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Enhanced Gas Recovery by Wettability Alteration to Reduce Water Blockage Around Wellbore

Gonzalo Mauricio Ceron Lopez

0000-0001-8861-2551

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DECLARATION

To the best of my knowledge and belief, this thesis contains no material previously published by any other person except where due acknowledgment has been made.

This thesis contains no material which has been accepted for the award of any other degree or diploma in any university.

Signed …………………………. (Gonzalo Mauricio Ceron Lopez)

Date: 20th of September 2023.

“ *Mi vida es hermosa porque existes tú*
Hermosos son mis días porque veo tu luz
Llevas ese fuego que hay en mi corazón
Para toda mi vida tú eres la razón, uh’

-Gondwana, 2002-

Dedicated to the tripod of my life: Pao, Marty and Suri. Without your love and sacrifice this piece of my life and my entire life would be meaningless.

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ABSTRACT

As a low-carbon fuel, natural gas is leading the transition to a sustainable and cleaner energy system. However, water blockage is seen to reduce gas deliverability significantly in many gas producing wells. This research project describes the synthesis and screening process followed to develop a novel environmentally friendly and cost-effective non-fluorinated chemical treatment using a new benzoxazine monomer as a wettability modifier to combat water blockage. In the first stage, a particular focus was placed on demonstrating the application of the novel chemical in moderate permeability rock samples, which was later complemented by a similar analysis in a complementary stage that assessed treating low permeability sandstone samples. In the initial stage, it was demonstrated that the chemical would adhere to silicate surfaces through a silane moiety followed by the application of a thermally accelerated ring-opening polymerization of the benzoxazine moiety. The performance of the treatment was evaluated using contact angle measurements, spontaneous imbibition tests, and core-flooding experiments at 60 ◦C and 10.35 MPa. After chemical treatment, the contact angle shifted from almost 0◦ to 90◦, implying that the treatment could alter the wettability from strongly water-wet to an intermediate gas-wetting state. Spontaneous imbibition measurements showed about a 65% reduction in the volume of water imbibed into the rock samples after chemical treatment, suggesting a substantial increase in the hydrophobicity of rock pore surfaces. Core-flooding experiments indicated that the chemical treatment increased gas relative permeability (by up to 22%) whilst decreasing residual water saturation (by up to 10%) hence helping to alleviate water blockage.

In the second stage of this research, it was demonstrated that the resin could be successfully applied in low-permeability sandstones (approximately 15 mD as opposed to 100 to 200 mD in the previous stage) to change the rock surface wettability from water-wet to intermediate gas-wet. In this stage, it was also shown that curing temperatures as low as 125 °C (as opposed to 180 °C used in the previous stage) could significantly change wettability, indicating surface functionalization through the silane moiety and ring-opening polymerization of the benzoxazine moiety. In drainage core flooding experiments at 2.5 wt.% resin loading, brine recovery increments of 6.3 to 6.9% were obtained for curing temperatures of 125 to 180 °C, respectively. A maximum 20% increment in the endpoint relative gas permeability was achieved at a curing temperature of 180 °C. These results demonstrated the suitability of this novel chemical for the treatment of low permeability rock formations that are often more prone to water blockage. A coupled experimental and numerical study conducted at core and wellbore scales demonstrated the potential effectiveness of this novel chemical treatment in improving gas productivity at the larger scales. Numerical reservoir simulations indicated a 2.9 to 10.6% improvement in gas deliverability for a treatment radius of 4 to 16 m, respectively.

Taken together, the research results indicate that this novel non-fluorinated benzoxazine monomer can successfully shift the wettability of sandstone rocks from a strongly water-wet to an intermediate gas-wet state and thus aid to mitigate water blockage at relatively low cost and in an environmentally friendly manner. Furthermore, this chemical can withstand extra high temperatures encountered in many deep low permeability gas reservoirs where water blockage may be highly pronounced.

PUBLICATIONS BY THE AUTHOR

The main technical outputs of this research work have been published in the following two journal papers:

1. Lopez, G.M.C., Myers, M.B., Xie, Q. *et al.* Wettability Alteration to Reduce Water Blockage in Low-Permeability Sandstone Reservoirs. *Transp Porous Med* 147, 401–428 (2023). https://doi.org/10.1007/s11242-023-01914-8

2. Gonzalo Mauricio Ceron Lopez, Matthew B. Myers, Quan Xie, Colin D. Wood, Ali Saeedi. Wettability alteration using benzoxazine resin: A remedy for water blockage in sandstone gas reservoirs. Fuel 291, 2021. 120189, ISSN 0016-2361, https://doi.org/10.1016/j.fuel.2021.120189.

Table of Contents

List of Figures

List of Tables

CHAPTER 1 Introduction

1.1. Background and Problem description

Many nations are seeking energy diversification that could reduce their dependence on fossil fuels. For instance, recent geopolitical events in 2022 have forced the European Union to seek cleaner alternatives to mitigate its dependency on fossil fuels. According to the International Energy Agency, the Stated Policies Scenario (STEPS), the Announced Pledges Scenario (APS) and the Near Zero Scenario provide optimistic development to mitigate the impact of global warming until 2050. However, there is not enough evidence that renewable and green energies could escalate to support the industries already dependent on fossil fuels until then. Therefore, as pointed out by many experts, natural gas has been recognised as an important participant in the energy transition to cleaner energy, principally due to its lower CO_2 emissions compared to burning oil and coal. The cleaner nature of natural gas is complemented by its relatively low cost. In addition, the infrastructure and technological advances in the supply chain have resulted in a significant increase in its supply in many regions of the world. However, to uphold the critical role of natural gas in the energy transition, it is essential to maintain and even boost its production in the next several decades, which in turn requires special attention and added investment in optimised recovery methods that could increase its deliverability.

The current global average gas recovery before abandonment is around 75%, which means approximately 30% of the Gas Initially In Place (GIIP) of a typical gas reservoir would remain unrecovered (Oldenburg, Stevens and Benson 2004). Low productivity of gas wells leading to their abandonment is a leading cause of low recovery factor in many gas fields. Several physical processes, such as water conning, water cross-flow and water invasion during workover/drilling operations, can lead to a substantial reduction in the productivity of gas wells (Bennion et al. 1996a). The majority of these processes likely trigger water blockage in the wellbore region, which can significantly decrease gas relative permeability resulting in reduced gas productivity. For example, gas production in Sindh, Pakistan drastically decreased from 30 to 9 MMscfd because of water crossflow from a water-saturated layer to the most productive interval (Khan, Noman and Hadi 2017). In another example, liquid blockage at Hatter’s Pond Field in Alabama, USA, reduced gas deliverability from 2.7 to 0.25 MMscfd due to water invasion during drilling operations.(Al-Anazi et al. 2003)

The water blockage phenomenon occurs due to the strong liquid-wet characteristic of the reservoir rock. Modifying the wettability from strong water-wetting to intermediate gas-wetting has the potential to mobilize the confined liquid relieving the limitation on the gas flow and improving gas productivity. However, to date, the application of mechanical techniques to alleviate water blockage do not provide a long-term solution while the long-term solutions involving chemical treatments use fluorinated components, which are expensive and environmentally unsafe. Hence, there is an urge in the technical community to identify a cost-effective and environmentally friendly wettability-altering chemical that can be fixed onto the rock surface through durable bonding. Furthermore, the chemical must be able to resist the harsh thermal conditions prevalent in many reservoirs. This research is tasked with the main aim of finding or developing a new chemical that meets the above specified requirements. In doing so, special attention would be paid to the surface characteristics and the way they control fluid-rock interactions in the porous space in sandstone rocks. In order to find a suitable chemical, other industry industrial sectors, particularly the paper and textile industry, which use chemical treatments to manufacture water-repellent products are explored to find a well-suited chemical.

To this end, a novel benzoxazine monomer that has been previously used in a wide variety of surface treatments on cotton, polyester, glass, silica wafers and paper to impart hydrophobic wettability characteristics was identified and synthesized (Gogoi et al. 2014; Liao et al. 2008; Liu et al. 2013; Tang, Hess and Breedveld 2015; Wang, Chang and Kuo 2011; Wang, Su, et al. 2006). This cost-effective and environmentally friendly monomer can be used to treat sandstone rock surfaces through a silane moiety, which improves its stability and longevity by limiting its mobility. Subsequent thermal treatment of the chemically functionalized porous sandstone rocks causes polymer formation, which changes the wettability of the rock. While this change in wettability is the mechanism for reducing water blockage, the thin polymer layer formed on the pore surfaces should not negatively impact the permeability in a significant way, i.e., it should not impede gas production by blocking the pore space. Moreover, the proposed chemical solution is expected to be durable and stable under high-temperature conditions, showing a potential application in deep gas reservoirs, which have become more common nowadays.

1.2. Research Objective

As indicate earlier, the primary aim of the proposed project is to develop a cost-effective and environmentally friendly chemical treatment to reduce wellbore water blockage. In achieving this main proposed goal, the following objectives will be pursued:

- To identify and select a non-fluorinated candidate chemical that can efficiently alter the wettability of reservoir rocks.
- To screen and select the most appropriate chemical formulation, temperature and solvent type to treat sandstone rock samples using laboratory techniques.

- To investigate the influence of rock permeability (moderate and low) on the outcome of wettability alteration with the identified chemical treatment using experimental approaches.
- To assess the performance of the final selected chemical solution(s) to increase gas production under dynamic reservoir conditions using core-flooding equipment through gas relative permeability, water saturation, and gas recovery measurement.
- To investigate the influence of the water blockage mitigation at the wellbore scale using a commercial reservoir simulation software package to quantify the improvement of the treatment at the larger scales.

1.3.Thesis organization

This thesis contains five chapters. The first chapter provides a brief introduction to the research program, where the background, problem description, and objectives are addressed providing a brief context for this research. Chapter 2 discusses the water blockage mechanisms and causes, mitigation techniques, and its relationship with rock-fluid interactions through a detailed literature review. In particular, the role of relative permeability, capillarity, and water saturation is described followed by a description of the particular properties of the novel benzoxazine resin as a suitable candidate chemical to alter the wettability of sandstone rocks.

Chapter 3 describes in detail the experimental equipment and material used to perform the necessary experiments as well as the particular procedures and protocols developed in conducting the envisaged experiments. This chapter also includes a description of the simulation software used for wellbore analysis and the upscaling of the laboratory-based results.

Chapter 4 presents a detailed description and interpretation of the experimental and numerical simulation results obtained. In doing so, appropriate references are made to the relevant literature and any agreement or disagreement with the previously published data are adequately addressed. The journal papers published constitute much of the information presented in this chapter.

Finally, Chapter 5 provides a brief review of the research highlights together with recommendations for further work built upon the results obtained in this research program.

CHAPTER 2 Literature Review

2.1. Introduction

The purpose of the current chapter is to conduct a detailed literature review on water blockage as a major productivity issue in sandstone gas reservoirs. In doing so, it will present a detailed discussion about the mechanisms associated with water entrapment in the wellbore area. Particular emphasis will be given to various fundamentals that characterise multiphase flow interactions controlling this important phenomenon, with a specific focus on wettability and capillary effect. In addition to the above, the chapter provides an overview of several techniques that have been developed to mitigate water blockage in gas reservoirs.

Towards the end of this chapter, a comprehensive description, including the properties and surface characteristics of a novel non-fluorinated monomer utilised in this research project is presented. The purpose of this monomer is to modify the wettability and surface properties of sandstone formations, which could offer promising solutions in the context of addressing water blockage challenges.

2.2. Common Gas Productivity Issues

For a gas field, the exploration phase focuses on characterising the rock formation and understanding the initial conditions of the fluid properties in the reservoir. This process leads to an estimate of the original hydrocarbon-in-place. In the subsequent development phase, the fluid dynamics are carefully analysed, which will employ any available production data. This analysis serves as a guide to predict future production and explore possible development scenarios. In achieving the above objectives, uncertainty analysis in predicting reservoir productivity can help optimize the reservoir development plan and extend the production life of a field. A major factor impacting the future performance of the reservoir and often requiring a rigorous uncertainty analysis is the reservoir drive mechanism. For gas reservoirs, although water drive can yield high gas recovery under optimal conditions but can bring about many major productivity issues. In fact, many common major productivity issues encountered in gas-producing wells are, in one way or another, associated with the introduction of water into the wellbore region.

