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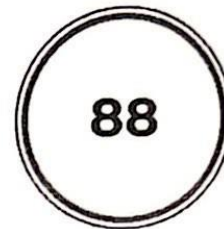
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Dedication:

I dedicate this modest paper:

To those who have always been there, pushing me to strive for more and always believing in me: to my loving parents.

To my siblings, it is for you that I continue to aim high and dream big, Tarek, Riad and my Sofia.

To my best friends, Adel and Riham, for always tolerating me, guiding me, and standing by me.

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ABBREVIATION:

Aq: Aqueous solution

C.I.N.A: Centre Industrial Nailli Abdelhalim

CIS: South Industrial Center

CRD: Research and Development Center

DAF: Administration and Finance Department

EDTA: Ethylenediaminetetraacetic Acid

Eff: Efficacy

EOR: Enhanced Oil Recovery

HMD: Hassi Messaoud

HSE (QHSE): Quality, Health, Safety, and Environment

IEA: International Energy Agency

I/O: Input/output

ISO: International Organization for Standardization

log: Logarithmic

LPG: Liquefied Petroleum Gas

N: Normality

OIP: Oil Initially in Place

pH: Potential of Hydrogen

TDS: Total Dissolved Solids

TEA: Triethanolamine

XRD: X-ray Diffraction

SUMMARY

Acknowledgment	I
Dedication:	II
CHAPTER I: LITERATURE REV... ..	3
I.1 Oil formation	3
I.2 Oil production process:	3
I.2.1 Upstream:	4
I.2.2 Midstream:	5
I.2.3 Downstream:	6
I.3 Water in the oil field.....	6
I.3.1 Injection water (water flood):	7
I.3.2 Wastewater.....	10
I.4 Water compatibility:	11
I.5 Mineral salt deposits:	13
I.5.1 Barium Sulfate (BaSO_4)	13
I.5.2 Strontium Sulfate (SrSO_4)	13
I.5.3 Calcium Sulfate (CaSO_4)	14
I.5.4 Sodium Chloride (NaCl):.....	14
I.5.5 Carbonates	14
I.6 Prevention of Deposits:	14
I.6.1 Curative Method:	14
I.6.2 Subtractive Method	15
I.6.3 Additive Method:	15
I.7 Deposit inhibitors:	15
I.8 The effects of oil emissions on the Hassi Messaoud region	16
I.8.1 Emission standards:	16
I.9 Research review.....	17
CHEPTER II: EXPERIMENTAL REVIEW	19

SUMMARY

II.1	The laboratory division description.....	19
II.2	Hassi Messouad Industrial zone description	20
II.3	Treatment stations.....	20
II.3.1	The CINA station:	20
II.3.2	The CIS station:.....	21
II.4	Sampling methodology:.....	21
II.4.1	Sample filtration:	22
II.5	Characterization.....	22
II.5.1	Physicochemical Analysis	22
II.5.2	Study of water compatibility.....	34
II.5.3	X-ray Diffraction (XRD) Analysis	36
II.5.4	Study of Anti-Deposit Products Effectiveness:	37
CHAPTER III: RESULTS AND DISCUSSION		39
III.1	Physicochemical analysis:	39
III.1.1	pH and conductivity	39
III.1.2	Water hardness:	40
III.1.3	Flame photometry	41
III.1.4	Argentimetry	41
III.1.5	Acidimetry	42
III.1.6	Hach DR 1900 Portable spectrophotometry	43
III.1.7	Total Dissolved Solids (TDS):.....	44
III.2	Water compatibility:	43
III.3	The XRD Results:	46
III.4	Effectiveness tests	47
CONCLUSION AND PROSPECTS		45

Bibliography

Appendix

FIGURES LIST

Figure I. 1: Oil production process	4
Figure I. 2 : Oil drilling rig	5
Figure I. 3 : Water flood	8
Figure I. 4: Schematic of the Continental Intercalary Aquifer in Algerian-Tunisian Basins	9
Figure I. 5: Hassi Messaoud reservoir station.....	10
Figure I. 6: Mineral deposits.....	12
Figure I. 7: Dead camel due to contamination of the groundwater.....	16
Figure I. 8: Pollution of the sands in the Hassi Messaoud region due to mud pits	17
Figure II. 1: The geological structure of the Hassi-Messaoud reservoir	20
Figure II. 2 : The different water samples.	21
Figure II. 3: wastewater filtration.	22
Figure II. 4 : pH meter.....	23
Figure II. 5 : Calcium dosage	24
Figure II. 6 : Magnesium dosage	25
Figure II. 7 : BWB XP Flame photometer.....	27
Figure II. 8: Argentometric titration.....	28
Figure II. 9 : Acidimetric determination.	30
Figure II. 10 : DR 1900 spectrophotometer.....	32
Figure II. 11: The analytical balance and the oven	33
Figure II. 12: Compatibility study	34
Figure II. 13: Deposits filtration.	35
Figure II. 14: The (60/40...90/10) dry deposits.....	36
Figure II. 15: The different inhibitors.	37
Figure II. 16: The effectiveness study.....	38
Figure III. 1 : The mixing ratios of the Albien/Cambrian... ..	45
Figure III. 2 : The mixing ratios of the Miocene/Cambrian.	47
Figure III. 3: The X-ray crystallographic analysis.....	46
Figure III. 4: The optimal dose of the SCW 83263 product	48
Figure III. 5: The optimal dose of the SCW 85372 product.	49
Figure III. 6 : The optimal dose of the CHIMEC3670 product.....	50
Figure III. 7: The optimal dose of SCW 83263 the product.....	51
Figure III. 8 : The optimal dose of the SCW 85372 product.	52
Figure III. 9 : The optimal dose of the CHIMEC3670 product.....	53

TABLES LIST

Table III. 1: pH and conductivity results of the various samples.	39
Table III. 2: Calcium and magnesium results of the various water samples.....	40
Table III. 3: Sodium and potassium results of the various water samples.	41
Table III. 4 : Chlorides results of the various water samples	41
Table III. 5: Carbonates and bicarbonates results of the various water samples.....	42
Table III. 6: Iron, barium and sulfate results of the various water samples	43
Table III. 7: The dissolved solids results of the various water samples.....	44
Table III. 8: The results of the compatibility study of the Albien/Cambrian water mixture...	44
Table III. 9 : The results of the compatibility study of the Miocene/Cambrian water mixture.	46
Table III. 10: The SCW 83263 effectiveness test results.	48
Table III. 11: The SCW 85372 effectiveness test results.....	49
Table III. 12: The CHIMEC 3670 effectiveness test results.	50
Table III. 13: The SCW 83263 effectiveness test results.	51
Table III. 14: The SCW 85372 effectiveness test results.	52
Table III. 15: The CHIMEC3670 effectiveness test results.	53

INTRODUCTION

INTRODUCTION:

Petroleum remains one of the world's most significant energy sources, underpinning a broad array of industrial, commercial, and domestic activities. The global demand for petroleum is substantial, with the International Energy Agency (IEA) reporting that the world consumed approximately 102.21 million barrels of oil per day in 2023 [1]. This substantial consumption highlights petroleum's critical role in supporting modern economies.

To meet this demand, the extraction and production of petroleum involve complex and resource-intensive processes, often requiring substantial quantities of water. Water is a crucial component in various stages of petroleum production, from drilling and hydraulic fracturing to enhanced oil recovery (EOR) and refining. EOR methods also utilize water to increase the amount of oil extracted from reservoirs. A common EOR technique is water flooding, where water is injected into the reservoir to displace oil and push it toward production wells, significantly boosting oil recovery rates, especially in mature fields where natural pressure has declined [2].

The role of water in petroleum production extends beyond facilitating extraction through methods like water flooding; it also necessitates a careful consideration of water compatibility. Understanding the chemical interactions between injected water and reservoir water is essential for optimizing recovery processes and minimizing production issues. Water compatibility studies are designed to assess how different water chemistries interact within a reservoir environment, particularly in terms of scale formation, reservoir rock wettability, and other chemical reactions that can affect oil recovery efficiency [3].

To manage and mitigate the issue of scaling, the oil and gas industry employs several strategies. One common approach is the use of scale inhibitors, chemicals that prevent the precipitation of minerals by either binding to the ions in the water or by modifying the properties of the water so that scaling is less likely to occur. These inhibitors can be injected along with the water during the secondary recovery phase to reduce the potential for scale formation.

Our study, conducted jointly within the "EX-CRD" Laboratories, focuses on the Hassi Messaoud region. It aims to prevent the formation of barium sulfate deposits by using injected inhibitors.

INTRODUCION:

In order to achieve that, the work will be plan is structured as follows:

The first chapter provides a literature review on the origins of petroleum and its production processes. It also covers details about water in oil fields, including the different types and their sources, and discusses water compatibility and the formation of deposits.

The second chapter describes the study site, followed by the methodologies and experimental protocols employed during the research.

The third and final chapter discusses the results and discussion of the various conducted experiments.

At the end, a conclusion resumes the main outcomes of the work with some prospects to enhance the research.

CHAPTER I: LITERATURE REVIEW

This chapter provides a comprehensive exploration into the multifaceted aspects of oil production processes, with a particular focus on the formation of crude oil, its extraction, and the integral role of water within oil field operations.

I.1 Oil formation:

Crude oil, a type of hydrocarbon, which is an organic raw material, that primarily comprises carbon and hydrogen, with additional constituents including sulfur, nitrogen and oxygen. It originates from the compression of organic remains of marine organisms within sedimentary rocks, notably sandstone, limestone, and shale, deposited in ancient oceanic environments. Over time, as successive layers of sediment accumulate on the seabed, the organic detritus integrates into the lithifying sediment, undergoing diagenesis [4]. Under specific thermal and pressure conditions prevailing deep within the earth's crust, these organic precursors undergo thermal degradation, thus transforming into liquid hydrocarbons [5].

The upward migration of oil and gas through porous rocks, driven by their lower density relative to water, is a consequence of buoyancy forces acting upon the hydrocarbon fluids. Geological structures such as folds, faults, and anticlines can serve as effective traps, impeding the vertical migration of oil and facilitating its accumulation into economically viable reserves. Following extraction, petroleum undergoes fractionation and chemical processing to yield an array of valuable products essential to diverse industrial sectors, thereby underscoring its significance as a cornerstone of modern civilization [4].

I.2 Oil production process:

The process of oil and gas production is divided into three major stages namely upstream, midstream, and downstream. See **Figure I. 1**.

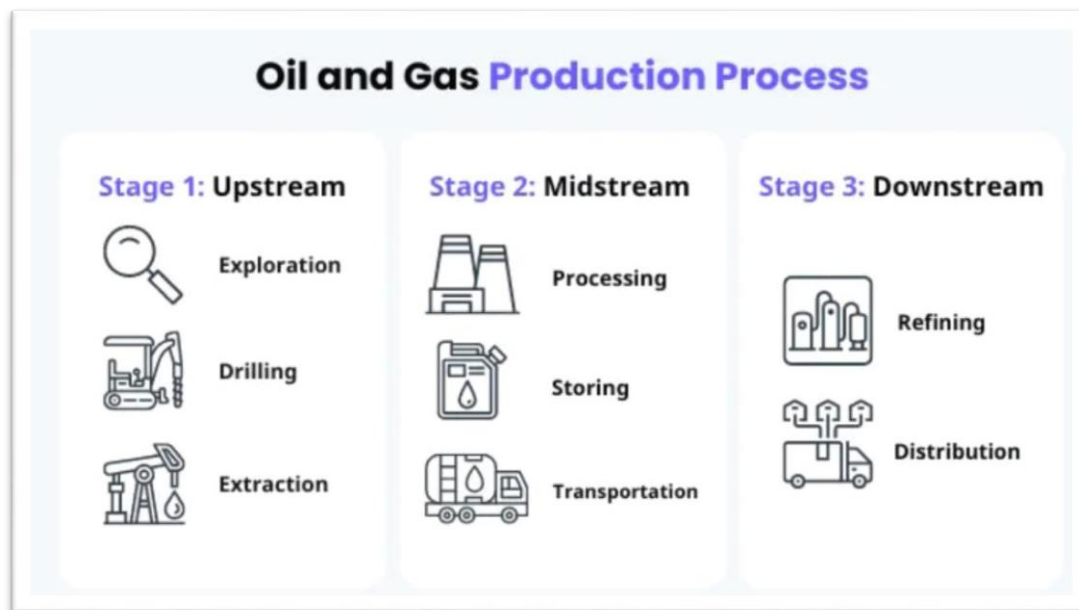


Figure I. 1: Oil production process [6].

I.2.1 Upstream:

- **Exploration:** The initial phase of oil and gas exploration encompasses a comprehensive array of processes and methodologies, such as seismic surveys to create images of subsurface structures, gravity and magnetic surveys to detect anomalies, and geological mapping to understand regional geology. These methods are employed by geologists to identify prospective sites. Once the site selection is completed, plans commence for drilling and extraction [7].
- **Drilling:** Oil drilling encompasses the procedural establishment of boreholes through the earth's surface, facilitating access to subterranean reservoirs. Employing specialized equipment, notably drilling rigs, optimized in design and functionality to withstand harsh environmental conditions and efficiently operate in remote locales, facilitates the establishment of wells for petroleum extraction [8].

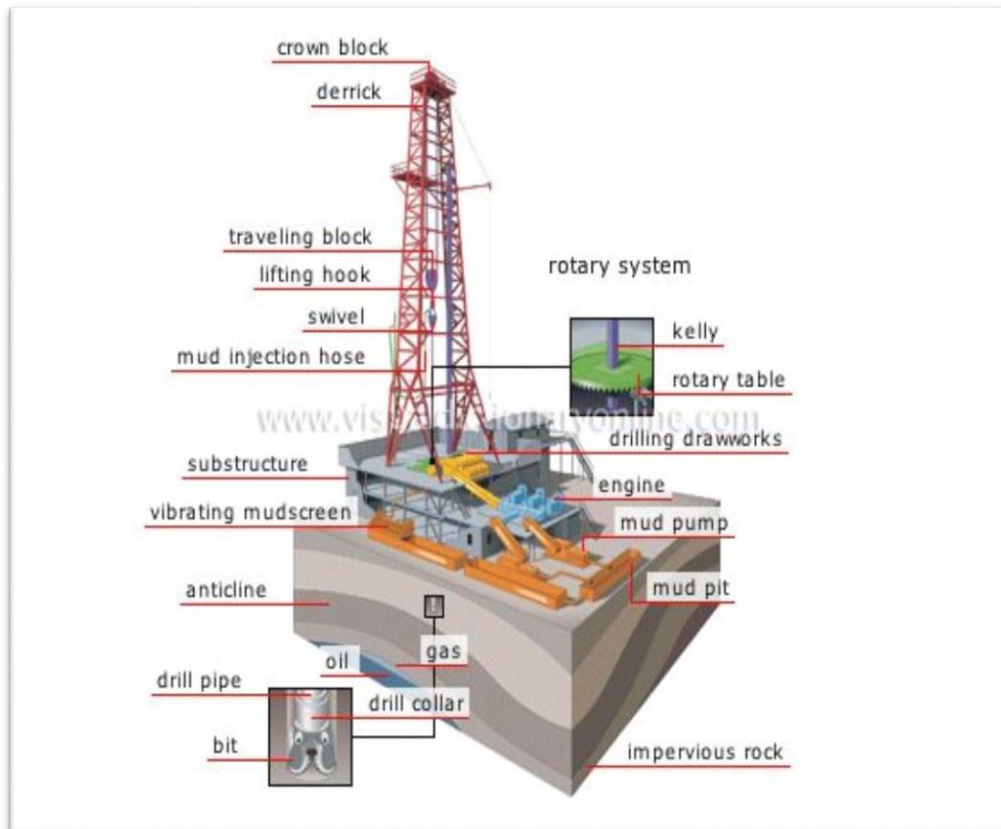


Figure I. 2 : Oil drilling rig [9].

