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**Rheology of bentonite-polymer systems:  
application to drilling fluids**

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## Abstract

*The objective of this study is to examine the rheological properties of bentonite suspensions, both with and without additives. Bentonite is a crucial component of water-based drilling mud. The specific additive employed in this study is carboxymethylcellulose. The second phase of the research focuses on investigating how the concentration of the bentonite suspension and the percentage of the additive impact the rheological parameters associated with the behavior of the fluid. Subsequently, an optimization analysis will be conducted based on the findings and discussions from the initial two phases. To characterize the fluid, a "Couette" type rheometer with coaxial cylinders and cone-plane configuration is used.*

## Résumé

*Le but de ce travail est d'identifier le comportement rhéologique des suspensions de bentonite avec ou sans présence d'additifs. La bentonite est le principal constituant de la boue de forage à base d'eau. L'additif utilisé dans ce travail est le carboxyméthylcellulose. La seconde partie du travail consiste à étudier l'influence de la concentration de la suspension de bentonite et le pourcentage de l'additif sur les paramètres rhéologiques intervenant dans la loi de comportement. Enfin, une étude d'optimisation sera menée sur la base des résultats trouvés et discutés dans les deux premières parties de ce travail. La caractérisation du fluide utilisé est effectuée à l'aide d'un rhéomètre de type « Couette » à cylindres coaxiaux et cône-plan.*

## ملخص

الهدف من هذا العمل هو تحديد السلوك الانسيابي لمعلقات البنتونيت مع أو بدون وجود مواد مضافة. البنتونيت هو المكون الرئيسي لطين الحفر المائي. المادة المضافة المستخدمة في هذا العمل هي كربوكسي ميثيل سلولوز. الجزء الثاني من العمل يتكون من دراسة تأثير تركيز معلق البنتونيت ونسبة المادة المضافة على المتغيرات الانسيابية المتضمنة في قانون السلوك. أخيرًا، سيتم إجراء دراسة التحسين بناءً على النتائج التي تم العثور عليها ومناقشتها في الجزأين الأولين من هذا العمل. يتم توصيف السائل المستخدم باستخدام مقياس ريومتر من نوع اللحاف مع أسطوانة متحدة المحور ومستوى مخروطي.

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BEN ABDI SOUMIA

BAYOU Manel

# Dedication

From the bottom of my heart, I dedicate this modest work:

To the one who gave me life, to the one who has done everything to make my life easier, my dear loving parents,

To my dear sisters Ahlem and Céline, for their constant encouragement and moral support,

To the memory of my uncle KARIM and my grandmother, who always dreamed of seeing me succeed,

To Ms. BOUISRI Nabila and NADI Souad for all their support and encouragement,

To my dear friends, for their support and encouragement,

To my entire family BAYOU and KHALFI, for their support throughout my academic journey,

A special dedication to someone who has been very motherly to me: Mrs. GUENDOUZ Fatiha. Please find in this modest work my sincere gratitude and appreciation,

May this work fulfill your long-standing wishes and be the result of your unwavering support,

Thank you for always being there for me.

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This work is dedicated to the ones who have been my guiding lights and unwavering support throughout this period.

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With deep gratitude and appreciation,

BEN ABDI Soumia

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# General Introduction

Rheology is the study of the flow and deformation of materials under stress. It is a branch of physics and materials science that deals with the behavior of complex fluids, such as polymers, suspensions, and emulsions, as well as soft solids, such as gels and pastes. Rheology is concerned with understanding the relationships between the forces applied to a material, its deformation, and its flow behavior. The properties of a material, such as its viscosity, elasticity, and yield stress, are critical in determining its rheological behavior. Rheological measurements are commonly used in a wide range of industries, including materials science, chemical engineering, food science, pharmaceuticals, cosmetics, and petroleum engineering. These measurements are used to design and optimize the processing and handling of materials, as well as to ensure that materials meet specific quality and performance standards. In summary, rheology is the study of how materials deform and flow under stress and is an essential tool for understanding and optimizing the behavior of complex fluids and soft solids [1].

In the petroleum sector, Rheology is used to design and optimize drilling fluids that are used to drill oil and gas wells. The viscosity and fluid behavior of the drilling fluids are critical to ensuring the efficient and safe drilling of the well. It is used also to design cement slurries that are used to cement the casing in place in oil and gas wells. The properties of the cement slurries, such as their viscosity and density, are critical to ensuring the successful completion of the well. Among the main objectives of rheology is the study of the flow behavior of oil and water in porous rocks in order to optimize the design of enhanced oil recovery techniques such as water flooding and polymer flooding. Finally, Rheology is used to study the flow behavior of crude oil and refined petroleum products in pipelines. Understanding the rheology of these fluids is critical to optimizing pipeline design and ensuring the efficient and safe transportation of these materials. Overall, rheology plays a crucial role in the design, development, and optimization of many processes and materials used in the petroleum industry [2, 3].

Polymers/clays are of great interest due to their wide and growing applications in industry. The polymer that is the subject of our work is carboxymethylcellulose (CMC) and bentonite as clay.

Moreover, the addition of polymers to bentonite suspensions causes a significant modification of its rheological properties. In general, the behavior laws of these materials turn out to be complex due to their shear-thinning character with yield stress and their viscoelastic behavior. The determination of the rheological properties of CMC/Bentonite dispersions, as well as the understanding of the interactions of a microscopic and physicochemical nature of these colloidal systems are essential elements for adapting the composition of the fluid to industrial conditions.

Our work consists mainly of five chapters:

Chapter 1 is dedicated to general notions of rheology. First, we will focus on the rheology of fluid materials, in particular the behavior of fluids in steady and oscillatory shear flow. Secondly, our interest will focus on the experimental devices and the various problems encountered in experimental rheology. Chapter 2 is devoted to the presentation of drilling fluids in the oil field while presenting the main functions of drilling fluids and their classification and also their compositions and properties. The rheology of bentonite suspensions is presented in chapter 3. We first present the procedure for the preparation of samples of bentonite suspensions and then the experimental study of these suspensions in water. In chapter 4, we study the rheology of aqueous solutions of CMC. A first part is dedicated to the bibliography study on CMC and the second is dedicated to the experimental study of aqueous solutions of CMC for several concentrations. The study and understanding of the rheological characteristics on the one hand of aqueous solutions of CMC and on the other hand of suspensions of bentonite in water, will subsequently facilitate the study of CMC/Bentonite/water mixtures. The last chapter focuses on the complete study of the rheology of bentonite suspensions in aqueous solutions of CMC. A single bentonite concentration was kept and the CMC concentrations were varied.

In conclusion, we will summarize the key findings of our study and provide an overview of the potential avenues for future research.



# Chapter 1

## Introduction to Rheology

### 1.1 Introduction

Rheology is a discipline that deals with the flow and deformation of materials under the influence of stresses. Rheology was developed to describe the properties of materials with behavior that is poorly defined and intermediate between that of a perfect elastic solid and that of a Newtonian fluid. The following section aims to define the main rheological parameters as well as the different types of fluid flow [4].

### 1.2 Overview of Rheology

The term rheology was created in the United States in 1929 by Eugene Cook Bingham (1878-1945). It refers to the study of the flow and deformation of materials (fluids) under the influence of applied stresses. Rheology encompasses the study of a wide range of materials and products, such as agro-food, cosmetic and pharmaceutical products, drilling muds, paper pulp, and many others.

#### 1.2.1 Objective of Rheology

The objective of rheology is to determine the rheological equation of state of a fluid by measuring its rheological parameters using instruments such as viscometers or rheometers. This rheological equation of state relates the shear rate  $\dot{\gamma}$  and shear stress  $\tau$  in the form of  $\tau = f(\dot{\gamma})$ . Knowing this equation allows for the experimental determination of the rheological properties of materials. It is important to note that the rheological equation of state not only depends on the

intrinsic characteristics of the fluid, such as its nature and physical properties, but also on external parameters such as temperature T and pressure P.

## 1.2.2 Shear Stress

The shear stress can be defined as the fundamental dynamic quantity in rheology. Let's consider two layers of fluid S1 and S2 in contact with each other that move relative to each other (Figure 1), resulting in the appearance of frictional forces that act tangentially to the surface of the layer  $\Sigma$ , these are the shear forces.

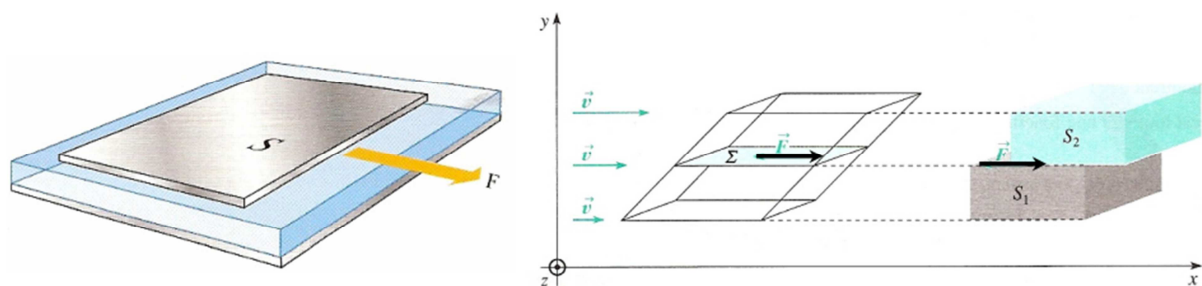


Figure 1 - Frictional force exerted on two adjacent layers during shear.

These shear forces are expressed by:

$$F = \mu \cdot S \cdot \frac{dv}{dy} \quad 1-1$$

With:

$\mu$  : Dynamic viscosity coefficient of the fluid.

$S$  : Surface of layers

$dv$  : Rate variation

$dy$  : Gap between two adjacent layers

$\frac{dv}{dy}$  : Velocity gradient

It is possible to relate these shear forces to the unit of surface on which they act and thus define the shear stress by:

$$\tau = \frac{dF}{dS} \quad 1-2$$

### 1.2.3 Shear Strain

To define shear deformation, we consider Flow between two parallel plates, for example, the experimental setup where the material is placed between two parallel plates, one of which is moving and the other is stationary. Let us consider the particles of matter that are present at time  $t=0$  in a certain cross-section. At a later time  $t$ , each particle of matter will have traveled the distance  $u(y, t)$ , where  $y$  represents the distance separating the particle of matter from the lower solid plane and allows the different plane layers of the material to be identified (Figure 2).

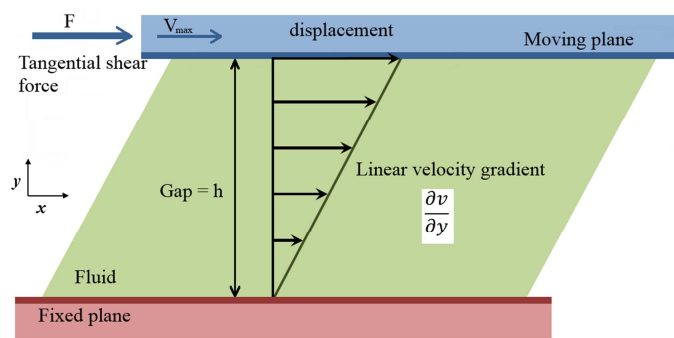


Figure 2 - Displacement gradient in a planar shear motion.

Shear deformation is defined in the case of plane symmetry by the equation

$$\gamma(y, t) = \frac{du(y, t)}{dy} \quad 1-3$$

### 1.2.4 Shear Rate

The shear rate expresses the effect or deformation due to shear stress by time; it corresponds to the transverse velocity gradient. In the case of flow between two parallel plates, we can write:

$$\dot{\gamma} = \frac{d}{dt} \left( \frac{du}{dy} \right) = \frac{d}{dy} \left( \frac{du}{dt} \right) = \frac{dv}{dy} \quad 1-4$$

### 1.2.5 Viscosity

This is a physical property of fluids. It expresses the effect of delay between two adjacent layers of the same fluid during its flow. Therefore, viscosity represents the resistance to the flow of a

system subjected to a tangential stress. Knowledge of this physical quantity is essential in the rheological study of a fluid. There are different types of viscosity, including:

### 1.2.5.1 Dynamic Viscosity

There are certain substances for which viscosity does not depend on the shear stress. These substances are called Newtonian fluids, and their viscosity coefficient is then called dynamic viscosity, denoted  $\eta$ .

$$\eta = \frac{\tau}{\dot{\gamma}} [Pa \cdot s] \quad 1-5$$

### 1.2.5.2 Kinematic Viscosity

Kinematic viscosity is of interest whenever viscosity depends on density (such as oils), where  $\rho$  is the fluid density in  $kg/m^3$ .

### 1.2.5.3 Relative Viscosity

In order to study solutions and dispersions, relative viscosity is often used, which is defined as follows:

$$\mu_r = \frac{\mu}{\mu_s} \quad 1-6$$

$\mu$  : Dynamic Viscosity of solution

$\mu_s$  : Dynamic Viscosity of solvent

### 1.2.5.4 Specific Viscosity

The study of solutions or dispersions aims to determine the respective influences of solids and solvents on rheological behavior. Other viscosity coefficients, such as the coefficient of relative viscosity mentioned below and the coefficient of specific viscosity given by

$$\mu_{sp} = \frac{\mu - \mu_s}{\mu_s} = \mu_r - 1 \quad 1-7$$

### 1.2.5.5 Intrinsic Viscosity

It is defined as

$$\mu_{in} = \lim_{C \rightarrow 0} \left( \frac{\mu_{sp}}{C} \right) \quad 1-8$$

$C$  : The concentration of solution

### 1.2.5.6 Complex Viscosity

In the case of viscoelastic fluids, complex viscosity is defined as follows

$$\mu^* = \frac{G''(\omega)}{\omega} - i \frac{G'(\omega)}{\omega} \quad 1-9$$

### 1.2.6 Rheogram

The rheogram is a graph that illustrates the mechanical behavior of a fluid when subjected to shear. It is obtained using rheometers and constitutes an essential database for mathematical modeling. This modeling allows for the creation of a rheological model representative of the behavior of the studied fluid. Typically, the rheogram shows how shear stress varies as a function of shear rate (Figure 3).

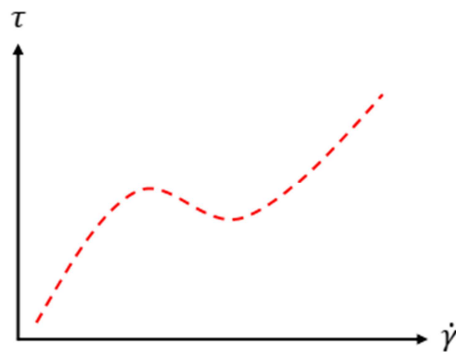


Figure 3 - Rheogram or rheological behavior curve of a thixotropic fluid.

### 1.2.7 Classification of Fluids

Rheological behavior can be used to distinguish between two main types of fluids.

#### 1.2.7.1 Newtonian Fluids

Shows that they display a linear rheological equation outlined by previous equation, they are also known as linear fluids

$$\tau = \eta \cdot \dot{\gamma} \quad 1-10$$

In this situation, stress and shear rate have a proportionate relationship, making viscosity independent of the applied shear but dependent on temperature and pressure. Figure 4 displays the rheograms of these different fluid kinds.

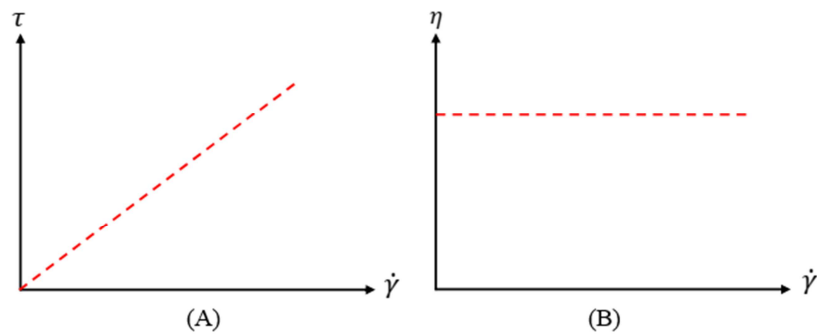


Figure 4 - (A) Rheogram of Newtonian Fluid, (B) Evolution of its Viscosity

### 1.2.7.2 Non-Newtonian Fluids

When a fluid's flow curve is nonlinear, it is said to be non-Newtonian. As a result, viscosity is no longer constant but rather varies with shear rate. Three categories of non-Newtonian fluids are distinguished by different rheological behaviors:

#### 1.2.7.2.1 Time Independent Non-Newtonian Fluids

These fluids are purely viscous, and the shear stress within a sample depends on the imposed shear rate. Time-independent non-Newtonian fluids are subdivided into three groups, each characterized by distinct rheological behaviors.