When analysing reservoir dynamics, if present, water influx is modelled as an effective mechanism affecting the recovery potential of a hydrocarbon reservoir. The water influx provides pressure support and effectively displaces the hydrocarbon phase until a water breakthrough is encountered. In many gas reservoirs, the undesirable breakthrough may occur at an earlier stage of production, leaving a significant volume of gas trapped in the formation. Such an event may occur early and uncontrollably when production wells produce under open- hole conditions (Karami, Manshad and

Ashoori 2014). This effect could cause water to bank up around the well and severely impact gas mobility, ultimately affecting the well productivity and field recovery (Armenta and Wojtanowicz 2002). Various mechanical solutions have been utilised to minimise the occurrence of this phenomenon (e.g., partial formation penetration, formation isolation, and inflow control devices) (Erarsian, Ayan and Lee 1991; Prakasa, Corona and Allen 2020).

In other cases, when the pressure support from the aquifer is not strong, the gas production is driven by a fluid expansion mechanism. However, a similar water-related problem to the above can be observed in the wellbore area via the introduction of water in this region via external sources. The water-based fluids used during drilling, completion, workover and/or fracking operations may infiltrate the rock formation and become trapped in the pore network of the rock formation and reduce gas productivity. This phenomenon is highly pronounced in formations with low permeability as they present large capillarity and a much greater tendency to trap water (Bennion et al. 1994; Methven 1971).

Many researchers have dedicated their efforts to characterising and addressing the issue of liquid blockage around the wellbore. Such efforts have not only involved conducting extensive analyses of data gathered for gas-producing formations worldwide but also evaluating this phenomenon experimentally.

Water-, oil-, and emulsion-based fluids were tested during drilling operations in the Cotton Valley Formation in Jones County, Mississippi. The studies found that wells drilled with water-based fluids had an efficiency of less than 50%, significantly impacting gas recoverability by 30 to 40% (Methven 1971). This substantial reduction in gas recoverability is attributed to the swelling of clays, migration of fines, and in particular water blockage, leading to reduced relative permeability to gas.

In 1993, Cimolai analyzed the effects of water blockage in horizontal wells within the Cadomin Formation, situated in a deep basin in west-central Alberta, Canada (Cimolai et al. 1993). The study revealed that irreducible water saturation was significantly affected by the intrusion of an aqueous phase used during drilling. Subsequently, it was suggested that employing a non-aqueous drilling fluid in horizontal drilling techniques could help avoid the abovementioned issue and benefit gas recoverability.

In further research, Bennion (1996) conducted a comprehensive experimental study of the Cadomin Formation, employing laboratory coreflood analysis, and demonstrated that the gas permeability of this low-permeability reservoir could decrease dramatically from 3.9 to 0.16 millidarcies (mD) after the introduction of water. Simultaneously, the residual water saturation exhibited a 2.5-fold increase compared to the initial in-situ water saturation determined from well logs. Another noteworthy case study relates to the Paddy formation in Alberta. In this reservoir, the initial water saturation was lower than the irreducible water saturation, a consequence of the reservoir geology, lithification, wettability, and temperature. Similar to the Cadomin Formation, coreflood analysis revealed a significant impact of water blockage, resulting in a reduction of gas permeability from approximately 100 md to 45 mD (Bennion et al. 1996a; Bennion, Thomas and Bietz 1996; Bennion et al. 1996b; Bennion, Thomas and Ma 2000a, 2000b).

Probably, the most notable finding related to the water blockage phenomenon originates from the analysis conducted on gas fields in the United States and Canada (Bennion et al. 1994; Engineer 1985; Khan, Noman and Hadi 2017; McLeod, McGinty and Smith 1966; Shen et al. 2014; Graham and Boyd 1967). Through their preliminary assessments, these authors have collectively identified low permeability as a critical characteristic of formation damage, significantly impacting water entrapment in the pores within the wellbore area (Figure 2.1). In 1965, a research study conducted by The Bureau of Mines in the United States revealed that reservoirs with permeability values between 0.1 and 100 mD were significantly impacted by water intrusion (Eakin, Miller and Eckard 1965). For their investigation, the researchers carefully selected fourteen gas production wells and six gas storage wells with apparent phase trapping.

Another productivity issue affecting gas deliverability and related to the introduction of the water phase is caused by the interaction between clay minerals and water. Common clay minerals (e.g. kaolinite, smectite, illite, and chlorite) tend to interact with the reservoir brine and subsequently swell and/or migrate within the rock pore space, significantly reducing fluid flow capacity and negatively impacting field productivity (Wilson, Wilson and Patey 2014).

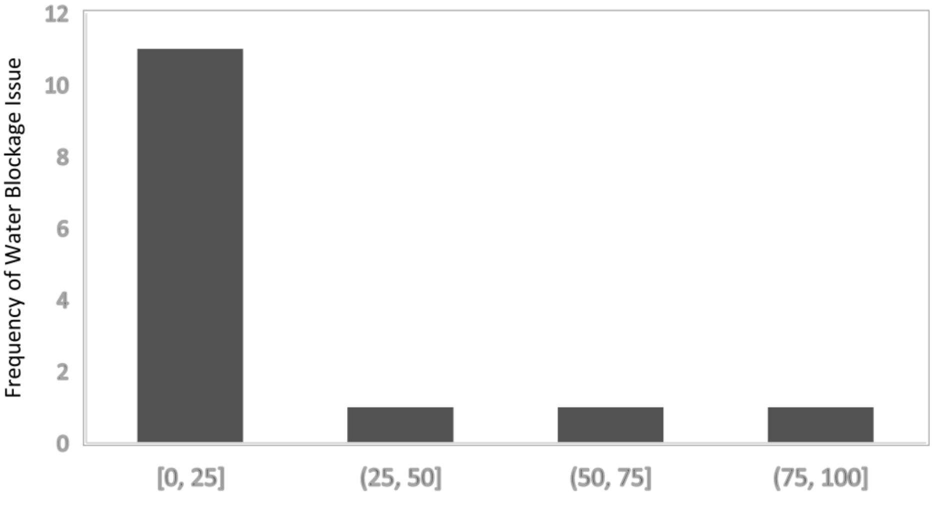


Figure 2.1. Low permeability formations often exhibit liquid blockage as a productivity problem.

While the earlier discussed water-related productivity issues may be of primary concern in dry gas reservoirs, in their gas condensate counterparts, the liquid condensate dropout around the wellbore can also result in issues similar to those caused by water and make the earlier discussed productivity issues even more pronounced (Al-Anazi et al. 2007; Noh and Firoozabadi 2008b, 2008a). Other potential productivity problems that may be encountered in gas reservoirs include formation collapse, emulsions, scaling/precipitation, and sand production (Muskat 1951).

2.3. Mechanisms of Water Blockage

As presented earlier, the water blockage effect in a gas reservoir is the build-up or severe accumulation of water-based fluids in the porous rock formation around the wellbore (Armenta and Wojtanowicz 2002; Li, Ge and Zhang 2015; Panga et al. 2007; Panga et al. 2006; Holditch 1979; Bennion et al. 1994). The water phase penetrates the formation pores and displaces the gas phase due to the capillary forces of the pore system (Antoci, Briggiler and Chadwick 2001; Bang et al. 2009; Bennion et al. 1994; Cheneviere et al. 2005; Cimolai et al. 1993; Engineer 1985; Khan, Noman and Hadi 2017; Eakin, Miller and Eckard 1965). If the reservoir rock formation is considered as a bundle of water-wet capillary tubes of different diameters filled with gas, the water phase enters on one side of the capillary tubes and displaces the gas phase by creating a differential pressure between the two steps (Bennion, Thomas and Bietz 1996; Deng and King 2018; Mirzaei Paiaman, Moghadasi and Masihi 2010).

Bennion et al. (1996) divided the process leading to water blockage into three straightforward stages, as shown in Figure 2.2. In the first stage, the larger pores are initially saturated with a predominant amount of the gas phase, while the liquid phase fills the narrowest capillary spaces in the rock system as well as forming a thin film over the surfaces of the large pores. This initial volume of water does not appreciably interfere with the gas phase, which flows preferentially through the most noticeable pores. In the second stage, the penetrating liquid (water) displaces the gas phase in the pores and fills many interconnected pores. So in a reservoir, the liquid volume around the wellbore increases significantly, creating a barrier to the gas flow. The final phase (phase 3) occurs after a pressure drop has occurred around the wellbore when the well starts producing and displaces some of the water phase that has entered the pores. Due to the capillary effect in the two-phase fluid system, a significant amount of liquid can become trapped in the pores retaining water as an immobile phase, despite the drawdown created around the wellbore.

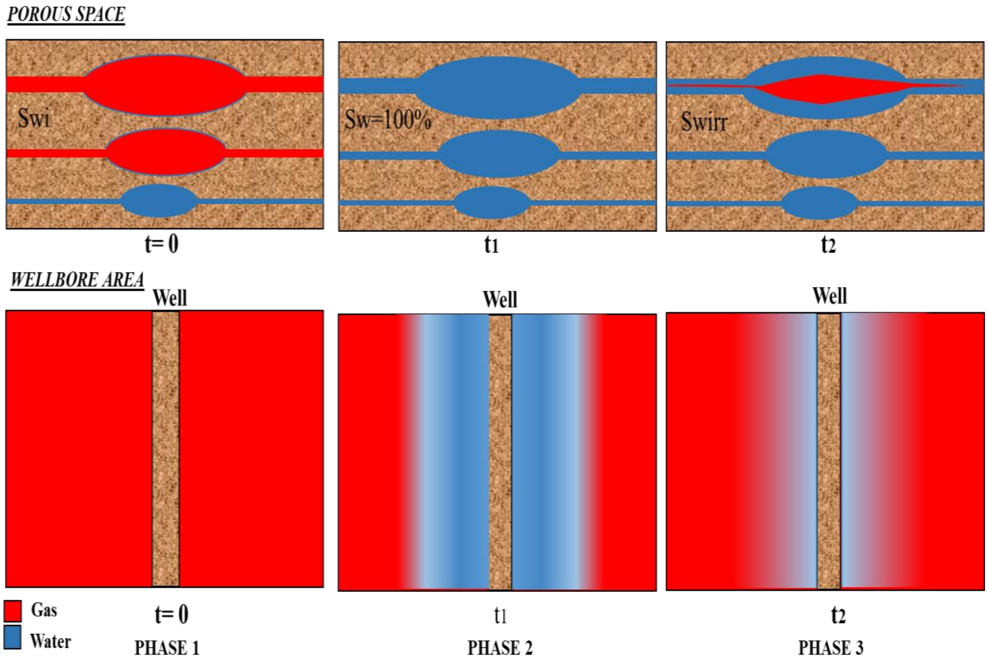


Figure 2.2. Water blockage stages in the porous system (modified from Bennion 1994).

Presented below are further insights into the process of water blockage and the responsible mechanisms, with a particular focus on the source of the water causing this issue.

2.3.1 Drilling or Completion Fluids. - Most fluids used in drilling and completion operations are water-based. Their direct application over the formation interval without casing affects gas production because of the direct contact with the interconnecting pores of the formation (Methven 1971). This rock-fluid interaction alters the original rock conditions and results in a drastic increase in water saturation in the pores of the rock due to the rapid spreading of water (Al-Anazi et al. 2005; Al-Anazi, Solares and Al-Faifi 2005; Bennion, Thomas and Bietz 1996). Utilising overbalanced drilling where the pressure exerted by the hydrostatic mud column (Ph) exceeds the bottom hole flowing pressure (BHP) tends to make the water blockage issue much more pronounced. The differential pressure (Ph *minus* BHP) created in the formation wall causes an opposite flow direction from the well into the formation. While drilling with underbalanced conditions (BHP > Ph) may be desirable in reducing the likelihood of water entrapment, this type of drilling condition is still prone to severe water blockage in low permeability formations due to the spontaneous imbibition effect caused by significant capillarity exerted by their small pore channels.

Water blockage tends to be even more pronounced during the drilling of horizontal wells. In such cases, the penetration rate is significantly reduced to avoid doglegs or trajectory deviations while maintaining underbalanced pressure conditions (e.g., dogleg, failure to reach the target). Therefore, the formation is exposed to water-based fluids for an uncontrolled and often significant duration of time. In addition, the low drawdown in horizontal wells impairs the ability to clean up the near wellbore region after drilling and clear the induced water blockage, which reduces the efficiency of horizontal well production. The increased severity of water blockage in horizontally drilled wells has been studied and reported by multiple researchers (Khansari 2009; Cimolai et al. 1993).

