

**LONG-TERM INVESTIGATION OF NANO-SILICA
GEL PERFORMANCE FOR WATER SHUT-OFF
TREATMENTS**

BY

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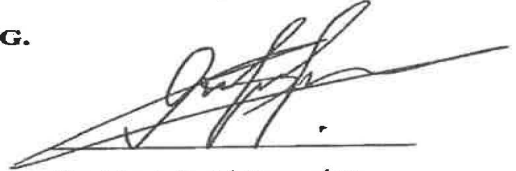
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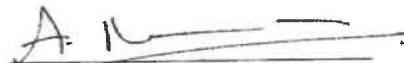
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To my mother Aida Salih may Allah give her health and happiness.

To my father, brother and sisters, may Allah protect you all.

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LIST OF ABBREVIATIONS

WOR	:	Water-oil ratio
RPM	:	Relative permeability modifiers
PAM	:	Polyacrylamide
HPAM	:	Hydrolyzed polyacrylamide
ESEM	:	Electron scanning electron microscope
SEM	:	Scanning electron microscope
CAC	:	Critical association concentration
LCST	:	Lower critical solution
UCST	:	Upper critical solution temperature
PPG	:	Preformed particle gels
SAP	:	Superabsorbent polymers
HQ	:	Hydroquinone
HMTA	:	Hexamethylenetetramine
HAHPAM	:	Hydrophobically associated with partially hydrolyzed polyacrylamide
GO	:	Graphene oxide
GNP	:	Graphene Nano-platelets
PCGEL	:	Personal computer gel
ANN	:	Artificial neural network
OWC	:	Oil-water contact
BWPD	:	Barrels of water per day
BOPD	:	Barrels of oil per day
PLT	:	Production logging tool

ICD	:	Inflow control device
CT	:	Computed Tomography
PEI	:	Polyethylene
NMR	:	Nuclear magnetic resonance

ABSTRACT

Full Name : Ahmed Ali Mohamed Ali

Thesis Title : Long-Term Investigation of Nano-Silica Gel Performance for Water Shut-off Treatments

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The oil and gas industry faces numerous challenges, among which the management of excessive water production is a significant concern. Silicate gels have long been utilized as water shut-off agents in petroleum fields to address excessive water production. In recent years, nano-silica gel has emerged as a promising alternative to traditional silicate gels, offering potentially improved plugging performance. However, the long-term effectiveness of these gels remains uncertain, posing challenges to sustained profitability. Therefore, coreflooding experiments spanning 6 months were conducted to evaluate the long-term plugging performance of nano-silica gel on permeable, fractured, and induced channel samples at 200 °F. Samples were treated initially with the nano-silica gel, then followed by endurance tests to ensure complete plugging. Then, samples were aged in formation water at 167 °F for 6 months, accompanied by endurance tests (up to 1000 psi) conducted in the first, third, and sixth months to assess gel plugging efficiency. Coreflooding experiments were accompanied by Computed Tomography (CT) scans for the treated samples to evaluate any degradation that occurred to the gel. Similar experiments were conducted using polyacrylamide/polyethylene (PAM/PEI) gel to build a long-term performance comparison between nano-silica gel and PAM/PEI gel. The results demonstrated that nano-silica gel achieved better long-term performance than PAM/PEI gel for 6 months. After 6 months, nano-silica gel was capable of reducing the permeability of the permeable sample to nearly zero with plugging efficiency not less than 99.98%, while the efficiency of PAM/PEI gel reduced to 99.85%. Similarly, Nano-silica gel maintained 100% plugging efficiency in the fractured sample (after 6 months) and 99.99% in the induced channel sample. On the other hand, a reduction to 99.15% plugging

efficiency was observed for PAM/PEI gel in the fractured sample. CT scan results indicate minimum degradation occurred to both gels with less significant impact on nano-silica gel, illustrating the capability of the gel to maintain its effectiveness and durability after 6 months.

ملخص الرسالة

الاسم الكامل: احمد علي محمد علي

عنوان الرسالة: تحقيق طويل الأمد في أداء جل النانو سيليكات لمعالجة تدفق المياه

التخصص: هندسة البترول

تاريخ الدرجة العلمية: مايو 2025

صناعة النفط والغاز تواجه تحديات عديدة، من بينها إنتاج المياه الزائدة وهو ما يشكل مصدر قلق كبير. تم استخدام جل السيليكا منذ فترة طويلة كعوامل لإيقاف تدفق المياه في حقول البترول. في السنوات الأخيرة، ظهر جل النانو سيليكات كبديل واعد لجل السيليكا التقليدي، و مما أعطى توقعات ان يقدم أداء افضل لمكافحة مشكلة إنتاج الماء الزائد. ومع ذلك، فإن فعالية هذه المواد على المدى الطويل تبقى غير مؤكدة، مما يشكل تحدياً للربحية المستدامة. لذا، تم إجراء تجارب حقن العينات على مدى 6 أشهر لتقييم فعالية جل النانو السيليكا على المدى الطويل على عينات مختلفة، عينة ذات مسامية، عينة متكسرة، وعينة بها قنوات عند 200 درجة فهرنهايت. تم علاج العينات في البداية بأصباغ جل النانو السيليكا، ثم تم إجراء ضغط تحمل تحت ضغط كبير لضمان إيقاف تدفق الماء بشكل كامل. ثم تم وضع العينات في ماء مالح عند 167 درجة فهرنهايت لمدة 6 أشهر، مصحوبة باختبارات الصمود (حتى 1000 رطل في البوصة المربعة) و التي أجريت في الشهر الأول والثالث والسادس لتقييم كفاءة الجل في منع مرور الماء. كما أجريت تجارب تصوير مقطعي للعينات المعالجة لتقرير أي تحلل حدث لجل. أيضاً تم إجراء تجارب مماثلة باستخدام جل بولي أكريلاميد/بولي إيثيلين على عينات مشابهة للتي استخدمت لجل النانو سيليكات بهدف مقارنة الاداء طويل الأجل بين جل النانو السيليكا و جل بولي أكريلاميد/بولي. أظهرت النتائج أن جل النانو السيليكا لديه أداء أفضل على المدى الطويل من بولي أكريلاميد/بولي إيثيلين لمدة 6 أشهر. بعد 6 أشهر، كانت جل النانو السيليكا قادراً على تقليل مسامية العينة المسامية إلى ما يقرب من الصفر بكفاءة لا تقل عن 99.98٪، بينما انخفضت كفاءة جل بولي أكريلاميد/بولي إيثيلين إلى 99.85٪. وبالمثل، حافظ جل النانو السيليكا على كفاءة 100٪ في العينة المكسورة (بعد 6 أشهر) و 99.99٪ في العينة ذات القنوات. من ناحية أخرى، لوحظ انخفاض إلى 99.15٪ في كفاءة جل بولي أكريلاميد/بولي إيثيلين في العينة المكسورة. أظهرت نتائج تصوير المقطعي حدوث تحلل بسيط لكلا المادتين مع تأثير أقل على أداء جل النانو السيليكا، مما يوضح قدرة الجل على الحفاظ على فعاليته مع مرور الزمن.

CHAPTER 1

INTRODUCTION

1.1 Background

During oil production under external fluid drive, the driving fluid is expected to uniformly propel the oil forward without leaving any behind. Conformance measures the effectiveness of the flood front in driving the oil towards the production interval.¹⁻³ However, reservoir heterogeneity, for various reasons, may accelerate the movement of the driving fluid (e.g., water) relative to the oil, resulting in significant amounts of un-swept oil remaining and excessive co-production of the driving fluid (water or gas).^{1,4} Such a scenario is termed a reservoir conformance problem^{1,5,6} and can arise due to factors associated with production or injection wells.⁷ Implementing techniques to improve the movement of un-swept oil is referred to as conformance control.^{2,4,8,9} Water shut-off falls under conformance control mechanisms, aiming to mitigate excessive water production through various strategies, thereby enhancing oil recovery and prolonging the product life cycle.¹⁰⁻¹²

Excessive water production is a common and challenging problem in the oil and gas industry associated with hydrocarbon production.¹³ The reservoir rock generally contains connate water and hydrocarbons. In addition to that, some reservoirs are surrounded by a vast aquifer. In such cases, water can flow from different sources into the wellbore and be produced along with hydrocarbons. Immediate treatment is required when the water production rate becomes above the economic level of water oil ratio (WOR).¹³ Problems arise when the water production rate starts to compete with oil production, which means no or little oil is produced¹⁴. Some studies reported a large volume of water produced with water. According to Bailey et al. (2000), each barrel of oil was associated with three barrels of water.¹⁵ This rate of production approximately equalled 75 billion barrels with \$40

billion for disposal at that time. Another study by Veil (2019) stated that total water production in the USA nearly reached 24.4 billion barrels in 2017.¹⁶ Therefore, water shut-off technologies were introduced to reduce water production, improve oil recover and apply effective reservoir management with minimum environmental impact.² Also, water control technologies will improve the well profitability for the operator by lowering the lifting cost, extending the productive well life, reducing the well maintenance cost and minimizing water disposal cost.^{10,13}

Excessive water production poses a common and formidable challenge in the oil and gas industry during production stages.¹³ Reservoir rock typically harbors both connate water and hydrocarbons, while some reservoirs are encompassed by extensive aquifers. Consequently, water from various sources can infiltrate the wellbore and be extracted alongside hydrocarbons. Prompt intervention becomes imperative when the water production rate surpasses the economically viable water-oil ratio (WOR).¹³ Complications arise when water production competes with oil production, leading to minimal or no oil production.¹⁴ Several studies have highlighted significant water volumes being produced alongside oil. Bailey et al.¹⁵ reported a ratio of three barrels of water for each barrel of oil, resulting in approximately 75 billion barrels of production with a disposal cost of \$40 billion at that time. Similarly, Veil¹⁶ et al. indicated that total water production in the USA nearly reached 24.4 billion barrels in 2017. Consequently, water shut-off technologies have been developed to mitigate water production, enhance oil recovery, and facilitate effective reservoir management with minimal environmental impact.² Moreover, water control technologies contribute to enhancing well profitability for operators by reducing lifting costs, extending productive well life, minimizing maintenance expenses, and lowering water disposal costs.^{10,13}

The successful water shut-off treatment depends primarily on detecting the real source of the water. Due to the heterogeneity of the reservoir and limitations of each technology, each water source has a certain effective solution to be applied. Once the real cause of the water is identified, an effective solution will be selected between the available mechanical and chemical methods. Mechanical methods are implemented by placing mechanical devices such as packers and tubing plugs into the wellbore. They are also conducted by

performing squeeze cementing around the wellbore. These mechanical methods are preferred for treating new wellbore problems. The chemical methods involve injecting chemical materials into the reservoir or near the wellbore, and these materials will start to either block or reduce the water flow after a certain period of placement. Polymer and silicate gels are considered one of the most traditional and effective chemicals to tackle water production.

1.2 Problem Statement

Water production is a common issue in oil fields undergoing water flooding or associated with a water aquifer. Researchers and engineers continually develop new mechanical and chemical solutions to address various sources of water. The mechanisms for reducing water production vary among different methods, and each method has its advantages and limitations due to varying reservoir characteristics. Therefore, a one-size-fits-all solution cannot be applied to every water problem. A new emerging technology in the oil and gas industry involves the utilization of nanomaterials in various sectors such as enhanced oil recovery (EOR), production, and drilling. Studies have shown that nanomaterials possess significant capabilities to enhance material performance for diverse applications.^{17–20}

Recently, a nano silica-based fluid has been introduced as a new development for silicate gels used in water shut-off treatments. Silicate gels offer several advantages, including environmental friendliness, low viscosity suitable for deep reservoir penetration, and thermal stability. Regarding nano-silica gel, recent reports indicate that this type of gel can achieve 100% plugging efficiency. However, extensive experimental work has yet to be conducted to assess the durability of nano-silica gel over an extended period and to compare it with other traditional gel types such as crosslinked PAM/PEI gel.

1.3 Objectives

Assessing the prolonged stability of gel under reservoir conditions is crucial for the success of water shut-off treatments. As nano silica gel emerges as a novel material for these treatments, it is mandatory to evaluate its long-term durability in reservoir conditions. Therefore, the objectives of this study involve the following:

1. Evaluate the effectiveness of nano silica-based gel as a water shut-off agent in a matrix characterized by high permeability and fractures, focusing on injectivity, and plugging efficiency.
2. Investigate the durability of nano-silica gel over 6 months under reservoir conditions in both permeable matrix and fractures.
3. Conduct a comprehensive comparison between the plugging performance of nano-silica gel and PAM/PEI gel over 6 months.

1.4 Proposed Work

This study involves conducting core flooding experiments with two different gel types using a specialized system designed for water shut-off treatments. Initially, samples will be treated with either nano silica gel or crosslinked PAM/PEI gel. Following treatment, the samples will undergo a 6-month aging process in formation water at elevated temperatures. Throughout this period, endurance tests will be implemented on the samples to assess the plugging efficiency of the gels. The findings of the study will establish a comprehensive understanding of gel performance over the 6-month duration.

CHAPTER 2

A REVIEW OF RECENT DEVELOPMENTS IN NANOMATERIAL AGENTS FOR WATER SHUTOFF IN HYDROCARBON WELLS¹

2.1 Abstract

Reducing water production from hydrocarbon wells is one of the major requirements to prolong the life span of the production wells. Gel treatment is commonly regarded as one of the traditional cost-effective methods for water shut-off applications. Different gel systems have been developed to overcome the challenges of performing a successful water shut-off treatment. Each gel system has its advantages and disadvantages. A new proposed technology is to enhance the gel performance by utilizing nanomaterials in its composition. Nanomaterials such as nano-silica, nano-clay, and graphene can significantly modify gel properties to improve plugging efficiency. This paper provides a brief review of the added value of using nanomaterials in the structure of polymer in-situ gel, preformed particle gel, and nano-silica-based fluid. Nanomaterials such as nano-clay, nano-silica, and nanographene are capable of adjusting the properties of in-situ gel, such as control of gelation time (9-10) hours and enhancing gel strength up to 4.5 times. Nanomaterials also improved the swelling ratio of preformed particle gel by up to 400%, accompanied by increased gel strength. Notably, nano-silica-based gels exhibit an exceptional plugging efficiency (100%). Additionally, the paper discusses how modelling can be used to overcome operational challenges in terms of placement and plugging performance.

¹ This chapter is copied from the manuscript: Ali, A.; Alabdrabalnabi, M.; Al Ramadan, M.; Aljawad, M.; Almohsin, A.; Azad, M. A Review of Recent Developments in Nanomaterial Agents for Water Shutoff in Hydrocarbon Wells. *ACS omega* **2024**.

2.2 Introduction

During oil production under an external drive fluid, the driving fluid targets to push the oil ahead to the production interval. Conformance measures the flood front efficiency of the driving fluid to push the oil towards the production interval.¹⁻³ However, the heterogeneity of reservoirs may assist the driving fluid (i.e. water) to move faster than oil, which results in leaving large amounts of oil unswept and leading to co-production of the driving fluid (water or gas).^{1,4} This is called a reservoir conformance problem,^{1,5,6} and it can occur in production or injection wells.⁷ Applying any technique to improve the movement of unwept oil is called conformance control.^{2,4,8,9} Water shut-off is classified under conformance control mechanisms by eliminating excessive water production using different strategies, which enhances the oil recovery and extends the production life cycle of the well.¹⁰⁻¹²

Undesired water production has received high attention from the petroleum industry to overcome the challenges associated with the produced water and thus improve the economic life of the wells.¹³ The reservoir rock generally contains connate water and hydrocarbons. In addition to that, some reservoirs are surrounded by vast aquifers. In such cases, water can flow from different sources into the wellbore and be produced along with hydrocarbons. Immediate treatment is required when the water production rate exceeds the economic level of the water-oil ratio (WOR).¹³ Problems arise when the water production rate starts to compete with oil production, which means no or little oil is produced.¹⁴ Some studies reported a large volume of water produced with oil. In 2000, According to Bailey¹⁵ et al., each barrel of oil was associated with three barrels of water worldwide and this amounted to approximately 75 billion barrels of water with a disposal cost of \$40 billion. Another study by Veil¹⁶ stated that total water production in the USA nearly reached 24.4 billion barrels in 2017. Therefore, water shut-off technologies are introduced to reduce water production, improve recovery efficiency, ensure effective reservoir management, and, in some cases, comply with environmental regulations.² Additionally, the water control technologies enhance profitability for the operator by lowering the lifting cost, extending the productive well life, reducing the well maintenance cost, and minimizing water disposal cost.^{10,13}

The critical parameter in planning a successful water shut-off treatment is conducting an accurate diagnosis of the root cause of water and then applying the suitable treatment for the problem.^{3,15,21–28} Investigation into several ineffective treatments has led to the conclusion that operators often do not perform an appropriate diagnosis in the beginning due to some reasons such as insufficient time, invested capital, and inadequate knowledge about the range of effectiveness for each method.^{10,29} Diagnosing the water production challenge should include information about the production wells and the field data. Data such as heterogeneity of reservoir, production drive mechanism, production data, and well geometry can help find the water entry point.³⁰ The diagnosis is conducted using production logging tools, pressure transient analysis, well log analysis, nodal analysis, relative permeability ratio, and production data analysis.^{30–35}

Gel treatments are considered one of the oldest methods to treat water production.^{3,36,37} They have shown their capability to plug the thief zones such as fractures, high permeability layers, etc.^{10,21} However, they face certain challenges that need to be addressed in terms of gelation control, gel stability, and thermal stability.^{38,39} The new developed improvement is by utilizing nanomaterials such as silica, clay and graphene in the composition of the gel. These materials have shown the capability to improve material performance for different uses. Over the last few years, there has been a noticeable increase in the usage of nanomaterials in the oil and gas industry.¹⁸ Nanomaterials are materials manufactured at nanoscale size, their size range from 1 to 100 nanometers. This size allows the material to exhibit unique properties distinct from the Bulk material. It was found that nanomaterials have a huge capability to improve material performance for different applications such as enhancing oil recovery, formation evaluation, and reservoir imaging.^{17–20} Many gel systems suffered from overcoming many challenges during water shut-off treatments such as gel instability under reservoir conditions, gelation time control, and gel propagation in the reservoir. Therefore, materials such as nano-silica, and nano-clay were introduced as a part of gel composition, and an incremental improvement in gel properties was found.

This study aims to discuss the recently developed gel systems that include only nanoparticles of silica, clay, zirconium oxide or graphene in their composition. The study shows the added value of these materials in the performance of polymer gels and silicate

gels to overcome operational challenges during water shut-off treatments. Besides, the study demonstrates the capability of gel modeling treatment for enhancing water shut off treatments.

2.3 History of Water Problem:

2.3.1 Sources of Water

Two types of water are produced with oil. Good water is produced naturally as part of the fractional flow process and does not compete with oil production at economically viable rates, so it is left untreated during production to avoid any negative impact on oil production.³ In contrast, Bad water also known as insufficient water hinders oil production. Immediate treatment is necessary for bad water to reduce its negative impact and increase oil production.^{3,15} Many sources have been identified to cause excessive water production. Generally, these can be classified into reservoir-related sources and wellbore-related sources. Below is a list of the most common ones:

2.3.1.1 Wellbore-related sources

Flow behind the pipe can occur when there is a channel between the water-bearing layer and the wellbore. The connection could be due to the partially or nonexistent primary cement in the interval between the water layer and production interval, or due to a bad cement job (cement failure). Another reason is the continuous microannulus between the cement and formation or the cement and the casing as illustrated in Figure 1.^{1,7,15,40}

Casing /Packer/Tubing leak can occur due to corrosion in the casing, tubing, or uninsulated seal of the packer as appeared (see Figure 2).^{1,22}

Migration of oil-water contact (OWC) can cause undesired water production because of water coning once the OWC starts rising and reaching the perforation of the target zone, as shown in Figure 3. This can predominantly occur if the perforations are placed close to the OWC, and the reservoir vertical permeability is high.

Barrier breakdowns can occur when fracture breaks through the impermeable layer or when acids are used to dissolve the rocks. This can result in the formation of a new fracture near the wellbore, which will eventually enable the water to migrate to the wellbore due to the pressure difference across the permeable layer.⁴¹

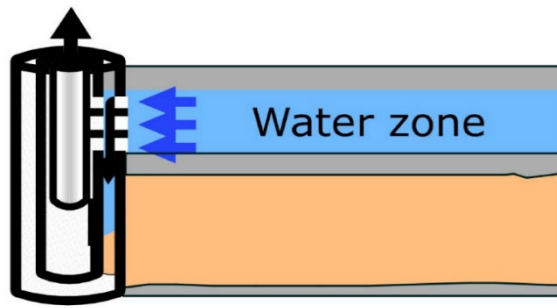


Figure 1 Flow behind pipe.

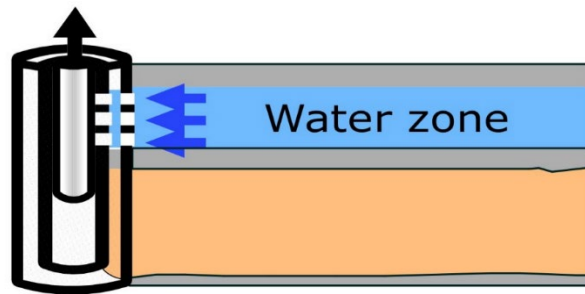


Figure 2 Tubing Leaks.

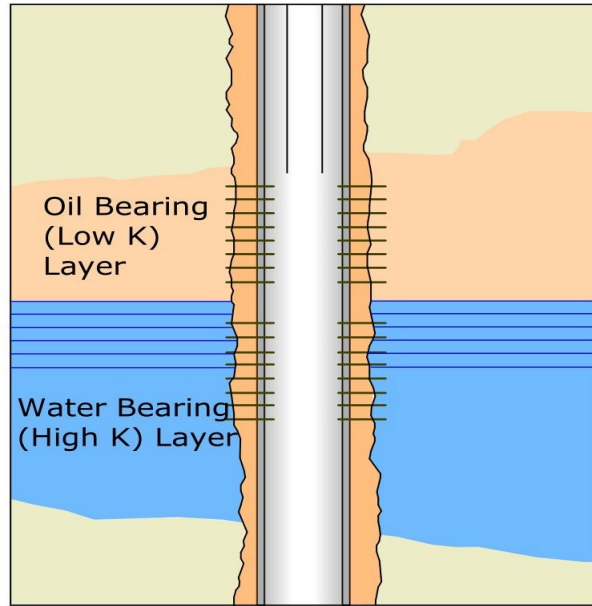


Figure 3 Rise of water oil contact.

2.3.1.2 Reservoir-related sources

Fracture between the injector and producer can allow water from the injection well to flow into the production well as illustrated in Figure 4. This is a common problem in waterflooded reservoirs, which leads to unwanted water production in a very short time through the fractures.¹⁵

Fissure/Fracture from a water layer can provide a path for water flow from the underlying water zone, also hydraulic fracturing can cause this problem (see Figure 5).⁷

Water coning can occur when the water rises up from the bottom of the reservoir and reaches the wellbore. Figure 6 illustrates this phenomenon. This is more likely to happen in wells with high water saturation and low permeability.²²

Watered-out layer with and without crossflow can occur when a water-saturated layer is sandwiched between two high permeability layers. Also, water can flow from the watered-out layer to the production well through the high permeability layers. the water source can be from either an active bottom water or injection well.^{1,15}

Channels through a high permeability zone can allow water to flow more easily through the reservoir, resulting in higher water production rates. This is a common problem in

reservoirs with high permeability streaks. This widely happens in reservoirs with either an active water drive or a water-flooding-treated reservoir.⁴²

Fingering can occur when water flows along high permeability channels in the reservoir. It is a condition whereby the interface of the oil-water layer creates a fingering profile (see Figure 7). The water bypasses horizontally a section of the reservoir as it moves. This phenomenon is common in a reservoir with a water injection well and viscous oil. It also can happen in a reservoir with a bottom water drive or gas cap expansion.^{1,13}

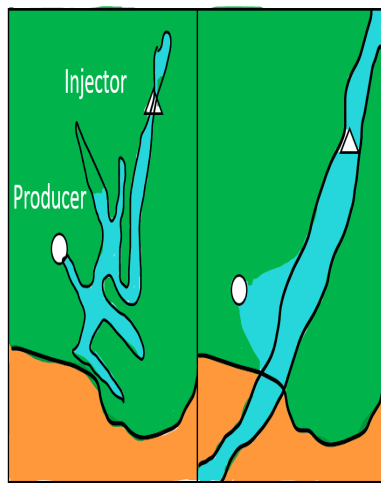


Figure 4 Fracture from the injector to producer.

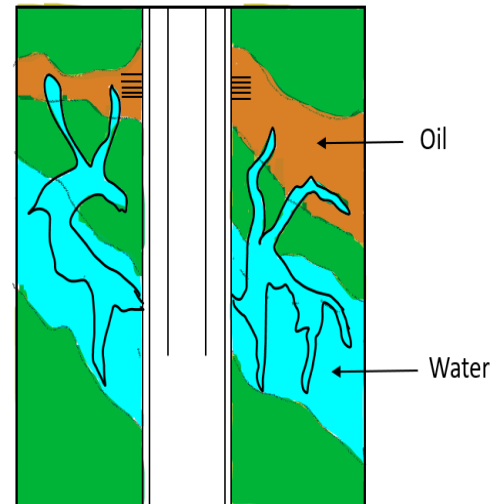


Figure 5 Fracture from a water layer.

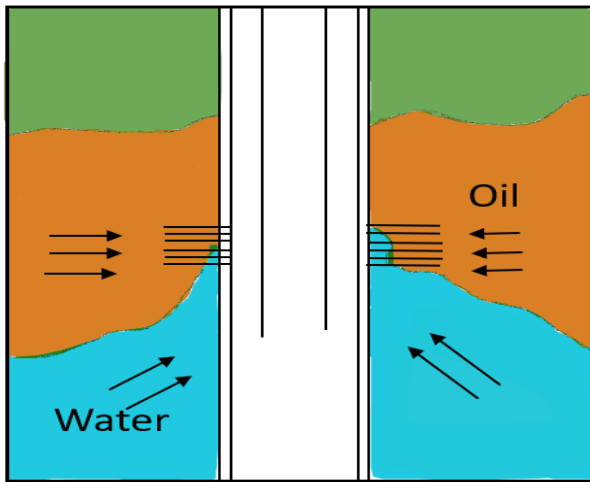


Figure 6 Water coning.

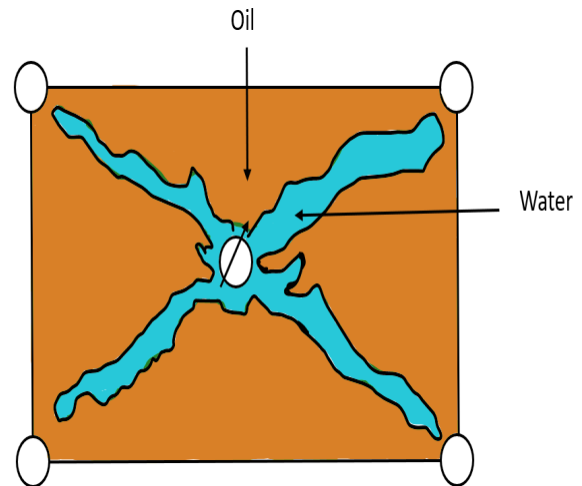


Figure 7 Fingering.

2.3.2 Water Shut-off Methods

In general, applying a certain method depends on the type of water problem in the reservoir (wellbore-related sources or reservoir-related sources).⁴³ Each method is effective in shut-off only specific water paths, and they could be classified into two types:

2.3.2.1 Mechanical methods

They involve placing a tool of high mechanical strength or cement into the wellbore to shut off the unwanted water source. The mechanical tools involve retrievable and straddle packers,^{43–46} plugs,⁴⁷ tubing patches,⁴⁸ and squeeze cementing.^{49–52} They are preferred for treating near wellbore problems such as channels behind casing or casing and tubing leaks. The advantage of the mechanical methods is that the effect will appear in a short time and is relatively inexpensive compared to other solutions.^{53,54} However, they are not feasible for treating reservoir-related sources such as fractures or high permeability zones.²¹ Additionally, incorrect placement of the plugging tool can lead to the loss of the producing oil zone.⁵⁵

2.3.2.2 Chemical methods

They involve injecting chemicals, such as gel, into the reservoir section or layer that provides an easy path for water to flow. This is implemented to plug the water-bearing zones and fractures, which can help to reduce water and increase oil production. The propagation of the chemical fluid reduces the water permeability in the targeted zones, and this forces the water to take other paths pushing the oil ahead to the production interval. These methods can also increase the water viscosity which improves the reservoir conformance and sweep efficiency. Their advantage over the mechanical solutions is the ability to treat both near-wellbore and reservoir-related sources. The results could last for months and up to years depending on reservoir characteristics. However, a disadvantage is that the efficiency of the chemical solution is highly affected by reservoir properties and its compatibility with the reservoir temperature and water salinity.^{10,56,57} The study focuses on discussing the chemical techniques that utilize the gels as blocking agents and how nanomaterials such as nano-silica can assist in overcoming some operational challenges during treatment. **Error! Reference source not found.** and Table 1 illustrate the most common chemical systems used for the last century, summarized below:

- **Inorganic gels**⁵⁸: They were discovered in early 1920s for blocking lost circulation zones and zone squeezing. Sodium silicate is the most common type. They have a very low viscosity and can easily be injected into deep reservoirs. They can provide an acceptable plugging efficiency with high thermal stability. Another type, aluminum, was developed to combat undesired water production in high temperature and low permeability reservoirs.^{59–61}
- **Monomer systems**: Monomer-based systems such as acrylamide, can be placed deep in the reservoir matrix. They have low viscosity, and after placement, they polymerize to form a gel with varying strength depending on the monomer type.
- **Polymer gels**⁶²: They are composed of polymer and crosslinking agent. Once they are placed into the target zone, they form a rigid 3D gel structure that blocks the water phase. Common types include Polyacrylamide (PAM) and hydrolyzed polyacrylamide (HPAM). Crosslinking agents could be metallic,

such as aluminum and chrome, or organic, such as phenol. Additionally, biopolymers such as xanthan can also be crosslinked to form a 3D gel.^{63,64}

- **Ungelled polymers**^{65,66}: It was found that some polymer types can reduce water permeability by a degree higher than oil permeability, which is called relative permeability modifiers (RPM). Polyacrylamide is one of these polymers that have this characteristic.
- **Resins**⁶⁷: These are thermosetting materials injected with a catalyst (acid or base) that start to react at bottomhole temperature to provide sufficient strength to seal fractures and channels. Phenol and epoxy are among the most common ones.

Viscous flooding (polymers)⁶⁸: In some situations, water production can be caused by an unfavorable mobility ratio, resulting in a poor sweep of viscous oil. Polymer flooding can enhance the mobility ratio and improve sweep efficiency by increasing the water viscosity during water flooding. HPAM and xanthan polymer are common for this job.

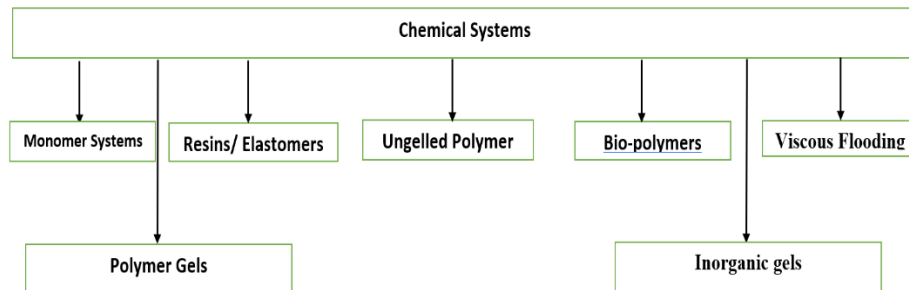
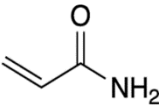
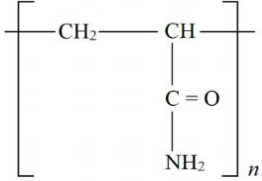
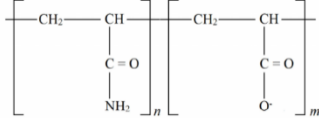
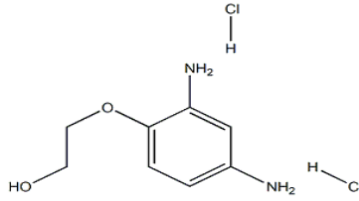
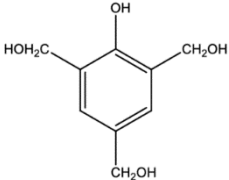


Figure 8 Chemical water shut-off systems.

Table 1 List of common chemical's structure for water shutoff applications.

Chemical System	Name	Chemical Structure
Inorganic Gels	Sodium Silicate	$ \begin{array}{c} \text{O} \\ \\ \text{Na}^+ \text{---} \text{Si} \text{---} \text{Na}^+ \\ / \quad \backslash \\ \text{O}^- \quad \text{O}^- \end{array} $

Monomer Systems	Acrylamide	
Polymers	Polyacrylamide	
	HPAM	
	Xanthan Gum	
Resins	Phenol-formaldehyde	

2.4 Utilizing Nanomaterials for Enhancing Gel Treatments:

The analysis process for this review starts with the initial demonstration of the actual challenges confronting three distinct gel types: in-situ polymer gel, preformed particle gel, and silicate gel. Figure 9 illustrates the systematic approach taken to assess the impact of nanomaterials on gel treatment. The influence of nanomaterials is divided into three distinct categories, each corresponding to a particular gel type. Enhancements in gels properties have been observed, primarily in terms of thermal stability, gelation time, gel strength, and

swelling performance. These improvements can be attributed to the application of four key types of nanomaterials, silica, clay, graphene, and zirconium oxide.

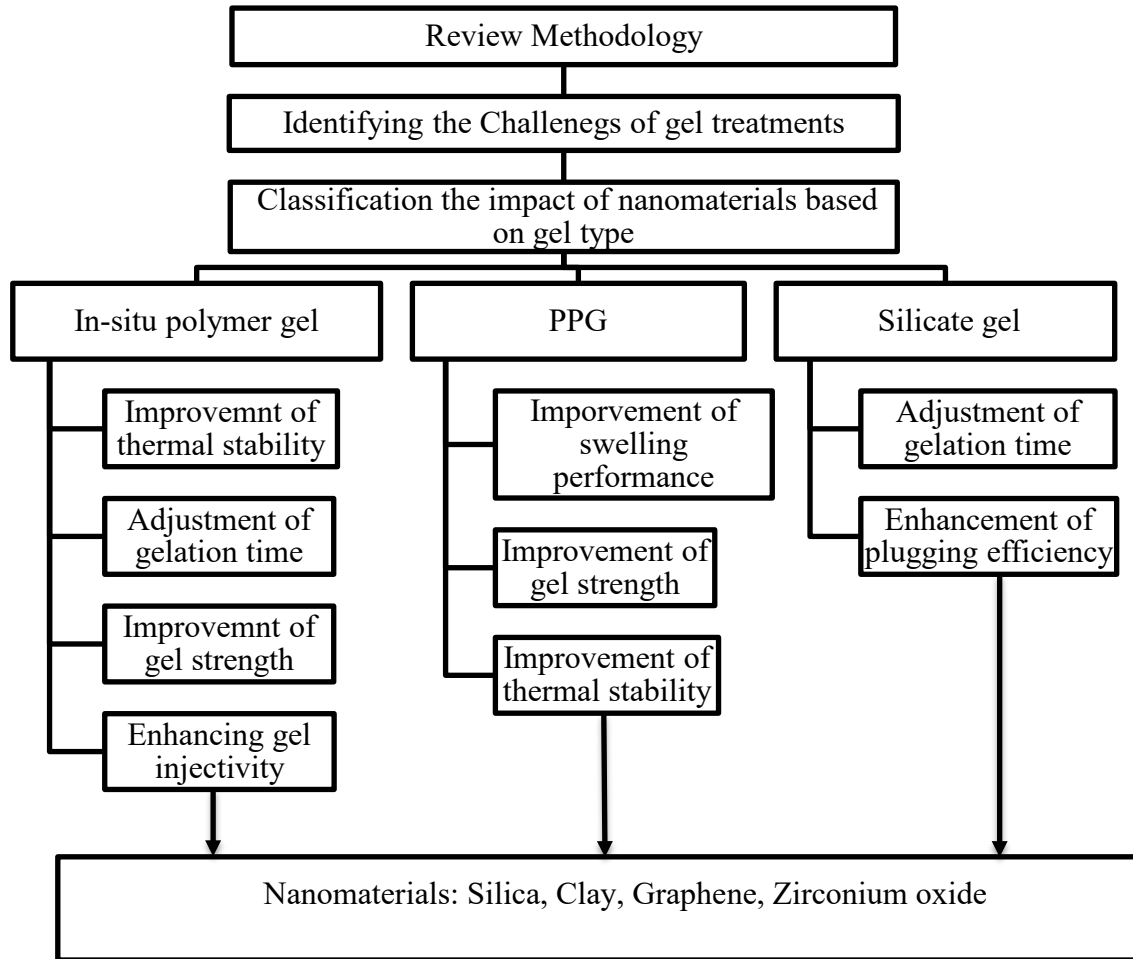


Figure 9 Review methodology for the impact of nanomaterials on gel treatments.

2.4.1 Challenges of Gel Treatments:

Gel treatments are one of the most common chemical water shut-off methods. They are effective and economical ways to reduce water production in mature reservoirs.⁶⁹ Polymer Gel can control water mobility by either reducing the permeability or plugging the high permeability zones and fractures.⁷⁰ This property improves the sweep efficiency and increases oil production correspondingly. Based on where the gelation takes place, subsurface or at the surface, the gel can be classified into the following:

2.4.1.1 In-situ Gel

It is a type of gel that forms a downhole in the reservoir.^{71,72} For conventional polymer gel, a mixture of polymer solution, crosslinker, and additives are injected downhole into the target zone. After the expected time and under a certain temperature, the mixture reacts to form a gel that plugs the zone partially or fully.⁷¹ Despite their popularity, many disadvantages were addressed such as a lack of gelation time control leading to an unpredictable depth of penetration,^{73,74} dilution by formation water,^{74–76} uncertainty of gelling due to shear in surface facilities and the reservoir,^{39,77,78} and potential damage of low permeability un-swept oil zone.⁷⁹

2.4.1.2 Preformed Gel:

Preformed gels (PPG) are a type of gel that is formed at the surface and then injected into the reservoir as particles. It is a new type of well-conformance technology that was first introduced by the Institute of Petroleum Exploration and Development (RIPED), PetroChina in 1996.⁷¹ They are made from superabsorbent polymers (SAPs), which are three-dimensional hydrophilic crosslinked polymers that swell but do not dissolve due to their inner physical and chemical nature.⁸⁰ PPGs are micro to millimeters in size and are used to plug fractures or channels of high permeability zones of a few darcies.⁸¹ Their plugging efficiency depends highly on particle strength and conduit inner diameter.⁸² Another advantage is the performance of plugging is less affected by operation and reservoir conditions such as shear rates, salinity, pH, and temperature.⁴ However, the application of these gels is limited to high permeable formation (not less than 500 mf) and fractures due to particle size constraints.⁴ Preformed gel types include partially preformed gels^{83,84}, preformed particle gels of millimeter to micro size (PPG),^{36,85,86} microgels,^{87–89} pH-sensitive crosslinked polymers,^{90–93} and Bright Water®.^{94,95} The main differences include the swelling capabilities, particle size, and the preferred reservoir conditions to be used.⁴ In addition to that, different types of mechanisms were used to combat water production such as partial plugging,^{71,96} relative permeability modification, large pores plugging, mobilizing capillary-trapped oil and monolayer or multilayer adsorption.^{71,88,97}

Figure 10 displays SEM images of swelling and aggregation of PPG and microgel in the porous media which will be reflecting on the achieved plugging efficiency. It distinctly demonstrates the contrasting plugging mechanisms between preformed particle gel and microgel when compared to in-situ gel. In preformed gel applications, plugging predominantly occurs due to swelling and aggregation of preformed gel within the pore structure. In contrast, in the case of in-situ gel, the transformation of the gelant solution from a liquid to a solid state within the pore system serves as the primary cause for shutting the water flow.

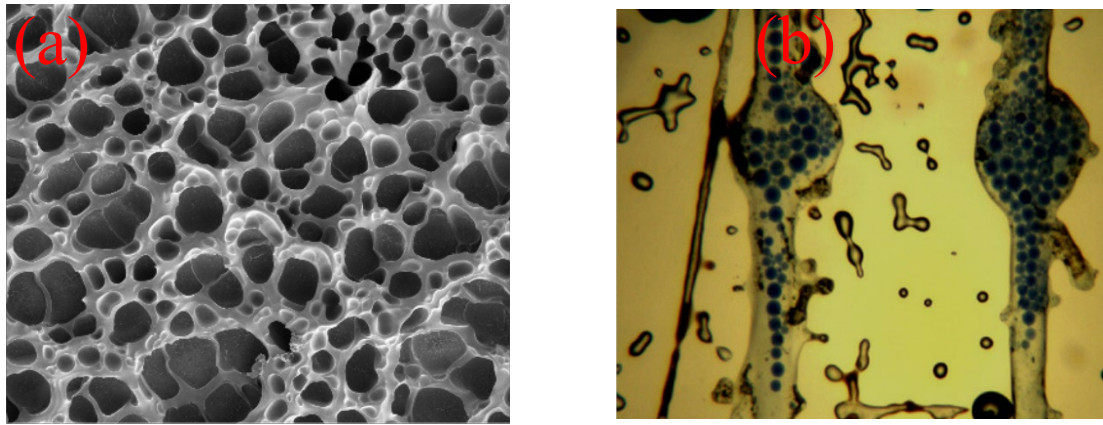


Figure 10 (a) Swelled PAM/Cs PPG,⁸⁵ (b) Distribution of microgel particles in the micro-visual mode.⁸⁵

2.4.1.3 Silicate gel

silicate-based gel is one of the oldest methods to tackle reservoir conformance problems.^{1,98} Their mechanism to mitigate water or gas production is similar to other gelling materials such as polymers or phenolic resins. It has the form of brittle gel, formed by the reaction between the silicate solution and an activator.⁹⁹ In the old days, HCl was used as an activator, but due to its hazardousness, different types of materials such as NaCl were successfully proved as gelation activators^{100,101}. The gelation happens as the result of chemical bonding between the particles which aggregate to form a semi-solid 3D network of long bead-like strings.¹⁰² In addition, the gelation time of silicate gels is highly affected by temperature and activator concentrations.¹⁰² Sodium silicate is considered the most

well-known silica solution.¹⁰¹ There are many advantages to applying silicate gels for water-shut-off applications. They are environmentally friendly, and the solution viscosity is similar to water, which provides good injectivity.¹⁰³ They also provide good thermal stability at elevated temperatures.^{104,105} The cost of applying silicate gels is relatively low, compared to other gel systems.^{104,106–108}

However, they have some drawbacks that have reduced their usage in recent years. The gel strength of silicate gel is less compared to polymer gels. The silicate gel has less gel strength when compared to polymer gels.¹ Another disadvantage is the gelation time, as it was found that the increase in gelation time could affect the gel strength negatively.¹

The focus of the study is only on these three gel systems, In situ Polymer gel, preformed particle gel, and silicate gel. These gels have operational common challenges in terms of gel placement and performance. Table 2 summarizes the common challenges that the face operator in the oil field. The challenges facing the three gel systems are diverse. In situ polymer gel contends with environmental sensitivity, complicated control of gelation time, and the potential for oil zone damage. Preformed gels confront a fundamental limitation, being generally unsuitable for low-permeability formations, necessitating alternative solutions in those cases. Silicate gels challenge precise control due to their rapid gelation and may struggle to maintain optimal gel strength over an extended duration, while their sensitivity to divalent ions can hinder effectiveness. Based on this observation, there is a clear need to improve the performance of the gel by making modifications to its composition. In recent times, three common nanomaterials, namely nano-silica, nano-clay, and nanographene, have been introduced into the gel composition to enhance its properties.

