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Review

A Review of Recent Developments in Nanomaterial Agents for Water Shutoff in Hydrocarbon Wells

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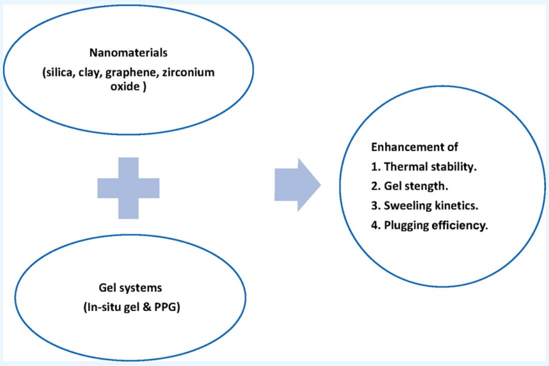
ABSTRACT: Reducing water production from hydrocarbon wells is one of the major requirements to prolong the life span of production wells. Gel treatment is commonly regarded as one of the traditional cost-effective methods for water shut-off applications. Different gel systems have been developed to overcome 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 nanosilica, nanoclay, 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 nanosilica-based fluid. Nanomaterials such as nanoclay, nanosilica, 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 the preformed particle−gel by up to 400%, accompanied by increased gel strength. Notably, nanosilica-based gels exhibit an exceptional plugging efficiency (100%). Additionally, the paper discusses how modeling can be used to overcome operational challenges in terms of placement and plugging performance.



1. INTRODUCTION

During oil production under an external drive fluid, the driving fluid targets pushing the oil ahead of the production interval. Conformance measures the flood front efficiency of the driving fluid to push the oil toward 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 coproduction 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, some reservoirs are surrounded by vast aquifers. In such cases, water can flow from different sources into the wellbore and be produced along with the 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 Bailey[15] 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 Veil[16] 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]

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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.[3,15,17−24] 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.[10,25] Diagnosing the water production challenge should include information about the production wells and field data. Data such as heterogeneity of reservoir, production drive mechanism, production data, and well geometry can help find the water entry point.[26] The diagnosis is conducted using production logging tools, pressure transient analysis, well log analysis, nodal analysis, relative permeability ratio, and production data analysis.[26−31]

Gel treatments are considered one of the oldest methods to treat water production.[3,32,33] They have shown their capability to plug the thief zones such as fractures, high permeability layers, etc.[10,17] However, they face certain challenges that need to be addressed in terms of gelation control, gel stability, and thermal stability.[34,35] 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 of improving material performance for different uses. Over the past few years, there has been a noticeable increase in the usage of nanomaterials in the oil and gas industry.[36] Nanomaterials are materials manufactured at nanoscale size, their size ranges from 1 to 100 nm. This size allows the material to exhibit unique properties distinct from those of 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.[36−39] 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 nanosilica and nanoclay 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. HISTORY OF WATER PROBLEM

2.1. 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:

2.1.1. 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]

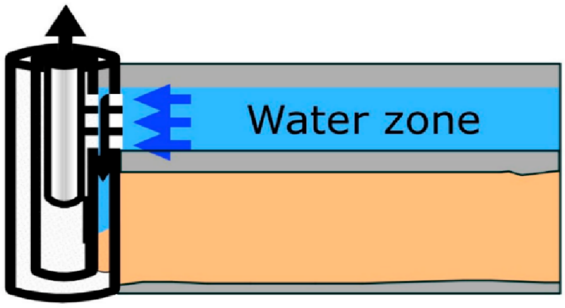


Figure 1. Flow behind pipe.

- **Casing/packer/tubing leak** can occur due to corrosion in the casing, tubing, or uninsulated seal of the packer as appeared (see Figure 2).[1,18]

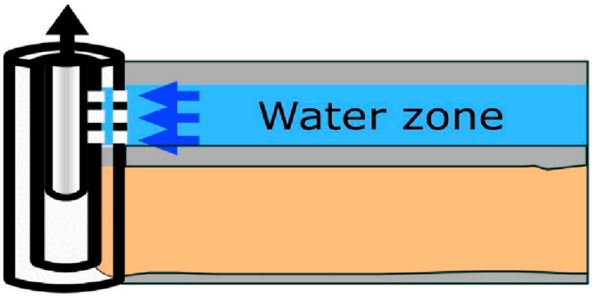


Figure 2. Tubing leaks.