- **Extraction:** Oil and gas extraction procedures predominantly involve the retrieval of conventional oil and natural gas from subterranean reservoirs and wells. This phase encompasses various techniques, including hydraulic fracturing (commonly referred to as fracking), which involves the injection of high-pressure fluid to fracture rock formations and enhance resource accessibility. Fracking fluids typically comprise a mixture of water, sand, and chemical additives such as guar gum, hydrochloric acid, and polyacrylamide, which reduces friction between fluid and pipe. Additionally, the recycling of fracking fluid is often integrated into extraction processes to minimize environmental impact and maximize resource utilization [10].

I.2.2 Midstream:

- **Processing:** Hydrocarbon-water separation constitutes a pivotal procedure designed to effect the segregation of oil and gas from water. This process is essential for the refinement and purification of hydrocarbon resources, ensuring the extraction of pure oil and gas components [6].

- **Storage:** The storage of oil and natural gas serves to mitigate fluctuations in supply and demand, thereby enhancing market stability. Crude oil, refined petroleum products, and finished oil derivatives are typically stored in aboveground tanks, while natural gases are often stored in subterranean reservoirs for safety considerations [11].
- **Transportation:** The transportation of hydrocarbon resources involves a multifaceted network of tankers and pipelines for conveying crude oil, while refined petroleum products are transported to market destinations via a diverse array of conveyance methods, including trucks, railroad cars, tankers, and additional pipelines [11].

I.2.3 Downstream:

- **Refining:** Petroleum refining facilities undertake the conversion of crude oil into a diverse array of components, serving as fuels for transportation, heating, and electricity generation, as well as feedstock for chemical manufacturing processes [12].
- **Distribution:** serving as the concluding stage of the process, distribution entails the transportation of refined petroleum products commercial enterprises, governmental entities, and the public.

I.3 Water in the oil field:

In the realm of the oil and gas sector, water assumes an important role, integral to numerous operational stages. Beginning with the initial drilling operations, water is utilized for various purposes, such as cooling drilling equipment and controlling downhole pressure. However, its significance extends far beyond the drilling phase. Throughout subsequent production processes, water serves as a vital component in reservoir management strategies, facilitating reservoir pressure maintenance through injection techniques [13].

The primary water classifications prevalent in the oil field context are water injection and produced water (wastewater). Water injection denotes the treated water intentionally introduced into reservoirs to facilitate secondary or enhanced oil recovery techniques, while produced water encompasses the aqueous byproduct extracted alongside hydrocarbons during production operations. These distinctions delineate the essential roles and sources of water within oil field activities, highlighting the nuanced water management strategies integral to hydrocarbon extraction processes [13].

I.3.1 Injection water (water flood):

Injection water serves as an essential method in the oil production process, aimed at augmenting reservoir pressure to enhance oil recovery from existing formations. Employed both onshore and offshore, injection water wells are strategically positioned to facilitate the pressurization of reservoirs, thereby displacing oil towards extraction points [14]. While conventional recovery methods typically allow for the extraction of approximately 30% of the oil within a reservoir through natural pressure, injection water substantially elevates this recovery factor. Typically, the use of water injection can increase the recovery factor by an additional 5-20 percentage points beyond the primary recovery factor. Given that the primary recovery factor is around 30%, the use of water injection can potentially raise the overall recovery factor to a range of approximately 35-50% [15].

The exact increase in the recovery factor depends on several factors, including the characteristics of the reservoir, the quality and effectiveness of the water injection process, and the overall management of the reservoir.

By introducing high-pressure water into reservoir formations, this technique effectively mobilizes additional volumes of oil initially in place (OIIP), thereby optimizing overall extraction yields. This secondary hydrocarbon recovery approach demonstrated in **Figure I. 2**, also known as water flooding, involves the injection of various types of water—ranging from produced water to treated or demineralized water—under controlled temperature and pressure conditions, thus prolonging the productive lifespan of reservoirs and sustaining production rates over extended periods [16].

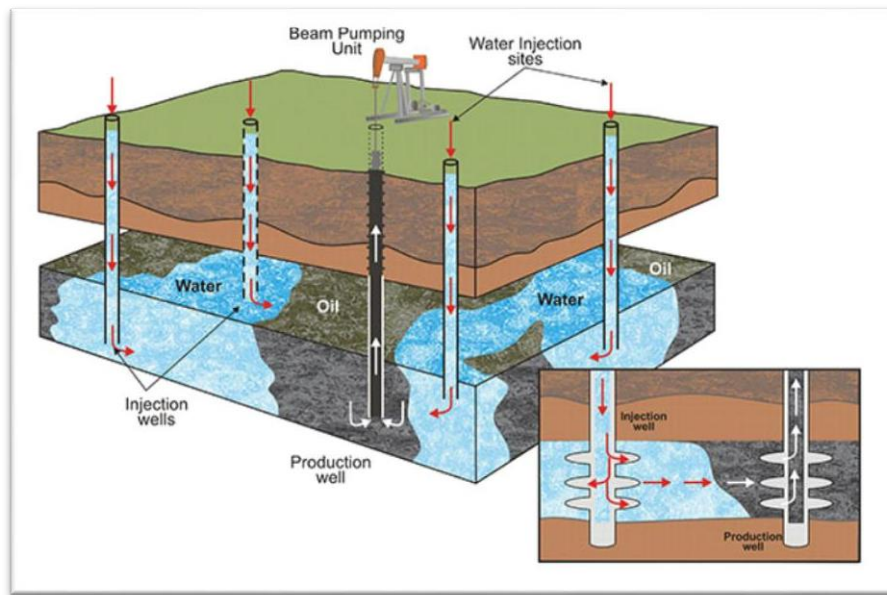


Figure I. 3 : Water flood [17].

I.3.1.1 Injection water sources:

Injection water in oil production involves the utilization of diverse water sources to augment oil recovery and sustain reservoir pressure.

Injection water appears in numerous forms:

- **Surface water:** Surface water comprises freshwater sourced from terrestrial bodies such as rivers, lakes, or reservoirs situated on the Earth's surface. It is prized for its accessibility and often-abundant flow rates. However, high oxygen levels and notable concentrations of suspended solids, encompassing sands, organic materials, and bacteria also mark surface water. Consequently, there is a risk of filter blockage in injection wells and bacterial corrosion of pipes. Thus, treatment may be required to ensure compliance with mandated quality standards prior to its utilization in injection operations within oil reservoirs [18].
- **Groundwater:** refers to the water stored beneath the earth's surface within permeable geological formations known as aquifers. These aquifers typically consist of porous rock or sediment layers capable of holding and transmitting water [19].

Among the various aquifers globally, the Albian aquifer and the Miocene aquifer hold significance due to their hydrogeological attributes and strategic importance in groundwater management.

- a) **The Albien aquifer:** derives its name from deposits laid down during the Albien Age of the Cretaceous Period, approximately 100 million years ago. This aquifer typically consists of sedimentary rocks such as sandstone, limestone, or conglomerate formations deposited during this geological epoch. Found at varying depths beneath the Earth's surface, the Albien aquifer often serves as a significant source of groundwater in regions where it is present [20].
- b) **The Miocene aquifer:** originates from deposits formed during the Miocene Epoch of the Neogene Period, which occurred approximately 23 to 5 million years ago. These aquifers are typically composed of sedimentary formations deposited during the Miocene epoch, such as sandstone, clay, or siltstone. The Miocene aquifer, like its Albien counterpart, plays a vital role in groundwater supply and management in areas where it is prevalent [21].

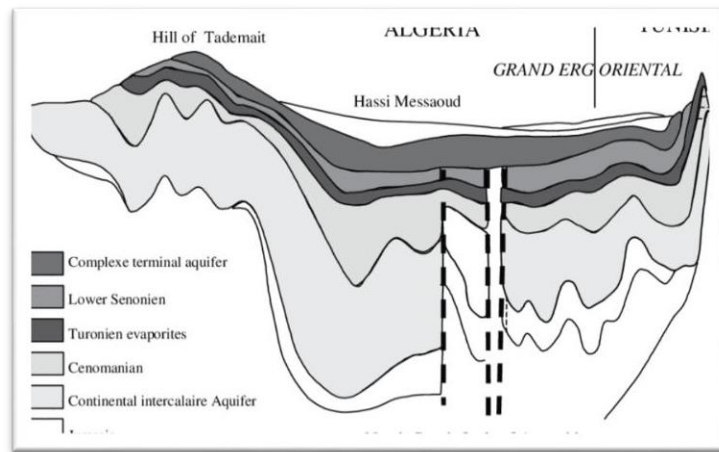


Figure I. 4: Schematic of the Continental Intercalary Aquifer in Algerian-Tunisian Basins [22].

- **Seawater:** Seawater, sourced from oceans and marine environments, is another potential option for water injection in oil production, particularly in offshore operations. Seawater may undergo desalination or treatment to mitigate its high salinity levels before injection [23].
- **Produced water:** Produced water constitutes the aqueous solution co-produced with oil and gas during extraction activities. This byproduct of oil production is often treated to remove impurities and contaminants before being reinjected into reservoirs for secondary recovery purposes [24].

I.3.2 Wastewater:

Wastewater, also referred to as reservoir water or formation water, can derive its source from either the underlying aquifer situated at the base of petroleum reservoirs or from condensation accompanying reservoir fluids in the vapor phase. It invariably coexists with crude oil within the producing reservoir. This aqueous component is frequently characterized by a substantial salinity level, often reaching saturation, with sodium chloride prevailing as the predominant salt. Moreover, reservoir water may exhibit notable concentrations of barium, strontium, and calcium ions, which can vary depending on the geological formation and the specific characteristics of the reservoir [2].

I.3.2.1 Wastewater sources:

Wastewater manifests in various forms:

- **Condensation Water:** This denotes the water vapor component accompanying reservoir fluids. It is theoretically expected to contain fewer chemical constituents and is typically produced at the wellhead through condensation, albeit in limited quantities.
- **Formation Water:** Generally, formation water refers to groundwater that has been confined within a geological formation for an extended duration. Its chemical and physical characteristics depend on the composition of the surrounding rock and prevailing geological processes. As an example, the Cambro-Ordovician stratigraphic sequence of the Hassi Messaoud field, which consists of a silico-clastic series uncomfortably overlying a metamorphic and eruptive basement. This sequence, illustrated in **Figure I.3**.

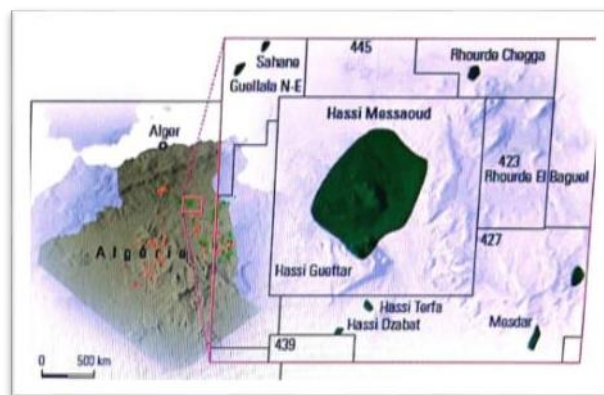


Figure I. 5: Hassi Messaoud reservoir station [25].

- **Interstitial Waters:** Also termed groundwater, interstitial waters occupy voids and fissures within soils and rocks beneath the earth's surface. Representing a substantial proportion of the planet's freshwater resources, interstitial waters serve diverse purposes, including irrigation, human and animal consumption, and industrial endeavors.

It primarily originates from the infiltration of rain and snowmelt into the soil, accumulating within porous and fractured rock substrates. Their sources may encompass snowmelt, groundwater recharge processes, and surface water percolation into the underlying geological strata [26].

- **Connate Waters:** Connate water is a type of underground water that was trapped in rocks when they formed. This ancient water has remained isolated from the atmosphere for most of its existence; making it a relic from earth's distant past [18].

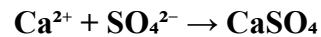
I.4 Water compatibility:

The oil industry relies heavily on the intricate interplay between various components, one of which is the compatibility of different types of water utilized in oil reservoirs. Understanding the compatibility between oil reservoir formation water and proposed source water is crucial, as their mixing can lead to the formation of precipitates, signaling incompatibility. Compatibility between waters is determined by the absence of precipitates upon mixing.

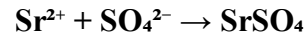
The compatibility or incompatibility of source and formation waters directly influences the success of water flooding techniques utilized for secondary oil recovery. Incompatibility between these waters can result in severe plugging and scale deposition issues, posing operational challenges and escalating costs. These problems arise when incompatible waters are mixed within the reservoir, remaining dormant until breakthrough occurs, subsequently leading to scaling in producing wells and equipment. As water flooding progresses, the dynamic nature of precipitation and scaling issues necessitates ongoing evaluation and potential treatment measures to mitigate operational disruptions [27].

The most common mineral deposits encountered are sulfate and carbonate-based minerals. Produced waters contain cations such as Ca^{++} , Sr^{++} , and Br^{++} , while injection waters contain anions such as SO_4^{2-} . When these waters are mixed, it can lead to the formation of deposits of CaSO_4 , SrSO_4 , and BrSO_4 [28].

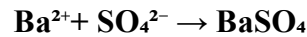
The mineral deposits commonly encountered after water injection-reservoir contact are:



“Calcium sulfate precipitation”



“Strontium sulfate precipitation”



“Barium sulfate precipitation”



Figure I. 6: Mineral deposits [29].

The effective management of water compatibility within oil reservoirs is paramount in reservoir engineering, significantly affecting operational efficiency, cost-effectiveness, and the ultimate success of oil recovery operations. Water compatibility refers to the ability of water samples to be mixed without undesirable chemical reactions occurring. Essentially, compatible waters possess similar chemical properties or do not react when combined. This concept holds significance across various fields such as chemistry, medicine, agriculture, and industry, where the blending of different solutions or chemicals is common practice to avoid adverse outcomes [3].

Elemental chemical analysis employs physicochemical parameters to theoretically approach such situations. These parameters encompass solubility product, salinity, and hardness, concentration of cations and anions, as well as pH (potential of hydrogen). By

utilizing these parameters, chemical analysis offers a deeper understanding of a substance or solution's composition and its response to diverse conditions [30].

I.5 Mineral salt deposits:

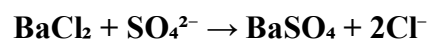
Mineral salt deposits form at various stages of oil production. They are numerous and vary in structure. Some are water-soluble (sodium chloride), others are acid-soluble (calcium carbonate), while still others are practically insoluble (barium sulfate, strontium sulfate, and calcium sulfate) [30].

I.5.1 Barium Sulfate (BaSO₄):

The issues posed by barium sulfate deposits stem from the incompatibility of two waters. Some reservoir waters contain dissolved barium salts (Ba²⁺). When these waters encounter surface water containing sulfates (SO₄²⁻), barium sulfate precipitates. This contact can occur during continuous washing practices to prevent salt deposits or during freshwater injection into the reservoir to maintain pressure. The injected water eventually reaches the producing wells, where mixing occurs and barium sulfate precipitation takes place.

