. The wide absorption band around 3459 cm⁻¹ could be attributed to the O-H vibrational stretch of the water molecules present in the brucite layer or on the surface of the ZIF-67 [218]. The band at 2978 cm⁻¹ can be attributed to the strong O-H-O stretch of the hydrogen bonding in the interlayer space connected to the intercalated CO₃²⁻ anion or water molecules [219], and the aromatic and aliphatic C-H stretching vibration of the methyl group in the imidazole ring [180]. The peak at 1646 cm⁻¹ corresponds to the O-H bending vibration of the water molecules intercalated in the interlayer space. The peak at 1580 cm⁻¹ is attributable to the presence of C=N stretching vibration in the imidazole ring. The absorption band characterizing the

asymmetric vibration of the CO_3^{2-} anion is located at 1361 cm^{-1} [220]. The peaks at 1146 and 988 characterize the stretching and bending vibrations of the C-N in the aromatic imidazole ring. The peak at 1411 cm^{-1} correspond to the C=C bonds in the imidazole ring [248]. The bands after 700 cm^{-1} are related to the lattice vibrations of the metal oxides [221]. Overall, the FT-IR spectra reveals the presence of CO_3^{2-} , O-H, imidazole rings and metal ions, confirming the formation of the nanocomposites.

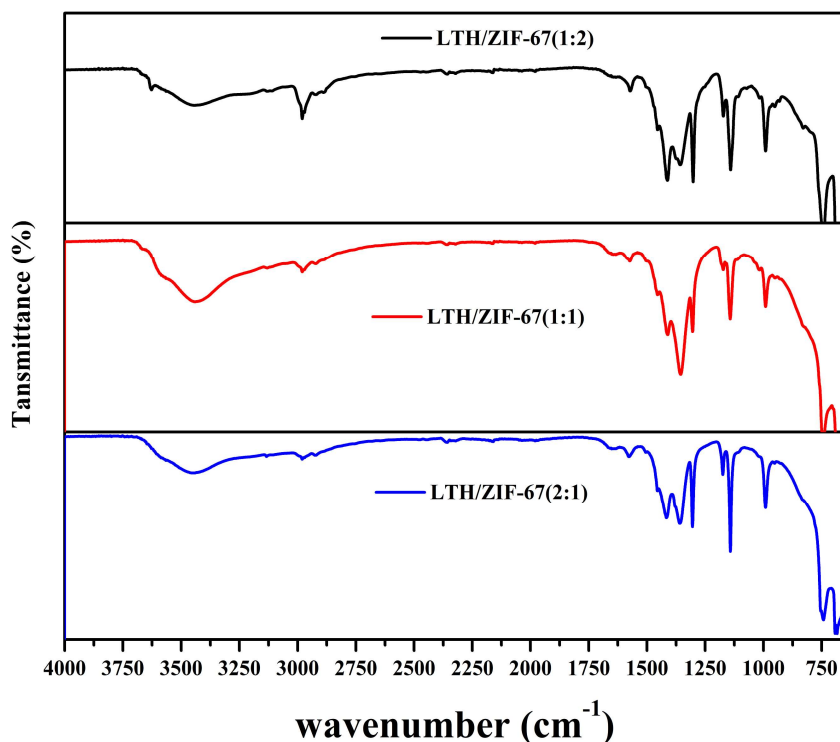


Figure 6-1: FT-IR Spectra of CuMgFe-LTH/ZIF-67 nanocomposites.

6.2.2 XRD analysis

The crystallographic patterns of the CuMgFe-LTH/ZIF-67 nanocomposites are depicted in Figure 6-2. The nanocomposites exhibited characteristic peaks of both ZIF-67 and LTH. The diffraction peaks positioned at $2\theta = 11.52, 23.12, 35.68, 38.96$ and 45.84° could be correlated to the (003), (006), (012), (015), and (018) miller indices respectively representing the crystallographic planes of the LTH structure in the synthesized

nanocomposite [211]. However, some characteristic peaks of ZIF-67 were missing or reduced in intensity. For LTH/ZIF-67(2:1), characteristic peaks of the ZIF-67 were observed at $2\theta = 7.76, 19.24, \text{ and } 32.60^\circ$ which correlates to the (011), (222), and (235) crystal planes of the ZIF-67 nanocrystals. For LTH/ZIF-67(1:1), peaks observed at $2\theta = 8.6, 13.96, 15.72, 19.44, 21.2, 25.72, 29.08, \text{ and } 32.60^\circ$ corresponds to the (011), (112), (022), (222), (114), (224), (044) and (235) crystal planes of the ZIF-67 nanocrystals. The LTH/ZIF-67(1:2) exhibited peaks at $7.36, 12.24, 13.36, 16.48, 18.12, 21.08, 25.04, 31.20, \text{ and } 32.76^\circ$ correlates to the (011), (022), (013), (222), (114), (233), (334) and (235) crystal planes associated with the ZIF-67 nanocrystals [181,183]. The result obtained from the XRD reveals the successful synthesis of the LTH/ZIF-67 nanocomposites.