##### a) Pseudo-plastic Fluid (Shear-thinning)

Shear thinning fluids exhibit a decrease in viscosity with increasing shear rate over time, meaning that the fluid becomes less viscous as shear rate increases. This behavior is reversible, and the fluid returns to its original viscosity when the shear rate is reduced or removed.

##### b) Dilatants (Shear-thickening)

Dilatant fluids, on the other hand, exhibit an increase in viscosity with increasing shear rate over time, meaning that the fluid becomes more viscous as shear rate increases. This behavior is also reversible, and the fluid returns to its original viscosity when the shear rate is reduced or removed.

### c) Plastic Fluid - Yield Stress Fluid

These are fluids that only flow when the applied stresses exceed a certain value called yield stress ( $\tau_c$ ). Beyond this value, the flow occurs under the effect of the effective stress ( $\tau - \tau_c$ ).

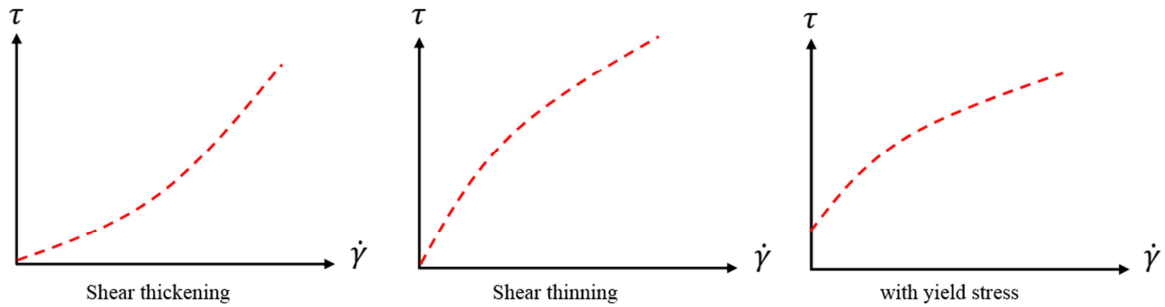


Figure 5 - Rheograms of the 3 most commonly encountered behaviors.

#### 1.2.7.2.2 Time Independent Non-Newtonian Fluids

Due to the non-instantaneous modification of the microscopic structure of these fluids, their rheological behaviors depend on time in addition to shear rates. Their rheological equations then take the form

$$\tau = f(\dot{\gamma}, t) \quad 1-11$$

These fluids behave as if the stresses experienced in the relatively recent past modified their present flow behavior. The rheograms resulting from the application of a deformation rate which increases and decreases regularly (charge-discharge) on the latter show hysteresis cycles (Figure 6).

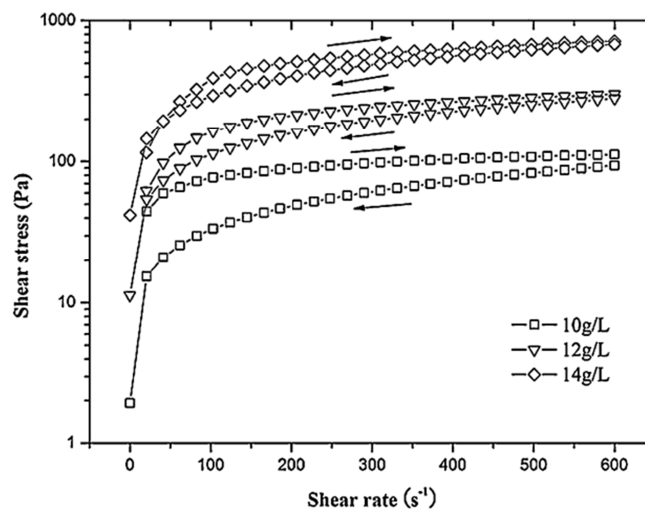


Figure 6 - Rheological curve resulting from a charge-discharge test for a time-dependent fluid [5].

The viscosity obtained during measurements under flow is not always constant under constant shear. Indeed, for certain complex fluids, this viscosity evolves during the observation time (Experiment), under fixed shear (or shear stress). If a fluid at rest subjected to shear (transition from a more structured state to a less structured state) sees its viscosity decrease at a constant shear rate, the fluid is said to be thixotropic, if on the other hand it increases, the fluid is anti-thixotropic [6, 7].

### 1.2.7.2.3 Viscoelastic Fluids

Viscoelastic fluids manifest under the effect of a stress, a behavior which depends at the same time on the deformation, on the shear rate and on time. Their rheological equation is of the following form:

$$\tau = f(\gamma, \dot{\gamma}, t) \quad 1-12$$

These fluids simultaneously possess viscous and elastic properties. Because of being subjected to a creep test (constant shear stress) as shown in Figure 7, these fluids deform in three successive times.

1. Instantaneous deformation which results from the elasticity of the fluid;
2. Elastic deformation damped by viscosity;
3. Purely viscous linear deformation.

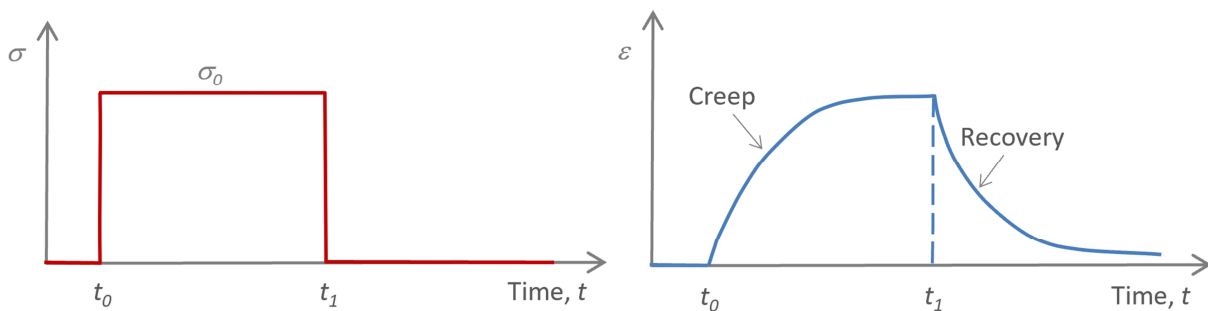


Figure 7 - Creep and recovery behavior of a viscoelastic fluid.



## 1.2.8 Rheological models

Table 1-Rheological laws of non-Newtonian fluids

Models	Rheological laws	settings
Ostwald de Weale [8]	$\tau = k \cdot \dot{\gamma}^n$	$k, n$
Ellis [9]	$\tau = \frac{\mu_0}{1 + \left(\frac{\tau}{\tau_{1/2}}\right)^{\alpha-1}} \cdot \dot{\gamma}$	$\frac{\tau_{1/2}}{2}, \mu_0, \alpha$
Prandlt-Eyring [10]	$\tau = \tau_0 + \sinh^{-1}(t_0 \dot{\gamma})$	$\tau_0, t_0$
Powell-Eyring [11]	$\tau = \mu_1 \dot{\gamma} + \frac{\mu_0}{t_0} \sinh^{-1}(t_0 \dot{\gamma})$	$\mu_1, \mu_0, t_0$
Sikso [12]	$\tau = \mu_0 \dot{\gamma} + k \dot{\gamma}^n$	$\mu_0, k, n$
Reiner-Philipoff [13]	$\tau = \left( \mu_0 + \frac{\mu_0 + \mu_\infty}{1 + (\tau/\tau_s)} \right) \dot{\gamma}$	$\mu_0, \mu_\infty, \tau_s$
Meter [14]	$\tau = \mu_0 \left[ \frac{1 + (\tau/\tau_m)^{\alpha-1} (\mu_\infty/\mu_0)}{1 + (\tau/\tau_m)^{\alpha-1}} \right]$	$\mu_0, \tau_m, \mu_\infty, \alpha$
Hamersma [15]	$\tau = \mu_\infty \dot{\gamma} + \tau_0 [1 - e^{-\alpha \tau}]$	$\mu_\infty, \tau_0, \alpha = \frac{\mu_\infty}{\mu_0 \tau_0}$
Cross [16]	$\tau = \left[ \mu_\infty + \frac{\mu_0 - \mu_\infty}{1 + (\lambda \dot{\gamma})^p} \right] \dot{\gamma}$	$\mu_0, \mu_\infty, \lambda, p$
Quemada [17]	$\tau = \left[ \mu_\infty \left( \frac{1 + (\lambda \dot{\gamma})^p}{\left(\frac{\mu_\infty}{\mu_0}\right)^{1/2} + \dot{\gamma}^p} \right)^2 \right] \dot{\gamma}$	$\mu_0, \mu_\infty, \lambda, p$
Kruger-Dougherty [18]	$\frac{\mu - \mu_\infty}{\mu_0 - \mu_\infty} = (1 + (\lambda \dot{\gamma})^p)^{-1}$	$\mu_0, \mu_\infty, \lambda, p$
Bingham [19]	$\tau = \tau_s + \mu_p \dot{\gamma}$	$\tau_s, \mu_p$
Herschel-Bulkley [20]	$\tau = \tau_s + k \dot{\gamma}^n$	$\tau_s, k, n$
Casson [21]	$\tau^{1/2} = \tau_s^{1/2} + k_c \dot{\gamma}^{1/2}$	$\tau_s, k_c$
Skelland [22]	$\tau = \tau_s + \frac{\mu_0 \dot{\gamma}}{1 + C(\tau - \tau_s)^m}$	$\tau_s, \mu_0, C, m$
Robertson-Stiff [23]	$\tau = K(\dot{\gamma}_0 + \dot{\gamma})^n$	$\dot{\gamma}_0, K, n$

The rheological model is used to describe the behavior using a function  $\tau(\dot{\gamma})$  or  $\dot{\gamma}(\tau)$ , which makes it possible to define the viscosity of a non-Newtonian fluid. The **Erreur ! Source du renvoi introuvable.** presents a number of rheological equations for fluids with non-Newtonian behavior.

## 1.2.9 Rheometry

Rheometers are devices for measuring the rheological properties of fluids according to the geometry of the measuring tool and the stress imposed on the fluid. There is a wide variety of rheometers.

### 1.2.9.1 Capillary Rheometer

Rotational instruments provide significantly lower shear rates compared to those encountered in processing. That is why, since Marzetti [24] and Dillon [25], extrusion instruments, including capillary rheometers, are increasingly used for the characterization of rubber materials.

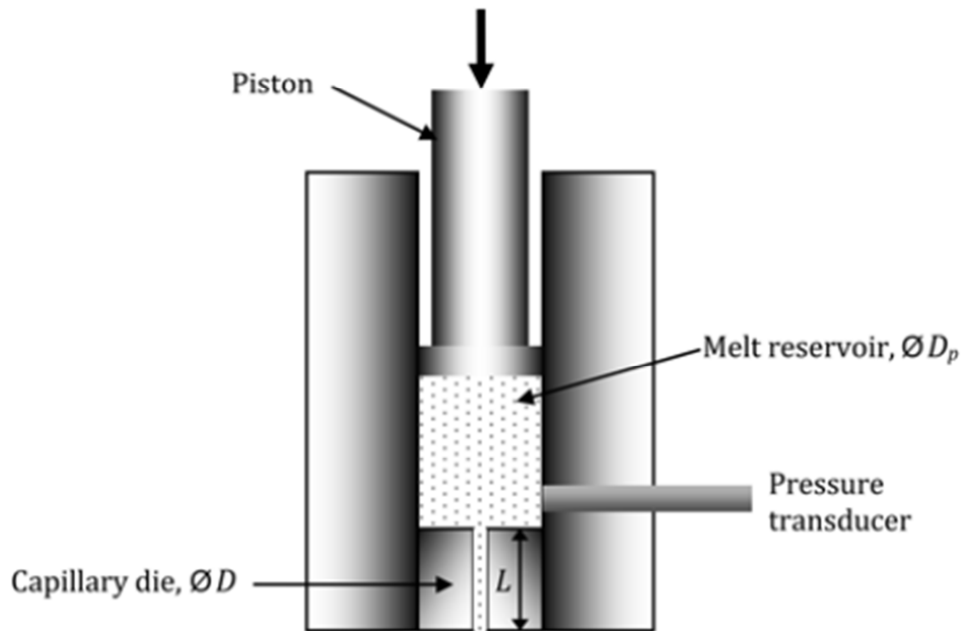


Figure 8 - Sketch of the capillary rheometer [26].

A capillary rheometer consists of a thermo-regulated cylindrical chamber where the materials are introduced, it is preheated, then it is pushed using a piston through a capillary as shown in Figure 8. The pressure is measured at using a sensor located upstream of the capillary, in the sheath. It is thus possible to determine the viscosity as a function of the shear rate. In capillary flow, the shear rate, like the stress, varies from zero on the capillary axis to a maximum value at the wall. To calculate the viscosity, it is necessary to use stresses and shear rates at the same point. The shear rate  $\dot{\gamma}$  is therefore commonly used.

### 1.2.9.2 Rotational Cone-Plate Rheometer

The cone-plane geometry consists of a disc and a cone of the same diameter and whose vertex is located on the disc (Figure 9). The cone and the disc are coaxial and rotate around their common axis at a relative speed  $\omega$ . The material to be analyzed is placed between the disc and the cone.

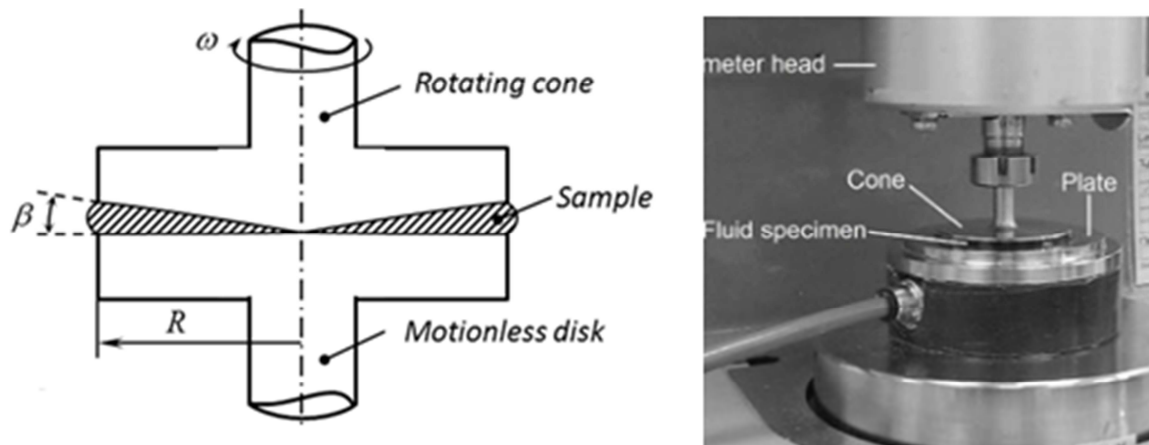


Figure 9 - Schematization of the cone-plate rheometer

### 1.2.9.3 Rotational Parallel-Plate Rheometer

This geometry is composed of two coaxial disks in relative rotation. The sample is placed in the same way as in the case of the plane cone geometry. Plane-plane geometry does not counteract variations in the velocity gradient within the sample as a function of distance from the central axis.

### 1.2.9.4 Coaxial Cylinders Rheometer

It is one of the most frequently used types of measurement cells. The operating principle of this rheometer consists in shearing the substance between two cylinders of revolution, coaxial with radius  $R_1$  and  $R_2$  and height  $h$  (Figure 10). The laminar shearing movement is obtained by imparting to one of the cylinders a uniform rotation (speed  $\omega$ ), the other cylinder remaining stationary or also rotating at an angular speed different from  $\omega$ .

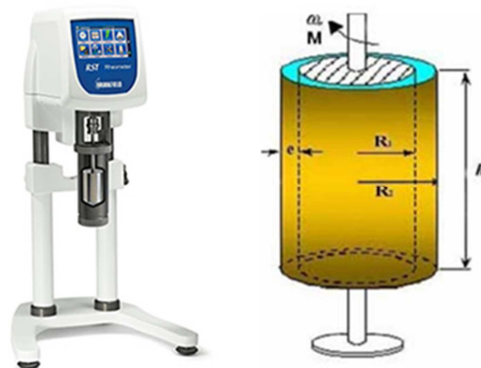


Figure 10 - Coaxial Cylinder Rheometer

## **Chapter 2**

### **Drilling Fluids Generalities**

#### **2.1 Introduction**

The process of "Petroleum Drilling" encompasses a series of procedures that facilitate accessing porous and permeable rocks situated in the subsurface, which are anticipated to hold liquid or gaseous hydrocarbons. The decision to implement this process is based on geological and geophysical studies conducted on a sedimentary basin. These studies provide insights into the structure of the subsurface and the possibilities of deposits [27]. The good choice of drilling fluid contributes to the success of a drilling operation while these fluids, commonly referred to as drilling mud, are considered complex due to their composition, which may include emulsions or suspensions of different elements, and their multiple functions. The rheological properties of these fluids, which include non-Newtonian behavior, Shear-thinning, thixotropic, and sensitive to temperature changing, are playing important role in the success of the drilling operation and may vary depending on the specific type of mud and operating conditions [27, 28].