Celestine, also known as celestite, is a mineral consisting of strontium sulfate (SrSO₄). It typically forms in sedimentary rock environments and is distinguished from barite, or natural barium sulfate, by flame coloration. While barium sulfate is frequently found in metallic veins. The crystals adhere to tubing walls, forming insoluble and very compact deposits [30].

Its formation occurs according to the reaction:



I.5.2 Strontium Sulfate (SrSO₄):

Strontium sulfate is much less soluble than calcium sulfate, with a solubility product of 2.8×10^{-7} mole/L, and like calcium sulfate, its solubility decreases with temperature. The precipitation of SrSO₄ can occur because of:

- Water evaporation.
- Temperature increase.
- Mixing of incompatible waters.

Strontium sulfate crystals are orthorhombic with very close meshes and porous in nature, with a tendency to adsorb foreign ions that can co-precipitate. SrSO_4 deposits are practically impervious even to acids [30].

I.5.3 Calcium Sulfate (CaSO_4):

Calcium sulfate salt deposits are slightly soluble, but even at concentrations close to their solubility limit; there is a risk of precipitation. One major cause of calcium sulfate deposition is the pressure drop along the well, while partial evaporation and the incompatibility of two waters (reservoir water and injection water) can also lead to precipitation. Calcium sulfate deposition can easily cause constrictions or even blockages in pipelines, potentially resulting in a failure to meet injection objectives due to decreased water production rates [30].

I.5.4 Sodium Chloride (NaCl):

Sodium chloride deposits are a frequent cause of salt deposition, leading to pipe diameter shrinkage. This issue arises from the mixing of sodium-rich water from wells with crude oil, which naturally contains high chloride content [30].

I.5.5 Carbonates

Carbonate deposits result from CO_2 departure precipitation due to temperature increase or pressure drop. The formation is slow due to long-lasting super saturation. The formation occurs according to the following reaction:



Although carbonates are highly soluble in acids, this solution is rarely used due to CO_2 release, which represents a significant corrosion constraint. Carbonates in tubing can be removed by water flushing with a coiled tubing unit (or even with an acetic acid solution) [30].

I.6 Prevention of Deposits:

I.6.1 Curative Method:

This method involves mechanical separation using reactors; however, its efficacy is limited, and it can cause tubing fissures [30].

I.6.2 Subtractive Method

This method involves removing the ions that form deposits. Majorly, the only feasible action is to eliminate sulfate ions present in the injection water, known as desulfation. There are two methods:

- Desulfation by ion exchange using anionic resins.
- Desulfation by precipitation with BaCl₂.

Both methods are effective but suffer from the drawback of being costly and requiring significant human and material resources for water treatment in an oil field [30].

I.6.3 Additive Method:

The additive method is best suited for deposit treatment as it inhibits crystalline growth using products known as deposit inhibitors. It follows that, among these options, only chemical inhibition appears to be technically and economically favorable [30].

I.7 Deposit inhibitors:

Deposit inhibitors primarily consist of molecules or small water-soluble macromolecules, classified into different classes based on their chemical functions or structures. Their mechanisms of action are categorized into three main categories, as described below:

- Nucleation inhibition: This involves the thermodynamic destabilization of nuclei by the adsorption of inhibitor molecules onto their growth sites.
- Dispersion of already formed crystals: This is achieved by maintaining aggregates in suspension through electrostatic or steric stabilization due to the adsorption of macromolecules, such as polyelectrolytes, onto their surface.
- Slowing down crystal growth: This occurs through the adsorption of inhibitor molecules onto the growth sites of deposits that are currently forming, thereby impeding their growth process [30].

I.8 The effects of oil emissions on the Hassi Messaoud region:

The expansion of the oil industry in the Hassi Messaoud area has resulted in the generation of hazardous effluents that pose risks to the ecosystem, including environmental and health concerns, stemming from oil drilling activities and the operation of production facilities.

Oil-contaminated wastewater poses a significant threat to soil, water, air, and human beings due to the hazardous nature of its oily content. These waters containing fats and oils can form films or superficial layers, obstructing air access in watercourses, leading to intoxication of aquatic organisms (thus, the destruction of aquatic fauna and flora), and consequently rendering any other beneficial use of water bodies impossible (such as fishing and agriculture).

The presence of various constituents in different oily wastewater discharges can result in soil quality deterioration, soil erosion, and air pollution with the emission of foul odors. If untreated wastewater is not disposed of under satisfactory hygiene conditions, it can lead to problems through infiltration, altering the quality of groundwater through organic pollution, salinization, acidification, increased iron content, discoloration, or poisoning. This causes numerous diseases. Therefore, it is necessary to treat these waters to enable their reuse to conserve water resources and preserve human health and the environment [31].

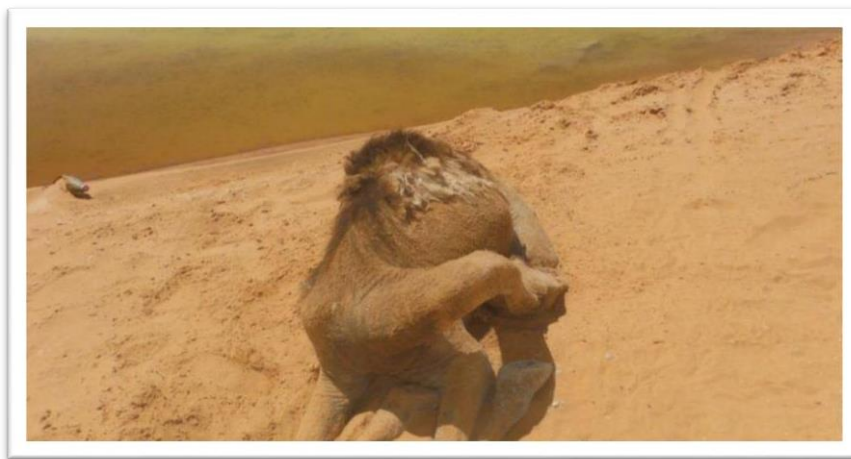


Figure I. 7: Dead camel due to contamination of the groundwater [31].

I.8.1 Emission standards:

Petroleum industrial discharges can be the source of various types of water pollution causing serious environmental problems. To allow for the balanced development of aquatic ecosystems and to prevent environmental issues, several countries establish discharge standards to mitigate

the negative impacts of treated industrial wastewater discharge into receiving environments. At the national level, Algerian regulations have dedicated a single document specifying discharge standards for industrial liquid effluents cited within Executive Decree No. 06-141 of April 19, 2006, defining the limit values of constituents for industrial liquid effluent discharge [31].



Figure I. 8: Pollution of the sands in the Hassi Messaoud region due to mud pits [31].

I.9 Research review:

In a comprehensive study, authored by Taha, A et al. The authors explored the critical role of water management in oil and gas operations, essential for both hydrocarbon mobilization and reservoir pressure maintenance, yet presenting the significant challenge of scaling. Scaling, caused by factors such as fluid incompatibility and temperature changes, is classified into acid-soluble carbonate scales (e.g., Calcium Carbonate) and acid-insoluble sulfate scales (e.g., Calcium Sulfate, Barium Sulfate, Strontium Sulfate). These scales significantly affect economic and operational efficiency by forming deposits from the reservoir to surface tanks [32].

Effective water management is pivotal, particularly in water-scarce regions where produced water (PW) reclamation can address freshwater shortages. Traditional treatment methods have proven insufficient, prompting the adoption of advanced technologies like physical, chemical, biological, and membrane processes. Integrated treatment approaches are necessary to meet environmental standards and facilitate PW reuse. Strategies for effective

management focus on minimizing generation, recycling, and safe disposal, considering environmental, technical, and economic factors [33].

Industry practices for scale prevention and removal include chemical inhibitors and mechanical interventions, highlighting the importance of understanding water properties to mitigate scaling risks. In another work done by Razavirad, Heidari et al. The compatibility between smart water for injection and formation water under varying temperature conditions was investigated, noting that temperature significantly influences sulfate concentration due to the transformation of sulfite to sulfate. In contrast, pressure variations have minimal impact on scale solubility. Their study utilized scanning electron microscopy and energy-dispersive X-ray spectroscopy to analyze scale composition, emphasizing the importance of water compatibility to prevent scale-related operational issues [34].

Further research by Jing et al. Examines scaling in water-injection pipe columns at the Daqing Oilfield, focusing on how different injection waters influence scale formation, particularly calcium carbonate, under varying temperatures. They found that scales are predominantly composed of iron compounds and organic materials, with temperature significantly affecting calcium ion concentrations. This underscores the need to manage water chemistry to control scale formation in oilfield operations [35].

Additionally, scaling issues in geothermal reinjection wellbores were investigated using water from the Xining Basin, China. Experiments measured scale deposition and adhesion on pipe walls, revealing that static conditions promote significant scaling, while operational conditions reduce this risk. An enhanced model predicts scale layer thickness based on deposition kinetics. Results suggest that extended injection times, higher rates, and increased temperatures effectively minimize scaling and blockage risks, highlighting critical measures for maintaining wellbore integrity in geothermal reinjection systems [36].

Overall, these studies highlight the multifaceted challenges of scaling in water management within the oil, gas, and geothermal industries. Effective strategies and advanced technologies are essential for preventing scale formation, ensuring operational efficiency, and addressing environmental concerns.

CHAPTER II: EXPERIMENT AND REVIEW

This chapter covers the following subjects: the description of the Laboratory division; an overview of the Hassi Messouad Industrial Zone; the sampling methodology and a discussion of the different experimental analyses, including physicochemical analysis and water compatibility; the DRX results; and the results of the effectiveness tests.

II.1 The laboratory division description:

The Laboratory Division, established in 1973, has undergone several stages of development since then. Initially, it benefited from the human and material resources of the hydrocarbon laboratories within the Hydrocarbons Division located in HYDRA, with the aim of providing scientific support in the field of hydrocarbon research and exploitation.

In 1975, under the designation of the Central Laboratory of Hydrocarbons, the structure was relocated to BOUMERDES for better installation and commissioning of equipment, enabling most laboratories to become operational in 1976-1977.

Since July 1987, it has been transformed into the Research and Development Center (CRD). The CRD is primarily involved in hydrocarbon research and exploitation, providing technical support through laboratory analysis and study. Additionally, the CRD, with its scientific focus, contributes to problem solving for operational divisions within the company.

In 2009, the CRD underwent a radical transformation, becoming the Laboratory Division. This change led to the absence of research with scientific advice, as well as a restructuring of the Human Resources Department, which subsequently became the Administration and Finance Department (DAF). This change was a result of the integration of the Finance and Planning Department. Furthermore, a Logistics Department was created, overseeing the Procurement and Resources Department, along with the Information Technology Development Group and IS I Group (Scientific and Technical Information).

In this new organization, the Quality / HSE (QHSE) (Quality, Health, Safety, and Environment) Department was established, reporting directly to the Laboratory Division, along with the creation of the position of Internal Security Assistant, which reports to the Division Manager.

The most significant aspect of this new organization was the involvement of the Laboratory Coordination HMD located in Hassi Messaoud, which oversees the central map library of Hassi Messaoud [37].

II.2 Hassi Messouad Industrial zone description :

The giant light oil field of Hassi Messaoud was discovered in 1956 by the MD1 well drilling, which penetrated the Cambro-Ordovician sandstone reservoirs at a depth of 3337 meters. The field, measuring 40 x 40 km, is located in the Algerian Sahara, 800 km south of Algiers. 1188 wells have been drilled, with over 85% currently active; miscible gas injection has been extensively implemented and, along with water injection, constitutes the main mechanisms for reservoir drainage [25].

Figure II- 1 illustrates the geological context of the field.

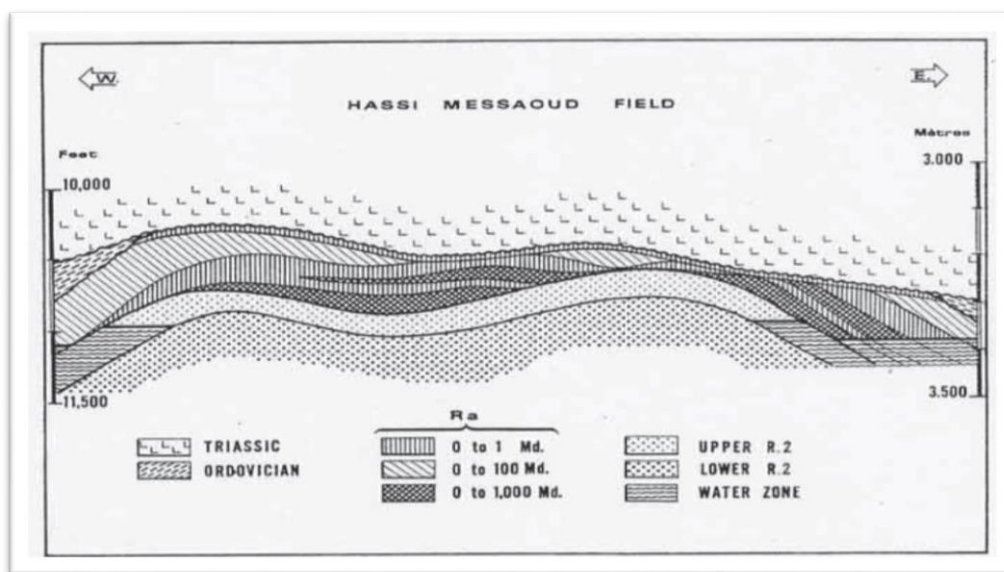


Figure II. 1: The geological structure of the Hassi-Messaoud reservoir [30].

II.3 Treatment stations [25]:

The Hassi Messaoud field consists of two distinct parts: the North CINA field and the South CIS field.

II.3.1 The CINA station:

The Centre Industrial Nailli Abdelhalim (C.I.N.A) is located in the central zone of the HMD field (within the North industrial zone) and processes the brine oil wells from the North zone. It consists of five 1000-liter tanks and one 2000-liter tank. It comprises a processing unit, a liquefied petroleum gas (LPG) unit, and a compression unit.

II.3.2 The CIS station:

It processes the brine oil wells from the Southwest zone and is located in the central zone of the HMD field (within the South Industrial Center). It has five 1000-liter tanks each and one 2000-liter tank. It comprises a crude oil processing unit, an LPG unit (1), an LPG unit (2), a refinery, a compression unit, and a central laboratory.

II.4 Sampling methodology:

The sampling choice is based on the Hassi Messaoud field for the following reasons:

- The deposition problem is more pronounced in this region.
- The risk of productivity loss or damage to well facilities due to the precipitation of BaSO_4 is more serious here, affecting practically all compositions and occurring in both downhole and surface conditions.

The objective of these analyses is to determine the composition as well as the ion content of the reservoir and injection waters. The waters involved in this study are:

- Injection water Albien extracted from the pressure maintenance well MDHA3.
- Injection water Miocene extracted from a pressure maintenance well.
- Wastewater Cambrian extracted from the oil-producing well NZN4.