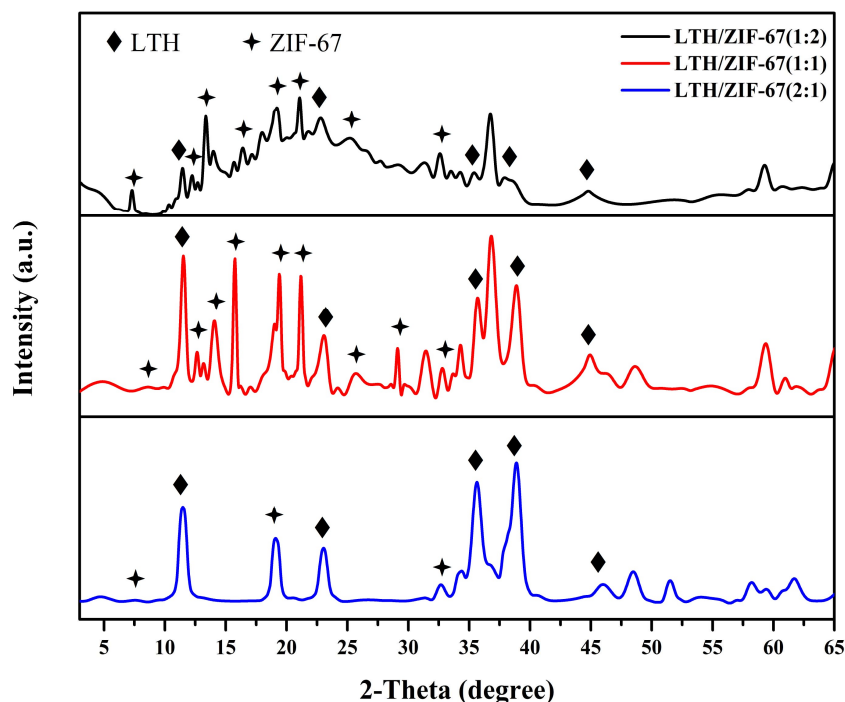


Figure 6-2: XRD Spectra of CuMgFe-LTH/ZIF-67 nanocomposites.

6.2.3 Thermogravimetric analysis

To evaluate the thermal stability of the synthesized nanocomposites, thermogravimetric analysis (TGA) was carried out on each sample. The TGA profiles of the nanocomposites

are presented in Figure 6-3. The TGA profiles shows several weight loss stages between 30 and 902 °C. The three nanocomposites exhibited similar profiles, weight loss stages, derivative weight peaks, and almost the same degree of thermal stability. The first significant weight losses are observed between ~120 to ~185°C, which are mainly due to loss of adsorbed or surface moisture. The dehydration of the hydroxyl and decarbonation of the CO_3^{2-} anions in the LTH occurs within the temperatures ranges of ~206 – ~280°C and ~308 – ~399 °C, respectively [222]. The major weight loss of the nanocomposite is noticed between ~424 – 541 °C owing to the loss of the 2-methylimidazole ligand [185]. Notably, the nanocomposite exhibited good thermal stability which makes it suitable to be utilized for drilling fluid applications. Up to a temperature of 400°C, the nanocomposites lost less than 30% of the initial weight.

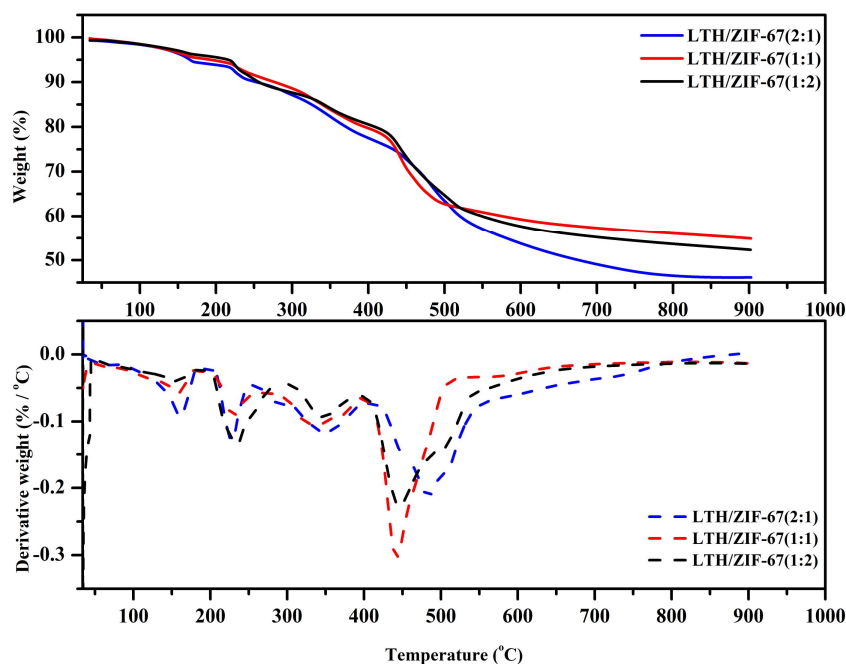


Figure 6-3: TGA profile of the nanocomposites.

6.2.4 Textural properties

The textural properties of the synthesized nanocomposites were evaluated using the N_2 adsorption-desorption isotherms analysis conducted at $-196\text{ }^\circ\text{C}$; the obtained isotherms are depicted in Figure 6-4. The CuMgFe-LTH/ZIF-67 nanocomposites exhibited type IV isotherms with a type-1 hysteresis loop according to the IUPAC classifications [223]. This indicates the existence of uniform mesopores with slight micropores. Table 6-1 summarizes the textural properties of the NCs. Comparatively, the LZ1 had the highest pore volume among the three NCs, whereas LZ3 had the lowest. The BET surface area of LZ3 was slightly and three times greater than those of LZ1 and LZ2, respectively. Consequently, the average particle sizes of LZ1 and LZ3 were almost three times larger than those of LZ2, implying that LZ1 and LZ3 could potentially achieve better H_2S removal. In addition, the existence of mesopores in the NCs is indicative of a potentially good H_2S scavenging capacity because the sites could easily engage the dissolved sulfide species on the surfaces of the NCs, as well as those inside these porous regions.