Table 2 Summary of the challenges of in-situ polymer gel, PPG, and silicate gel.

Gel system	Mechanism	Challenges	Examples
In situ Polymer gel	Gellant is placed into the target zone and over a certain period, it will be transformed into a solid gel.	- Gelation is affected by environmental conditions. - Control of gelation time is difficult. - Possible damage to the oil zone.	Crosslinked PAM gels ⁴
PPG	The gel is initially generated at the surface before being injected into the reservoir.	- It cannot propagate formation with permeability less than 1 D. - Limited application for the reservoir of an extreme permeability.	PPG (China) ⁸¹
Silicate gel	The gel is formed into the formation by the reaction of silicate solution with an activator under a certain temperature.	- Rapid gelation time. - The gel strength is low for an extended period. - Sensitive to the formation's minerals (divalent ions).	Sodium silicate gel ¹⁰¹

The key to a successful water shut-off treatment lies in accurately diagnosing the root cause of water intrusion and applying suitable remedies.^{3,15,21–28..} Understanding the reservoir's recovery mechanism and tracing the source of the produced water are crucial. Tracers and logging services help identify these sources. Once identified, specific solutions can be applied. Table 3 illustrates some of the previous successful filed applications for gel treatments. In-situ polymer gels and silicate gels are commonly used for near-wellbore issues like casing and tubing leaks, as well as sealing high-permeability zones. Preformed particles are preferred in China for their effectiveness in treating fractures over in-situ gels.

Table 3 Successful field applications for gel treatments.

Applied chemical system	Cause of Water Problem	Reference
In-situ polymer gel	Casing leaks	3,109
	Tubing leaks	40,109
	High permeable thief zones	110
	2D coning	111,112
	Natural fracture system connected to water zones	113,114
Preformed particle gel	Super permeability channels	115
	Low permeability fractured reservoirs	116
	Communication between the injection and the production wells	71
	High permeable layers	71

Silicate gel	Casing leaks	117
	High Permeable layers	118
	Fault reservoir with extremely high permeability	119,120

2.4.2 The Positive Impact of Nanomaterials on Gel Treatments:

This study will focus on gel properties improvements by utilizing nanomaterials for in-situ gels and preformed gels to combat excessive water production as illustrated below:

2.4.2.1 The impact on in-situ polymer gels

Polymer gels are commonly used as a cost-effective technique for reservoir conformance problems.¹²¹ Due to their nature, polymer gels provide many advantages such as good injectivity, deep penetration in the reservoir, increasing the viscosity of water, and changing the fluid's permeability for different zones. However, several challenges exist in implementing proper gel treatment techniques, such as aggregation to high polymer concentrating above critical association concentration (CAC), instability or degradation at high temperature in the reservoir, and insufficient gelation time to place a gel in the target zone. Utilizing nanomaterials has shown an improvement in gel properties as follows:

2.4.2.1.1 Enhancement of thermal stability

Temperature is one of the most important factors that affect the conversion of polymer solution into a solid gel that seals the target zone. In the design of polymer gel, two critical temperatures are significant for gel placement, the lower critical solution temperature (LCST) and the upper critical solution temperature (UCST). The range between them identifies the transition zone from flowing solution to a solid gel.¹²² Another important factor is the degradation temperature at which the polymer degrades and becomes flexible, affecting negatively sealing performance¹²³. Therefore, researchers have been working to illustrate the valuable impact of adding nanoparticle materials to strengthen polymer

stability at elevated temperatures and extend the transition zone. Some of these nanoparticles include the following:

Zirconium hydroxide: Zirconium hydroxide ($\text{Zr}(\text{OH})_4$) of nanoparticles size that has been investigated to improve the thermal stability of gels. They are highly applicable as a crosslinker agent due to several hydroxyl groups existing in their composition.¹²⁴ These hydroxyl groups can react with the polymer chains in the gel, forming strong bonds that help to prevent the gel from degrading at high temperatures. The usage of nanoparticles of zirconium hydroxide has improved the thermal stability of PAM crosslinked with hydroquinone (HQ) and hexamethylenetetramine (HMTA).¹²⁵ The thermal stability increased by 3 or 5 °C and reached up to 187 °C compared to the gel without nanoparticles. The new interaction between the hydroxyl group and amide group led to a stronger gel with limited gel mobility that required more energy to break the gel structure.

Nano-silica & Nano-clay: Nano-silica (SiO_2) and nano-clay have shown their capabilities to improve the thermal stability of gels. Nano-silica has a high specific surface area and can absorb heat, which helps to prevent the gel from degrading at high temperatures. Nano-clay has a high thermal conductivity, which helps to transfer heat away from the gel, which also helps to prevent the gel from degrading. Lie¹²⁶ et al. observed that adding nanoparticles of silica improves the strength of polyacrylamide crosslinked with HQ and HMTA. Figure 11 illustrates two gel structures for the gel, with and without nano-silica particles. The ESEM images clearly demonstrate the massive aggregations and arrangements of silica nanoparticles that existed in uniformly distributed three-dimensional network structures of the gel. These are new arrangements assist in creating stronger structure, reflected in the higher gel strength for gels incorporating nano-silica particles.

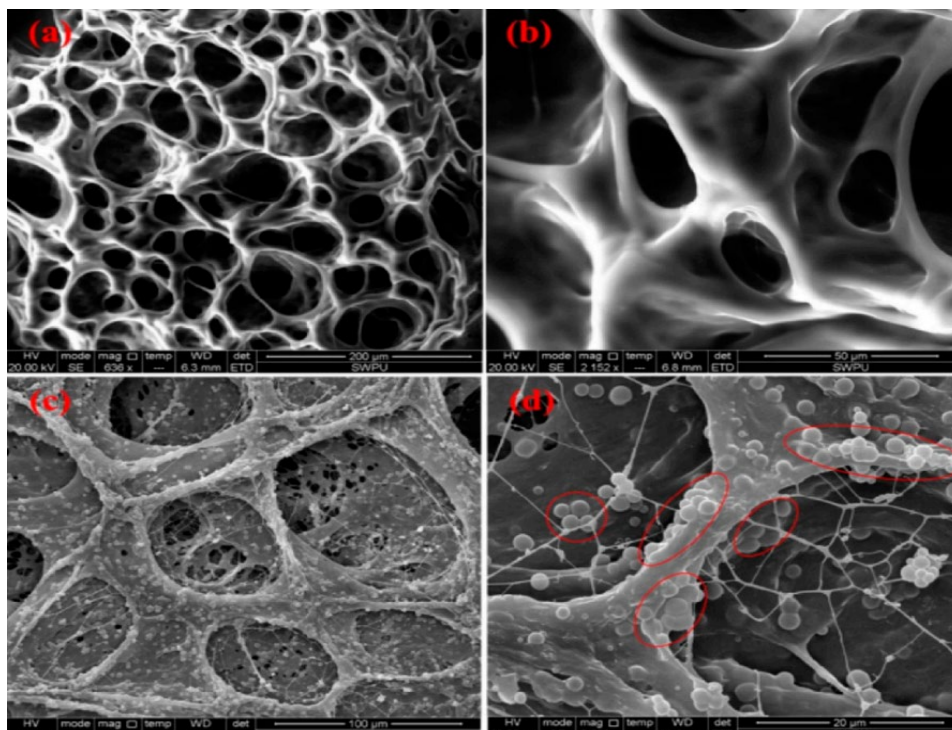


Figure 11 ESEM images of gel samples enhanced by varying concentrations of nano-silica particles, (a) & (b) without nano-silica; (c) & (d) 2% nano-silica concentration.¹²⁶

Asadizadeh¹²⁷ et al. obtained the same results when analyzing the effect of SiO₂ on the a gel composed of hydrolyzed polyacrylamide crosslinked with chromium (III) acetate. The gel showed significant flexibility, elongating to 1150% at very high temperatures. Furthermore, the recorded inflection temperature for a gel with nano-silica was higher than the one without nano-silica particles.

Despite these advantages, the usage of nanoparticles silica is limited to its compatibility with the polymer type. Nano-clay also has been addressed by some researchers. It has improved the performance of gel at high temperatures in many studies. In a study performed by Cheraghian¹²⁸ et al., adding nano-clay to PAM hydrogel increased the oil recovery by 5.8% at elevated temperatures (80 °C).

The use of nano-silica and nano-clay to improve the thermal stability of gels is a promising new technology for combating water production in oil reservoirs. This technology can help to extend the life of gels and improve their performance at high temperatures.

Nano-Graphene: Graphene is a carbon-based material that can be used at the nanoscale. It has very acceptable mechanical and thermal properties that improve the performance of nanocomposite gel. An experimental study was conducted by Shen¹²⁹ et al. to investigate the effect of Graphene Oxide on polyacrylamide hydrogels. The results showed an increase in the thermal stability of the nanocomposite gel due to a denser structure caused by the increased cross-linking density.

2.4.2.1.2 Adjustment of gelation time

The gelation time is the time it takes for a gel to form. It is important to be able to control the gelation time so that the gel can be injected into the reservoir and gel at the right location. Nanoparticles can be used to adjust the gelation time of gels. Nanoparticles can aggregate and connect to the polymer chains, forming a 3D network that is stronger with adjustable gelation time.

In the same study performed by Lie¹²⁶ et al., nanoparticles of silica have improved the gelation time of polyacrylamide crosslinked with hydroquinone and hexamethylenetetramine. Another study was conducted by Singh¹³⁰ et al. by utilizing nano fly ash with PAM polymer crosslinked with chromium acetate. The results of the study showed an increase in the gel strength with a reduction in gelation time (9-10) hours. In addition, the low activation energy supported rapid gel formation.

2.4.2.1.3 Improvement of gel strength:

The gel strength is the ability of a gel to withstand shear forces. It is important for gels to have high gel strength so that they can withstand the shear forces in the reservoir and be effective at plugging water production zones. Nanoparticles can be used to improve the strength of gels. Nanoparticles can form a network that strengthens the gel and makes it more resistant to shear forces.

Nano-silica: Lie et al¹²⁶ investigated the effect of nano-silica on PAM hydrogel. The results showed that the increase in the concentration of silica nanoparticles led to an increase in gel strength and storage modulus of nanocomposite gel. Chen¹³¹ et al. also added nano-silica to PAM/PEI hydrogel to investigate the impact on gel syneresis, plugging efficiency, and stability at elevated temperatures. It was found that a high decrease in the degree of syneresis caused further improvement in gel strength. The classification of the gel strength code has changed from class F (highly deformable non-

flowing gel) to class I (rigid gel). In addition to that, the results of sand pack experiments illustrate a high residual resistance factor which reflects the high plugging efficiency.

Nano-Graphene: Graphene was observed to add an improvement in the strength of the gel, Shen et al.¹³² investigated the effect of graphene oxide (GO) nanoparticles on PAM hydrogel. The increase in crosslinking density led to a denser structure with a higher modulus when compared to the original gel without nanoparticles. Similar results were observed by Lie¹³² et al., the nanocomposite GO-PAM had tensile strength higher by 4.5 times and more than 300% elongation.

In another study, Almohsin¹³³ et al. introduced a nanocomposite PAM by including graphene-based zirconium oxide, a superb mechanical strength was observed at elevated temperatures. The structure of the gel was homogenous and stable, and it shows the capability to trap the water even at elevated temperatures.

2.4.2.1.4 Enhancing gel injectivity

The evaluation of gel injectivity stands as a pivotal criterion for the effective deployment of gels in field applications, necessitating rigorous assessment prior to field trials. In a study conducted by Almohsin¹³³ et al., the injectivity of a developed polyacrylamide (PAM) gel incorporating graphene and zirconium oxide nanoparticles, was examined through core flooding experiments. Six pore volumes of the gelant were injected at a temperature of 320 °F. Throughout the injection process, a minimal increase in pressure was observed, stabilizing at 28 psi, indicative of the favorable injectivity characteristics exhibited by the nano-based gel formulation.

Pereira¹³⁴ et al. explored the effectiveness of HPAM gel integrated with nanoparticles for water shut-off purposes. They assessed injectivity by measuring gelant viscosity at varying shear rates. The viscosity of gelant, with and without clay nanoparticles, ranged from 18.0 to 19.1 mPa·s at a shear rate of 300 s⁻¹. At lower shear rates, viscosity values were between 67.5 and 76.9 mPa·s. These findings suggest that the addition of nanoparticles minimally affects gel injectivity. Ali¹³⁵ et al. also investigated gel injectivity using sulphonated PAM gel incorporating Fe₂O₃ and NiO nanoparticles. Their study revealed that the gel with nanoparticles experienced a minimal pressure drop during the initial 2 pore volumes compared to the gel without nanoparticles. However, as the injection progressed, the nano-based gel exhibited a higher pressure drop. This phenomenon can be attributed to the

aggregation and adsorption of nanoparticles within the core samples. Consequently, the study suggests using nanoparticles of a size that matches the expected treated pore size to optimize gel injectivity.

2.4.2.2 Impact on preformed particle gel

Preformed particle gels are composed of dried crosslinked polymers in the form of adjustable particle sizes.⁸¹ The injection process of these gels is simpler than the in-situ gels as the aqueous solution is composed of one component. When PPGs come in contact with water, they absorb it and expand to a few hundred times their original size.⁷¹ The swelling ratio depends mainly on its composition along with the surrounding environmental conditions such as salinity, pH, and temperature⁷¹. As they are prepared on the surface, this helps prevent some drawbacks of in-situ gels such as lack of gelation time control, dilution by formation water, and gelation variation caused by shear degradation.⁷¹ The new proposed technology is to enhance particle gels performance by incorporating some nanomaterials into their composition, below is the list of some types:

2.4.2.2.1 Improvement of swelling performance and thermal stability:

Nano-silica and Nano-clay: Khoshkar¹³⁶ et al. reported the advantages of using nanomaterials in preformed particle gel composition and their positive effects on serving water shut-off objectives for the fractured reservoir. In their study, a small amount of nano-clay and nano-silica were added to 9 PPG samples of different compositions (which are called N-PPG). To investigate the effectiveness and performance of N-PPG, static bulk tests, dynamic good tests, and micromodel model tests were performed to examine various parameters such as swelling capacity, pH value, temperature, and particle size.

Their results showed that the existence of nanomaterials improved the maximum swelling ratio and lesser syneresis rates compared to PPG without nanomaterials added. In a comparison of N-PPG and PPG made without nanomaterials, the swelling capacity of N-PPG was not affected by a pH value in the range of 3 – 10, which opens a potential usage of N-PPG for a wide range of pH values. They recommended that for any specific reservoir, the optimum particle size and the injection rate should be identified to obtain effective water shut-off treatment.¹³⁶

Graphene Nanoplates: Paprouski¹³⁷ et al. conducted laboratory experiments to investigate the effect of new additives on the swelling performance and thermal stability of preformed particle gel. The additive is composed of sodium silicate solution and Graphene Nano-platelets (GNP). Compared to the base synthesized PPG, it provides an acceptable swelling performance as well as higher thermal stability and dehydration resistance. The results showed that the samples that had a combination of silicate sodium and Nano graphene had a higher storage modulus compared to the base samples without nano-graphene. Over the wide range of frequencies, the values of G' were greater than G'' , which illustrates the elasticity of the composed gel. In addition to this point, it was found that the addition of nano-graphene along with the presence of silicate sodium has shown small sensitivity to temperature and time.

3.2.2.2 Improvement in gel strength and thermal stability:

Nano-clay: a study by Tongwa and Bai⁸⁰ proposed a new Preformed Particle Gel using a nanomaterial in the main composition, called nanocomposite hydrogel. The proposed gel is composed of monomer, initiator, crosslinker, additives, and nano-clay called laponite XLG (L-XLG) which does not exist in the conventional hydrogel (see Figure 12).

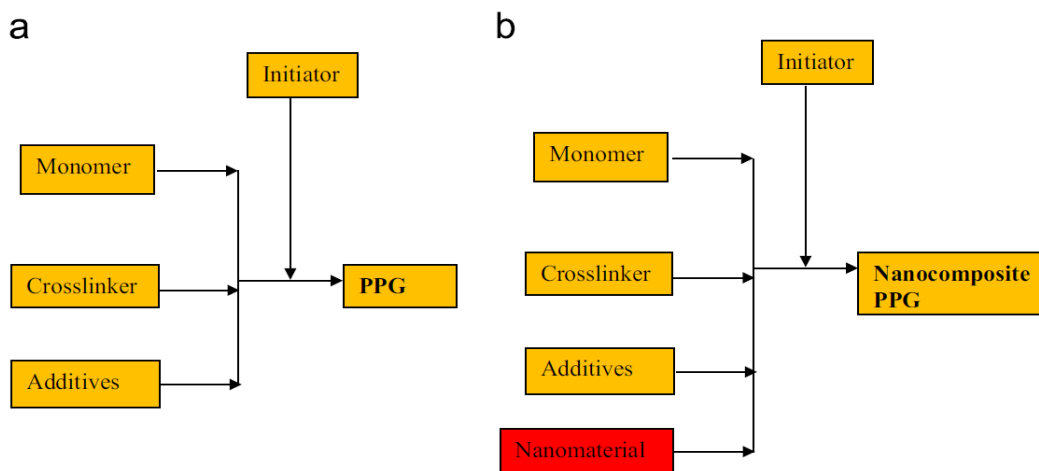


Figure 12 Nano Composite PPG.⁸⁰

Viscoelastic properties, such as elastic moduli, were used to evaluate the mechanical performance of nanocomposite preformed particle gel. A significant increase in elastic modulus was noticed along with an increase in the concentration of nanomaterials, leading to further improvement in gel strength properties as illustrated in **Error! Reference source not found.**⁸⁰ **Error! Reference source not found.** shows the changes in elastic modulus with increase in concentration of LXLG concentration. The lowest value for the elastic modulus was for the gel without nanomaterials (800 Pa), and it greatly increased with the addition of nanomaterials.

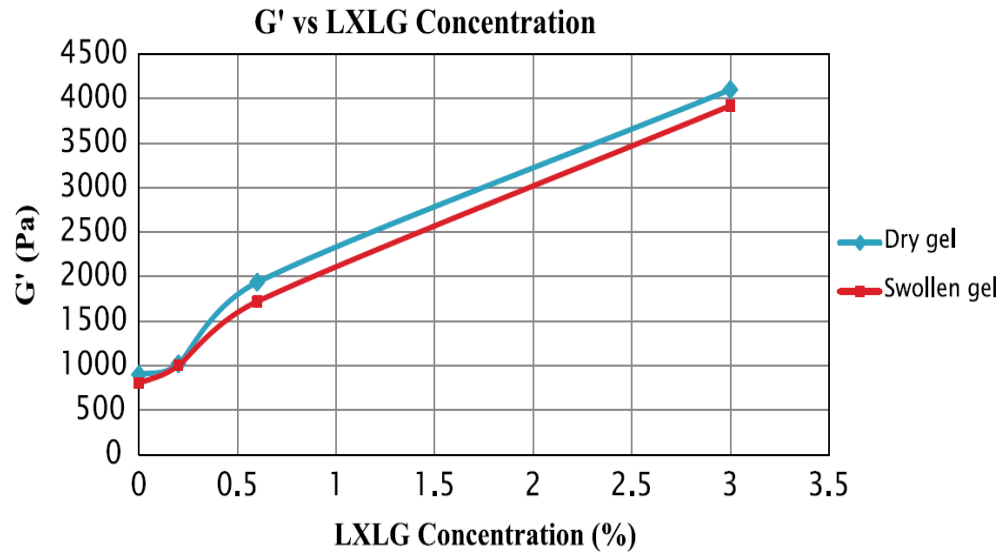


Figure 13 Effect of nano-clay concentration on gel strength.⁸⁰

The swelling performance was also evaluated in formation water and 1% brine solution. The results showed an obvious increase in the swelling kinetics of gel with nanomaterials in formation water, the swelling ratio was 180%, and in 1% brine solution (NaCl), it exceeded 400%.

For thermal stability, a significant increase in thermal stability for a long period was obtained for a gel with nanomaterial (up to years). This improvement supports the idea of adding nanomaterial to gel composition to serve water shutoff objectives for an extended period. However, it was noticed that after degradation, there was a substantial increase in viscosity. The viscosity of nanocomposite gel was 4,437 cp, which is much higher than the viscosity of gel with no nanomaterial (170 cp). This suggests that nanocomposite gel can

be used to first plug the thief zones and then after degradation, form a high viscous polymer solution that boosts water and polymer flooding.⁸⁰

Pandit et al.¹³⁸ conducted a study to assess a newly formulated PPG reinforced with bentonite nano-clay and nano-silica. The system demonstrated exceptional thermal stability over a two-year period at 120 °C. Moreover, the research examined the plugging efficiency of the gel, revealing a high rate of 97.6% for a 1 wt% reinforced preformed particle gel. These results suggest promising opportunities for utilizing the developed material in water shut-off applications.

2.4.2.3 Silicate Gel:

Recently, Nano-silica based fluids were introduced to the industry as an alternative to sodium silicate gels. Many studies investigated temperature limitation, activator concentration, and plugging efficiency. The real challenges for applying the silicate gel is the rapid gelation time along with maintaining a good plugging efficiency over an extended period. Through utilizing nano-silica solution, a better performance was observed and can be illustrated as below:

2.4.2.3.1 Adjustment of Gelation Time

Boul¹³⁹ et al. conducted experiments using different sizes and shapes of nano-silica to examine their effect on gelation time under a temperature range from 50 to 150 °F. Three tests were conducted on six nano-silica samples with different initial activity and shapes; the tests included the inversion test which measures the approximate gelation time of the different samples, Small-Amplitude Oscillatory Shear (SAOS), and Turbiscan™ tests that both confirm the gelation time precisely. The results led to the conclusion that nano-silica of non-spherical shapes could provide superior gelation time at temperatures as low as 50 °F, and also the samples with high aspect ratio built stable gels in a shorter period than the spherical ones.

Almohsin¹⁴⁰ et al. performed lab experiments to examine certain chemical properties that assist in evaluating the performance of nano-silica based systems for water shut-off applications. In their study, the authors examined the effect of temperature on gelation time as well as how to adjust it by modifying the concentration of the activator. The results of experiments showed that the increase in temperature greatly accelerates the gelation time,

as the gelation time is required to be sufficient for successful gel placements. In addition to this point, increasing activator concentration led to a shorter gelation time under a wide range of temperatures from 50 to 200 °F.

Karadkar¹⁴¹ et al. also performed lab experiments on using nano-silica based fluid for water shut-off applications. To examine the rheology behavior, they conducted experiments on rheology tests with different concentrations of activator at 200 °F. Using the viscosity buildup against time, it was found that gelation time was less sensitive to a higher concentration of 24% and 25% and was susceptible at a lower concentration from 21% to 23%. It was possible to optimize the gelation time from 125 to 490 mins.

2.4.2.3.2 Enhancing the Plugging Efficiency

Karadkar¹⁴¹ et al. conducted core flooding experiments to assess the injectivity and stability of the gel after placement (endurance test), the results were convenient as there was only a 10 psi increase for injection of five pore volume, this indicates the gel has a convenient injectivity. After placement, both N₂ and brine could not flow through the core plug (confirming excellent plugging efficiency).

In a study conducted by Almohsin¹⁴⁰ et al. to evaluate the injectivity and endurance of the nano-silica solution, core flooding experiments were conducted on Brea-Sandstone outcrop cores, four pore volumes were injected with a small increase in differential pressure, and by the continuous increase in the differential pressure until 4,000 psi a small leak off was recorded 0.0018 cm³/min. Microscope and SEM were used to examine the sliced pieces of the cores to determine the depth of invasion of the fluid, and they both confirmed that nano-silica-based fluid was capable of invading all the samples.

Based on these aforementioned experimental studies on different types of gel, it is obvious that nanomaterials such as nano-silica, nano-clay, and graphene can enhance gel performance for water shut-off treatments. In addition to that, Table 4 summarizes the impact of nanomaterials on improving the performance of these gels in terms of gel strength, gelation time, and thermal stability.

Table 4 Summary of nanomaterials' impact on gel properties.

Nanomaterial	Gel Type	Gel System	Impact	Reference
Silica		PAM crosslinked with HQ and HMTA	Increasing the maximum temperature of the stable gel from 137.8°C to 155.5°C by adding 0.3% nano-silica.	126
		HPAM crosslinked with chromium (III) acetate	Elevating the stable gel's maximum temperature from 140.8 to 157.9 by incorporating 2000 ppm of SiO ₂ nanoparticle.	127
	In situ Polymer gel	HPAM crosslinked with chromium (III) acetate	Elevating the stable gel's maximum temperature from 140.8 to 157.9 by incorporating 2000 ppm of SiO ₂ nanoparticle.	127
	PPG	Acrylamide, AMPSNa (2-Acrylamido-2-methyl-1-propane sulfonic acid sodium salt monomer) with linking agent polyethylene glycol diacrylate	Enhancing the swelling ratio with lesser syneresis. The gel becomes more temperature-durable.	136
		Nano-silica based fluid	Accelerating gelation time at low temperatures as 50 °F.	139
	Silicate Gel	Nano-silica solution with activator	Adjust the gelation time at a wide range of temperatures between 50 °F and 200 °F.	140
			Achieving 100% plugging efficiency with acceptable injectivity.	
			Achieving 100% plugging efficiency for both water and nitrogen.	141
Clay			Increasing Young's modulus of the gel enhances the gel strength.	80

	PPG	Acrylamide crosslinked polyethylene glycol diacrylate	Increasing the long-term thermal stability of the gel for up to 12 months.	
Graphene		PAM crosslinked by N,N-methylenebisacrylamide (BIS)	Increasing the thermal stability of the hydrogel by building a strong interaction between graphene sheets.	129
			Enhancing the gel strength by increasing the cross linking density.	
	In situ polymer gel	PAM cross-linked with N,N'-methylenebisacrylamide	Increasing the gel tensile strength by 4.5 times more than 300% elongation.	132
		PAM crosslinked with Metal Oxide/Two dimensional Nanosheets ZrO ₂ /RGO	Providing a superb mechanical strength was observed at elevated temperatures.	133
	PPG	PPG	Increasing the gel strength with superior rheological properties.	137
	In situ Polymer gel	PAM crosslinked with Chromium (III) acetate	Enhancing the gel strength with a higher thermal stability.	130
Zirconium hydroxide	In situ Polymer gel	PAM crosslinked with hydroquinone and hexamethylenetetramine	Improving the thermal stability of the gel to temperature up 187 °C.	125

2.5 Treatment Modelling and Field Cases

2.5.1 Gelation Time Modelling

Gelation time (GT) is one of the essential parameters for designing successful water shutoff treatments. Most mathematical models for polymer gels fundamentally include one dependent variable, “GT” and three independent variables, temperature, polymer

concentration, and crosslinker concentration.^{142,143} To study the gelation kinetics of water shutoff in-situ gels, steady shear rate measurements have been widely used.^{144–147}

The Arrhenius equation¹⁴⁸ (Equation 2.1) represents the effect of absolute temperature on reaction rate. It details the mechanism of a chemical reaction, and it applies to most of the chemical reactions. Hurd and Letteron¹⁴⁹ developed an empirical model (see Equation 2.2) correlating the gelation time of silicic acid gels with temperature close to the Arrhenius equation. They validated this correlation using experimental data with some assumptions. Below are the beliefs they followed to develop the model¹⁴²:

- The gelation reaction is classified as an ordinary chemical reaction with the n^{th} -order rate law.
- The experimental data matches the Arrhenius equation.
- The reacted silica at the gelation point remains the same at all reaction temperatures.

$$\ln k = \ln A - \frac{E_a}{R} \frac{1}{T} \quad (2.1)$$

$$\ln t = \ln c - \ln k - (n - 1) \ln a \quad (2.2)$$

Where a is the fractional conversion, c is simply a constant depending on the value of a , n is the reaction order, t is the gelation time, and k is the rate constant.

The developed model by Hurd and Letteron¹⁴⁹ was verified by Jorden et al. Jorden¹⁵⁰ et al. using PAM/Cr(III) gel system to examine the effect of temperature on GT. They proved that many chemical reactions can be analyzed using the Arrhenius equation.

From the Arrhenius-type equation, Broseta¹⁵¹ et al. similarly validated the relationship between GT and temperature. His research focused on the PAM/Cr (III) acetate system. He investigated that the GT is a function of multiple parameters: temperature, polymer and crosslinker concentrations, brine salinity, and degree of hydrolysis. Additionally, he verified that temperature has the highest impact on GT compared to other parameters, and it followed the Arrhenius equation. Marfo¹⁵² et al. studied a water shutoff gel consisting of an acrylamide-acrylate copolymer crosslinked with a polyamine crosslinker. Using statical

analysis software, he developed a predictive GT model (Equation 3) for temperature, crosslinker concentration, and water salinity.

$$GT = 38.4333 - \frac{13}{75}T + \frac{19}{30}S - \frac{67}{30}C + \frac{1}{100}TC - \frac{1}{300}TS \quad (2.3)$$

Equation (2.3) was very efficient ($R^2 \sim 98\%$) where GT is in hours, T in °F, S is the salinity of mixed water (%) and C is the crosslinker concentration (wt%).

2.5.2 Modelling Water Shutoff Performance

Xianchao¹⁵³ et al. predicted the water shutoff performance in horizontal wells utilizing the gel flow physics during and after gel treatment by modifying the personal computer gel (PCGEL) simulator that involves black oil and in situ gel models. The degradation process of the gel was considered using viscosity and the time-varying residual resistance factor (RRF) models. They also integrated the non-Newtonian fluid behavior within pressure drop calculations along the wellbore. After that, the coupled model was solved numerically. Finally, the coupled model presented outstanding and reliable prediction results utilizing an actual horizontal water shutoff treatment field scenario.

Alghazal and Ertekin¹⁵⁴ proposed an artificial neural network (ANN) as a machine learning module for deep polymer gel conformance treatments in fractured reservoirs. This module was benchmarked with commercial simulators as it minimizes the complexity of a simulation module. The developed ANN module outperformed commercial simulators with higher processing speed and less computational complexity. In addition, the module utilizes reference simulation modules to construct the dataset for the ANN module. Additionally, the module involves the chemical reaction of Polyacrylamide-based polymer with a Chromium Acetate crosslinker. The physical properties of the polymer and produced gel were generated from experimental data. The ANN module included various parameters based on reservoir properties and conformance design factors. After injecting the gel treatment, the predicated model has two indicators that rely on oil and water rate profile enhancement.

Meshalkin¹⁵⁵ et al. presented a three-dimensional computer model that simulates the process of water shutoff performance within high water cut oil zones. The model considers

the geophysical characteristics of the bottomhole formation zone, as well as the rate and amount of water control solutions that are injected in it. The model's effectiveness was validated by comparing the calculated values of water cut and oil production rate with actual well performance data after water shutoff treatment. This confirms that the model is sufficiently accurate and can be applied to increase energy and resource efficiency in oil production.

The study by Ferreira¹⁵⁶ et al. focused on the creation, training, and validation of a neural network model that can predict the performance of wells following gel treatment injection. This model is designed to rank wells that are candidates for water shutoff treatments based on potential production results, thereby enhancing the design of future treatments, and optimizing the use of economic resources. The researchers explored various configurations of the neural network, including adjustments to the number of layers, neurons, and transfer functions, to enhance the model's accuracy.

2.5.3 Limitations of Proposed Models

The existing coupled numerical models in the literature for water shutoff using gel treatments emphasize on simulating conventional black oil or compositional multi-phase flow and account for the water treatment process by basically modifying the production index or permeability around the wellbore. For instance, these models do not fully integrate a dynamic model between the wellbore and the reservoir. They lack a wellbore model that can handle the non-Newtonian flow behaviour of gels, coupled with a gel-blocking prediction model in the reservoir that simulates gel propagation and blocking. The current state-of-the-art in coupled modelling does not fully address or integrate these two key aspects. The existing coupled models simplify the gel blocking effects and do not capture the complete dynamic interactions involved.^{153,157,158}

Despite the availability of numerical simulation tools for designing water shutoff treatments, there exists a gap between prediction accuracy and field performance due to inadequate consideration of fluid composition and reservoir properties during the design and optimization stage. Consequently, this can significantly impact the efficiency of the treatment and, eventually, the project's economic viability.

2.5.4 Field cases in Oil Wells

Water production in oil and gas wells is a common challenge faced by the petroleum industry. Water breakthrough can reduce the productivity of the well, increase the risk of formation damage, and lead to environmental problems. To mitigate the adverse effects of water breakthrough, various water shutoff treatments have been developed and implemented. This section analyzes field cases focusing on the utilization of polymer gels (preformed gels, foamed gels, in-situ crosslinked gels), resins, and Nano-silica. The treatments are compared based on their advantages and disadvantages, considering the reservoir temperature for each case.

2.5.4.1 Polymer Gels

In-situ crosslinked gels offer the advantage of being pumped as a low-viscosity fluid and then subsequently crosslinked in the reservoir to form a gel. In-situ crosslinked gels have been successful in high-temperature reservoirs of more than 150 °C, but they may face challenges related to gel degradation and incomplete gelation.^{11,40,159}

A modified organically crosslinked polymer gel was successfully field tested in an oil producer located in the Meleiha concession in Egypt's Western Desert. The well initially produced 1900 BOPD with a 30% water cut, but production declined over time and the well was shut in due to low productivity. The well was produced from two intervals in a sandstone reservoir. The upper interval was depleted to 777 psi, while the lower interval maintained 3300 psi due to a strong aquifer. The polymer gel was selected to treat the upper depleted interval using coiled tubing to achieve a treatment penetration radius of 3 ft by having eight hours of gelation time. This zone had a temperature of 200 °F. After pumping the treatment, the well was shut in for two days. The upper interval was then positive pressure tested to 3500 psi. The lower interval was opened and had an initial oil rate of 2500 BOPD with zero water cut.¹⁶⁰

Preformed particle gel (PPG) technology has been effectively employed in many mature oil fields across China, including Daqing, Zhongyuan, Liaohe, Shengli, Tuha, Dagang, and Jidong. These fields exhibit a range of challenging conditions such as high salinity and temperature in Zhongyuan, severe channels and high temperature in Dagang, and natural fractures in Tuha. By 2007, around 2,000 wells across Chinese oil fields had been treated

using PPG, with the amount of dried PPG per treatment ranging from 3,000 to 40,000 kg. All PPG injection operations were conducted without issues of reduced injectivity.^{75,82,161}

In 1999, the first successful treatment using preformed particle gels (PPGs) was implemented in the SINOPEC reservoir, located in the Zhongyuan oilfield, China.^{71,162,163} Since then, PPGs of millimeter size have been extensively utilized in China, with over 4000 wells benefiting from their application for conformance control and the reduction of permeability in fractures and highly permeable channels.^{9,161}

Foamed gels provide improved mobility control during injection and have shown success in water shutoff applications. The foaming process enhances gel placement and distribution. Their thermal stability allows for application in reservoirs with temperatures more than 100 °C. However, challenges exist in maintaining gel stability and overcoming issues related to foam generation and transport.^{164,165}

A gel foam water shutoff system was tested in Huoshaoshan fractured oilfield Well H1304 on November 11, 2005. The treatment was successfully tested in an oil producer in a fractured reservoir with low permeability and a temperature of 55°C. Since January 2009, oil production has increased by 7800 m³, demonstrating good economic benefits. In this well, the fluid production rate did not decrease while the water cut decreased greatly because of the treatment.¹⁶⁶

2.5.4.2 Resins

Resins, such as phenol-formaldehyde and epoxy-based resins, have been employed for water shutoff treatments. They exhibit excellent mechanical strength and chemical resistance, making them suitable for harsh reservoir conditions. Resins can withstand high temperatures (e.g., up to 150 °C) and are effective in treating highly permeable zones. However, they can be challenging to inject due to their high viscosity, and the curing process may take an extended time, limiting their applicability.^{167,168}

A phenol-formaldehyde system was successfully trial tested in a vertical oil producer located in the GA field in western India. The reservoir was characterized by extremely low permeability, a high temperature of 130-150 °C, and highly consolidated, homogeneous, thin sandstone with high gravity oil. The pre-treatment flowback experienced a 100% water

cut with 317 BWPD of water production. The main factors were determined to be a rise in oil-water contact (OWC) and water coning. The planned gel volume was 16 m³. Because of low injectivity, the actual injected volume was around 5 m³. It effectively blocked about a 4.5-meter radius of the formation. The treated well produced around 200 barrels of oil per day for several months after the treatment. The water cut dropped from 100% to 48%.^{169,170}

2.5.4.3 Nano-silica gel

Nano-silica particles can be used as water shutoff additives and fluid-based systems due to their ability to reduce water permeability. They have been effective in both low and high-temperature reservoirs, with varying particle sizes and concentrations. Nano-silica is an eco-friendly material that has been utilized by oil producers for water and gas shutoff applications.^{171,172} Nano-silica treatments can be easily injected and exhibit good thermal stability up to 350 °F.^{140,173,174}

Nano-silica was successfully field tested in a horizontal oil producer. The well was drilled across a carbonate formation with 3,000 ft of reservoir contact including seven compartments with 38 ICDs. Before treatment injection, the well was thoroughly diagnosed utilizing noise log, and temperature survey. The pre-job analysis confirmed that excess water production was coming from the middle compartment which impacted the integrity of mechanical packers resulting in cross-flow behind the casing. The length of this compartment was 500 ft which contains six ICDs. The water shutoff treatment was pumped through coiled tubing after setting an inflatable packer above the compartment and a bridge plug below it. The post-treatment analysis (PLT, noise, and temperature logs) and flowback have proven the increase in oil production from the other compartments and an 80% reduction in water production.¹⁷⁵

2.5.4.4 Nano-based particulate gel

The Southeast Kuwait field has been produced from sandstone formation. A production test was conducted on a cased hole oil producer and indicated 90% of water cut out of 300 BPD of total produced liquids. The test revealed that water came from a 12 ft section of the perforated interval. A decision has been made to isolate the water zone through coiled tubing utilizing a particulate gel as a single nano-additive. The post-treatment flowback

showed an increment in oil production to 1,000 BOPD and only 1% of water cut. This particulate gel has been considered a reliable and cost-effective fluid to seal off the water zone layer. The system was smoothly mixed and injected into the targeted zone.^{176,177}

2.6 Research Gap and Future Development

Water shutoff treatments in oil and gas wells utilize various techniques and materials, each with its advantages and limitations. Polymer gels, resins, and Nano-silica have been applied in a wide range of reservoir temperatures. Preformed gels offer thermal stability but require careful placement. Resins exhibit excellent mechanical strength but may have limited injectability. Nano-silica treatments are versatile and can be applied in ultra-high temperatures. Further research and field studies are necessary to optimize water shutoff treatments based on specific reservoir conditions. The advancement in the utilization of nanomaterials can play a major role to enhance gels' performance, some of future challenges can be illustrated as below:

(1) In-situ and preformed particle polymer gel:

- While studies have demonstrated the positive impact of nanomaterials like nano silica, nano-clay, and nano-graphene, future research should explore a wider range of nanomaterial approved their applicability in EOR applications, such as Aluminum Oxide (Al_2O_3), Titanium dioxide (TiO_2) and Zinc Oxide (ZnO). The compatibility with different polymers and compositions is also an area of research that needs further investigation. Understanding the most effective nanomaterial-polymer combinations can enhance the applicability of these gels.
- Long-term stability and performance, as well as potential degradation, are areas demanding further investigation. Understanding how these gels behave over extended periods within reservoirs is essential. This includes assessing the longevity of gel stability and identifying potential degradation mechanisms to ensure the continued effectiveness of these gels in preventing water flow.
- Nanomaterials significantly enhance the mechanical properties of the gel while ensuring thermal stability. This makes them a viable solution for

applications in harsh environments, including temperatures exceeding 300 °C and environments with high salinity levels. Further investigations are needed in this area.

- The transition from laboratory experiments to field applications is a critical research gap. Extensive lab work and field trials are needed to validate the practicality and effectiveness of nanomaterial-enhanced gels in actual reservoirs with different characteristics.

(2) Nano-silica based gel:

- Studies have indicated that gelation time is sensitive to temperature variations. Future work can work deeper into the mechanisms underlying this sensitivity and explore additives to mitigate the impact of temperature on gelation time. This is essential for ensuring that silicate gels can be placed successfully over a wide range of temperatures.
- While the research has confirmed that nano-silica can enhance the plugging efficiency of silicate gels, additional studies can focus on the long-term stability and endurance of these gels under reservoir conditions. This includes assessing their injectivity, stability, and plugging efficiency over extended periods to confirm their effectiveness in preventing unwanted water flow.
- Given its outstanding plugging efficiency of 100%, nano-silica gel presents itself as a viable alternative to polymer in-situ gels. Notably, its low viscosity and environmental friendliness further enhance its appeal for various scientific applications.

2.7 Conclusions

Polymer and silicate gels are considered the most widely applied chemical systems for water shut-off applications. The use of nanomaterials in water shut-off applications has the potential to significantly improve the efficiency and effectiveness of these treatments. The placement process is highly affected by the gelation time as a critical factor along with the impact the reservoir characteristic. Therefore, modelling treatment will assist in

improving agents' performance as water shut off agents. Eventually, the impact of nanomaterials could be concluded to:

1. Nanomaterials such as nano-clay, nano-silica, and nanographene, can play a major role in adjusting the properties of in situ gel such as control of gelation time (9-10) hours, enhancing gel strength up 4.5 times, and maintain thermal stability at high temperature (187 °C).
2. Adding nanomaterials to the composition of PPG could help to adjust swelling ratio by percentage up to 400% and improve the strength of the formed gel to withstand the reservoir conditions (elastic modulus 4,437 Pa).
3. The experimental results of nano-silica gel showed improvement in the plugging efficiency up to 100%, which enhances the idea of potential usage as a plugging material along with other advantages of silicate systems.

CHAPTER 3

LONG-TERM INVESTIGATION OF NANO-SILICA GEL

AS A WATER SHUT-OFF AGENT IN PERMEABLE

MATRIX²

3.1 Abstract

The oil and gas industry faces numerous challenges, among which the management of excessive water production is a significant concern. Nano-silica gel is a newly developed silicate gel for water shut-off applications. No investigation has been conducted to evaluate the gel's performance over an extended period. The objective of this study is to evaluate the long-term performance of nano-silica gel in a permeable matrix over 6 months, while also comparing this performance with polyacrylamide/polyethyleneimine PAM/PEI gel. Coreflooding experiments were conducted to evaluate the performance of the nano-silica gel of 75/25 wt% (nano-silica/activator) and PAM/PEI gel (9/1 wt%) on carbonate core samples at 200°F. The experiment involved initial permeability assessment, gel placement, and endurance tests up to 1000 psi. Additional measurements of computed Tomography (CT) scan and nuclear magnetic resonance (NMR) were implemented, CT scans visualized density changes and NMR measured fluid distribution in the pore system. Then, Samples

² This chapter is copied from the manuscript: Ali, A.; Al-Ramadan, M.; Aljawad, M.; Alabdrabalnabi, M.; Almohsin, A.; Sultan, A.; Azad, M. Long-term Investigation of Nano-Silica Gel as a Water Shut-off Agent in Permeable Matrix.

were aged at 167 °F for six months, with durability tests (up to 1000 psi) conducted in the first, third, and sixth months to assess gel plugging efficiency. The results demonstrated nano-silica gel's remarkable plugging efficiency, achieving a reduction in permeability from 144.85 to 0.001 mD initially and sustaining pressures up to 1000 psi with minimal leak-off rates. After 6 months, nano-silica gel maintained plugging efficiency above 99.98%, while PAM/PEI gel efficiency reduced to 99.85%. The nano-silica gel exhibited better long-term performance with a maximum leak-off rate of 0.25 cc/min 6 months, compared to 2.165 cc/min for the PAM/PEI gel. The nano-silica gel achieved better long-term performance than PAM/PEI gel with a maximum leak-off rate of 0.25 cc/min in 6 months (2.165 cc/min for PAM/PEI gel). CT scan analysis confirmed effective gel placement within the pore systems, and minimal degradation occurred over time with less significant impact on the efficiency of nano-silica gel compared to PAM/PEI gel.