2.3.2. Hydraulic fracturing. – In most low-permeability reservoirs, a standard method of improving gas productivity is fracturing the formation to increase overall absolute permeability around the wellbore. The fracking fluid phase used during the hydraulic fracturing process is often a combination of proppant and water. The widespread application of water is due to its immediate availability, lower environmental impacts, no major health and safety implications and considerably low cost compared to other possible carrier fluids (Ma, Sobernheim and Garzon 2016). A large amount of water used in this technique remains in direct contact with the formation and covers the entire fracture surface for an extended time, similar to the underbalanced drilling of horizontal wells. The above combination of various factors makes the formation damage caused by water entrapment around the fracture faces highly pronounced (Wang and Zhou 2021). It is worth noting that the pore surface of sandstone rocks is often preferentially water-wetted in the presence of a gaseous phase so that the water phase does not encounter strong resistance or limitations to penetrate the smallest and largest pores of the formation, resulting in severe damage in formations with low permeability. (Holditch 1979).

2.3.3. Conification and crossflow. – Adequate data collection and analysis in the early stages of field development plays a key role in determining the source of water inflow and subsequent conification that can result in productivity impairment. The source of water inflow is generally the aquifers and approaches the production interval primarily through fractures, faults, or heterogeneous strata (Bennion et al. 1996a). In an open borehole system, water from the bottom layers may also flow through the borehole to reach the upper productive layers, resulting in a crossflow invasion and displacement of the gas phase as a result of capillary forces (Li, Ge and Zhang 2015; Li and Zhang 2011).

A common technique for directly removing water accumulation and crossflow problems is mechanical intervention (e.g., partial formation penetration, replacement of casing, packer installation) by isolating the water source when the problem is detected in the casing. Nevertheless, installing mechanical devices to remove the blockage is not feasible if the problem is related to the bulk of the reservoir.

2.4. Factors Affecting Water Blockage

Regardless of the source of water, the severity of water blockage around the wellbore largely depends on a number of critical properties of the fluid-rock system, including initial water saturation, surface wettability, absolute permeability, capillary pressure, and relative permeability functions. The following sub-sections of the chapter present an in-depth examination of how the above factors control water blockage and its underlying mechanisms.

2.4.1. Fluid Properties

In addressing the liquid blockage issue in a gas reservoir, adequate knowledge of the type of reservoir fluid plays a vital role in understanding and modelling the dynamic behaviour and interaction between the rock and fluid phases. In the context of gas reservoirs in general, the in-situ gas mixture may broadly be categorised as dry gas and gas condensate (McCain 1990; Fan 2006). When only the dry gas phase is present in the pore space of the reservoir, the primary concern regarding liquid blockage is water invasion in the vicinity of the wellbore. However, in the case of a gas condensate reservoir, in addition to water blockage, condensate banking can also lead to a notable reduction in gas mobility (Engineer 1985). The differentiation between these two phenomena is paramount, as each may require its own mitigation strategy. A detailed analysis of the phase behaviour of reservoir fluid can provide field operators with the necessary knowledge to characterise any future productivity impairment where the liquid blockage is believed to be the primary suspect.

The composition of the in-situ gas is the main characteristic distinguishing dry gas from wet gas or gas condensate. Lighter alkanes, such as methane and ethane, predominate in the dry gas composition. In contrast, other light-molecular alkane components (propane, butane, pentane, and hexane) may also be present in the mixture in small concentrations. In addition, nitrogen and carbon dioxide may also be present, while small amounts of $C7+$ (alkanes with higher molecular weight than heptane) could coexist under reservoir conditions to produce gas at the surface (McCain 1990; Archer and Wall 1986). In Figure 2.3, the quality curves show the two phases' overall concentrations below the dew point pressure line and within the two-phase region. In contrast, only the gas phase exists at temperatures exceeding the cricondentherm. Point P1 represents the initial reservoir pressure (beyond the cricondentherm line) when only a single gas phase is present in the reservoir. During production, the pressure drops to P2 due to pressure drawdown. Despite the pressure drop, the composition of the gas phase does not change abruptly and no liquid condensate can form in situ. As the gas mixture enters the wellbore and flows towards the surface, it will experience a reduction in pressure and temperature. Subsequently, depending on its composition, the gas mixture may undergo a phase change, and liquid hydrocarbon could form and drop out inside the production tubing (P3).

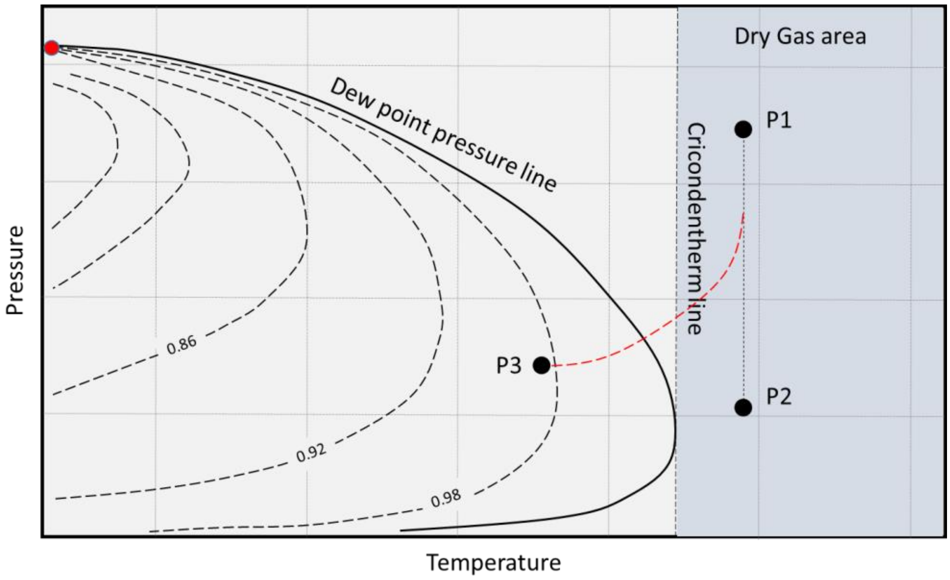


Figure 2.3. Pressure – Temperature diagram – Dry gas Reservoir (Modified from McCain 1990).

In the case of a gas condensate reservoir, the low molecular weight alkanes still predominate in the hydrocarbon mixture, however, compared with a dry gas mixture, there is an increase in the proportion of high molecular weight alkanes (McCain 1990; Archer and Wall 1986). In such reservoirs, the temperature is situated between the cricondentherm and the critical point value. The liquid phase dropout takes place in situ when the average reservoir pressure reaches the dewpoint (Thomas, Bennion and Andersen 2009). In the pressure-temperature diagram shown in Figure 2.4, the initial reservoir pressure is marked by P1, which is located above the dew point line (Pdp). As the reservoir depletes, the pressure approaches P2 within the two-phase region, and the condensate or liquid phase in the mixture grows (Figure 2.4). This behaviour alters various properties of the reservoir fluid, such as a sharp decrease in gas viscosity due to the dropout of the heavier components into the liquid mixture (Fan 2006). Localised condensate dropout can occur around the wellbore even when the reservoir pressure is above the dew point value due to significant pressure drawdown.

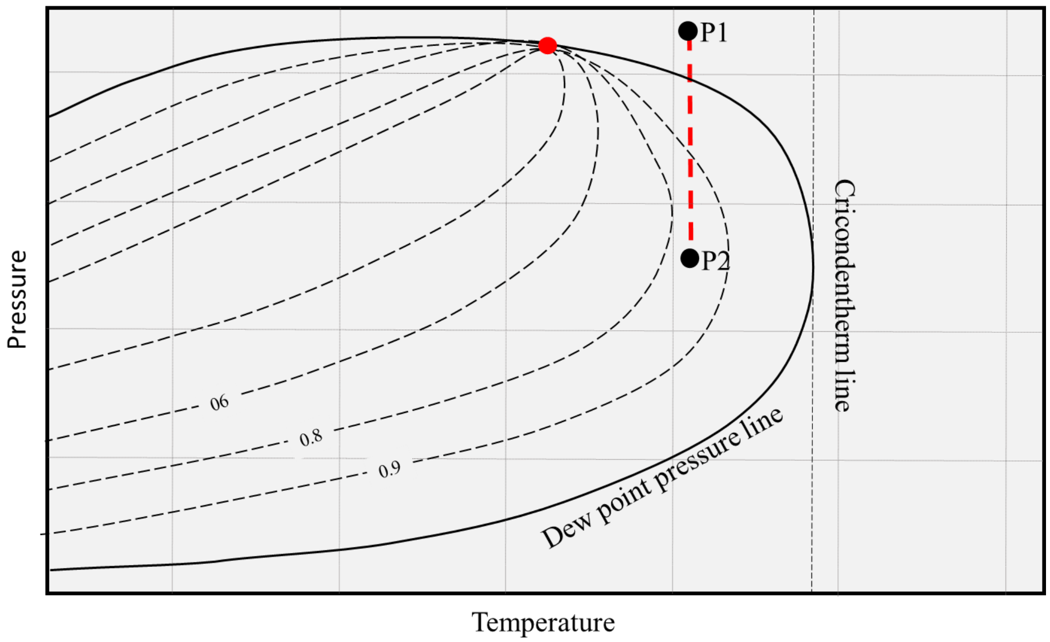


Figure 2.4. Normal Phase behavior in a Gas Condensate Reservoir Fluid (Modified from McCain 1990).

Liquid trapping becomes particularly pronounced in gas-condensate reservoirs when bottom hole pressure falls below the dew point pressure, and condensate phase saturation occurs around the wellbore (Al-Anazi, Solares and Al-Faifi 2005; Bang et al. 2009; Noh and Firoozabadi 2008b). This phenomenon is known to lower the relative permeability to the gas phase by more than 90% (Bang et al. 2009). The Cal Canal Field, for example, suffered from high saturation levels of connate water and excessively high-pressure drawdown. After ten months of production, the water volume increased due to the expansion of the connate water and the nearby water inflow. The bottom hole flowing pressure also reached the dewpoint value, creating a condensate phase built up around the wellbore, reducing the gas deliverability to a greater extent than the water blockage (Engineer 1985).

2.4.2. Rock Properties

The capacity and quality of a field to produce gas largely depend on its specific rock properties, which must be thoroughly analysed and understood to plan its production phase. In addition, the anticipated interactions between the reservoir rock and in-situ fluids require a detailed characterisation before attempting to address productivity issues such as liquid blockage. In the context of this research, the primary factors of concern include absolute and relative permeability, wettability and capillary pressure. In the next few sections, the above critical properties will be defined, and their importance and influence discussed in detail, emphasizing their control on the water blockage phenomenon as the primary subject matter of this research.

2.4.2.1. Absolute and relative permeability

When a porous medium is 100% saturated with a single fluid, the particular property of the medium that characterises fluid movement in its pores is the absolute permeability. Through experimental work, Darcy investigated the fluid flow in the porous media (Darcy 1856), developing an empirical correlation between various parameters of the system, with absolute permeability being a medium-specific constant included in the correlation (Figure 2.5 and Equation 2.1). This relationship was developed with a number of constraints and assumptions. The main assumptions that limit the application of the Darcy equation are: a) the pore space must be 100% saturated with a single fluid, b) the fluid flow in the pore space is uniform and laminar, c) there must be no chemical interaction between the pore surface and the flowing fluid. Considering these assumptions, the Darcy equation, in its initial form, does not apply to multiphase flow systems.

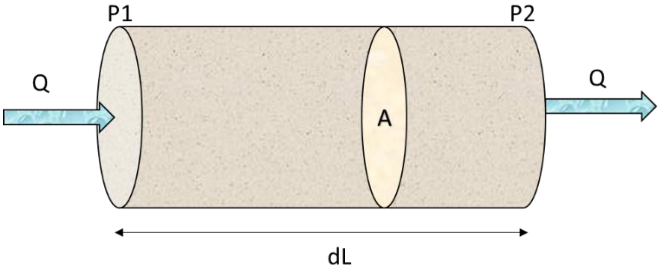


Figure 2.5. The Darcy Law experiment for one-phase linear flow.

$$Q = -\frac{k\ A\ \partial P}{\mu\ \ \partial L} \qquad \text{Equation 2.1}$$

Q = fluid flow rate [m^3/s]

k = absolute rock permeability (m^2)

A = cross-sectional area (m^2)

µ = fluid viscosity (Pa s)

dL = length of the rock sample (m)

dP = Differential pressure (P2 – P1) (Pa)

The absolute permeability of a rock is controlled by the pore network of the rock, which in turn is affected by the size, shape, distribution, and packing of its grains. Additionally, the degree of cementation and clay content also have a strong impact on the pore and pore throat sizes. Several example case studies demonstrating a link between the significance of the water blockage issue and the absolute permeability of the reservoir were briefly presented earlier (Figure 2.1). Such a link has strong roots in the relationship between permeability and capillary pressure characteristics of a rock. This important relationship and its impact on the water blockage issue will be discussed in further detail in subsequent sections of this chapter.