- **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]

2.1.2. 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]

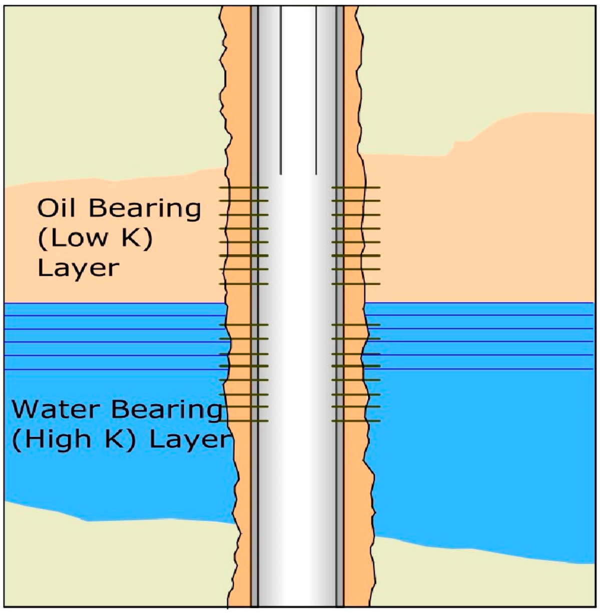


Figure 3. Rise of water−oil contact.

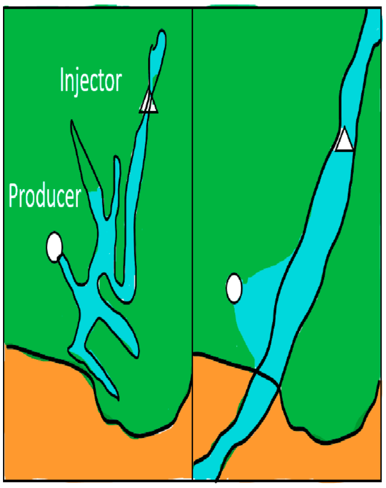


Figure 4. Fracture from the injector to producer.

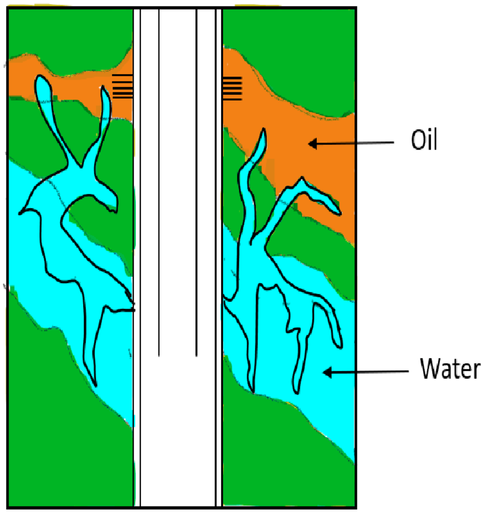


Figure 5. Fracture from a water layer.

- **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.[18]

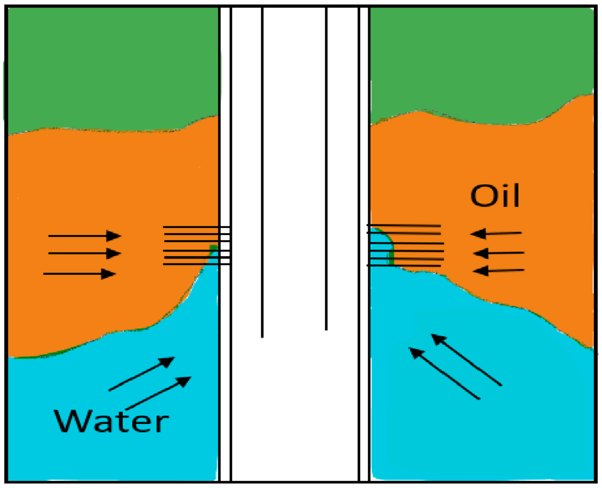


Figure 6. Water coning.