#### **2.2 Overview of Drilling Fluids**

Since the last century, the development of oil operations has been of great importance. Exploiting an oil deposit requires several operations, including

- Locating the reservoir rock and confirming the presence of hydrocarbons;
- Evaluating the economic feasibility of development;
- Drilling and bringing oil and gas wells into production.

Furthermore, the success of a drilling operation is largely ensured by the proper choice of drilling fluid. In this chapter, we will present the main roles and characteristics of drilling fluids [28].

## **2.3 Definition of Drilling Fluids**

Drilling fluid, also known as drilling mud, is any fluid that circulates in a well for removal of cuttings from a well hole. It is a system composed of different liquid components (water, oil) and/or gaseous components (air or natural gas) containing in suspension other mineral and organic additives (clays, polymers, surfactants, cuttings, cements, etc.).

## **2.4 Principle Functions of Drilling Fluids**

The drilling fluid or the drilling mud has a specific purpose in the operation of an oil drilling, it is responsible for the smooth running of this operation and this thanks to the well-studied physico-chemical properties to ensure its functions in the well. They are divided into two: primary and secondary functions.

### **2.4.1 Primary Functions**

#### **a- Preventing the intrusion of formation fluids into the wellbore:**

In order to avoid the intrusion of the fluids contained in the reservoirs encountered during oil drilling, the drilling fluid must exert sufficient hydrostatic pressure to balance the reservoir pressures. The desired hydrostatic pressure is maintained by adjusting the density between maximum and minimum values [29].

#### **b- Wellbore wall protection and stability**

Hydrostatic pressure is controlled by the density of the drilling fluid. This pressure must be high enough to hold the walls of the well but not so high as to prevent fracturing of the rock. The calculation of the necessary density is therefore essential. The drilling fluid must have physical and chemical characteristics such that the hole maintains a diameter close to the nominal diameter of the tool [30]. The tightening is often caused by an insufficient hydrostatic pressure of the mud column which cannot balance the pressure of the rocks. The filtration of part of the liquid phase of the drilling fluid in the permeable formations creates a film on the walls of the

borehole, this film is called the filter-cake (Figure 11), its deposit makes it possible to consolidate and reduce the permeability of the walls of the well [30].

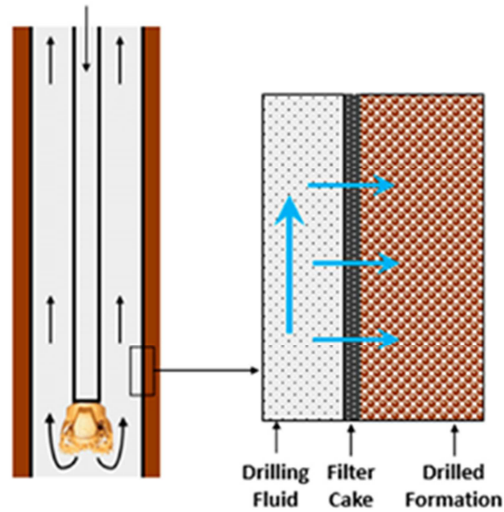


Figure 11 - The Filter-Cake

**c- Transport of cuttings and wellbore cleaning**

The drilling fluid must rid the well of the particles of the drilled formations which are in the form of rock debris called “cuttings” or “debris” [30]. The circulation of the drilling fluid rising in the annulus must carry the cuttings from the bottom of the well to the surface. Three parameters influence the cleaning efficiency of the annular: the fluid velocity in the annular, the yield-point and the viscosity of the drilling fluid [31] in order to avoid problems of rod string jamming (Figure 12).

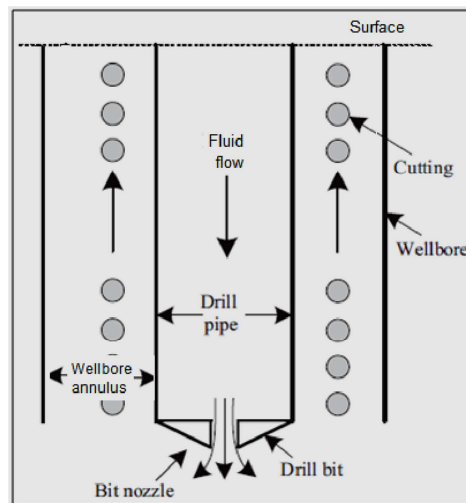


Figure 12 - The transport of cuttings on the surface

#### d- Suspending cuttings in the wellbore:

The drilling fluid must allow the cuttings to be kept in suspension in the well during stoppages [30], to avoid the deposition and precipitation of solids which causes a jamming called stuck-pipe, the gelling power of the drilling fluid is the rheological parameter which provides this so-called Gel-Strength function (Figure 13).



Figure 13 - The gelling power of the drilling fluid

### 2.4.2 Secondary Functions

#### a- Cooling and lubrication of the drill bit and the drill string

Due to its passage on the surface, the circulating drilling fluid is at a temperature lower than that of the formations, which allows it to effectively reduce the overheating of the drill string and the tool (Figure 14). This overheating is due to the transformation of part of the mechanical energy into calorific energy [32].



Figure 14 - Cooling of the drilling tool

## **b- Provision of information about the encountered formations**

The drilling fluid makes it possible to obtain permanent information on the evolution of the formations and fluids encountered. This information is obtained:

- By the rising cuttings with the circulation of the fluid.
- The evolution of the physical and/or chemical characteristics of the drilling fluid.
- The detection of gases or other fluids mixed with the drilling fluid.

There are indeed other roles such as:

- Transmission of hydraulic power to the drilling tool.
- Supply of energy necessary to operate the downhole motors and turbines.
- Protect drilling equipment against corrosion and abrasiveness and personnel against toxicity.

## **2.5 Classification of Drilling Fluids**

Generally, drilling fluids have been classified into three categories based on the base fluid used in their preparation: air, water, or oil. We distinguish

### **2.5.1 Water – Based Mud**

These fluids are the most commonly used in drilling operations. They are typically composed of clay suspensions (such as bentonite), inert solids (such as carbonates), and viscosity-enhancing polymers (such as Xanthan). Filtrate reducers (such as carboxymethylcellulose and synthetic polymers) are also added to the composition [33]. These fluids are less expensive and less polluting [34]; however, the thermal degradation of polymers used in these formulations presents a major drawback for successful drilling operations (for example, the thermal stability range of Xanthan is between 120 and 138 °C). This type of fluid can be classified into two categories [35, 36]; (a) Soft muds (bentonite muds) and (b) Saline muds.

### **2.5.2 Oil – Based Mud**

Oil-based muds are chosen for their stability at high temperatures, lubrication, and wellbore stabilizing properties, although they have specific characteristics that make them difficult to handle compared to water-based muds. Their use may entail some challenges, such as special



handling requirements and environmental issues [37]. Oil-based muds are inverse emulsions with the continuous phase being an organic or mineral oil (crude oil, diesel oil, etc.) and the dispersed (discontinuous) phase being an aqueous solution of up to 50% by volume, which maintains the advantage of having the oil as the external phase [38]. Viscosifying agents, emulsifiers, stabilizers, thinners, and weighting agents are then added. These fluids exhibit insensitivity to contaminants (such as NaCl, KCl, clay, etc.), reduced friction of the drill string against the wellbore walls, and limited damage to the formation, resulting in improved productivity, unless they pose ecological issues (pollution) as they can contaminate cement slurry, and they can be expensive. Currently, non-toxic oil-based fluids (such as vegetable oils) are increasingly being used, along with water-based fluids.

### **2.5.3 Gas – Based Mud**

These are fluids where the continuous phase is gas mixed with water in varying proportions, either naturally from the formation being drilled or intentionally added. The gas can be air, natural gas, foam (foams are dispersions of a relatively large volume of gas in a relatively small volume of liquid), or mist [35].

## **2.6 Circulation of drilling fluids**

The drilling mud is in continuous circulation throughout the duration of the drilling as well both in the sounding and on the surface. The fluid is prepared in the sludge tanks; it is injected inside the stems up to the tool, then it goes up through the annular space loaded with cuttings formed at the front of size Figure 15. On leaving the well, it undergoes various treatments (screening, dilution, addition of product, ...) in such a way as to eliminate the transported cuttings and to readjust its characteristics physico-chemical and rheological compared to important values (before injection)

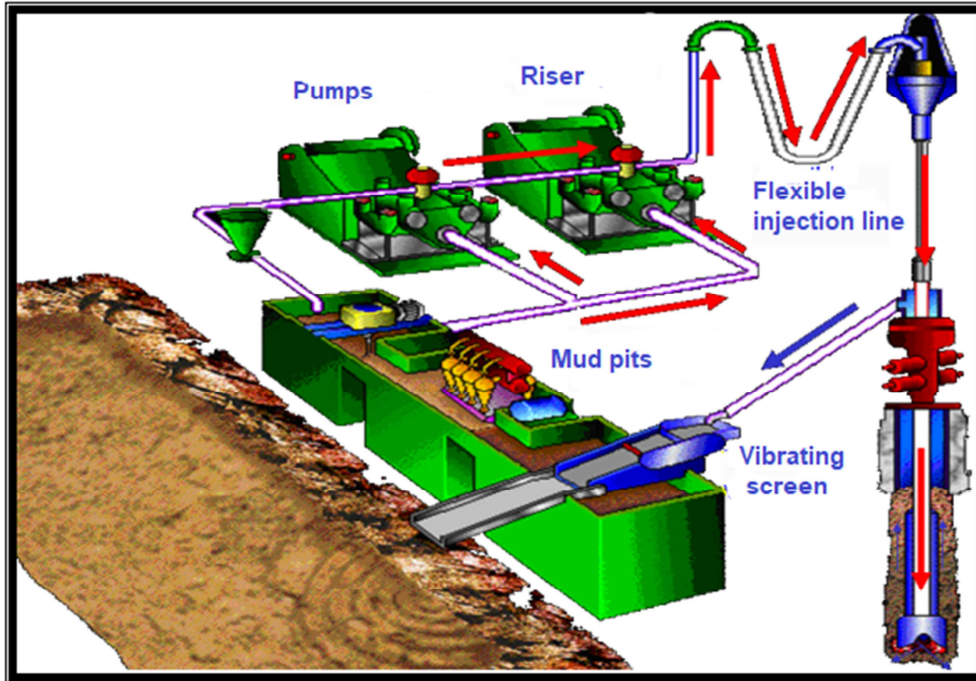


Figure 15 - Diagram of mud circulation on the drilling site

## 2.7 Drilling Fluids Composition

Drilling fluids must possess a wide range of characteristics, some of which are even contradictory. For instance, drilling fluids must be very viscous to assure cuttings removal, but the viscosity shouldn't be excessive to prevent formation fracturing and to reduce pressure losses from flow. As a result, the drilling fluid is given the appropriate qualities by the addition of numerous multifunctional components. As shown in Table 2, these components can be loosely divided into 20 categories.

Table 2- The main additives used in drilling fluids

1	Alkalinity Controller	11	Lubricant
2	Bactericide	12	Stuck pipe remover
3	Anti -calcium	13	Clay Swelling Inhibitor
4	Corrosion Inhibitor	14	Separation Facilitator
5	Anti – foaming agent	15	High temperature stabilizer
6	Foaming agent	16	Deflocculant
7	Emulsifier	17	Viscofier
8	Filtrate reducer	18	Weightening agent
9	Flocculant	19	Brine
10	Colmatant	20	Mineral or Organic Oil

As an example, clays (such as Bentonites and organophilic clays) and polymers (like polyanionic cellulose (PAC), hydroxyethyl cellulose (HEC), and biopolymers (similar to xanthan gum, guar gum) are all included in the category of viscosifiers. Barite ( $\text{BaSO}_4$ ) or calcium carbonate ( $\text{CaCO}_3$ ) can be employed as weighing agents. Starches, carboxymethylcellulose (CMC), or resins can be used as filtrate reducers (which help solidify the filter cake to limit filtrate invasion). Clays, potassium chloride (KCl), glycerol, and different polymers can all act as swelling inhibitors. Exotic additives such as granular materials (nut shells), fibrous materials (wood fibers, sugarcane), or lamellar materials (oyster shells, cereals) can be utilized as plugging agents, too [39, 40].

## **2.8 Properties of Drilling Fluids**

The majority of drilling mud properties should be measured and reported daily. The following basic properties are used to determine and control mud behavior when drilling: viscosity, density, filter cake, solids content and quality and type of water contained.

### **2.8.1 Density**

Defined as weight per unit volume of sludge. It is expressed in lb/gal, lb/ft<sup>3</sup> or kg/m<sup>3</sup>, or in SG. The pressure exerted by the hydrostatic column depends on the density and the depth, however it is convenient to express the density in psi/ft, or kg/cm<sup>3</sup>/m.

### **2.8.2 Viscosity**

It can be defined as the resistance of the mud to flow. It is affected by several factors such as: mud density, whole size and condition, rate of advancement, flow rate and pressure. The viscosity is a function of three parameters: the continuous phase viscosity, the plastic viscosity and the elastic limit (yield point).

### **2.8.3 Plastic Viscosity**

It represents the part of the flow resistance caused by the friction between the suspended particles and the viscosity of the base liquid. It is a function of the size, shape and number of particles.

#### **2.8.4 Elastic limit (yield point)**

It represents the measurement of forces between particles in the mud. In other words, it is the initial flow resistance or the stress required for the fluid to start flowing.

#### **2.8.5 Freeze stress (Gel strength)**

It represents the same measure of the inter-particle forces of the mud as determined by the YP, except where the mud is at rest.

#### **2.8.6 Filter cake**

The solids contained in the mud depositing on the well walls form what is called: “Filter cake”, the fluid which invades the formation is said: “Filtrate”. The mud fluids lost in the formation are: ‘Filtrations’ or mud losses.

#### **2.8.7 Water quality and type**

There are three factors that can affect drilling fluid performance: pH, salt content and water hardness (water containing Ca or Mg becomes difficult to hydrate the bentonite).

## **Chapter 3**

### **Rheology of bentonite suspensions**

#### **3.1 Introduction**

The base of "Water-based drilling mud" is made up of aqueous suspensions of clay where the drilling mud must be able to meet certain requirements, particularly those imposed by the temperature and pressure encountered during drilling. The properties of the mud depend on its composition; in fact, the elements that make up its composition and contribute in building its structure. Water-based muds are made up of aqueous suspensions of bentonite while no study on bentonite drilling mud can be conducted without a prior study of the main component, which is the montmorillonite clay.

#### **3.2 Bentonite's Origin**

The alteration and hydrothermal transformation of ash-rich volcanic tuffs lead to the neoformation of clay minerals, mainly belonging to the group of smectites. The clay rocks thus formed are called bentonite, named after the deposit located near Fort Benton (Wyoming, United States). It contains more than 75% montmorillonite. This mineral was first discovered in 1847 near Montmorillon, in the Vienne region of France, by Damour and Salvétat, and identified by Knight in 1886. Bentonite is a term used for montmorillonite. The bentonites discovered since 1888 contain at least 75% montmorillonite [41].

### 3.3 Definition of Bentonite

The term BENTONITE refers to clay materials for industrial use, mainly composed of smectites and more particularly montmorillonite. Bentonite is a clay rock that is friable, soft, and smooth to the touch, and its color depends on the closely associated mineral compounds and impurities (Figure 16). It can be white, gray, or slightly yellow. It is characterized by a high capacity for adsorption, ion exchange, and swelling [42].



Figure 16 - Bentonite

### 3.4 Structure of Bentonite

Montmorillonite is the main constituent of bentonite (Figure 17). It is a 2:1 phyllosilicate (smectite family) in which the negative charge of the layer is electrically balanced by an equal charge of exchangeable cations (  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{H}^+$ ,  $\text{K}^+$ ,  $\text{NH}^+$  and  $\text{Na}^+$  ) located mainly between these silicate layers; these cations do not belong to the structure and have some mobility [41].