While absolute permeability is a critical rock property, it is often considered insufficient to characterise the dynamic behaviour of the system when more than one immiscible fluid coexist in the reservoir (e.g., water, gas, oil). In other words, the dynamic flow properties of a real hydrocarbon reservoir can only be characterised by the ability of its pore system to transmit a rather multiphase fluid system in its interconnected pores. Such an important technical necessity has led to the definition of effective and relative permeability.

After Darcy's pioneering work, the understanding of fluid flow in porous media advanced further by researchers who attempted to measure fluid conductivity of sandstone rocks using a two-phase flow system, specifically water and gas (Muskat et al. 1937). Empirical correlations, known as the "Laws of flow", were established from these experiments, which linked multiphase fluid velocities to differential pressure and fluid viscosities. These correlations ultimately led to the development of an equation characterising multiphase flow under conditions representative of subsurface hydrocarbon reservoirs. Subsequently, the concept of effective permeability emerged, referring to the ability of an interconnected pore system to transmit fluids when other fluids coexisted. With the replacement of ‘absolute’ permeability with its ‘effective’ counterpart, the amended Darcy Equation (Equation 2.2) was capable of modelling fluid flow in real hydrocarbon reservoirs.

$$Q_f = -\frac{k_f\ A\ (P_1 - P_2)}{\mu_f \quad \partial L} \qquad \text{(Equation 2.2)}$$

In the equation 2.2 the subscript “f” refers to the fluid phase (oil, water or gas).

Relative permeability is the ratio of the effective permeability of a given fluid to the absolute permeability of the system (Equation 2.3). The relative permeability of a given fluid depends on the wettability state, capillary pressure characteristics, saturation level and pore structure of the rock as well as the specific interactions taking place between fluids and the rock surface. Figure 2.6 shows the relative permeability curves for a two-phase flow system, where the water is the wetting phase and gas is the non-wetting phase. In the graph, the endpoints of the relative permeability for the non-wetting phase (k_{rg}’) and the wetting phase (k_{rw}’) represent the maximum mobility value of one phase at the lowest saturation of the other coexisting phase. The shape of the relative permeability curves also indicates the pore heterogeneity of the reservoir and the level of interference between the fluids when flowing through the pore network of the rock simultaneously. It is also worth noting that when two fluids (e.g., gas and water) coexist in the same porous medium, the sum of the relative permeabilities of the two fluids cannot exceed "1".

$$kr_w = \frac{k_w}{k_{abs}} \quad ; \quad kr_g = \frac{k_g}{k_{abs}} \quad ; \; kr_o = \frac{k_o}{k_{abs}} \qquad \text{(Equation 2.3)}$$

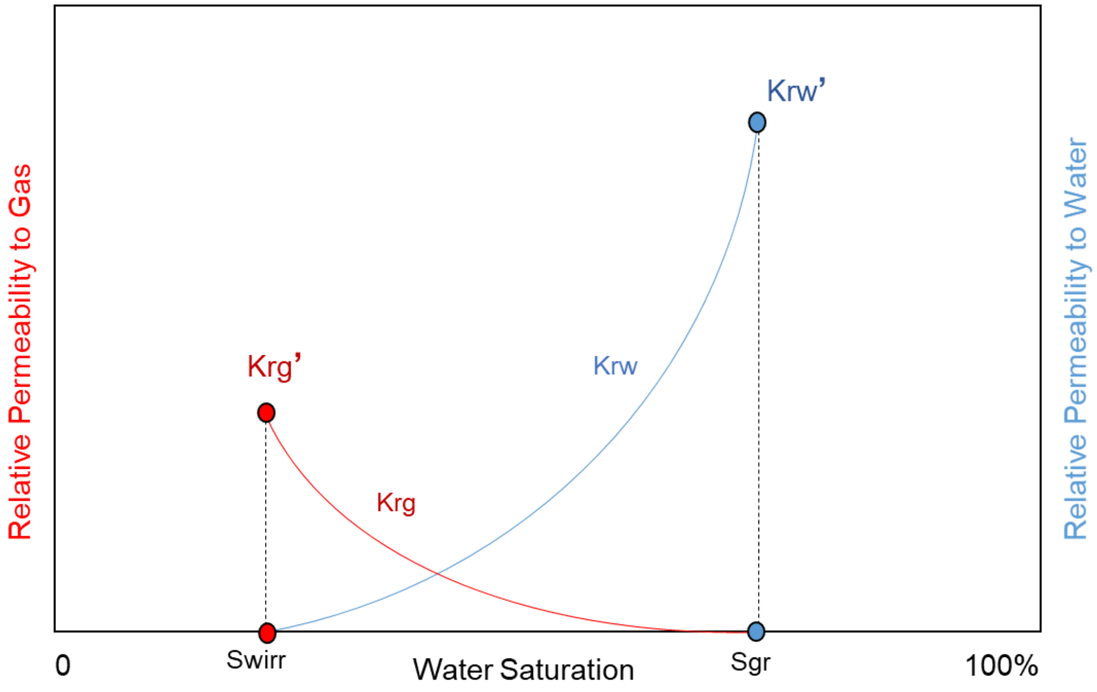


Figure 2.6. A set of typical relative permeability curves for a gas-water system with water being the wetting phase.

2.4.2.2. Wettability

In a multiphase flow system, wettability is a primary attribute that affects fluid distribution and saturation level, relative permeability characteristics, and capillary pressure by influencing the interaction between fluids and pore surfaces (Anderson 1986; Morrow 1990).

Wettability is a measure of attraction between a fluid and a solid surface in the presence of another immiscible fluid, with the wetting phase being the one most attracted to the surface (Ahmed 2019). In a gas-liquid-rock system, for example, the wetting strength of the rock may range from strongly liquid-wet to strongly gas-wet. The strong liquid-wet condition is generally exhibited by the ability of the liquid phase (e.g., water, oil, condensate) to penetrate a wide range of pore size distributions (from very small to large), with the gas phase being capable of the same in a gas-wet system. In general, the "gas-wet" and "strongly gas-wet" conditions are highly rare. Achieving such conditions is also challenging because it is difficult for the gas phase to displace a denser liquid phase and replace it as the preferred phase attracted to the rock surface. It is worth noting that there are wettability states other than strong wetting, referred to as intermediate or neutral, where for example in a gas-liquid-rock system, the pore surfaces have a tendency to be wetted by both gas and liquid phases simultaneously (Anderson 1986; Guancheng 2018). Some heterogeneous reservoirs may also be characterised by the fractional wettability state, where rock minerals can influence and alter the tendency of the pore surfaces to interact with a particular fluid phase in the same rock. For example, part of a pore space may be water-wet, while the remaining portion may be oil-wet, depending on the mineral composition of the surfaces. When evaluating the wettability state of a rock, the wetting phase should not be confused with the fluid phase that may be initially saturating the pores of the rock. For example, having a rock formation fully saturated with water initially does not necessarily mean water is the wetting-phase.

Any attempt to understand the wettability characteristics of a solid in the presence of a multiphase fluid system needs to take into account the interactions between all elements of the fluids-rock system. When a fluid reaches the pores, a molecular interaction occurs in the solid-fluid interface called the total free energy or surface tension (Arsalan, Buiting and Nguyen 2015; Fowkes 1964). Fowkes introduced the term surface tension, which refers to the interaction between gas-solid or liquid-solid, as opposed to interfacial tension, which refers to the interaction between two fluids. The term surface tension depends on the dispersion force of a liquid – London attraction (γ^d) and polar forces (γ^p), which mainly rely on the interaction between polar effects and other bonding effects (Equation 2.4, Equation 2.5) (Park and Seo 2011; Fowkes 1964). The molecular interaction at the rock surface is comparable to the interfacial tension that occurs during a liquid-liquid interaction.

$$\gamma_S = \gamma_S^d + \gamma_S^p \qquad \text{(Equation 2.4)}$$

$$\gamma_L = \gamma_L^d + \gamma_L^p \qquad \text{(Equation 2.5)}$$

The concept of wettability plays a fundamental role in understanding the multiphase flow characteristics of a reservoir. It represents an intrinsic property of the reservoir that does not require a mathematical equation to determine its value. Young first observed a relationship that allowed for a more qualitative assessment of wettability when a solid surface interacts with a liquid droplet on a substrate, with air acting as the bulk phase (Young 1805). This interaction involves three surface tensions that coexist in mechanical equilibrium among the two fluids (air-liquid-solid surface).

Figure 2.7 depicts the interaction of the rock surface with liquid and gas as an example two-phase fluid system. The symbols γ represent the surface tension, while the subscripts S, L, and G denote the corresponding phases (solid, liquid, or gas, respectively) (Equation 2.6) (Zisman 1964).

$$\gamma_{S-G} - \gamma_{S-L} = \gamma_{L-G} \cos\theta \qquad \text{(Equation 2.6)}$$

γ_{S-G} = Surface free energy of the gas phase.

γ_{S-L} = Surface free energy of the solid surface.

γ_{L-G} = Surface tension liquid-gas.

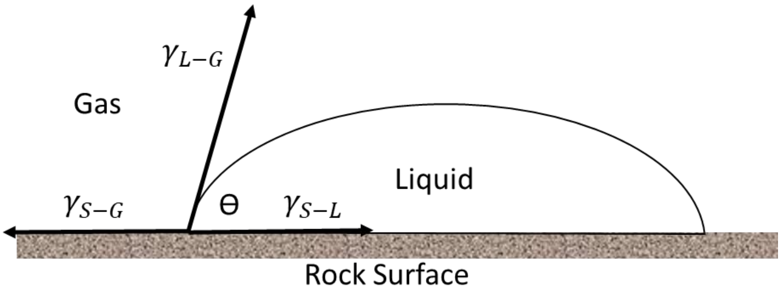


Figure 2.7. Rock surface interactions with multiphase fluids.

Taking into account the earlier discussed concepts relating to the particular interactions between a solid surface and a multiphase fluid system, the contact angle (θ) has been recognised as a simple but effective parameter in evaluating the wettability state of the solid (Figure 2.8). When the contact angle is less than 90 degrees, the liquid is considered as the wetting phase, resulting in a liquid-wet system and, if water is the liquid phase, exhibiting hydrophilic characteristics. If the contact angle is greater than 90 degrees, the gas phase is regarded as the wetting phase, resulting in a gas-wet system and, if water is the liquid phase, showing hydrophobic properties. Finally, if the contact angle is about 90 degrees, the two fluids tend to wet the rock surface to the same extent, a state referred to as intermediate or neutral-wetting.

The wettability character of a fluid-rock system can be used to broadly divide the fluid-fluid displacements that take place in the pore space of the rock into the two categories of imbibition and drainage. During an imbibition displacement, the wetting phase would displace the non-wetting phase leading to an increase in its saturation. The opposite would take place during a drainage flood causing an increase in the non-wetting phase saturation.

To summarise, wettability is a critical characteristic of a subsurface fluid-rock system controlling its multiphase flow properties. It controls how fluids may position themselves relative to the surface of the rock under both static and dynamic conditions. Wettability also has primary control over the capillary pressure and relative permeability characteristics of the system. Therefore, the wettability state of the system has a profound impact on the severity of the earlier discussed water blockage. In fact, wettability alteration is considered an effective mitigation technique for liquid blockage around the wellbore. The subsequent sections of this chapter will elaborate on the above in much greater depth.

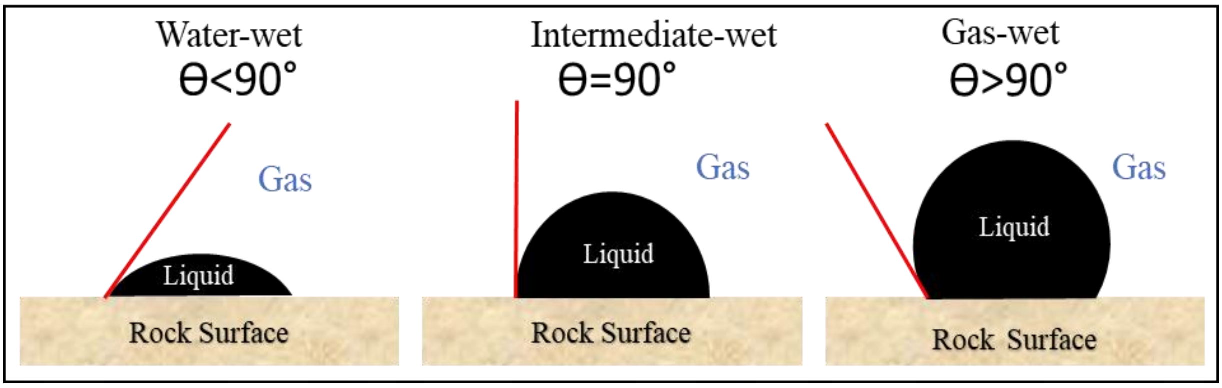


Figure 2.8. Rock surface interactions – Contact Angle (Modified from (Zisman 1964; Anderson 1986)).