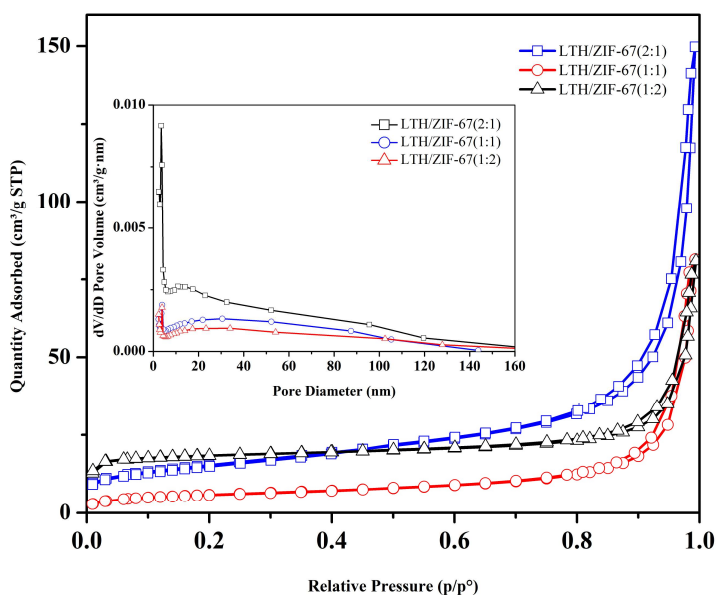


Figure 6-4: Nitrogen (N_2) Adsorption/desorption Isotherm for CuMgFe-LTH/ZIF-67 nanocomposites.

Table 6-1: Textural properties of the NCs.

NCs	BET surface area (S_{BET}) (m^2/g)	Pore volume (V_{p}) (cm^3/g)	Average pore size (d_{p}) (nm)	Average particle size (nm)
LZ1	54.22	0.23	9.20	187.54
LZ2	21.07	0.13	14.64	552.84
LZ3	67.04	0.10	4.67	177.22

6.2.5 Screening of CuMgFe-LTH/ZIF-67 nanocomposite

From the results presented in the earlier chapter, the ZIF-67 and CuMgFe-LTH have exhibited remarkable H_2S removal performance when compared with other nanomaterials that have been reported in the literature for such applications. As such, we sought to investigate the performance of their nanocomposite towards H_2S removal. This was done by preparing three CuMgFe-LTH/ZIF-67 nanocomposites with varying ratios of 2/1, 1/1, and 1/2, denoted a LZ1, LZ2, and LZ3 respectively, which were tested for H_2S removal. The result obtained from the test is presented in Table 6-2. The nanocomposite was incorporated into the aqueous drilling fluid formulation at 0.25 wt.%. From the result, the nanocomposite almost had the same breakthrough time. However, the LZ1, exhibited better performance with the highest saturation time of 1319.50 min. Hence, the LZ1 nanocomposite was then utilized for further studies in this chapter and subsequent sections.

Table 6-2: H_2S removal and rheological performance of the CuMgFe-LTH/ZIF-67 nanocomposites screening at 0.25 wt.%.

NC	AV	YP	PV	(YP/PV)	GS (10 s)	GS (10 min)	BT (min)	ST (min)	FL (ml)
LZ1	21.09	8.81	15.36	0.57	4.50	22.11	545.00	1319.50	17.2
LZ2	29.97	15.26	20.45	0.75	7.24	36.39	536.50	839.50	16.8
LZ3	30.99	9.00	15.17	0.59	5.28	22.89	523.00	1049.00	17.00

6.2.6 Hydrogen sulfide removal

Figure 6-5 depicts the H₂S scavenging performance of the LZ1 nanocomposite. The breakthrough time obtained for the aqueous drilling fluid formulation containing 1.0 wt.% LZ1 (abbreviated as LZ1-BM, hereafter) was about 1011.5 min (i.e., 16.86 h) which corresponds to an H₂S removal capacity of 140.77 mg H₂S/g scavenger. Up until the breakthrough time, the LZ1-BM was capable of continuously removing all the H₂S from the entering gas stream with no H₂S present in the outlet gas stream. Beyond the breakthrough time, the H₂S concentration in the gas effluent gradually increased up to the saturation time, at which the amount of H₂S in the outlet stream is the same as that in the inlet stream. At saturation, most of the H₂S scavenging sites on the LZ1 are utilized. The H₂S scavenging capacity of the LZ1-BM at the saturation time of 25.91 h reached 184.76 mg H₂S/g scavenger. Compared to the base mud without any scavenger (BM), which only reached breakthrough and saturation after 34.5 and 325 min, respectively, the LZ1-BM exhibited a very remarkable H₂S scavenging capacity, as seen in Figure 6-5. Comparing with the pristine ZIF-67 and CuMgFe-LTH drilling fluid formulations presented in earlier chapters, the order of H₂S removal is as follow; ZIF-67< LZ1<CuMgFe-LTH. The addition of the CuMgFe-LTH to the ZIF-67 improved the H₂S scavenging capacity of the drilling fluid formulation when compared to the formulation with the pristine ZIF-67. This addition increased the breakthrough and saturation capacities by 20.12 and 12.97%, respectively. The H₂S removal capacities of the LZ1 nanocomposite is shown in Table 6-3. Comparing the saturation periods obtained at the two distinct LZ1 concentrations of 0.25 wt.% and 1.0 wt.% (thus for the screening test and further studies), it was observed that the ST increased by only 235 min at the highest dosage of 1.0 wt.%. This shows that the sites for the scavenging of the H₂S and its associated sulfide species were readily accessible at 0.25

wt.% concentration than at 1.0 wt.%. In other words, the available sites on LZ1 scavenger were not fully utilized at the highest dosage, which implies that the sorption capacity of H₂S could potentially be extended if 100% utilization of the scavenging sites could be achieved.