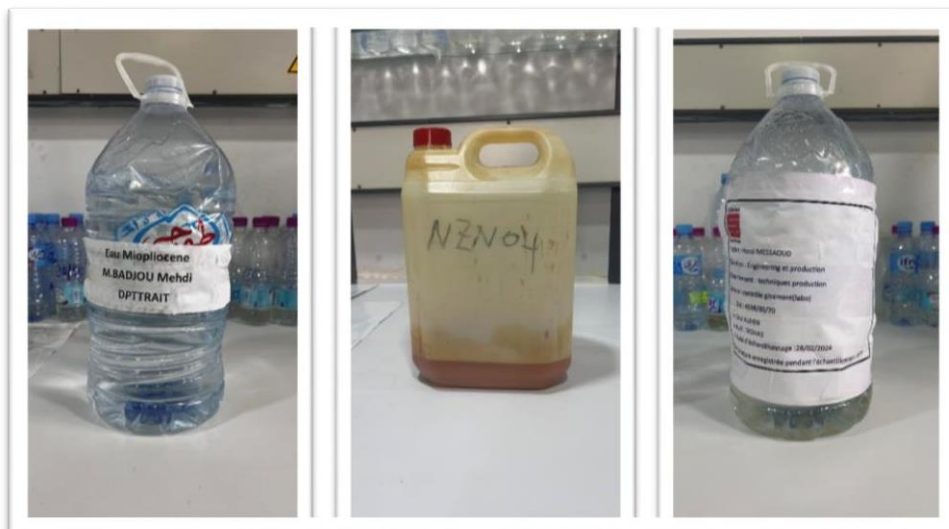


Figure II. 2 : The different water samples.

II.4.1 Sample filtration:

Before proceeding with physico-chemical analyses, the water must be pre-filtered to remove suspended matter, sands, some types of oils, and to eliminate the discoloration of oily waters (wastewater) that can influence analysis results.

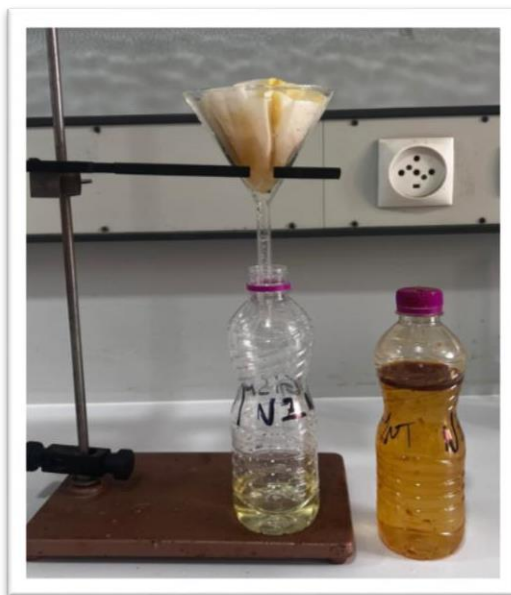


Figure II. 3: wastewater filtration.

II.5 Characterization:

II.5.1 Physicochemical Analysis :

For every water compatibility study, a specific physico-chemical analysis is necessary. This analysis is justified by the actions and interactions of the parameters listed below.

II.5.1.1 pH and conductivity:

This is a potentiometric method using a glass electrode specific to H^+ ions. The concept of pH, indicating the acidity of a solution, reflects the concentration of H^+ ions (H_3O^+) through the relationship $pH = -\log [H_3O^+]$ [30].

A pH meter, consisting of an electronic millivolt meter connected to two electrodes within a probe, measures the voltage (potential difference) between these electrodes, directly relating to the solution's pH.

To measure pH, first, calibrate the pH meter with standard buffer solutions, then rinse and blot the electrode. Immerse the probe in the solution, allowing the readings to stabilize, and record the pH value.

For conductivity, switch to conductivity mode, calibrate if necessary, and rinse and immerse the probe in the solution again. After stabilization, record the conductivity value. Finally, rinse the electrode and store it properly.



Figure II. 4 : pH meter.

II.5.1.2 Determination of water hardness:

Complexometry is an analytical technique utilized to assess water hardness. Determining water hardness involves measuring the concentration of calcium and magnesium ions present in the water. It serves as a crucial parameter for evaluating water quality due to its potential adverse effects, including the formation of limescale deposits, decreased effectiveness of soaps and detergents, and clogging of pipes and equipment [30].

- **Calcium concentration determination (dosage):**

In an aqueous solution, calcium is primarily found in its ionic form (Ca^{2+}) (aq). It plays a crucial role in determining water hardness. Additionally, it functions as a pH stabilizer due to its buffering properties [38].

In order to measure the calcium concentration by complexometry according to the ISO 6058-1984 (E) standard [39], we must follow the procedure outlined below.

We begin the by taking a 10 ml sample (PE) in a beaker. To this sample, we add 5 drops of NaOH and 5 drops of TEA to adjust the pH, which is crucial for the accurate performance

of the indicator and the EDTA titration. Following this, we introduce a small amount of Murexide, a color indicator that helps us visually track the progress of the titration. We place the mixture under agitation using a magnetic stirrer to ensure thorough mixing of the reagents. Using an automatic burette, we then titrate the mixture with the EDTA solution, carefully observing the color change from pink to violet. This color change signifies the end point of the titration, where all the calcium ions have reacted with the EDTA. Finally, we note the volume V_1 indicated on the automatic dosimeter, which is used to calculate the calcium concentration in the sample.



Figure II. 5 : Calcium dosage.

Results expression:

$$[Ca^{++}](Mg/L) = \frac{V_1 \times N \times D \times 40,08 \times 10^3}{PE}$$

- V_1 : volume of EDTA titrated in milliliters
- N : normality of the EDTA solution
- $N=0.01$
- D : dilution
- PE : sample intake of the water in ml.
- $PE=10ml$
- 40.08×10^3 : atomic mass of Ca^{++} in mg.

- **Magnesium concentration determination (dosage):**

Magnesium occurs naturally in groundwater, typically in the form of dissolved magnesium ions (Mg^{2+}) (aq). The concentration of magnesium in groundwater can vary depending on several factors, such as geology and the composition of rocks through which the groundwater passes. It can also contribute to water hardness.

To measure the magnesium concentration by complexometry according to the ISO 6058-1984 (E) standard, we need to adhere to the following procedure.

We start by taking a 10 ml sample of the solution to be analyzed and placing it in a beaker. We then adjust the pH of the sample by adding 5 drops of a buffer solution with $\text{pH} = 10$. Next, we add a small amount of Eriochrome Black T indicator to the sample, which initially turns the solution purple. Placing the beaker on a magnetic stirrer ensures continuous mixing during the titration process. Using an automatic burette, we titrate the sample with the EDTA solution until the solution changes color from purple to pure blue, indicating the endpoint where all magnesium ions have been complexed with EDTA. Finally, we record the volume of EDTA solution used (V_2) to reach this endpoint, thus determining the magnesium concentration in the sample.



Figure II. 6 : Magnesium dosage.

Results presentation:

$$[Mg^{++}](Mg/L) = \frac{(V2 - V1) \times N \times D \times 24 \times 32 \times 10^3}{PE}$$

- V2: volume of EDTA titrated in milliliters
- N: normality of the EDTA solution
- N=0.01
- D: dilution
- D= 1(no dilution)
- PE: sample intake of the water in ml.
- PE=10ml
- 40.08×10^3 : atomic mass of Mg^{++} in mg.

Note:

- TEA is used to prevent iron complexation.
- NaOH is used to create a basic environment.

II.5.1.3 Flame spectrophotometry:

Flame spectrophotometry offers significant advantages over classical chemical methods for analyzing the mineral composition of various products. It enables precise quantification of low concentrations of sodium, potassium, etc. Its suitability for rapid serial analysis enhances its utility [30].

Sodium:

Sodium is regarded as a conservative element in groundwater because once dissolved, there are no significant reactions that remove it from the water. Normally, precipitation only introduces a small amount of sodium into groundwater. However, abnormally high concentrations can result from salt leaching or percolation through salty soils, as well as infiltration of brackish waters.

CHAPTER II

EXPERIMENTAL REVIEW

Potassium:

Potassium is typically the least abundant major element in waters after sodium, calcium, and magnesium; it rarely ranks third among cations. Potassium may be present in groundwater as dissolved potassium ions (K^+). Its occurrence in groundwater can be influenced by various factors, such as geology, the chemical composition of surrounding rocks, and geochemical processes.

To determine the concentrations of sodium (Na^+) and potassium (K^+) using a flame spectrophotometer, we follow a precise procedure:

First, we prepare standard solutions of sodium hydroxide and potassium hydroxide with known concentrations, labeled as C1, C2, C3, C4, and C5. These standard solutions are subjected to absorption measurements using a BWB XP Flame photometer. The absorption values obtained from these measurements are then used to plot a concentration versus absorption curve, also known as the calibration curve for Na^+ and K^+ . By analyzing the absorption values of the unknown samples and comparing them to this calibration curve, we can accurately determine their corresponding concentrations. The results are directly displayed on the spectrophotometer, providing a clear and precise measurement of sodium and potassium levels in the samples.



Figure II. 7 : BWB XP Flame spectrophotometer.

The concentration value is displayed on the apparatus.

II.5.1.4 Argentimetry:

Argentimetry refers to a set of precipitation titration methods that utilize a solution containing Ag^+ ions, typically silver nitrate (AgNO_3). These methods are used to determine the concentration of anions such as halides, thiocyanates (SCN^-), cyanides (CN^-), mercaptans, and fatty acids. The objective is to determine the concentration of chloride ions (Cl^-) in a sample using silver nitrate (AgNO_3) titration, with potassium chromate (K_2CrO_4) serving as a color indicator [30].

Chlorides:

Chlorides, important inorganic anions, are found in varying concentrations in natural waters, usually as sodium chloride (NaCl) and potassium chloride (KCl) salts, and are commonly used as indicators of pollution [30].

To determine the chloride concentration via the argentometric volumetry method in accordance with NF ISO 9297-2000 [40], the procedure is as follows:

Starting with a 10 ml aliquot of the sample, we transfer it into a beaker. Next, we add five drops of potassium chromate (K_2CrO_4) solution, which serves as an indicator. Placing the beaker on a magnetic stirrer ensures continuous mixing. Using a graduated burette, we titrate the sample with a 0.05 N silver nitrate (AgNO_3) solution. During the titration, we carefully observe the solution until a brick-red color appears, indicating the onset of the endpoint. This color change signifies that the chloride ions have fully reacted with the silver ions to form silver chloride. We note the volume of AgNO_3 solution used, recorded as V on the burette. This volume is then used to calculate the chloride concentration in the sample.



Figure II. 8: Argentometric titration.

Results presentation:

$$[Cl^-] \text{ mg/L} = \frac{10^3 \times V \times N \times D \times 35,457}{PE}$$

- V: The volume of AgNO₃ solution added in milliliters.
- N: Normality of the AgNO₃ solution
- D: Dilution factor.
- PE: Volume of the water sample for analysis in milliliters.
- 35.457 × 10³: Atomic mass of chlorine in milligrams.

II.5.1.5 Acidimetry:

Acidimetry primarily involves direct or residual titrimetric analysis of alkaline substances (bases) using a certain quantity of acid. It is commonly used in the analytical control of various substances such as carbonates (CO₃²⁻) and bicarbonates (HCO₃⁻).

Carbonates and bicarbonates:

These elements are significant, as they constitute the natural buffer for water. These ions influence the pH of water, which determines the type of ion or ions present in a water sample. They can combine with cations to form insoluble mineral deposits. Most carbonate deposits are soluble in hydrochloric acid.

To determine the levels of carbonate (CO₃²⁻) and bicarbonate (HCO₃⁻) in a water sample, the alkalinity is assessed using a titration method involving pH measurement.

We start by preparing a 25 ml sample of the water in a beaker. We place the beaker on a magnetic stirrer to ensure continuous agitation of the sample. Using a pH meter see **Figure II. 2**, we monitor the pH of the water as we titrate with a 0.05 N HCl solution. Gradually, we add the HCl from a burette, carefully noting the volume of acid dispensed. The first endpoint is reached when the pH of the sample drops to 8.3, which indicates the neutralization of bicarbonates. We continue titrating until the pH further drops to 4.3, marking the neutralization of carbonates. We record the volume of acid used at each of these pH levels. This volume data (V) will be used to calculate the concentrations of carbonate and bicarbonate ions in the water sample.



Figure II. 9: Acidimetric determination.

Results expression:

$$[CO_3^{2-}] \text{ mg/L} = \frac{V \times N \times 60 \times 10^3}{PE}$$

$$[HCO_3^-] \text{ mg/L} = \frac{V \times N \times 61 \times 10^3}{PE}$$

- V1: Volume of acid (in ml) required for neutralization at pH 8.3
- V2: Volume of acid (in ml) required for neutralization at pH 4.3
- N: Normality of the acid solution
- PE: Sample volume of the water under analysis (in ml)
- Atomic mass of carbonates: 60.103 mg
- Atomic mass of bicarbonates: 61.103 mg

II.5.1.6 Hach DR 1900 Portable Spectrophotometry:

Hach spectrophotometry is a method for analyzing substances by measuring their absorption of light. It is commonly used to determine the concentrations of various substances such as iron, barium, and sulfate [30].

Iron:

Iron levels in oilfield waters vary and can indicate active corrosion. Iron counts are used to monitor corrosion rates in sweet systems (those without hydrogen sulfide) and can signal issues like bottom hole or surface equipment blockages in acidic systems where iron is present as iron sulfide, often-indicating corrosion, bacterial activity, or incompatible water mixtures.

Sulfate:

Sulfates are naturally found in minerals, with calcium, barium, and strontium sulfate being common in water resources. High sulfate levels in groundwater usually have natural origins but can also result from industrial effluents or atmospheric deposition.

Barium:

Barium is significant for its ability to combine with sulfate ions, forming highly insoluble barium sulfate that can cause severe blockages.

To determine the concentrations of Ba^{2+} , Fe^{2+} , and SO_4^{2-} in a sample solution, we follow a specific procedure using a HACH DR 1900 spectrophotometer.

Initially, we fill a specialized 10 ml cuvette with the sample solution up to the marked line. The cuvette is then wiped clean with a cloth to remove any water traces and fingerprints, ensuring accurate readings. We turn on the spectrophotometer by pressing the I/O button and place the cuvette containing the sample inside. Using the menu on the spectrophotometer, we select the desired ion for measurement and press the Zero button to calibrate the device. After removing the cuvette, we add the corresponding ion capsule to the solution. Finally, we place the cuvette back into the spectrophotometer and press the "Measure" button to obtain the concentration reading of the ion, expressed in mg/l. This procedure is repeated for each ion (Ba^{2+} , Fe^{2+} , and SO_4^{2-}) to determine their respective concentrations in the sample.



Figure II. 10: DR 1900 spectrophotometer.

Results expression:

The concentration results for the different ions are displayed on the HACH DR 1900 spectrophotometer.

II.5.1.7 Determination of Total Dissolved Solids (TDS):

Total dissolved solids (TDS) represent all substances that do not volatilize under specific physical conditions. These conditions must be established to minimize alteration of the substances comprising this extract. TDS measurement serves as an indicator of the overall mineral content of water.

To measure the Total Dissolved Solids (TDS) in a water sample, we follow a precise procedure using sodium fluoride (NaF) and specialized equipment.

We begin by placing a small amount of sodium fluoride into an anti-climbing capsule and drying it in an oven set at 105°C for one hour. After drying, we cool the capsule in a desiccator and then weigh it using an analytical balance with a precision of 0.0001g. This initial weight is recorded as P1.