2.4.2.3. Initial water saturation

With reference to the diagram presented in Figure 2.2 outlining the three stages involved in the formation of water blockage, in the initial stage, the entire reservoir (including the wellbore region) is saturated with water (wetting phase) and gas (non-wetting phase) with this initial water saturation only accounting for water present in smaller pores and thin film covering the surfaces of large pores. Water saturation would then dramatically increase as external water enters the wellbore area during the second stage. Once production commences during the third stage, the water phase is partially removed by gas displacement until a residual value is reached. The significance of a water blockage issue resulting from the events taking place during the second and third stages strongly depends on the initial water saturation and how different it is from that achieved at the end of the third stage. Various research work and field data indicate that the new water saturation is often significantly higher than the initial water saturation. As evident from the relative permeability curves presented in Figure 2.6, with an increase in water saturation, the mobility (i.e. relative permeability) of the gas phase would reduce, hence the pronounced water blockage issue encountered in numerous gas reservoirs. This important point is visually depicted in Figure 2.9 below, which shows how water blockage may significantly reduce the mobility of the gas phase by reducing its relative permeability (from Point 1 to Point 3) due to the drilling fluid invasion (Bennion et al. 1994).

Bennion et al. (1996) hypothesised that the reduction in water saturation in the formation could result from changes in pore geometry due to the diagenetic process and subsequent lithification. The increase in overburden pressure leads to greater rock compaction, causing grains to rearrange and change shapes and sizes. This phenomenon can reduce the quality of the reservoir by decreasing porosity and permeability and significantly degrade previously favourable flow conditions.

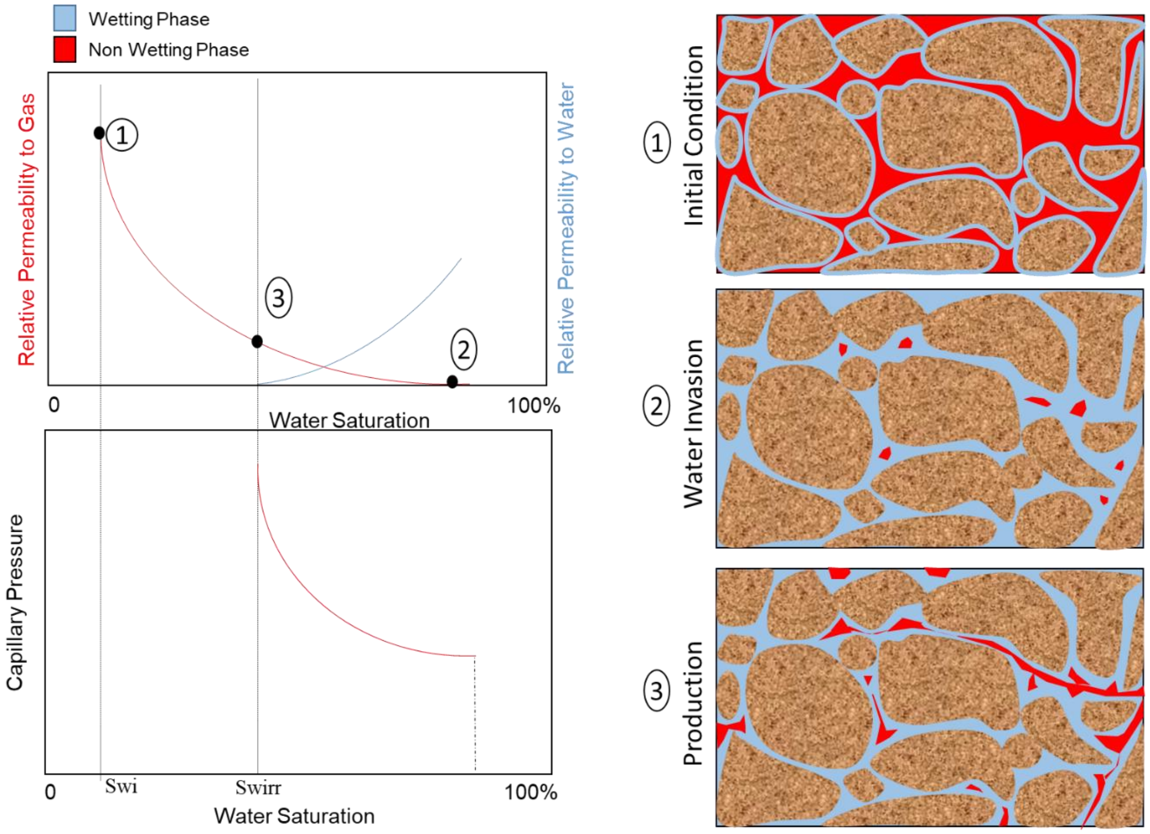


Figure 2.9. Relative permeability (above) and the capillary pressure (below) curves during water blockage (Modified from Bennion, 1994).

2.4.2.4. Capillary Pressure

Capillary pressure refers to the differential pressure between the two immiscible fluids, the non-wetting and the wetting phases, in a narrow capillary tube (Equation 2.7). The process involves the interaction between two immiscible fluids whereby the denser liquid moves within the walls of the capillary tube (Figure 2.10) until it reaches a particular height, creating a fluid meniscus with a concave, straight or convex shape at the interface of the two fluids (Chesworth et al. 2008; Gerhard and Kueper 2003). The shape of this interface, characterised by the radius of curvature (Rc), depends on the rock surface's wettability, fluid saturation, pore geometry, and mineralogy. To describe this relationship, Young-Laplace proposed a mathematical expression that incorporated the geometric relationship between the radii of curvature (Rc) and the capillary tube (r) (Tiab and Donaldson 2016). The final result was a straightforward representation of the capillary strength in the system (Equation 2.8).

$$P_c = P_{non-wetting} - P_{wetting} \quad \text{(Equation 2.7)}$$

$$P_c = \frac{2\gamma \cos\theta}{r} \qquad \text{(Equation 2.8)}$$

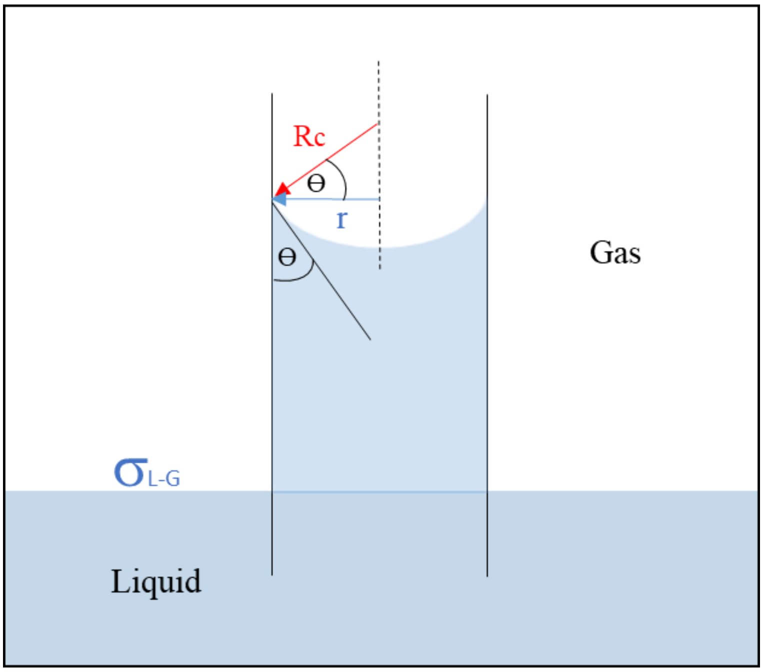


Figure 2.10. Capillary Rise System.

In the Young-Laplace equation indicates that the capillary force in the porous space is directly proportional to the interfacial tension, which refers to an interface formed between two liquids where the total molecules of liquid 1 (L1) attract the molecules that are in the interfacial zone of liquid 1. The L2 dispersion forces in a reduced geometric mean attract the same molecules of the interface (Figure 2.11). Consequently, the interfacial tension between liquid L1 and liquid L2 is the sum of the surface tension of each liquid and the subtraction of the L1 and L2 dispersion forces (Equation 2.9) (Fowkes 1964).

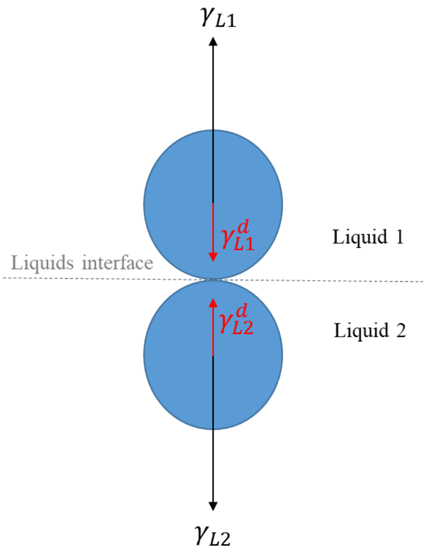


Figure 2.11. Interfacial Tension – Two fluids interaction (Modified from Fowkes,1964).

$$\gamma_{L1L2} = \gamma_{L1} + \gamma_{L2} - 2\sqrt{\gamma_{L1}\gamma_{L2}} \qquad \text{(Equation 2.9)}$$

The Young-Laplace equation also signifies the fact that capillary pressure is inversely proportional to the radius of the pore channels (pore throats) in a rock formation. As mentioned earlier, it is widely known that lower permeability rocks have narrower pore channels/throats and therefore present a stronger capillary pressure. A dimensionless function proposed by Leverett characterises the reservoir heterogeneity by relating porosity and absolute permeability to the capillary pressure function (Equation 2.10) (Leverett 1941). This relationship clearly signifies that capillary pressure is inversely proportional to absolute permeability. It is also shown in Figure 2.12 how capillary curves may differ for a range of permeability values from values as low as 0.01 md to as high as 1000 mD. As evident from the figure, when reservoir permeability decreases, the capillary curve shifts to the right and up, increasing the irreducible water saturation and the capillary entry pressure (Pe). Additionally, the shape of the capillary curve becomes more flat and less convex with an increase in the permeability (Bennion, Thomas and Ma 2000a). The above-presented discussion can be used to explain why when the absolute permeability is low, the non-wetting phase may not be effective in displacing the wetting phase reducing its saturation much even when the pressure drawdown is drastically increased, an issue not much less pronounced when the absolute permeability is high.

$$J\ (S_w) = \frac{P_c(S_w)\sqrt{k/\emptyset}}{\gamma\ cos\theta} \qquad \text{(Equation 2.10)}$$

Finally, the Young-Laplace equation clearly describes the dependence of capillary force on the wettability state of the rock. For example, a strongly water-wet rock presents significantly higher capillary pressure towards retaining the water phase in its pores against the gas flow by exhibiting a larger contact angle. In other words, due to the rock wettability condition, the non-wetting gas phase cannot surpass the wetting water phase in a gas-liquid-rock system, for example, when water blockage occurs.