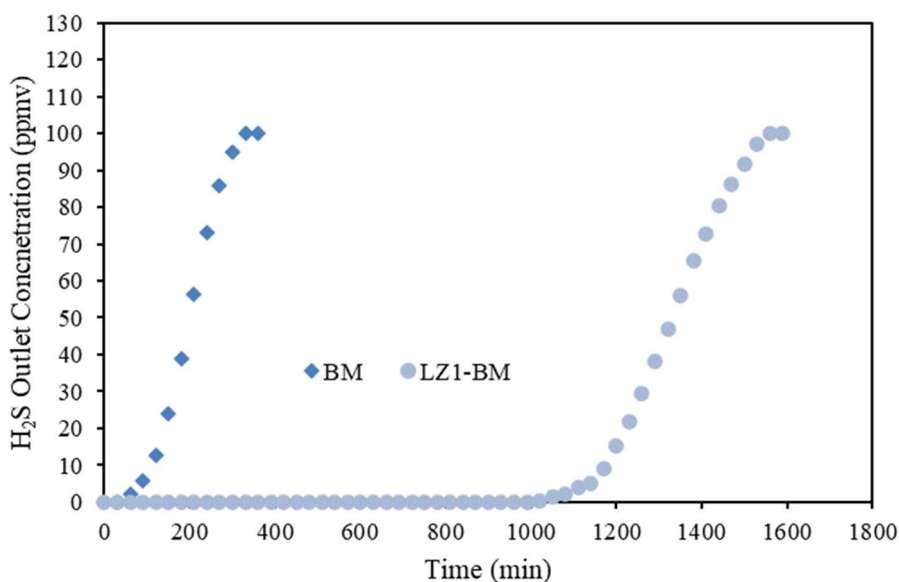


Figure 6-5: H₂S scavenging performance of the BM and LZ1-BM in a continuous breakthrough experiment (LZ1-BM contains 1 wt.% CuMgFe-LTH/ZIF-67(2:1)).

Table 6-3: Breakthrough time, breakthrough capacity, saturation time, saturation capacity of drilling muds.

Parameters	BM	LZ1-BM
Breakthrough time (min)	34.5	1011.5
Saturation time (min)	325	1554.5
Breakthrough capacity (mg/g)	-	140.77
Saturation capacity (mg/g)	-	184.76
Breakthrough capacity (mg/L)	52.3	1513.27
Saturation capacity (mg/L)	294.6	1986.18

6.2.7 Filtration properties

API filter press tests were performed to get insights into the amount of filtrate that will be lost, and the thickness of the mud cake layer formed. The fluid loss property is an essential

aspect of drilling fluid behavior and has significant implications for wellbore stability and overall fluid performance [199,225]. Figure 6-6 depicts the API LPLT fluid loss volumes of the BM and LZ1-BM. The filtrate volume of the BM is approximately 12.2 mL, while the LZ1-containing formulation at 1.0 wt.% resulted in a volume of 13.6 mL. The addition of the LZ1 nanocomposite led to an increase in the filtrate volume. However, it is important to note that the obtained filtrate volume remains within the recommended range for LPLT conditions. Ideally, when introducing nanoparticles (NPs), the filtrate volume should decrease due to the increase in solid content. Also, the permeability of the deposited filter cake layer and, consequently, the fluid loss volume are primarily influenced by the particle size, additives within the drilling fluid, and the extent of nanoparticle dispersion [226]. Additionally, agglomeration has the potential to impact fluid loss volume through the formation of permeable cake layers, leading to an increase in filtrate volume [89,200]. This increase is evident in the LZ1-BM formulation, which showed a 11.48% rise in filtrate volume. Despite this increment, the nanocomposite still remains within the recommended limit of 15 mL, indicating its ability to effectively control fluid loss and mitigate the issue. Furthermore, the LZ1-BM formulation provides an added advantage by improving H₂S scavenging performance. This advantageous trait makes the LZ1 nanocomposite an exceptionally favorable additive for drilling fluid applications.

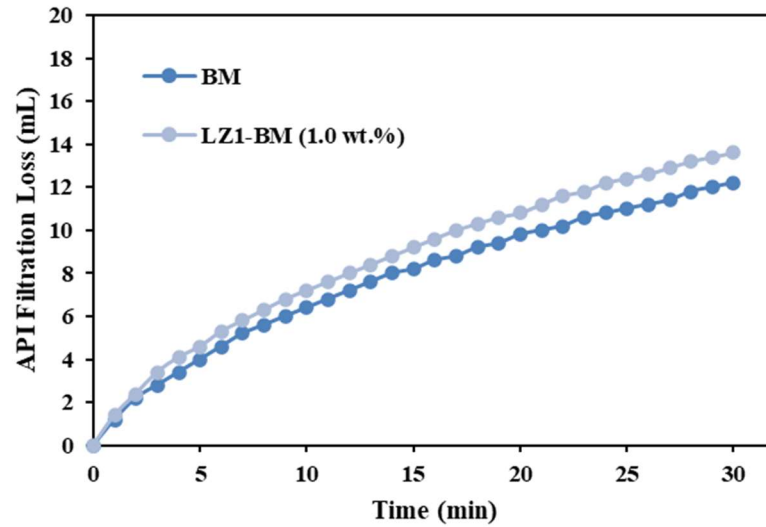
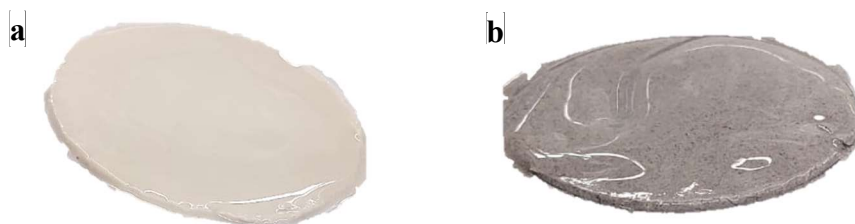


Figure 6-6: API LPLT filtrate loss of the BM and the LTH-BM formulations.

Furthermore, we also conducted measurements of the filter cake thickness. The filter cake layer plays a critical role as it acts as a barrier, preventing further loss of filtrate into the formation and aiding in maintaining the integrity of the wellbore [229]. A range of factors, such as mud properties, operating conditions, and formation properties, can influence the thickness of the filter cake [230,231]. Ensuring proper control of the filter cake thickness is essential because it enhances cutting transport and helps regulate well pressure [90]. The thickness of both BM and LZ1-BM filter cake layers is provided in Table 6 3. Our results indicate that incorporating the 1.0 wt.% LZ1 nanocomposite into the BM formulation had no impact on the thickness of the filter cake layer. Both the base mud (BM) and the nano-mud (LZ1-BM) had a filter cake layer thickness of 3/32 inch. The incorporation of the LZ1 nanocomposite is observed not to have enhanced the filter layer thickness. Putting together this observation with the FL volume lost, the formulations with the LZ1 exhibited appreciable control over the loss of filtrate and prevented excessive loss of fluid from the base mud. A physical illustration of the filter cakes obtained are presented in Figure 6-7.