Following this, we take a 5 ml sample of the water for analysis and pour it into the capsule containing the dried sodium fluoride. We gently agitate the mixture to ensure complete dissolution of the NaF. The capsule is then returned to the oven to allow complete evaporation

of the water. After the water has evaporated, the capsule remains in the oven for an additional 20 minutes to ensure complete removal of all moisture.

After this heating period, we transfer the capsule back to the desiccator to cool. Once cooled, we weigh the capsule again to obtain the final weight, recorded as P2. This final weight represents the total weight of the capsule along with the quantity of dry salts left from the water sample. By comparing P1 and P2, we can determine the amount of total dissolved solids in the water sample.



Figure II. 11: The analytical balance and the oven.

Results expression:

$$\text{Total Dissolved Solids (mg/L)} = \frac{(P1-P2).D.10^3}{PE}$$

- P1: Weight in mg of the capsule + NaF.
- P2: Weight in "mg" of the capsule + NaF + dry residue.
- PE: Sample volume of the water in ml.
- D: Dilution factor.

II.5.2 Study of water compatibility:

The study of water compatibility is a crucial process in various industries, especially in oil and gas exploration. It involves assessing the compatibility of different water sources, such as injection water and reservoir water, to determine if they can be safely mixed. The first parameter to check is visual inspection, which involves observing water turbidity, color variations, and unusual smells that may indicate the presence of sediments, minerals, bacteria, or chemicals. Additionally, an analytical approach is employed, which includes filtration of precipitates, drying of the recovered deposit, and analysis of the recovered solution to determine its chemical composition.

The experimental procedure outlined entails a systematic investigation into the compatibility of water sources, utilizing a series of meticulous steps and specialized equipment.

Initially, a set of nine labeled 25ml beakers is arranged atop a multiple stirring plate, serving as the vessels for the experimental solutions. Subsequently, using precision instrumentation such as a 100ml graduated cylinder, reservoir water is incrementally added to each beaker in ascending volumes, while injection water is proportionately introduced in descending volumes, thus establishing a gradient of water mixing ratios.

Following this, the beakers are subjected to agitation for a defined period of one hour upon placement on the multipoint stirrer, ensuring thorough homogenization of the solutions.



Figure II. 12: Compatibility study.

Subsequent to this stirring phase, the filtrate from each solution is isolated via vacuum filtration, employing nine 0.4 μ m filter papers individually placed within labeled watch glasses. This filtration process is facilitated by a vacuum filtration setup, which efficiently separates solid particulates from the liquid phase, yielding clarified solutions in the respective beakers while retaining the filter papers for subsequent analysis.



Figure II. 13: Deposits filtration.

Following filtration, the beakers containing the filtrates along with the retained filter papers are transferred to an oven for a predetermined duration of two hours, enabling the complete evaporation of residual moisture and subsequent drying of the filter papers. Upon completion of the drying process, the filtrates are subjected to analytical scrutiny to ascertain the concentrations of sulfates, barium, and calcium. This analytical assessment encompasses the determination of sulfates and barium utilizing a DR1900 spectrophotometer, whereas the determination of calcium entails the utilization of complexometry, a technique based on the formation of complex ions for quantitative analysis. Through this comprehensive experimental regimen, a nuanced understanding of water compatibility is attained, critical for informed decision-making in industrial applications.

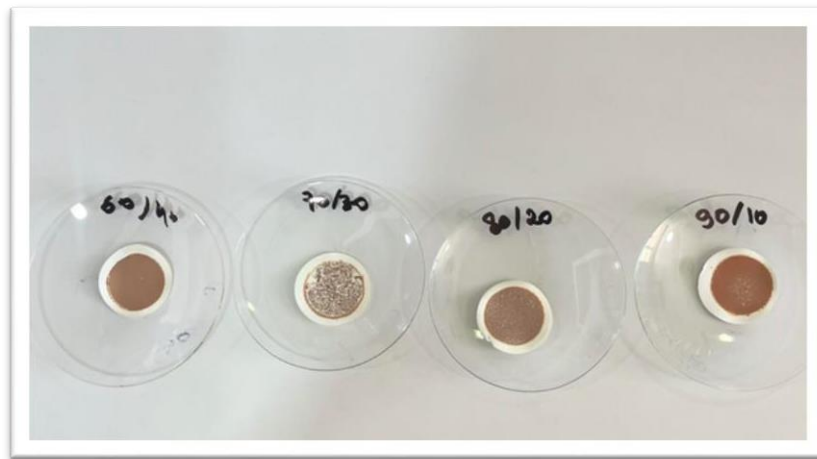


Figure II. 14: The (60/40...90/10) dry deposits.

Results expression:

$$\text{The mass of deposits (g)} = P_2 - P_1$$

- P1: Mass of watch glass + empty filter paper.
- P2: Mass of watch glass + filter paper + the deposit after drying.

II.5.3 X-ray Diffraction (XRD) Analysis:

After conducting a compatibility study between Cambrian and Miocene waters, and the Cambrian and Albien waters the resulting deposit underwent laboratory chemical and water treatment preparation. This comprehensive procedure allows for a thorough understanding of the mineral composition of the deposit and provides valuable insights into the compatibility between the two types of water.

To determine the moisture percentage, dry the deposit at 105°C until it achieves a constant weight. Then, heat the deposit to 525°C to eliminate organic matter, allowing for the determination of its percentage by comparing weights before and after heating. Collect the remaining residue, which represents the mineral matter. Conduct an X-ray diffraction (PANalytical X'Pert PRO MPD) analysis on this mineral residue to characterize its mineralogical composition. This method effectively differentiates between moisture, organic matter, and mineral content, culminating in a detailed mineralogical profile of the sample [30].

II.5.4 Study of Anti-Deposit Products Effectiveness:

Finally, anti-deposition products are tested on the critical mixing ratio, which is the proportion of the two water mixes that yields the maximum deposition. This ratio is determined by evaluating the mass of deposits formed for various mix proportions of the two waters during a compatibility study. During this study, we used three inhibitors: SCW 83263 (A), SCW 85372 (B), and CHIMEC 3670 (C).

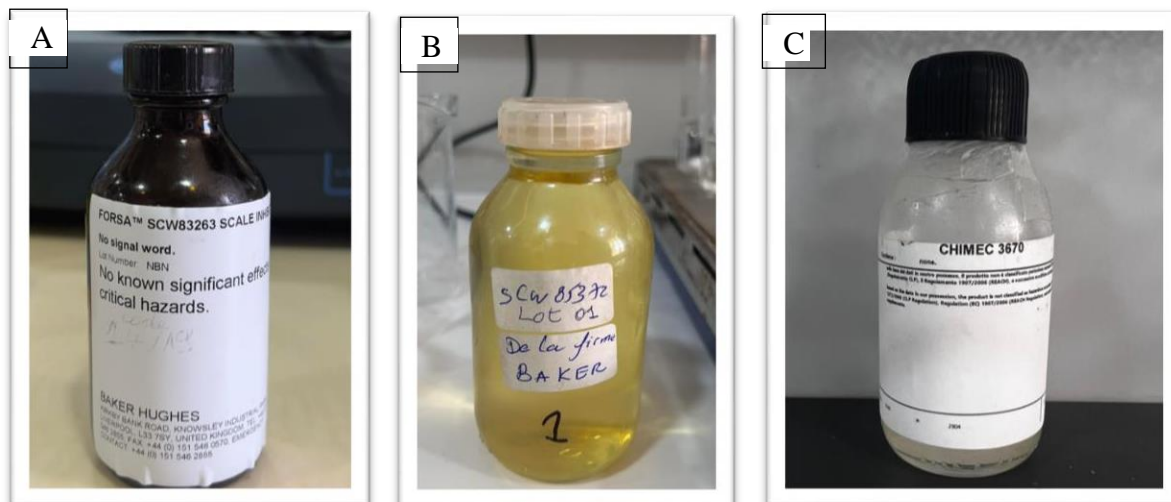


Figure II. 15: The different inhibitors.

To begin, arrange six labeled beakers on the multiple stirring plate. Using an automatic pipette, add 50, 100, 150, 200, and 250 μL of the inhibitor to each of the 5 turbid beakers, leaving one beaker as a blank control. Agitate the mixtures for 1 hour using a multipoint stirrer and magnetic stir bars. After the agitation period, measure the turbidity in all six beakers with a turbid meter. Based on these turbidity measurements, calculate the efficiency of the inhibitor. Repeat this entire procedure for each different inhibitor to ensure accurate comparison and assessment.

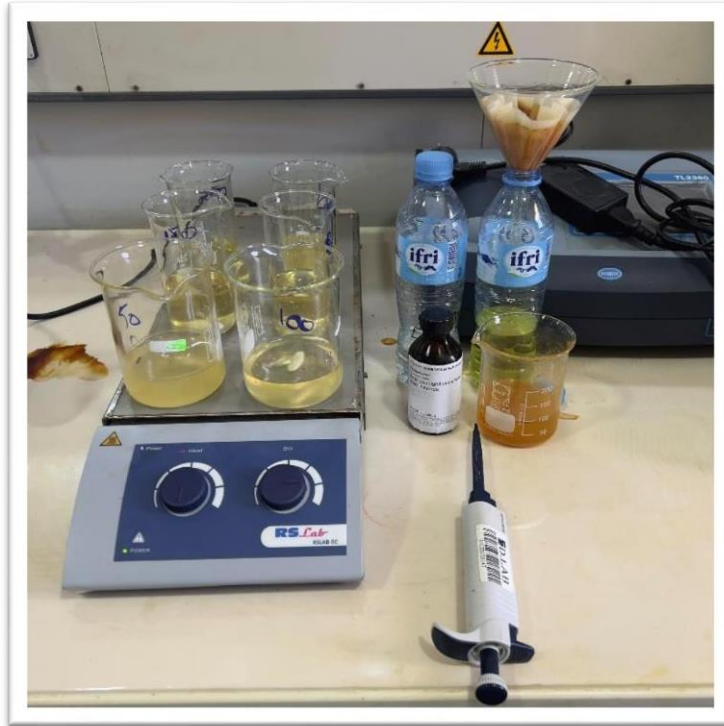


Figure II. 16: the effectiveness study.

Results expression:

The effectiveness of the anti-deposits products was evaluated by measuring turbidity, which is calculated using the following expression:

$$Eff(\%) = \frac{(T0 - T1)}{(T0)} \cdot 100$$

CHAPTER III: RESULTS AND DISCUSSION

This chapter provides an analysis and discussion of the obtained results from the experimental work.

III. 1 Physicochemical analysis:

The subsequent sections present the manifold results derived from the physicochemical analysis conducted on both injection and formation wells.

III.1.1 pH and conductivity:

The following table displays the pH and conductivity measurements for the different water samples.

Table III. 1: pH and conductivity results of the various samples.

Sample Parameters	ALBIEN	MIOCENE	CAMBRIAN
pH at 20 °C	7.5	8.40	2.4
Conductivity ms/cm	2.60	1.80	2.23

The table above demonstrates that the Albien and Miocene water samples have similar values, both exhibiting basic pH levels. Conversely, the Cambrian water sample demonstrates an acidic characteristic, with a pH value of 2.4, which is notably below seven. Moreover, the conductivity values for all types of water are comparable, ranging from 1.80 to 2.60.

The pH levels of geological formations like those of the Albien, Miocene, and Cambrian, can vary due to various factors, including the composition of rocks, presence of minerals, and environmental conditions during their formation. The Albien and Miocene waters are low in salinity with pH levels (7.5 and 8.40, respectively), while the Cambrian has an acidic pH level (2.4).

III.1.2 Water hardness:

The table displays the concentrations of calcium and magnesium in the waters that were tested.

Table III. 2: Calcium and magnesium results of the various water samples.

Sample parameters	ALBIEN		MIOCENE		CAMBRIAN	
	mg/L	meq/L	mg/L	meq/L	mg/L	meq/L
Ca ⁺⁺	178.35	9.91	138.28	6.90	27855.6	1392.78
Mg ⁺	130.11	10.70	43.65	3.59	11369.6	935

It is evident from our observations that the Cambrian water sample exhibits a notably higher concentration of metals compared to the injection waters, which demonstrate similar levels of calcium and magnesium.

The elevated levels of calcium and magnesium in the Cambrian water, as compared to the Albien and Miocene waters, reflect the distinct geological characteristics and processes associated with each geological period. The Cambrian period, with its unique geological formations rich in calcium- and magnesium-bearing minerals, facilitates the release of these ions into the water through weathering and hydrological processes. In contrast, the Albien and Miocene waters exhibit lower concentrations of calcium and magnesium, likely due to differences in the mineral composition and hydrological dynamics of their respective geological formations.

III.1.3 Flame spectrophotometry:

The **Table III.3** provides both contain sodium and potassium results for the different water samples.

Table III. 3: Sodium and potassium results of the various water samples.

Sample Parameters	ALBIEN		MIOCENE		CAMBRIAN	
Unite	mg/L	meq/L	mg/L	meq/L	mg/L	meq/L
Na⁺	257.78	11.2	163.56	7.11	75238.58	3271.24
K⁺	39.18	1.00	18.86	0.48	5979.52	153.32

The Cambrian sample shows an extraordinarily high concentration of sodium and potassium, which is significantly greater than the concentrations in the Albien and Miocene samples. The Albien sample has a moderate concentration of the two metals, while the Miocene sample has the lowest concentration of the three.

The high levels of K⁺ and Na⁺ ions in Cambrian water are primarily due to its unique geochemical characteristics.

III.1.4 Argentimetry:

The chloride concentrations in different water samples are presented in this table.

Table III. 4 : Chlorides results of the various water samples.

Sample Parameters	ALBIEN		MIOCENE		CAMBRIAN	
Unite	mg/L	meq/L	mg/L	meq/L	mg/L	meq/L
Cl⁻	531.85	15	297.84	8.40	212742	6000

The Cambrian sample shows an exceptional high chloride level 212742 mg/ (6000 meq/l), much higher than those found in the other samples.

The higher chloride levels observed in Cambrian waters indicate geological formations or environmental conditions conducive to the accumulation or influx of chloride ions. Conversely, the modest chloride concentration in the Albien and Miocene waters reflect contrasting geological compositions or hydrological processes governing ion transport and accumulation in that particular region.

III.1.5 Acidimetry:

The following results show the carbonate and bicarbonate content of the different waters.

Table III. 5: Carbonates and bicarbonates results of the various water samples

Sample Parameters	ALBIEN		MIOCENE		CAMBRIAN	
	mg/l	meq/l	mg/l	meq/l	mg/l	meq/l
Unite						
CO_3^{--}	0.00	0.00	18	0.60	0.00	0.00
HCO_3^-	213.5	3.5	93.03	1.52	0.00	0.00

The Albien and Cambrian samples exhibit no detectable carbonate levels, while the Miocene sample denotes a meager concentration of 18mg/L (0.60 meq/L). Regarding bicarbonates, the Albien sample displays the highest concentration at 213.5 mg/L, signifying a substantial occurrence. In contrast, the Miocene sample has a lower bicarbonate concentration of 93.03 mg/L (1.52 meq/L), and the Cambrian sample shows no detectable bicarbonates, mirroring its carbonate content.

The variation of bicarbonate and carbonate levels between the three sources due to differences in their pH levels, the presence of dissolved CO_2 , and the geological and environmental factors affecting each water source.

III.1.6 Hach DR 1900 Portable spectrophotometry:

The next results are for the iron, barium and sulfate tests.