3.2 Introduction

In petroleum fields, the persistent challenge faced by oil companies worldwide is the occurrence of excessive water production during well production life¹. Excessive water production refers to the unwanted influx of water alongside oil. It occurs when water production competes with oil production due to certain wellbore problems,^{7,15,22} geological factors, and reservoir characteristics.^{7,13,15,22} The produced water not only reduces the oil recovery but also increases operational costs by requiring more extensive separation and water treatment or disposal processes. Additionally, it can damage production equipment and reservoirs, leading to reduced productivity and increased risks of failure. Therefore, managing excessive water production is crucial for maintaining profitability and minimizing environmental impact in petroleum operations. In 2000, Bailey¹⁵ et al. documented a worldwide ratio of three barrels of water produced for every barrel of oil, amounting to a significant 75 billion barrels of co-produced water, with disposal expenses estimated at \$40 billion. Pappas²³ and co-authors specified that the United States independently produced about 24.4 billion barrels of co-produced water. These numbers indicate the negative impact of the produced water on well productivity.

Different mechanical and chemical methods were applied to tackle the water production problem. Gel treatments are considered one of the most cost-effective chemical methods to treat different water problems such as flow behind pipes, high permeable layers, fractures, and water coning.^{4,69,82,178–180} They can be classified into two types: organic gel (polymer gels) and inorganic gels (silicate gels).¹⁸¹ This study focuses on the application of a newly developed silicate system to mitigating water production problems from permeable layers. Over the last decade, silicate gels have been commonly employed method for addressing excessive water production, representing one of the earliest techniques used for this purpose. By injecting specially formulated silica gel (silica solution mixed with activator) into the wellbore or reservoir matrix, impermeable barriers are formed to block water flow.^{99,100} This targeted approach minimizes production disruptions and maximizes reservoir sweep efficiency, thereby enhancing overall hydrocarbon recovery. This gel system offers several operational advantages, including good injectivity due to its lower viscosity and convenient thermal stability at elevated temperatures. Moreover, silicate gels are cost-effective compared to polymer gels and are environmentally friendly.^{106–108} However, their application has certain drawbacks, such as reduced gel strength over time, rapid gelation, and sensitivity to divalent ions in the formation.^{101,106,181} Maintaining high gel strength is crucial for water shut-off treatments because the applied material is expected to function efficiently for extended periods, sometimes lasting for years.

In recent years, the emergence of nanomaterials has become a focal point in the oil and gas sector. Nanomaterials exhibit promising capabilities in enhancing material performance for diverse applications, including enhanced oil recovery,¹⁸ reservoir imaging,²⁰ and water shut-off.¹⁸¹ Numerous studies have demonstrated their capability to plug pore throats,^{182–184} making them well-suited for water shut-off treatments. A notable advancement in the field of water shut-off systems involves the adoption of nano-based silica gel over traditional silicate systems. The newly developed nano-silica gel incorporates nano-sized silica particles, in contrast to the larger silica particles used in previous silicate systems. This distinction enables the gel to exhibit superior plugging performance characteristics for water shut-off applications. Several studies have been conducted to comprehend the gelation behavior of nano-silica gel under various conditions. Boul¹³⁹ et al. conducted

experiments to explore the relationship between particle size and shape on gelation behavior at low temperatures (50 °F). Their findings indicated that non-spherical nanoparticles could prolong the gelation time. Similarly, Almohsin¹⁴⁰ et al. investigated gelation behavior across different temperatures, observing that higher temperatures shorten the gelation time. However, manipulations of the activator concentration can influence gelation time. Additionally, Karadkar¹⁴¹ et al. delved deeper into the sensitivity of gelation time to activator concentration. Their experiments revealed that the gelation time of nano-silica gel is more sensitive to activator concentrations of 24% and 25%, while showing less sensitivity to lower concentrations of 21% and 23%.

The effectiveness of gel plugging is crucial for water shut-off applications, especially its durability over extended periods. Several studies have investigated the plugging capabilities of nano-silica gel. Almohsin et al.¹⁴⁵ conducted a 15-day endurance test on treated core samples with a permeability of 400 md, showcasing the gel's durability over two weeks with minimal leak-off rates at 300° F. Karadkar⁷ et al. evaluated the plugging efficiency of nano-silica gel on Berea sandstone samples with a permeability of 190 mD at 200 °F. After gel treatment, brine injection led to a significant increase in differential pressure, indicating effective pore space plugging. An 8-hour endurance test at 2,500 psi differential pressure exhibited no leak-off rates.⁷ Furthermore, Almohsin¹⁴⁰ et al. investigated nano-silica gel plugging on higher permeability (700 mD) formations. During a 12-day endurance test with continuous pumping at 4000 psi, an average leak-off rate of 0.0018 cc/min was observed.¹⁴⁰ Despite the insights gained from these studies regarding the short-term performance of nano-silica gel, there's still a lack of thorough assessments regarding its long-term effectiveness.

The objectives of this study are to assess the long-term durability of nano-silica gel within a permeable matrix over a 6-month period and to compare its performance with that of in-situ polymer gel, specifically polyacrylamide/polyethyleneimine (PAM/PEI) gel. Previous research has demonstrated the ability of PAM/PEI gel to achieve 100% plugging efficiency in Berea sandstone core samples at 90 °C.¹⁴⁴ Furthermore, it has showcased significant effectiveness in reducing water flow in challenging environments, achieving a remarkable 99.8% reduction in permeability over a 6-month period.¹⁸⁵ Through a comparative analysis

between nano-silica gel and PAM/PEI gel using similar sample characteristics, the superiority of one gel over the other can be determined.

3.3 Materials and Experimental Procedure

3.3.1 Chemicals

In this study, two gel systems were employed: nano-silica gel and PAM/PEI gel. The nano-silica gel consists of a mixture of nano-silica solution and activator, both supplied by Saudi Aramco. The components are combined in specific proportions to allow sufficient gelation time for proper gel placement. To prepare a 75/25 wt% (silica/activator) nano-silica gel, a certain volume of the silica solution was prepared in a 500ml beaker, and its weight was measured. Then, based on the desired percentage, an equivalent volume of activator was prepared and added to the silica solution. The mixture was stirred for 10 minutes until it reached a consistent state suitable for injection. The silica nanoparticles are discrete, possessing a smooth, spherical shape. The average particle size distribution of the nano-silica was 14 nm, determined using the FPIA-3000 (Malvern) particle size analyzer. The initial gel mixture exhibits an average viscosity of 6 cp, which accelerates with temperature as a result of gelation.

The second gel system, called PAM/PEI gel, consists of PAM (polyacrylamide) and PEI (polyethyleneimine). PAM, obtained from SNF Floerger in the form of an aqueous solution, was used without any further treatment. It had a concentration of 20 wt% active ingredients and a molecular weight ranging from 250 to 500 kg/mol, as specified by the supplier. PEI, functioning as a cross-linker, was provided in a solution form. To prepare a 30 mL sample of PAM/PEI solution with a weight ratio of 9:1, 13.5 mL of PAM was initially mixed with 15.5 mL of water and stirred for about one minute. Subsequently, 1 mL of PEI was added to the mixture, which was then stirred for an additional 10 minutes. For measuring permeability and conducting endurance tests, a brine solution containing sodium chloride at a concentration of 0.1M per liter was utilized.

3.3.2 Methodology

3.3.2.1 Study Plan:

The plan for this study involves conducting an initial gel treatment on permeable limestone samples, followed by an endurance test to confirm the initial plugging efficiency. Once the sample is plugged with gel, it will undergo three aging stages over a period of 6 months. A comprehensive experimental plan for the 6-month duration is illustrated in Figure 14. After the first aging period of one month, an endurance test was conducted to evaluate the plugging efficiency. Simultaneously, a computed tomography (CT) scan was performed on the core sample to detect any gel degradation. These steps of the endurance test and CT scan were repeated for the second aging stage (2 months) and the third aging stage (3 months). By the end of the sixth month, the plugging performance of the gel was evaluated and compared to its initial performance, along with determining the rate of degradation. This systematic approach provided insights into the long-term effectiveness and stability of the gel treatment.

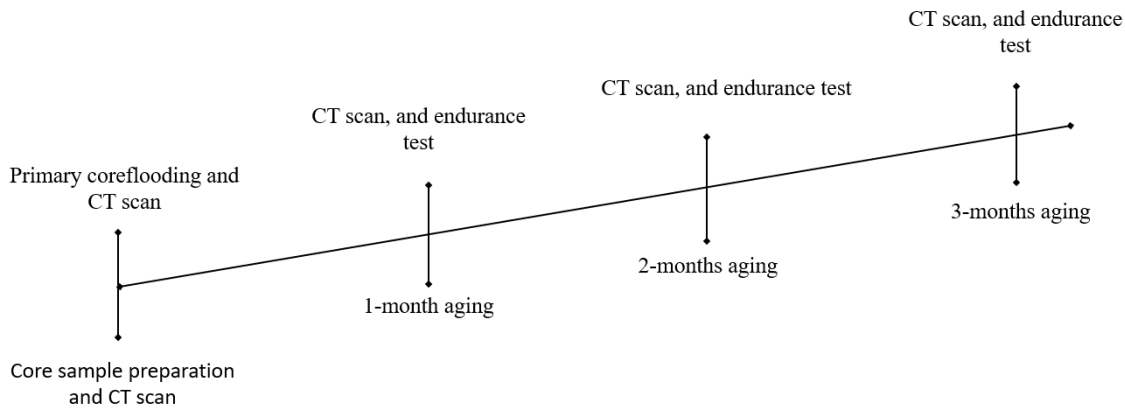


Figure 14 Investigation methodology.

3.3.2.1.1 Coreflooding

Coreflooding experiments were conducted to mimic the gel treatment operation and assess the initial plugging efficiency of the gel. The experiment involved three stages: a pretreatment stage to assess the initial samples' permeability, a gel injection stage, and a post-treatment stage to evaluate the efficiency of gel sealing. A schematic diagram in Figure 15 illustrates the components of coreflooding system used in the study. This system

consists of a 1.5-inch core holder equipped with two pressure transducers to measure both inlet and outlet pressures. Two pumps are incorporated, with one applying confining pressure to the core holder and the other injecting fluid through two accumulators – one for gel situated outside the oven and another for brine placed inside the oven. To maintain consistent pressure and replicate reservoir conditions, a back pressure regulator is employed and set at 400 psi. Additionally, medical CT scans and nuclear magnetic resonance (NMR) measurements are utilized to characterize the pore system of the samples before and after gel treatment.

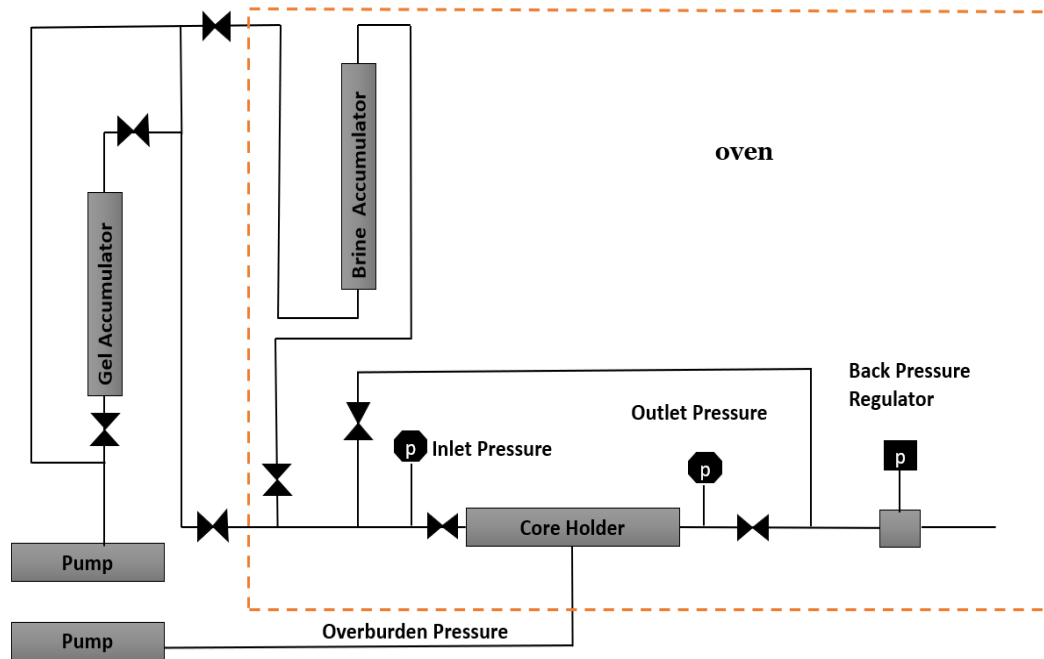


Figure 15 Coreflooding system.

To conduct the coreflooding experiments, initial assessments of core sample properties, including porosity and bulk volume, were conducted. Subsequently, a medical CT scan was performed on the dry sample to obtain detailed imaging. Following this, the core sample was saturated with brine (0.1M per liter), and T_2 NMR measurements were taken to analyze the pore system characteristics in the saturated state. The prepared core sample was then introduced into the coreflooding system, operating at 200 °F. Brine injection ensued, employing various flow rates, while corresponding pressure drop recordings were

made to assess initial permeability. Subsequent to brine injection, a gelant solution equivalent to 5 to 7 pore volumes was injected, followed by cleaning of the system lines to remove residual silicate gel. After a curing period of 48 hours for the treated sample, brine injection was resumed under constant differential pressure, and the leak-off rate was recorded at 200 °F. From the obtained leak-off rate and differential pressure, the plugging efficiency can be calculated by Equation (1), described below:

$$\text{Plugging efficiency (\%)} = \frac{\text{Initial Permeability} - \text{Final Permeability}}{\text{Initial Permeability}} \quad (3.1)$$

1. CT scan and NMR T₂ measurement:

To attain optimal plugging efficiency with the gel, it's essential to uniformly place an adequate amount of gel along the target zone. In our experiment, CT scan and NMR measurement were used to identify how the gel is distributed and its penetration length along the sample length. CT provides a detailed insight into the pattern of gel penetration. Scans were conducted both pre- and post-gel treatment, and the results were presented in terms of CT numbers. These numbers, measured in Hounsfield units, indicate the intensity of the transmitted X-ray beam and correspond to specific density values in g/cm³.¹⁸⁶ Therefore, alterations in CT numbers reflect changes in density. The density shift, as indicated by changes in CT numbers, is directly linked to the invasion of the gel.

NMR T₂ measurement serves as another tool to assess the impact of gel on the pore system characteristics of the core sample. This measurement, conducted before and after gel treatment, relies on the principles of nuclear magnetic resonance, which exploits the behavior of atomic nuclei in a magnetic field to understand pore structure and fluid characteristics. Specifically, in the context of pore size analysis, NMR T₂ measurement probes the dynamics of fluids within porous materials. The T₂ relaxation time represent the time for the NMR signal to decay to a certain percentage of its initial intensity. By subjecting the fluid-saturated sample to a magnetic field and radiofrequency pulses, we can observe the decay of the NMR signal, which is influenced by fluid mobility and distribution within the pore space. This analysis provides insights into the alteration of fluid distribution induced by gel treatment.

When examining fluid within porous materials, T_2 relaxation is influenced by three distinct phenomena: bulk relaxation, surface relaxation, and diffusion relaxation. T_2 relaxation time measurements are obtained utilizing the conventional Carr-Purcell-Meiboom-Gill (CPMG) pulse sequence. This sequence can be represented by a mathematical model:

$$Pl \frac{1}{T_2} = \frac{1}{T_{2,bulk}} + \rho_2 \frac{S}{V} + D \frac{(\gamma G t_e)^2}{12} \quad (3.1)$$

T_2 bulk represents the relaxation component associated with the unconfined bulk fluid, particularly significant when relaxation isn't limited by pore geometry. It's notable that T_2 bulk is inversely proportional to fluid viscosity.¹⁸⁷ ρ_2 denotes surface relaxivity, reflecting relaxation enhancement due to surface interaction, while S/V represents the surface area to volume ratio of the pore space. Surface relaxation dominates overall relaxation when fluid directly interacts with pore geometry. D refers to the fluid's self-diffusion coefficient, γ is the gyromagnetic ratio of proton nuclei, g signifies internal magnetic field gradients (in saturated rocks, due to variations in magnetic susceptibility between solid grain matrix and liquid phase), and t_e stands for echo time between NMR CPMG spin echoes. Typically, diffusion relaxation has minimal impact on carbonate rock samples acquired with low magnetic field instruments (like the 0.05 T system used here). Thus, the NMR signal at low magnetic fields from fluid-saturated rocks mainly depends on collective properties of bulk fluid and surface relaxation characteristics, as associated with the first and second terms on the right side of Equation (2), respectively.

3.4 Results and Discussion

3.4.1 Experiment 1 (Nano-silica gel)

In this experimental investigation, a limestone core sample designated as A1 was specifically chosen for its moderate permeability. The dimensions of the sample are provided in Table 5, while the solutions employed in the experiment are described in Table 6. The prepared solution of nano-silica gel has a concentration of 75% nano-silica and 25% activator, designed to provide enough gelation time during placement and avoid any plugging. The brine used is composed mainly of NaCl, used in the pretreatment stage for measuring the core sample permeability and in the post-treatment stage to conduct an endurance test.

Table 5 Core sample dimensions for sample A1.

Sample	Length (inch)	Diameter (inch)	Porosity (%)	Pore volume (ml)	Permeability (mD)
A1	2.83	1.5	21.88	17.99	100-200

Table 6 Chemical solutions of Exp. 1.

Stage	Solution
Pre-treatment	Brine (0.1 M per liter)
Gel placement	Nano silica gel (75% silica, 30% activator)
Post treatment	Brine (0.1 M per liter)

3.4.1.1 Primary flooding stages:

The experiment comprises three distinct stages illustrated in Figure 16. Firstly, the sample's initial permeability was evaluated by injecting a brine solution. Brine was injected with four different flow rates to a total of 10 pore volumes at 200 °F. The average brine permeability was approximately 132.01 millidarcies (mD).

After completing the assessment of the sample's initial permeability, the subsequent phase of the experiment focused on the injection of gel. This gel injection stage aimed to deliver between 5 to 7 pore volumes of nano-silica gel into the sample for optimal placement. The injection process involved the continuous flow of the nano-silica solution over 90 minutes, maintaining a steady flow rate of 1.5 cc/min. As a result, the total volume of gel injected into the sample amounted to approximately seven times the pore volume. Throughout the gel injection process, the variations in pressure drop were carefully monitored, as illustrated in Figure 16. Remarkably, the recorded pressure drop exhibited only a minimal increase, indicating a satisfactory level of gel injectivity for seven pore volumes. Additionally, the resistance factor, which reflects the sample's resistance to flow, was closely observed throughout the injection process, as depicted in Figure 17. The calculated

resistance factor, in conjunction with the observed lower differential pressure, provided further evidence of acceptable injectivity within the sample matrix.

After the completion of the gel placement phase, the sample underwent a curing period lasting 24 hours. Subsequently, an endurance assessment was conducted to evaluate the gel's pore-plugging capabilities. This involved subjecting the sample to gradually escalating levels of differential pressure, spanning from 250 psi to 1000 psi, as appeared in Figure 16. At each differential pressure level, a specific duration was maintained while monitoring the leak-off rate to examine the efficiency of the gel plugging process. Initially, the pressure was set at 250 psi for a duration of 30 minutes, during which no leak-off rate was observed, indicative of exceptional gel plugging within the pore spaces. Following this, the pressure was elevated to 500 psi and sustained for another 30 minutes, again exhibiting no detectable leak-off. Subsequent increments in pressure to 750 psi for 30 minutes revealed the appearance of initial droplets, with an average leak-off rate measured at 0.069 cc/min. To assess the durability of the gel, the pressure was further escalated to 1,000 psi and maintained for an extended period of 3 hours. Throughout this duration, the leak-off rate was recorded to be approximately 0.115 cc/min. The obtained results underscore the remarkable pore-plugging capabilities of the nano-silica gel, demonstrating an impressive plugging efficiency of 99.99%.

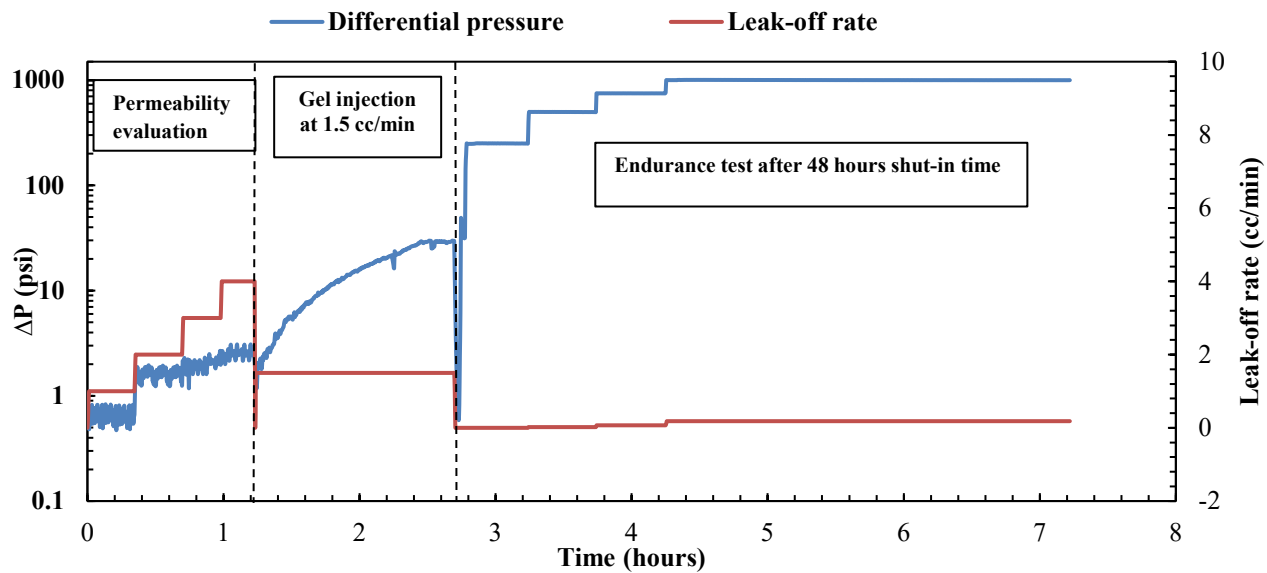


Figure 16 Experiment 1 coreflooding stages.

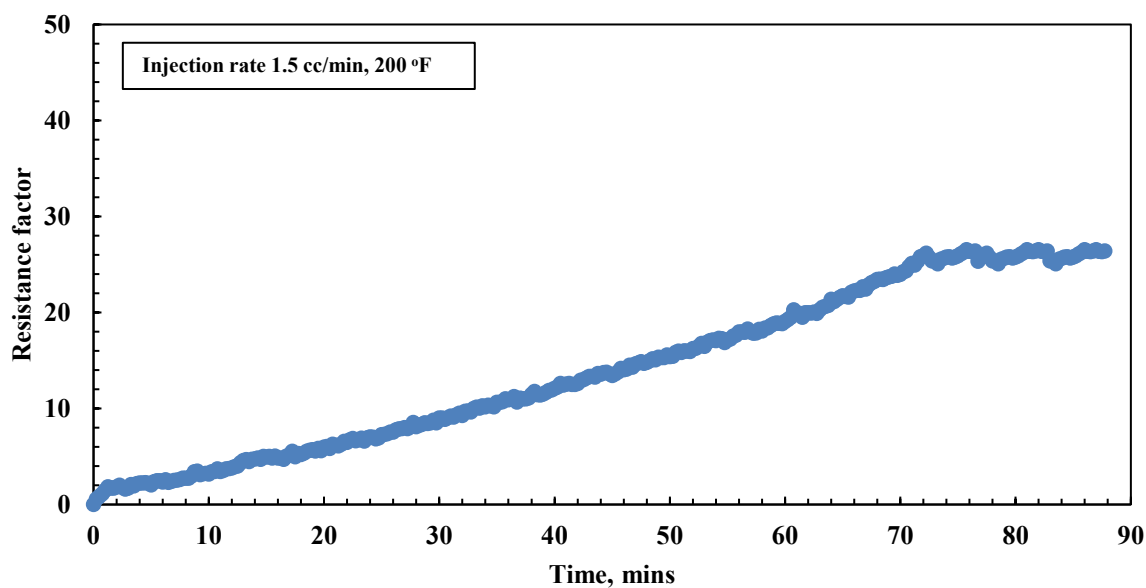


Figure 17 Resistance factor during nano-silica gel injection.

3.4.1.2 CT scan and NMR analysis:

3.4.1.2.1 CT scan:

To visualize the alteration in pore space following gel placement, CT scans were conducted before and after gel treatment. Figure 18 presents different slices of the core sample, showing the pore spaces before gel treatment (empty) and after gel placement. Darker colors indicate lower CT numbers or density, while brighter colors represent higher CT numbers (density). Comparing the slices, it's evident that after gel treatment, the sample exhibits a higher density distribution, indicating the presence of the gel in these pore spaces. Additionally, the average CT number of each slice along the sample length increased after gel injection from 2084.91 to 2273.00, confirming the uniform distribution of the gel along the sample length.

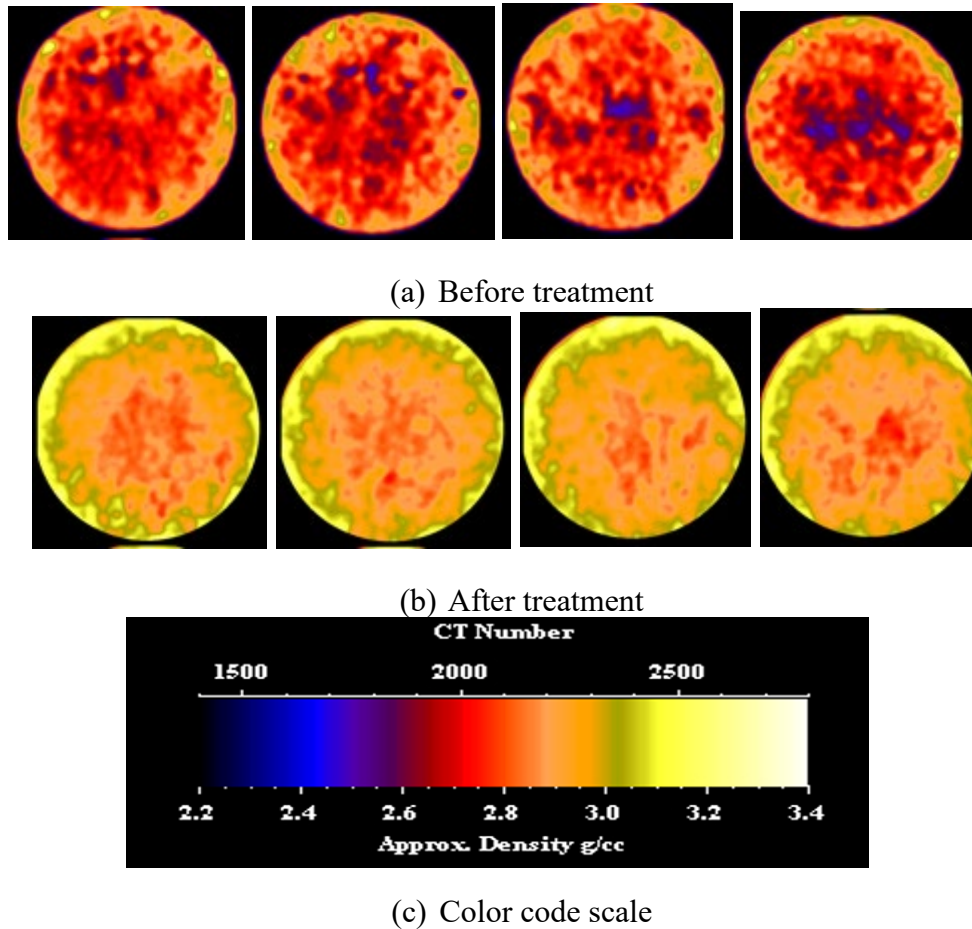


Figure 18 (a) CT scan images of dry samples before nano-silica gel injection; (b) CT scan images after nano-silica gel treatment; (c) Color code scale.

3.4.1.2.2 T₂ NMR measurement:

Initially, NMR assessments were carried out on both brine solution and nano-silica gel bulk fluids. The T₂ peaks corresponding to bulk-free brine and bulk-free nano-silica are indicated by black and red vertical dashed lines, respectively, in Figure 19. It is evident from the figure that water's relaxation time (around 2818 ms) is longer than that of nano-silica gel (approximately 32 ms), primarily due to a significant disparity in viscosity. When NMR measurements were conducted on the sample saturated with brine, it became apparent that the core manifests a bi-modal pore size distribution. Micropores demonstrate a shorter relaxation time, while macropores exhibit longer relaxation times. After gel treatment, the T₂ peak of the micropores shifted significantly to the left, becoming very close to the peak of nano-silica gel as the bulk fluid. This indicates that the gel has displaced most of the brine, causing a shorter relaxation time. Similarly, the T₂ peak of the macropores shifted, and T₂ values approached zero in the previous spot of the T₂ peak before gel placement. These results indicate that the gel has displaced the brine from the pore spaces extensively, leading to the achieved plugging efficiency.

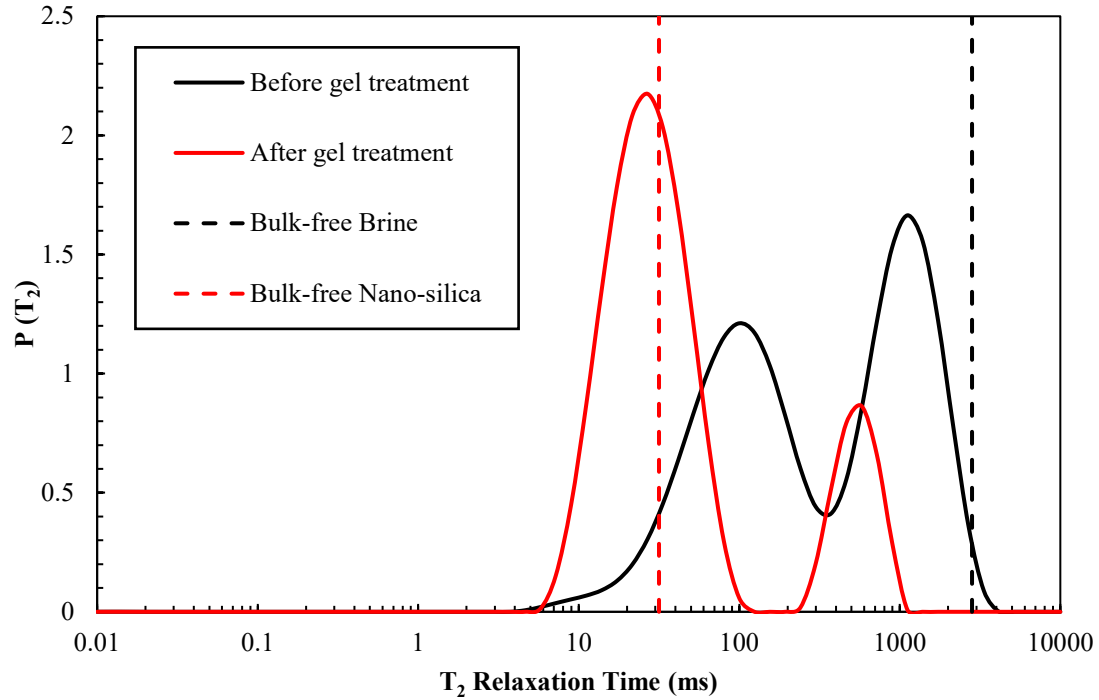


Figure 19 Average NMR T_2 before and after nano-silica gel treatment.

3.4.1.3 Gel durability over 6 months

First month: The sample underwent a 1-month aging period in formation water at 167 °F, followed by a 4.5-hour endurance test at 200°F, with the results displayed in Figure 20. The test was initiated with a 30-minute pressure hold at 250 psi, during which no leak-off rate was observed at the outlet. Subsequently, the pressure was increased to 500 psi for 30 minutes, then to 750 psi for an additional half-hour. The maximum leak-off rate during this period did not surpass 0.088 cc/min, a value very close to the leak-off observed in the post-treatment under the same differential pressure. To assess gel durability, the pressure was sustained at a constant 1,000 psi for 3 hours, resulting in a reported leak-off rate of 0.125 cc/min. Remarkably, the maximum leak-off rate remained steady, aligning with the post-treatment level, indicating the gel's durability at high differential pressure and sustained plugging efficiency at 99.99%.

Third month: Following the first month endurance test, the sample was immersed in formation water at 167 °F for an additional two months. Subsequently, another endurance

test was conducted under varying differential pressures, reaching up to 1000 psi at 200°F. As shown in

Figure 20, a slight increase in the leak-off rate was observed in the third month compared to the first month. Initially, the pressure was held at 250 psi for 30 minutes, during which the leak-off rate was minimal at 0.06 cc/min. Subsequently, as the pressure was raised to 500 psi for 30 minutes, a slight increase in the leak-off rate was observed (0.078 cc/min). Further increasing the pressure to 750 psi for 30 minutes resulted in a leak-off rate of 0.135 cc/min, indicating a minor degradation of the gel. To assess the gel's durability, the pressure was maintained at a constant 1000 psi for 3 hours, with the reported leak-off rate reaching 0.225 cc/min. Comparing this leak-off rate after 3 months with the post-treatment values (as shown in Figure 16), a slight increase was noted. However, the gel exhibited continued effectiveness, achieving an exceptional plugging efficiency of 99.986%, and remained durable after 3 months.

Sixth month: Following the third-month endurance test, the sample was immersed in formation water for an additional three months at 167 °F. The endurance test was conducted using the same methodology, gradually increasing the differential pressure up to 1,000 psi at 200 °F. The gel's performance during the sixth month is depicted graphically in Figure 20. An observable similarity in the leak-off rate compared to the third month was noted, indicating no further degradation of the gel. Under a pressure of 500 psi for 30 minutes, the leak-off was approximately 0.151 cc/min. This rate increased to 0.211 cc/min when the pressure was raised to 750 psi. Sustaining a pressure of 1,000 psi for 3 hours led to the leak-off rate stabilizing at 0.240 cc/min, closely resembling the rate observed in the third month (0.225). These findings confirm that the gel retained its plugging capabilities, achieving a plugging efficiency of 99.983%.

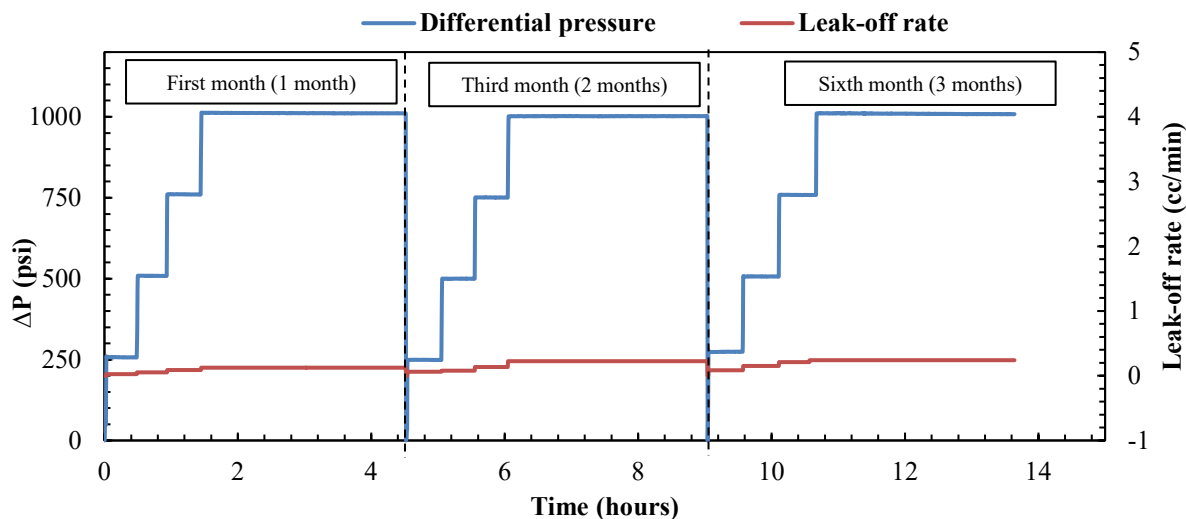


Figure 20 Durability tests over 6 months for nano-silica gel treated sample (A1).

To monitor changes in the porous media over time, CT scans were conducted at various stages over the 6-month period following aging and endurance tests, as appeared in Figure 21. Generally, during aging, there was an increase in CT numbers, indicating higher density, possibly due to water invasion into the core sample. However, after each endurance test, CT numbers decreased to values very close to those after the initial treatment. This suggests that some water may have displaced part of the gel. The CT number after the initial treatment was 2273, which increased to 2296.72 after 1 month of aging and further to 2279.99 in the third month. After 6 months, the CT number following the endurance test was 2279.99, indicating minimal degradation of the gel. Nevertheless, the gel maintained a high plugging efficiency for water flow, indicating that it still occupied most of the connected pore spaces.

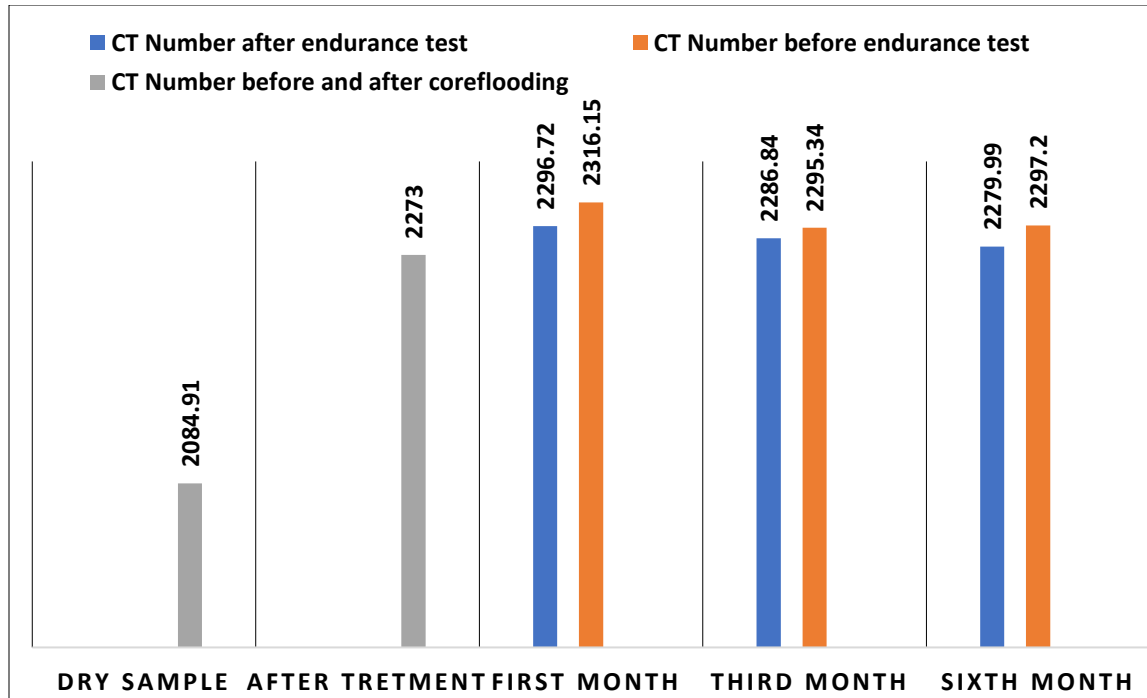


Figure 21 Average CT numbers in different stages for nano-silica gel treated sample.

3.4.2 Experiment 2 (PAM/PEI gel)

In this experimental setup, a limestone core sample labeled as **A2** was specifically chosen due to its similar characteristics to sample **A1** from the previous experiment, allowing a valid comparison of the plugging performance between nano-silica gel and PAM/PEI gel. Sample dimensions are provided in Table 7, while the solutions utilized in the experiment are described in Table 8. The PAM/PEI gel solution, with a concentration of 9/1 wt% (PAM/PEI), was formulated to allow adequate gelation time during placement without causing plugging during injection. The brine solution used in this experiment maintains a similar concentration to that of experiment 1, ensuring consistency in experimental conditions for a precise comparison of results.

Table 7 Dimensions of core sample A2.

Sample	Length (inch)	Diameter (inch)	Porosity (%)	Pore volume (ml)	Permeability (mD)
A2	2.97	1.5	20.54	17.91	100-200

Table 8 Chemical solutions for experiment 2.

Stage	Solution
Pre-treatment	Brine (0.1 M per liter)
Gel placement	PAM/PEI (9/1) %wt
Post treatment	Brine (0.1 M per liter)

3.4.2.1 Primary Coreflooding Stages:

The experiment consists of three distinct stages, as depicted in Figure 22. Initially, the sample's initial permeability was assessed by injecting a brine solution. Brine was injected at four different flow rates totaling 10 pore volumes as in the previous experiment, all conducted at 200 °F. The average permeability of the brine was approximately 144.85 millidarcies (md). Interestingly, this permeability closely matches the sample permeability observed in Experiment 1.

After assessing the sample's initial permeability, the subsequent phase of gel injection started directly. This phase plan is to inject between 5 to 7 pore volumes of PAM/PEI gel into the sample for optimal placement. A PAM/PEI gel with a concentration of 9/1 %wt was chosen for treating the sample. Gel injection occurred over a 90-minute period at a flow rate of 1.5 cc/min, with the total injected gel volume approximately seven times the pore volume. The pressure drop observed during gelant injection is depicted in Figure 22, showing that the maximum pressure drop did not exceed 50 psi, indicating acceptable matrix injectivity. Additionally, the resistance factor, representing the sample's resistance

to flow, was closely monitored throughout the injection process, as shown in Figure 23. The obtained resistance factor values were not excessively high, indicating the gel's capability to displace water within the pore spaces.

Following the completion of gel placement, the sample underwent a 24-hour curing period. Subsequently, an endurance test was conducted to evaluate the gel's pore-plugging capabilities. Brine injection was performed under constant pressure conditions, starting at 50 psi and incrementally increasing to 100, 250, and finally 1000 psi, as depicted in the accompanying Figure 22. Initially, the core sample sustained a pressure of 250 psi for 30 minutes with no detectable leak-off rate. Subsequently, the pressure was raised to 500 psi and maintained for 30 minutes, also without observable leak-off. The pressure was then further increased to 750 psi for 30 minutes and subsequently to 1000 psi for 3 hours. The first water droplet was observed at 1000 psi, with a reported leak-off rate not exceeding 0.02 cc/min. These results confirm the gel's effective plugging capability for water flow. Additionally, the nano-silica gel treatment resulted in a remarkable reduction in the sample's original permeability from 144.85 to 0.001 mD. The residual resistance factor (RRF) of 106,251.01, representing the ratio of initial permeability to the resulting permeability after gel treatment, highlights the significant impact of the gel on reducing core sample permeability.