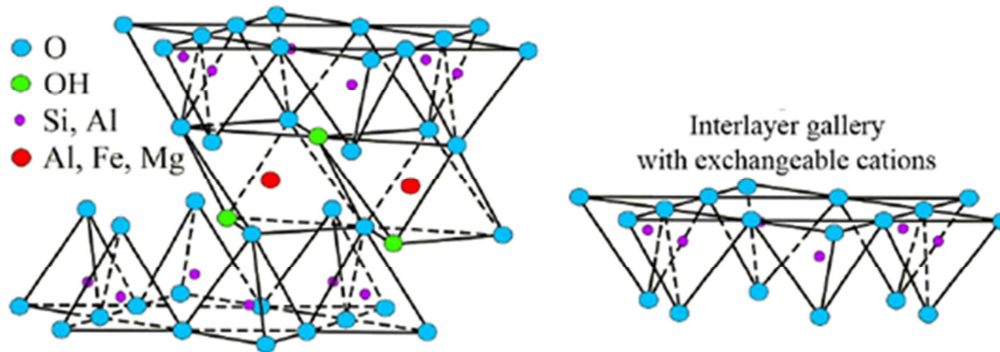


Figure 17 - Structure of Montmorillonite

### 3.5 The chemical formula of montmorillonite

The idealized formula of a unit cell of montmorillonite can be written as [43]:



With :

- R = Mg, Fe, Mn, Zn, Ni
- Ce (exchangeable cations) = Ca, Na, Mg

### 3.6 The multi-scale structure of montmorillonite

To describe the structure at different scales and its specific properties, this is made possible by the use of experimental techniques such as Small-Angle X-ray Scattering (SAXS), Transmission Electron Microscopy (TEM), and Scanning Electron Microscopy (SEM). Montmorillonites have the particularity of presenting different levels of organization depending on the observation scale. Different characteristic "objects" of this multi-scale structure are schematically represented in Figure 18 [44].

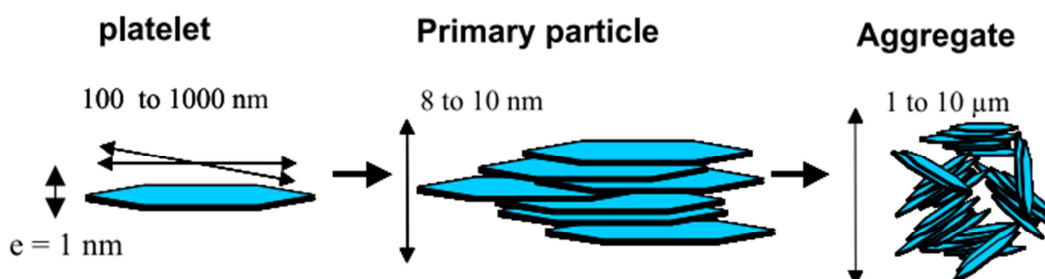


Figure 18 - The multi-scale structure of montmorillonite

#### **a- The layer**

The sheets are the basic structural units defining the mineral nature, clay type, physicochemical properties, and macroscopic behavior. The sheet is the successive horizontal stacking in the X and Y directions for the half-cell, and has the shape of a disc or platelet with dimensions of about one hundred to one thousand nanometers in length and ten Angstroms in thickness. These platelets are very flexible, especially in the presence of water, so they are deformable [45].

#### **b- The particle**

Several crystals can associate to form a particle, and the stacking of sheets is achieved by attractive electrostatic forces between the compensating ions and the sheets. The thickness is approximately 8 to 10 nanometers for the size of the primary particle, which remains nearly constant. This means that when a montmorillonite is swollen, the interlayer space is increased, and there are fewer sheets in a particle [45].

#### **c- The aggregate**

The term "aggregate" refers to clays in a powdery state, which is a collection of small particles having a more or less rectangular shape called "primary particles" oriented in all directions. These particles are connected to each other by Coulombian forces or by deposits of hydroxides or organic matter. Aggregates have a size that varies from 0.1 to 10 microns, as shown in the Figure 18 [45].

### **3.7 Types of Bentonite**

One of the essential characteristics of montmorillonites is to possess exchangeable cations with the surrounding environment. In nature, the most commonly encountered cations are calcium and sodium. Therefore, two types of bentonites can be distinguished [46]:

**a- Sodium bentonites:** Also called "Wyoming" or "western" bentonite. Its sodium oxide content of >2% gives it a high swelling index between 15 and 20.

**b- Calcium Bentonites:** where calcium is the majority exchangeable cation, they have a lower swelling and adsorption power than sodium bentonites.



### 3.8 Application of bentonite

The Table 3 shows the application and use of clay in different sectors [47]:

Table 3- The application and use of clay in different sectors

Usage sectors	Examples of applications
Drilling Industry	<ul style="list-style-type: none"> <li>• Mineral Ingredient for drilling ( Drilling Mud )</li> <li>• Binder</li> </ul>
Pharmaceutical & Cosmetic Industry	<ul style="list-style-type: none"> <li>• Binding ointments.</li> <li>• Facial Mask</li> <li>• Makeup Products</li> </ul>
Plant Production	Soil productivity improvement
Construction Material	Ingredient of Cement
Chemical Industry	Pesticide carrier
Fertilizers	Fertilizer additive
Industry of Paper	Coating
Dye Industry	Varnish and thixotropy control
Food Industry	Clarification of fruit juices and cocoa butter

### 3.9 Physicochemical characteristics of bentonite

#### 3.9.1 Chemical Composition of Bentonite

Bentonite is the commercial term for montmorillonite. The latter represents more than 80% of the total ore. The rest is impurities. The analysis of some bentonites is presented in Table 4 below [48]:

Table 4- Chemical Composition of Bentonite in different regions

Samples ( % )	Wyoming (USA)	Almeria (Spain)	Maghnia (Algeria)
$SiO_2$	54.55	47.7	51.52
$Al_2O_3$	20.12	21.59	19.03
$Fe_2O_3$	2.23	1.53	1.98
$TiO_2$	0.21	0.25	/
$FeO$	1.48	/	/
$CaO$	0.95	2.46	0.16
$MgO$	1.99	2.82	3.08
$MnO$	0.01	0.07	/
$Na_2O$	2.48	0.18	1.17
$K_2O$	0.31	0.20	0.36
$H_2O$	16.04	23.72	23.20
(%)	100.37	100.52	99.86

The mineralogical analysis by X-ray diffractometry of the bentonite used to prepare our samples revealed the presence of the following phases

- Quartz  $\text{SiO}_2$
- Dolomite  $\text{Mg Ca CO}_3$
- Calcite  $\text{Ca CO}_3$
- Gypse  $\text{Ca SO}_4 (\text{H}_2\text{O})_2$
- Barite  $\text{Ba SO}_4$
- Goethite  $\text{Fe}_3\text{O}(\text{OH})$
- Feldspaths
  - Albite calcian  $\text{Ca NaAlSi}_3\text{O}_8$
- Argiles
  - Illite  $(\text{K, H}_3\text{O})(\text{Al, Mg, Fe})_2(\text{Si, Al})_4\text{O}_{10}$
  - Montmorillonite  $\text{H}_1\text{Al}_2\text{Ca}_{0.5}\text{O}_{12}\text{Si}_4$  mostly

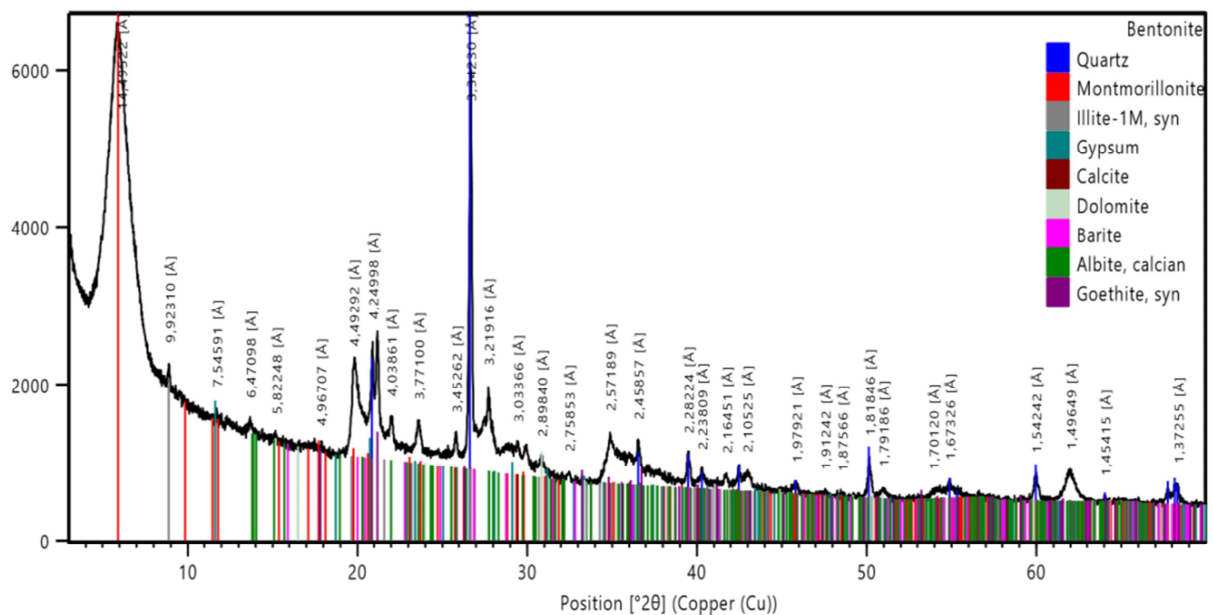


Figure 19 - Diffractogram of bentonite sample

At the end of the XRD analysis, it can be concluded that the "bentonite" sample is mainly composed of bentonite and illite type clay, quartz and, incidentally, dolomite, calcite, gypsum, barite, goethite and calcic albite.

### **3.9.2 Swelling**

The swelling property of bentonite results mainly from the interactions of interlayer cations with water molecules, which penetrate into the interlayer space. The latter is filled with two or more molecular layers of water. The majority of ions in the external medium lead to the development of the electrical double layer, which has the effect of pushing the layers apart. Good commercial bentonites swell 15 to 20 times their initial volume.

### **3.9.3 Plasticity and Density**

Due to their richness in colloidal particles, bentonites are highly plastic. The range of the plasticity index (PI) of bentonites is high and varies from 700 to 500 % depending on the nature of the bentonite. Bentonites are capable of retaining a large amount of water in a "rigid" form (LI = liquidity index) to form a plastic state. Calcium montmorillonites have liquidity index values ranging from 100 to 200%, while sodium montmorillonites have values ranging from 350% to over 700%. The measured density of raw bentonite is equal to 2.00 g/cm<sup>3</sup>.

### **3.9.4 pH Measurement and Color**

pH = 9.83 indicates the basicity of the bentonite, which could be attributed to the presence of soluble basic salts such as alkaline carbonates, bicarbonates or silicates, which are usually present in bentonites. Bentonite is white in color, with a grayish, sometimes bluish, pink, red, or even greenish tint.

## **3.10 Rheological characterization of bentonite suspensions**

The main focus of this chapter is to investigate the rheology of bentonite suspensions at various concentrations ranging from 1 to 8%, without incorporating any additives. The primary objective is to comprehend the rheological behavior of these clay suspensions in their restructured and destructured states, while highlighting the challenge of result reproducibility. By doing so, we will be able to examine how the addition of a polymer affects the rheological properties of clay suspensions.

### 3.10.1 Sample preparation

The preparation is made by mixing the bentonite powder, with the desired concentration (1, 2, 3, 4, 5, 6, 7 and 8% by weight), in distilled water. To ensure swelling and homogenization of the fluid, the suspensions obtained are magnetically stirred continuously for 48 hours. Then, we leave the sample for 15 days at rest for the swelling operation to end and we can then have the reproducibility of the results [49]. The rheograms were plotted just after 5 min of pre-shearing. This protocol would make it possible to have a destructured state of the suspension.

### 3.10.2 Characterization device

We carried out the rheological measurements using an Anton Paar MCR 302 rheometer of the cone-plane type and 60 mm in diameter (Figure 20).



Figure 20 - The Rheometer type MCR 302 from the company Anton Paar

The characterization of the flow of the complex fluid prepared is done with a rotational rheometer. The device consists of a rotation axis connected to a motor which can be either at imposed speed or at imposed torque and a measuring cell. The cell is made up of a fixed part (stator) and a mobile part (rotor). Thus, the fluid to be studied is then confined in the space between the rotor and the stator commonly called gap or air gap. Different cells can be used depending on the desired flow geometry. The cells used are the Couette cell, which makes it possible to produce cylindrical flows of the cone–plane type.

The sample is placed between a plate and a cone of radius  $R$ , the axis of rotation of the cone is perpendicular to the plane of the plate. The generatrix of the cone makes an angle with the plane of the plate. The end of the cone is truncated to separate the cone and the plane by a constant distance ("gap") of the order of a micrometer. This gap must be precisely maintained so as not to interfere with the conical symmetry of the module. The plate is fixed; on the other hand, the cone is subjected to a torque which causes a shearing movement by rotation.

Table 5- Characteristics of the cone-plane geometry used in the rheometer

<b>Parameter</b>	<b>Cone-plane Geometry</b>
Diameter $D$ (mm)	20-60
Air gap $h$ (mm)	Depends on $\theta < 4$ and the $D$ of the cone
Sample volume $V$ (ml)	Weak ( $\sim 0.5 - 2$ )
Mechanical and thermal inertia	Weak
Shear rate in the measurement volume $\dot{\gamma}$	Almost constant
High shear rates	Achievable because $\theta$ is very small
Oscillating frequency range	Large
Low viscosity measurements	Possible with diameter $D = 60$ mm
Measurements of high viscosities	Possible with diameter $D = 20$ mm
Measurements on samples with large particles	No
Ease of use	Yes

In Table 5, we present the characteristics of the geometry used to perform the rheological tests. The rheometer is controlled by a microcomputer which allows the measurement points to be entered, processed and analyzed by an installed “Rheoplus software”. This device can also be connected to a printer for printing reports.

### 3.10.3 Structure-flow interaction

A complex fluid possesses an internal structure that surpasses that of a "simple" liquid, with a size scale referred to as mesoscopic. This size range lies between the microscopic and macroscopic scales. Supramolecular structures in the system result in significantly longer relaxation times compared to a "simple" liquid. We comprehend that larger structures correspond to extended time periods, as exemplified by the following analogy. Consider a dilute solution containing hard spheres that undergo Brownian motion. The diffusion coefficient of these spheres can be determined using the Stokes-Einstein relation

$$D = \frac{k_B T}{6\pi\eta R} \quad 3-1$$

Where  $\eta$  represents the solvent viscosity,  $R$  denotes the sphere's radius,  $k_B$  represents the Boltzmann constant, and  $T$  represents the temperature. The time required for a sphere to diffuse a distance equal to its radius,  $\tau$ , can be approximated as

$$t \sim \frac{R^2}{D} \sim \frac{6\pi\eta R^3}{k_B T} \quad 3-2$$

While applicable solely to hard spheres in a solution, this equation allows us to comprehend the proportional relationship between a characteristic length and a corresponding time

$$t \sim \frac{\eta R^3}{k_B T} \quad 3-3$$

Additionally, we have observed that subjecting a fluid to shear introduces a distinct time parameter. The shear rate possesses the dimension of inverse time, denoted as  $t' = 1/\dot{\gamma}$ , thereby having the dimension of time. The ratio of the time related to the internal structure of the fluid and the time associated with its shearing defines a dimensionless number, the Deborah number

$$De = \frac{t}{t'} \quad 3-4$$

When  $De \ll 1$ , the characteristic time of the flow significantly exceeds the microscopic characteristic time. As a result, the fluid's structure has ample time to relax before experiencing

the influence of shear. Consequently, there is no interaction between the structure and the flow. This scenario applies to simple liquids.

In contrast, when  $De \sim 1$ , the fluid's structure does not have enough time to relax under shear. As a result, the internal organization can be altered by the shear, leading to changes in the macroscopic behavior of the fluid. This signifies an interaction between the structure and flow.

The nonlinear relationship between stress  $\tau$  and shear rate  $\dot{\gamma}$ , as observed in rheology, indicates that some underlying changes are occurring at the microscopic structure level. However, it's important to note that rheology is a macroscopic tool that only provides insights into the macroscopic effects, such as variations in apparent viscosity or the emergence of normal stress.

### 3.10.4 Stress plateau and shear bands

In this chapter, our focus is on studying bentonite suspensions, which fall under the category of complex fluids. These fluids display a stress plateau in their flow curve, depending on the shear rate. Figure 21 illustrates two examples of such flow curves. In the figure, we observe a distinct horizontal plateau, accompanied by an "S"-shaped curve known as a "loop" due to its resemblance to a van der Waals loop seen in phase transitions.