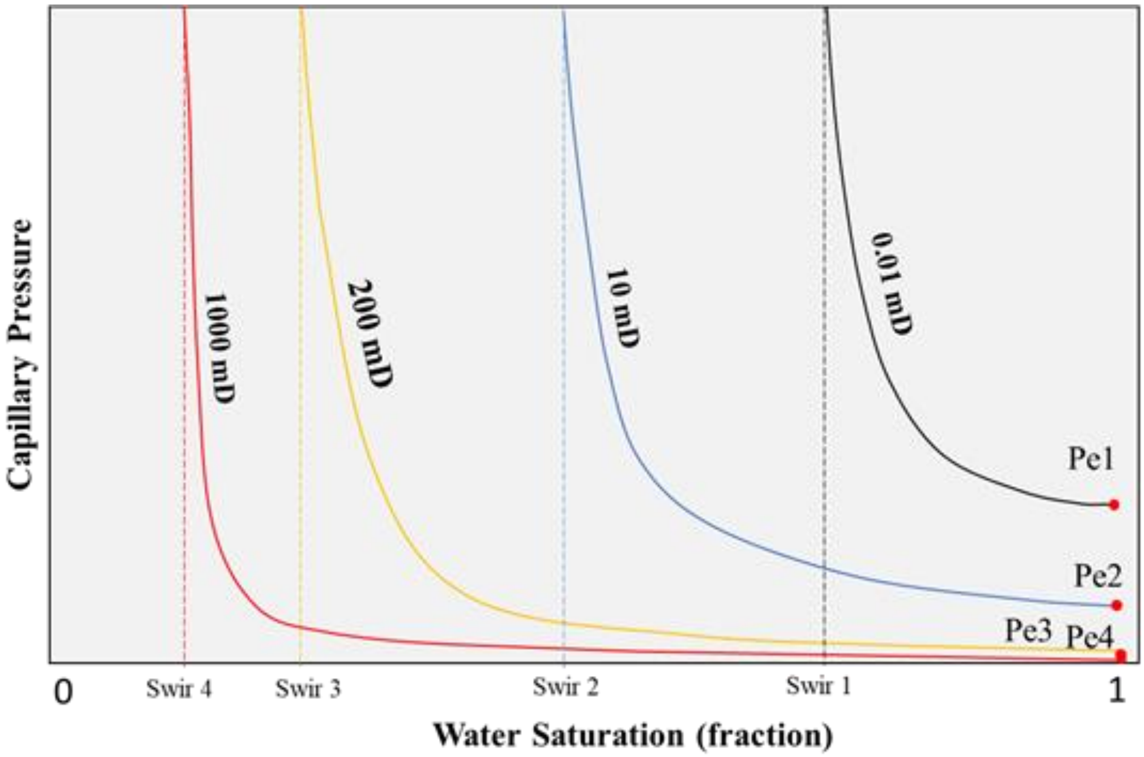


Figure 2.12. Capillary pressure vs. water saturation in water-wet rocks (Modified from Bennion,2000).

With the presence of the gas phase, the wettability of most of the gas reservoirs can be characterised as strongly water-wet, while neither the intermediate-wet nor the gas-wet condition is frequently observed. Therefore, the rock surface preferentially attracts the wetting water phase under reservoir conditions in any imbibition or drainage process. As a result, the capillary entry pressure (Pe) required to displace the wetting phase is appreciable and tends to be considerably high in moderate to low permeability rocks in particular (Figure 2.12).

2.5. Water Blockage Remediation

Numerous mechanical, chemical and operational techniques have been proposed to remediate water blockage whose detailed descriptions can be found in various published literature. Such techniques often help to remove/reduce water blockage by manipulating the earlier discussed attributes of the fluid-rock system as major factors, directly or indirectly, controlling water blockage. Unfortunately, such techniques have their own major drawbacks, from being temporary solutions to posing major risks to the environment or being uneconomic.

Companies frequently aim to employ routine practices for addressing wellbore damage or blockage, intending to avoid interventions that could lead to additional costs and non-productive downtime. As a result, a commonly used approach for tackling water blockage is incrementing the pressure drawdown. If this approach is found ineffective, other more involved techniques such as gas injection and hydraulic fracturing may be implemented. In more complex cases, techniques that modify rock and fluid properties could also be employed.

The current section of this chapter is to present a detailed overview of the techniques presented in the literature and discuss their particular advantages and disadvantages.

2.5.1. Operational Techniques

2.5.1.1. Pressure drawdown – After the water invasion during the drilling operation, the well begins to produce due to a pressure differential around the wellbore; the produced gas removes part of the water blockage in the pore system, by partially reducing water saturation in the wellbore region. This reduction is usually minimal in low permeability reservoirs under normal operating conditions (Parekh and Sharma 2004). Often an extremely high-differential pressure is required to reduce the water saturation to levels close to the initial water saturation. Thus, the differential pressure is increased by reducing the bottom hole flowing pressure, generating a drastic growth in the flow rate to reduce the residual water that remains in the pores and, in turn, upturn the relative permeability to gas. When performing this procedure, many aspects must be considered and paid attention to. For example, there must be an optimal assembly of the completion string and equipment, considering the production at high flow rates and drastic pressure variation, generating additional expenses. As seen in Figure 2.12, the lower the absolute permeability, the higher the capillary forces and imposing a drawdown increment may only lead to minimal variations in the water saturation (Bennion et al. 1996a). Holditch (1979) indicated that the effect of the water blockage may be effectively addressed if the pressure drawdown is much higher than the capillary pressure end effect (Holditch 1979). On the contrary, in low permeability reservoirs, the control of capillary strength on water blockage is much higher than the pressure drawdown (Settari et al. 1996). Therefore, while this approach is very desirable in most highly permeable gas reservoirs, its application in intermediate to low permeability gas reservoirs may be limited.

2.5.1.2. Gas Injection – this technique is primarily related to injecting a dehydrated gas such as CO_2 or tanked liquid nitrogen to reduce water blockage. This technique has been reported to increase gas production by around 20% by reducing water saturation (Eikeland and Hansen 2007). Before implementing this strategy, identifying the source of water that invades the wellbore region is critical. If the water is introduced by an active aquifer, the gas injection approach may be found obsolete due to the high capacity of the water source and the anticipated repetitive nature of the water blockage issue (Eikeland and Hansen 2007). The degree of heterogeneity of the rock formation is also an important factor in dictating the effective of this remediation technique. In heterogeneous formations or faulted reservoir systems, low fault transmissibility, or vertical/lateral discontinuity in the formation may partially or fully isolate the wellbore from the aquifer leading to better and longer lasting outcomes.

2.5.2. Well Stimulation Techniques

2.5.2.1. Hydraulic Fracturing – This technique involves hydraulic fracturing or acid fracturing to increase the absolute permeability around the wellbore and, consequently, reduce the capillary strength responsible for water blockage (Bang et al. 2008; Bennion, Thomas and Ma 2000a). Extending the length of the fracture until the trapped fluid area is surpassed could remove the trapped fluid with the drawdown generated during gas production.

While hydraulic fracturing can result in desirable outcomes but can introduce its own productivity issues. The fracking process involves the use of a water-based fluid mixture composed of additives and proppant agents. After fracking, this fluid may accumulate in the formation next to the surface of the fracture requiring a proper cleaning practice to avoid negative impacts on gas productivity. Doing so involves is costly and may offer a temporary solution, considering that during the clean-up of the formation, the pressure drawdown cannot entirely remove the trapped water (Montgomery and Berthelot 1990). In addition, possible damage around the fracture due to clay swelling or other reactions between the rock and fracking fluid can add to the complexity of the situation at hand (Holditch 1979; Montgomery and Berthelot 1990; Sherman and Holditch 1991)

2.5.2.2. Interfacial Tension Modifiers – To mitigate water blockage near the wellbore, water-miscible solvents (e.g., methanol, ethanol, isopropanol) or a combination of water-alcohol or solvent-gas can also be injected into the area around the wellbore. The application of these techniques may successfully reduce the interfacial tension of the aqueous phase by dilution, lower the capillary strength of the system resulting in the removal of the liquid phase and thus reducing the water blockage (Du et al. 2000; Jamaluddin et al. 2001; Al-Anazi et al. 2003; Alzate et al. 2006). Once the water interfacial tension reduction is achieved, the differential pressure between the non-wetting and the wetting phase decreases, resulting in liquid removal by evaporation due to alcohol. In 1947, Youster pioneered alcohol treatment in gas reservoirs, where the use of alcohol reached positive results for water vaporization. Later in 1965, Eakin proposed using a combination of alcohol and surfactant to remove the presence of water and possible oil in the formation. In another research work, the application of alcohol was successful. However, the application of surfactants faced substantial limitations due to their low effectiveness under dynamic conditions and the poor formation penetration caused by their high molecular weight (McLeod, McGinty and Smith 1966).

The main advantage of this remediation technique lies in its straightforward application at the field scale with low-cost solvent injection over a short period with immediate productivity improvements (Eakin, Miller and Eckard 1965). Unfortunately, these techniques are short-term remedies that require recurrent well shutdowns for further application when the liquid blockage problem occurs periodically.

2.5.3. Wettability Alteration by the Use of Polymers

A polymer comprises a group of monomers with either hydrophobic or hydrophilic characteristics. They are water-soluble when they possess hydrophilic groups in their structure, while others can dissolve only in organic solvents. Conformational entropy increases when a polymer is diluted in a solvent, which means the freedom of movement of the monomer segments that conform to the polymer structure. When using polymers to alter the wettability of rock surface, a high-quality solvent is needed to overcome the critical absorption energy in the solution-surface interaction and ensure chemical durability over the rock surface (Torn 2000). Therefore, a rigorous chemical screening (polymer and solvent) process is essential towards achieving optimal outcomes.

Polymers could be retained in the porous space by adsorption, mechanical entrapment, and hydrodynamic retention (Al-Hajri et al. 2018). During the wettability alteration process in a gas-water system by chemical treatment, the adsorption process involves polymer molecular interaction with the rock surface; in this process, the polymer segment- substrate interaction is higher than the solvent-substrata interaction, ensuring a durable covalent bond. Moreover, in terms of durability, physical and chemical forces will act over the rock surface, providing long-term polymer segment-rock bonding.

Important factors affecting the effectiveness of polymers are their molecular weight, chemical concentration, rock surface charge, and formation lithology. In terms of solubility, polymers are less soluble when their molecular weight increases. Also, increasing their concentration can cause pore throat obstruction due to excessive amounts of chemicals in the pore system. The typical sedimentary rocks where the hydrocarbon accumulates are carbonate and sandstone. Quartz, as the main constituent of sandstone rocks, is negatively charged at neutral pH, and carbonates comprise positively charged calcite. It is commonly known that quartz surface absorbs organic bases while carbonates organic acids. Also, anionic or non-anionic compounds create a bond with calcite, while cationic tend to bond with silica (Chiappa et al. 1999; Azam et al. 2013). Due to the high surface area and negative charge, an increment in the clay volume increases the adsorption of cationic polymers, while it has an adverse effect on anionic polymers (Figure 2.13) (Chiappa et al. 1999).

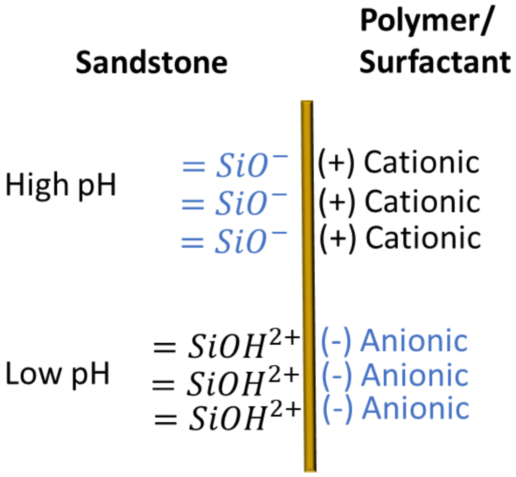


Figure 2.13. The rock surface – polymer interaction.

2.5.3.1. Fluorinated Polymerization Treatment – As indicated above, altering the rock wettability in the near-wellbore region is a longer-term solution as achieved by treating reservoir rocks with chemicals that have an affinity to the surface, thus changing their characteristics (Ahmadi et al. 2010). Evaluating the surface free energy of a substrate and the contact angle measurement provide initial indicators of the degree of wettability alteration. In contrast, the more complex and time-consuming displacement tests could provide detailed insights into the durability of the treatment under representative dynamic conditions.