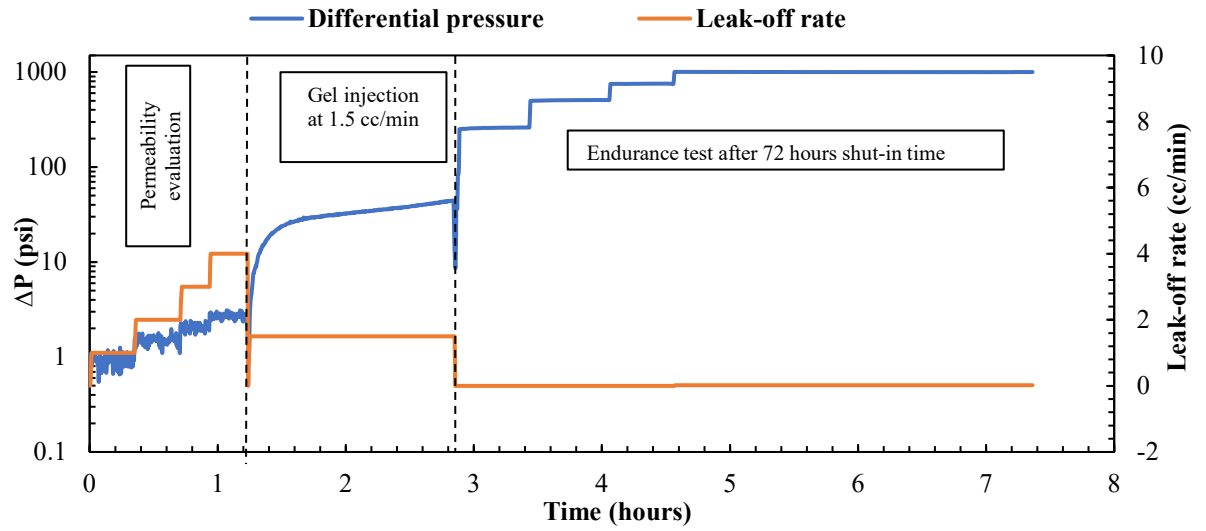


Figure 22 Coreflooding stages for PAM/PEI gel treated sample.

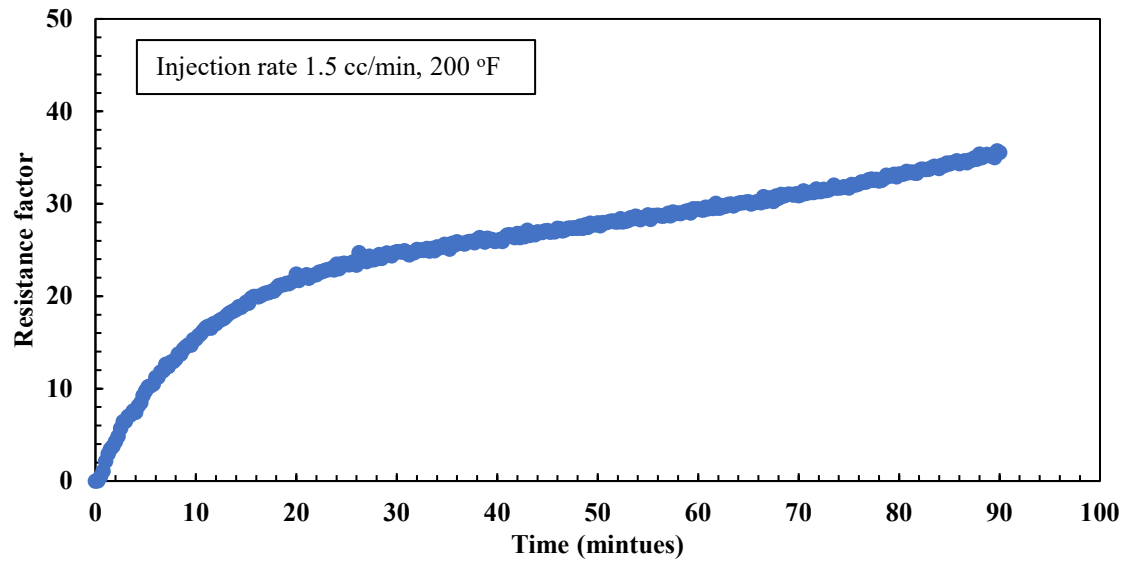


Figure 23 Resistance factor during PAM/PEI gel injection.

3.4.2.2 CT scan and NMR analysis

3.4.2.2.1 CT scan:

A CT scan was conducted on sample A2, both before and after PAM/PEI gel treatment. Figure 24 displays CT images for different slices of the dry sample and after treatment. It is apparent that the gel caused a change in the density distribution of the sample, with a wider spread of higher density distribution compared to the low-density distribution observed before gel placement. This change can be attributed solely to the invasion of the gel. Before gel treatment, the average CT number of each slice was 2105.64, while after treatment, it increased to approximately 2300.64. This significant shift indicates the uniform distribution of the gel along the sample length and reflects the high plugging efficiency achieved by the gel.

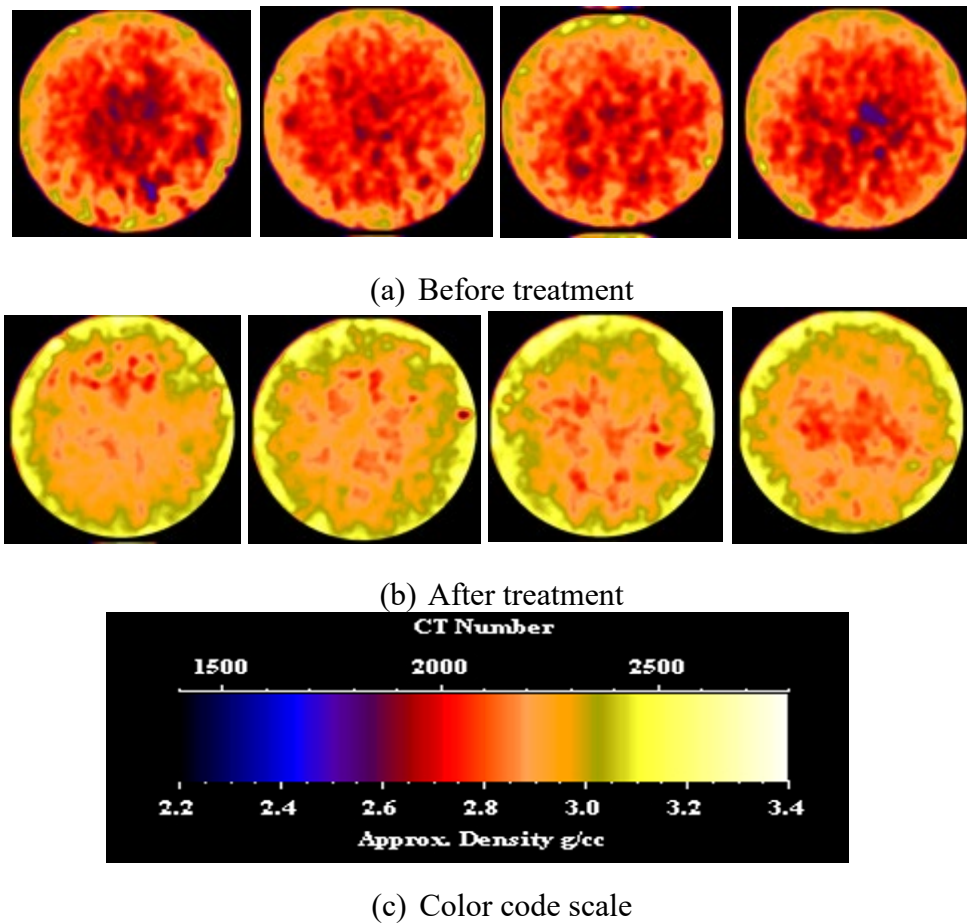


Figure 24 (a) CT scan images of dry samples before PAM/PEI gel injection; (b) CT scan images after PAM/PEI gel treatment; (c) color code scale.

3.4.2.2.2 NMR T_2 measurement:

Initially, NMR measurements were conducted on brine solution and nano-silica gel bulk fluids. The T_2 peaks for bulk-free brine and bulk-free nano-silica are displayed as black and red vertical-dashed lines in Figure 25, respectively. It's apparent from Figure 25 that water's relaxation time (around 2818 ms) exceeds that of PAM/PEI gel (approximately 630 ms), mainly due to a significant disparity in viscosity. The core sample is composed of two predominant pore size systems: micropores and macropores. By comparing the NMR T_2 peaks, it's evident that the gel displaced the brine from both pore systems, with the relaxation time of the gel closely resembling that of a bulk fluid (exhibiting a shorter relaxation time compared to the peak of the bulk fluid). These findings, in conjunction with those obtained from CT scan analysis, clearly demonstrate that the achieved plugging efficiency results from effective gel placement within the pore systems.

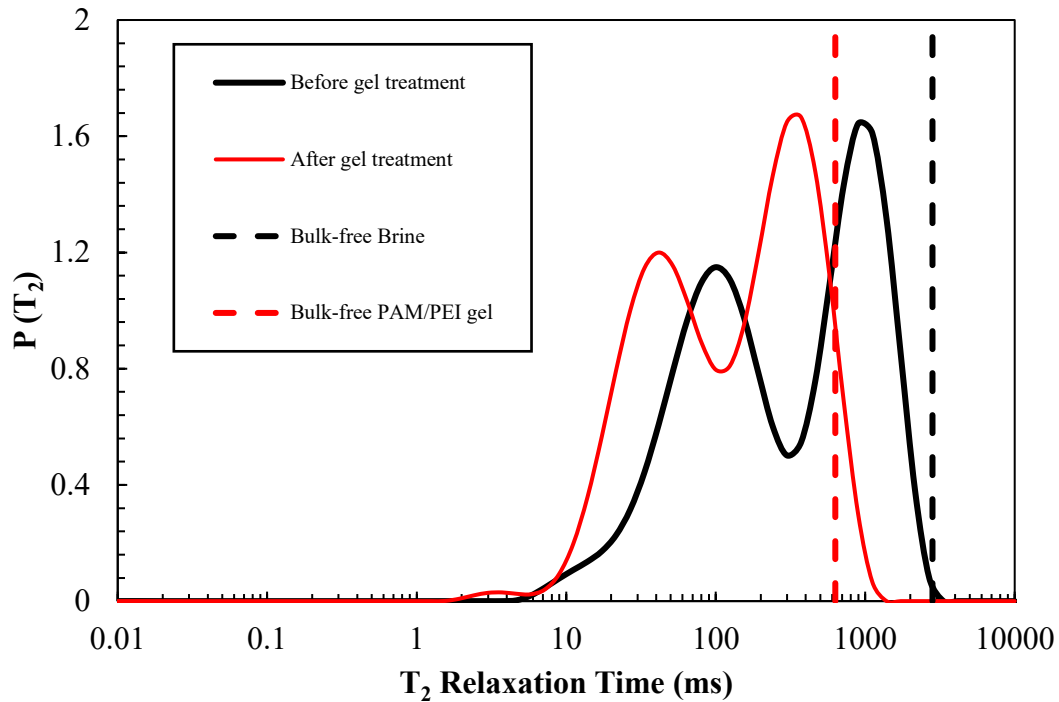


Figure 25 Average NMR T_2 before and after PAM/PEI gel treatment.

3.4.2.3 Durability tests over 6 months:

First month: The sample underwent aging in formation water for 1 month at 167 °F, followed by an endurance test lasting 4.5 hours at 200 °F. The results of this test are

depicted in Figure 26. The test began with a 30-minute pressure hold at 250 psi, during which no leak-off rate was observed at the outlet. Subsequently, the pressure was raised to 500 psi for 30 minutes, then to 750 psi for an additional half-hour. The maximum leak-off rate during this period did not exceed 0.003 cc/min. To examine gel durability, the pressure was maintained at a constant 1000 psi for 3 hours, with the reported leak-off rate being 0.02 cc/min. Remarkably, the maximum leak-off rate remained consistent with the post-treatment level, indicating no degradation of the gel and its sustained plugging efficiency of 100%.

Third month: Following the first month endurance test, the sample underwent an additional 2-month immersion in formation water at 167 °F, followed by another endurance test under varying differential pressures, reaching up to 1000 psi at 200 °F. The results of this third-month endurance test are illustrated in Figure 26. Initially, the pressure was held at 250 psi for 30 minutes, during which the leak-off rate was minimal at 0.02 cc/min. Subsequently, as the pressure was raised to 500 psi for 30 minutes, a slight increase in the leak-off rate was observed (0.059 cc/min). Further increasing the pressure to 750 psi for 30 minutes resulted in a leak-off rate of 0.332 cc/min, indicating a minor degradation of the gel. To assess the gel's durability, the pressure was maintained at a constant 1,000 psi for 3 hours, with the reported leak-off rate reaching 0.601 cc/min. Comparing this leak-off rate after 3 months with the post-treatment values (as shown in Figure 22), a slight increase was noted. However, the gel exhibited continued effectiveness, achieving an exceptional plugging efficiency of 99.96% and remained durable after 3 months.

Sixth month: Subsequent to the third-month endurance assessment, the sample underwent an additional immersion in formation water for three months at 167 °F. The endurance test was conducted under varied differential pressures, reaching up to 1000 psi at 200 °F. The gel's performance during the sixth month is depicted graphically in Figure 26. An observable rise in the leak-off rate compared to the third month was noted, indicating further degradation of the gel. Under a pressure of 500 psi for 30 minutes, the leak-off was around 1.33 cc/min. This rate increased to 1.86 cc/min when the pressure was raised to 750 psi. These values were approximately 3.5 times those observed in the third month. Sustaining a pressure of 1,000 psi for 3 hours resulted in the leak-off rate stabilizing at

2.167 cc/min. While it's evident that the gel has undergone degradation, it retained its ability to reduce water flow by 99.86%.

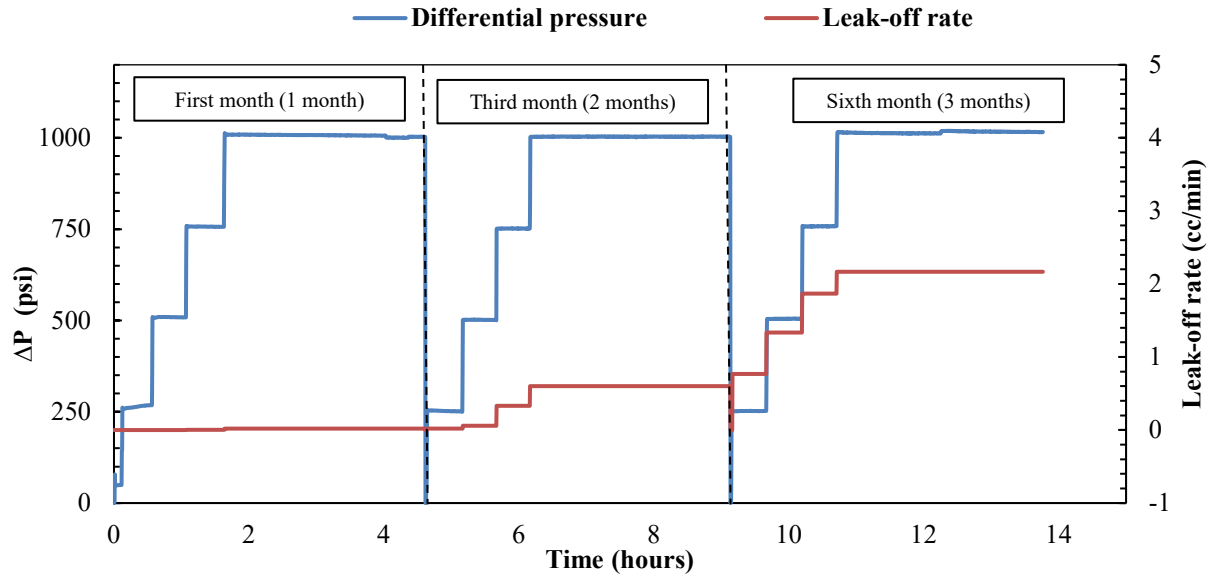


Figure 26 Durability tests over 6 months for PAM/PEI gel treatment.

Similar CT scan stages were employed to assess the sample treated with PAM/PEI gel over the 6-month period, following aging and endurance tests as in Figure 27. A consistent pattern of change in CT numbers was observed during these measurements, characterized by an initial rise in CT numbers after the first month, followed by a decline after each aging period and endurance test. Initially, the CT number after the treatment with PAM/PEI gel was 2301, which decreased to 2286.04 and 2280.28 in the first and third months (endurance test), respectively. Notably, a significant decrease was evident after 6 months, with the CT number dropping to 2255.6. This decline suggests that some water displaced part of the gel. This trend in CT numbers corresponds with the achieved plugging efficiency, as a noticeable increase in the leak-off rate was observed. Nevertheless, the PAM/PEI gel still effectively reduced sample permeability, indicating that it occupied most of the connected pore spaces.

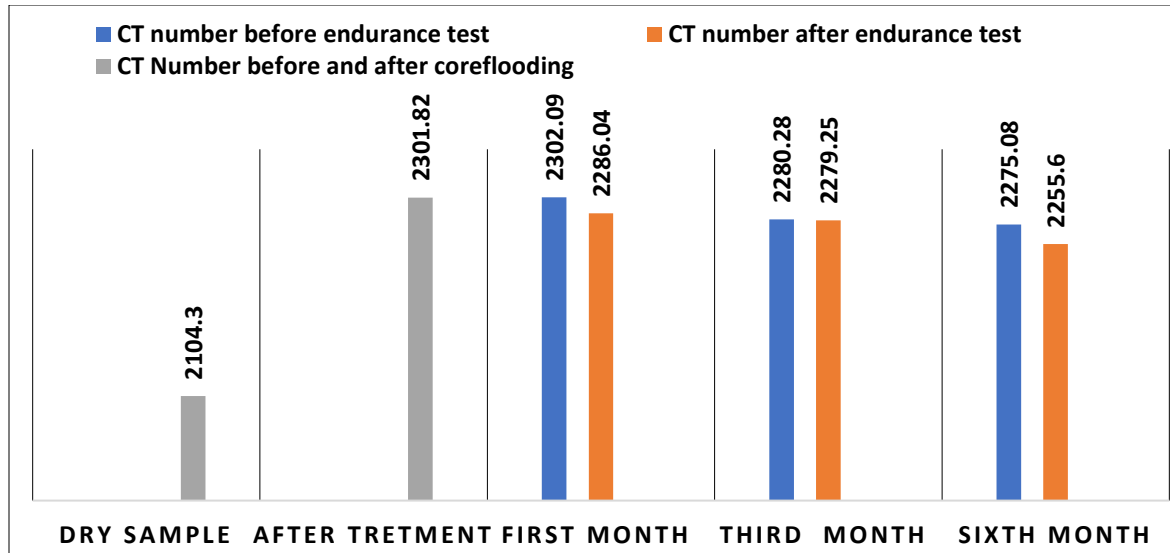


Figure 27 Average CT numbers in different stages for PAM/PEI gel treated sample (A2).

3.4.3 Comparison of the Long-term Effectiveness of Nano-silica gel and PAM/PEI gel:

In this investigation, similar sample characteristics were subjected to treatment using both nano-silica and PAM/PEI gels, enabling a direct comparison of their performance over 6 months. Figure 28 presents an overview of the plugging efficiency of these two gels during this period. Both nano-silica and PAM/PEI gels exhibited high plugging efficiency in brine. Initially, both gels effectively reduced permeability to zero under high differential pressure (1000 psi). However, experimental findings suggest that nano-silica gel experienced a lower degradation rate over the 6-month duration compared to PAM/PEI gel. Nano-silica gel maintained a plugging efficiency of over 99.98%, with only a minimal decrease of approximately 0.01% from the initial treatment. These results demonstrate that nano-silica gel can sustain its durability over an extended period, addressing a significant concern associated with older silica gels. In contrast, PAM/PEI gel, initially displaying exceptional plugging efficiency of 100%, experienced a decrease to 99.856% over the 6 months (a 0.144% decrease). This reduction in plugging efficiency of PAM/PEI gel is a reflection of the increase in the leak off-rate to 2.165 cc/min in the sixth month. The leak-off rate of PAM/PEI gel is 9 times the leak-off rate of nano-silica gel in the sixth month. This indicates that nano-silica gel achieved a better performance than PAM/PEI gel over 6 months,

demonstrating the capability to provide high levels of plugging efficiency comparable to other in-situ gel systems such as PAM/PEI gel, thereby opening up more applications for nano-silica gel in various conditions.

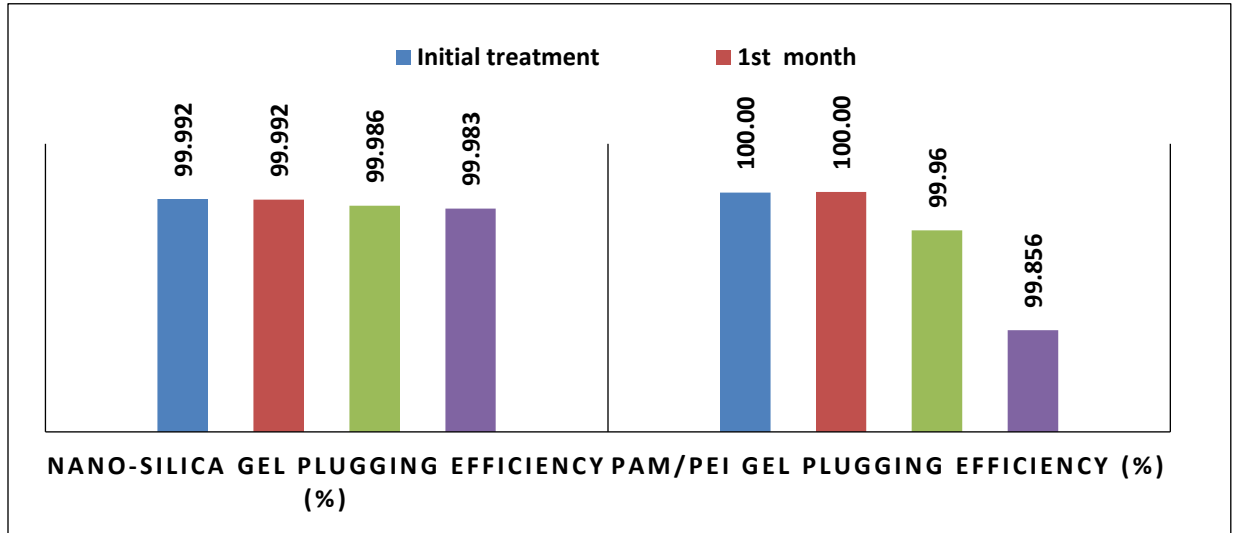


Figure 28 Comparison of plugging efficiency of nano-silica gel and PAM/PEI gel.

Experimentally, nano-silica gel demonstrated superior long-term performance compared to the effective PAM/PEI gel. PAM/PEI gel demonstrated its capabilities for water shut-off applications even under harsh conditions.¹⁸⁵ Consequently, the study suggests broader applications for nano-silica gel over in-situ polymer gels. Silicate gels are cost-effective water shut-off agents, notably cheaper compared to polymer gel.¹⁰⁶ Additionally, they offer the advantage of low viscosity, making them suitable for deep reservoir invasion.¹⁰⁶ These inherent advantages position the newly developed nano-silica gel with significant potential for addressing water production challenges.

3.5 Conclusion

Gel treatments are widely used to address water-related issues in permeable matrix. Ensuring the long-term effectiveness of these gels is crucial for maximizing profitability. This study investigated the performance of a newly developed nano-silica gel over a period of 6 months to assess its potential as a long-term solution. The key findings are:

- Nano-silica gel achieved a remarkable plugging efficiency of 99.99% under high differential pressure (1000 psi).
- Over the 6-month period, nano-silica gel maintained its effectiveness, with a plugging efficiency of over 99.98%.
- PAM/PEI gel initially blocked water flow with a plugging efficiency of 100% under 1000 psi differential pressure.
- The plugging performance of PAM/PEI gel has slightly decreased over 6 months, with a final plugging efficiency of 99.985%.
- Over 6 months, nano-silica gel achieved better plugging performance than PAM/PEI gel.
- CT scan confirmed minimal degradation occurred to both gels over 6 months with less significant impact on the efficiency of nano-silica gel compared to PAM/PEI gel.

CHAPTER 4

NANO-SILICA GEL FOR WATER SHUT-OFF IN

FRACTURED RESERVOIRS: EXPERIMENTAL

INSIGHTS AND PROMISING RESULTS³

4.1 Abstract

In the oil industry, the pervasive challenge of water production during hydrocarbon extraction presents operational and environmental complexities, impacting costs, oil recovery efficiency, and environmental sustainability. Over the last decade, many chemical systems were developed to mitigate this problem. As the nanomaterials showed its capability to add improvement in EOR and drilling applications, it becomes a demanding to incorporate such materials in water shut-off applications. This paper delves into examining the potential of nano-silica gel to prevent water flow in fractures. While prior research has explored its utility in high permeable matrix, this study extends the investigation to fractures that contribute to unproductive water production. In this study, a fractured limestone sample featuring a groove (middle) with a depth of 0.5 to 0.7 mm was created intentionally to simulate reservoir fractures. injected using a core flooding system

³ This chapter is copied from the manuscript: Ali, A.; Al-Ramadan, M.; Aljawad, M.; Alabdrabalnabi, M.; Almohsin, A.; Sultan, A.; Azad, M. Nano-Silica Gel for Water Shut-Off in Fractured Reservoirs: Experimental Insights and Promising Results. In *SPE EOR Conference at Oil and Gas West Asia*; SPE, 2024; p D021S018R004.

to ensure precise gel placement. The core flooding experiment was implemented at 200 °F and involved three stages: 1) a pre-treatment stage for evaluating initial permeability, 2) an injection stage for the gel solution, and 3) a post-treatment stage for the constant pressure endurance test. Subsequently, the sample underwent a 3-month aging process in formation water at 167° F. Endurance tests were conducted in both the first and third months to reevaluate the plugging efficiency at 200 °F. The experimental findings demonstrated the gel's effectiveness in plugging water flow in both the fracture path and matrix, achieving initially a 100% plugging efficiency. The gel was durable to high differential pressure up to 1500 with minimal leak-off rate of 0.09 ml/min. There was a substantial reduction in the average permeability across the sample, decreasing from 37.19 mD to 0.0012 mD. Analysis of the pore system through CT scans before and after treatment confirmed successful gel placement in the inlet and outlet fracture sections, as well as an invasion into the matrix. The CT scans also verified the uniform distribution of the gel along the sample length. Additionally, the gel was capable of maintaining exceptional plugging efficiency of 99.98% after 3 months from the initial treatment.

4.2 Introduction

Unproductive water production in oil fields represents a significant challenge that can have substantial economic and operational consequences. This phenomenon occurs when an undesirable amount of water is co-produced along with oil and gas during extraction processes.¹ Oil reservoirs often contain a mixture of hydrocarbons and water, but the proportion of water production can become problematic when it surpasses the economically viable limit.¹³ The consequences of excessive water production are multifaceted. Economically, it leads to decreased oil recovery rates, higher operational costs, and a potential decline in the overall profitability of oil fields.^{1,15} Operationally, the handling and disposal of large volumes of produced water present environmental concerns and logistical challenges.^{15,188–190} Furthermore, the presence of water can have detrimental effects on the infrastructure and equipment used in oil extraction and processing. The existence of such a problem required immediate treatment to maintain or extend the productive life cycle of the well.

The water production comes from two primary sources: wellbore-related sources and reservoir-related sources.^{1,8} Wellbore-related factors involve flow behind pipe, tubing, or packer leaks.^{7,15,22} Reservoir-related factors are represented in fractures or channels,^{7,15} water coning,²² and fingering,¹³ which are easily contributing to increased water production. This study concerns the water production due to the existence of fractures. Fractures within the geological structure, whether natural or induced, act as conduits for fluid movement, enabling water to bypass oil-bearing zones and reach the wellbore.^{1,82,191–193} This disruption in fluid dynamics leads to a higher co-production of water during oil production. The identification and characterization of these fractures are crucial for effective reservoir management, allowing the implementation of targeted strategies to mitigate their impact and optimize oil production.

One of the cost-effective chemical techniques to mitigate water problem is gel treatment.^{4,69} Polymer and silicate solutions stand out as prevalent gel systems employed in water shutoff applications.^{21,101,194} The fundamental mechanism involves injecting a gelant solution, a fluid with gel-forming properties, which undergoes a transformation into a solid 3D gel network. This solidified gel network serves to minimize or entirely prevent the flow of water. Silicate gels, also known as sodium silicate or colloidal silica gels, have been widely used over the last decade. The gel is primarily composed of silicon and oxygen as it is formed by the reaction between silica solution and activator, NaCl).^{99,100} The gel exhibits unique properties that make it well-suited for sealing off water-producing zones in subsurface formations. Silicate gels offer several advantages for water shut-off applications. Their compatibility with a wide range of reservoir conditions, including temperature and salinity variations, makes them versatile for diverse geological structure.¹⁰⁴ Additionally, their relatively low viscosity during injection ensures ease of transport through the wellbore,¹⁰³ facilitating uniform distribution in the targeted zones. The environmentally friendly nature of silicate gels further adds to their appeal, as they do not pose significant risks to the ecosystem.^{106–108}

However, there are some drawbacks of using silicate gels for water shut-off applications include variability in gelation times, limitations in high-temperature reservoirs, sensitivity to divalent ions in the formation and decreased gel strength for long period.^{101,106} In recent

years, a new developed system was derived from silicate gels and called nano-silica gel. Several studies were conducted on this system, Boul¹³⁹ et al. explored the impact of particle size and shape on gelation time, finding that non-spherical nanoparticles extend gelation time at low temperatures, while Almohsin¹⁴⁰ et al. observed an acceleration at higher temperatures, with adjustable gelation through activator concentration. Karadkar¹⁴¹ et al. investigated rheological behavior, noting lower sensitivity at higher concentrations. Core flooding experiments by Karadkar Karadkar on Berea sandstone confirmed plugging capabilities at 200°F, with no flow during an 8-hour endurance test.¹⁴⁰ also tested nano-silica gel on Berea sandstone, demonstrating efficient plugging with a leak off rate of 0.0018 cm³/min after 317 hours at 4000 psi differential pressure. Furthermore, Alabdrabalnabi¹⁴⁷ et al. examined and analyzed the gelation kinetics of a nano-silica gel considering the cooldown effect during water shut-off injection by evaluating the effect of temperature and activator on gelation time.

Prior research on gel applications has not extensively explored the potential use of nano-silica gels for treating fractures, which are recognized as significant contributors to excessive water production. This study seeks to investigate the application of nano-silica gel specifically for treating fractures.

4.3 Materials

4.3.1 Chemicals

During the coreflooding experiment, two solutions were employed: NaCl brine solution and a nano-silica gel. Brine, with a concentration of 0.1M per liter, was initially injected for permeability assessment and subsequently used during the endurance test. The second solution, the nano-silica gel, consists of a nano-silica solution and an activator. During the aging process of the treated core sample, formation water of 120,000 ppm was prepared (NaCl and CaCl₂ are the main components).

4.3.2 Core Sample Characteristic

In this study, limestone core sample was utilized for core flooding experiments, and it has a distinct configuration with dimensions of 1.5-inch diameter and 3-inch length. The core sample has a fractured with groove as displayed in Figure 29. The sample was prepared

by cutting the sample into two equal halves, creating a groove with a length of 2 inches and a depth ranging from 0.5 to 0.7 mm in the middle of one of the halves. Subsequently, the two parts were conjoined using a shrinkage tube with heating.

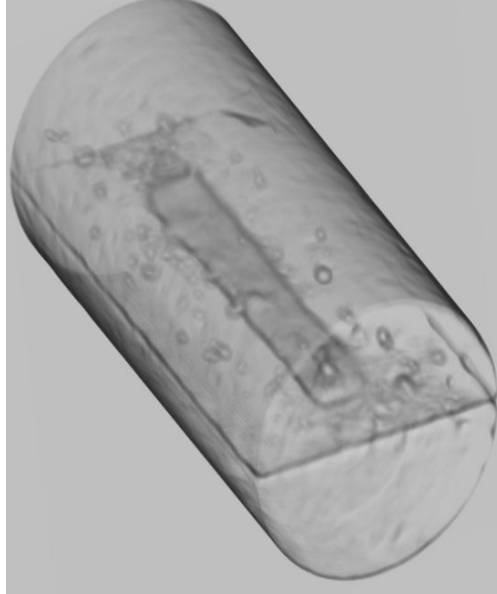


Figure 29 Fracture sample with groove.

4.3.3 Experimental Procedure

To assess the efficiency of nano-silica gel in mitigating fractures, core flooding experiments were conducted to simulate water shut-off treatments. The experimental process comprises three stages: a pre-treatment phase to assess the initial permeability of the sample, the injection of the gel, and a post-treatment phase to evaluate the efficiency of gel plugging. The schematic diagram in **Figure 30** illustrates the core flooding system used in this study, featuring a 1.5-inch core holder equipped with pressure transducers for recording inlet and outlet pressures. Two pumps are integrated, with one applying confining pressure to the core holder and the other injecting fluid through two accumulators – one for gel outside the oven and another for brine inside the oven. To maintain uniform pressure and replicate reservoir conditions, a back pressure regulator is set at 400 psi. Alongside the gel treatment, medical CT scans are employed to characterize the sample's

pore system before and after the gel treatment. The comprehensive experimental procedure can be illustrated as follows:

1. Determine sample properties: (porosity, permeability, bulk volume)
2. Perform a medical CT scan on the dry sample.
3. Saturate the core sample with brine (0.1M per liter).
4. Position the core sample into the core flooding system (temperature: 200° F).
5. Inject brine at various flow rates and document the resulting pressure drop.
6. Introduce the gelant solution, equivalent to 5 to 7 pore volumes of the core sample.
7. Clean the system lines of any residual silicate gel.
8. Allow the treated sample to cure for 24 hours.
9. Inject brine under constant differential pressure and record the leak-off rate (temperature: 200 °F).
10. Retrieve the core sample and conduct a medical CT scan.

After the initial treatment and completing the endurance test, the sample will be subjected to an aging process in a cell filled with formation water at 167 °F for a duration of 1 month. Following this aging period, an endurance test will be conducted to reassess the plugging efficiency. Subsequently, the sample will undergo another round of aging in the cell for an additional 2 months at 176° F. After the 2-month aging period, a third endurance test will be carried out to evaluate the plugging efficiency in the third month.

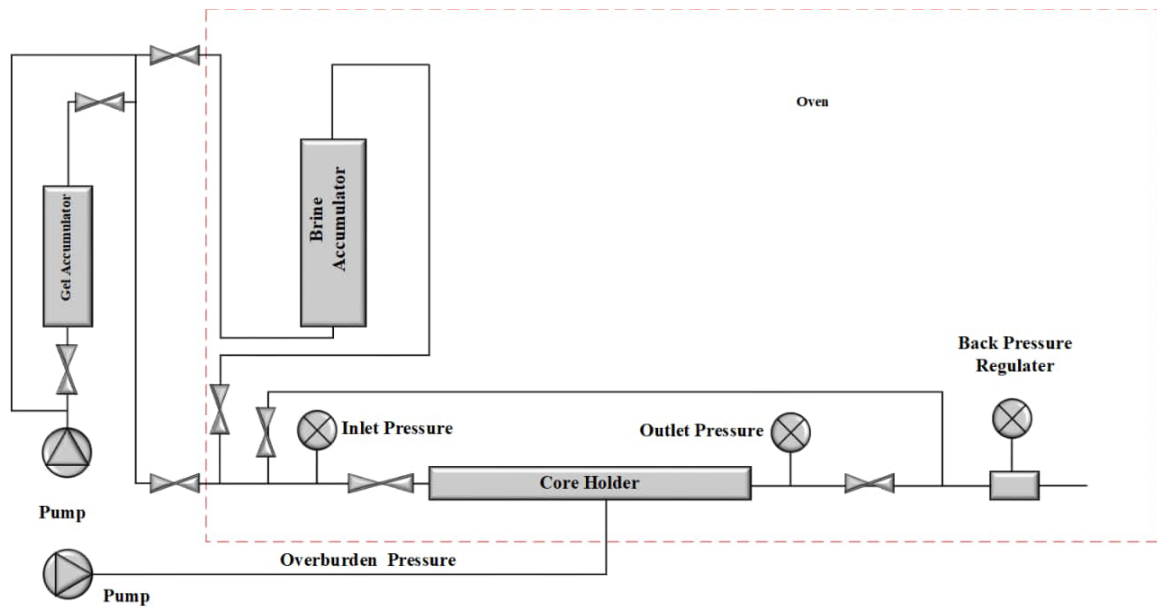


Figure 30 Core flooding system for nano-silica gel treatment.

4.4 Results and Discussion

In this experiment, a fractured sample was employed, and its dimensions are specified in Table 9. The solutions utilized in the experiment are detailed in Table 10. The designated concentration of the nano-silica gel was 77 (wt%) nano-silica and 23 (wt%) activator. A NaCl brine solution with the same concentration will be utilized for both the pre-treatment and post-treatment stages.

Table 9 Core A1 dimensions.

Sample	Length (inch)	Diameter (inch)	Porosity (%)	Pore volume (ml)
A1	1.5	3	17.46	15.17

Table 10 The used Chemical solutions during core flooding experiment.

Stage	Solution
Pre-treatment	Brine (0.1 M per liter)
Gel placement	Nano silica gel (77 wt% silica, 23 wt% activator)
Post-treatment	NaCl Brine (0.1 M per liter)

4.4.1 Coreflooding

As displayed in **Figure 31**, there are three stages to conduct the gel treatment, pre-treatment stage, gel injection and post-treatment stage. During the post-treatment stage, brine was injected at four different flow rates. The average permeability of the brine, measured at a temperature of 200° F, was approximately 28.36 millidarcies (mD). Notably, the calculated permeability is six times greater than the permeability of the core sample without the fracture section in the middle (around 4 mD). This observation underscores the significant contribution of the fracture section to the brine flow.

For gel placement, sufficient nano-silica gel was injected into the core sample to ensure it is fully saturated by the gelant. The injected gelant was composed of 77% silica and 23% activator. This concentration allowed a gelation time of approximately 5 hours at 200 °F. The solution was injected over a 40-minute period with a constant flow rate of 1.5 cc/min, approximately four times the pore volume. **Figure 31** depicts the pressure drop observed during gel injection, the injection was conducted in two stages that explained a gradual drop in the pressure between the two stages. The sample exhibited low injectivity due to gel invasion into the low permeability matrix, resulting in a substantial differential pressure. Notably, the reported resistance factor during the 30-minute injection period reached up to 200 with a small drop between the two stages as the result of pressure drop between them (refer to **Figure 32**), indicating a considerable contrast in gel performance compared to a high-permeability matrix (low resistance factor).

After 24 hours of shut-in time, the post-treatment stage started by conducting an endurance test under high differential pressure. Brine injection occurred with a gradual increase in pressure, and the leak-off rate was monitored as displayed in Figure 31. Initially, the pressure was held constant at 250 psi for 30 minutes with zero observed leak-off rate. Subsequently, the pressure was increased to 500 psi and maintained for 30 minutes, again with no observed water droplets in the outlet. The first reported leak-off rate of 0.02 ml/min occurred when the pressure reached 1000 psi (held constant for 30 minutes). Following this, the pressure was further increased to 1500 psi and sustained for 3 hours, during which the leak-off rate remained minimal at 0.09 ml/min. These findings affirm the gel's effectiveness in plugging water flow through the fracture and the surrounding matrix.

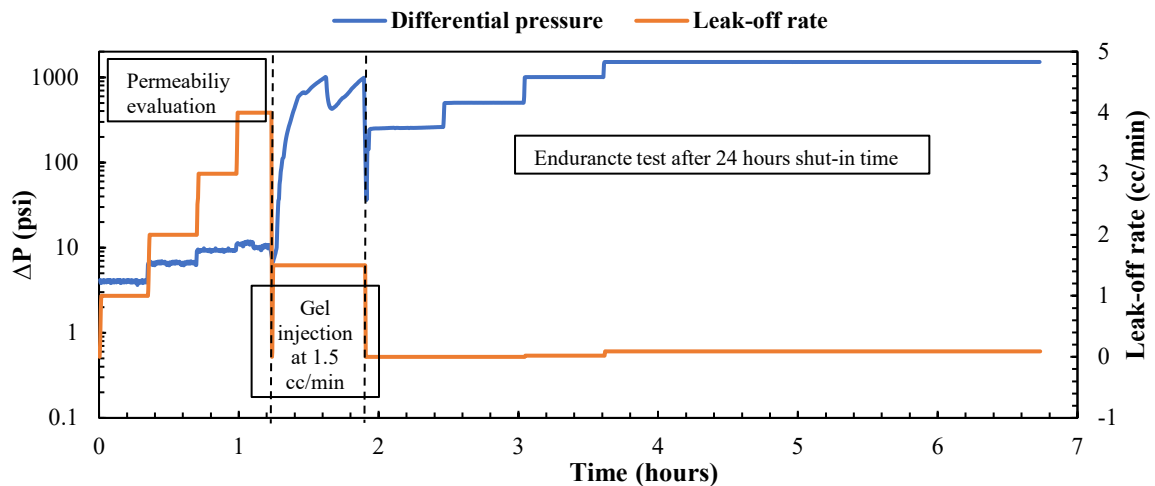


Figure 31 Post-treatment endurance test.

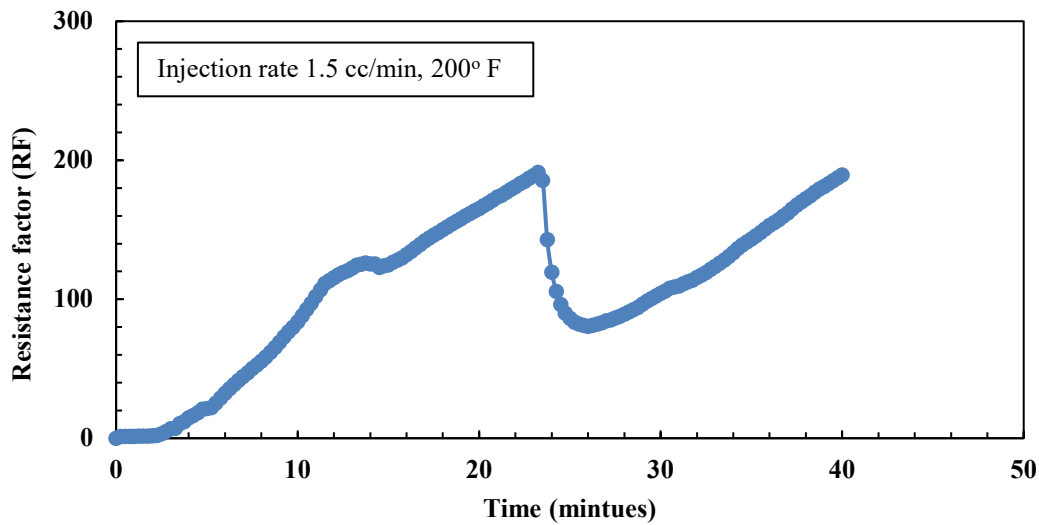


Figure 32 Resistance factor during gelant injection.

The impact of the nano-silica gel on the fracture sample is summarized in Table 11. Only 3 pore volumes of nano-silica solution were injected into the core sample due to the high differential pressure experience during the gelant injection. A sharp continuous increase in the pressure drop was noticed as the gelant solution started to invade the low permeable matrix around the fracture. The high values of resistance factor can clearly explain the challenging condition for the nano-silica gel to invade the matrix. However, this injected amount was sufficient enough to plug the fracture path and the matrix as the sample achieved 100% plugging efficiency. The sample initial permeability was 37.19 mD, but after gel treatment the permeability significantly dropped to 0.0012 mD.

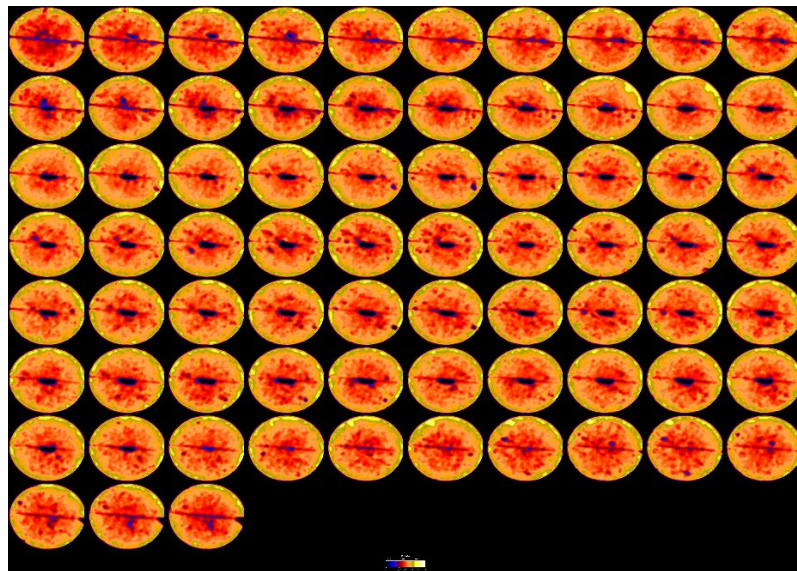
Table 11 The impact of gel treatment on the core sample.