- **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

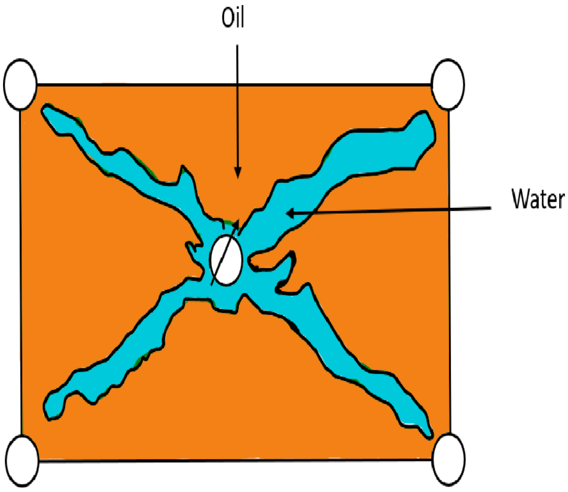


Figure 7. Fingering.

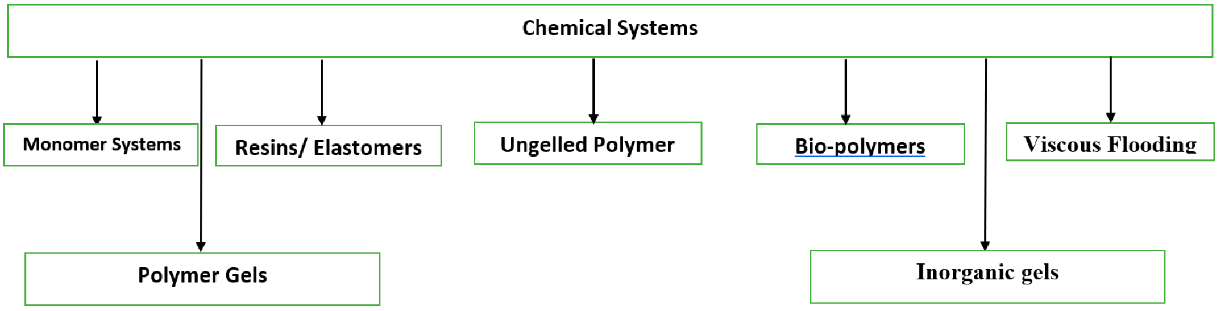
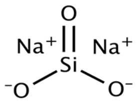
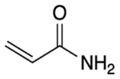
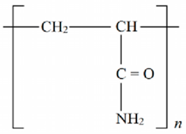
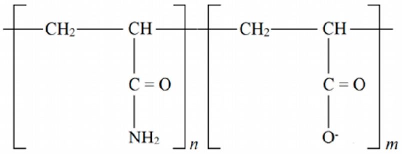
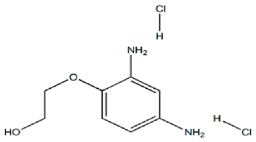
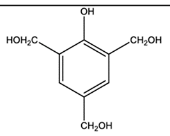


Figure 8. Chemical water shut-off systems.

Table 1. List of Common Chemicals' Structures for Water Shutoff Applications

Chemical System	Name	Chemical Structure
Inorganic Gels	Sodium Silicate	
Monomer Systems	Acrylamide	
Polymers	Polyacrylamide	
	HPAM	
	Xanthan Gum	
Resins	Phenol-formaldehyde	

injection well and viscous oil. It also can happen in a reservoir with a bottom water drive or gas cap expansion.[1,13]

2.2. 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 shutting off only specific water paths, and they could be classified into two types:

1. **Mechanical methods** 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.[17] Additionally,

incorrect placement of the plugging tool can lead to the loss of the producing oil zone.[55]

2. **Chemical methods** 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 nanosilica can assist in overcoming some operational challenges during treatment. Figure 8 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 cross-linking 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). Cross-linking agents could be metallic, such as aluminum and chrome, or organic, such as phenol. Additionally, biopolymers such as xanthan can also be cross-linked 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.

3. 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 gel 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.