Table III. 6: Iron, barium and sulfate results of the various water samples.

Sample Parameters	ALBIEN		MIOCENE		CAMBRIAN	
	mg/L	meq/L	mg/L	meq/L	mg/L	meq/L
Fe⁺⁺	4.37	0.15	0.00	0.00	4.37	0.15
Ba⁺⁺	0.00	0.00	0.00	0.00	459.72	6.69
SO₄⁻	751.43	15.65	500	10.41	0.00	0.00

Our examination reveals that Iron is discernible in both the Albien and Cambrian water samples, with identical concentrations of 4.37 mg/L (0.15 meq/L). However, the Miocene samples show no discernible iron content.

Barium is notably absent in the injection water samples, while the Cambrian sample presents a notable concentration of barium, reaching levels as high as 459.72 mg/L (6.69 meq/L).

The Albien sample showcases the highest sulfate concentration at 751.43 mg/L (15.65 meq/L), followed by the Miocene sample at 500 mg/L (10.41 meq/L). Nevertheless, the Cambrian sample lacks any detectable sulfate presence.

The Albien, Miocene, and Cambrian waters exhibit relatively low concentrations of ferrous ions (Fe²⁺). This may be due to the absence of abundant iron-bearing minerals, oxidizing conditions favoring the formation of insoluble iron compounds, and transport/weathering processes that limit the release or accumulation of iron ions in the water.

The Albien and Miocene waters exhibit significant sulfate ion concentrations, which is typical for surface waters. Conversely, the Cambrian water lacks sulfate ions but contains elevated levels of barium.

III.1.7 Total Dissolved Solids (TDS):

The results below stand for the TDS values in the analyzed waters.

Table III. 7: The dissolved solids results of the various water samples.

Sample Parameters	ALBIEN	MIOCENE	CAMBRIAN
TDS mg/L	2110	1295	346500

Dissolved solids are notably elevated in the Cambrian water 346500 mg/L, while the Albien sample displays a moderate content 2110 mg/L and the Miocene water shows the lowest concentration 1295 mg/L.

The high TDS concentration in the Cambrian water could be indicative of extensive mineral dissolution or evaporation processes, whereas the lower TDS concentrations in the Albien and Miocene waters might be due to factors such as dilution, filtration, or selective mineral precipitation.

III.2 Water compatibility:

The findings of the compatibility study of the Albien/Cambrian water mixture are presented in the following table.

Table III. 8: The results of the compatibility study of the Albien/Cambrian water mixture

Mixtures ratio (A/C)	Mass of deposits obtained (mg/L)	ALBIEN/CAMBRIAN		
		Ca ⁺⁺	Ba ⁺⁺	SO ₄ ⁻⁻
0/100	0	27855	459	0
10/90	270	25158	351	0
20/80	341	22924	189	0
30/70	526	19015	Tr	0
40/60	626	15952	0	Tr
50/50	512	12834	0	142
60/40	390	10962	0	271
70/30	359	7723	0	387
80/20	243	5457	0	500
90/10	158	2575	0	595
100/0	0	178	0	751

Tr: Trace

The **Table III. 1** shows that the amount of the obtained deposit increases until it reaches a maximum at a mixing ratio of (40/60). This represents the critical ratio.

The Cambrian waters and the injection water are incompatible across the entire range of mixing ratios. The mass of the deposit obtained increases until it reaches a maximum at a mixing ratio of (40/60). This incompatibility is mainly because of the presence of the calcium (Ca⁺⁺), barium (Ba⁺⁺), and sulfate ions (SO₄⁻⁻). The interaction of these distinct chemical constituents leads to the precipitation of deposits.

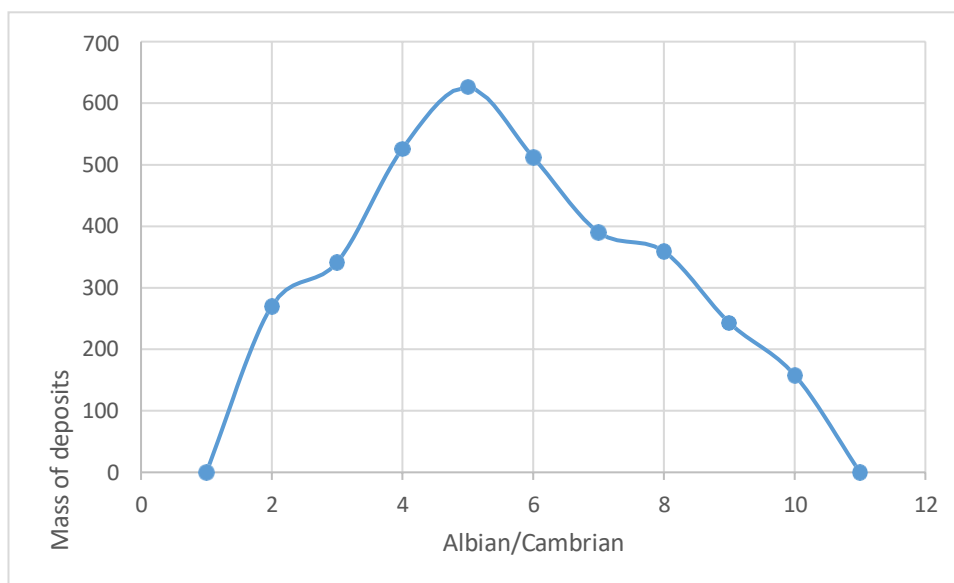


Figure III. 1: The mixing ratios of the Albian/Cambrian.

Moreover, the results of the compatibility study between the Miocene and Cambrian waters refer to **Table III. 9**.

Table III. 9: The results of the compatibility study of the Miocene/Cambrian water mixture.

Mixtures ratio (M/C)	Mass of deposits obtained (mg/L)	MIOCENE / CAMBRIAN (mg/L)		
		Ca ⁺⁺	Ba ⁺⁺	SO ₄ ⁻⁻
0/100	0	31062	280	0
10/90	207	27955	31	0
20/80	223	24835	27	0
30/70	400	21794	10	0
40/60	557	18678	0	0
50/50	975	15597	0	0
60/40	652	12500	0	7.0
70/30	563	9428	0	12
80/20	375	6333	0	21
90/10	253	3221	0	35
100/00	0	138.28	0	500

The mass of the deposit obtained increases progressively and peaks at a 50/50 mixing ratio, indicating this as the optimal ratio.

The Cambrian waters and the Miocene water are incompatible at all mixing ratios. The mass of the deposit obtained increases until it reaches a maximum at a mixing ratio of (50/50). The incompatibility primarily arises from the presence of calcium (Ca⁺⁺), barium (Ba⁺⁺), and sulfate ions (SO₄⁻⁻). Their interaction induces the precipitation of deposits.

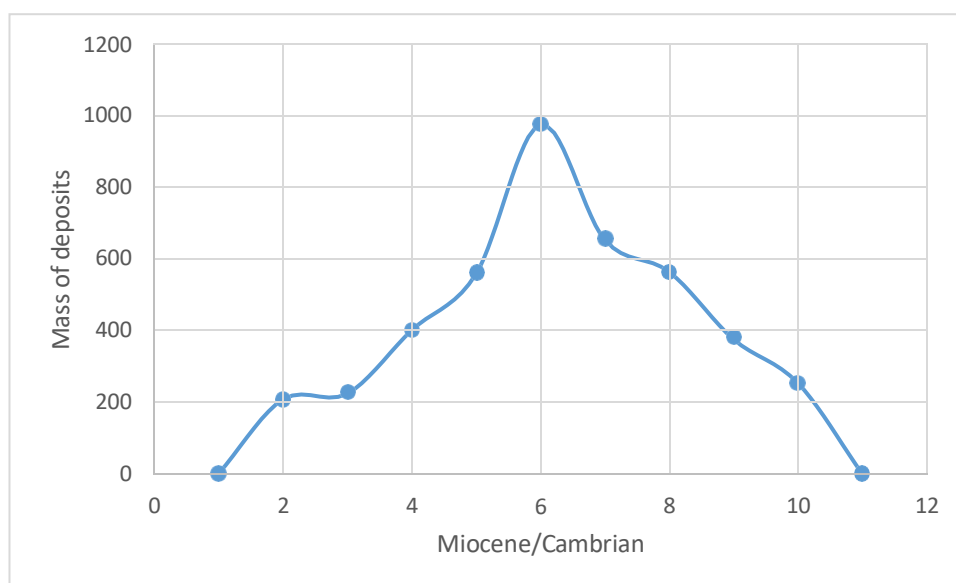


Figure III. 2 : The mixing ratios of the Miocene/Cambrian.

III.3 The XRD Results:

The illustration indicates the diffractogram of the deposits.

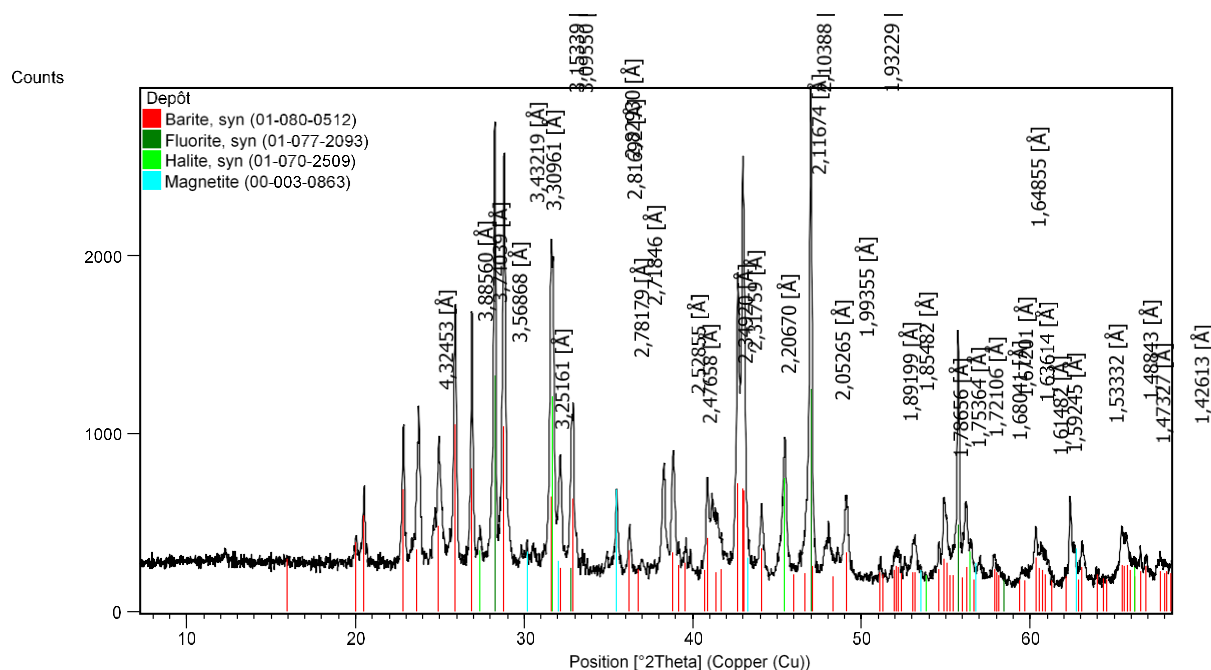


Figure III. 3: The X-ray crystallographic analysis.

The X-ray crystallographic analysis of the deposition sample revealed the following mineral phases (see diffractogram).

- **Barite:** BaSO₄ (Barium sulfate)
- **Fluorite:** CaF₂ (Calcium fluoride)
- **Halite:** NaCl (Sodium chloride)
- **Magnetite:** Fe₃O₄ (Iron oxide)

X-ray diffraction characterization revealed that the deposit is primarily composed of barium sulfate (barite), fluorite, a halite-type salt, and a small concentration of the iron oxide magnetite. The formation of the deposits is attributed to the chemical interactions between the ions in the water mixtures. As the mixture ratio changes, the concentrations of calcium (Ca⁺⁺), barium (Ba⁺⁺), and sulfate (SO₄^{- -}) vary, leading to different levels of saturation and the potential for precipitation of these compounds.

III.4 Effectiveness tests:

The ensuing sections detail the diverse results obtained from the effectiveness tests performed on the Albien/Cambrian and Miocene/Cambrian combinations.

1. Albien/Cambrian:

The results mentioned below are from the effectiveness test with the SCW 83263 inhibitor.

Table III. 10: The SCW 83263 effectiveness test results.

Inhibitor doses (ppm)	Turbidity after 1 ^H (NTU)	Efficiency (%)
Reference (0)	23	-
50	422	29.43
100	396	33.77
150	184	69.23
200	81	86.45
250	02	99.66
300	00	100

The effectiveness of the inhibitor improves as its concentration increases. At lower doses (50 and 100 ppm), the inhibitor shows limited efficacy, resulting in high turbidity and low efficiency. Marked reductions in turbidity and significant gains in efficiency are observed at concentrations of 150 ppm and above. The highest efficiency (100%) is achieved at 300 ppm, where turbidity is eliminated.

For optimal performance and the maintenance of low turbidity levels, it is advisable to utilize inhibitor doses of 200 ppm or greater. This high concentration ensures that there is enough inhibitor to interact with the particles, reducing their ability to scatter light and thus lowering turbidity.

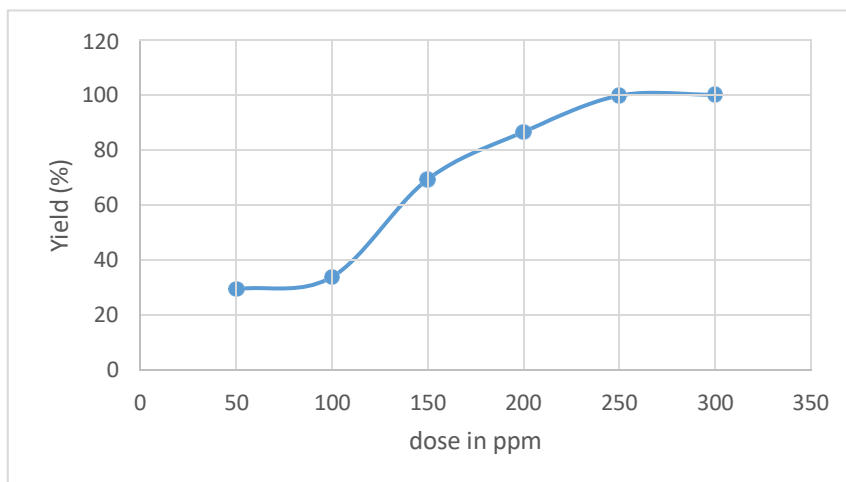


Figure III. 4: The optimal dose of the SCW 83263 product

The following results, conducted from the SCW 85372 effectiveness test.

Table III. 11: The SCW 85372 effectiveness test results.

Inhibitor doses (ppm)	Turbidity after 1 ^H (NTU)	Efficiency (%)
Reference (0)	598	-
50	496	17,05
100	427	28,59
150	385	35,61
200	36	93,97
250	00	100
300	00	100

The effectiveness of the inhibitor increases with respect to the concentration. Indeed, at lower doses, such as 50 and 100 ppm, the inhibitor exhibits limited effectiveness, leading to higher levels of turbidity and reduced efficiency. However, at concentrations of 150 ppm and beyond, there are noticeable reductions in turbidity accompanied by significant improvements in efficiency. The pinnacle of efficiency, reaching 100%, is attained at doses of 250 ppm and 300 ppm, effectively eradicating turbidity at these levels.