	Pre-treatment	Post-treatment
K (mD)	37.19	0.0012
Plugging efficiency %	100	
Residual resistance factor (RRF)	31128.31	

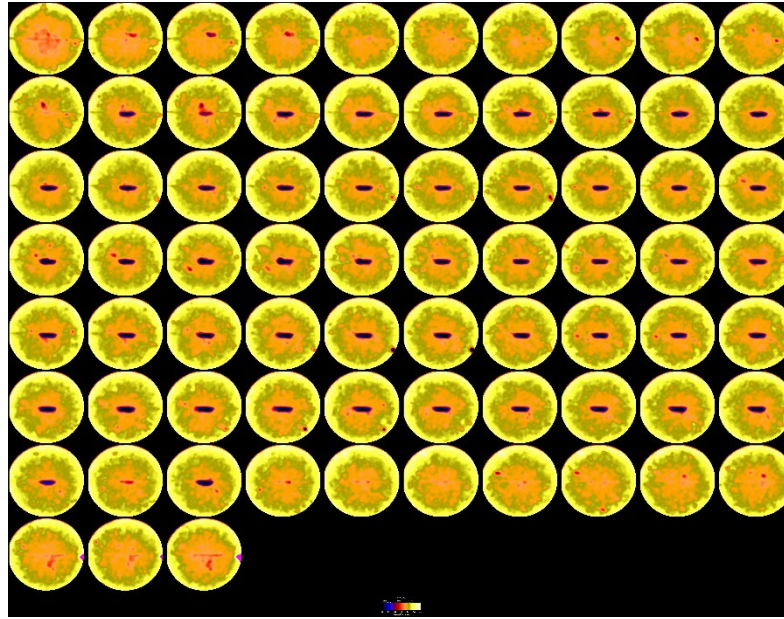
Resistance factor (RF)	200
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4.4.2 CT Scan Analysis

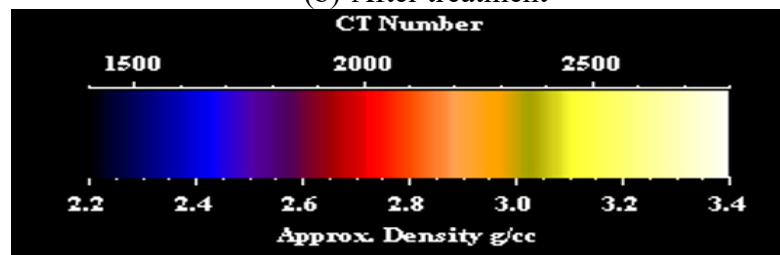
CT scans were performed on the core sample both before and after gel treatment, with results expressed in CT numbers. CT numbers, measured in Hounsfield units, reflect the intensity of the transmitted X-ray beam and correspond to specific density values in g/cm^3 .¹⁸⁶ Each change in CT number signifies a shift in density distribution. The fractured sample in this study featured three fracture sections: a 0.5-inch inlet fracture, a 2-inch groove (0.05 mm deep), and a 0.5-inch outlet fracture. These sections were interconnected to form a single path for water flow. In the pre-treatment CT scan, these sections appeared brighter, indicating a low-density distribution as displayed in **Figure 33**. As for the post-treatment, a noticeable transition to a darker color occurred in the inlet and outlet fracture sections, signifying a shift from low-density to high-density distribution and indicating successful gel placement. However, there was no indication of gel placement in the groove section. This observation from the CT scan led to the conclusion that the gel was effectively placed in the smaller fracture sections, particularly in the middle section, impeding water flow. Moreover, an obvious change in the surrounding matrix confirmed the gel invasion to the matrix.



(a) Before treatment



(b) After treatment



(c) Color code scale

Figure 33 (a) CT scan slices before gel treatment (b) CT scan slices after gel treatment (c) color code scale.

CT scanning was employed to analyze the gel penetration pattern in the core sample. The histogram in **Figure 34** illustrates the CT number distribution per slice along the sample length. Before treatment, the average CT number was 2382.11, which increased to 2165.99 after treatment. This significant shift confirms the uniform distribution of the gel throughout the sample, indicating a consistent and effective penetration pattern.

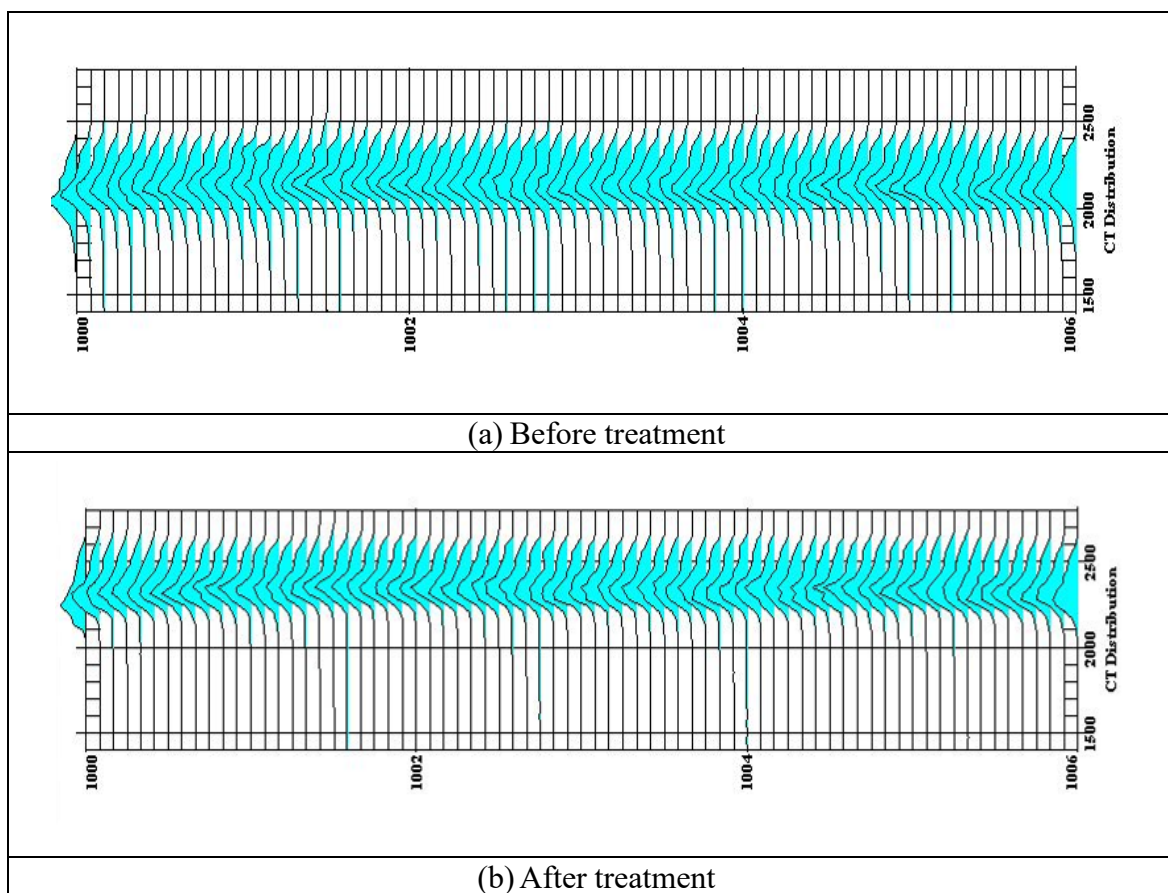


Figure 34 (a) CT distribution before gel treatment; (b) CT distribution after gel treatment.

4.4.3 Evaluation of Gel Durability Over 3 Months:

First month: following the post-treatment endurance test, the sample underwent aging in formation water for a duration of 1 month at 167 °F, followed by another endurance test lasting 4.5 hours at 200° F. The results of this test are illustrated in **Figure 35**. The test commenced with a 30-minute pressure hold at 250 psi, during which no leak-off rate was observed at the outlet. Subsequently, the pressure was increased to 500 psi for 30 minutes, and then to 1000 psi for an additional half-hour. The maximum leak-off rate during this period did not exceed 0.085 ml/min. Following these stages, the pressure was maintained at a constant 1500 psi for 3 hours, and the reported leak-off rate was 0.145 ml/min. This observation affirms that the gel retained its initial plugging efficiency, with a reported plugging efficiency of 99.99%.

Third month: subsequent to the first month endurance test, the sample underwent an additional 2-month immersion in formation water at 167 °F, followed by another endurance test under varying differential pressures, reaching up to 1500 psi at 200° F. The results of this third-month endurance test are depicted in Figure 35. Initially, the pressure was held at 250 psi for 30 minutes, during which no leak-off rate was observed at the outlet. Following this, the pressure was raised to 500 psi for 30 minutes and then to 1000 psi for an additional half-hour. The maximum leak-off rate during this period did not exceed 0.1 ml/min. Subsequently, the pressure was maintained at a constant 1500 psi for 3 hours, and the reported leak-off rate was 0.175 ml/min. Upon comparing the obtained leak-off rate after 3 months with the post-treatment values (refer to Figure 31), a slight increase in the leak-off rate was noted. However, the gel demonstrated continued effectiveness, achieving an exceptional plugging efficiency of 99.98% and remained durable after 3 months.

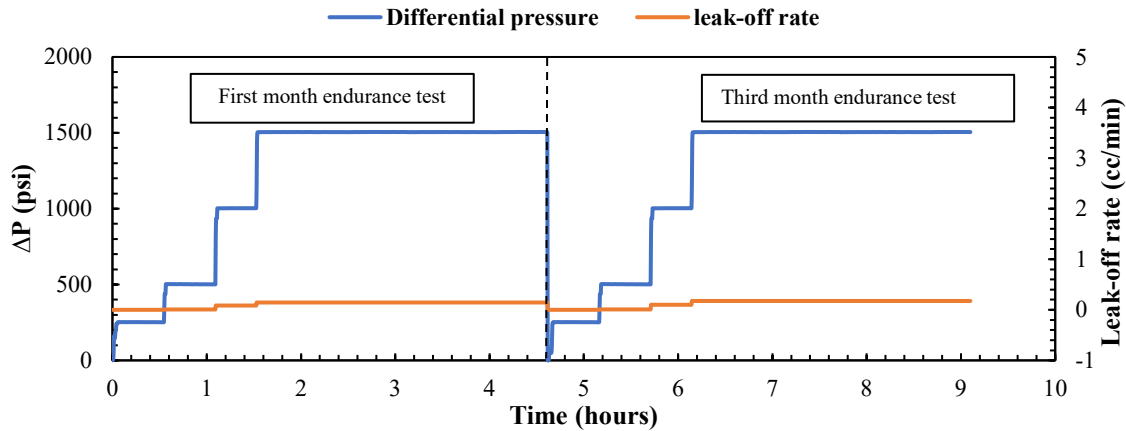


Figure 35 Gel durability over 3 months.

4.5 Conclusion

In recent studies, the newly developed nano-silica gel has demonstrated its ability to effectively plug high-permeability matrix with an exceptional plugging efficiency. This study focuses on evaluating the gel's performance in fractures, which are recognized as significant contributors to excessive production. The findings of the study can be concluded to:

- Nano-silica effectively sealed the fracture path in the designed fracture sample.
- The plugging efficiency was remarkably high, akin to its performance in the highly permeable matrix.
- Nano-silica exhibited notable durability under high differential pressure, withstanding pressures up to 1500 psi.
- CT scans verified the placement of nano-silica gel predominantly in the smaller fracture path rather than in the groove, prompting further investigations into factors influencing gel performance in fractures.
- The gel has maintained its high plugging efficiency under high differential pressure for 3 months.

CHAPTER 5

EXPERIMENTAL STUDY OF NANO-SILICA GEL AS A WATER SHUT-OFF AGENT IN FRACTURED RESERVOIRS⁴

5.1 Abstract

Excessive water production in the oil industry is a persistent challenge, impacting operational costs and environmental concerns related to produced water disposal. Fractures and channels are widely recognized as significant sources of water production in reservoirs produced under the water drive mechanism. Recent investigations have shown the efficiency of nano-silica gel in mitigating water production in high-permeability formations. However, these studies have not thoroughly evaluated its performance in addressing fractures as potential pathways for water migration. Therefore, this study investigates the performance of nano-silica gel in fractures and channels, which are major sources of water production. Four carbonate core samples of 1.4-inches diameter and 3-inch length were utilized: two containing an induced fracture and the other featuring an open channel. Core samples underwent coreflooding experiments, Computed Tomography (CT) scans, and nuclear magnetic resonance (NMR) T_2 measurements. The coreflooding system was utilized to treat carbonate samples with two gels: a nano-silica gel solution

⁴ This chapter is copied from the manuscript: Ali, A.; Al Ramadan, M.; Aljawad, M. S.; Elsayed, M.; Almohsin, A. Experimental Study of Nanosilica Gel as a Water Shut-Off Agent in Fractured Reservoirs. *Energy & Fuels* **2024**.

comprising 75 (wt%) nano-silica and 25 (wt%) activator, and PAM/PEI gel of (9/1) wt%. The injection of a sufficient volume of the gel ensured successful placement and curing at a high temperature of 200 °F. The nano-silica demonstrated exceptional plugging efficiency, with a remarkable 100% reduction in permeability and enduring durability under varying differential pressures, reaching up to 1,000 psi. This performance was at the same level of plugging success obtained with PAM/PEI gel with 9/1 (wt%) concentration. CT scans and NMR analysis further confirm the uniform distribution of both gels and the successful displacement of brine from fractures and channels.

5.2 Introduction

One of the challenging problems in the oil industry is reducing the excessive water production that accompanies hydrocarbon production.¹ It poses several significant challenges to oil producers, including increased production costs, reduced oil recovery efficiency, and potential environmental hazards associated with the handling and disposal of produced water. In 2000, Bailey¹⁵ et al. reported a global ratio of three barrels of water production to every barrel of oil, resulting in a substantial 75 billion barrels of co-produced water, with disposal costs estimated at \$40 billion. Pappas²³ et al. revealed that the United States alone produced approximately 24.4 billion barrels of co-produced water. These reports confirm that the produced water can highly affect the economics of the producing wells, and immediate treatment should be applied when this problem starts to appear.

Water shut-off involves the application of various techniques to mitigate the excess water production associated with hydrocarbon extraction. A successful water shut-off treatment requires a consistent analysis to accurately identify the root cause of the water entry point, followed by the application of an appropriate solution.^{7,8} Sources of water can be categorized into two primary types: wellbore-related and reservoir-related sources.^{1,8} Wellbore-related sources are related to production wells like flow behind pipes and tubings or packer leaks.^{7,15,22} The second type is reservoir-related sources such as high permeability zones¹, fractures^{7,15}, water coning²², and fingering.¹³ Water shut-off methods generally fall into two common categories, mechanical methods used to address near-wellbore problems and involve the placement of materials like cement,⁴⁹ or mechanical devices such

as packers,⁴⁴ plugs, and tubing patches.⁴⁷ The second method involves chemical techniques, which entail injecting chemical substances into the reservoir to obstruct the water path.²¹ Chemical methods are versatile and can be applied to both wellbore and reservoir-related sources, and gel treatments are considered one of the most prevalent and effective chemical approaches.^{4,69,82,178–180}

This study focuses on fractured reservoirs due to their significant contribution to excessive water production. Fractures can provide an easy path for water from the injector to the producer or a pathway for top or bottom water drive. By reducing permeability through fractures, water can be redirected to unwept zones, pushing oil towards the production interval. The placement of gels to plug fractures has been addressed in many studies.^{3,84,178,191,196} Polymer and silicate gels are the most common gel systems used for water shut-off applications.^{99,100,197,198} Polymer gels are classified into two types: in-situ gel and preformed gel. Newly developed preformed particle gels are more applicable for treating and plugging fractures compared to in-situ gel due to uncertainties in gelation and gel extrusion problems associated with in-situ gel.^{71,81}

Silicate gels are one of the common gel treatments and represent one of the oldest methods for mitigating excessive water production.⁹⁸ The mechanism of plugging water paths is similar to the in-situ polymer treatments by forming a 3D semi-solid structure, and the gel is formed by the reaction between the silica solution and the activator solution (HCl, NaCl).^{99,100} This gel system poses many operational advantages, such as good injectivity due to low viscosity¹⁰³ and convenient thermal stability at elevated temperature.¹⁰⁴ Additionally, silicate gels are cheaper than polymer gels and environmentally friendly.^{106–108} Nevertheless, its application comes with certain drawbacks, including reduced gel strength over an extended period, rapid gelation, and sensitivity to divalent ions in the formation.^{101,106,181}

Recently, researchers have recognized that nanomaterials hold significant potential for enhancing material performance as they were applied in improving oil recovery, formation evaluation, and reservoir imaging.^{18,20,101,181} Silica nanoparticles, with their distinctive morphological characteristics and high surface area, have demonstrated the ability to effectively plug pore throats, as reported in studies conducted by Elkatatny¹⁸² et al., Jin¹⁸³

et al., Lyu¹⁸⁴ et al. Additionally, silica nanoparticles have been employed to enhance gas production from gas wells, with modified nano-silica using fluor surfactants to alter rock wettability from liquid-wetting to gas-wetting.¹⁸³ Nano-silica-based gel, which has been the subject of numerous investigations for water shut-off applications, contains nano-silica and activator solutions that react to form the gel. Several studies have examined the gelation behavior under various conditions. Boul¹³⁹ et al. delved into the impact of particle size and shape on gelation time at low temperatures, revealing that non-spherical nanoparticles can extend the gelation time at very low temperatures (50 °F). Another study conducted by Almohsin¹⁴⁰ et al. to examine the influence of temperature on gelation time, and they found that higher temperatures significantly accelerate the gelation process. Furthermore, it was observed that gelation can be adjusted by varying the activator concentration. In a related area, Karadkar¹⁴¹ et al. investigated the rheological behavior and reported that gelation time exhibits higher sensitivity to higher concentrations of 24% and 25%, and less sensitivity to lower concentrations of 21% and 23%. These findings contribute to our understanding of how nano-silica-based gels can be tailored and optimized for water shut-off applications.

Several studies have explored the plugging capabilities of nano-silica gel for water shut-off applications. Karadkar¹⁴¹ et al. conducted coreflooding experiments on Berea sandstone sample with initial brine permeability of 190 mD. The sample was treated with the gel at 200 °F and then left to cure for 24 hours. Subsequently, the brine was injected at 1 ml/min and a sudden increase in the pressure to 1,400 psi which confirms the plugging capability.¹⁴¹ Additionally, during the endurance test no flow was noticed when continuing pumping for 8 hours (back pressure was set at 2,500 psi).¹⁴¹ Almohsin¹⁴⁰ et al. also investigated the plugging efficiency of the nano-silica gel using Berea sandstone core sample with high permeability (700 mD liquid permeability). The endurance test was conducted until 4,000 psi differential pressure for 317 hours, and the measured leak-off rate was only 0.0018 cm³/min.¹⁴⁰ The previous results can encourage the application of nano-silica gel as an alternative to the polymer in-situ gel along with the aforementioned advantages.

The objective of this study is to assess the efficiency of applying nano-silica gel to fractures and channels, comparing its performance to that in a high-permeability matrix. Previous research has primarily focused on validating the efficiency of nano-silica gel in high-permeability matrix. However, none of these studies have investigated whether the gel is capable to plug the fractures, which represent another prevalent source of excessive water production. The study aims to compare the performance of nano-silica gel with a traditional polymer gel, specifically polyacrylamide/polyethyleneimine (PAM/PEI) gel. PAM/PEI gel has demonstrated its effectiveness in achieving 100% plugging efficiency in Berea sandstone core samples at a temperature of 90 °C.¹⁴⁴ Furthermore, this gel has proven capable of reducing water flow in harsh environments, achieving a notable 99.8% reduction in permeability over a 5-month period.¹⁸⁵ By conducting a comparison under similar sample characteristics, the study intends to quantify the extent of improvement in the performance of the nano-silica gel system for fracture applications.

5.3 Materials and Experimental Procedure

5.3.1 Chemicals

Two gel systems were used in this study, nano-silica gel and PAM/PEI gel. The nano-silica gel system consists of two components: a nano-silica solution and an activator were both in the solution form (supplied by Saudi Aramco). To prepare a nano-silica gel with a 75/25 wt%, initially, a certain volume of nano-silica solution was placed in a beaker and recorded its weight. Then, an equal amount of activator solution was added to match the desired weight percentage. The mixture was gently stirred for at least 10 minutes until it reached a suitable consistency for injection. The silica nanoparticles are discrete, possessing a smooth, spherical shape. The average particle size distribution of the nano-silica was 14 nm, determined using the FPIA-3000 (Malvern) particle size analyzer. The initial gel mixture exhibits a viscosity of 6 cp, which accelerates with temperature as a result of gelation.

The second gel system is PAM/PEI gel, comprised of PAM and PEI. PAM was provided by SNF Floerger as an aqueous solution. It was utilized without additional treatment. The PAM solution had a concentration of 20 wt% active ingredients, and its molecular weight fell within the range of 250-500 kg/mol, as indicated by the supplier. The PEI, serving as

a cross-linker, was utilized in solution form. To prepare a sample volume of 30 mL of PAM/PEI solution with a weight percentage of (9/1), 13.5 mL of PAM was initially combined with 15.5 mL of water and stirred for approximately one minute. Following this, 1 mL of PEI was introduced into the mixture, which was then stirred for an additional 10 minutes. For permeability measurement and endurance test, brine solution was used, contains sodium chloride with a concentration of 0.1M per liter.

5.3.2 Coreflooding

To evaluate the effectiveness of nano-silica gel for plugging fractures, coreflooding experiments are conducted to simulate the water shut-off treatment. The experiment has three stages, pretreatment stage to evaluate sample initial permeability, gel injection and post- treatment stage to evaluate the gel plugging efficiency. The schematic diagram, depicted in Figure 36, illustrates the coreflooding system utilized in the study. This system includes a 1.5-inch core holder equipped with two pressure transducers for recording both inlet and outlet pressures. Two pumps are integrated, with one responsible for applying confining pressure to the core holder and the other for injecting fluid through two accumulators – one for gel placed outside the oven and another for brine kept inside the oven. To maintain consistent pressure and replicate reservoir conditions, a back pressure regulator is utilized and set at 400 psi. In conjunction with the gel treatment of the samples, medical CT scans and NMR measurements are employed to characterize the sample's pore system before and after the gel treatment.

To conduct the coreflooding experiments, the following steps were undertaken: Firstly, the core sample properties, including porosity and bulk volume, were initially evaluated. A medical CT scan was then conducted on the dry sample for detailed imaging. Subsequently, the core sample was saturated with brine (0.1M per liter), and T_2 NMR measurements were taken to assess its pore system characteristics in the saturated state. The prepared core sample was then placed into the coreflooding system, operating at 200 °F. Brine injection follows, utilizing various flow rates, with corresponding pressure drop recordings for initial permeability evaluation. The experiment progressed to injecting a gelant solution equivalent to 5 to 7 pore volumes, and subsequent cleaning of system lines from silicate gel is carried out. Following a 48-hour curing period for the treated sample, brine injection

is resumed under a constant differential pressure, and the leak-off rate is recorded at 200 °F.

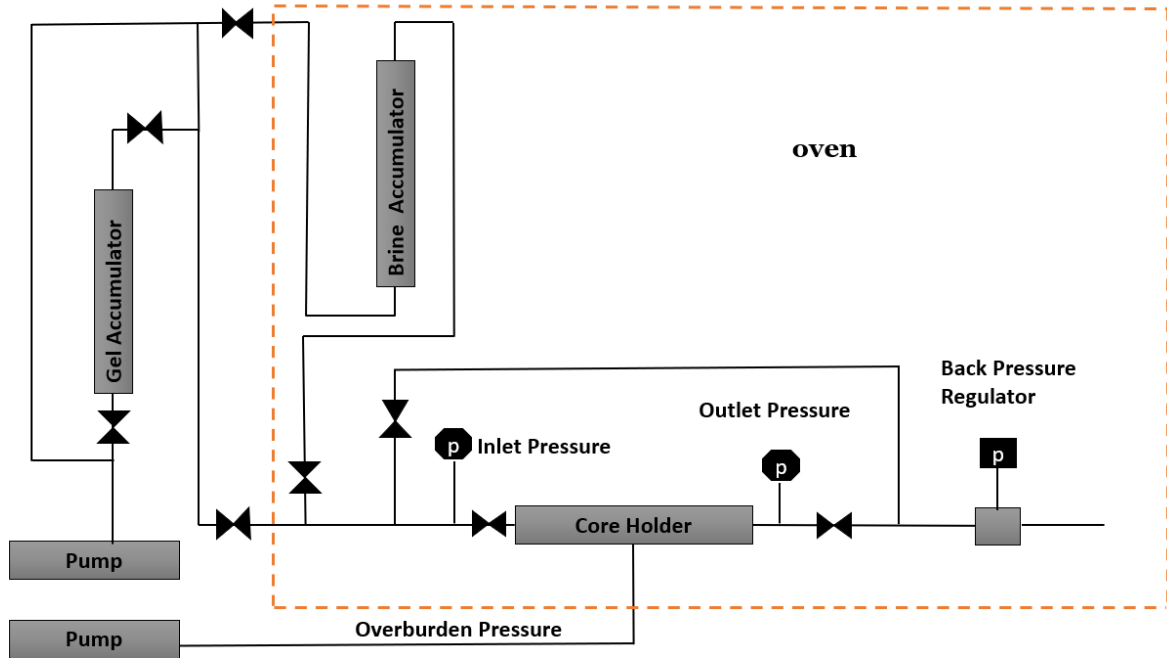


Figure 36 Core flooding system for gel treatment.

5.3.3 CT scan and NMR T₂ Measurement

The primary objective of using the medical CT scan is to validate the penetration of the nano-silica gel into both the induced fracture and the matrix. It also enables a comprehensive understanding of the pattern of gel penetration. Scans were conducted both before and after gel treatment, and the results are depicted in terms of CT numbers. The CT number, expressed in Hounsfield units, signifies the intensity of the transmitted X-ray beam and is equivalent to a specific density value in g/cm³.¹⁸⁶ Consequently, any change in the CT number corresponds to a change in density.

Another tool to evaluate the gel impact on the pore system characteristic of the core sample is NMR T₂. The measurement was conducted both before and after gel treatment. It relies

on the principles of nuclear magnetic resonance, where the behavior of atomic nuclei in a magnetic field is used to gain insights into the structure and properties of materials. In the context of pore size understanding, NMR T_2 measurement is used to probe the dynamics of fluids within porous materials. The T_2 relaxation time is a measure of the time it takes for the NMR signal to decay to a certain fraction of its initial intensity. For a sample confined in porous media is placed in a magnetic field and subjected to radiofrequency pulses, the NMR signal decay, or relaxation, is influenced by the mobility and distribution of fluids within the pore space. This decay is directly related to the characteristics of the fluid properties, pore size and connectivity.

When measuring fluid confined in porous media, T_2 relaxation is governed by three different phenomena: bulk, surface, and diffusion relaxation. The T_2 relaxation time measurements are acquired using the conventional CPMG pulse sequence^{199,200} which can be modelled as:

$$\frac{1}{T_2} = \frac{1}{T_{2,bulk}} + \rho_2 \frac{S}{V} + D \frac{(\gamma G t_e)^2}{12} \quad (5.1)$$

$T_{2,bulk}$ is the relaxation component related to the free-bulk fluid, and it becomes significant when the relaxation is not restricted by the pore geometry. It worth mentioning that the $T_{2,bulk}$ is inversely proportional to fluid viscosity.¹⁸⁷ ρ_2 is the surface relaxivity corresponding to the relaxation enhancement due to the surface interaction, S/V is the surface area to volume ratio of the pore space. The surface relaxation component dominates the overall relaxation when the fluid is in direct interaction with the pore geometry. D is the fluid's self-diffusion coefficient, γ is the gyromagnetic ratio of a proton nuclei, g is the internal magnetic field gradients (in saturated rocks, these effects arise due to variations in magnetic susceptibility between the solid grain matrix and the liquid phase); t_e is the echo time between NMR CPMG spin echoes. Typically, the impact of diffusion relaxation has negligible impact for carbonate rock samples acquired with low magnetic field instruments (such as the 0.05 T system used herein). Therefore, the NMR signal at low magnetic fields

from rocks saturated with fluid mainly depends on the collective properties of the bulk fluid and the surface relaxation characteristics of the system. These aspects are associated with the first and second terms on the right side of Equation (1), respectively.

5.4 Results and Discussion

5.4.1 Experiment 1 (Nano-silica gel on fractured sample)

The fractured sample is a limestone core sample utilized to simulate coreflooding experiment on fracture, and it has a distinct configuration with dimensions of 1.5-inch diameter and 3-inch length. The mid-fracture sample has an induced fracture that runs along the length of the core sample, as depicted in Figure 37. The middle section in the sample was considered to represent a small fracture which was created by cutting the sample into two equal halves and subsequently rejoining them using a shrinkage tube with heating.

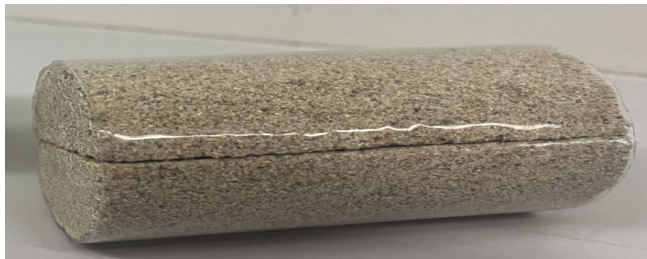


Figure 37 Fractured sample.

5.4.1.1 Coreflooding

There were three stages to conduct the coreflooding experiment, pre-treatment stage, gel injection and post-treatment stage as displayed in Figure 38. In the pre-treatment stage, sample permeability was initially evaluated. It was assessed using the brine solution, with 10 pore volumes injected at four distinct flow rates as displayed in Figure 38. The calculated average sample permeability was determined to be 184.73 mD, significantly exceeding the original sample's permeability in the nonexistence of an induced fracture, which was 70 mD. This outcome signifies that the created fracture remains open and provides an additional channel for water flow.

Before commencing the gel injection, the system underwent heating to reach a temperature of 200 °F. To ensure the successful placement of the gel, the plan involved injecting approximately 6 to 7 pore volumes of nano-silica gel. The prepared solution consisted of 75% nano-silica and 25% activator, providing a suitable gelation time of 3.5 hours. With a constant injection rate of 1 ml/min, approximately 6.3 pore volumes were injected, as illustrated in Figure 38. During the injection, a gradual increase in the differential pressure was observed due to the rising viscosity of the gelant. However, it's worth noting that the measured differential pressure during the injection process remained within an acceptable range, and the target volume was successfully pumped. This outcome indicates that the injectivity of the treatment was satisfactory.

The last stage, post-treatment stage, involved conducting an endurance test at high differential pressure to evaluate the plugging efficiency. The gel was allowed to cure for 48 hours at a temperature of 200 °F. Then, the endurance test commenced with a gradual increase in differential pressure until it reached 250 psi as depicted in Figure 38. This pressure was maintained for a duration of 30 minutes, during which no flow was observed. Subsequently, the pressure was held steady at 500 psi for another 30 minutes and then at 750 psi for 3 minutes, with no observable flow leakage from the system outlet. This observation serves as an initial indication of the gel effectively plugging the pore spaces. To investigate the durability of the gel, the differential pressure was then increased to 1000 psi and maintained for a continuous 3-hour period. The leak-off rate during this phase was minimal, measuring only 0.054 ml/min. The durability for high pressure drop was confirmed with this observed zero leak-off rate under holding pressure of 4000 psi/ft. These results clearly demonstrate the gel's exceptional plugging capability, achieving a plugging efficiency of 100%. The permeability dropped significantly to 0.046 millidarcies (mD), which is notably lower than the pre-treatment permeability of 184.73 mD. The gel exhibited an impressive residual resistance factor of 39,746.9 (ratio of permeability before treatment to permeability after treatment), This high residual resistance factor signifies the tremendous impact of the gel in reducing water permeability, reaffirming its substantial capability for effectively plugging induced fractures, reaffirming its substantial plugging capability for the induced fracture. The attained plugging capacity aligns closely with the

gel's performance as reported in the study conducted by Almohsin¹⁴⁰ et al. treating a high-permeability matrix of 700mD. In that investigation, the gel exhibited a 100% plugging efficiency alongside a leak-off rate of 0.0018 cc/min.

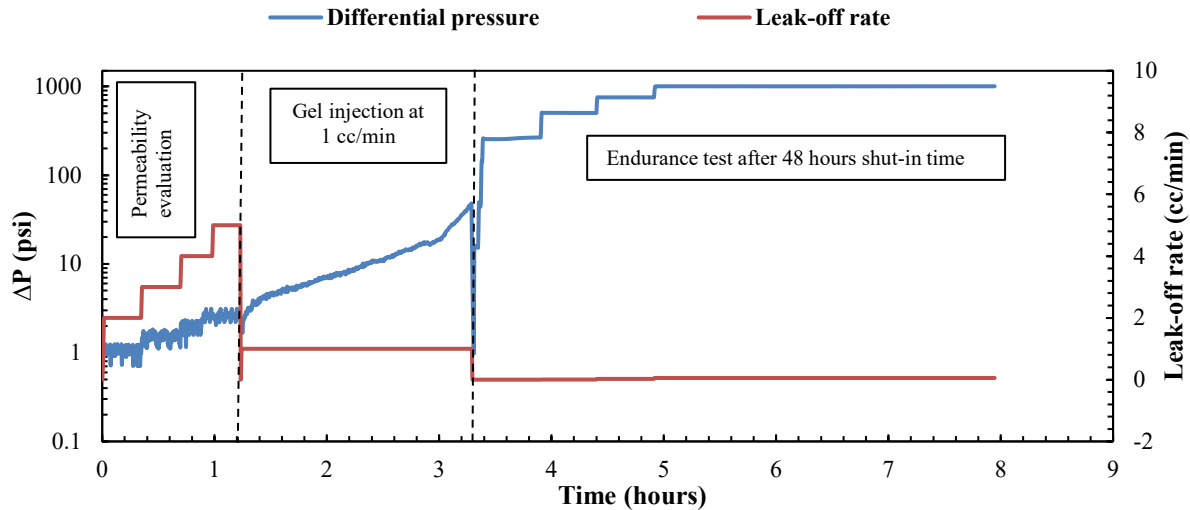
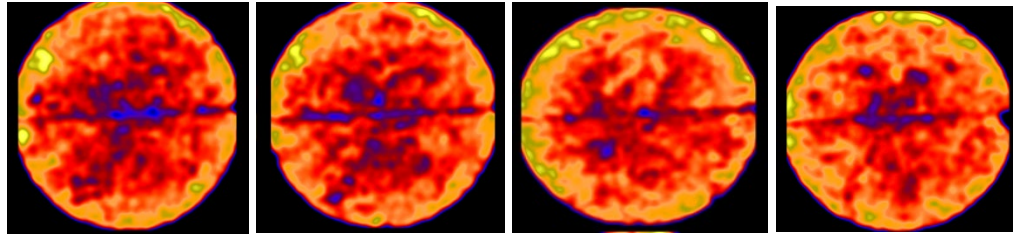


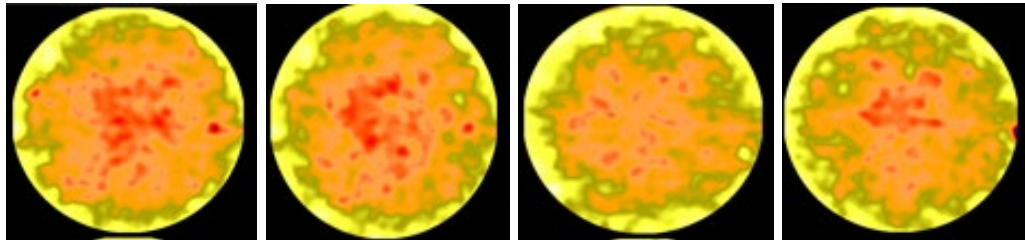
Figure 38 Coreflooding experiment 1 (200 °F).

5.4.1.2 CT Scan Analysis

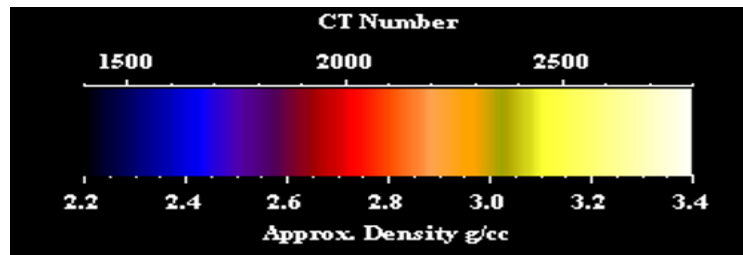
Figure 39 displays various slices at different positions along the length of the core sample. The color code illustrates the variation in CT numbers or density. By referencing the color code scale, one can clearly point out the differences between slices before and after gel treatment. Darker colors indicate lower CT numbers or density, while brighter colors represent higher CT numbers (density). From Figure 39, it becomes evident that the gel has been effectively placed in both the induced fracture and the matrix. After treatment, there is a more widespread presence of brighter spots in the central zone (fracture) as well as in the matrix. This shift from darker to brighter colors indicates an increase in the density of the porous media, which can only be attributed to the injected gel.



(a) Before treatment



(b) After treatment



(c) Color code scale

Figure 39 (a) CT scan images of different fracture sample slices before nano-silica treatment; (b) CT scan images of different slices of the fractured sample after nano-silica gel treatment; (c) color code scale (Experiment 1).

Before treatment, the average CT number for each slice hovered around 2104.28 along the length of the core sample. Following gel treatment, there was a clear shift, with the average CT number now centered around 2321.18. This increase in the average CT number throughout the core sample underscores that the gel was successfully distributed along the entire length of the sample. In sum, the analysis of the CT scans has provided conclusive evidence that the gel was effectively placed within the induced fracture along the entire length of the core sample. This outcome aligns with the exceptional plugging efficiency demonstrated by the gel.

5.4.1.3 Pore size characteristics using NMR T_2 Measurement

Initially, NMR measurements were performed on a brine solution and nano-silica gel bulk fluids. The T_2 peaks for bulk-free brine and bulk-free nano-silica are represented as black and red vertical-dashed lines as shown in Figure 40, respectively. In Figure 40, It is evident that water's relaxation time (~ 2818 ms) is longer than that of nano-silica gel (~ 32 ms), primarily due to a substantial difference in viscosity. When performing NMR measurements on the sample saturated with brine, it becomes apparent that the core exhibits bi-modal pore size distribution. Micropores have a shorter relaxation time, while macropores, associated with the induced fracture, appear in the region with longer relaxation times. The nano-silica gel was then introduced into the core during injection until no brine was detected from the outlet. The T_2 peak shifted to the left aligning closer to that of the bulk-free nano silica while there is very minor T_2 relaxation component arising in longer relaxation times. This behavior indicates that brine still exists in the macropores samples in extremely less amount after nano-silica gel injection and it is significantly influenced by surface relaxation effects. Figure 41 represents a schematic visualization of the fluids' distribution within the macropores. Comparing the T_2 relaxation time distribution behavior of the before and after gel injection, it becomes evident that the gel has significantly reduced the brine content in the macro pores associated with the induced fracture.

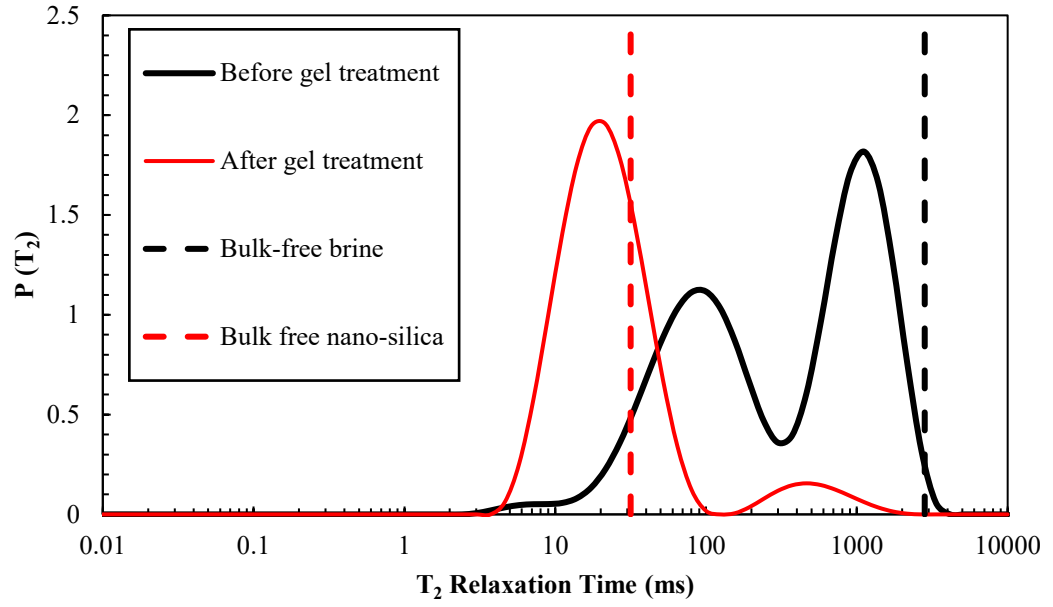


Figure 40 Average T_2 distribution for the mid-fracture sample (Experiment 1).

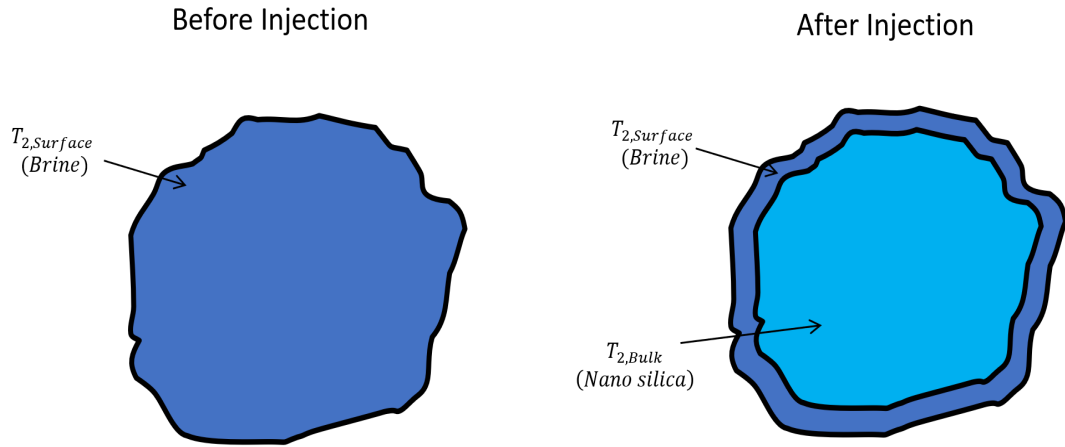


Figure 41 Fluids distribution before and after gel treatment.

To ensure full saturation of fluid inside the rock core, NMR saturation profiles were acquired along the length of the sample. Figure 42 shows a uniform saturation profile of

fluid before and after injection of fluids. This indicates the full gel penetration along the sample length.