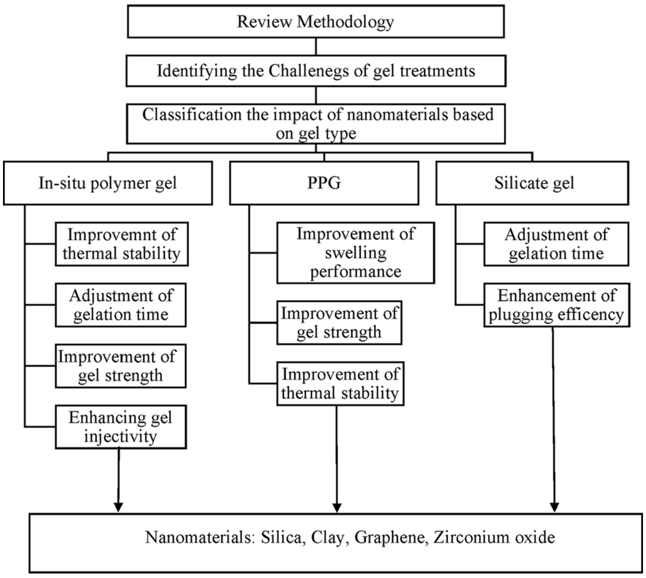


Figure 9. Review methodology for the impact of nanomaterials on gel treatments.

3.1. 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, correspondingly, increases oil production correspondingly. Based on where the gelation takes place, subsurface or at the surface, the gel can be classified into the following:

3.1.1. 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, cross-linker, and additives is injected downhole into the target zone. After the expected time and under a certain temperature, the mixture reacts to form a gel that

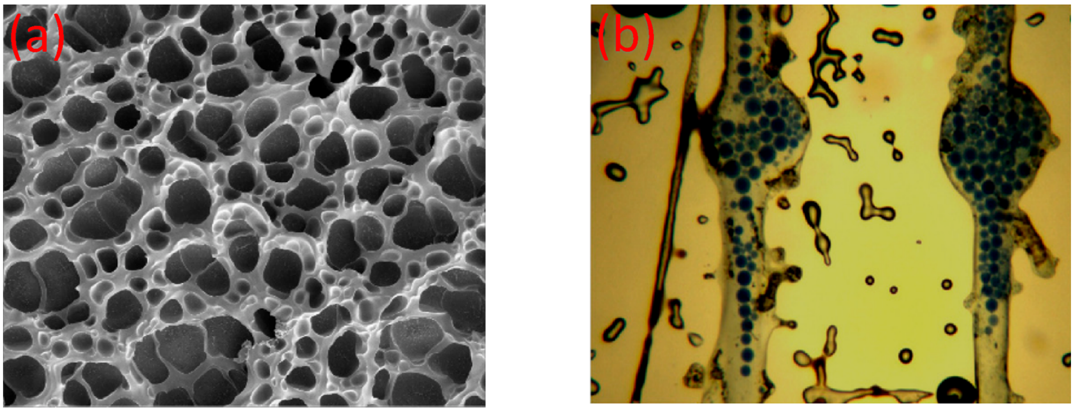


Figure 10. (a) Swelled PAM/Cs PPG[85] and (b) distribution of microgel particles in the microvisual model[87]

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.	Cross-linked 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]

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,[35,77,78] and potential damage of low permeability unswept oil zone.[79]

3.1.2. Preformed Gel. Preformed gels (PPG) are a type of gel that are 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 cross-linked 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 decries.[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),[32,85,86] microgels,[87−89] pH-sensitive cross-linked 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 reflect 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.

3.1.3. 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 that of 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 semisolid 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 of 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 that of 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 operators face 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 nanosilica, nanoclay, and nanographene, have been introduced into the gel composition to enhance its properties.