Table 6-4: API LPLT filter cake thickness.

Formulation	Cake Thickness		FL (ml)
	1/32 inch	(mm)	
BM	3	2.38	12.2
LZ1-BM (1.0 wt.%)	3	2.38	13.6

**Figure 6-7: Photos of the API LPLT filter cake of (a) BM and (b) LZ1-BM formulations.**

6.2.8 Effect of CuMgFe-LTH/ZIF-67 on the rheological properties

The influence of the LZ1 nanocomposite on the plastic and apparent viscosity is presented in Figure 6-8. As displayed in Figure 6-8, the values of the AV are greater than the PV for all the formulations prepared. Further, the AV increases gradually from 25.15 to 52.54 cP with the increase of LZ1 nanocomposite content from 0.0 to 1.0 wt.%. Similarly, the PV increases from 18.30 to 32.00 cP within the same range. This general increase in viscosity is as a result of the increase in solid content and the association between the drilling fluid additives [232]. Unlike the trend of the viscosity observed in previous chapters, the PV and AV do not exhibit any declining trend at lower nanocomposite dosages. The AV and PV increased by about 4.25 and 3.17%, respectively, with the addition of 0.05 wt.% LZ1 nanocomposite. The increase in the content of the viscofiers (i.e., xanthan gum and starch) might have improve 3D or gel like network formation in the drilling fluid which might

have been enhance by the nanocomposite and hence, resulted in the observed gradual increase in the viscosities.

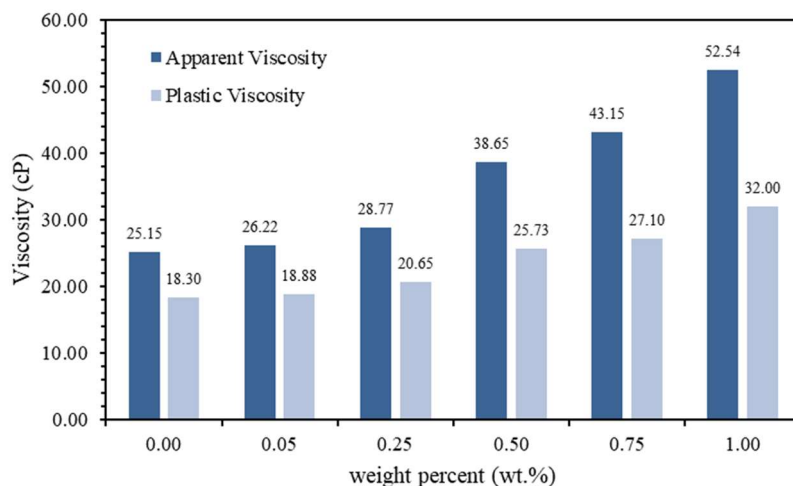


Figure 6-8: Influence of NPs on PV and AV of the formulated WBM.

Figure 6-9 depicts the influence of LZ1 nanocomposite on the yield point (YP) and carrying capacity. As presented in Figure 6-9, the YP and carrying capacity of the formulated water-based drilling muds increase upon the addition of the LZ1 nanocomposite. The YP and carrying capacity gradually increase with increasing LZ1 nanocomposite content from 13.70 to 41.10 Ib/100 ft² and 0.75 to 1.28 Ib/100 ft²/cP, respectively. The YP and carrying capacity increased by about 7.15 and 4%, respectively, with the addition of 0.05 wt.% LZ1 nanocomposite. The LZ1 nanocomposite was found to be good for increasing the yield point and carrying capacity. This increase in these rheological properties indicates that the LZ1 nanocomposite can improve the hole cleaning performance of the drilling fluid. The observed trend could be attributed to the increase in electrostatic interaction between the drilling fluid particles [238]. Further, the increase in PV discussed earlier which is as a

result of the increase in solid contents and formation of strong gel or 3D network within the drilling fluid system is likely to contribute to the increase in carrying capacity.

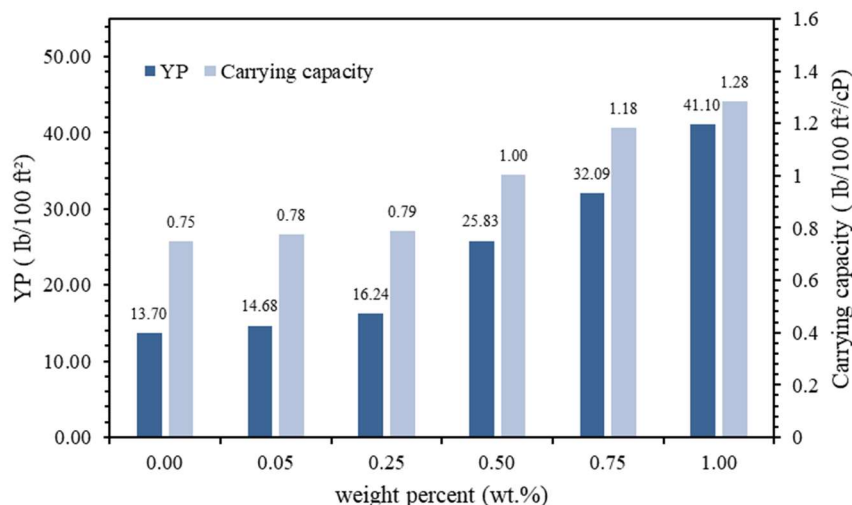


Figure 6-9: Influence of NPs on YP and Carrying Capacity of the formulated WBM.