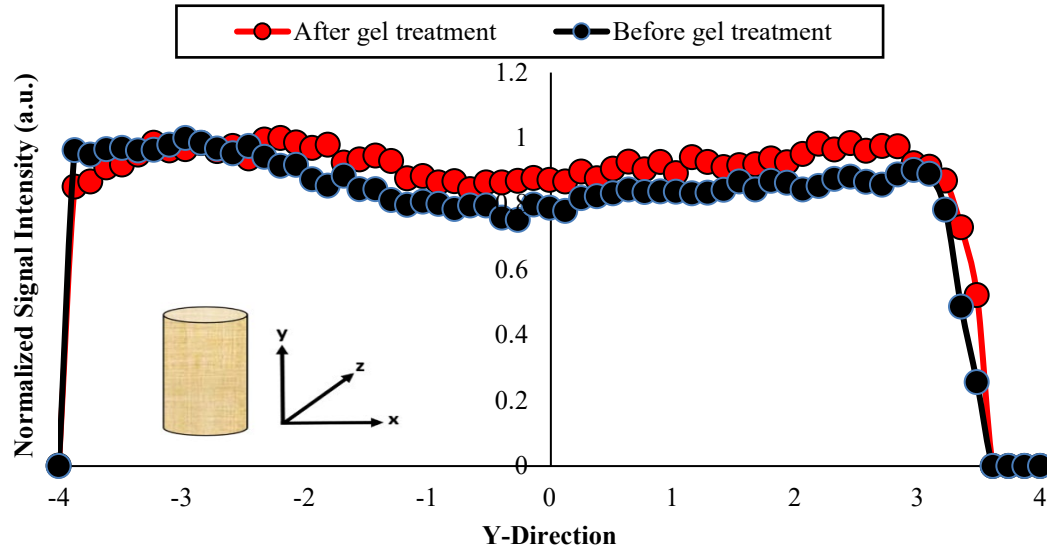


Figure 42 Fluids saturation profile before and after nano-silica gel treatment.

5.4.2 Experiment 2 (nano-silica gel on an induced-channel sample)

The sample characteristics differ from the previous sample for experiment 1, as it has opening channel created by HCl acid as displayed in Figure 43.



Figure 43 A CT scan of the sample with induced channel.

5.4.2.1 Coreflooding

The initial sample's permeability assessment was conducted using the same NaCl solution with a concentration of 0.1M per liter. The injection involved seven pore volumes at different flow rates of 1, 2, 3, and 4 ml/min as displayed in Figure 44. The resulting average permeability was determined to be 440.60 millidarcies (mD), a significant increase compared to the original sample's permeability before the creation of the channel (wormhole), which was less than 50 mD. This outcome highlights the substantial influence of the open channel on brine flow.

Prior to initiating the gel injection, the system was heated to a temperature of 200 °F. The gel solution remained consistent as in the previous experiment, comprising 75% nano-silica and 25% activator, which maintained a gelation time of 3.5 hours. With a steady injection rate of 1 ml/min, the entire injection process was efficiently completed in less than an hour, delivering approximately 6.13 pore volumes, as visually represented in the accompanying Figure 44. During the injection, as expected, a gradual increase in differential pressure was observed due to the gelant's increasing viscosity. Compared with brine injection, the higher reported differential pressure provided a clear indication of gel penetration into the matrix surrounding the channel. Importantly, it's noteworthy that the measured differential pressure consistently remained low within an acceptable range throughout the injection process. This observation confirms successful gel penetration into both the channel and matrix. The successful injection of the target gel volume ensures a sufficient amount of gel for effective plugging.

After shutting in the system for 48 hours, the nano-silica gel was completely cured for 48 hours. The endurance test was implemented using the same procedure by applying different differential pressures and observing the leak-off rate in the outlet. In Figure 44, the test began with a gradual increase in differential pressure until it reached 250 psi. This pressure was maintained for 30 minutes, during which no flow was observed. Subsequently, the pressure was held constant at 500 psi for another 30 minutes, and then at 750 psi for 30 minutes with no detectable flow leakage from the system outlet. This observation serves as an initial indication that the gel has effectively plugged both the channel and the matrix pore spaces. To assess the durability of the gel, the differential pressure was then raised to

1000 psi and maintained continuously for 3 hours. The leak-off rate during this phase was minimal, measuring only 0.05 ml/min. The nearly negligible leak-off rate observed underscores the durability and robustness of the gel, particularly under a holding pressure of 4000 psi/ft. The permeability significantly decreased to 0.0049 millidarcies (mD), a substantial reduction from the pre-treatment permeability of 440.19 mD. These results demonstrate the exceptional plugging capability of the gel, achieving a plugging efficiency of 100% along with the large value of the residual resistance factor achieved (115567.4). This significant value reflects the tremendous impact of the gel reducing water permeability. The performance closely resembles the plugging efficiency demonstrated in Karadkar¹⁴¹ et al.'s study, where the gel exhibited a leak-off rate of zero under differential pressures of up to 2500 psi. Furthermore, when compared to the gel's performance in Almohsin¹⁴⁰ et al.'s study, which focused on a highly permeable matrix of 700 mD, both treatments displayed consistent plugging efficiency of 100%.

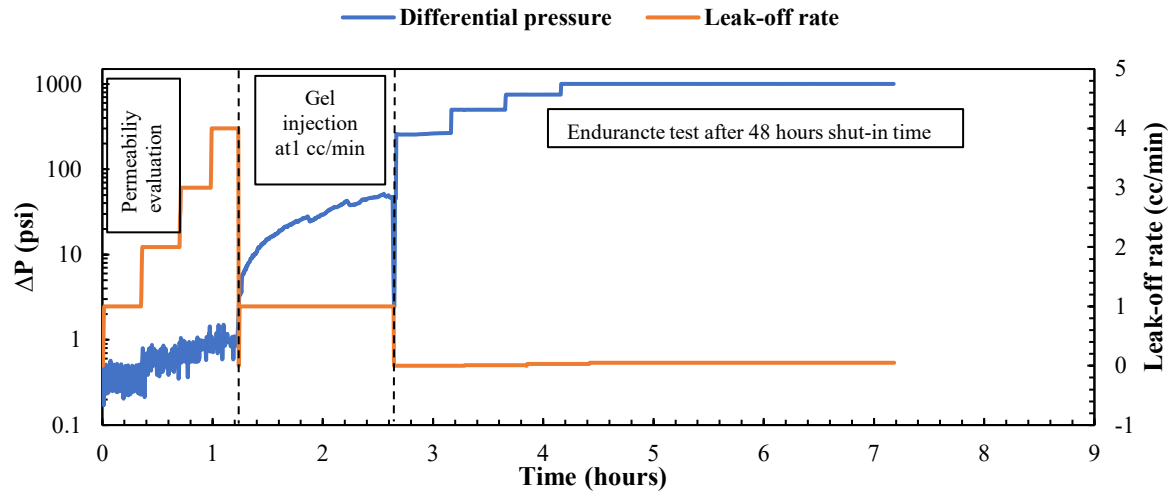


Figure 44 Coreflooding experiment 2 (200 °F).

5.4.2.2 CT Scan Analysis

Gel invasion was analyzed considering medical CT scan results on the sample before and after gel treatment. Figure 45 presents various slices at different positions along the length of the core sample. By referencing the color code scale, Darker colors indicate lower CT numbers or density, while brighter colors represent higher CT numbers (density). The sample channel appears as a small circular spot with a dark color, while after treatment,

these spots' color has changed to blue color. The change refers to a larger change in density in this position. Clearly, this confirmed that the nano-silica gel was successfully placed into the channel. To gain insights into the gel invasion pattern, the average CT number was obtained per slice. Prior to treatment, the average CT number for each slice consistently measured around 2,363.31 along the length of the core sample. After the gel treatment, a slight shift became evident, with the average CT number now centered around 2,368.39. This increase in the average CT number across the entire core sample emphasizes the successful placement and distribution of the gel along its entire length. In summary, the CT scan results provide compelling evidence that the gel was effectively positioned within the induced channel spanning the full length of the core sample. This outcome aligns seamlessly with the exceptional plugging efficiency demonstrated by the gel.

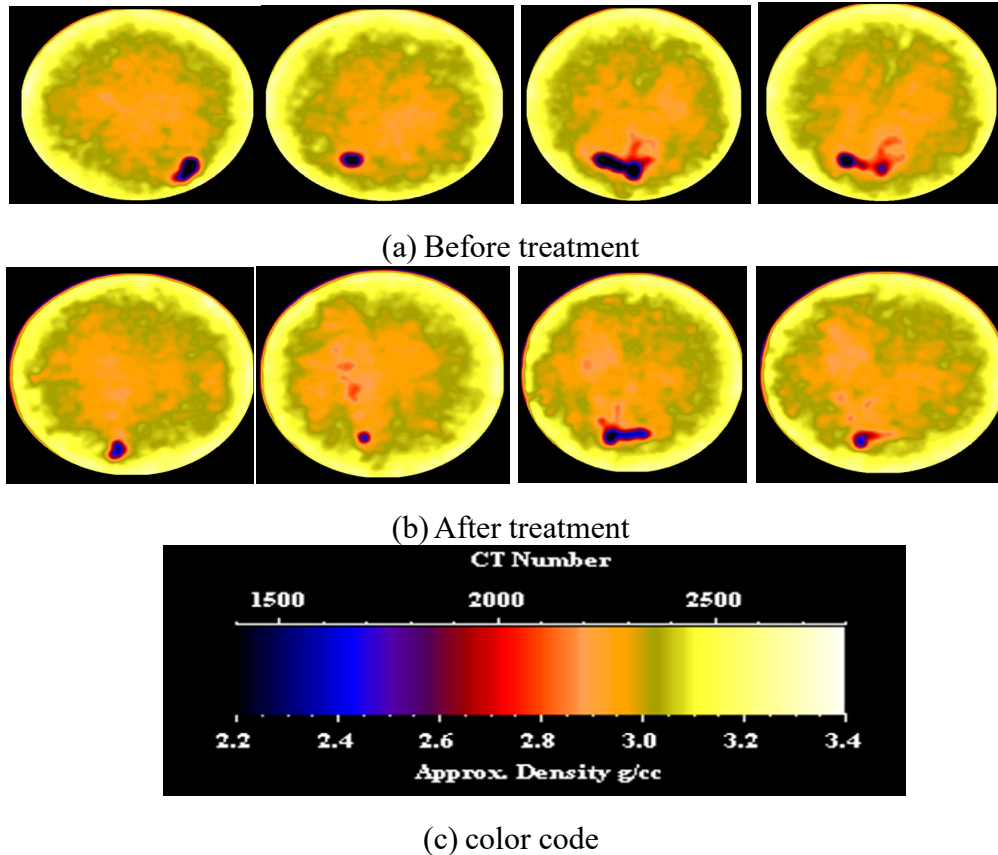


Figure 45 (a) CT scan for different slices before treatment; (b) CT scan for different slices after treatment; (c) color code scale.

3.2.5 Pore size characteristics using NMR T_2 Measurement

NMR measurements were conducted both before and after the gel treatment, as shown in Figure 46. The T_2 curve for the sample saturated with brine reveals the presence of three distinct pore systems, including two micro systems and a third macro system that incorporates the open channel. Following the injection of the gel, it is evident that the gel filled a portion of the micropores, causing the T_2 peak of the larger micropores to shift towards the T_2 peak of the bulk-free nano-silica. However, it's worth noting that it remains larger than the T_2 peak of the free bulk gel. This suggests that the gel may not be optimally centered within the middle of the micropores, particularly when compared to experiment 1 (refer to Figure 46). In the case of the macropores, the T_2 distribution distinctively confirms that the gel has completely displaced the brine from the channel. The T_2 value has decreased to zero in the location corresponding to the previous T_2 peak, indicating the complete removal of the brine from these channels. To further validate the penetration of the nano-silica gel throughout the entire sample length, Figure 47 presents the fluid saturation profile in the core sample before and after gel treatment. Here, only minimal changes were observed, demonstrating the uniform distribution of the gel along the entire sample length and the successful penetration of the gel into the rock sample.

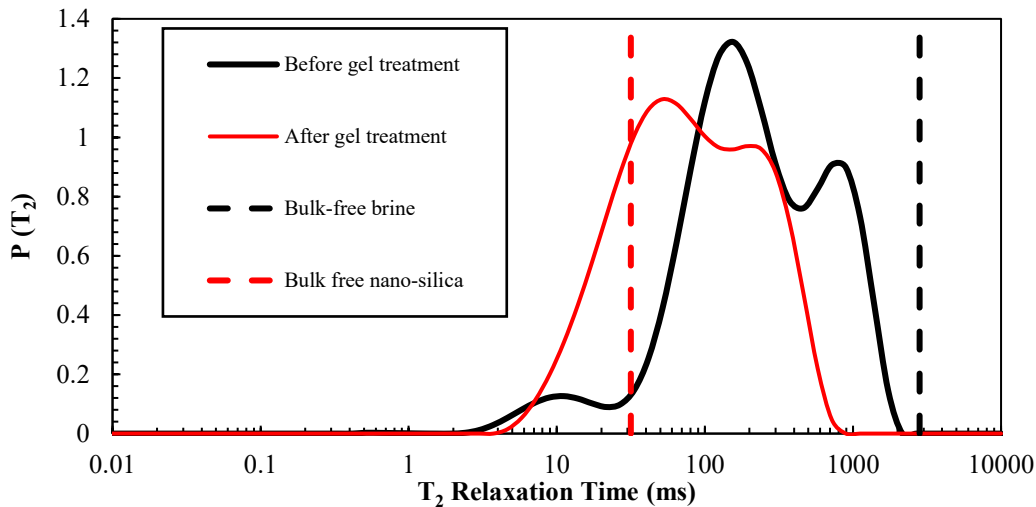


Figure 46 Average T_2 distribution for the induced channel sample (Experiment 2).

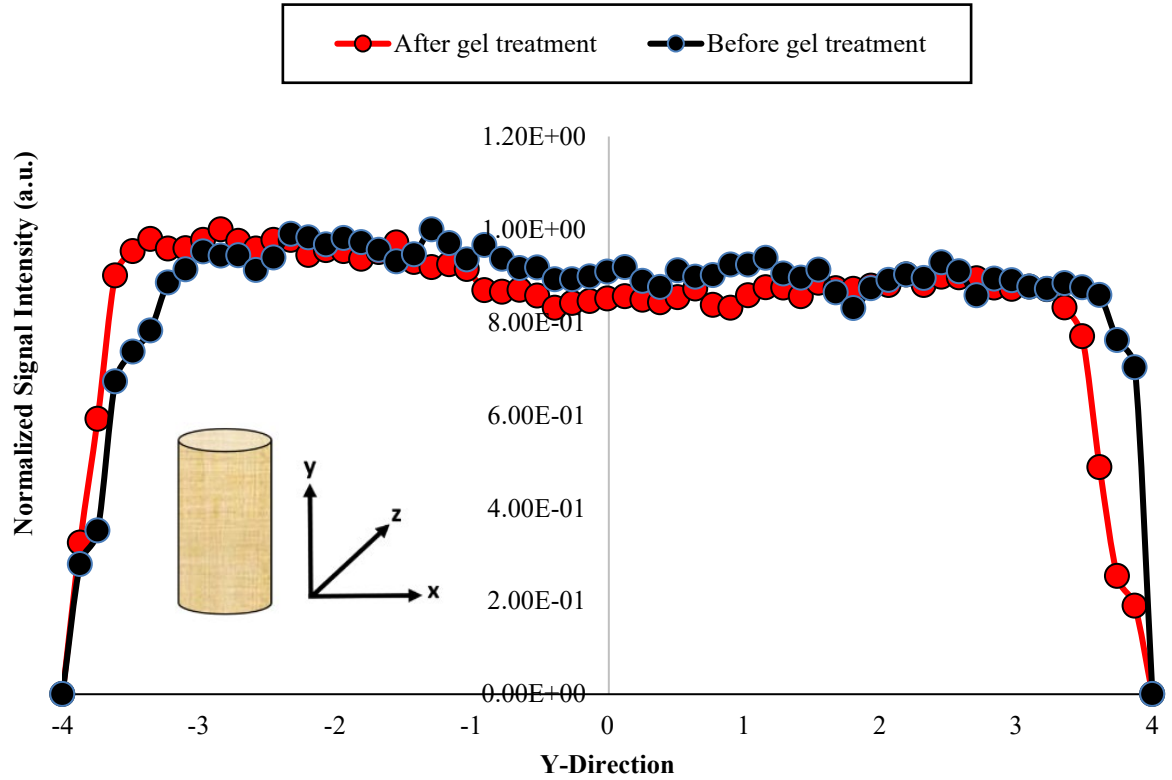


Figure 47 Fluids saturation profile (Experiment 2).

5.4.3 Experiment 3 (PAM/PEI gel on the mid-fracture sample)

5.4.3.1 Coreflooding

A mid-fracture sample, similar to the one displayed in Figure 37, was chosen for treatment with PAM/PEI gel. The sample has similar characteristics to the sample in experiment 1. The initial sample permeability was evaluated using the brine solution, which was injected at four distinct flow rates as appeared in Figure 48 . The calculated average sample permeability was determined to be 184.73 millidarcies (mD), significantly exceeding the original sample's permeability in the absence of an induced fracture, which was 70 mD. This result indicates that the created fracture remains slightly open, providing an additional path for water flow.

A PAM/PEI gel was prepared with a concentration of 9/1 %wt. The gel injection was conducted over a 130-minute period at a flow rate of 1 ml/min, with the total injected gel volume approximately seven times the pore volume. The pressure drop observed during

the gelant injection is depicted in Figure 48, and the maximum pressure drop did not exceed 40 psi, indicating acceptable matrix injectivity.

After a 72-hour shut-in period, the PAM/PEI gel was fully cured. The endurance test was conducted following the same procedure, applying various differential pressures and observing the leak-off rate at the outlet (refer to Figure 48). The test commenced with a gradual increase in differential pressure until reaching 250 psi, maintained for 30 minutes with no observable flow. Subsequently, the pressure was held constant at 500 psi for another 30 minutes and then at 750 psi for an additional 30 minutes, with no detectable flow leakage from the system outlet. This observation suggests an initial indication that the gel effectively plugged both the channel and the matrix pore spaces. To evaluate the durability of the gel, the differential pressure was then raised to 1000 psi and maintained continuously for 3.5 hours. After 2 hours at 1000 psi, water droplets were observed at the outlet, measuring only 0.25 ml/min. The minimal leak-off rate observed under a holding pressure of 4000 psi/ft validates the durability of the gel and underscores its ability to sustain plugging capability over an extended period. The permeability experienced a significant reduction to 0.0181 millidarcies (mD), marking a substantial decrease from the pre-treatment permeability of 242.58 mD. These results demonstrate the effective plugging capability of the gel, achieving a plugging efficiency of 99.99% in both the matrix and the fracture with residual resistance factor of 13380.59. The substantial residual resistance

factor value indicates that the gel has effectively reduced water permeability, confirming its applicability for plugging fractures.

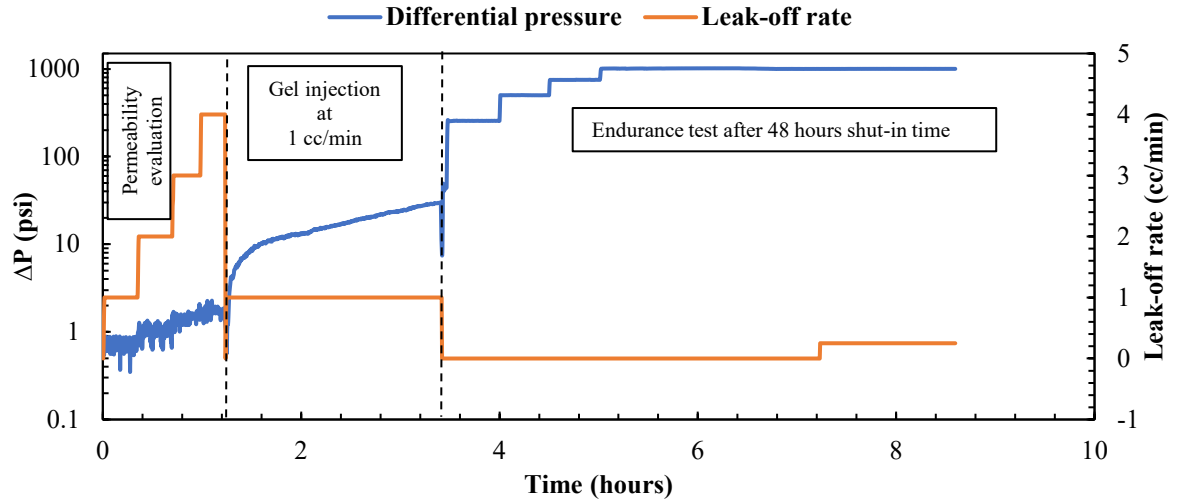


Figure 48 Coreflooding experiment 3 (200 °F).

5.4.3.2 CT scan analysis

A CT scan was conducted before and after gel treatment, and the core sample exhibited an obvious shift in CT distribution, visually confirming the successful invasion of the gel into the fractured section as displayed in Figure 49. Comparison of CT slices revealed a density transition, indicating effective gel placement. In addition, a shift in average CT numbers per slice from approximately 2096.92 pre-treatment to 2279.09 post-treatment, affirming the gel's successful distribution along the entire core sample length. This CT scan analysis provides conclusive evidence of the effective gel placement within the induced fracture along the complete length of the core sample.

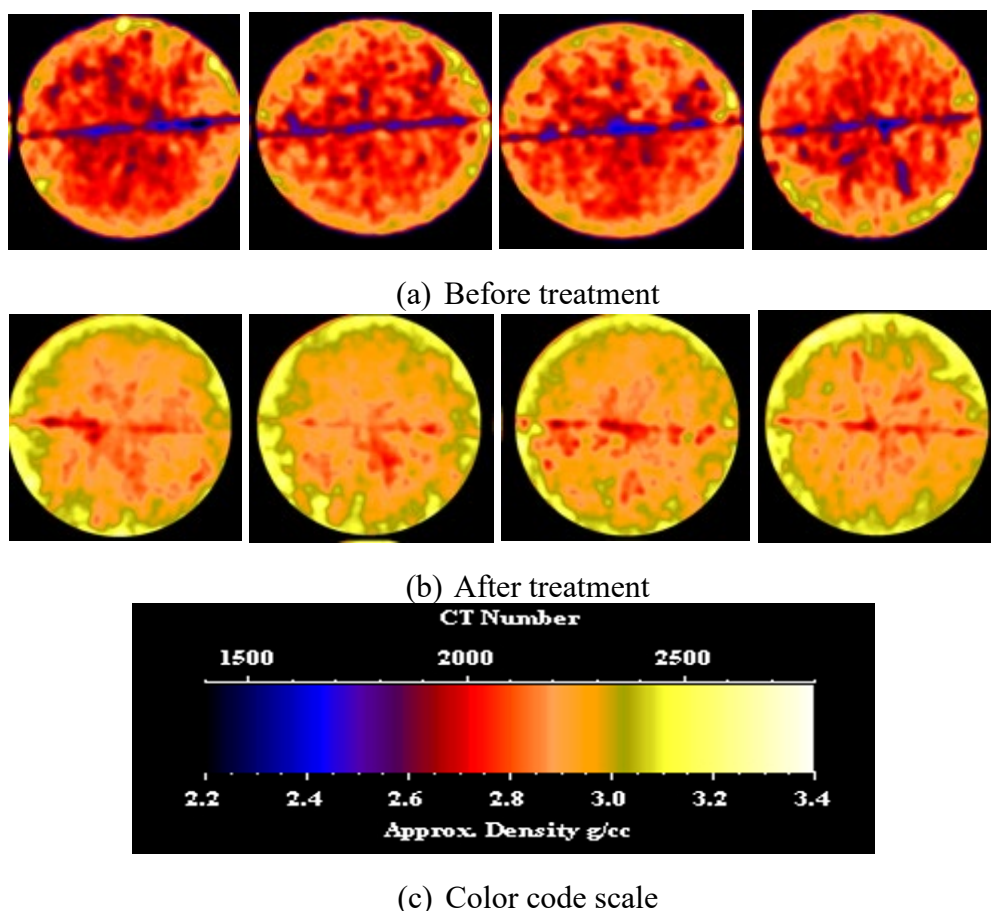


Figure 49 (a) CT scan images of different slices before PAM/PEI treatment; (b) CT scan images of different slices after PAM/PEI gel treatment; (c) color code scale.

5.4.3.3 Pore size characteristics using NMR T_2 Measurement

Initially, NMR measurements were conducted on brine solution, and PAM/PEI fluids, with the T_2 peaks for bulk-free brine and bulk-free PAM/PEI, represented as black and red vertical-dashed lines in Figure 50, respectively. The longer relaxation time of water (~ 2818 ms) compared to PAM/PEI (~ 630 ms) is attributed to their substantial viscosity difference. NMR measurements on the brine-saturated sample reveal a bi-modal pore size distribution, with micropores exhibiting shorter relaxation times and macropores, linked to the induced fracture, displaying longer relaxation times. The introduction of nano-silica gel into the core caused the T_2 peak to shift left, aligning closer to bulk-free nano-silica, with minimal T_2 relaxation component in longer times, suggesting residual brine in macropores post-gel injection. A comparison of T_2 relaxation time distribution before and after gel injection revealed a significant reduction in brine content in the macropores associated with the

induced fracture. To identify the invasion of the nano-silica gel throughout the entire sample length, Figure 51 shows NMR saturation profiles were acquired along the length of the sample. A minimal change was observed in the saturation profile of the fluid after injection of gel solution. This could indicate that the gel responsible for the plugging efficiency was more concentrated on the injection side.

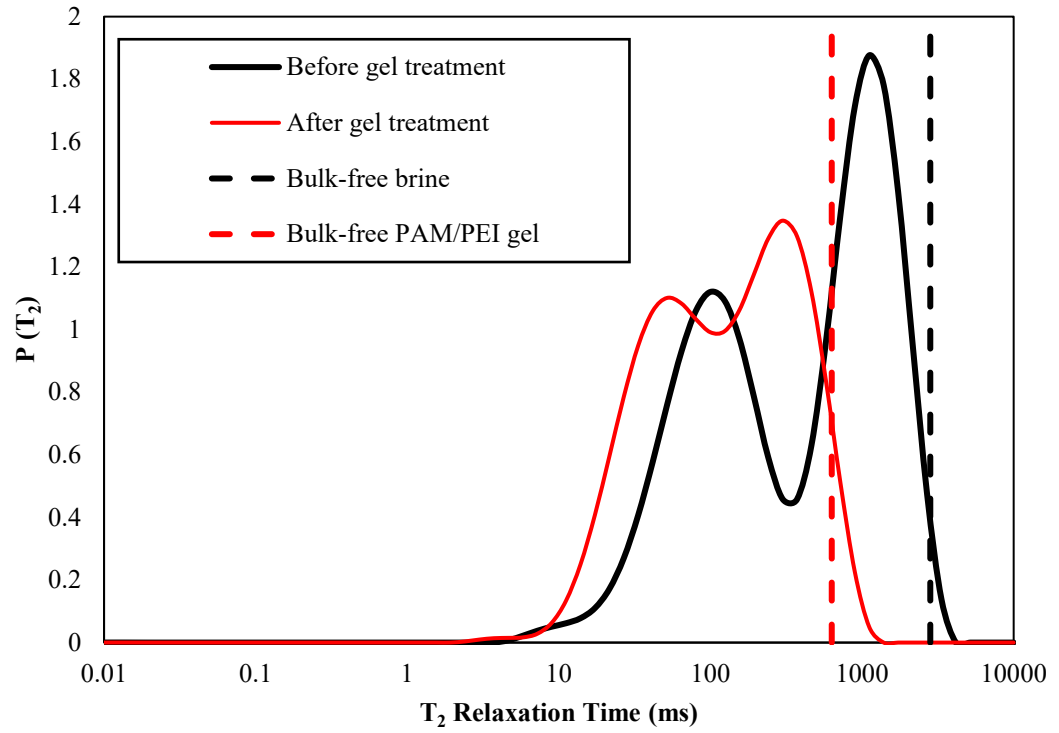


Figure 50 Average T_2 distribution for the mid-fracture sample (Experiment 3).

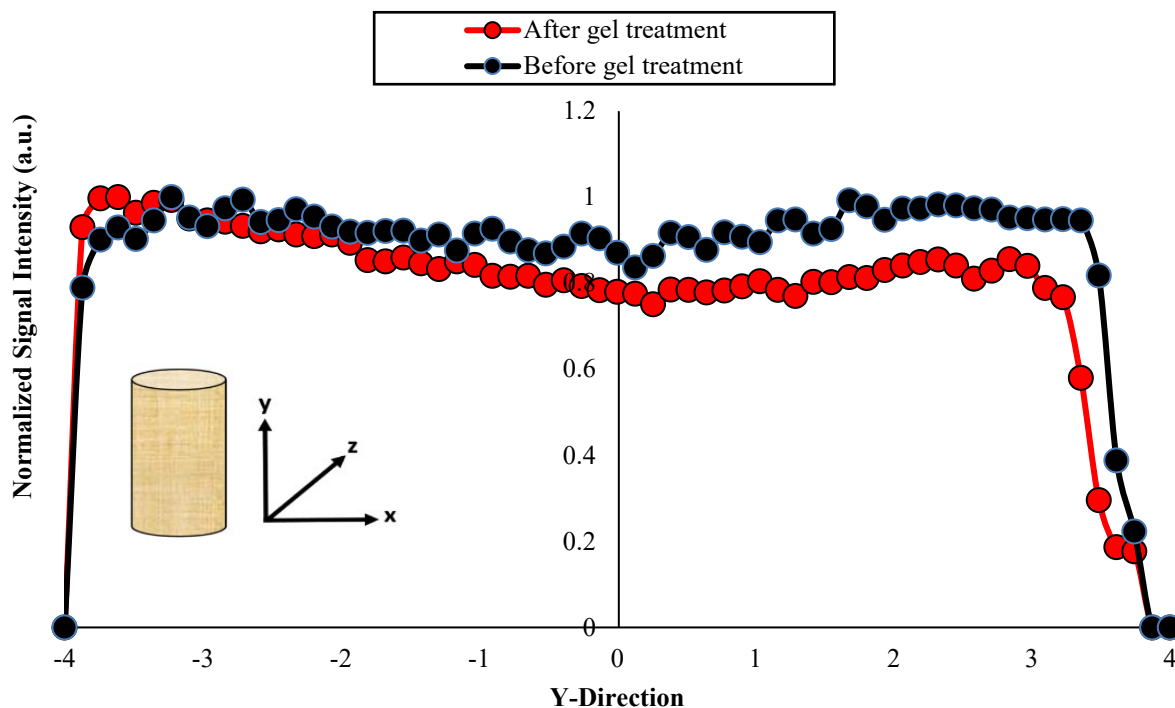


Figure 51 Fluids saturation profile (Experiment 3).

5.4.4 Experiment 4 (PAM/PEI gel on an induced channel sample)

5.4.4.1 Coreflooding

A carbonate core sample was selected for treatment with PAM/PEI gel. The sample has a channel (wormhole), as displayed in Figure 43, but it is closed in the outlet part. The initial sample permeability was assessed using a brine solution injected at four distinct flow rates as depicted in Figure 52. The calculated average sample permeability was determined to be 10.48 millidarcies (mD). The closure of the channel from the outlet resulted in a relatively low permeability as the brine was compelled to move through the low permeable matrix.

A PAM/PEI gel was prepared with a concentration of 9/1 %wt. The gel injection was carried out over a 30-minute period at a flow rate of 1 ml/min, with the total injected gel volume approximately 3 times the pore volume. Due to the low permeability, a high-pressure drop was observed during the gelant injection, as depicted in Figure 52. The

obtained pressure drop indicates that the gel was forced to move through the low permeable matrix, ensuring the placement of the gel in both the matrix and the channel.

After a 72-hour shut-in period, the PAM/PEI gel was fully cured. The endurance test was conducted following the same procedure, applying various differential pressures and observing the leak-off rate at the outlet (refer to Figure 52). The test commenced with a gradual increase in differential pressure until reaching 250 psi, maintained for 30 minutes with no observable flow. Subsequently, the pressure was held constant at 500 psi for another 30 minutes and then at 750 psi for an additional 30 minutes, with no detectable flow leakage from the system outlet. This observation suggests an initial indication that the gel effectively plugged both the channel and the matrix pore spaces. To evaluate the durability of the gel, the differential pressure was then raised to 1000 psi and maintained continuously for 3 hours. After 2 hours at 1000 psi, few water droplets were observed at the outlet, measuring only 0.001 ml/min. The nearly zero leak-off rate observed at 4000 psi/ft holding pressure confirms the durability of the gel and its ability to effectively plug water flow over an extended period of time. The gel achieved a plugging efficiency of 100%. Post-treatment, the permeability experienced a significant reduction to zero millidarcies (mD), marking a substantial decrease from the pre-treatment permeability of 10.48 mD. These results demonstrate the effective plugging capability of the gel, achieving a plugging efficiency of 99.99% in both the matrix and the fracture. The substantial residual resistance factor of 762625.06 further highlights the significant reduction in water permeability attributed to the presence of the gel.

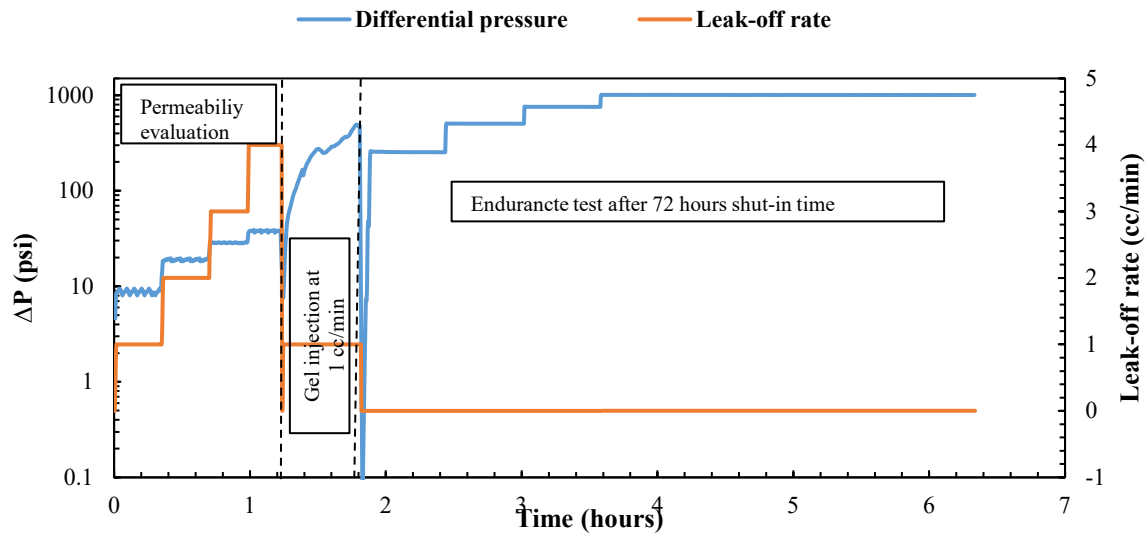


Figure 52 Coreflooding experiment 4 at 200 °F.

5.4.4.2 CT scan analysis:

In a similar track, a medical CT scan was conducted on the sample both before and after gel treatment, as illustrated in Figure 53, showcasing various slices at different positions along the core sample length. The pre-treatment appearance of the sample channel is seen as a small circular spot with a dark color (low density), which transforms to a blue color with a smaller size after gel treatment (higher density), indicating a notable increase in density in this position. This change provides confirmation that the PAM/PEI gel was effectively placed into the channel. The average CT number for each slice revealed a slight shift after gel treatment, with the average CT number centered around 2424.67 compared to the pre-treatment average of 2305.12. This increase in average CT number across the entire core sample emphasizes the successful placement and distribution of the gel along its complete length. In summary, the CT scan results provide compelling evidence of the effective positioning of the gel within the induced channel spanning the entire length of the core sample, aligning seamlessly with the exceptional plugging efficiency demonstrated by the gel.

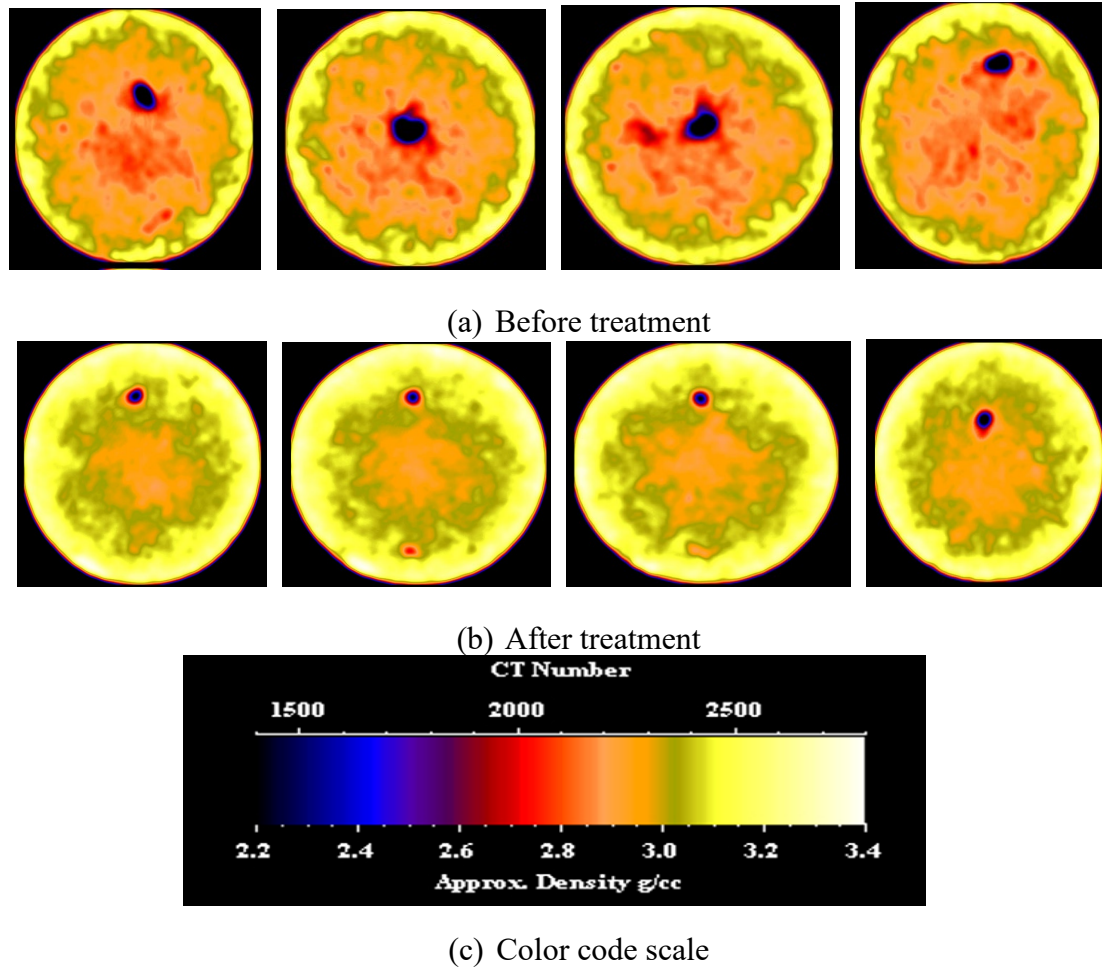


Figure 53 (a) CT scan images of different slices before PAM/PEI gel treatment; (b) CT scan images of different slices after gel PAM/PEI gel treatment; (c) color code scale.

5.4.4.3 Pore size characteristics using NMR T2 Measurement

Initially, NMR measurements were conducted on brine solution, and PAM/PEI fluids, with the T_2 peaks for bulk-free brine and bulk-free PAM/PEI represented as black and red vertical-dashed lines in Figure 54, respectively. As appeared in Figure 54, the sample has a bi-modal pore size distribution, as micropores are exhibiting shorter relaxation times, and macropores, linked to the channel, displayed longer relaxation times. Invasion of nano-silica gel into the core causes the T_2 peak to shift left, aligning closer to bulk-free nano-silica, with a small T_2 relaxation component in longer times, suggesting residual brine in macropores post-gel injection. Comparison of T_2 relaxation time distribution before and

after gel injection reveals a significant reduction in brine content in the micropores and sufficient placement of the gel in the macropores incorporating the channel. To identify the invasion of the nano-silica gel throughout the entire sample length, NMR saturation profiles were acquired along the length of the sample. Figure 55 shows a minimal change in the saturation profile of the fluid after injection of gel solution.

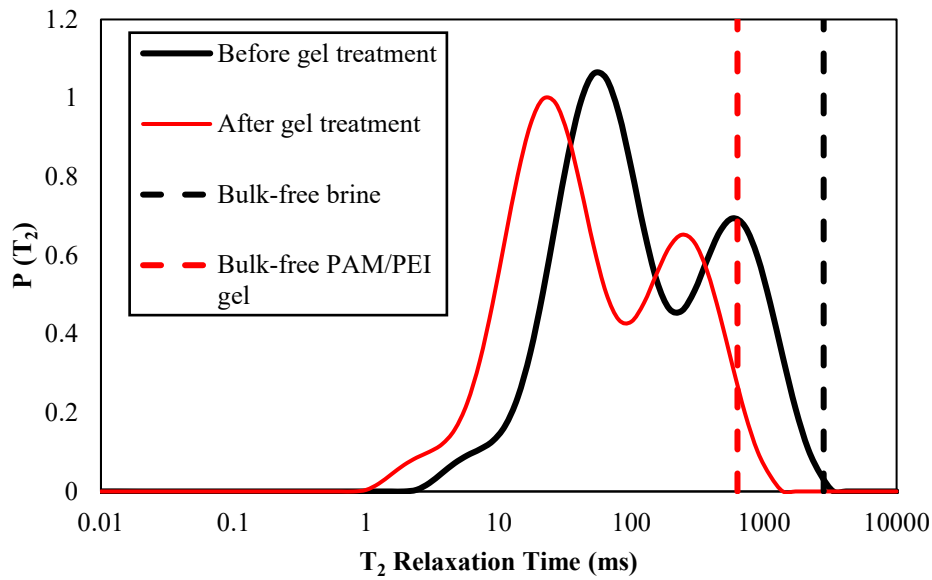


Figure 54 Fluids saturation profile along the induced channel sample (Experiment 4).

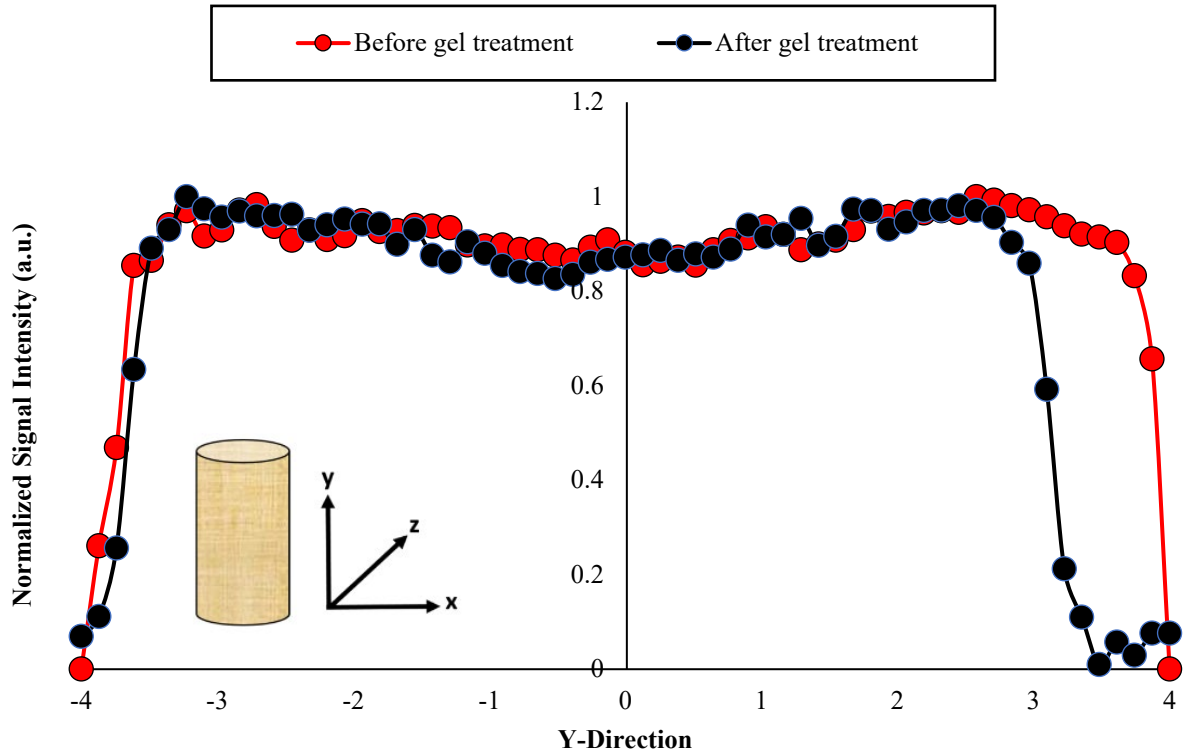


Figure 55 Fluids saturation profile along the induced channel sample (Experiment 4).