The key to a successful water shut-off treatment lies in accurately diagnosing the root cause of water intrusion and applying suitable remedies,[3],[1517−24] 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

3.2. Positive Impact of Nanomaterials on Gel Treatment.

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:

3.2.1. 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 concentration 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:

3.2.1.1. Enhancement of Thermal Stability.

Temperature is one of the most important factors that affects the conversion of polymer solution into a solid gel that seals the target zone. In the design of the 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 performance.[123] Therefore, researchers have been working to illustrate the valuable impact of adding nanoparticle materials to strengthen the polymer stability at elevated temperatures and extend the transition zone. Some of these nanoparticles include the following:

Zirconium Hydroxide. Zirconium hydroxide ($Zr(OH)_4$) of nanoparticle size has been investigated to improve the thermal stability of gels. They are highly applicable as as a cross-linker 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 cross-linked with hydroquinone (HQ) and hexamethylenetetramine (HMTA).[125] The thermal stability increased by 3 or 5 °C and reached up to 187 °C compared with 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.

Nanosilica and Nanoclay. Nanosilica (SiO_2) and nanoclay have shown their capabilities to improve the thermal stability of gels. Nanosilica has a high specific surface area and can absorb heat, which helps to prevent the gel from degrading at high temperatures. Nanoclay has a high thermal conductivity, which helps to transfer heat away from the gel, which also helps to prevent the gel from degrading. Lie[126] et al. observed that adding nanoparticles of silica improves the strength of polyacrylamide cross-linked with HQ and HMTA. Figure 11 illustrates two gel structures for the gel, with and without nanosilica particles. The ESEM images clearly demonstrate the massive aggregations and arrangements of silica nanoparticles that exist in uniformly distributed three-dimensional network structures of the gel. These are new arrangements that assist in creating stronger structure, reflected in the higher gel strength for gels incorporating nano-silica particles.

Asadizadeh[127] et al. obtained the same results when analyzing the effect of SiO_2 on the a gel composed of hydrolyzed polyacrylamide cross-linked with chromium(III) acetate. The gel showed significant flexibility, elongating to 1150% at very high temperatures. Furthermore, the recorded inflection

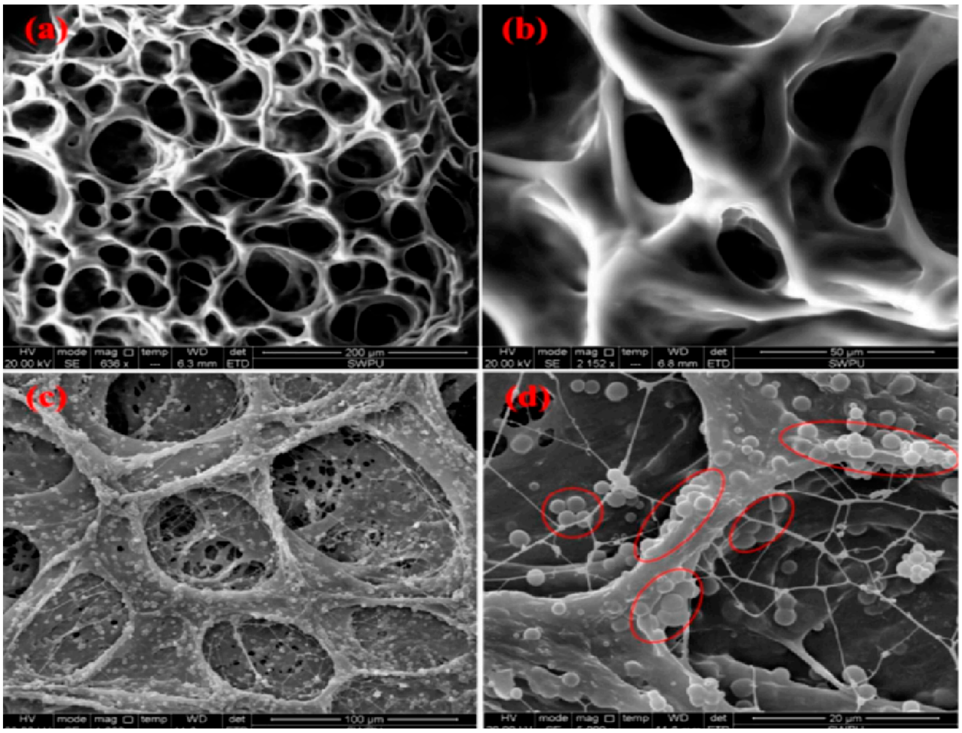


Figure 11. ESEM images of gel samples enhanced by varying concentrations of nanosilica particles: (a, b) without nanosilica and (c, d) 2% nanosilica concentration.[126]

temperature for a gel with nanosilica was higher than the one without nanosilica particles.