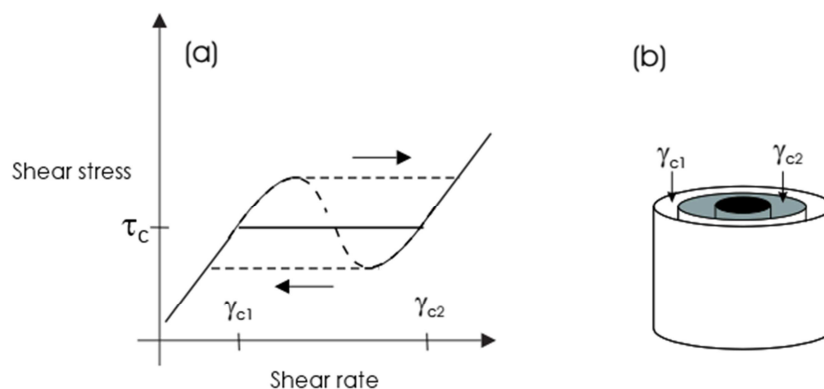


Figure 21 – (a) Horizontal plateau in the flow curve corresponding to shear-thinning behavior, (b) case of "gradient-banding": shear bands coexisting at the same stress in the direction of the velocity gradient in the case of a horizontal plate.

In the case of a shear-thinning fluid (Figure 21.a), experimental observations show that imposing stress leads to a hysteresis between stress increase and decrease (dotted line in Figure 21.a). Conversely, when imposing shear rate, the system exhibits a loop, traversing all stress states. On this loop, the dotted part where the stress is decreasing corresponds to a mechanically unstable

zone. Let us understand why this plateau is surprising: at a given stress  $\tau_c$  correspond two shear rates  $\dot{\gamma}_{c1}$  and  $\dot{\gamma}_{c2}$  and therefore also two viscosities. The fluid is bistable. The plateau can be understood as follows: Once the fluid reaches the critical shear rate  $\dot{\gamma}_{c1}$ , it forms shear bands. These bands consist of one strip sheared at the rate  $\dot{\gamma}_{c1}$  and another at the rate  $\dot{\gamma}_{c2}$ . The proportion of the fluid sheared at  $\dot{\gamma}_{c2}$  on the plate gradually increases, reducing the band sheared at  $\dot{\gamma}_{c1}$ . The measured shear rate confirms the Levier law, which states the following:

$$\dot{\gamma} = \beta_1 \dot{\gamma}_{c1} + \beta_2 \dot{\gamma}_{c2} \quad 3-5$$

$\beta_1$  and  $\beta_2 = 1 - \beta_1$  are respectively the proportions of fluids sheared at the shear rate  $\dot{\gamma}_{c1}$  and  $\dot{\gamma}_{c2}$ . Note that in this model, the two fluids 1 and 2 are Newtonian, since their shear rates  $\dot{\gamma}_{c1}$  and  $\dot{\gamma}_{c2}$  are constant. When the plate is placed horizontally, the entire fluid is subjected to the same stress level, denoted as  $\tau_c$ . To achieve this, shear bands are formed in the direction of the velocity gradient, allowing different shear rates within the fluid. This intriguing occurrence is commonly referred to as "gradient-banding" (Figure 21.a) [50, 51]. The flow curve with a horizontal plateau, commonly found in complex fluid systems, was initially observed in polymer solutions. The theoretical model developed by Doi and Edwards, building upon De Gennes's concept of creeping polymers, establishes a constitutive equation that accurately predicts a flow curve exhibiting a loop [52].

As shear increases, polymers align with the flow direction. At a critical shear rate equal to the inverse of the creep time, the chains align and contribute less to stress. This alignment continues until a second critical shear rate is reached, beyond which stress starts increasing again. The stress does not decrease to zero even at infinite shear rates. In this process, the increase in viscosity is influenced by the solvent. Two theoretical approaches explain the emergence of a plateau and/or a loop in the flow curve. The first approach interprets the plateau as an indication of a shear-induced non-equilibrium phase transition. The second approach attributes it solely to a mechanical instability phenomenon.

#### **3.10.4.1 Shear-induced non-equilibrium phase transition approach**

When a horizontal stress plateau occurs, it is assumed that the fluid divides into separate shear bands  $\dot{\gamma}_{c1}$  and  $\dot{\gamma}_{c2}$ , and the applied shear rate  $\dot{\gamma}$  follows the Levier law. The stress curve, characterized by a peak, followed by a negative slope and then a minimum, bears a resemblance



to a van der Waals loop observed in liquid-vapor transitions, among others. This similarity to an equilibrium phase transition has been explored by Olmsted et al. In their study of an isotropic rigid rod system, they demonstrate that the coupling between order parameter fluctuations and shear results in the emergence of a nematic phase [51, 53, 54]. Furthermore, Porte et. al. developed a method for analyzing horizontal plateaus using a variational principle [55].

The authors propose a phenomenological explanation that involves an effective non-equilibrium potential, which considers the energy stored within the material under shear. By minimizing this potential, the critical stress is determined, and the model interprets the plateau as an indication of a non-equilibrium thermodynamic phase transition induced by shear. Strong experimental evidence supporting this interpretation has been presented for concentrated giant micelle systems [56] and polymer systems [57, 58].

#### **3.10.4.2 Mechanical instability approach**

For giant micelles, a microscopic model was developed by Cates and co-workers, which integrates the mechanisms of creep and reversible scission. This model predicts a non-monotonic relationship between stress and strain decay, similar to Figure 20.a. Additionally, it suggests the formation of distinct shear rate bands, as observed in the flow structuring phenomenon [59-63]. This model relies solely on elastic factors, where the alignment of micelles in the flow leads to a reduction in stress under shear. When the break-recombination time ( $t_{break}$ ) is greater than the creep time ( $t_{rep}$ ), the micelles have sufficient time to untangle before breaking, and creep becomes the dominant mechanism. Conversely, when  $t_{break} \leq t_{rep}$ , the Cates model predicts that a single characteristic time governs stress relaxation, namely  $t = \sqrt{t_{break} \cdot t_{rep}}$  [60]. Because of the cut-recombination phenomena, all the segments relax in the same way and forget their initial configuration.

The solution exhibits quasi-Maxwellian behavior, defined by its characteristic time  $t$  and elastic modulus  $G_0$ . It has been demonstrated in this scenario [62] that the flow curve displays a stress maximum at a shear rate of  $\dot{\gamma} = 2.6/t$ , corresponding to a stress value of  $\tau_c = 0.67 G_0$ . These theoretical findings were subsequently verified [62] in the Rehage and Hoffman system [64]. The presence of the stress plateau and loop is solely attributed to elastic effects. Distinguishing between shear-induced phase transitions and mechanical instability is challenging in

experimental settings. Phenomenologically, it is difficult to determine whether it is the fluctuations of an order parameter, elastic effects, or a combination of both that contribute to the occurrence of inhomogeneous flow. Concentration fluctuations may also have an influence in this regard. Schmitt et al. examined the impact of flow-concentration coupling on the prevalence of mechanical instability versus shear-induced phase transition [65], as well as on the orientation of different flow bands. Notably, variations in concentration between these bands can lead to a tilting of the plateau [50]. When dealing with a proximity to an equilibrium phase transition, such as the nematic-isotropic transition for giant micelles, and observing a distinct shear-induced nematic phase, it is probable that the interpretation in terms of a non-equilibrium phase transition is accurate. However, if an induced nematic phase is not detected, making a definitive determination becomes challenging.

#### **3.10.4.3 Wall slip**

In other fields, such as polymer engineering, horizontal plateaus are frequently observed, particularly in the flow curves of polymer melts, and are interpreted in a significantly different manner from what has been discussed thus far. Consider the scenario of a fluid sliding strongly along a wall: the apparent viscosity measured by a rheometer experiences a sudden decrease, resulting in the observation of a plateau similar to that depicted in Figure 20. When a stress of  $\tau_c$  is applied, the measuring system no longer encounters any resistance, causing the measured velocity gradient to abruptly transition from  $\dot{\gamma}_{c1}$  to  $\dot{\gamma}_{c2}$ . A slip at the wall generates an extremely high shear rate within an infinitesimally thin region in close proximity to the wall. The distinction between flow separation into "bands" and wall slip can be ambiguous. In the context of wall slip, the occurrence of a horizontal plateau primarily indicates mechanical instability [66].

#### **3.10.5 Flow curves**

For three different concentrations of the bentonite suspension 3%, 4% and 5% by weight, we followed the evolution of the shear stress and the viscosity as a function of the shear rate (Figure 22).

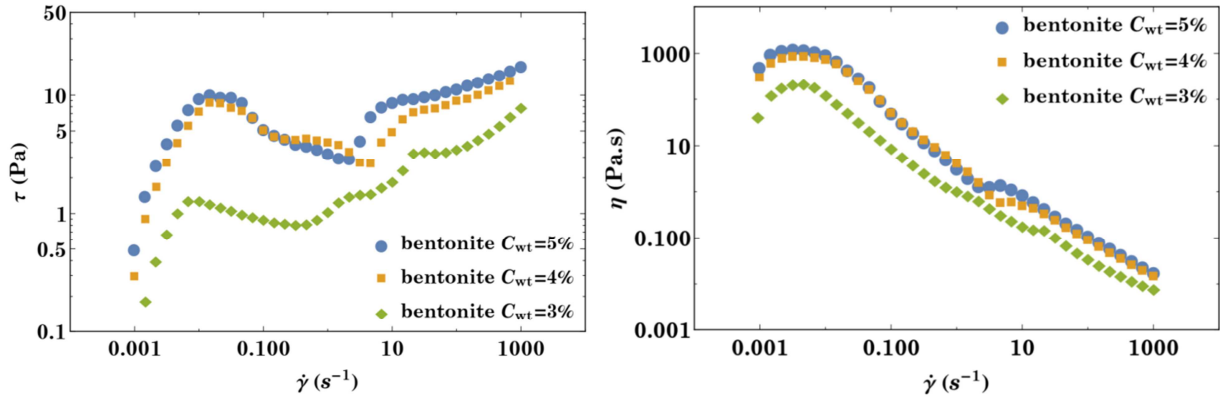


Figure 22 – Left: Flow curves of three different bentonite concentrations

On the shear stress-shear rate curve, we observe a stress plateau which indicates the existence of a mechanically unstable zone and shear bands are created within the sample for the three concentrations studied in our work.

### 3.10.6 Dynamic tests

Viscoelasticity refers to the dual nature of certain materials that combine viscous and elastic characteristics during deformation. Viscous materials, like honey, resist shear flow and exhibit strain that increases over time when subjected to stress. Elastic materials, on the other hand, deform under stress and quickly return to their original state once the stress is removed. In rheology, linear viscoelastic materials exhibit behavior that falls between that of an ideal elastic solid (represented by a spring with modulus  $G$ ) and a viscous Newtonian liquid (represented by a damper with viscosity  $\eta$ ). The elasticity of a material signifies its capacity to store and release energy after deformation, while the viscosity reflects its ability to dissipate energy. Most materials, including polymers, demonstrate viscoelastic behavior.

Viscoelastic materials exhibit time-dependent responses to stress, whether in creep or stress relaxation, whereas purely elastic materials do not. When subjected to constant stress or strain, viscoelastic materials behave like liquids and demonstrate viscous flow.

Various models can be used to describe linear viscoelasticity. Maxwell's model is applicable to viscoelastic liquids, while the Kelvin-Voigt model serves as a basic model for viscoelastic solids. Additionally, there are the Zener model and the Burgers model specifically designed for these two cases, respectively. In linear viscoelasticity, a constitutive law can be associated with a

material, which makes it possible to calculate the response to a given stress history. This is Boltzmann's principle of superposition.

By employing the principle of time-temperature equivalence, it becomes possible to determine the complete viscoelastic behavior of a material across a wide temperature range and over time, using a relatively small number of measurements of a viscoelastic quantity, such as an elastic modulus, conducted at different temperatures. Complex numbers (consisting of two components) are commonly employed to incorporate the duality between viscosity and elasticity when studying materials under dynamic stress. To represent the complex modulus  $G^*(t)$  for shear stress, the following notation is often used:

$$G^* = \frac{\sigma}{\epsilon} = G' + i G'' \quad 3-6$$

Where:

$\sigma$  and  $\epsilon$ , dynamic stress and strain, respectively;

$G'$ , the real part of  $G^*$ , called storage modulus, which characterizes the stiffness of the viscoelastic material. it characterizes the elastic behavior (the energy conserved and totally restored by the material);

$G''$ , the imaginary part of  $G^*$ , called loss modulus or dissipation modulus, which characterizes the viscous behavior [the energy dissipated (in the form of heat)].

The loss factor or damping factor is written:

$$\tan \delta = \frac{G''}{G'} \quad 3-7$$

Where  $\delta$  is the phase or loss angle, or phase shift, between stress and strain. The loss factor represents the fraction of energy dissipated during a load cycle.

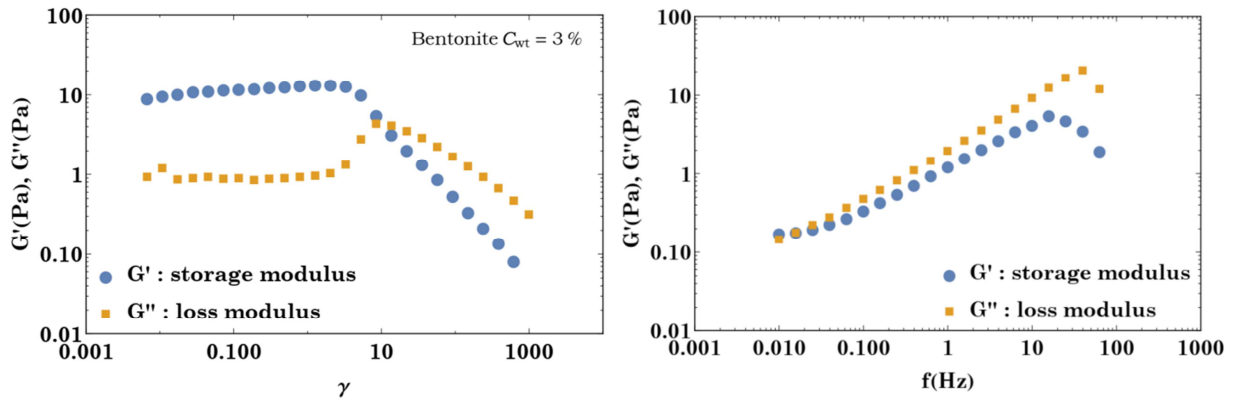


Figure 23 – Left: Evolution of  $G'$  and  $G''$  versus deformation in order to determine the linear deformation zone. Right: Dynamic test of bentonite suspension with à 3% by weight concentration

In order to determine the interval of small deformations where the regime is considered to be linear, we plotted in Figure 23 (left) the evolution of  $G'$  and  $G''$  as a function of the deformation. The linear domain is that which corresponds to practically constant values of  $G'$  and  $G''$  as a function of the deformation. This test is important to fix a value of deformation belonging to the linear field to make the dynamic test which we present on Figure 23 (on the right). Through this curve, we observe the dominance of the viscous part for this frequency range. That said, the viscous character is more significant in bentonite suspensions than the elastic one.

## Chapter 4

# Rheology of CMC Aqueous Solutions

### 4.1 Introduction

Carboxymethylcellulose (CMC) is a derivative of natural cellulose, formed after its reaction with alkali and chloroacetic acid. Purified CMC is a grayish-white granular substance, presented in a non-toxic, odorless, biodegradable powder. It does not promote allergic reactions in humans [67]. Unlike cellulose, CMC can be dissolved in hot or cold water. CMC is available in different viscosity levels. Among the most important properties that make it useful in several applications, is the possibility of obtaining a high viscosity at low concentrations, its ability to act as a thickener [68, 69]. In this chapter we will focus closely on the bibliographical study of CMC. The second part will be devoted to the experimental study of CMC, at different concentrations.

### 4.2 Definition

Abbreviation for carboxymethylcellulose, CMC is a derivative of cellulose (Figure 24), has been employed since 1947 in various water-based drilling fluids as a filtrate reducer or as a viscosifier. Cellulose is the most abundant renewable resource on earth. It is made up from photosynthesis and produced at around  $10^9$  to  $10^{12}$  tons per year and 5% of all felled timber is converted into cellulose [70]. Pure cellulose is not soluble in either cold or hot water due to intramolecular hydrogen bonding between the 3-position hydroxyl groups and intermolecular hydrogen bonds between the 6 hydroxyl groups and oxygen [71].

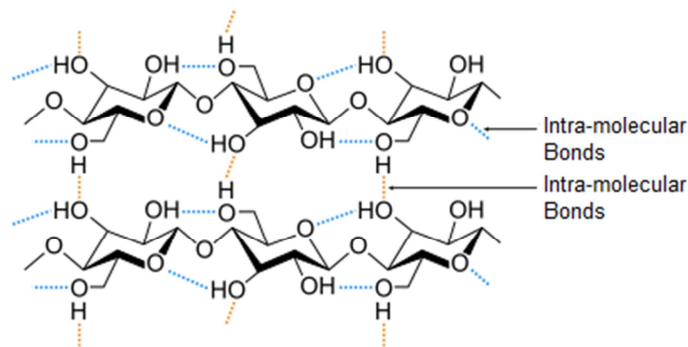


Figure 24 - Cellulose

Therefore, it can only be used as a filtrate reducer if its solubility in water is increased and this is done by introducing specific groups into the molecule. These groups can be, inter alia, carboxymethyl, hydroxyethyl or sulfomethyl radicals. The first two groups are practically the only ones used for the production of products for drilling muds [72].