5.4.5 Observations on the effectiveness of nano-silica gel in comparison to PAM/PEI gel:

The core samples treated with nano-silica exhibit similar characteristics to those treated with PAM/PEI gel, allowing for a meaningful comparison of their performance. As shown in Table 12, nano-silica gel demonstrated exceptional performance in plugging fractures and channels, achieving 100% plugging efficiency in both cases, comparable to PAM/PEI gel. The gel remained durable under high differential pressure, up to 1000 psi, aligning closely with findings in previous studies,^{145,172} where it effectively plugged high-permeability matrices. Furthermore, the table presents the residual resistance factor for both gels, representing a valuable indicator of the gel's impact on the initial sample permeability. The observed high values of the residual factor are above 30,000 for the nano-silica gel and above 13000 for the PAM/PEI gel. The nano-silica gel strongly

illustrates a notable reduction in sample permeability, indicating the exceptional effectiveness of the gels in preventing water flow.

Table 12 Performance comparison between nano-silica gel and PAM/PEI gel.

	Plugging efficiency %		Residual resistance factor	
	Nano-silica gel	PAM/PEI gel	Nano-silica gel	PAM/PEI gel
Mid-fracture sample	100%	100%	39746.94	13380.0
An induced-channel sample	99.99%	100%	115567.0	762625.1

The identification of gel invasion through medical CT scans and NMR measurements aligns with the achieved plugging efficiency. Analyzing pore size via NMR indicates that nano-silica gel displaced water to a greater extent than PAM/PEI gel. In core samples with channels, nano-silica gel completely displaced water, while PAM/PEI gel left some water in the channel. Despite this, the achieved plugging efficiency suggests that the injected gel volumes were sufficient to prevent water flow.

5.5 Conclusion

Fractures and channels are one of the easy paths for water flow from the reservoir to production interval. The research effectively highlights the outstanding efficiency of nano-silica gel in addressing water-related challenges in reservoirs with fractured or channelized conditions. The findings of this study can be summarized as follows:

- Nano-silica gel effectively sealed the designed fractures and channels with 100% plugging efficiency, reducing permeability to nearly zero.
- Nano-silica gel demonstrated high injectivity with low pressured drop, sustained durability under varying differential pressures up to 1000 psi with maximum leak-off rate of 0.054 ml/min.

- PAM/PEI gel was capable to plug the designed fracture and channel with 100% permeability reduction, and the gel showed high durability for 1000 psi with leak-off rate nearly zero.
- Both CT scans and NMR proved confirmation for consistent gels penetration and distribution throughout the core samples.

CHAPTER 6

LONG-TERM INVESTIGATION OF NANO-SILICA GEL

FOR WATER SHUT-OFF IN FRACTURED

RESERVOIRS⁵

6.1 Abstract

Silicate gels have long been utilized as water shut-off agents in petroleum fields to address excessive water production. In recent years, nano-silica gel has emerged as a promising alternative to traditional silicate gels, offering potentially improved plugging performance. However, the long-term effectiveness of these gels remains uncertain, posing challenges to sustained profitability. Therefore, a comprehensive study spanning 6 months was conducted on fractured and induced channel samples treated with nano-silica gel of 75/25 wt% (silica/activator) at 200 °F. A comparative analysis was made with samples treated using polyacrylamide/polyethyleneimine PAM/PEI gel (9/1 wt%) to compare the performance of both systems. Throughout the aging period in formation water at 167°F, endurance tests were conducted at regular intervals, complemented by computed tomography (CT) scans to monitor any potential degradation. The results revealed nano-silica gel's superior long-term performance in plugging fractures and channels compared

⁵ This chapter is copied from the manuscript: Ali, A.; Al Ramadan, M.; Aljawad, M. S.; Almohsin, A. Long-Term Investigation Of Nano-Silica Gel For Water Shut-Off In Fractured Reservoirs .

to PAM/PEI gel. Even after 6 months, the nano-silica gel maintained a remarkable 100% plugging efficiency at 1,000 psi, with a maximum leak-off rate of 0.088 cc/min in the mid-fractured sample and 0.027 in the induced channel sample. In comparison, PAM/PEI gel exhibited a reduction in efficiency to 99.15% in the fractured sample (5.5 cc/min maximum leak-off rate) and 99.99% in the induced channel sample (0.036 c/min maximum leak-off rate). Moreover, CT scans confirmed minimal degradation in both gels, with nano-silica gel showing a lesser impact compared to PAM/PEI gel. These findings highlight the potential of nano-silica gel as a more durable water shut-off agent for managing water production in fractures and Channels.

6.2 Introduction

In the oil industry, excessive water production poses a significant challenge, with unwanted water accompanying hydrocarbon.¹ The excessive water production not only reduces operational efficiency and profitability but also raises logistical, economic, and environmental concerns.^{1,201} Handling, treating, and disposing of co-produced water requires additional resources, driving up operational costs and lowering overall profitability.¹ Water shut-off techniques aim to mitigate excessive water production from reservoirs by restricting or eliminating water flow into production wells, thereby improving hydrocarbon recovery efficiency and reservoir performance. Numerous studies have highlighted the detrimental impact of produced water on well productivity. For instance, Bailey¹⁵ et al. found that globally, three barrels of water were produced for every barrel of oil extracted, resulting in a significant volume of 75 billion barrels of co-produced water worldwide, with disposal costs estimated at \$40 billion. Additionally, Pappaset²³ et al. revealed that the United States alone generated approximately 24.4 billion barrels of co-produced water. These statistics underscore the critical need for prompt water production treatments.

Two common solutions for mitigating water production in oil wells are mechanical and chemical methods. Mechanical methods involve placing cement^{49–52} or mechanical tools like packers and plugs in the wellbore to block water flow.^{47,48} On the other hand, chemical methods involve placing durable materials around the wellbore or into the reservoir.^{1,201} Over the last decade, various chemical systems have been developed, such as monomers,

resins, and gel systems. Among these, gel treatments are considered one of the oldest and most cost-effective methods for addressing wellbore or reservoir-related issues.^{4,69,82,178–180} These gels can be categorized into organic gels, like polymer gels, and inorganic gels, like silicate gels. Silicate gels, in particular, have been extensively used to control excessive water production. By injecting a specially prepared silica gel mixture into the wellbore or reservoir, a 3-D gel structure is formed, effectively preventing water flow.^{99,100} This method minimizes production disruptions, enhances reservoir sweep efficiency, and increases overall hydrocarbon recovery. Silicate gel systems offer operational advantages such as easy injection due to their low viscosity and stable performance at high temperatures. Moreover, they are cost-effective and environmentally friendly compared to polymer gels.^{106–108} However, challenges exist, including decreasing gel strength over time, rapid gel formation, and sensitivity to certain ions in the formation.^{101,106,181}

In recent years, nanomaterials have emerged as promising additives in the petroleum industry, offering enhanced performance across various applications such as enhanced oil recovery, reservoir imaging, and formation evaluation.^{18,20,101,181} Studies have demonstrated their effectiveness in blocking pore throats, highlighting their suitability in water shut-off treatments.^{182–184} Research by Ali¹⁸¹ et al. summarized the impact of incorporating nanomaterials like nano-silica and nano-clay into polymer gels, revealing improvements in gel properties, including gel strength and thermal stability. Furthermore, investigations into nano-silica gel highlighted its superior performance compared to larger particle sizes in silicate gel systems, making it an excellent candidate for water shut-off applications. Moreover, rheological studies have shed light on the behavior of nano-silica gel under different conditions. For instance, Boul¹³⁹ et al. found that non-spherical particles exhibit prolonged gelation times at 50°F. Almohsin¹⁴⁰ et al. delved into the influence of temperature on the gelation time of nano-silica gel, observing an acceleration with increasing temperature. Additionally, their study identified higher concentrations (24% and 25%) as significantly affecting gelation time, with lower sensitivity observed at concentrations of 21% and 23%. These findings underscore the potential of nano-silica gel in water shut-off treatments and contribute valuable insights into its rheological behaviour under varying conditions.

The plugging efficiency of nano-silica gel has been extensively studied in both permeable matrices and fractures. Almohsin¹⁴⁵ et al. evaluated the gel's performance in a high permeable matrix, achieving successful plugging of a 400-md core sample at 300 °F over two weeks. Similarly, Karadkar¹⁷² et al. reported 100% plugging efficiency for nano-silica gel on a 190-md Berea core sample, with no observed leak-off rate under 2500 psi differential pressure for eight hours. Additionally, Almohsin¹⁴⁰ et al. examined the gel's effectiveness in plugging core samples with higher permeability (700 mD) over a 12-day endurance test, achieving an average leak-off rate of 0.0018 cc/min under continuous pumping at 4000 psi.¹⁴⁰ For gel performance in fractures, Ali¹⁹⁵ et al. investigated the performance of nano-silica gel in fractures and channels, demonstrating approximately 100% plugging efficiency with a minimal leak-off rate at 200 °F. While these studies highlight the exceptional plugging efficiency of nano-silica gel initially, none have assessed its performance over an extended period. Addressing this gap is crucial given the historical drawback of decreased gel strength over time observed in conventional silicate gel systems.

The objectives of this study encompass two primary aims: first, to evaluate the long-term durability of nano-silica gel within fractures and channels over a period of six months, and second, to conduct a comparative analysis of its performance against in-situ polymer gel, specifically polyacrylamide/polyethyleneimine (PAM/PEI) gel. Prior studies have highlighted the capability of PAM/PEI gel to attain 100% plugging efficiency in Berea sandstone core samples at a temperature of 90 °C.¹⁴⁴ Additionally, it has demonstrated notable effectiveness in mitigating water flow in harsh conditions, achieving an impressive 99.8% reduction in permeability over 6 months.¹⁸⁵ By performing a comparative analysis between nano-silica gel and PAM/PEI gel using similar fractured sample characteristics, it is feasible to determine the superiority of one gel over the other.

6.3 Materials and Experimental Plan:

6.3.1 Chemicals

Two gel systems were utilized in this study: nano-silica gel and PAM/PEI gel. Nano-silica gel is composed of a mixture of nano-silica solution and activator, both provided by Saudi Aramco, mixed in specific weight proportions to ensure sufficient gelation time for optimal

placement. To prepare a 75/25 wt% nano-silica gel, a predetermined volume of the silica solution was measured in a 500 ml beaker, and its weight was determined, followed by the addition of an equivalent volume of activator based on the desired ratio. The mixture was stirred for 10 minutes until achieving a uniform consistency suitable for injection. The silica nanoparticles exhibit a discrete, smooth, spherical shape, with an average particle size distribution of 14 nm as analyzed by the FPIA-3000 (Malvern) particle size analyzer. Initially, the gel mixture presents an average viscosity of 6 centipoises (cp), which increases with temperature due to gelation.

The second gel system, referred to as PAM/PEI gel, comprises two primary solutions: PAM (polyacrylamide) and PEI (polyethyleneimine). PAM, obtained from SNF Floerger in the form of an aqueous solution, was utilized without further treatment, featuring a concentration of 20 wt% active ingredients and a molecular weight ranging from 250 to 500 kg/mol, as specified by the supplier. PEI, serving as a cross-linker, was provided in solution form. To prepare 30 mL of PAM/PEI gel with a 9/1 wt%, 13.5 mL of PAM was initially combined with 15.5 mL of water and stirred for approximately one minute. Following this, 1 mL of PEI was introduced to the mixture, which was then stirred for an additional 10 minutes. For conducting endurance tests, a brine solution containing sodium chloride, mainly at a concentration of 0.1M per liter, was utilized.

6.3.2 Methodology

6.3.2.1 Experimental plan:

The study plan involves initially treating fractured core samples with gel, followed by an endurance test to verify the initial plugging efficiency. Subsequently, the gel-plugged sample will undergo three aging stages in formation water over six months. A detailed experimental plan for this duration is outlined in Figure 56. After the first month of aging, an endurance test was conducted to reevaluate the gel plugging efficiency, while a computed tomography (CT) scan was performed simultaneously to detect any gel degradation. These procedures were repeated after the third and sixth months of aging. After the sixth month, the gel's plugging performance was evaluated and compared to its initial effectiveness while also determining the degradation rate. This systematic approach provides valuable insights into the long-term efficiency and stability of the gel.

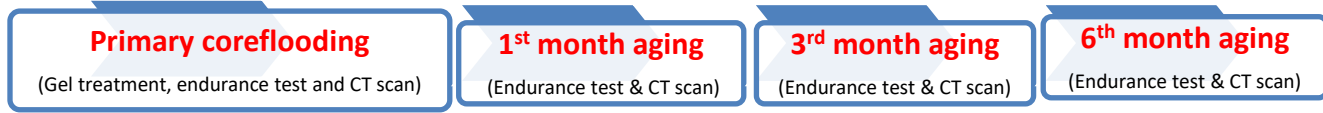


Figure 56 Experimental plan.

6.3.2.2 Coreflooding system

A fully equipped coreflooding system was utilized to conduct the initial gel treatment and endurance test on the fractured sample. Figure 57 shows the main components of the coreflooding system. This system includes a 1.5-inch core holder fitted with two pressure transducers to measure inlet and outlet pressures accurately. Additionally, it features dual pumps: one for applying confining pressure to the core holder and the other for injecting fluid via two accumulators—one outside the oven for gel and another inside for brine. To maintain pressure consistency and replicate reservoir conditions, a back pressure regulator is employed, set at 400 psi. Moreover, medical CT scans were utilized to characterize the density distribution of the samples before treatment, after treatment, and during the aging stages.

To ensure effective gel treatment, a sufficient amount of gel was injected into the sample at a very low rate of 1 cc/min throughout 1.5 to 2 hours, aligned with the gelation time of the injected gel. Subsequently, the system underwent a thorough cleaning to remove any remaining gel residue before being shut-in for 48 to 72 hours to allow complete curing of the gel. Once the gel was fully cured, the endurance test commenced by subjecting the sample to various differential pressures at 200°F while monitoring the leak-off rates. The leak-off rate with differential pressure can be used to estimate the sample's permeability after treatment. Plugging efficiency was calculated using Equation (1), as described below:

$$\text{Plugging efficiency (\%)} = \frac{\text{Initial Permeability} - \text{Final Permeability}}{\text{Initial Permeability}} \quad (6.1)$$

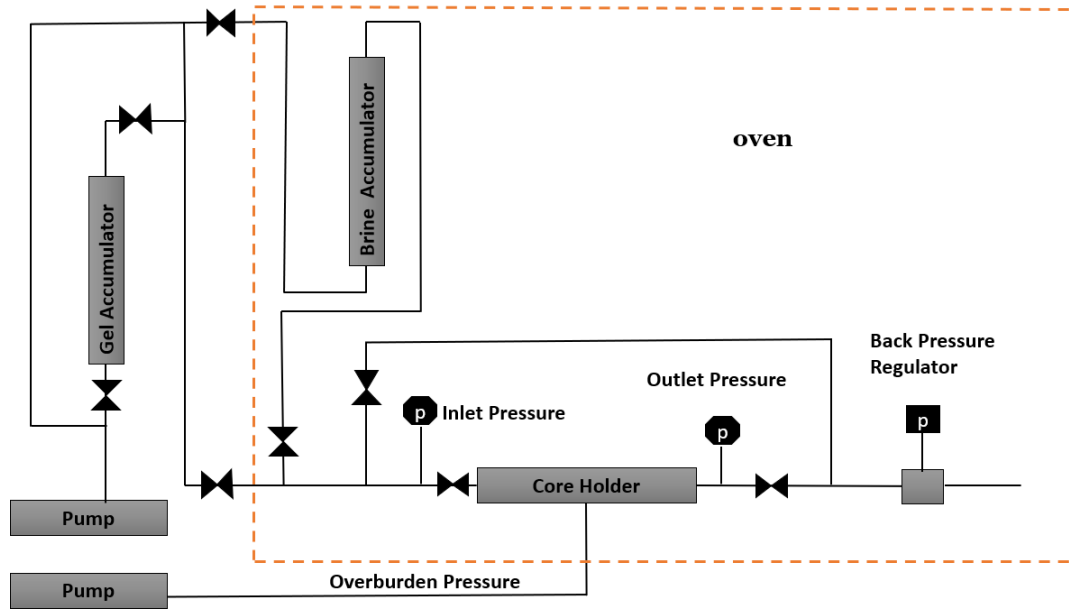


Figure 57 Coreflooding system.

6.3.2.3 CT scan

To ensure optimal plugging efficiency with the gel, it is crucial to have a uniform distribution of an adequate amount of gel throughout the sample. In the experiments that were conducted, a medical CT scan was utilized to identify the distribution pattern and penetration length of the gel precisely along the sample length. CT scans were conducted before treatment, after treatment, and at each aging stage over 6 months. The results were obtained in terms of CT numbers, which represent the intensity of the transmitted X-ray beam and correspond to specific density values in g/cm^3 .¹⁸⁶ Therefore, variations in CT numbers directly indicate changes in density, reflecting the extent of gel invasion.

6.4 Results and Discussion

6.4.1 Gels Performance on the Fractured Samples

6.4.1.1 Experiment 1 (Nano-silica gel on fractured sample)

In this study, a limestone fractured sample was employed, with a fracture deliberately created in the middle section of the sample. A 3D CT scan image of the sample is depicted in

Figure 58. The preparation involved cutting the original sample into two similar halves, which were then reconnected using a shrinkage tube with heating. Details regarding the dimensions and properties of the sample are provided in Table 13. Notably, the fractured sample exhibited a permeability of 184.73 md, significantly higher than that of the original sample.

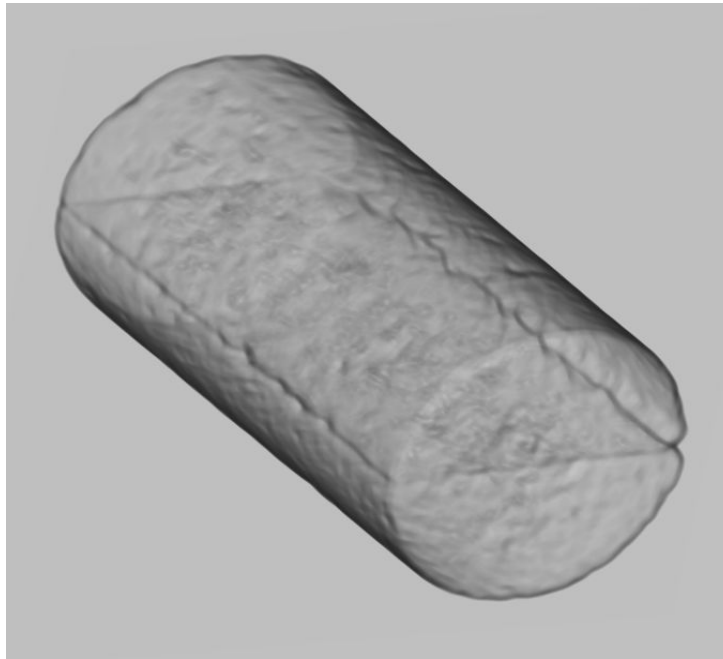


Figure 58 3D CT scan image of sample F1.

The nano-silica gel has a concentration of 75% nano-silica and 25% activator, designed to provide enough gelation time during placement and avoid any plugging. The brine used is composed mainly of NaCl, used in in the post-treatment stage to conduct an endurance test.

Table 13 Core sample dimensions for sample F1.

Sample	Length (inch)	Diameter (inch)	Porosity (%)	Pore volume (ml)	Permeability (mD)
F1	3.0	1.5	21.88	19.79	184.73

6.4.1.1.1 Gel treatment:

The treatment stage commenced under reservoir conditions at 200 °F, with the coreflooding system preheated before initiating the injection process. Nano-silica gel was prepared using a mixture comprising 75 wt% nano-silica and 25 wt% activator, allowing for gel formation with a gelation time of 3 to 4 hours, suitable for completing the injection at a flow rate of 1 cc/min. Figure 59 illustrates the immediate pressure drop observed during gel injection, attributed to the increasing viscosity of the solution with temperature. Over 3.5 hours, a total injected volume equivalent to 6.3 pore volumes was achieved, with a pressure drop of less than 50 psi and a gel resistance factor of 17.9 (ratio of pressure drop for the gel to pressure drop for the water), indicating satisfactory gel injectivity.

Following the injection process, the system underwent cleaning and then was shut in for 48 hours to allow the gel to cure. After this period, the gel-plugging performance was evaluated by conducting an endurance test under various differential pressures while monitoring the leak-off rate as depicted in Figure 59. Initially, the sample was subjected to 250 psi for 30 minutes, followed by 500 psi for an additional 30 minutes, with no observed leak-off rate during either period, indicating the high plugging efficiency of the nano-silica gel. Subsequently, the pressure was raised to 750 psi and maintained for 30 minutes, with no droplets observed in the outlet. To assess gel durability, the differential pressure was further increased to 1000 psi and maintained for 3 hours. The leak-off rate during this period remained very low at 0.054 cc/min, with a holding pressure of 4000 psi/ft, underscoring the gel's plugging capabilities under high differential pressure. The gel effectively obstructed both the fracture path and the permeable matrix, achieving a plugging efficiency of 100%. Moreover, it exhibited a high residual resistance factor of 39,746.9 (ratio of initial permeability to final permeability), significantly reducing the sample permeability from 184.73 mD to 0.0046 mD. These results align closely with

previous findings on nano-silica gel conducted by Almoshin¹⁴⁰ et al., highlighting the exceptional plugging capabilities of the gel.

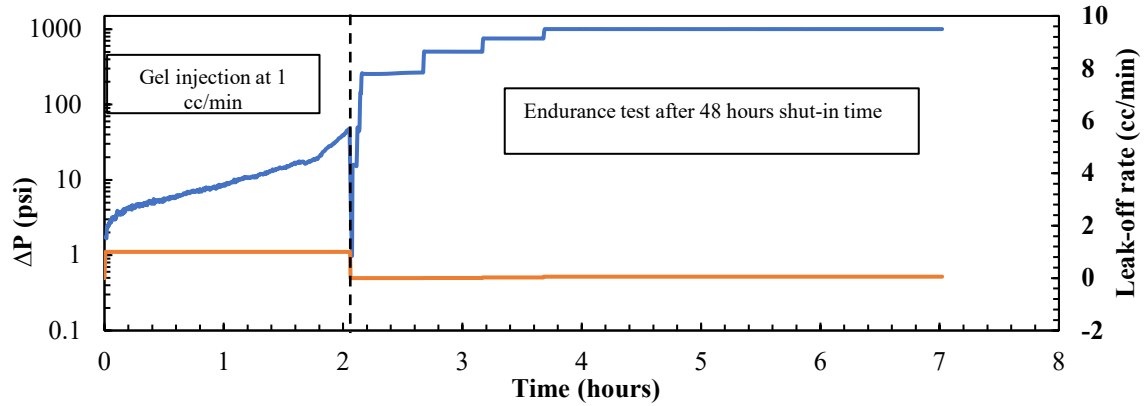


Figure 59 Nano-silica gel treatment on the fractured sample F1.

CT scans were performed on sample F1, both pre and post nano-silica gel treatment. Figure 60 showcases CT images depicting various slices of the dry sample and the treated sample. It is evident that the gel induced a shift in the density distribution of the sample, resulting in a broader spread of higher density compared to the initial low-density distribution observed prior to gel application. This alteration can be attributed to the infiltration of the gel. In the middle section, particularly in the fracture area, a clear shift to higher density is evident, attributable to the presence of the gel. Prior to gel treatment, the average CT number of each slice was recorded at 2104.28, while post-treatment, this value increased significantly to approximately 2321.18. Such a substantial change signifies successful placement and uniform distribution of the gel along the sample length, effectively sealing the fracture path and achieving the desired plugging efficiency.

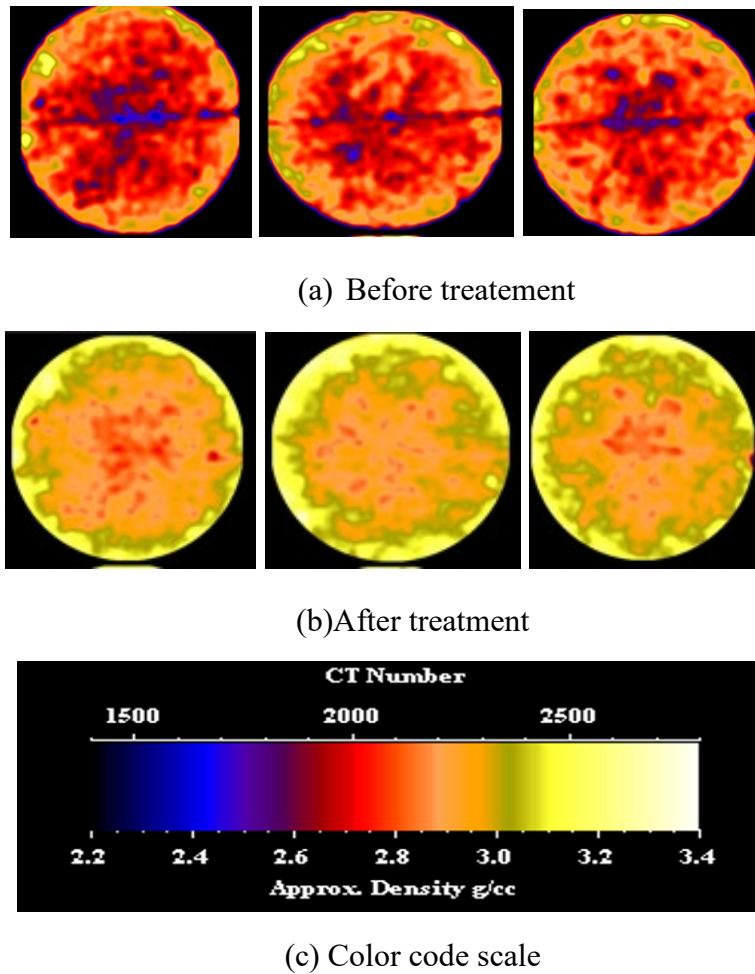


Figure 60 CT scan of the fractured sample before nano-silica gel treatment; (b) CT scan of the fractured sample after nano-silica gel treatment; (c) Color code scale.

6.4.1.1.2 Gel durability over a 6-month period:

First-month aging: The treated fractured sample underwent aging within a cell filled with formation water at a temperature of 167 °F for one month. Following the aging period, an endurance test lasting 4.5 hours was conducted to assess the plugging efficiency of the sample, as illustrated in Figure 61. The test commenced with a 30-minute pressure hold at 250 psi, during which no leak-off rate was observed at the outlet. Subsequently, the pressure was incrementally raised to 500 psi for another 30 minutes, then further increased to 750 psi for an additional half-hour. During this period, the leak-off rate consistently

remained below 0.036 cc/min, which closely resembled the post-treatment leak-off observed under the same differential pressure. To evaluate the durability of the gel, the pressure was maintained at a constant 1,000 psi for 3 hours, resulting in a reported leak-off rate of 0.058 cc/min. Remarkably, the maximum leak-off rate remained stable and nearly identical to the post-treatment leak-off rate (0.054 cc/min), affirming the gel's durability under high differential pressure and maintaining its plugging efficiency at 100%.

Third-month aging: After the initial month of endurance testing, the sample underwent further immersion in formation water at 167 °F for an additional two months. Following this period, a subsequent endurance test was carried out, involving the injection of brine under different pressure differentials, reaching a maximum of 1000 psi at 200 °F. As depicted in Figure 61, a slight uptick in the leak-off rate was observed during the third month compared to the first. Pressures of 250, 500, and 750 psi were maintained for 30 minutes each, with the maximum leak-off rate remaining minimal at 0.056 cc/min. To assess the gel's endurance, the pressure was kept constant at 1000 psi for 3 hours, resulting in a reported leak-off rate of 0.088 cc/min. Comparing this third-month leak-off rate with the post-treatment values (as depicted in Figure 3), a very slight increase was noted. Nevertheless, the leak-off rate remained extremely low, with the overall plugging efficiency of the gel staying at 100%, showcasing its exceptional sealing capabilities.

Sixth month: After the third-month endurance test, the sample underwent an additional three months of immersion in formation water at 167 °F. The endurance test followed the same procedure, gradually escalating the differential pressure up to 1,000 psi at 200 °F. The performance of the gel during the sixth month is visually illustrated in Figure 61. A noticeable similarity in the leak-off rate compared to the third month was observed, indicating the gel's stability and consistent performance. At 500 psi for 30 minutes, the leak-off was around 0.052 cc/min. This increased slightly to 0.061 cc/min at 750 psi. When held at 1,000 psi for 3 hours, the leak-off stabilized at 0.091 cc/min, similar to the rate obtained in the third month (0.088 cc/min). Nevertheless, the maximum leak-off rate obtained is exceedingly low, confirming the gel's remarkable effectiveness in sealing the fractured sample. These findings after 6 months confirm that the nano-silica gel maintained its durability, achieving a plugging efficiency of 100%.

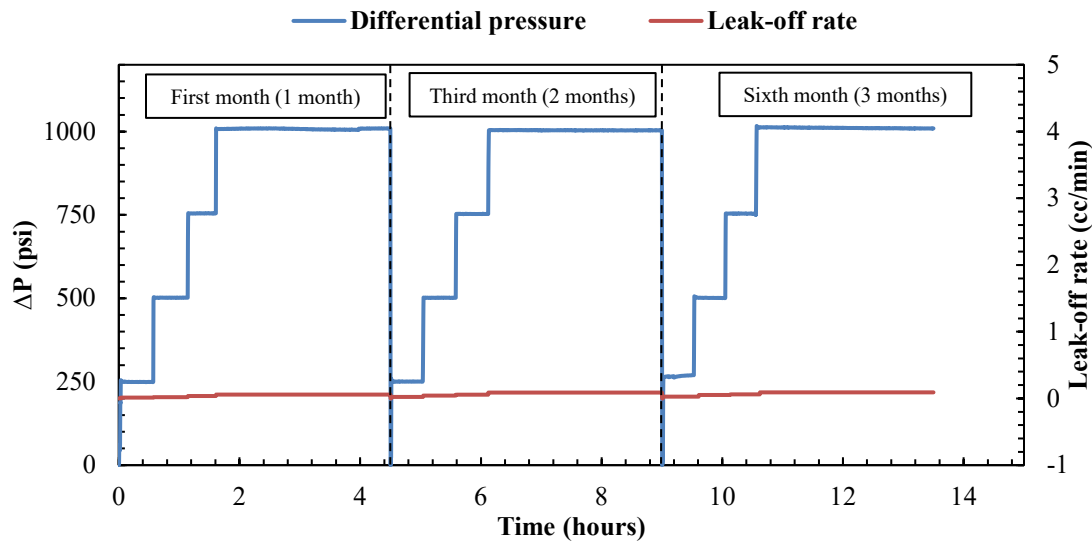


Figure 61 Nano-silica gel plugging performance over 6 months (fractured sample).

To assess potential gel degradation by analyzing changes in pore space, CT scans were conducted at intervals over the 6-month period following aging and endurance tests, as depicted in Figure 62. Typically, after each aging phase, CT numbers displayed an increase, suggesting higher density, likely attributed to water infiltration into the core sample. Initially, the CT number post-initial treatment was 2321.18, rising to 2341.11 after 1 month of aging. However, it subsequently decreased to 2341.11 after the first month of endurance testing. Following each endurance test, CT numbers declined to values surpassing post-treatment levels as water displaced some of the gel. After 6 months, the CT number post-endurance test was 2312.21.99, indicating minimal gel degradation. This interpreted the slight increase in the leak-off rate after 6 months. However, the gel maintained high plugging efficiency for water flow, confirming its occupation of the fractured path and pore spaces within the matrix.

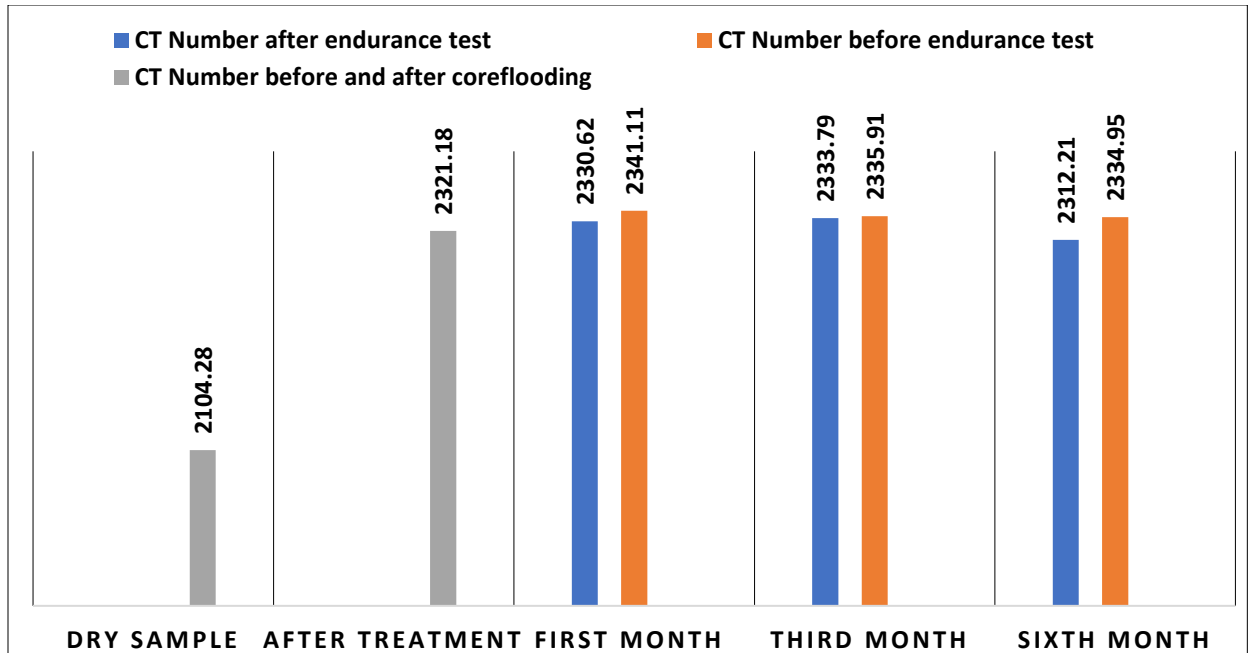


Figure 62 Average CT Number in different stages for the fractured sample F1.

6.4.1.2 Experiment 2 (PAM/PEI gel on the fractured sample)

For this study, a fractured sample, designed similarly to that used in Experiment 1, was employed. The dimensions and properties of the sample are outlined in Table 14. Notably, the fractured sample exhibited a permeability of 242.58 md, which is significantly higher than that of the original sample (70 mD).

Table 14 Core sample dimensions for sample F1.

Sample	Length (inch)	Diameter (inch)	Porosity (%)	Permeability (mD)
F2	3.0	1.5	20.54	242.58

6.4.1.2.1 Gel treatment:

Under reservoir conditions at 200 °F, the PEM/PEI gel treatment phase began following the preheating of the coreflooding system. Formulated with a concentration of 9/1 %wt, the PAM/PEI gel was then injected. Figure 63 depicts the immediate pressure drop observed during the injection process. Over the course of 2 hours, 7 pore volumes were

injected, with the maximum pressure drop staying below 40 psi. This resulted in a gel resistance factor of 30, suggesting effective gel injectivity.

Following the injection phase, the system underwent a cleaning procedure and then remained shut-in for a period of 72 hours to facilitate the curing of the gel. Subsequently, an evaluation of the gel's plugging performance was conducted through an endurance test, which involved subjecting it to varying levels of pressure differentials while monitoring the rate of leakage, as illustrated in Figure 63. Initially, the sample endured 250 psi for 30 minutes, followed by an additional 30 minutes at 500 psi, with no observable leakage during either phase, indicating the initial high efficiency of the PAM/PEI gel in plugging the fractured sample. The pressure was then escalated to 750 psi and maintained for 30 minutes, with no detection of water droplets at the outlet. To assess the durability of the gel, the pressure was further increased to 1000 psi and sustained for 3 hours. During the last hour of maintaining the pressure at 1000 psi, water droplets began to emerge, with a leak-off rate recorded at 0.25 ml/min. The gel effectively obstructed both the fracture path and the permeable matrix, achieving a remarkable plugging efficiency of 99.99%. Additionally, it demonstrated a substantial residual resistance factor of 13,380.59, leading to a significant reduction in sample permeability from 242.58 mD to 0.0181 mD. These findings validate the gel's capacity to impede water flow in fractures.

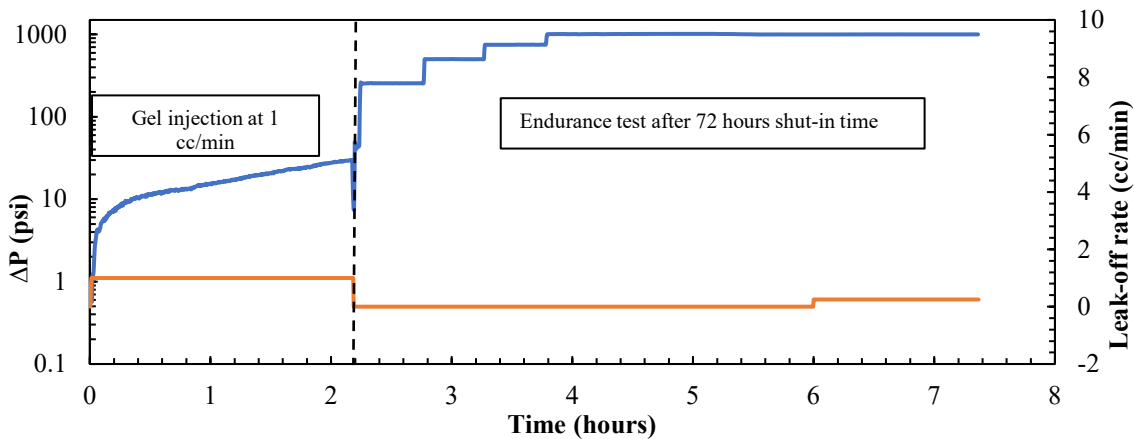


Figure 63 PAM/PEI gel treatment in the mid-fractured sample F2.

CT scans were conducted on sample F2 both before and after PAM/PEI gel treatment, with

Figure 64 displaying CT images showcasing various slices of both the dry sample and the treated sample. Evidently, the gel induced a change in the density distribution of the sample, resulting in a broader spread of higher density compared to the initial low-density distribution observed before gel application. This alteration is attributed to gel infiltration. Notably, in the middle section, particularly within the fracture area, a distinct shift to higher density signifies the presence of the gel. In pre-gel treatment, the average CT number of each slice was 2096.92, whereas post-treatment, this value substantially increased to approximately 2279.09. This significant change validates the successful placement and uniform distribution of the gel throughout the sample length, encompassing both the fractured path and the surrounding matrix.

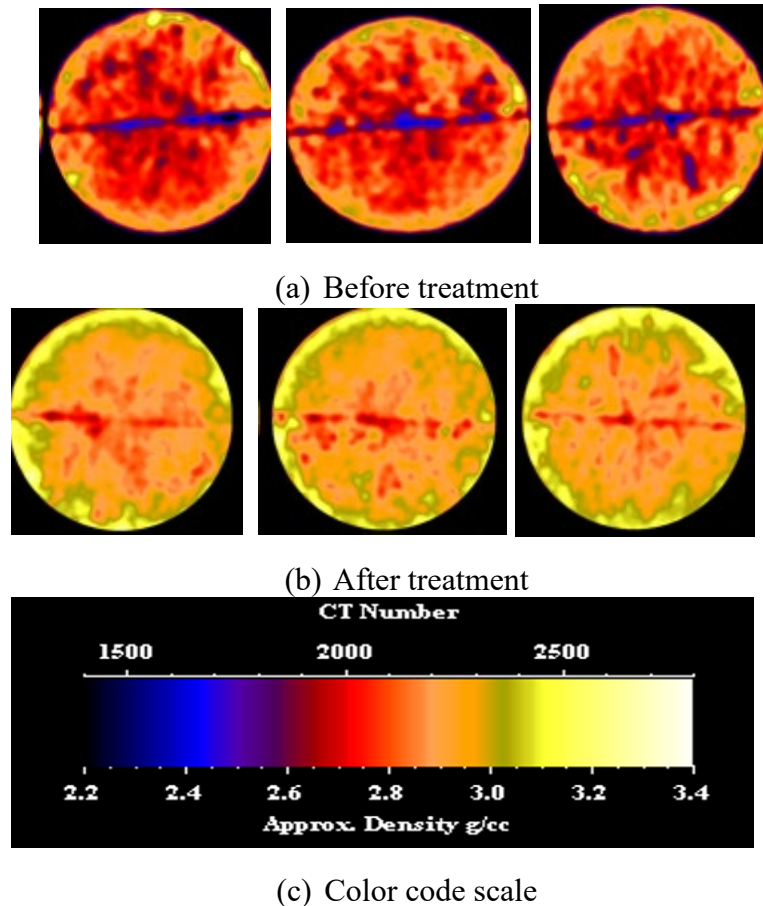


Figure 64 CT scan of the fractured sample before PAM/PEI gel treatment; (b) CT scan of the fractured sample after PAM/PEI gel treatment; (c) Color code scale.

6.4.1.2.2 Gel durability over a 6-month period:

First-month aging: Following the initial treatment, the fractured sample underwent aging in formation water within a cell at a temperature of 167° F for one month. Subsequently, the endurance test commenced with the injection of brine at various differential pressures, as displayed in Figure 65. Initially, a 30-minute pressure hold at 250 psi revealed a noticeable leak-off rate of 0.5 cc/min, significantly higher than the post-treatment rate of zero leak-off. Gradually increasing the pressure to 500 psi for 30 minutes resulted in a leak-off rate of 1.233 cc/min, and further increasing the pressure to 750 psi for 30 minutes led to a rise in the leak-off rate to 2.067 cc/min. These observed leak-off rates were higher than the post-treatment rate, indicating an initial indication of gel degradation. To assess the gel's durability, the pressure was maintained at a constant 1,000 psi for 3 hours, resulting in a reported leak-off rate of 2.98 cc/min. Consequently, the reported plugging efficiency of the PAM/PEI gel decreased to 99.88% after one month, indicating a slight degradation of the gel.

Third-month aging: Following the initial month of endurance testing, the sample underwent an additional two months of immersion in formation water at 167 °F. Subsequently, a subsequent endurance test was conducted at 200 °F in two stages: one using constant pressure and the second using constant flow rate. As depicted in Figure 65, a rise in the leak-off rate was observed in the third month compared to the first month. Pressures of 250 and 500 psi were sustained for 30 minutes each, with the leak-off rate increasing to 4.79 cc/min and then to 5.33 cc/min, respectively. These leak-off rates were considerably higher than those observed in the first month, indicating further degradation of the gel over the previous two months. Afterward, the test mode was changed to a constant flow rate to obtain accurate results about the sample permeability. Four different flow rates were applied, starting with 1 cc/min, then 2, 3, and finally 4 cc/min. The total injected volume through the treated sample was 10 pore volumes, resulting in a plugging efficiency of 99.55%. It is evident that the gel degraded after 3 months, as the plugging efficiency decreased from 100% in the post-treatment to 99.55%.