Another important rheological characteristic of drilling fluids is their gel strength. This property shows how well the fluid can maintain a gel-like structure while it is not in motion or under completely static conditions [191]. The thixotropic nature of drilling fluids, demonstrated by their gel strength, plays a crucial role in preventing cuttings from settling when circulation is paused. This ensures that the cuttings remain suspended and do not accumulate at the bottom of the wellbore [37]. Moreover, the gel strength of the drilling fluid contributes significantly to wellbore stability by providing support to the walls, reducing fluid invasion into the formation, and lowering the risk of differential sticking [239,240].

In Figure 6-10, it is evident that the 10-s gel strength (GS) is smaller than the 10-min GS, indicating the impact of static periods during drilling fluid on its rheological property. The 10-min GS is determined after allowing a 10-min static period for the LZ1 nanocomposite

and other drilling fluid additives to reorganize in a way that minimizes free energy through electrostatic surface charge compensation [84]. This reorganization leads to the creation of a more robust gel structure compared to the 10-s static time, resulting in a higher GS.

Moreover, as the concentration of the LZ1 nanocomposite increased, both the gel strength at 10-s and 10-min showed a corresponding increase. It is a common characteristic for nanoparticles in drilling fluids or other aqueous dispersions to carry surface charges [238,241]. As the concentration of these nanoparticles in the fluid rises, their zeta potential and surface charge also increase [241]. This leads to a higher abundance of colloidal and surface-charged particles in the fluid, resulting in a strengthened gel strength. Also, the presence of polymers like xanthan gum and starch in the fluid contributes to the formation of a stronger gel, further impacting its strength. Therefore, the enhanced gel strength observed after adding the LZ1 nanocomposite can be attributed to the charges of the LZ1 nanocomposite, which likely strengthened the gel structure and the network of drilling fluid additives through electrostatic interactions [84]. Interestingly, similar outcomes have been reported in the published literature involving other types of nanoparticles [242,243].

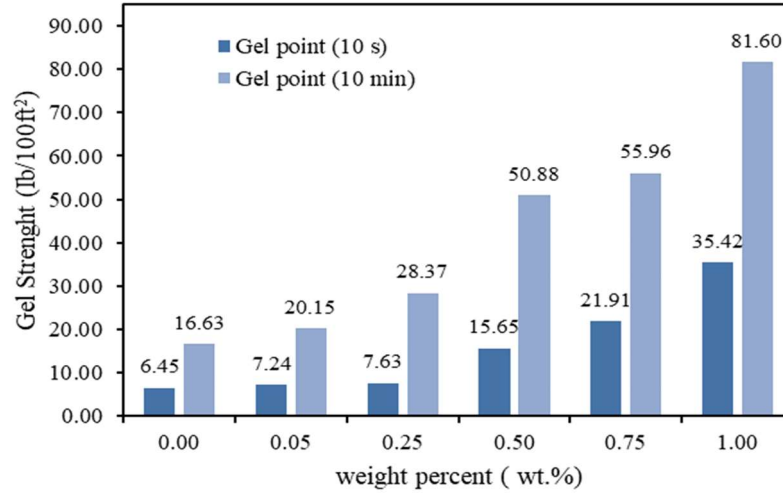


Figure 6-10: Influence of NPs on the 10 s and 10 min gel strengths of the formulated WBM.

6.2.9 Rheological modelling of the WBMs

Table 6-5 presents the predicted model parameters for the drilling fluid formulations. Based on the R^2 values obtained, the Herschel-Bulkley and Sisko models are found to be the most suitable ones for describing the behavior of all the prepared formulations, as their R^2 values are closest to unity. The order of the models that best track the shear rate-shear stress curve of the formulation is as follows: Herschel-Bulkley > Sisko > Bingham > Ostwald power law. The fitting of shear rate-shear stress data is shown in Figure 6-11 for both the base mud (BM) and all LZ1-BM formulations. Furthermore, the dimensionless flow index (n) obtained using the Herschel-Buckley, Ostwald power law, and Sisko models for both the base mud (BM) and all LZ1-BM formulations is less than 1, indicating that they all behave like pseudoplastic or shear-thinning fluids. Moreover, the dimensionless flow index demonstrates a decreasing trend with increasing LZ1 content, which is favorable, as lower values of the dimensionless flow index indicate proper hole cleaning [244]. Interestingly, the incorporation of LZ1 resulted in an increase in the coefficient of viscosity of the drilling

mud. This suggests that LZ1 could be utilized to enhance the capacity to remove cuttings from drilled wells, suspend and transport them to the surface, and maintain wellbore stability [246].

Table 6-5: Rheological parameters of water-based drilling fluids containing LZ1 at different concentrations.

NC (wt.%)		BM	0.05	0.25	0.5	0.75	1.00
Newtonian model	μ_P	0.058	0.061	0.067	0.092	0.104	0.128
	R^2	0.860	0.840	0.841	0.739	0.655	0.558
Bingham model	μ_P	0.045	0.046	0.051	0.063	0.066	0.071
	τ_o	9.100	10.238	11.203	20.211	27.222	40.289
	R^2	0.988	0.990	0.987	0.988	0.990	0.989
Herschel Buckley	τ_o	6.716	8.034	8.466	17.075	24.890	40.040
	k_H	0.207	0.188	0.238	0.269	0.196	0.080
	n	0.783	0.800	0.780	0.793	0.843	0.982
	R^2	1.000	0.999	0.999	0.998	0.996	0.990
Ostwald power law model	k_P	1.207	1.499	1.673	5.206	9.978	20.756
	n	0.542	0.516	0.514	0.387	0.305	0.221
	R^2	0.971	0.961	0.965	0.932	0.894	0.825
Sisko model	k_2	0.036	0.038	0.041	0.053	0.058	0.071
	k_1	5.306	6.590	6.804	14.859	23.216	40.289
	n	0.168	0.138	0.156	0.098	0.051	0.001
	R^2	0.999	0.998	0.999	0.997	0.994	0.999