### 4.3 Carboxymethylation

The conversion of cellulose into derivatives is carried out by simple chemical modification. It is well known that the solubility of cellulose derivatives strongly depends not only on the degree of substitution (DS) but also on the distribution of substituents in the glucose units and along the cellulose chain.

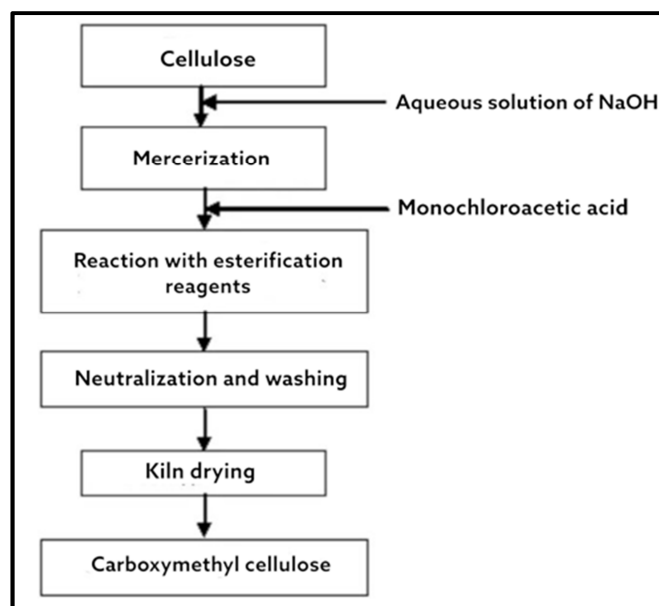


Figure 25 -Process of Carboxymethylation

Kötz et al [73] studied the characterization of synthesized CMC samples from the point of view of macromolecular and electrochemical data. The experimental procedures of carboxymethylation are shown in Figure 25.

#### 4.4 Chemical Structure, Na-CMC

The CMC therefore has the skeleton of cellulose made up of a sequence of glucoses as shown in Figure 26 below. The presence on each glucose monomer of three hydroxyl groups, linked to carbons C2, C3 and C6, allows the formation of hydrogen bridges between cellulosic structures. This interaction between the linear chains of cellulose is at the origin of the insolubility of this natural polymer in many solvents. This structure of the inter-chains is reinforced by the rigidity of the skeleton and can lead to the formation of crystalline zones in the cellulose. The degree of crystallinity varies according to the origin of the cellulose [74, 75].

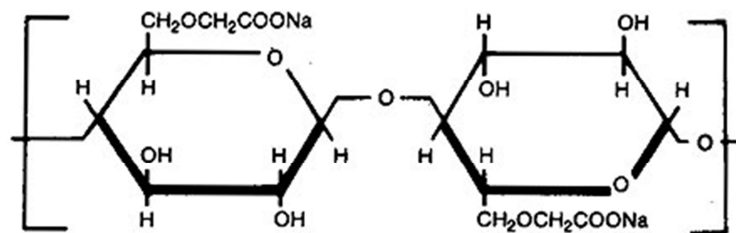


Figure 26 - Structure of Na-CMC

#### 4.5 Utilisation du CMC :

CMC (CarboxyMethylCellulose) is widely used in various industries, including the textile industry as a sizing agent, in paint resin emulsions and printing inks. In the oil industry, due to its high water retention capacity, it is used in drilling muds to increase their stability and prevent swelling of clay layers [75]. In the paper industry, CMC acts as a strengthener and increases the water retention of coating mixes (Figure 27). It is preferred due to its strong thickening and stabilizing properties [69]. CMC is also found in detergents, soaps, thickeners, and other cosmetic products.



## APPLICATION

### CMC / sodium carboxymethylcellulose



Figure 27 - Application of CMC

In the food industry, it is added as a thickener or emulsion stabilizer to products such as frozen dairy, dry beverage mixes, frosting, syrups, and baked goods. High-purity categories of CMC are used as additives to prolong the shelf life of food products. CMC is also used in pharmaceutical, ceramic, and other biological applications that require viscosity properties [74].

## 4.6 Specification

The CMC can be used for various functions; its most important features are solubility, rheology, and surface adsorption. These main properties facilitate that CMC can control different properties of aqueous systems stabilizing effects such as water retention and thixotropy. There are different parameters that define the properties of the CMC:

**Purity:** CMC is produced with sodium salt giving purity to the product.

**Viscosity:** one of the most interesting characteristics of CMC which can vary from low to high. It is measured by digital viscometers at certain temperatures and different percentages of dissolution (1%, 2% or 4%).

**Degree of substitution:** the average number of sodium carboxymethyl groups per anhydroglucose unit in the cellulose structure. This parameter is important in various fields of application of the product.

**Physical Form:** CMC can be produced in powder or granular form.

## 4.7 Rheological characterization of CMC solutions

### 4.7.1 Sample preparation

In this study, we used a sodium carboxymethylcellulose (Na-CMC) of molar mass 700000g/mol. This Na-CMC is supplied by Sigma-Aldrich. Na-CMC is an anionic polymer derived from cellulose, it is soluble in water. The CMC is prepared as follows: it is dissolved in demineralized water; stirring is done with a magnetic stirrer at a constant temperature. This allows the homogenization of the CMC, without modifying the structure of the polymer. The studied concentrations of CMC vary from 0.25 to 2% by weight.

### 4.7.2 Flow curves

In Figure 28, the rheograms of CMC solutions show that the apparent viscosity rises with the concentration, as seen in the log-log plot of  $\tau$  versus  $\dot{\gamma}$ . This effect is attributed to greater intermolecular interactions between CMC molecules. Notably, there is no observable yield stress for any of the concentrations examined, indicating that the behavior of CMC solutions in water is non-Newtonian.

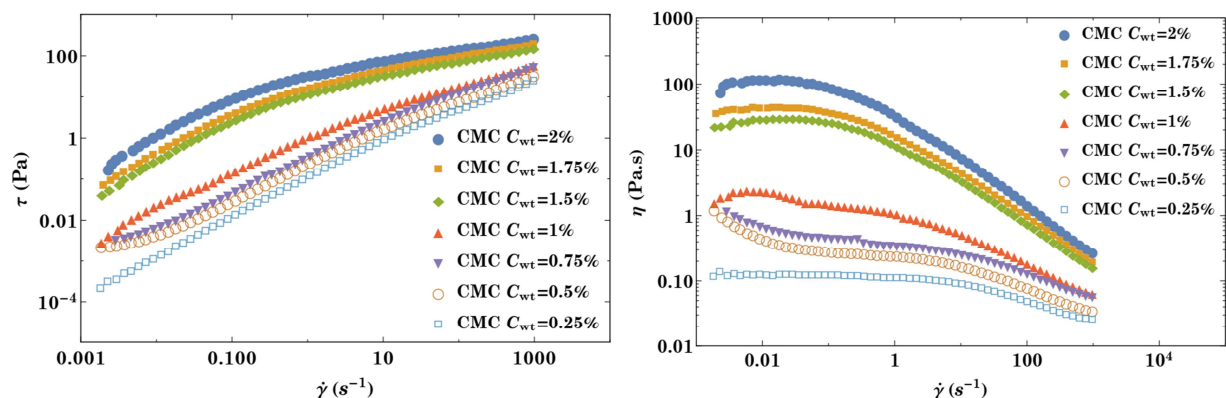


Figure 28 - on the left: Rheograms of aqueous solutions of CMC, on the right: evolution of the corresponding viscosities

### 4.7.3 Modeling

In Figure 29, the flow and viscosity curves are plotted for a concentration of 2% in order to compare three models that can describe the rheological behavior of CMC solutions. Even though Ostwald's and Sisko's models offer solutions to various non-Newtonian fluid flow issues, based on the current flow curves available, these laws are unsuitable. They inadequately describe behavior at low shear rates and lack a clear interpretation of the microscopic parameters represented by  $k$  and  $n$ . The Cross model, defined in chapter I is given by :

$$\tau = \left[ \eta_{\infty} + \frac{\eta_0 - \eta_{\infty}}{1 + (\lambda\dot{\gamma})^p} \right] \dot{\gamma} \quad 4-1$$

This formula relates the viscosity at gradient  $\dot{\gamma}$ , zero shear viscosity  $\eta_0$ , infinite shear viscosity  $\eta_{\infty}$ , a characteristic relaxation time of the fluid  $\lambda$ , and a dimensionless parameter  $p$ , which measures the rate of viscosity decrease in the fluidization zone. Specifically, when  $p$  is equal to zero, the behavior is considered to be Newtonian.

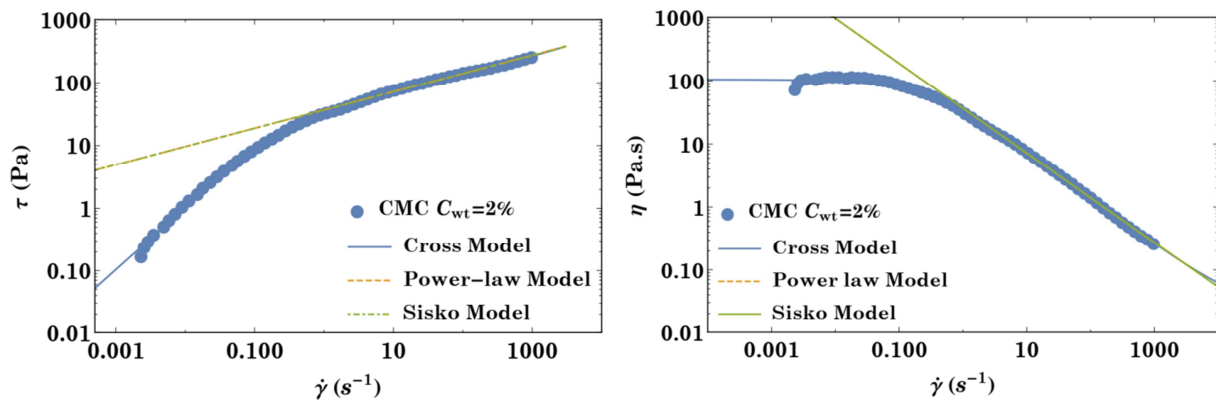


Figure 29 – Comparison between three rheological models to describe the behavior of CMC solutions with a concentration of 2% by weight

The flow curves and viscosity as a function of shear rate are shown in Figure 30 by adding the Cross model to visualize the concordance between the experimental points and the theoretical model. It is noted that there is a good agreement between the two and especially for high concentrations.

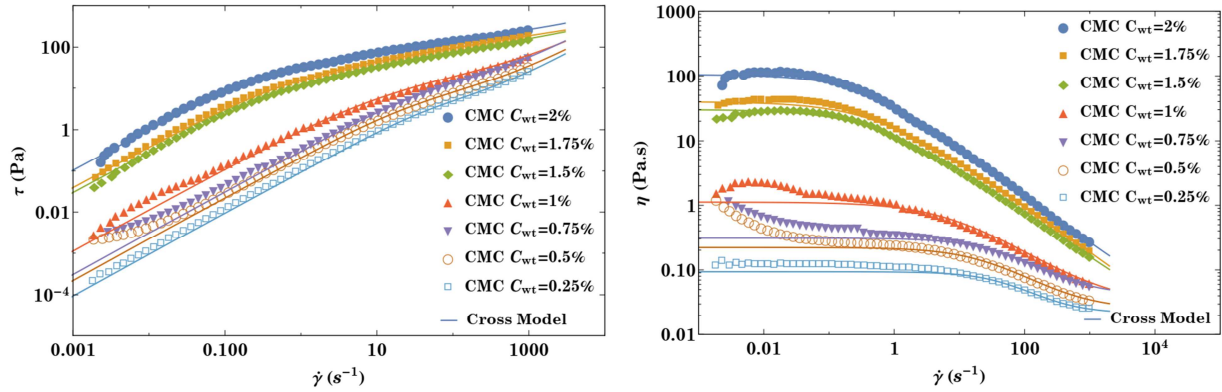


Figure 30 - Evolution of shear stresses and viscosities as a function of the shear rate adjusted by the Cross model

The rheological parameters intervening in the law of behavior through the Cross model for the aqueous solutions of CMC are presented in Table 6.

Table 6- Rheological parameters of the Cross model

CMC (%)	$\eta_0$ (Pa.s)	$\eta_\infty$ (Pa.s)	$\lambda$ (s)	$p$
0.25	0.0936	0.0216	0.0160	1.0597
0.5	0.2202	0.0248	0.0308	0.8492
0.75	0.3069	0.0407	0.0206	0.8970
1	1.1202	0.0299	0.1165	0.7189
1.5	30.2027	0.0077	1.8185	0.7042
1.75	39.7076	$4.0785 \times 10^{-8}$	1.8129	0.7131
2	105.0208	0.0199	2.6241	0.7688

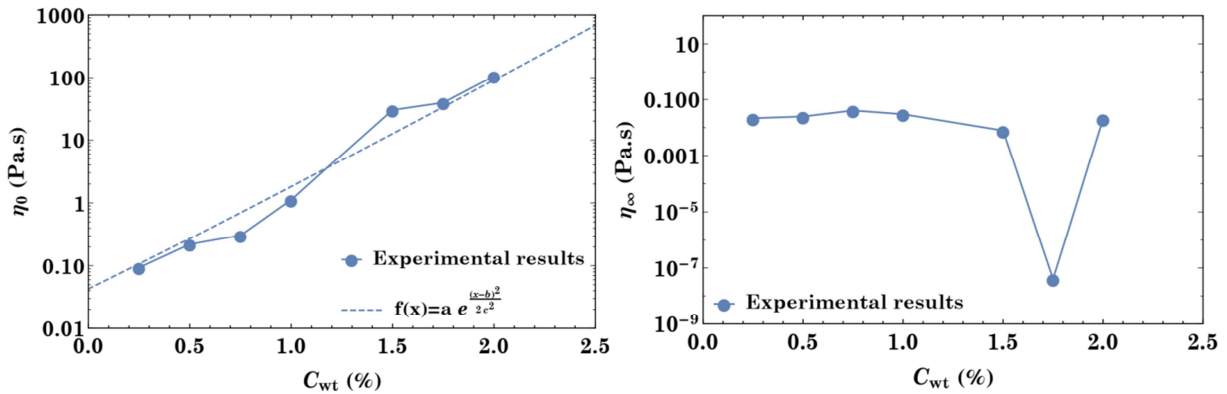


Figure 31 - Evolution of the initial and final viscosities as a function of the concentration

Through Figure 31 and Figure 32, we notice that the initial viscosity and the relaxation time increase with the concentration. On the other hand, the infinite viscosity and the parameter  $p$  remain practically constant with increasing concentration.

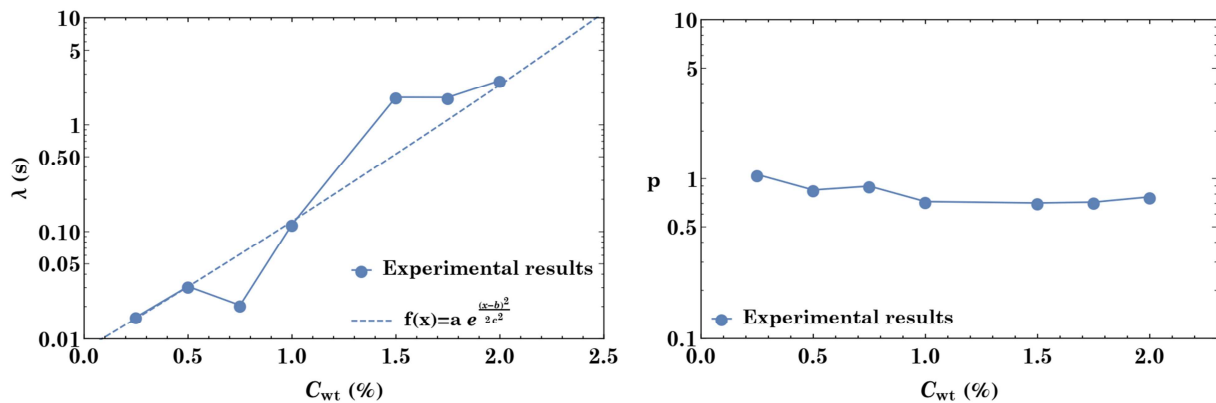


Figure 32 - Evolution of the parameter  $p$  and the relaxation time as a function of the concentration

#### 4.7.4 Dynamic tests

In a dynamic test, a test material undergoes controlled oscillation, where the frequency controls the deformation rate. The deformation is intentionally kept minimal to preserve gel structures. By varying frequencies, two fundamental parameters are obtained:  $G'$  (storage modulus), which represents the elastic properties, and  $G''$  (loss modulus), which reflects the viscous properties. The frequency range for measurement depends on the sample and study objectives.