Despite these advantages, the usage of silica nanoparticles is limited to its compatibility with the polymer type. Nanoclay also has been addressed by some researchers. It has improved the performance of the gel at high temperatures in many studies. In a study performed by Cheraghian[128] et al., adding nanoclay to PAM hydrogel increased the oil recovery by 5.8% at elevated temperatures (80 °C).

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

Nanographene. Graphene is a carbon-based material that can be used on the nanoscale. It has very acceptable mechanical and thermal properties that improve the performance of the nanocomposite gel. An experimental study was conducted by Shen[129] 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.

3.2.1.2. 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 the gels. Nanoparticles can aggregate and connect to the polymer chains, forming a 3D network that is stronger with an adjustable gelation time.

Nanosilica and Nano-Fly Ash. In the same study performed by Lie[126] et al., nanoparticles of silica have improved the gelation time of polyacrylamide cross-linked with hydroquinone and hexamethylenetetramine. Another study was conducted by Singh[130] et al. by utilizing nano fly ash with PAM polymer cross-linked 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 the rapid gel formation.

3.2.1.3. 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 the water production zones. Nanoparticles can be used to improve the strength of the gels. Nanoparticles can form a network that strengthens the gel and makes it more resistant to shear forces.

Nanosilica. Lie et al.[126] 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 the nanocomposite gel. Chen[131] 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 the 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.

Nanographene. 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 Lie[132] et al., the nanocomposite GO-PAM had tensile strength higher by 4.5 times and more than 300% elongation.

In another study, Almohsin[133] et al. introduced a nanocomposite PAM by including graphene-based zirconium oxide, a

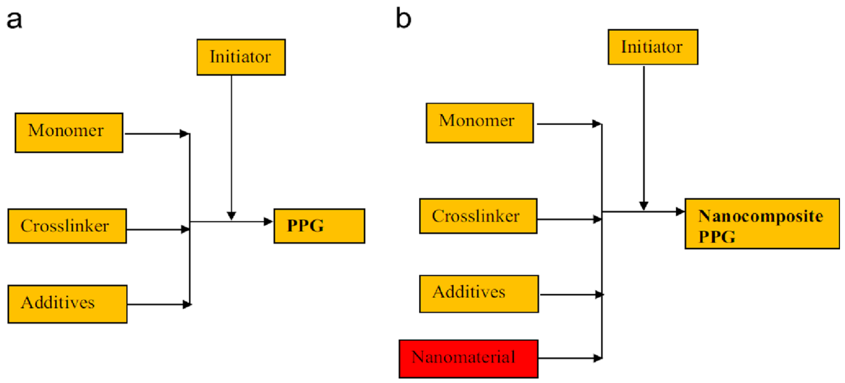


Figure 12. Nanocomposite PPG.[80]

superb mechanical strength was observed at elevated temperatures. The structure of the gel was homogeneous and stable, and it shows the capability to trap the water even at elevated temperatures.

3.2.1.4. Enhancing Gel Injectivity. The evaluation of gel injectivity stands as a pivotal criterion for the effective deployment of gels in field applications, necessitating a rigorous assessment prior to field trials. In a study conducted by Almohsin[133] 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.

Pereira[134] et al. explored the effectiveness of HPAM gel integrated with nanoparticles for water shut-off purposes. They assessed the injectivity by measuring the 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, the viscosity values were between 67.5 and 76.9 mPa·s. These findings suggest that the addition of nanoparticles minimally affects the gel injectivity. Ali[135] et al. also investigated gel injectivity using sulfonated PAM gel incorporating Fe_2O_3 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.

3.2.2. Impact on Preformed Particle–Gel. Preformed particle gels are composed of dried cross-linked polymers in the form of adjustable particle sizes.[81] The injection process of these gels is simpler than that of 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 temperature.[71] 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:

3.2.2.1. Improvement of Swelling Performance and Thermal Stability. Nanosilica and Nanoclay. Khoshkar[136] 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 lower 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 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. Paprouschi[137] 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 nanographene had a higher storage modulus compared to the base samples without nanographene. 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. Nanoclay. Another study by Tongwa and Bai[80] proposed a new preformed particle–gel using a nanomaterial in the main composition, called nanocomposite hydrogel. The proposed gel is composed of monomer, initiator, cross-linker, additives, and nano-clay called laponite XLG (L-XLG), which does not exist in the conventional hydrogel (see Figure 12).