Given the notable reduction in turbidity and the commendable efficiency achieved at 200 ppm, this concentration appears to be adequate for practical needs. Nonetheless, for situations demanding absolute elimination of turbidity and optimal efficiency, doses exceeding 250 ppm may be necessary. These higher concentrations provide a guarantee of complete removal of turbidity and ensure the highest level of effectiveness, should such requirements arise.

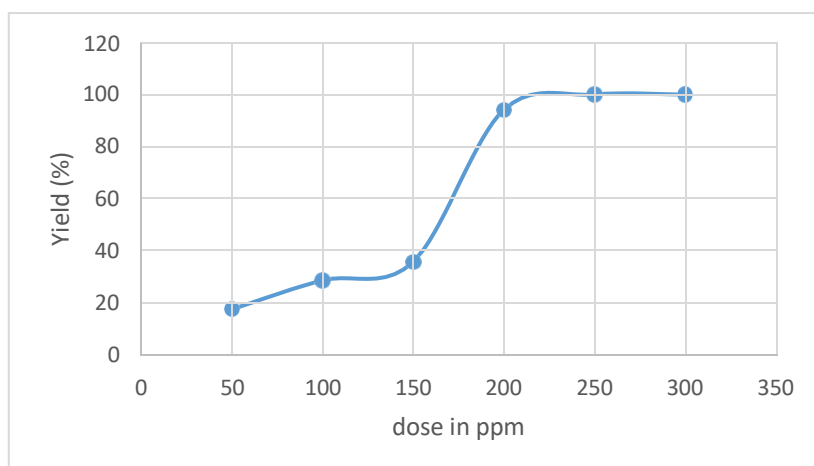


Figure III. 5: The optimal dose of the SCW 85372 product.

The ensuing outcomes, derived from the CHIMEC 3670 effectiveness assessment.

Table III. 12: The CHIMEC 3670 effectiveness test results.

Inhibitor doses (ppm)	Turbidity after 1 ^h (NTU)	Efficiency (%)
Reference (0)	499	-
50	490	17,65
100	470	21,01
150	400	32,77
200	320	46,22
250	180	69,75
300	375	36,97

The product efficiency of CHIMEC 3670 reaches its maximum (69.75%) at 250 ppm. However, by increasing this dosage, a considerable decrease in efficiency is observed, attributed to the presence of crystals and notably the occurrence of turbidity.

The results demonstrate the effectiveness of the inhibitor in reducing turbidity; with optimal performance observed at doses around 200-250 ppm.

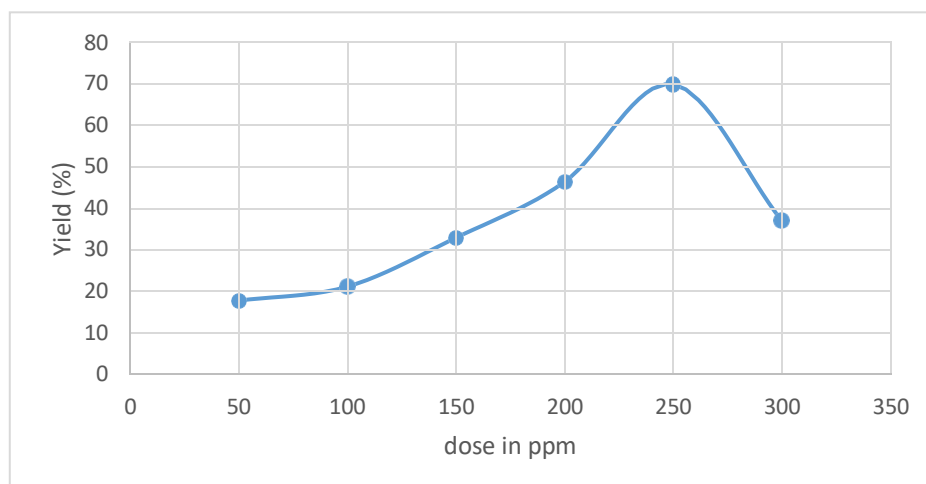


Figure III. 6 : The optimal dose of the CHIMEC3670 product.

2. Miocene / Cambrian:

The table set out below shows the results of the effectiveness tests with the SCW 83263 inhibitor.

Table III. 13: The SCW 83263 effectiveness test results.

Inhibitor doses (ppm)	Turbidity after 1 ^H (NTU)	Efficiency (%)
Reference (0)	261	-
50	250	4,21
100	180	31,03
150	117	55,17
200	43	83,52
250	3	98,85
300	3	98,85
400	3	98,85

The data reveal a clear trend the turbidity level drops in contrast to the inhibitor doses. An apparent turning point is evident at concentrations of 200 ppm and above. Efficiency increases sharply with dose, peaking at 250 ppm with 98.85% effectiveness. Efficiency remains constant at 300 ppm and 400 ppm, indicating saturation. This suggests an optimal dosage range of 200-250 ppm for significant turbidity reduction.

The curve in **Figure III. 5** plotted on the axis system linking the yield of product SCW 83263 to its concentration (in ppm) shows the necessary dose (250 ppm) to achieve maximum efficiency of 98, 85%. Beyond this treatment dose, the water is clear.

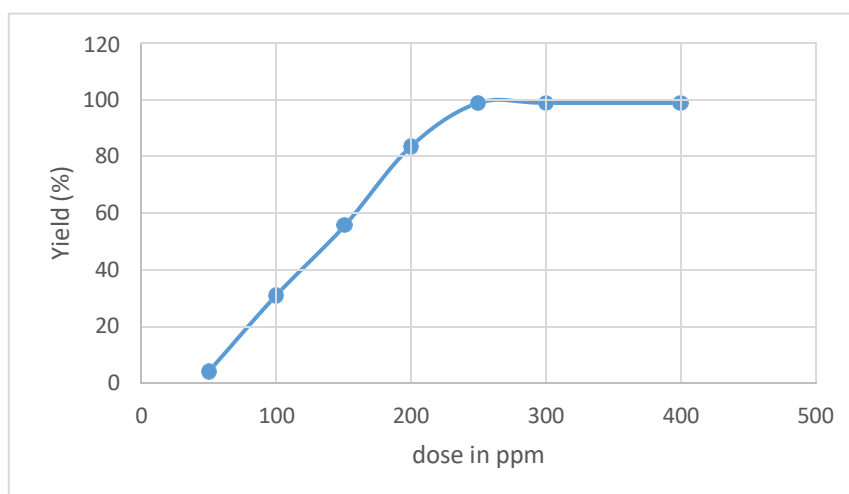


Figure III. 7: The optimal dose of SCW 83263 the product.

Below is the table displaying the results of the effectiveness tests conducted with the SCW 85372 inhibitor.

Table III. 14: The SCW 85372 effectiveness test results.

Inhibitor doses (ppm)	Turbidity after 1 ^H (NTU)	Efficiency (%)
Reference (0)	261	-
50	243	6,89
100	240	8,04
150	127	51,34
200	80	69,34
250	3	98,85
300	3	98,85
400	3	98,85

The observations depict a substantial augmentation in turbidity as inhibitor doses increase. Efficiency, depicted by the percentage decrease in turbidity, demonstrates a notable escalation with rising doses. Particularly noteworthy is the significant drop in turbidity observed at 200 ppm and higher, where efficiency reaches a plateau, remaining consistently high at 98.85% for doses of 250, 300 and 400 ppm. This indicates a saturation point in inhibitor

effectiveness beyond 200 ppm, underscoring the necessity of optimizing dosage for practical applications.

The graph depicted in Figure 6, on the axis system correlating the yield of SCW 85372 product to its concentration (in ppm), illustrates that a dosage of 250 ppm is necessary to achieve a maximum efficiency of 98, 85%. Beyond this treatment dosage, the water becomes clear.

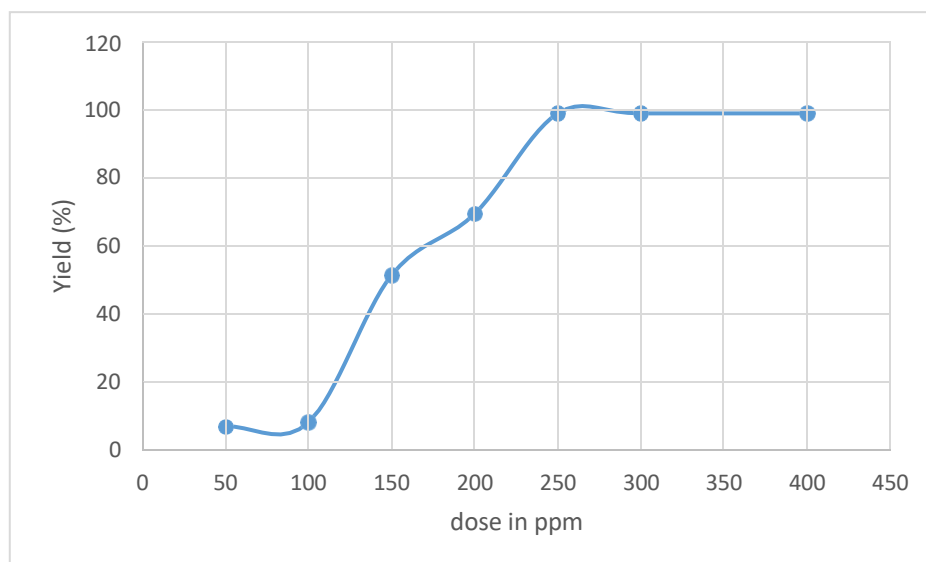


Figure III. 8: The optimal dose of the SCW 85372 product.

The table below shows the CHIMEC3670 effectiveness test results.

Table III. 15: The CHIMEC3670 effectiveness test results.

Inhibitor doses (ppm)	Turbidity after 1 ^H (NTU)	Efficiency (%)
Reference (0)	261	-
50	252	3,44
100	250	4,21
150	247	5,36
200	234	10,34
250	230	11,87
300	230	11,87

The product CHIMEC3670 achieves its maximum effectiveness of 11.87% at a treatment dose of 250 ppm.

Throughout the range of test doses, the effectiveness of the CHIMEC3670 inhibitor appears to be inadequate. Despite increasing the dosage from 50 to 300 ppm, there is only a marginal reduction in turbidity after 1 hour, with the highest efficiency recorded at a mere 11.87% at 250 ppm. This indicates a lack of substantial impact on controlling particulate matter across the tested concentrations.

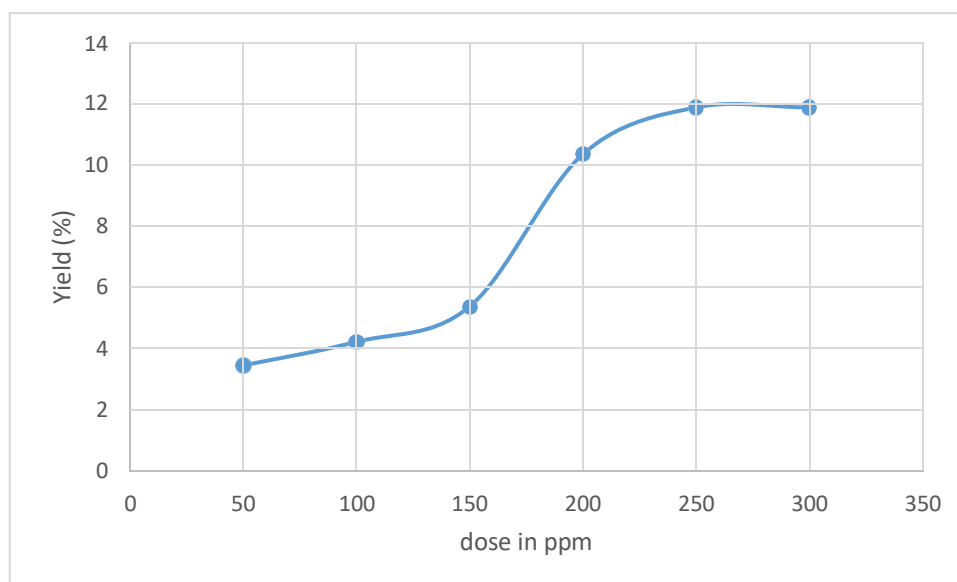


Figure III. 9 : The optimal dose of the CHIMEC3670 product.

CONCLUSION AND PROSPECTS:

CONCLUSION AND PROSPECTS:

Based on the analysis and chemical treatment of various samples taken from the Hassi Messaoud field, the following conclusions can be drawn:

- The surface installations develop deposits primarily composed of barium sulfate when pressure maintenance water is injected.
- The injection waters in Hassi Messaoud are high in sulfate, with concentrations ranging from 500 to 750 mg/L. The formation water of the region is rich in barium, with a concentration of approximately 0.45972 g/L.
- Injection water and formation water are incompatible at any mixing ratio, leading to the formation of barium sulfate deposits, due to the interaction between the sulfates in the injection water and the barium in the formation water.
- The critical mixing ratio for Miocene/Cambrian waters is 50/50, with a maximum potential deposit weight of 975 mg/L. While the critical mixing ratio for Albion/Cambrian waters is 40/60, with a maximum potential deposit weight of 626 mg/L.
- Laboratory tests of the SCW 83263 product on mixtures of untreated injection water (Albian) and formation water (Cambrian) demonstrated 100% efficiency in inhibiting barium sulfate deposits at a dose of 300 ppm, with no deposits observed at this concentration. The same product showed 98.85% efficacy for mixtures of Miocene and Cambrian water.
- Similarly, the SCW 85372 product showed 100% efficacy at a dose of 250 ppm for the same untreated Albion-Cambrian water mixture and 98.85% efficacy for the Miocene-Cambrian mixture. We have identified and evaluated these two inhibitors as the optimal solution. To address the scaling problem in the Cambrian wells of the Hassi Messaoud region.

To further enhance this work, it would be beneficial to:

- Conduct a compatibility study under downhole conditions.
- Test the effectiveness of the products in downhole conditions.
- Perform industrial tests on-site to definitively evaluate the performance of each product under real production conditions.

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APPENDIX:

Appendix A: The Na⁺ calibration curve.

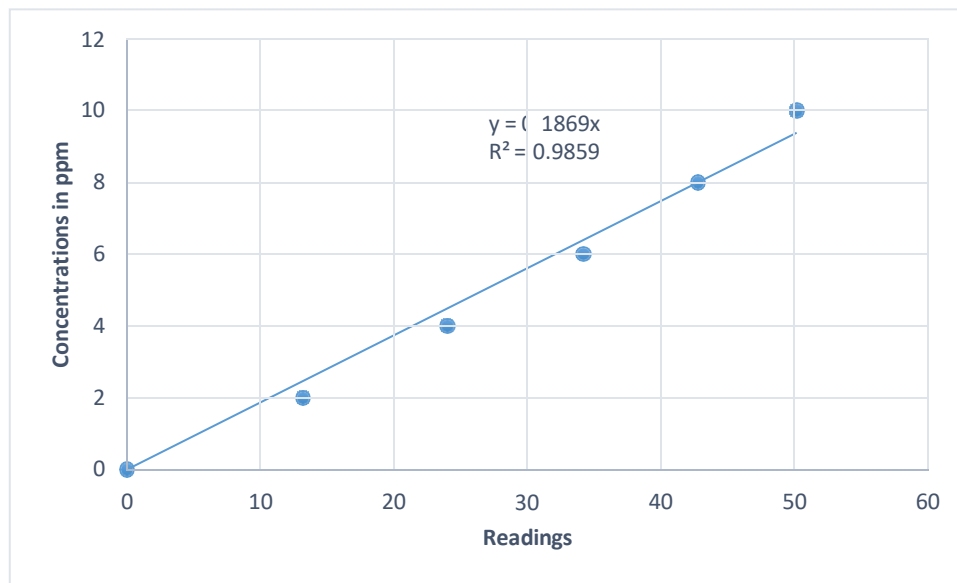


Figure 1 : The Na⁺ calibration curve.