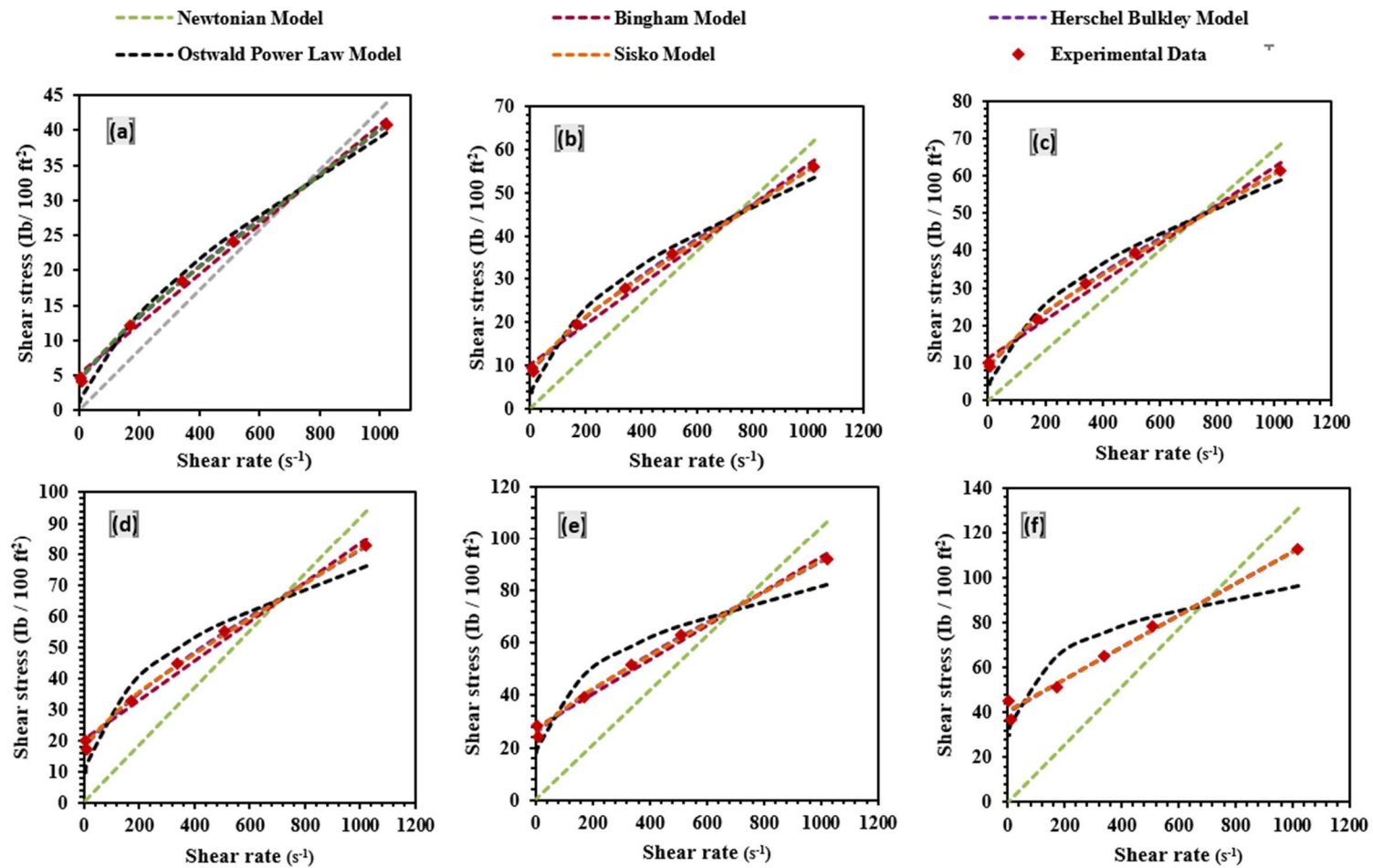


Figure 6-11: Rheological modelling of the (a) the base mud, and the NCs containing mud at (b) 0.05 wt.%, (c) 0.25 wt.%, (d) 0.50 wt.%, (e) 0.75 wt.% and (f) 1.0 wt.% concentrations, respectively.

6.3 Summary

CuMgFe-LTH/ZIF-67 has proven to be a compelling additive, significantly improving the performance of H₂S scavenging in water-based drilling muds (WBM). Furthermore, incorporating CuMgFe-LTH/ZIF-67(2:1) in WBMs offers a practical way to enhance various rheological properties, such as apparent and plastic viscosities, yield point, gel strength, and overall carrying capacity. The addition of the CuMgFe-LTH/ZIF-67(2:1) caused an increase in all the rheological parameters. The CuMgFe-LTH/ZIF-67(2:1) - containing muds display pseudoplastic behavior (shear thinning), indicating that introducing these nanocomposites to the base mud results in a favorable fluid flow behavior. Further, it is worth noting that the increase in filtration loss on addition of the 1.0 wt.% CuMgFe-LTH/ZIF-67(2:1) is negligible and remains within the recommended range. Overall, utilizing CuMgFe-LTH/ZIF-67(2:1) in drilling applications offers several advantages, underscoring its promising commercial potential in the oilfield industry.