The efficacy of reducing the surface free energy of the rock has been experimentally tested by researchers, obtaining values lower than 20 mN/m when testing the rock surface with polar and non-polar liquids (water and decane) (Esmaeilzadeh, Taghi Sadeghi and Bahramian 2018; Fahimpour and Jamiolahmady 2014; Fahimpour, Jamiolahmady and Sohrabi 2012; Sharifzadeh et al. 2015). Researchers studied the rock surface's wettability alteration by fluorinated compounds that increased the contact angle from 0° to more than 90° in sandstone rock samples, providing an abrupt shift of wettability towards intermediate-wet from a strongly water-wet case (Li and Firoozabadi 2000; Tang and Firoozabadi 2002; Fahes and Firoozabadi 2005). In later studies, various fluorocarbon polymers have improved the thermal and chemical stability of treatment at reservoir conditions, reaching intermediate to gas-wet conditions (Li et al. 2011; Wang et al. 2013; Zhang et al. 2014; Wang et al. 2015). A particular case is the use of perfluoroalkyl alkyl chemicals that can decrease rock's surface free energy while increasing the contact angle from 0° to almost 140°. The hydrolysis-condensation process that involves the application of the chemical solution composed primarily of perfluorinated alkyl silane can improve the durability of the chemical adsorption while maintaining the gas-wet condition (Erfani Gahrooei and Ghazanfari 2017; Esmaeilzadeh et al. 2015; Fahes and Firoozabadi 2005; Fahimpour, Jamiolahmady and Sohrabi 2012; Karandish et al. 2015; Kumar, Pope and Sharma 2006; Saboori et al. 2017; Sharifzadeh et al. 2015; Tang and Firoozabadi 2002; Wang et al. 2013; Wu and Firoozabadi 2010a). A group of researchers reached superhydrophobicity over sandstone samples using fluorinated nano-components reaching water contact angle values of more than 150 (Franco-Aguirre et al. 2018; Jin et al. 2016; Mousavi, Hassanajili and Rahimpour 2013; Saboori et al. 2017).

In general, fluorinated components can create an ideal hydrophobic or superhydrophobic condition over the rock surface; nonetheless, most of the fluorochemicals represent an environmental concern. For instance, long-chain fluoro alkanes accumulate strong molecular carbon-fluorine bonds that are difficult to biodegrade (Winkens et al. 2017; Rice 2015; Park et al. 2013). Additionally, the complexity of the process associated with chemical synthesis increases the cost of their field application, making them unfeasible to use at large scale.

2.5.3.2. Non-Fluorinated Polymerization Treatment - Silylation is a non-fluorinated functionalisation technique that uses silanes to modify the free energy of a substrate's surface and decrease its hydrophilic condition. Silanes are the most well-known coupling agents used to ensure retention in a substrate. Their principal function is to support polymers to adhere to the rock's surface. The hydroxyl group could do it in most silane polymers. Some silanes used as coupling agents are APS-aminopropyltriethoxy silane, glycidoxy-propyl-methoxy silane (GPS), and 3-aminopropyl trimethoxy silane (APTMOS). The silylation technique could be classified into two categories based on the solvent or carrier fluid used during treatment. The first category corresponds to the conventional silylation technique that involves the application of liquids or vapour as a solvent. In contrast, the other category involves using a supercritical fluid (e.g. CO_2) as a carrier fluid to modify the surface properties of the material (Sanli and Erkey 2015).

Silane as a coupling agent could be applied over the rock surface with fluorinated or non-fluorinated chemicals to alter wettability from liquid-wet to gas-wet. For example, a low molecular weight FC-759 polymer in combination with the Si-OH moiety increases the bonding strength between sandstone and chalk surfaces (Tang and Firoozabadi 2003). The perfluorinated silane polymer enhanced the adsorption of the chemical in sandstone and carbonates due to the Si-O- Si chain attached to the rock surface after a sol-gel chemical synthesis process (Sharifzadeh, Hassanajili and Rahimpour 2012; Wu and Firoozabadi 2010b). The organosilanes, combined with a liquid solvent (alcohol, toluene, acetone), can be used to treat the rock surface by conventional silylation. The organosilane's main component is a methyl group with hydrophobic characteristics (e.g., Methyltrimethoxysilane) that can lower the surface free energy of the treated surface.

As evident from the above discussions, wettability alteration using chemical treatment of the near wellbore region is regarded as a promising technique in combating liquid/water blockage. This approach offers major advantages (e.g. longevity, less complex application, etc.) over other approaches presented and discussed earlier. However, the chemicals studied by various researchers so far suffer from a number of drawbacks including being expensive, pose a risk to the environment, cannot withstand high temperatures, or require complex synthesis procedures. The current PhD research has examined the use of the novel benzoxazine resin to treat sandstone rock surfaces and achieve a reasonable degree of wettability shift. This resin offers many advantages over other chemicals used for the same purpose. The remainder of this chapter is dedicate to providing essential insights into specific properties of this resin that make it a suitable candidate for sandstone surface treatment.

2.6. Novel Benzoxazine Resin

Benzoxazine resins were first synthesised in 1944, and their fundamental characteristics were understood during the 50s and 60s. However, the development of small oligomers, cross-linked and self-curable benzoxazine, was not completely developed until the 80s. In 1994, the unique properties of this resin were clearly described. Presented below are some of the essential properties of the benzoxazine resins as highlighted in the literature (Wang, Su, et al. 2006; Ishida 2011):

- Near-Zero Volume Changes – Experimentally, it has been determined that the monomers expand by less than 1% during the polymerization process due to molecular packing; this value tends to decrease with the increment of curing time at a constant curing temperature (Ishida and Low 1997).
- Low Water Absorption – Ishida observed that water absorption testing in benzoxazine monomers showed less than 1.9% water saturation in aniline-based benzoxazine; this value is lower in methylamine-based benzoxazine. The water absorption level would vary with the type of amine used in the benzoxazine synthesis process (Ishida and Allen 1996).
- High Thermal Resistance – The resin has very high-temperature tolerance. This characteristic depends on the phenol used during monomer synthesis, with the degradation process starting at around 260 °C. For example, Polybenzoxazine aniline-based (BA) starts degrading at 315 °C. (Ishida,2011)
- Very High Char Yield - The char yield indicates the flammability of a polymer, with those chemicals with a high char yield value considered flammable resistant. Benzoxazine

monomers (BA-m, BA-A, MP-tmos) have a high value of char yield. The BA-m and BA-a possess a char yield value between (35 – 75%) while the same for MP-tmos is 92% (Ishida 2011; Liu et al. 2013).

Low Surface Free Energy - When treating glass surfaces, researchers achieved low surface free energy values of less than 19 mN/m, lower than Teflon. Contact angle measurements of different polar (i.e. water) and non-polar liquids (i.e. diiodomethane and ethylene glycol) showed values higher than 100° (H.-C. Lin 2009; Liao et al. 2008).

The benzoxazine resin is a monomer primarily constituted of phenol, formaldehyde, and amine, as shown in Figure 2.14 (Ishida 2011). The benzoxazine molecule's principal characteristic is an oxazine ring with oxygen and nitrogen atoms in the structure. The most common monomer is the 1-3 Bezoxazine, where the prefix number indicates the oxygen and nitrogen position in the oxazine ring. Some examples of different benzoxazine names are provided in Table 2.1. The word dihydro is associated with ring-opening polymerization, which is significant in surface treatment. Each monomer name and abbreviation has been selected based on the phenol and amine components used during the chemical synthesis (Gogoi et al. 2014; Wang, Su, et al. 2006; Wang, Wang, et al. 2006). For example, if bisphenol A and methylamine are used during benzoxazine synthesis, their abbreviation is BA-m. After synthesis, the resulting chemical possesses a benzene and oxazine ring with radicals attached to the structure (Ishida 2011).

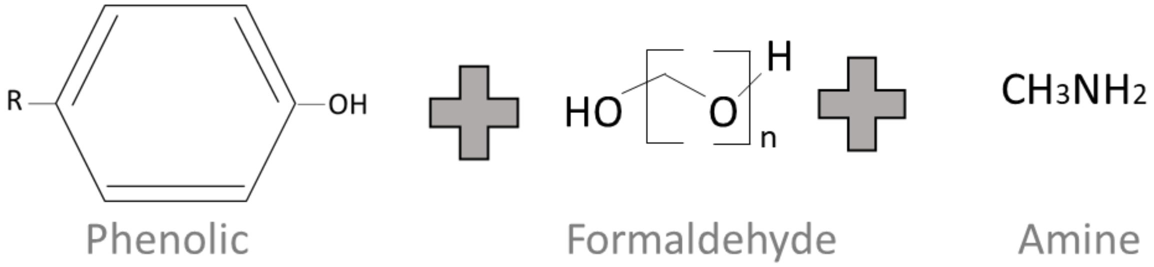


Figure 2.14. The principal components of benzoxazine monomer.

Table 2.1. Examples of Chemical names.

REFERENCE	CHEMICAL
(Wang, Su, et al. 2006)	2,2-bis(3-phenyl-3,4-dihydro-2H-1,3-benzoxazinyl propane **(BA-a)** 2-bis(3-methyl-3,4-dihydro-2H-1,3-benzoxazinyl)propane **(BA-m)**
(Gogoi et al. 2014)	2,2-bis(3-methyl-3,4-dihydro-2H-1,3-benzoxazinyl)propane **(Benz-b)**

	3-tert-butyl-3,4-dihydro-8-allyl-2H-1,3-benzoxazine **(Benz-m)**

2.6.1. Polymerization of benzoxazine resins

The benzoxazine monomer cannot reach low surface energies without undergoing thermally accelerated polymerization. When polymerization occurs, the oxazine ring in the monomer structure opens to act as a cationic initiator promoting the corresponding polymerization. It has been documented that intramolecular and intermolecular forces interact during polymerization (Figure 2.15). The former grows when the curing temperature increases, while the subsequent increases with time (Ishida 2011; Ishida and Allen 1996; Ishida and Low 1997). These forces directly influence lowering the surface free energy of the treated substrate.

The surface energy of the treated substrates will depend on the curing time and temperature. To elaborate on this statement, the surface free energy of separate substrates treated with two monomers (aniline and methylamine-based benzoxazine) is plotted in Figure 2.16 for different curing time and temperatures. In both cases, the surface free energy decreases when the curing temperature increases, reaching a constant value at 180 °C (Wang, Su, et al. 2006; Wang, Wang, et al. 2006). It can also be observed from this figure that the surface free energy is drastically affected when the temperature exceeds the limit. In other words, an extended curing time at high temperatures (higher than 180 °C) results in benzoxazine's thermal degradation.

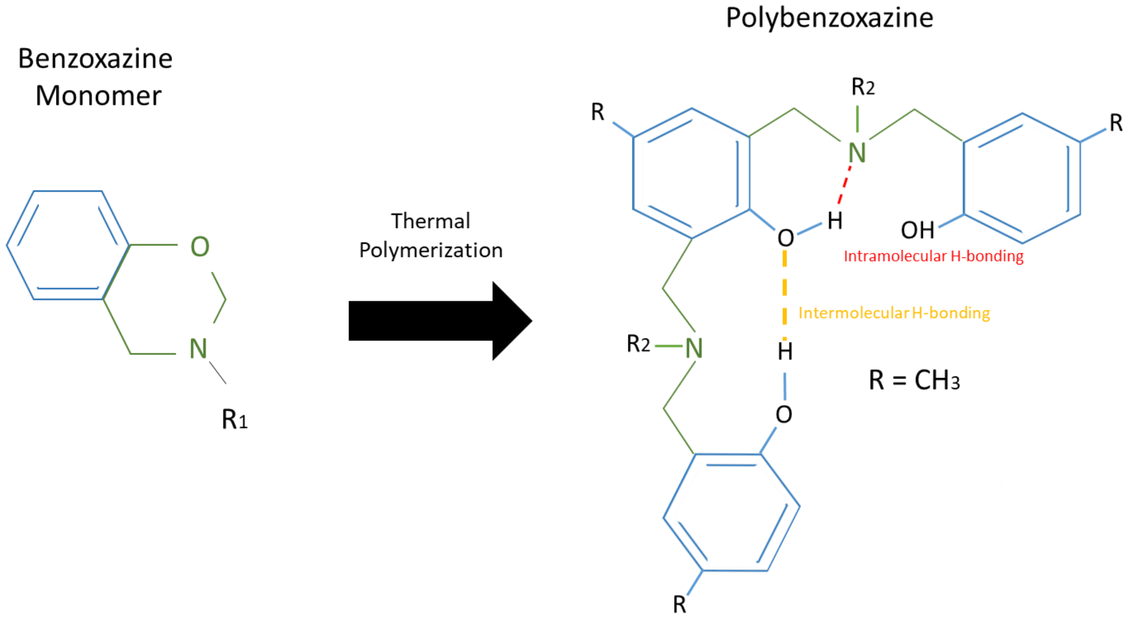


Figure 2.15. Intermolecular and intramolecular forces during thermal polymerization of benzoxazine monomer (modified from Ishida 1997).