Appendix B: The K⁺ calibration curve.

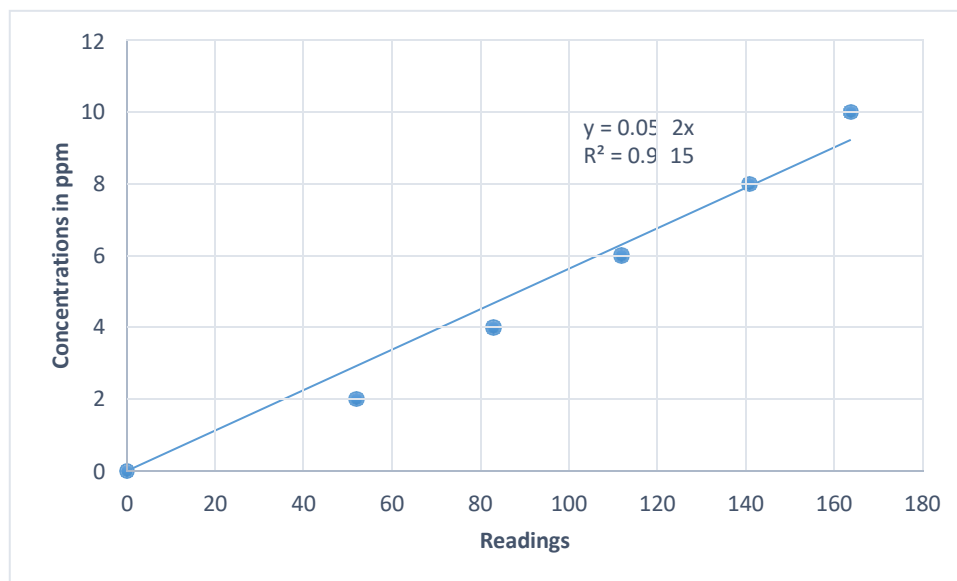


Figure 2 : The K⁺ calibration curve.

APPENDIX:

Appendix C: Diagram for carrying out a compatibility study in the laboratory.

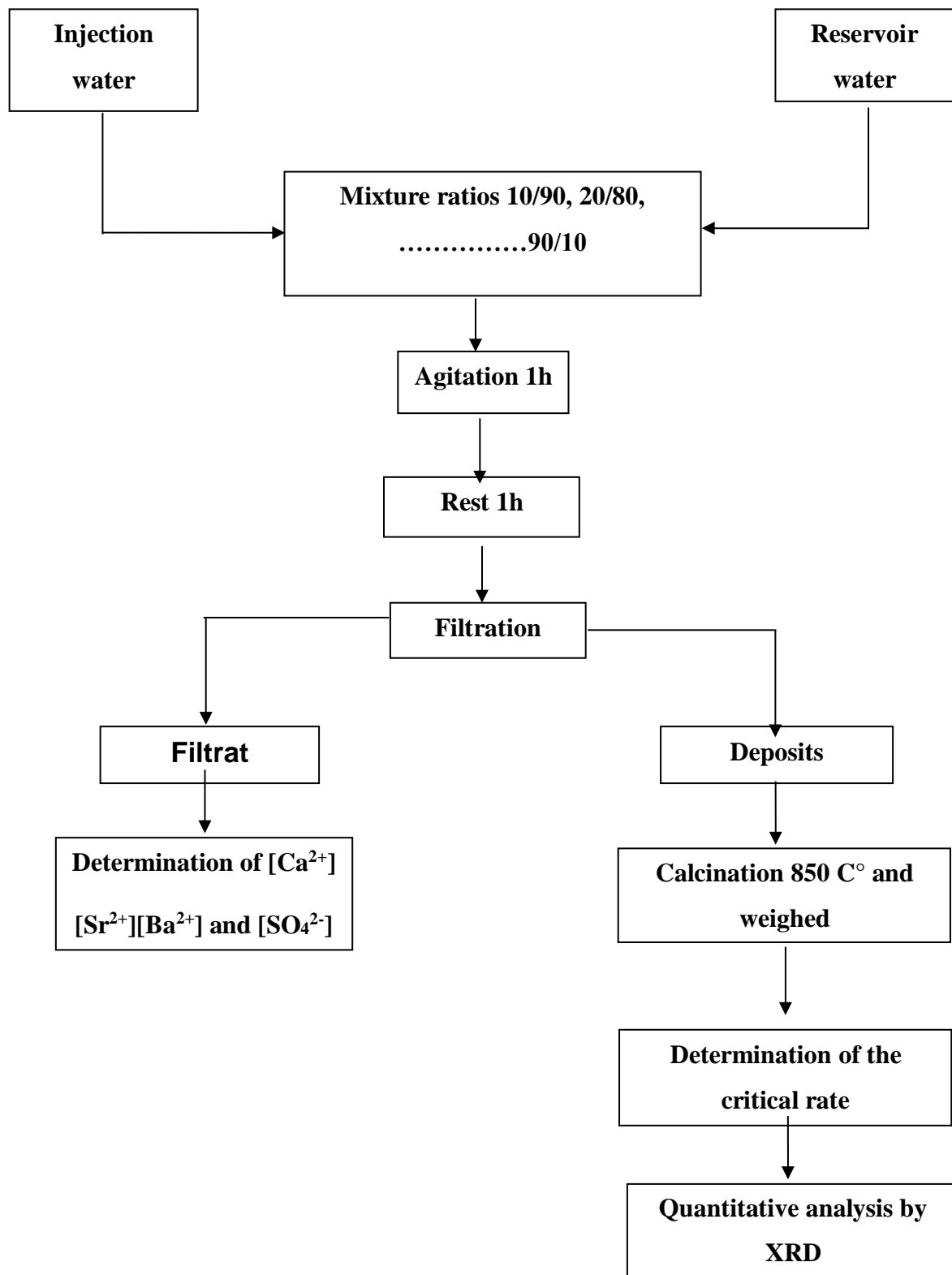


Figure 3 : Diagram for carrying out a compatibility study in the laboratory.

APPENDIX:

Appendix D: Evaluation scheme for an anti-deposit product.

The study was carried out according to the following scheme:

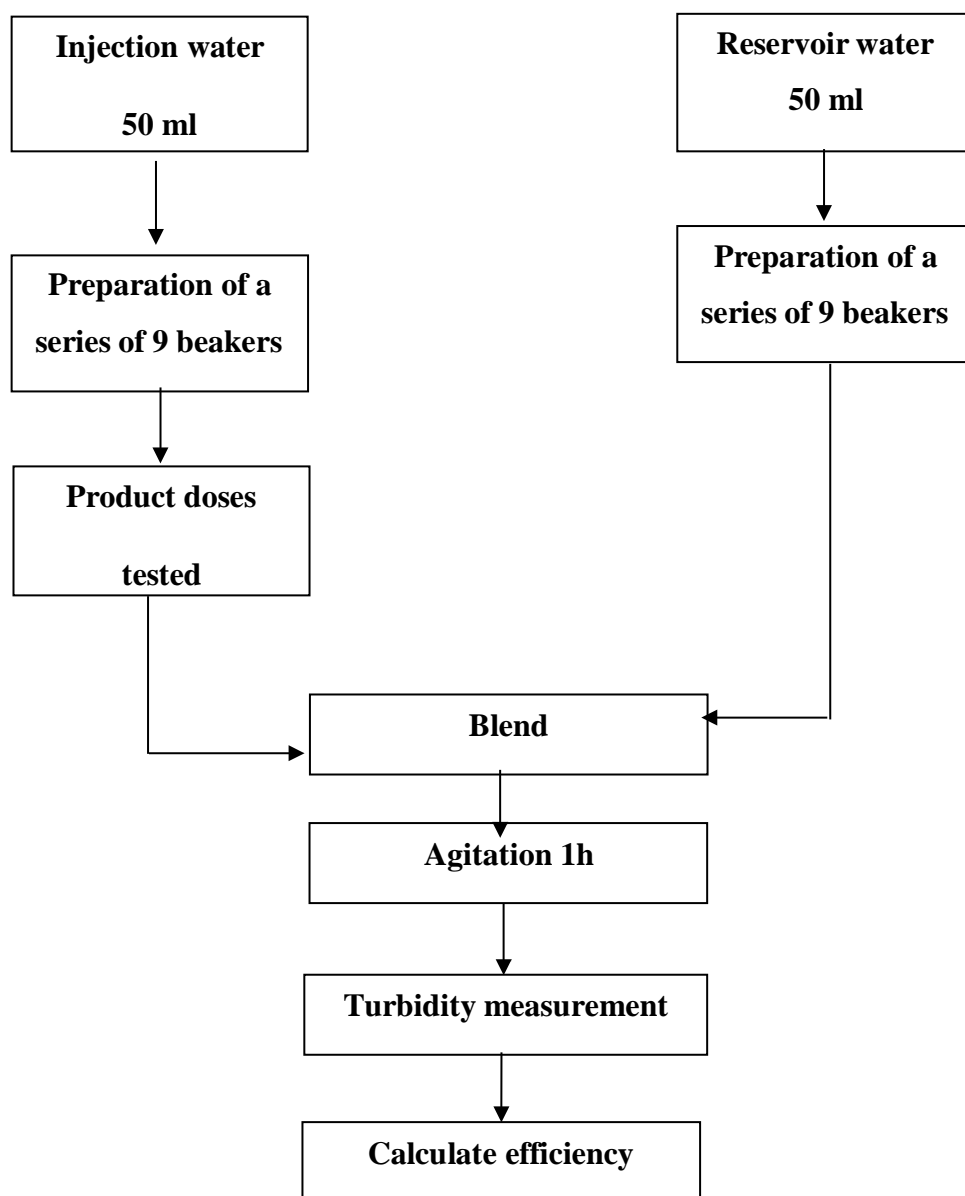


Figure 4 : Evaluation scheme for an anti-deposit product.

Appendix E: Schematic of an X-ray diffractometer.

The X-ray diffraction technique determines the arrangement of atoms within a structure and provides information at the Angstrom scale. Diffraction analyses were conducted using a PANalytical X'Pert PRO MPD diffractometer.

APPENDIX:

The analytical data obtained and interpreted are directly stored on the Dell P4 microcomputer that controls the X'Pert PRO MPD.

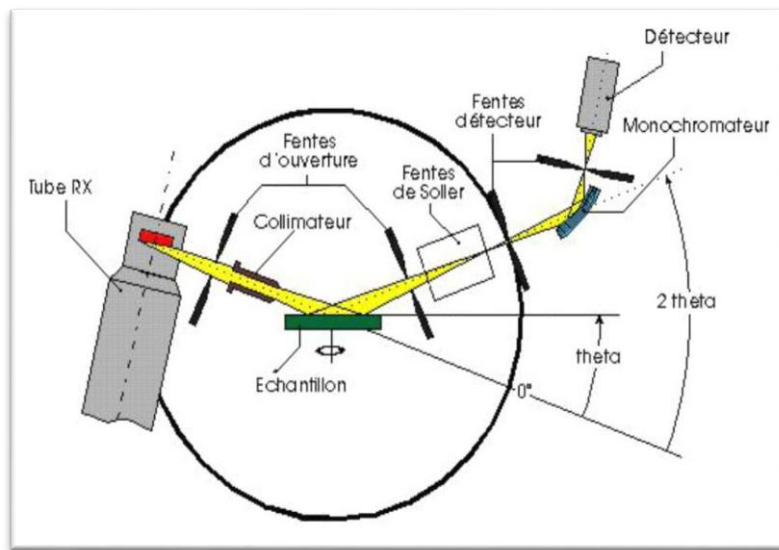


Figure 5 : Schematic of an X-ray diffractometer.

Appendix F: The turbidity test.

The turbidity test is conducted according to the ISO 7027-1999 standard using the "HACH 2100N" laboratory turbidity meter (Loveland, CO, USA).



Figure 6 : Turbidity meter.

Initially, the turbidity meter is calibrated using the "GELEX secondary turbidity standard kit," which includes glass bottles tightly sealed and containing different turbidity ranges (0-2, 20-200, 200-400, 400-4,000, 4,000-10,000 NTU). The procedure involves placing the standard in the reference cell slot of the turbidity meter, starting with the lowest turbidity range standard (0-2 NTU). Successive standards are then placed in the measurement cell, progressing from the

APPENDIX:

lowest (0-2 NTU) to the highest (4,000-10,000 NTU) turbidity range. The principle behind this test is to evaluate the effectiveness of deposit inhibitors at the critical mixing ratio of injection water to formation water, where deposition is most pronounced.

ABSTRACT:

Abstract

The major inconveniences of oil extraction by water injection are scaling and the formation of deposits in petroleum wells. This study focuses on these issues by analyzing water samples (injection water and reservoir water) taken from the wells of the Hassi-Messaoud field. The objective is to identify the constituents present in these samples through physico-chemical and mineralogical analyses.

To eliminate this problem, a water compatibility test is conducted to determine the optimal mixing ratio and the nature of the formed deposits. The study concludes with an efficiency test of three different inhibitors to identify the most effective one for preventing these issues.

Keywords: Compatibility, water injection, reservoir water, deposits, efficiency, inhibitors.

Résumé

Les inconvénients majeurs de l'extraction de pétrole par injection d'eau sont l'entartrage et la formation de dépôts dans les puits pétroliers. Cette étude se concentre sur ces problèmes en analysant des échantillons d'eau (eau d'injection et eau de gisement) prélevés dans les puits du champ de Hassi-Messaoud. L'objectif est d'identifier les constituants présents dans ces échantillons grâce à des analyses physico-chimiques et minéralogiques.

Pour but d'éliminé cette problématique, un test de compatibilité de l'eau est réalisé afin de déterminer le ratio de mélange optimal et la nature des dépôts formés. L'étude se conclut par un test d'efficacité de trois inhibiteurs différents pour identifier le plus efficace pour prévenir ces problèmes.

Mots clés : Compatibilité, injection d'eau, eau de gisement, dépôts, efficacité, inhibiteurs.

ملخص:

العيوب الرئيسية لاستخراج النفط عن طريق حقن المياه هي التكلس وتكوين الرواسب في آبار النفط. تركز هذه الدراسة على هذه المشاكل من خلال تحليل عينات الماء (مياه الحقن ومياه المتكون الصخري) المأخوذة من آبار حقن حاسي مسعود. الهدف هو تحديد المكونات الموجودة في هذه العينات من خلال التحاليل الفيزيائية الكيميائية والمعدنية.

من أجل حل هذه المشكلة، يتم إجراء اختبار توافق المياه لتحديد نسبة الخلط المثلى وطبيعة الرواسب المتكونة. وتختتم الدراسة باختبار كفاءة ثلاثة مثبطات مختلفة لتحديد الأكثر فعالية في منع هذه المشاكل.

الكلمات الرئيسية: التوافق، حقن المياه، المتكون الصخري، الرواسب، الفعالية، المثبطات.