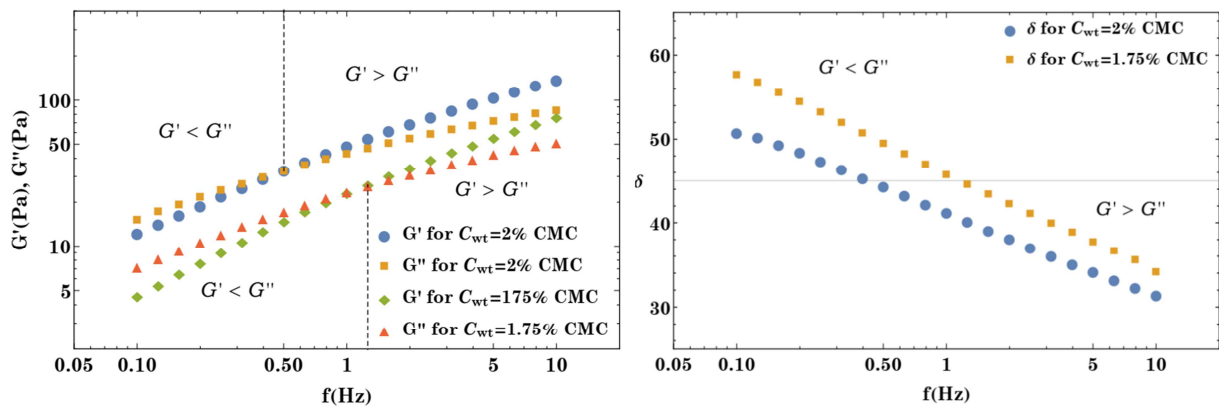


Figure 33 - Evolution of storage and loss moduli in addition to deflection angle versus frequency

Patterns obtained from frequency sweep experiments categorize  $G'$  and  $G''$  into three typical types. In a dilute solution of macromolecules,  $G'$  is generally smaller than  $G''$  across most frequencies. As the concentration increases, molecule interactions become more significant, forming an entangled or semi-dilute solution. An entangled solution exhibits a distinct cross-over point where  $G'$  equals  $G''$  or  $\tan(\delta)$  equals 1. Below this point, the material behaves fluid-like, while above it, the material behaves solid-like. The frequency corresponding to the cross-over

point is known as the relaxation frequency. In the case of gel formation,  $G'$  becomes dominant ( $G' > G''$ ), and both  $G'$  and  $G''$  become relatively unaffected by frequency. If ideal cross-links are established through permanent covalent bonding, the moduli remain completely independent of frequency. In our case (Figure 33), the relaxation frequencies for the concentrations  $C_{wt}=1.75\%$  and  $C_{wt}=2\%$  are respectively 1.26 Hz and 0.5 Hz.

## Chapter 5

# Rheology of Bentonite/CMC Suspensions

### 5.1 Introduction

Investigating the rheological characteristics of complex fluids containing solid particles, particularly clay, is highly significant due to their wide range of applications. These systems play crucial roles in various fields such as civil engineering, pharmaceutical formulations, the food industry, and fiber science and technology. Incorporating clay particles into polymers offers a means to enhance the fire resistance of fibers derived from these polymers. Additionally, clay/polymer mixtures find application in drilling muds. Bentonite demonstrates a remarkable capacity for swelling and adsorbing substantial quantities of polymer onto its surfaces.

Moreover, it has the potential to form colloidal structures that exhibit yield properties and viscoelastic behavior even at relatively low concentrations of clay. Carboxymethylcellulose (CMC) is an anionic polymer that readily dissolves in water. This fundamental characteristic governs its essential physical properties, including solubility, rheological behavior, and adsorption capabilities.

Presently, numerous research studies are dedicated to investigating nanocomposites that involve the dispersion of clay within a polymer matrix. Oscillation measurements provide valuable insights into the microstructure of these dispersions. By exploring the nonlinear regime, distinctions in behavior have been identified between the dispersion within the molten polymer and within a solution of the same polymer in clay/polyamide systems. These observations suggest

the presence of distinct modes of polymer-particle interactions that contribute to these differences [76].

In recent times, extensive research has been conducted to examine the behavior of model laponite/polyoxyethylene aqueous solution systems. By combining traditional rheological measurements with flow birefringence, it has been observed that as the velocity gradient increases, a sequential phenomenon occurs. Firstly, there is the alignment of particles within the flow, followed by the stretching of the polymer chains. These phenomena are attributed, at least in part, to the interactions between the polymer and the particles [77]. In the linear domain of oscillation, the impact of pH and chain length is emphasized, along with the effect of dispersion aging [78]. This allows for the consideration of various modes of gelation in the system, including edge-to-edge associations, polymer adsorption onto particles, and/or the formation of bridges between them [79].

When clay is added to the polymer solution, the polymer adsorbs onto the surfaces of the clay. The interactions occurring during this adsorption process involve a competition between Van der Waals forces, hydrogen bonds, and electrostatic forces of attraction or repulsion [75].

This physical phenomenon of anchoring polymer chains onto the surfaces of clay particles is accomplished by segments of the chain known as "trains." Between two consecutive trains, the macromolecules form a "loop" (Figure 34). The segment of the chain preceding the first train or following the last one is referred to as the "tail." The adsorption process is influenced by the flexibility and dimensions of the polymer chains, which are closely connected to the molecular chemical structure, the repulsions between charged groups on the chain, the charge density of the polymer, and the ionic concentration of the medium. In the case of CMC-Bentonite dispersions, the interactions can be broadly categorized into two groups:

In the first group, the interaction primarily involves electrostatic forces between the anionic polymer chains and the positively charged sites on the edges of the clay particles. However, this particular interaction is improbable in our case because, at a pH level of approximately 10, both the edges and faces of the clay particles exhibit a negative charge [80]. In the second group, the interaction occurs between the negative charges of the clay and the anionic polymer through one of the following three mechanisms:



- Ion exchange occurs between the  $OH^-$  ions of the clay surfaces and the anionic part of the polymer.
- Hydrogen bonds can form between clay particles and polymer chains
- The  $Ca^{2+}$  cation, or any other naturally occurring cation in bentonite, can establish electrostatic bridges between the anionic part of the polymer and the surface of the clay particle

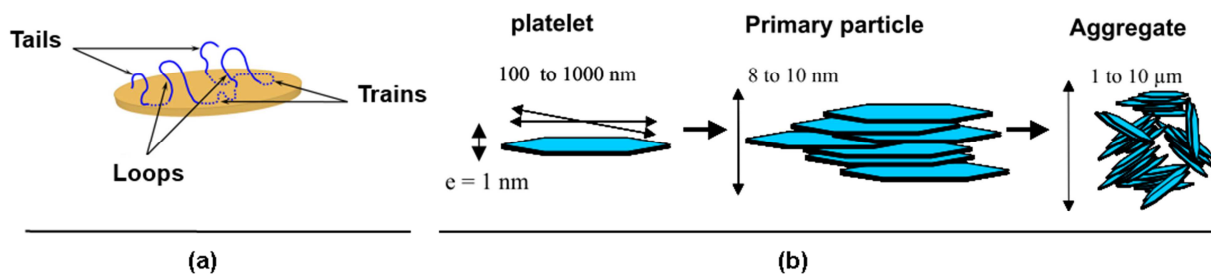


Figure 34 – (a) Fixing of a polymer chain on a clay particle surface [80]. (b) Schematic representation of the multi-scale organization of montmorillonite [81].

The addition of bentonite to the CMC solution enhances the formation of bridging bonds. This selected method increases the likelihood of interaction between the polymer chain and multiple clay particles. With the increased concentration of CMC, these bonds are further strengthened, leading to a more intricate three-dimensional structure of the clay particles. Consequently, the viscosity of the system increases due to increased flow difficulties. Figure 33 illustrates an agglomerate of bentonite before and after shearing along a specific plane. The polymer adheres to the exposed surfaces of newly formed smaller agglomerates resulting from shearing. The CMC chains remain situated between the clay particles, rendering the polymer-clay suspension reliant on the structural state of the polymer.

## 5.2 Simple preparation

Understanding the rheological properties of the polymer-clay solution system is a highly intricate task. To address this complexity, it is crucial to investigate the mechanical history of the system. In order to obtain consistent and reproducible results, we have implemented a sample preparation protocol. Failing to properly control the fluid's state before and during rheometric experiments renders it impossible to reliably and consistently determine its intrinsic properties. By studying

the aging process of bentonite dispersions in CMC aqueous solutions, we can gain valuable insights into the rheological behavior of CMC/Bentonite mixtures, as well as the interactions between the polymer chains and the clay sheets [82]. The studied fluids are dispersions of bentonite in aqueous solutions of CMC. The products used are supplied by Biochem Chemopharma and Sigma-Aldrich Companies. Aqueous solutions (demineralized water) of CMC are prepared from polymers associated with a wide range of viscosity, which corresponds to a molar mass of 700000 g/mol. The CMC concentration varies from 0 to 2% by mass.

The protocol which was adopted for the preparation of the samples is as follows: the bentonite is mixed with 100 g of demineralised water. After stirring for 24 hours, the powdered CMC is added at the desired concentration, and the mixture is stirred using a magnetic stirrer until homogenization. This protocol was too long to perform, for the high concentrations of CMC. The procedure involves stirring the bentonite suspension for duration of 2 hours, followed by the dispersion of CMC powder with concentrations ranging from 0.25% to 2% by mass.

The mixture is then stirred for several hours using a magnetic stirrer. Similarly, the bentonite dispersions in the CMC solutions are also subjected to stirring using a magnetic stirrer. It is important to point out that the sample preparation protocols as well as other parameters such as temperature have a great influence on the final state of the dispersions and the reproducibility of the results of the rheological measurements.

### **5.3 Flow curves**

Flow curves for mixtures containing 3% bentonite and different concentrations of CMC ranging from 0.25% to 2% in addition to the evolution of the corresponding viscosities as a function of shear rates are presented in Figure 35. What is remarkable on these curves is the fact that the increase in the concentration of CMC decreases the mechanical instabilities within the bentonite suspension and for the concentration of 2% by mass of CMC the shear bands phenomenon disappears and the monotony of the stress as a function of the shear rate is established. Also the viscosity increases considerably by increasing the concentration of the CMC in the mixture.

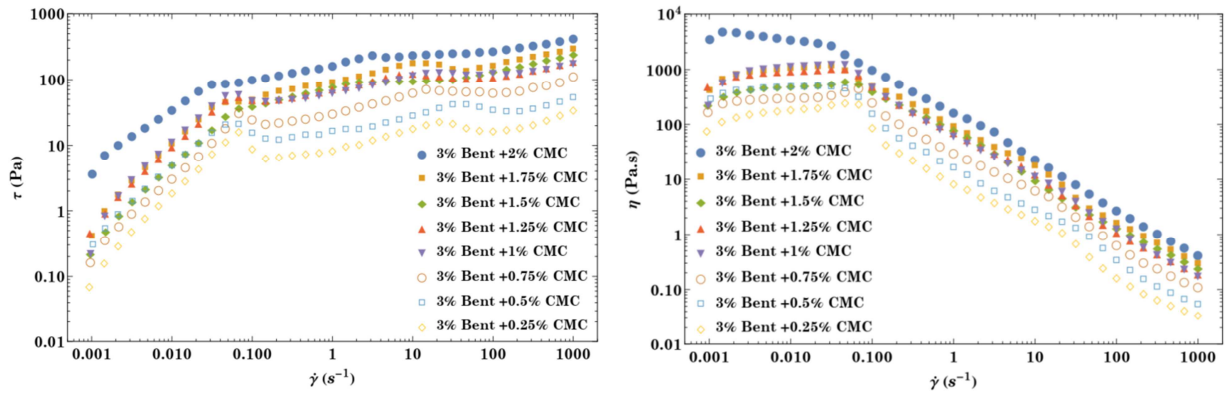


Figure 35 – Flow curves and viscosity as a function of shear rate for different concentration of CMC in the suspension of bentonite with 3% by weight

### 5.3.1 Modeling

The rheograms of the bentonite dispersions in CMC aqueous solutions are modeled based on the flow curves obtained after reaching equilibrium during the aging study (starting from the 15th day). The Herschel-Bulkley model is employed to describe the rheological behavior of these fluids:

$$\tau = \tau_0 + k\dot{\gamma}^n$$

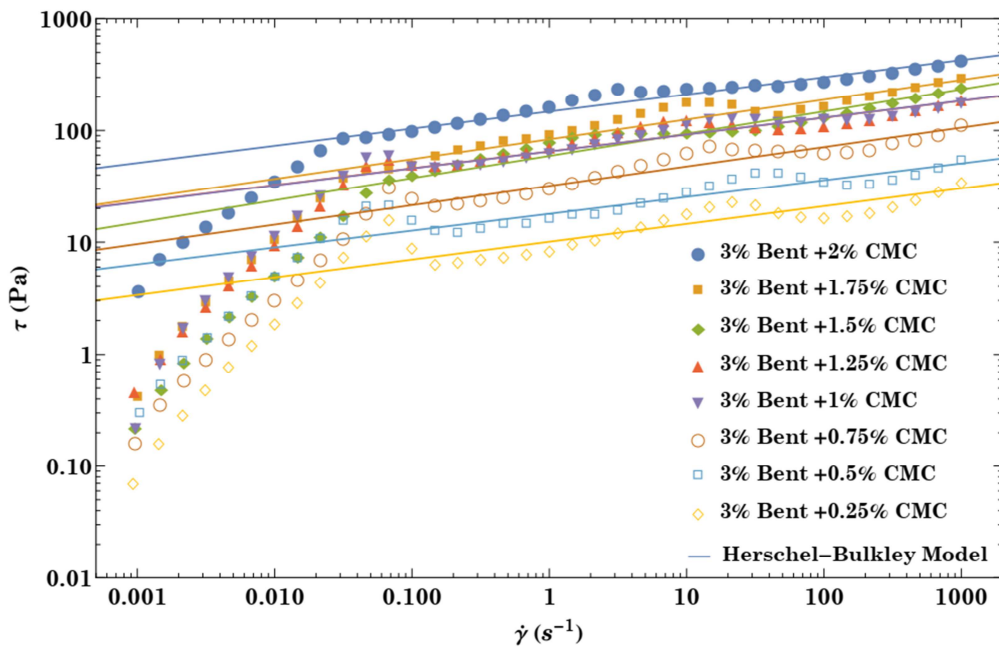


Figure 36 – Flow curves for different concentrations of CMC modeled by Herschel-Bulkley constitutive equation.

In Figure 36 we plot the flow curves for different concentrations of CMC added to the same suspension of bentonite at a concentration of 3%. What is remarkable is that the Herschel-Bulkley model describes well the behavior of all the samples but for high values of the shear rate. It is largely sufficient especially in the industrial field where the shear rates exceed  $1 \text{ s}^{-1}$ .

The rheological parameters involved in the Herschel-Bulkley model and for all the concentrations of CMC added to the bentonite suspension are summarized in Table 7

Table 7- Rheological parameters of the Herschel-Bulkley model

CMC (%)	$\tau_0 \text{ (Pa)}$	$k \text{ (Pa} \cdot \text{s}^{\frac{1}{n}})$	$n$
0.25	$1.273 \times 10^{-7}$	10.087	0.1591
0.5	$6.981 \times 10^{-7}$	17.921	0.1505
0.75	$2.006 \times 10^{-7}$	31.918	0.1736
1	$1.228 \times 10^{-7}$	64.838	0.1516
1.25	$1.238 \times 10^{-7}$	64.970	0.1508
1.5	$1.519 \times 10^{-7}$	59.208	0.1990
1.75	$7.960 \times 10^{-8}$	83.344	0.1775
2	$5.794 \times 10^{-8}$	147.821	0.1536

In what follows, we will study the influence of the concentration of the polymer on the rheological parameters of the bentonite/CMC mixture.

### 5.3.2 Influence of concentration on rheological parameters

In chapter 4, we characterized the CMC solution. It is not-yielded fluid and is well described by Cross's four-parameter law. On the other hand, the bentonite suspension presents a yield stress.

Based on Figure 37, it can be observed that the addition of CMC to the bentonite suspension at a constant concentration reduces its yield stress, despite an increase in viscosity with higher CMC concentrations. However, this effect is not desirable in drilling muds because a fluid with a yield stress is always preferred to prevent the settling of drilling cuttings in case the drilling process is halted.