Viscoelastic properties, such as elastic moduli, were used to evaluate the mechanical performance of the 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 Figure 13. Figure 13 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.

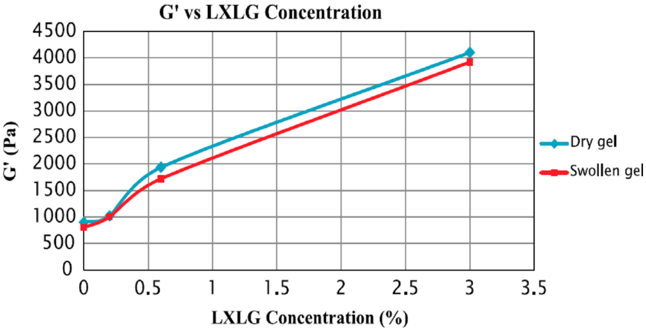


Figure 13. Effect of nanoclay concentration on gel strength.[80]

The swelling performance was also evaluated in formation water and a 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 a nanomaterial (up to years). This improvement supports the idea of adding nanomaterials to the 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.

3.2.3. Silicate Gel. Recently, nanosilica-based fluids were introduced to the industry as an alternative to sodium silicate gels. Many studies investigated the temperature limitation, activator concentration, and plugging efficiency. The real challenge 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:

3.2.3.1. Adjustment of Gelation Time. Boul[139] 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.

Almohsin[140] 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 the 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 the activator concentration led to a shorter gelation time under a wide range of temperatures from 50 to 200 °F.

Karadkar[141] 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 min.

3.2.3.2. Enhancing the Plugging Efficiency. Karadkar[141] 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 N_2 and brine could not flow through the core plug (confirming excellent plugging efficiency).

In a study conducted by Almohsin[140] 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 cm^3/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 nanosilica-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, Table 4 summarizes the impact of nanomaterials on improving the performance of these gels in terms of gel strength, gelation time, and thermal stability.

5. Treatment Modeling and Field Cases.

5.1. Gelation Time Modeling. 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]

Table 4. Summary of Nanomaterials' Impact on Gel Properties

Nanomaterial	Gel Type	Gel System	Impact	Reference
Silica	In situ polymer gel	PAM cross-linked with HQ and HMTA	Increasing the maximum temperature of the stable gel from 137.8 to 155.5 °C by adding 0.3% nanosilica.	126
		HPAM cross-linked 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-propanesulfonic acid sodium salt monomer) with linking agent polyethylene glycol diacrylate	Enhancing the swelling ratio with lesser syneresis.	136
			The gel becomes more temperature-durable.	
	Silicate gel	Nanosilica based fluid	Accelerating gelation time at low temperatures as 50 °F.	139
		Nanosilica 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	PPG	Acrylamide cross-linked polyethylene glycol diacrylate	Increasing Young's modulus of the gel enhances the gel strength.	80
			Increasing the long-term thermal stability of the gel for up to 12 months.	
Graphene	In situ polymer gel	PAM cross-linked by N,*N*-methylenebis(acrylamide) (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.	
		PAM cross-linked with *N*,*N*′-methylenebis(acrylamide)	Increasing the gel tensile strength by 4.5 times more than 300% elongation.	132
		PAM cross-linked 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
Fly ash	In situ polymer gel	PAM cross-linked with chromium(III) acetate	Enhancing the gel strength with a higher thermal stability.	130
Zirconium hydroxide	In situ polymer gel	PAM cross-linked with hydroquinone and hexamethylenetetramine	Improving the thermal stability of the gel to temperature up 187 °C.	125

The Arrhenius equation[148] (eq 1) represents the effect of absolute temperature on reaction rate. It details the mechanism of a chemical reaction and applies to most of the chemical reactions. Hurd and Letteron[149] developed an empirical model (see eq 2) correlating the gelation time of silicic acid gels with temperature close to the Arrhenius equation. They validated this correlation by using experimental data with some assumptions. Below are the beliefs they followed to develop the model:[142]

- 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.