Sixth month: Following the third-month endurance test, the sample underwent an additional three months of aging in formation water at 167 °F. Subsequently, the endurance

test was repeated using the same procedure, initially with constant pressure and then transitioning to a constant flow rate. Figure 65 illustrates the gel's performance after the sixth month, revealing a noticeable increase compared to the third month. At 250 psi for 30 minutes, the leak-off rate was measured at 7.33 cc/min, approximately 1.5 times the leak-off rate observed in the third month, indicating further degradation of the gel. Afterward, the test mode was switched to a constant flow rate, beginning with 1 cc/min and gradually increasing to 2, 3, and finally 4 cc/min. The total injected volume reached 10 pore volumes, resulting in an average permeability of 2.06 mD, which is higher than the post-treatment permeability of 0.018 mD. The plugging efficiency of the PAM/PEI gel after six months was approximately 99.15%.

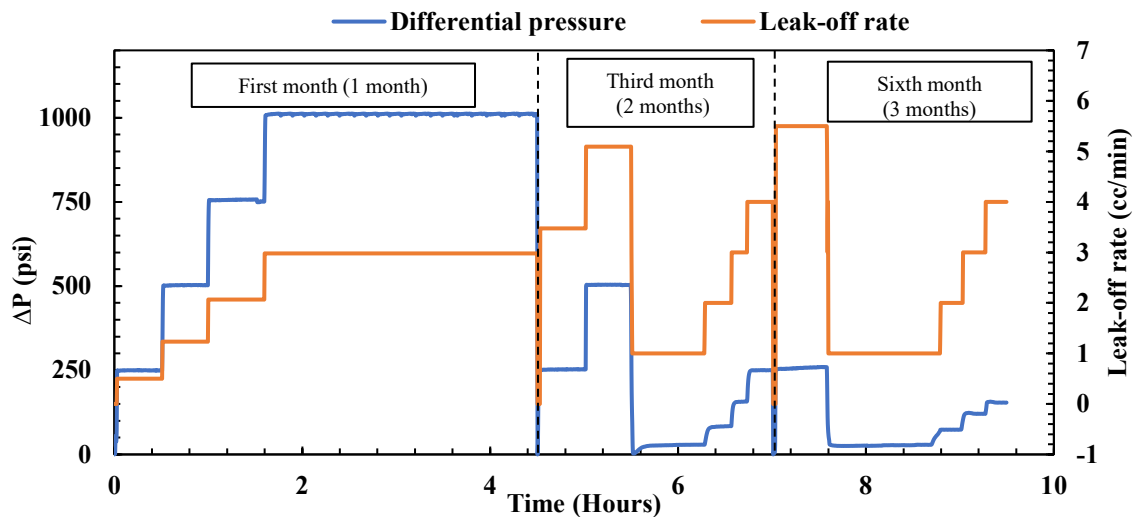


Figure 65 PAM/PEI gel performance over 6 months (mid-fractured sample).

Throughout the aging and endurance test phases, CT scans were conducted at the same intervals over the 6-month period, as illustrated in Figure 66. Initially, the CT number post-initial treatment was 2279.09, rising to 2311.5 after 1 month of aging. However, it subsequently decreased to 2296.55 after the first month of endurance testing. This reduction indicates an initial degradation of the gel in the first month. Linking this observation with the noticeable change in the leak-off rate in the first month suggests potential degradation of the gel, particularly in the fractured area where water flow is

facilitated under high differential pressure. After 6 months, the CT number post-endurance test was 2285.26, which is lower than the values observed in the first month (more degradation). This interprets the increase in the leak-off rate after 6 months.

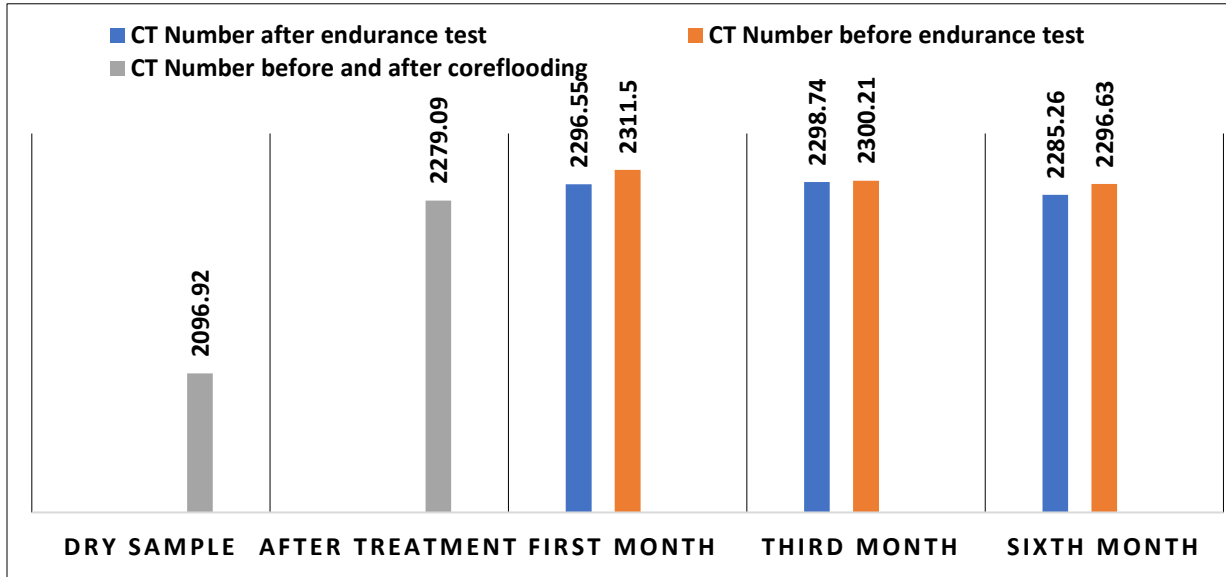


Figure 66 Average CT number in different stages for the fractured sample F2.

6.4.1.3 Comparison of Pels performance in the Fractured Samples

Similar fractured samples characteristics were treated by nano-silica gel and PAM/PEI gels. This assists to construct a valid comparison between the gel's performance over 6 months. Figure 67 displays the plugging efficiency of both gels over 6 months at different stages. In general, it appears that over an extended period nano-silica gel was more effective than the PAM/PEI gel. Nano-silica gel maintained its durability with plugging efficiency remaining at 100%. PAM/EPI gel efficiency clearly decreased from 99.99% to 99.15% over 6 months. Additionally, The maximum leak-off rate of PAM/PEI gel at 250 psi was 5.5 cc/min, which is 5 times the leak-off rate obtained by nano-silica gel on the fractured sample. This confirms that nano-silica gel exhibits superior performance compared to PAM/PEI gel over the span of 6 months.

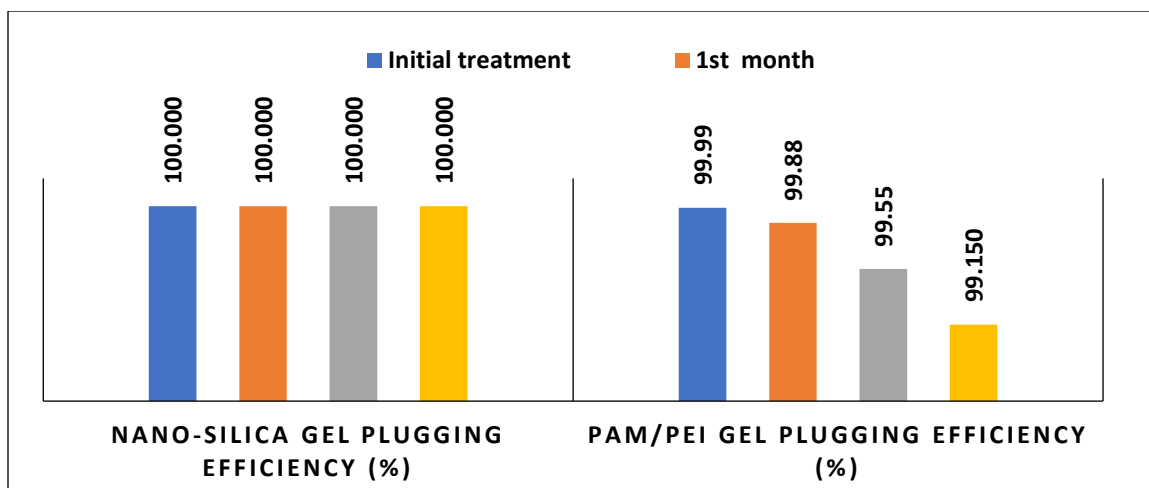


Figure 67 Performance comparison of nano-silica and PAM/PEI gels in the fractured sample.

6.4.2 Gels Performance on the Induced Channel Samples

6.4.2.1 Experiment 3 (Nano-silica gel on the induced channel sample)

This investigation employed a sample with a distinct characteristic—a channel (wormhole) created by hydrochloric acid (HCl). A 3D CT scan image of the sample is depicted in Figure 68. Further details regarding the dimensions and properties of the sample are outlined in Table 15. Notably, the sample exhibits a permeability of 440.6 md, significantly higher than that of the original sample (less than 50 mD).



Figure 68 3D image of the induced channel sample W1.

Table 15 Core sample dimensions for sample W1.

Sample	Length (inch)	Diameter (inch)	Porosity (%)	Permeability (mD)
W1	3.0	1.5	15.70	440.60

6.4.2.1.1 Gel treatment

Similarly, the experiment was conducted under reservoir conditions at 200 °F and an overburden pressure of 2000 psi, with the coreflooding system heated before starting the injection process. Utilizing a gel concentration similar to that in Experiment 1, the prepared gel consisted of 75 wt% nano-silica and 25 wt% activator, providing a gelation time of 3 to 4 hours. Figure 69 illustrates the observed pressure drop during gel injection at a rate of 1 cc/min, with continuous pressure observed due to the increasing viscosity of the solution with temperature (gelation). After 1.4 hours, a total injected volume of 6.3 pore volumes was achieved, with the maximum pressure drop being less than 50 psi and a gel resistance factor of 47.2. This higher resistance factor compared to experiment (1) is attributed to the gel's invasion into a low permeability matrix surrounding the channel. The successful injection of the target volume with a low-pressure drop indicates acceptable injectivity, ensuring the presence of gel in both the matrix and channel.

Following the gel injection phase, the system underwent cleaning and was then sealed for 48 hours to facilitate gel curing. Subsequently, the gel-plugging performance was evaluated by applying varying differential pressures as depicted in Figure 69. Initially, the sample was subjected to 250 psi for 30 minutes, followed by 500 psi for an additional 30 minutes, with no observed leak-off rate during either period, indicating efficient water flow blockage by the nano-silica gel in both channel and matrix areas. Droplets first appeared when applying 750 psi for 30 minutes, with a reported leak rate of 0.03 cc/min. To assess gel durability, the differential pressure was increased to 1000 psi and maintained for 3 hours, during which the leak-off rate remained very low at 0.05 cc/min, with a holding pressure of 4000 psi/ft, highlighting the gel's exceptional plugging capabilities under high differential pressure. The gel effectively obstructed both the channel path and the

permeable matrix, achieving a plugging efficiency of 100%. Additionally, it demonstrated a high residual resistance factor of 90,802.96, significantly reducing the sample permeability from 440.60 mD to 0.0049 mD. These findings closely corroborate those of experiment (1).

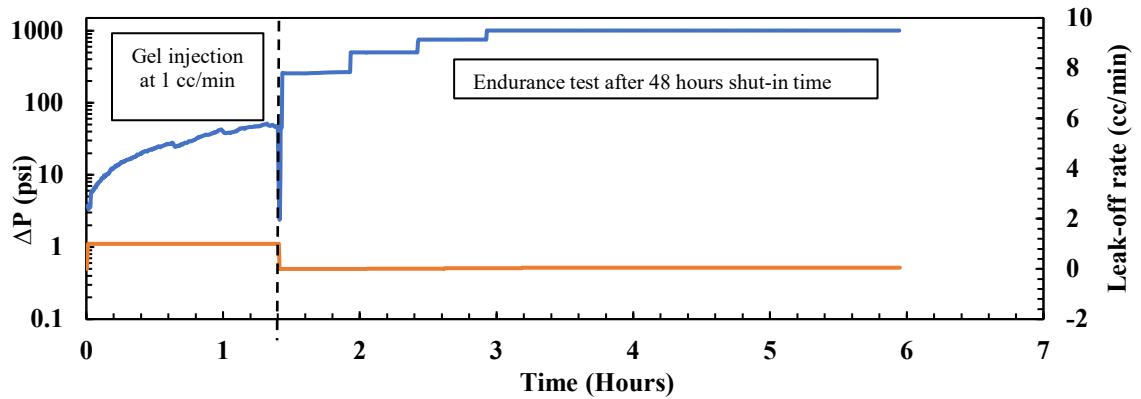
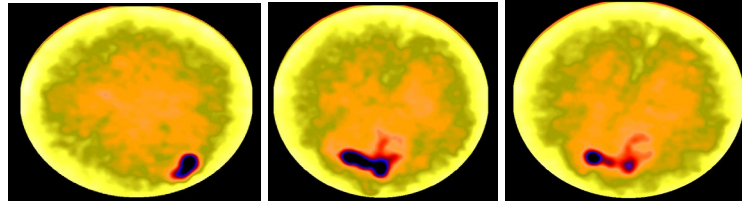
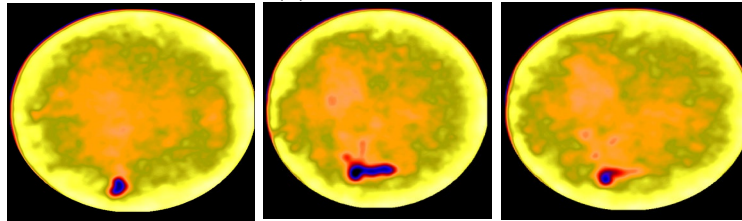


Figure 69 Nano-silica gel treatment on the induced channel sample W1.

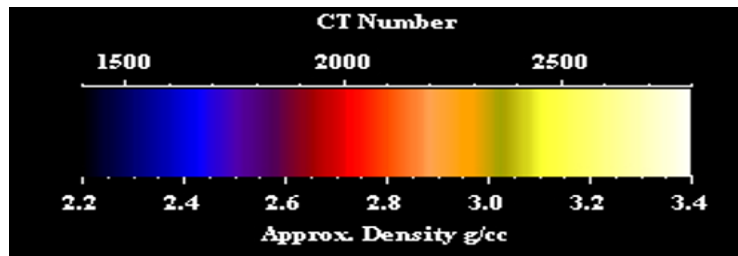
CT scans were conducted on sample W1 before and after nano-silica gel treatment. Figure 70 presents CT images of various cross-sections of both the untreated and treated samples. Before the gel treatment, the channel is characterized by a circular spot with dark colour (low density). Following the application of the gel, a noticeable change in colour to blue was observed (higher density). The presence of the gel changed the density distribution of the sample in the induced channel along the sample length. Before gel treatment, the average CT number of each slice was 2363. Post-treatment, this value significantly rose to approximately 2368.39. This marked increase confirms the successful placement and even distribution of the gel throughout the sample length in the induced channel and the surrounding matrix.



(d) Before treatment



(e) After treatment



(f) color code

Figure 70 CT scan of the induced channel before nano-silica gel treatment; (b) CT scan of the induced channel after nano-silica gel treatment; (c) Color code scale.

6.4.2.1.2 Gel durability over a 6-month period:

First-month aging: The induced sample, having undergone treatment, was aged within a cell filled with formation water at a temperature of 167 °F for one month. Following this aging period, an endurance test was initiated by injecting brine at various differential pressures, as illustrated in Figure 71. The test began with a 30-minute pressure hold at 250 psi, followed by another 30 minutes at 500 psi. During this hour, the leak-off rate was very minimal, measuring at 0.037 cc/min. Subsequently, the pressure was gradually increased to 750 psi for an additional half-hour, with the leak-off rate consistently remaining below

0.046 cc/min. To assess the durability of the gel, the pressure was maintained at a constant 1,000 psi for 3 hours, resulting in a reported leak-off rate of 0.09 cc/min. Although the maximum leak-off rate was slightly higher than the values observed in the post-treatment stage (0.05 cc/min), the reported leak-off rates were extremely low, indicating that the nano-silica gel maintained its plugging performance with a plugging efficiency of 100%.

Third-month aging: Following the initial month of endurance testing, the sample underwent further immersion in formation water at 167 °F for an additional two months. Subsequently, a subsequent endurance test was conducted at 200 °F. As depicted in Figure 71, a minor rise in the leak-off rate was noted in the third month compared to the first. Pressures of 250, 500, and 750 psi were sustained for 30 minutes each, with the maximum leak-off rate remaining minimal at 0.09 cc/min. To evaluate the gel's endurance, the pressure was maintained at a constant 1000 psi for 3 hours, yielding a reported leak-off rate of 0.125 cc/min. Comparing this third-month leak-off rate with the post-treatment values (as depicted in Figure 70), a slight increase was observed. However, the leak-off rate remained extremely low, with the overall plugging efficiency of the gel remaining at 100%, demonstrating its outstanding sealing capabilities.

Sixth month: After the third-month endurance test, the sample underwent an additional three months of aging in formation water at 167 °F. The endurance test followed the same procedure, gradually escalating the differential pressure up to 1,000 psi at 200 °F. The gel's performance after the sixth month is visually depicted in Figure 71. A slight increase was observed after the sixth month compared to the third month. At 500 psi for 30 minutes, the leak-off measured around 0.072 cc/min. This increased slightly to 0.124 cc/min at 750 psi. When maintained at 1,000 psi for 3 hours, the leak-off stabilized at 0.182 cc/min, higher than the rate obtained in the third month (0.125). Nevertheless, the maximum leak-off rate obtained is exceptionally low, confirming the gel's remarkable effectiveness in sealing the induced channel sample. These findings after 6 months affirm that the nano-silica gel maintained its durability, achieving a plugging efficiency of 100%. The results obtained also indicate that the nano-silica gel performs similarly in both fractured and induced channel samples.

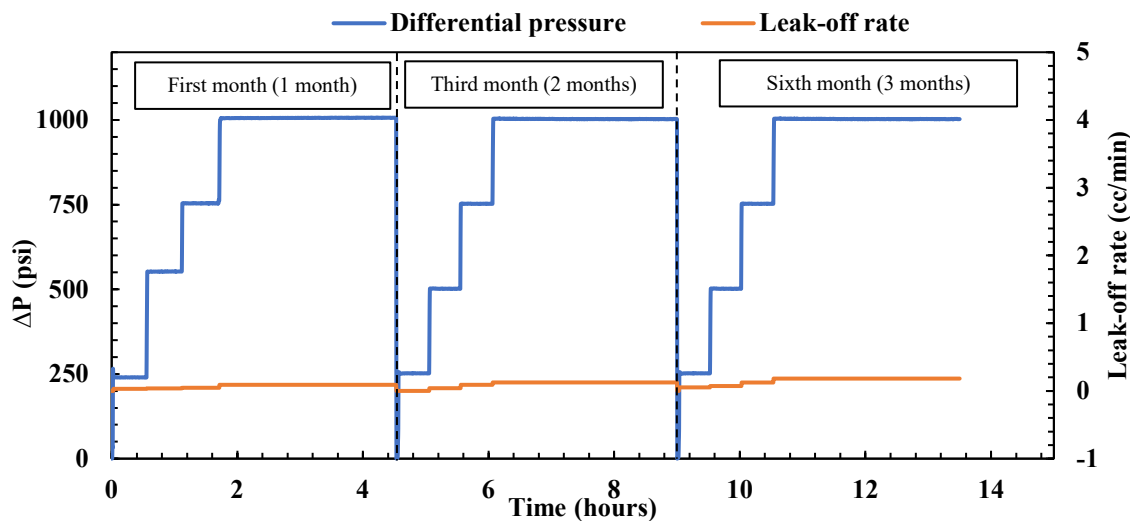


Figure 71 Nano-silica gel plugging efficiency over 6 months (induced channel sample).

During both the aging and endurance test phases, CT scans were conducted at regular intervals over the course of 6 months, as shown in Figure 72. Initially, the CT number after the initial treatment was 2368.39, which then rose to 2378.64 after 1 month of aging. However, it subsequently decreased to 2367.3 after the first month of endurance testing. After the third month, there was a slight increase in the CT number following the endurance test, likely due to increased water invasion. After 6 months, the average CT number decreased to 2363.84, which is lower than the post-treatment values. This indicates minimal degradation occurred to the gel. Nevertheless, the achieved plugging efficiency of the gel remains very high, underscoring that the gel still occupies most of the induced channel and the surrounding matrix.

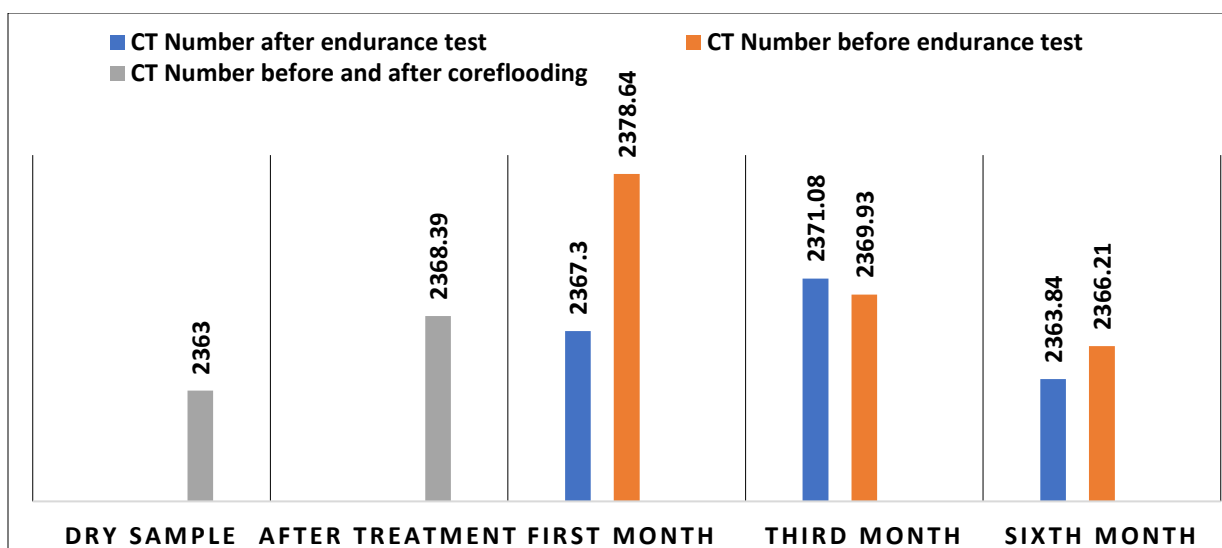


Figure 72 Average CT number in different stages for the induced channel sample W1.

6.4.2.2 Experiment 4 (PAM/PEI gel on the induced channel sample)

In this experiment, a limestone sample containing an induced channel was employed. The channel was sealed from one side to facilitate the invasion of the PAM/PEI gel into the matrix. Detailed information regarding the dimensions and properties of the sample can be found in the accompanying Table 16. It is worth mentioning that the induced channel sample has a permeability of 10.48 mD.

Table 16 Core sample dimensions for sample W2.

Sample	Length (inch)	Diameter (inch)	Porosity (%)	Permeability (mD)
W2	3.0	1.5	13.04	10.48

6.4.2.2.1 Gel treatment:

In this experiment, the same concentration of PEM/PEI gel as in experiment 1 (9/1 wt%) was utilized. The injection process was finalized in approximately 30 minutes at 200 °F, as illustrated in Figure 73. The injection stage persisted for 30 minutes at a flow rate of 1 cc/min. The considerable pressure drop observed was attributed to the gel invasion into the

low-permeability matrix, ensuring its placement in both the channel and the matrix. The total injected volume amounted to three times the pore volume.

Following the gel injection, the system underwent cleaning and then was sealed for a duration of 72 hours to enable the gel to solidify at 200 °F. Subsequently, the endurance test was conducted by injecting brine under various differential pressures and monitoring the leak-off rate, as depicted in Figure 73. Initially, the sample endured 250 psi for 30 minutes, followed by an additional 30 minutes at 500 psi, without any observable leakage during either phase, indicating the initial high plugging efficiency of the nano-silica gel in sealing the induced channel sample. The pressure was then increased to 750 psi and sustained for 30 minutes, with no water droplets detected at the outlet. To evaluate the durability of the gel, the pressure was further raised to 1000 psi and maintained for 3 hours. The gel effectively blocked both the channel path and the permeable matrix, exhibiting a minimal leak-off rate of 0.001 cc/min. The gel achieved a remarkable plugging efficiency of 100%, as it demonstrated a significant residual resistance factor of 771,082.4, resulting in a notable reduction in sample permeability from 10.48 mD to zero mD. These results confirm the gel's ability to prevent water flow in channels.

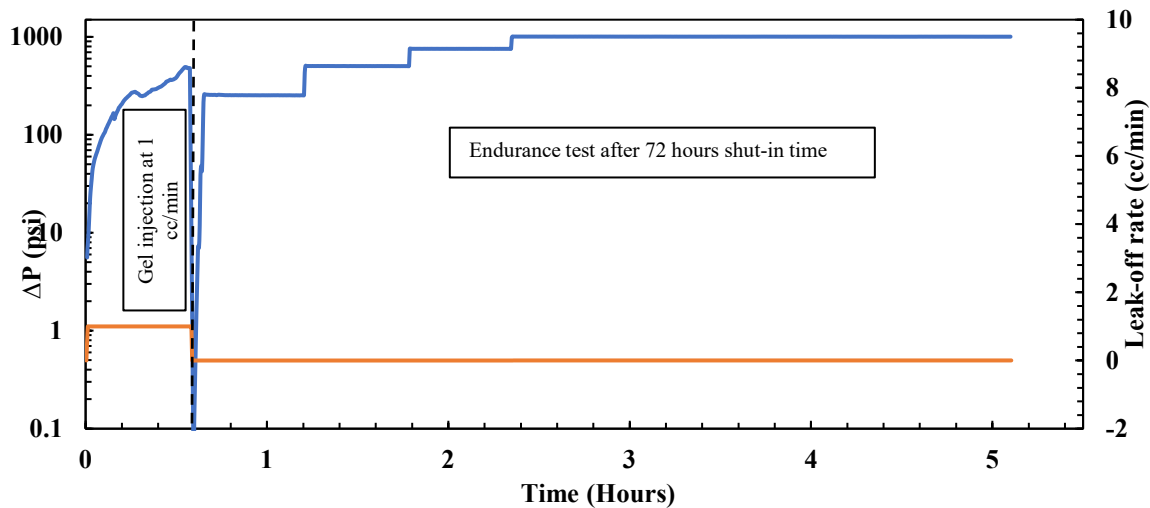


Figure 73 PAM/PEI gel treatment on the induced sample W2.

To visually assess the impact of gel invasion on pore space, CT scans were conducted before and after gel treatment. Figure 74 displays various slices of the core sample, with

the induced channel appearing as a small dark spot in each slice, indicative of low density. Following treatment, the color of these spots changed to blue, with a smaller size, suggesting a higher density distribution and confirming the presence of the gel within the channel. Furthermore, the average CT number of each slice along the induced sample length increased post-gel injection from 2305.12 to 2424.67, confirming the uniform distribution of the gel throughout the sample length.

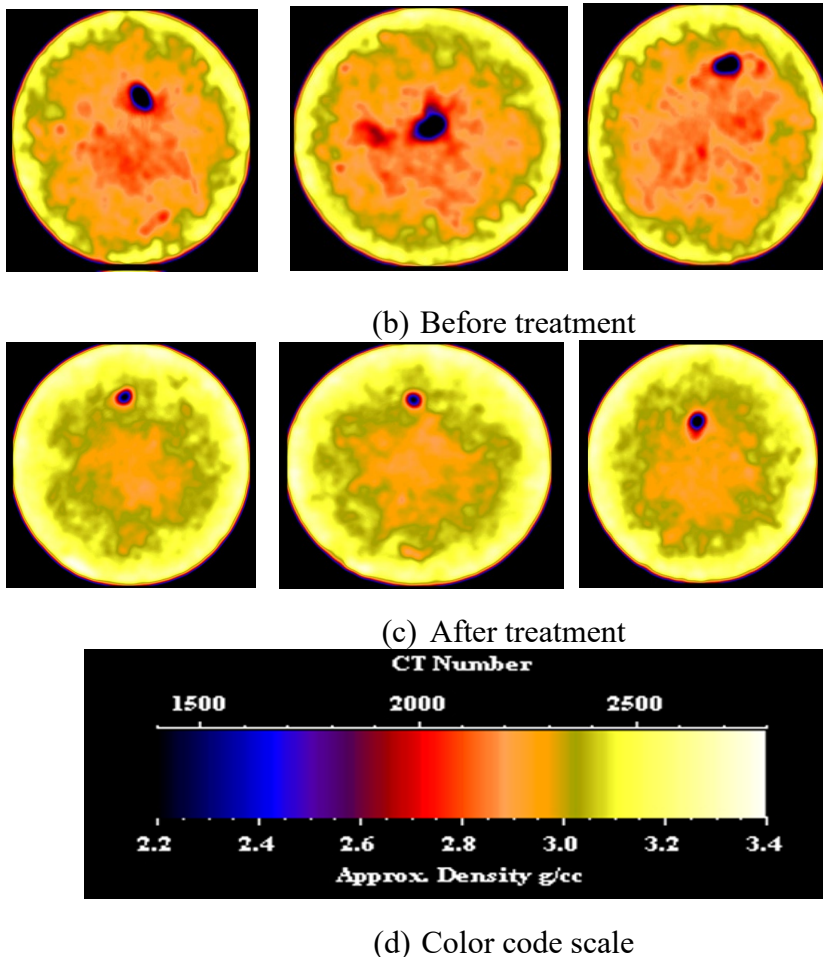


Figure 74 CT scan of the induced channel before PAM/PEI gel treatment; (b) CT scan of the induced channel after PAM/PEI gel treatment; (c) Color code scale.

6.4.2.2.2 Gel durability over 6 months:

First month: The sample endured a one-month aging period in formation water at 167 °F, followed by a 4.5-hour endurance test at 200 °F, as depicted in Figure 75. The test commenced with a 30-minute pressure hold at 250 psi, revealing no observable leak-off rate at the outlet. Subsequently, the pressure increased to 500 psi for 30 minutes and further to 750 psi for an additional half-hour. Throughout this period, the maximum leak-off rate remained below 0.004 cc/min, closely resembling the post-treatment level under the same differential pressure. To assess gel durability, a constant pressure of 1,000 psi was sustained for 3 hours, yielding a reported leak-off rate of 0.009 cc/min. Remarkably, the maximum leak-off rate remained consistent, indicating the gel's stability at high differential pressure and sustained plugging efficiency at nearly 100%.

Third month: Following the first-month endurance test, the sample was replaced in formation water at 167 °F for an additional two months. Subsequently, another endurance test was conducted under varying differential pressures, reaching up to 1000 psi at 200 °F. As depicted in Figure 75, a slight increase in the leak-off rate was observed in the third month compared to the first month. Initially, the pressure was maintained at 250 psi for 30 minutes, during which no water droplets were observed. Subsequently, as the pressure was raised to 500 psi for 30 minutes, no leak-off rate was observed. The subsequent increase in pressure to 750 psi for 30 minutes led to a leak-off rate of 0.02 cc/min, indicating a minor increase. To assess the gel's endurance, the pressure was sustained at a constant 1,000 psi for 3 hours, resulting in a reported leak-off rate of 0.036 cc/min. Comparing these leak-off rates after 3 months with the post-treatment values, as depicted in Figure 3, a slight increase was observed. However, this leak-off rate was extremely low, and the gel exhibited continued effectiveness, achieving an exceptional plugging efficiency of 99.99%.

Sixth month: Following the third-month endurance test, the sample underwent an additional three-month immersion in formation water at 167 °F. The endurance test was conducted similarly, with a gradual increase in the differential pressure up to 1,000 psi at 200 °F. The gel's performance during the sixth month is depicted in Figure 75, showing a slight resemblance in the leak-off rate compared to the third month, indicating minimal gel degradation. Under a pressure of 500 psi for 30 minutes, the leak-off rate was

approximately 0.065 cc/min. This rate increased to 0.164 cc/min when the pressure was raised to 750 psi. Sustaining a pressure of 1,000 psi for 3 hours led to the leak-off rate stabilizing at 0.211 cc/min, notably higher than the rate in the third month (0.036). These findings suggest minimal gel degradation over the past 3 months. However, the PAM/PEI gel retained its plugging capabilities, achieving a plugging efficiency of 99.91% after 6 months from the initial treatment.

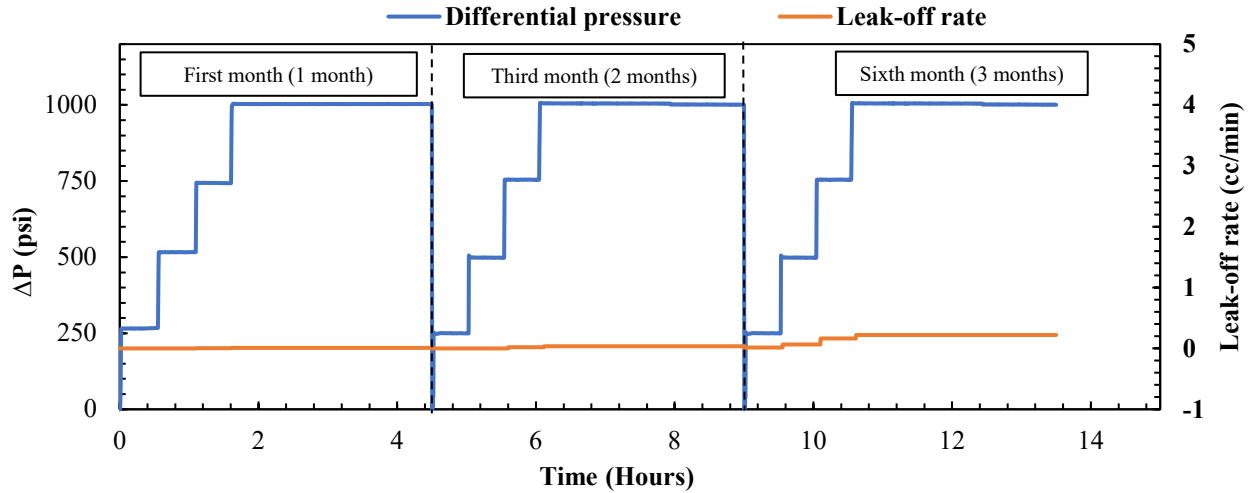


Figure 75 PAM/PEI gel performance over 6 months (induced channel sample).

CT scans were performed at various intervals over the 6-month period, following aging and endurance tests, as depicted in Figure 76. Generally, during aging, there was a rise in CT numbers, indicating increased density, likely due to water intrusion into the core sample. The CT number post-initial treatment was 2424.67, which climbed to 2429.58 after 1 month of aging. Subsequently, it decreased to 2431.52 after the endurance test. Following each endurance test, CT numbers dipped below post-treatment values as water displaced a portion of the gel. Following 6 months, the CT number post-endurance test was 2279.99, suggesting minimal gel degradation. However, the gel retained high plugging efficiency for water flow, indicating its occupation of most connected pore spaces.

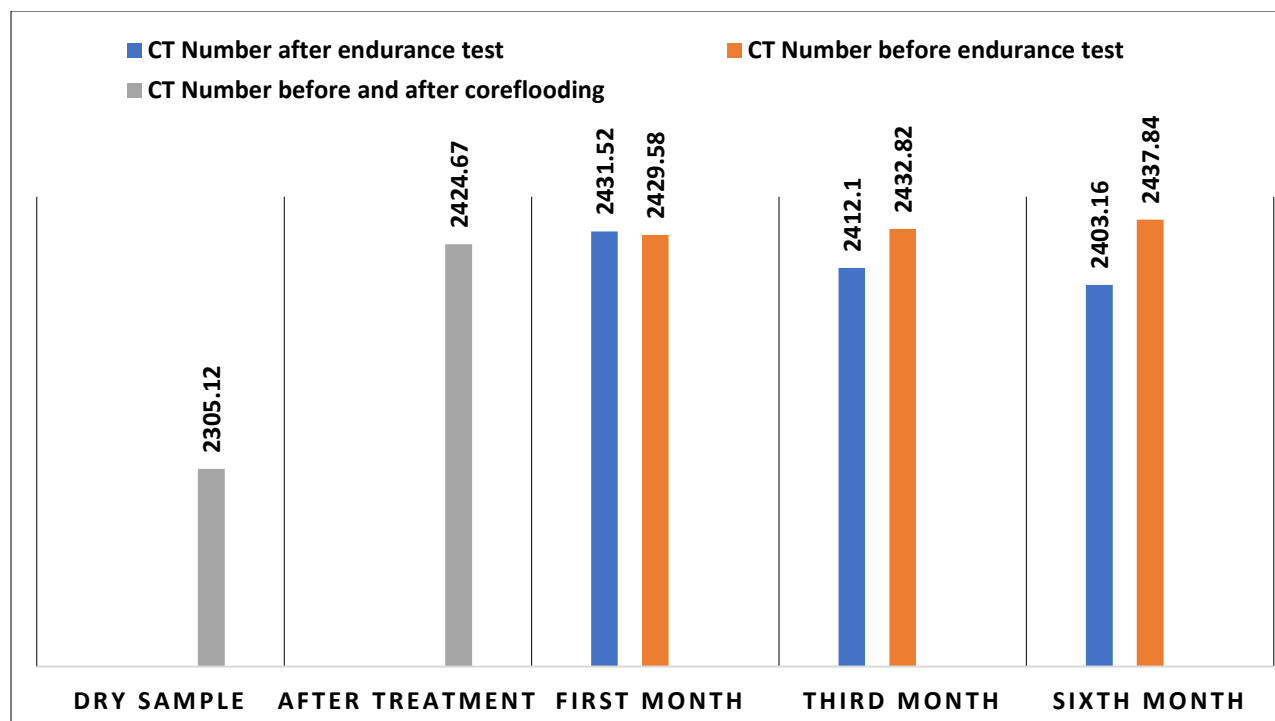


Figure 76 Average CT number in different stages for the induced channel sample W2.

6.4.2.3 Comparison of gels performance in the induced channel samples

Two induced channel samples were treated with nano-silica gel and PAM/PEI gels, and their plugging efficiency over 6 months was compared in Figure 77. Both gels demonstrated sustained high plugging efficiency throughout the 6-month period. However, in the third month, nano-silica gel exhibited slightly better performance than PAM/PEI gel, which showed minor degradation affecting its performance in the last three months. Specifically, after 6 months, the leak-off rate for PAM/PEI gel was 0.221 cc/min, which was 1.2 times higher than that of nano-silica gel. This suggests that nano-silica gel may offer better long-term stability and effectiveness for water shut-off applications compared to PAM/PEI gel.

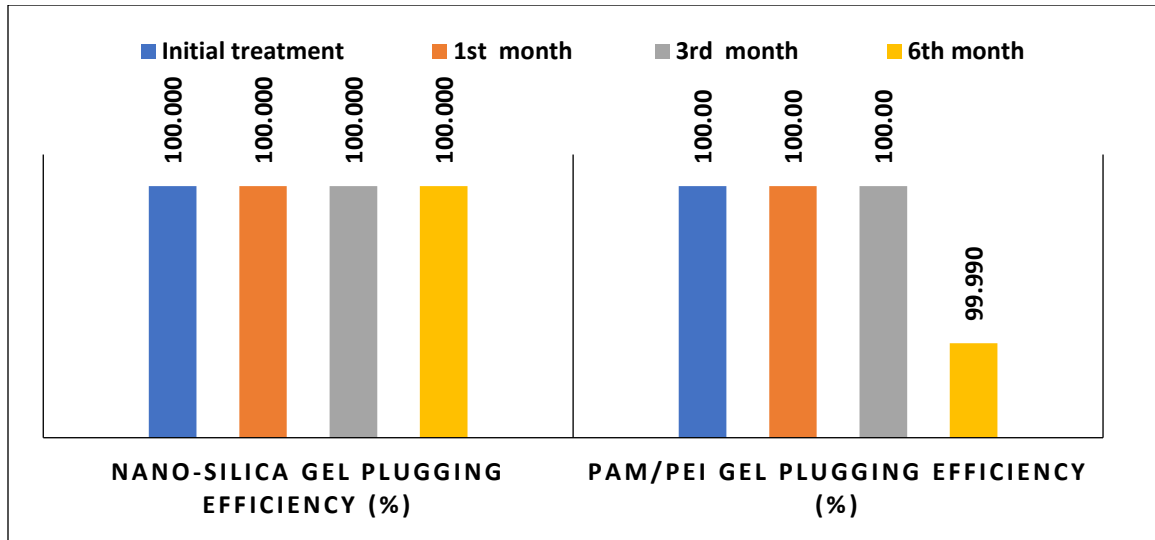


Figure 77 Comparison of plugging efficiency of nano-silica gel and PAM/PEI gel in the channel sample.

6.5 Conclusion

Nano-silica gel, a novel silicate gel introduced in recent years, has garnered attention for its potential in mitigating water-related issues by plugging fractures and channels. Despite its initial effectiveness, the long-term performance of these gels remains uncertain, posing a challenge in ensuring sustained profitability. To address this concern, this study delved into the performance of the nano-silica gel over a span of 6 months in fractured and induced channel samples, aiming to ascertain its viability as a durable, long-term solution. Key findings involve:

- Nano-silica gel maintained 100% plugging efficiency for 6 months in both fractured and induced channels.
- Nano-silica gel remained durable under high differential pressure (up to 1,000 psi) for 6 months.
- PAM/PEI gel's plugging efficiency decreased to 99.15% in the fractured sample after 6 months but remained at 99.99% in the induced channel sample.
- CT scans showed minimal degradation in both gels over 6 months, with less impact on nano-silica gel efficiency.
- Nano-silica gel had a better long-term stability and effectiveness than PAM/PEI gel for water shut-off in fractures and channels.

CHAPTER 7

CONCLUSIONS AND RECOMMENDATIONS

7.1 Conclusions

Silicate gels are among the oldest chemical techniques used to address excessive production issues in the oil industry. However, their utilization has been less compared to in-situ polymer gel due to challenges in placement and reduced plugging performance over time. In recent years, Nano-silica gel, a novel alternative introduced as a replacement for traditional silicate gel, has garnered attention for its potential in mitigating water-related issues by plugging permeable matrices, fractures, and channels. Despite its initial effectiveness, the long-term performance of these gels remains uncertain. The study focused on investigating the long-term plugging performance of nano-silica gel over a 6-month period, yielding the following key findings:

- Nano-silica gel achieved a remarkable plugging efficiency of 99.98% after 6 months.
- It maintained its durability at a high differential pressure of 1000 psi after 6 months.
- Nano-silica gel effectively plugged mid-fractured and induced samples by approximately 100% for the duration of 6 months.
- Furthermore, it exhibited durability to 1000 psi differential pressure in fractures and channels after 6 months.
- Over the 6-month period, nano-silica gel demonstrated better long-term performance than PAM/PEI gel, with a higher plugging efficiency.
- CT scan analysis indicated minimal degradation occurred in both gels, with less significant impact observed on the nano-silica gel.

7.2 Recommendations

The findings from the study have confirmed the capability of the newly developed nano-silica gel to serve as a water shut-off agent across different sample characteristics. The study also implicitly suggests broader applications for nano-silica gel over in-situ polymer gels, given its additional advantages such as low viscosity and environmental friendliness. Building on these achievements, several recommendations are proposed:

- Investigate the performance of nano-silica gel under harsh conditions.
- Assess the impact of fracture size and geometry on the performance of nano-silica gel.

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