Increasing the viscosity is good but not enough to remove the yield stress in the drilling mud. Some sort of optimization must be performed on the Bentonite-CMC mixtures in order to set the appropriate rheological parameters for the drilling operation. These rheological parameters depend on the size and weight of the grains constituting the cuttings.

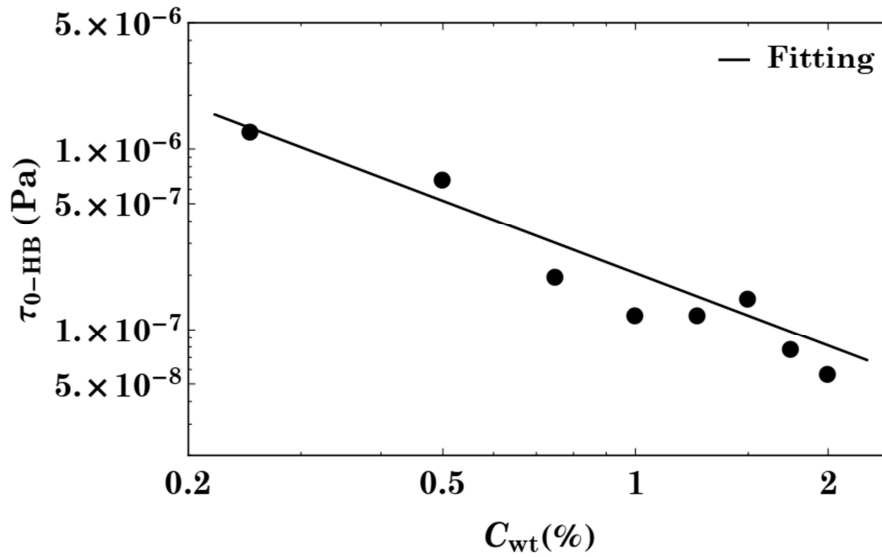


Figure 37 – Yield stress  $\tau_0$  as a function of the concentration of CMC added to the bentonite suspension of concentration 3%

On the other hand, the consistency of the mixture increases with the concentration of CMC. This is proven by Figure 38 which shows an increase in consistency with concentration. A very rapid increase from  $5 Pa \cdot s^{1/n}$  to  $200 Pa \cdot s^{1/n}$  for a variation of 0.25% to 2% of CMC. We note here the influence of concentration so that a small change induces a large change in consistency.

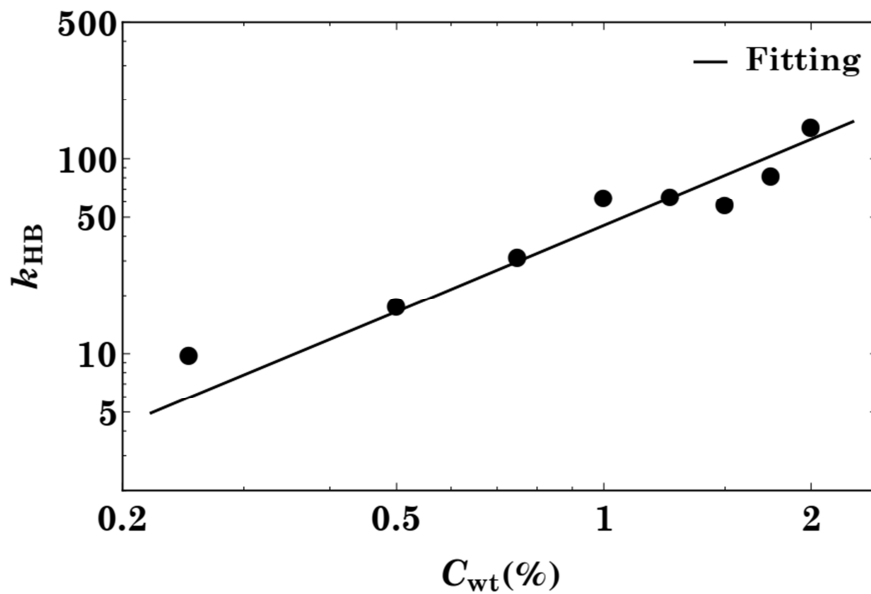


Figure 38 – Consistency as a function of the CMC concentration in the Bentonite-CCM mixture for a fixed bentonite concentration of 3% by weight

The structure index presented in Figure 39 shows an independence of its evolution from the concentration of the polymer added to the suspension. It can therefore be concluded through this curve that the concentration of CMC in the bentonite suspension practically does not affect the internal structure of the mixture. It remains in future work to determine the influence of other physical parameters such as pH and temperature on the internal structure of the mixture.

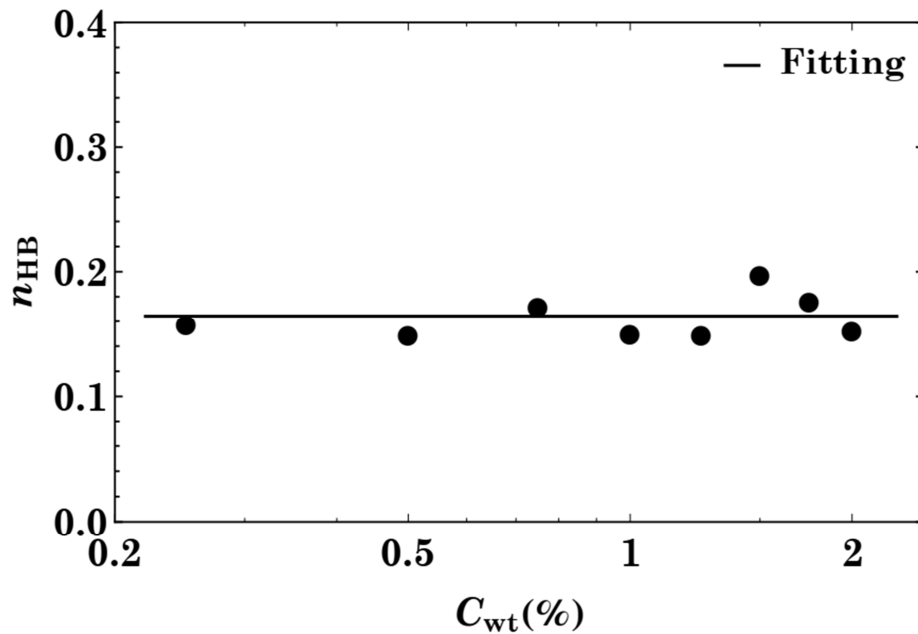


Figure 39 – Evolution of the structure index as a function of the concentration of the CMC for a fixed bentonite concentration of 3% by weight.

## 5.4 Dynamic test

In this section, our focus will be on two types of developments. Firstly, we will examine the deformation-based evolution to determine the range of the linear regime. Subsequently, based on the tests conducted for this type of evolution, we will proceed with the second type of test, which involves studying the rheological parameters of our mixtures at different frequencies.

### 5.4.1 Strain dependence

In Figure 40, we have plotted the shear stress and the angle of deflection within our samples as a function of strain for a concentration of 2% CMC and 3% bentonite. We plotted them to confirm the linear dependence between the stress and the strain on the one hand and also between the

angle of deviation and the strain on the other hand. that way we are sure that our device works without problem and the measurements that will give us are correct.

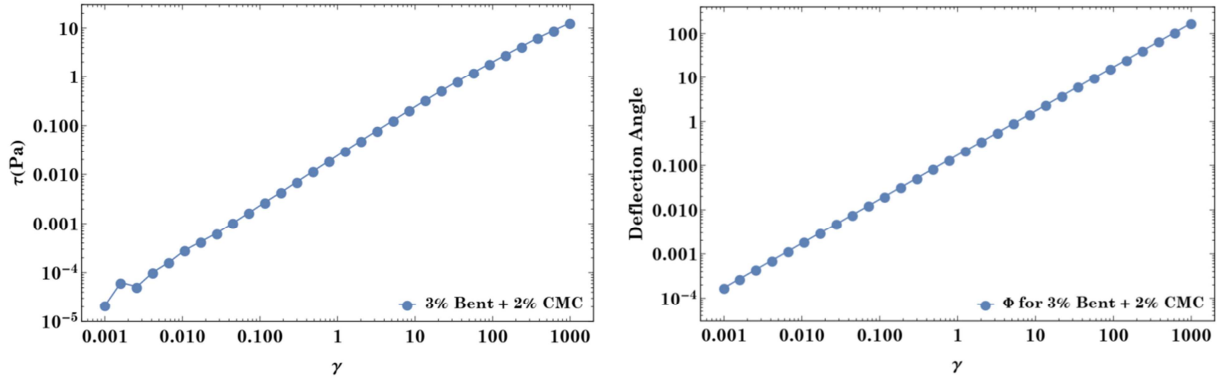


Figure 40 –Evolution of stress and deflection angle as a function of a strain

Figure 41 presents the most significant test in our study. The plot depicts the evolution of the storage modulus ( $G'$ ) and the loss modulus ( $G''$ ) as a function of deformation. This data is crucial as it provides valuable insights into the limit of the small deformation domain within which all our tests are conducted, ensuring we operate within a linear deformation regime. We can derive this information either from  $G'$  and  $G''$  or from the damping factor, which represents the tangent of the ratio between the loss modulus and the storage modulus.

The figure clearly illustrates a linear deformation regime within the range of [0.01-10]. Consequently, when performing frequency tests, it is essential to select a deformation value that falls within this interval.

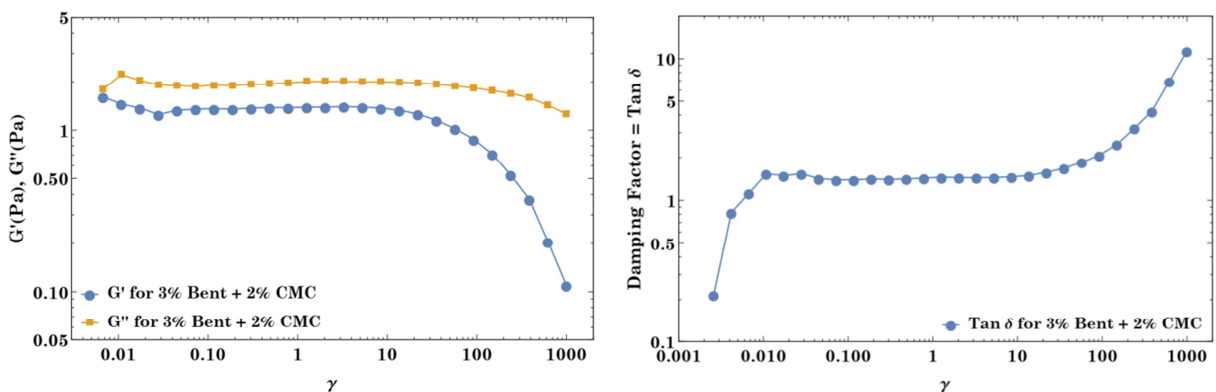


Figure 41 –Evolution of storage and loss moduli (at left) and the damping factor (at right) as a function of the strain.

## 5.4.2 Frequency dependence

The dynamic study of our sample of 2% CMC and 3% bentonite is made by tracing the evolution of the modules of conservation and loss according to the frequency. Figure 42 shows these evolutions. We notice that the loss modulus is greater than the conservation modulus over the whole range of frequencies, which proves the dominance of the viscous character in the deformation than the elastic character. The evolution of the complex viscosity is shown in the same figure on the right.

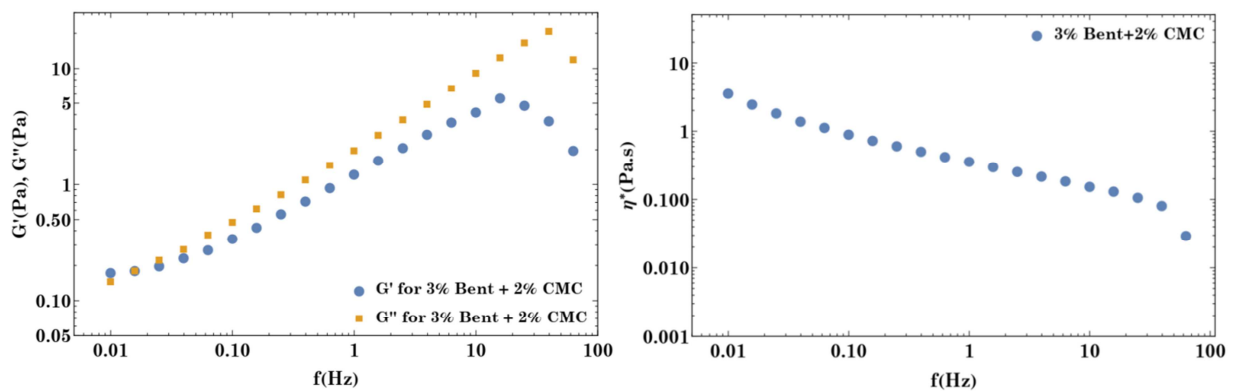


Figure 42 –Storage and loss moduli as a function of frequency (at left) and complex viscosity as a function of frequency (at right)

The complex viscosity is given by the expression:

$$\eta^* = \frac{G^*(\omega)}{i\omega} = \frac{G' + iG''}{i\omega} = \frac{G''}{\omega} - i \frac{G'}{\omega} = \eta'(\omega) - i \eta''(\omega) \quad 5-1$$

A decrease in the complex viscosity as a function of the frequency is observed, which always reflects the shear-thinning character of the mixture.



## General Conclusion

Drilling mud systems utilize two main categories of polymers: synthetic polymers and natural polymers. Naturally occurring polymers include starch, hydroxyethyl cellulose (HEC), guar, and carboxymethylcellulose (CMC). On the other hand, synthetic polymers such as polyacrylamide, polyacrylate, and partially hydrolyzed polyacrylamide (PHPA) are commonly employed in drilling mud systems. This study has made a significant contribution to the rheological characterization of three key fluids that play a crucial role in the composition of drilling muds. These fluids include the bentonite suspension, carboxymethylcellulose (CMC), and the mixture of bentonite and CMC.

The rheology of bentonite suspension and the flow curves for three different concentrations reveal a highly interesting physical phenomenon that has been extensively discussed in the literature: the phenomenon of stress plateaus and shear bands. This phenomenon has been interpreted through three different approaches: the non-equilibrium shear-induced phase transition approach, the mechanical instability approach, and the wall slip approach.

The rheology of the aqueous solution of CMC exhibits a non-Newtonian rheological behavior without a yield stress. The constitutive law that accurately describes its behavior is the four-parameter Cross model. We tracked the variation of these parameters with respect to the concentration of CMC. We observe an increase in both the initial viscosity and relaxation time as the concentration increases. However, the infinite viscosity and the parameter  $p$  remain relatively constant as the concentration increases.

Through the dynamic testing of two samples with concentrations of 1.75% and 2%, we were able to conclude that our fluid is a semi-solid or entangled solution that exhibits a distinct crossover point where  $G'$  is equal to  $G''$ . Below this point, the material behaves like a fluid, while above it, the material behaves like a solid. The relaxation frequencies for these two concentrations are 1.26 Hz and 0.5 Hz, respectively.

In the rheology of the bentonite/CMC mixture, what is noteworthy in the flow curves of these mixtures containing 3% bentonite and varying concentrations of CMC ranging from 0.25% to 2%, as well as the corresponding viscosity evolution with shear rates, is the observation that increasing the concentration of CMC reduces mechanical instabilities within the bentonite suspension. At a concentration of 2% CMC by mass, the phenomenon of shear bands disappears, and a consistent relationship between stress and shear rate is established. Furthermore, the viscosity increases significantly with an increase in CMC concentration in the mixture. The Herschel-Bulkley model is employed to describe the rheological behavior of these mixtures.

By adding CMC to the bentonite suspension at a consistent concentration, the yield stress of the suspension decreases, although its viscosity increases at higher CMC concentrations. Nevertheless, this outcome is undesirable in drilling muds as it is preferable to have a fluid with a yield stress to prevent the settling of drilling cuttings in the event of a pause in the drilling process. Conversely, the consistency of the mixture rises in tandem with the concentration of CMC. The evolution of the structure index remains independent of the polymer concentration added to the suspension. Thus, it can be concluded that the concentration of CMC in the bentonite suspension has minimal impact on the internal structure of the mixture.

Our study was limited to investigating the effect of the polymer concentration, specifically carboxymethylcellulose (CMC), on the rheological parameters of the Herschel-Bulkley model used to describe the behavior of the Bentonite/CMC mixture. An important aspect for our future work involves examining the influence of temperature and pH on its rheological properties. Another perspective is to explore the use of xanthan gum or guar gum, which have been recently employed as constituents in drilling muds.

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