CHAPTER 7

CONCLUSION AND RECOMMENDATION

7.1 Conclusion

The continuous removal of hydrogen sulfide (H_2S) gas in a bubble column and the rheological properties of aqueous drilling fluid formulations were investigated in this study using novel drilling fluid nano-additives (i.e., ZIF-67, CuMgFe-LTH, and their nanocomposites). Analytical characterizations indicated that the nano-additives were successfully synthesized and had good thermal stability for drilling fluid applications. The formulated base mud showed low H_2S removal capacities, whereas the respective formulations with these nano-additives showed significantly improved H_2S scavenging capacities. The breakthrough capacities of 117.2, 216.3, and 140.8 mg H_2S /g scavenger, equivalent to 1259.8, 2325.2, and 1513.3 mg/L of drilling fluid, respectively, were obtained for ZIF-67, CuMgFe-LTH, and CuMgFe-LTH/ZIF-67(2:1) nanocomposite, respectively. At saturation, 163.6, 263.0, and 184.8 mg H_2S /g scavenger, equivalent to 1758.1, 2881.4, and 1986.2 mg/L of drilling fluid, respectively, were removed. Moreover, the rheological behavior of the base formulation, including nano-drilling fluids, was best described by the Herschel-Buckley and Sisko rheological models. Furthermore, the pseudoplastic (i.e., shear thinning) behavior of the additive-containing formulations confirms that their incorporation into the base formulation provides and maintains favorable fluid flow behavior. These findings indicate that the nano-additives developed in this study are effective, promising, and excellent candidates for enhancing the H_2S scavenging performances of aqueous drilling fluids. Furthermore, the additives utilized herein not only mitigated H_2S release per se, but also significantly augmented the rheological parameters

and exhibited appreciable control of the filtration properties of the formulated water-based drilling fluids.

7.2 Recommendations

Metal–organic frameworks (MOFs) and layered triple hydroxides (LTHs) are among the most recent classes of nanomaterials that are incredibly promising in diverse areas of research, particularly for environmental remediation and mitigation of exposure to toxic substances. For the first time, these materials have been utilized in aqueous drilling fluid formulations owing to their remarkable thermal and chemical stability. Notably, these materials are suitable for utilization in upstream well development, particularly where H₂S is prevalent, based on the findings of the present work. Nevertheless, there are still some gaps that should be examined in future studies. These are some recommendations to be tackled in future research work:

- i. Explore the rheology and performance of the nanomaterial towards H₂S removal under high-pressure and high-temperature (HPHT) conditions.
- ii. Investigate the long-term stability of the nanomaterial in the aqueous drilling fluid formulations.
- iii. Evaluate the influence of nanocomposites of MOFs and LTHs with polymers and/or surfactants on the rheology and performance of drilling fluids.
- iv. Examine in detail the structure-rheology relationship of MOFs and LTHs on the performance of drilling fluids.
- v. Investigate the performance of MOFs and LTHs towards shale recovery, shale swelling, and salt tolerance in aqueous drilling formulations.

- vi. Development techniques that could facilitate the regeneration of the spent H_2S scavenger to allow multiple cycles of H_2S removal.

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Vitae

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Research Outcome

Journal Publications:

- **Iddrisu, M.**, Onaizi, S.A. (2023). H₂S scavenging performance and rheological properties of water-based drilling fluids comprising ZIF-67. *Geoenergy Science and Engineering* 228, 212007. <https://doi.org/10.1016/j.geoen.2023.212007>.
- **Iddrisu, M.**, Al-Sakkaf, M. K., Bahadi, S. A., Zahid, U., Drmosh, Q. A., Ahmed, U., & Onaizi, S. A. (2023). Waste to a commodity: the utilization of waste cooking oil for the formulation of oil-based drilling mud with H₂S scavenging capability bestowed by the incorporation of ZIF-67. *Emergent Materials*, 1–10. <https://doi.org/10.1007/s42247-023-00531-x>.
- **Iddrisu, M.**, Bahadi, S. A., Al-Sakkaf, M. K., Ahmed, U., Zahid, U., Drmosh, Q. A., & Onaizi, S. A. (2023). Harnessing zeolitic imidazolate framework-8 (ZIF-8) nanoparticles for enhancing H₂S scavenging capacity of waste vegetable oil-based drilling fluids. *Emergent Materials*, 1–12. <https://doi.org/10.1007/s42247-023-00535-7>.

- **Iddrisu, M.**, Al-Amrani, W. A., Merghani, A. A., Drmosh, Q. A., & Onaizi, S. A. (2023). Effects of detergent on enzyme adsorption onto solid surfaces. Emergent Materials, 1–8. <https://doi.org/10.1007/s42247-023-00578-w>.
- Bahadi, S.A., **Iddrisu, M.**, Al-Sakkaf, M.K., Elgzoly, M.A.A., Al-Amrani, W.A., Ahmed, U., Zahid, U., Drmosh, Q.A., Onaizi, S.A., 2023. Chemically versus thermally reduced graphene oxide: effects of reduction methods and reducing agents on the adsorption of phenolic compounds from wastewater. Emergent Mater 1–13. <https://doi.org/10.1007/s42247-023-00514-y>
- Bahadi, S.A., **Iddrisu, M.**, Al-Sakkaf, M.K., Elgzoly, M.A.A., Drmosh, Q.A., Al-Amrani, W.A., Ahmed, U., Zahid, U., Onaizi, S.A., 2023. Optimization of methyl orange adsorption on MgFeAl-LTH through the manipulation of solution chemistry and synthesis conditions. Emergent Mater 1–13. <https://doi.org/10.1007/s42247-023-00513-z>.
- **Iddrisu, M.**, Onaizi, S.A. Effect of layered triple hydroxide/ZIF-67 nanocomposite on the rheology and H₂S removal performance of water-based drilling fluid. (Under preparation).
- **Iddrisu, M.**, Onaizi, S.A. Aqueous Drilling Fluid Comprising CuMgFe-Layered Triple Hydroxide: Rheology, Filtration loss and H₂S Scavenging Performance. (Under preparation).

Submitted Patent Applications:

- Onaizi, S.A., **Iddrisu, M.**, (2023). Enhancing H₂S Scavenging in Drilling Operations through the Integration of CuMgFe-Layered Triple Hydroxide in Water-Based Drilling Fluids.
- Onaizi, S., **Iddrisu, M.** (2023). Incorporating imidazole-based material into water-based drilling fluids for effective H₂S scavenging during drilling operations.