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

$$\ln t = \ln c - \ln k - (n - 1)\ln a \quad (2)$$

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 Letteron[149] was verified by Jorden et al. Jorden[150] 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, Broseta[151] 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 cross-linker concentrations, brine salinity, and degree of hydrolysis. Additionally, he verified that the temperature has the highest impact on GT compared to other parameters, and it followed the Arrhenius equation. Marfo[152] 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 (eq 3) for temperature, cross-linker concentration, and water salinity.

$$\mathrm{GT} = 38.4333 - \frac{13}{75}T + \frac{19}{30}S - \frac{67}{30}C + \frac{1}{100}TC - \frac{1}{300}TS \quad (3)$$

Eq 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 cross-linker concentration (wt %).

5.2. Modeling Water Shutoff Performance. Xianchao[153] 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 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 Ertekin[154] 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 a 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 the 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 is injected, the predicated model has two indicators that rely on oil and water rate profile enhancement.

Meshalkin[155] 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 the energy and resource efficiency in oil production.

The study by Ferreira[156] 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.

5.2.1. Limitations of Proposed Models. The existing coupled numerical models in the literature for water shutoff using gel treatments emphasize simulating conventional black oil or compositional multiphase 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 behavior 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 modeling 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.

5.3. 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 the 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 cross-linked gels), resins, and nano-silica. The treatments are compared based on their advantages and disadvantages, considering the reservoir temperature for each case.

5.3.1. Polymer Gels. In-Situ Crosslinked Gels. In-situ cross-linked gels offer the advantage of being pumped as a low-viscosity fluid and then subsequently cross-linked 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 cross-linked 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 at two intervals in a sandstone reservoir. The upper interval was depleted to 777 psi, while the lower interval was maintained at 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 h of gelation time. This zone had a temperature of 200 °F. After pumping the treatment, the well was shut in for 2 days. The upper interval was then positive pressure tested at 3500 psi. The lower interval was opened and had an initial oil rate of 2500 BOPD with zero water cut.[160]

Preformed Gels. 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]

5.3.2. Foamed Gels. Foamed gels provide improved mobility control during injection and have shown success in water shutoff applications. The foaming process enhances the 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 m^3, 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]

5.3.3. 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 at 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 a high gravity oil. The pretreatment flowback experienced a 100% water cut with 317 BWPD of water production. The main factors were determined to be a rise in the oil-water contact (OWC) and water coning. The planned gel volume was 16 m^3. Because of the low injectivity, the actual injected volume was around 5 m^3. 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]

5.3.4. Nanosilica 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 a noise log and temperature survey. The prejob 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 an inflatable packer was set 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]

5.3.5. Nano-Based Particulate Gel. The Southeast Kuwait field has been produced from a sandstone formation. A production test was conducted on a cased hole oil producer and indicated 90% of water was 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 to be 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]

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 nanosilica 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. Nanosilica treatments are versatile and can be applied in ultrahigh 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 the future challenges can be illustrated as below:

6.1. In-Situ and Preformed Particle Polymer Gel.

- While studies have demonstrated the positive impact of nanomaterials like nano silica, nanoclay, and nanographene, future research should explore a wider range of nanomaterial approved their applicability in EOR applications, such as Aluminum Oxide (Al2O3), Titanium dioxide (TiO2) 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.

6.2. Nanosilica-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 nanosilica 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%, nanosilica 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.

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 on the reservoir characteristic. Therefore, modeling treatment will assist in improving agents' performance as water shut off agents. Eventually, the impact of nanomaterials could be concluded as follows:

1. Nanomaterials, such as nanoclay, nanosilica, 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 nanosilica 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.

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■ NOMENCLATURE

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 nanoplatelets
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

Symbols

a	Fractional conversion
c	Constant
n	Reaction order
t	Gelation time (hours)
k	Rate constant
T	Temperature (°F)
S	Mixed water salinity (%)
GT	Gelation time (hours)
C	Cross-linker concentration (wt %)

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