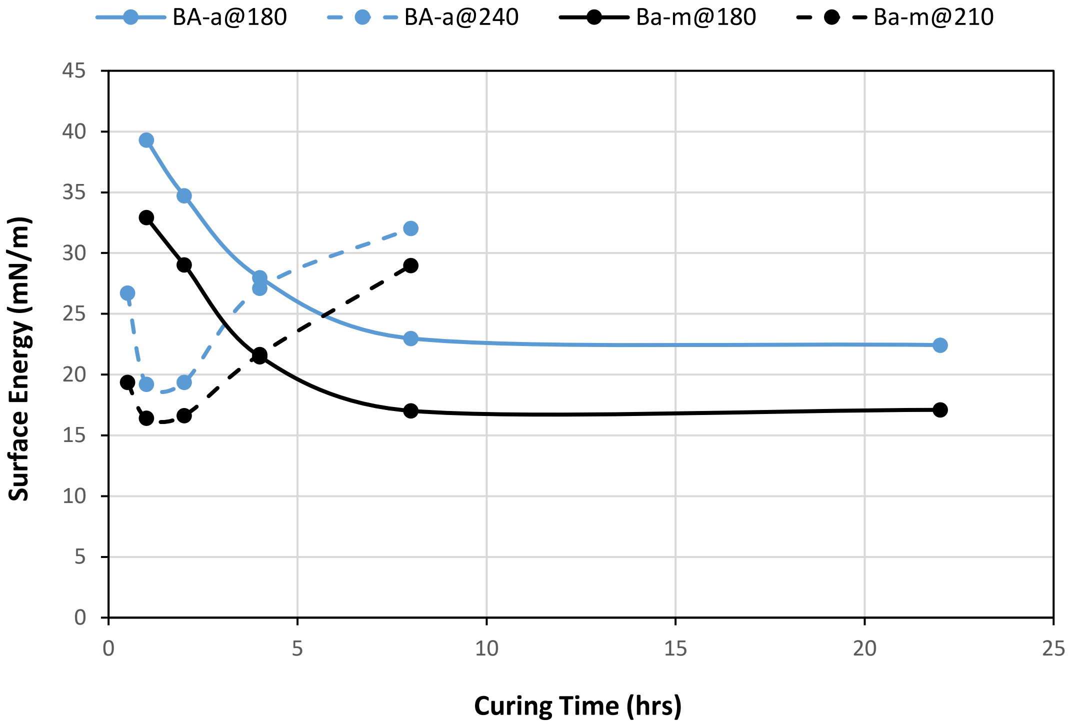


Figure 2.16. Surface Energy at different curing times and temperatures – aniline (BA-a) and methylamine-based (BA-m) benzoxazine (Modified from Wang, 2006).

2.6.2. Benzoxazine application in other research areas

Recent research work around the benzoxazine resin have unveiled a diverse range of applications across the materials industry, primarily due to its impressive thermoresistant properties. This resin has now been widely used in various manufacturing sectors, including adhesives, aerospace composites, coatings, and electronics (Tietze and Chaudhari 2011). Moreover, the resin has become an essential substance in making a diverse range materials, including cotton, polyester, glass, silica wafers, and paper, capable of repelling fluids by modify their surface characteristics (Gogoi et al. 2014; Liao et al. 2008; Liu et al. 2013; Tang, Hess and Breedveld 2015; Wang, Chang and Kuo 2011; Wang, Su, et al. 2006).

The most common benzoxazine monomers (BA-m and BA-a) could repeal polar and non-polar fluids such as water, ethylene glycol, and diiodomethane when spin-coating or immersing glass substrates in a benzoxazine solution. (Liu et al. 2006; Wang, Chang and Kuo 2011). BA-m and BA-a can reduce surface energy of glass substrates to 17 mN/m 22 mN/m, respectively, under a curing temperature of 180 °C and polymerization time ranging from 4 to 22 hours (Wang, Su, et al. 2006). Wang et al. attributed the above slight difference between these two monomers in lowering the surface energy to the amine component used during the resin monomer synthesis. Short-chain amines have been observed to increase intramolecular force interactions between the hydroxyl and nitrogen atoms in the oxazine ring (Wang, Chang and Kuo 2011; Wang, Su, et al. 2006; Liu et al. 2013; Qu and Xin 2011). To reach even lower surface energy values, Liu et al. used a combination of aniline-based benzoxazine and 3-aminopropyl trimetoxysilane (APTMOS) to decrease water repellency in glass slides. The final result suggested that the benzoxazine monomer (PTBP-tmos) could reach surface energy values as low as 15 mN/m (Liu et al. 2013). In their research analysis, Liu et al. also proposed a modified benzoxazine resin synthesis by incorporating coupling agents such as the APTMOS. Those coupling agents provided a more durable covalent bonding with a rock substrate (Park and Seo 2011; Sharifzadeh, Hassanajili and Rahimpour 2012; Liu et al. 2013). Figure 2.17 shows the rock surface functionalization through the silane moiety. The effect of the APTMOS and benzoxazine moiety after thermal polymerization will be evaluated by the methodology proposed in the following chapter.

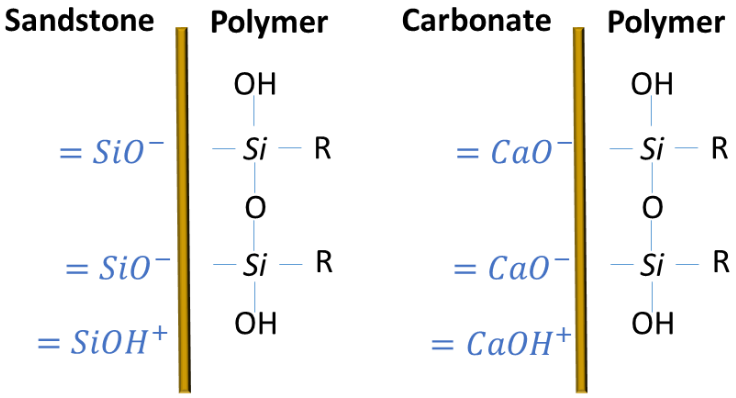
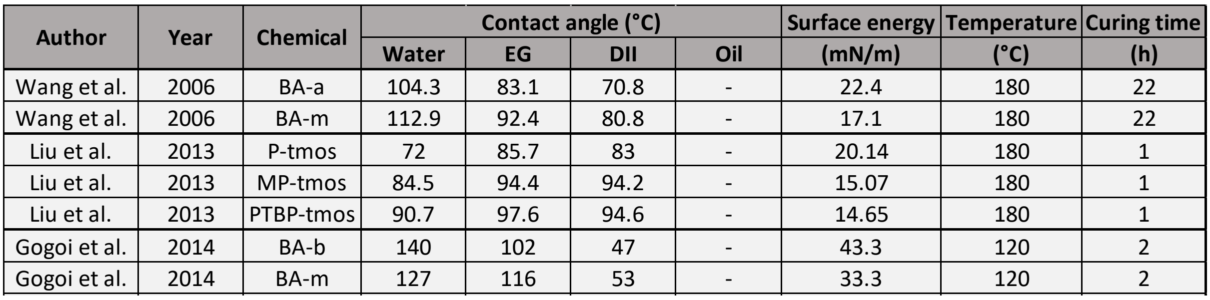


Figure 2.17. Sandstone and APTMOS moiety surface interaction (Modified from Park,2011and Liu,2013).

Table 2.2. Properties of different Benzoxazine resins.



Author	Year	Chemical	Contact angle (°C)				Surface energy	Temperature	Curing time
			Water	EG	DII	Oil	(mN/m)	(°C)	(h)
Wang et al.	2006	BA-a	104.3	83.1	70.8	-	22.4	180	22
Wang et al.	2006	BA-m	112.9	92.4	80.8	-	17.1	180	22
Liu et al.	2013	P-tmos	72	85.7	83	-	20.14	180	1
Liu et al.	2013	MP-tmos	84.5	94.4	94.2	-	15.07	180	1
Liu et al.	2013	PTBP-tmos	90.7	97.6	94.6	-	14.65	180	1
Gogoi et al.	2014	BA-b	140	102	47	-	43.3	120	2
Gogoi et al.	2014	BA-m	127	116	53	-	33.3	120	2

In this chapter, the concept of water blockage in gas producing wells, issues associated with this phenomenon, as well as the most common techniques to alleviate the water blockage were presented and discussed in detail. In doing so, the fundamental characteristics of multiphase flow impacting this important phenomenon (wettability, relative permeability, and capillarity) were also reviewed. At the end of the chapter, a background explanation of the particular characteristics of the novel non-fluorinated benzoxazine resin was presented. As briefly mentioned, this resin has been used in this PhD research to alter the wettability of sandstone rock samples. In achieving this important goal, the information included in the relevant literature about the application of this resin in other industries has been used as a guide.

The primary purpose of presenting the above information and discussions in this chapter was to provide an introduction to the upcoming chapters that will include detailed descriptions of the laboratory methods and procedures used in applying the resin to a range of sandstone rock samples and evaluating the resultant wettability shift. These chapters will also present a detailed critical discussion of the laboratory results obtained and the attempt made to upscale the laboratory scale data to a larger wellbore scale using numerical simulation.

Chapter 3 Experimental Equipment, Materials, and Procedures

To achieve the objectives set for this research, as outlined in the previous two chapters, a series of laboratory-scale experiments were carried out. The experimental program was carefully designed using the guidelines and protocols found in the relevant literature. To examine the implications of the laboratory-generated data at a larger scale, the experimental work was complemented by a wellbore-scale numerical simulation using an industry standard software package.

This chapter will present a detailed discussion about the equipment and material used in conducting the planned experimental investigations. It will also present the details of the experimental procedures followed and discuss their relevance and particular order in helping achieve the objectives set for the study. The chapter will also present essential information about the numerical simulation model constructed in order to upscale the results of the laboratory work.

3.1. Experimental Equipment and Software

3.1.1. Dean-Stark Apparatus

The rock samples used in this study were cut out of quarried sandstone blocks, which were expected to contain inorganic salt residues from the sample cutting process. Therefore, they were cleaned using a standard Dean-Stark apparatus. The apparatus (Figure 3.1) is a glass distillation assembly, composed of the flask that contains a solvent (methanol in this work) in its main body and a section to hold the rock sample. Additionally, a heating mantle allows the increment of temperature up to around 100 C. the detailed procedure followed in cleaning the samples will be provided in Section 3.2.

3.1.2. Automated Porosi-Permeameter

The AP-608 automated porosi-permeameter (Coretest Inc., USA) was used to measure the porosity and absolute permeability of the sandstone rock plugs. This equipment uses a procedure based on Boyle’s Law to measure the porosity of a core plug in a core holder subjected to confining pressures of up to 9,500 psi. It also uses a pulse decay technique to accurately measure permeability by monitoring the passage of a pre-determined volume of gas through the plug under a specified pore pressure set point.

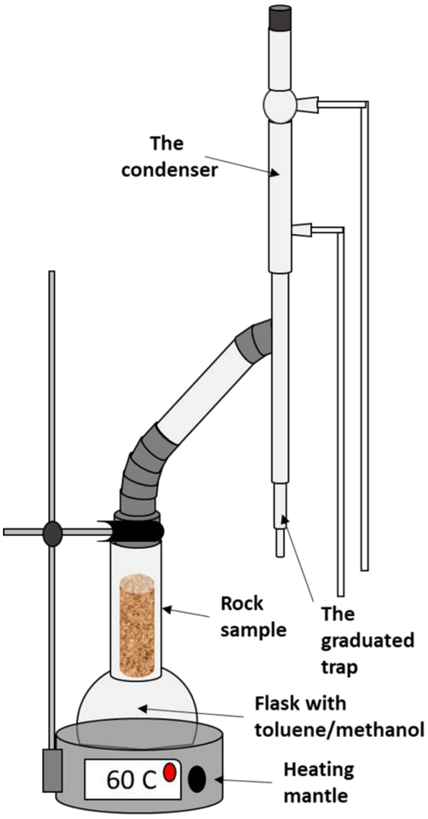


Figure 3.1. A schematic of the Dean Stark equipment used in this research.

3.1.3. Spontaneous Imbibition and Contact Angle Measurement Equipment

As indicated in the previous chapters, this research aimed to investigate the application of a novel chemical treatment to alter the wettability of rock samples to address water blockage in gas-producing wells. Therefore, pre- and post-treatment wettability evaluations were at the core of this research. After conducting a detailed literature review, it was decided to do the wettability evaluation at two scales using contact angle measurement on substrates complemented by spontaneous imbibition experiments conducted at the core scale. The details of the experimental apparatus and procedures used in carrying out these tests are provided in Section 3.3.1.

3.1.4. Coreflooding Setup

A robust coreflooding apparatus was used to reproduce the high pressure-high temperature dynamic multiphase flow conditions generally encountered in a gas reservoir as realistically as possible to demonstrate the effectiveness of chemical treatment in alleviating water blockage. Figure 3.2 shows a schematic of the coreflooding system.

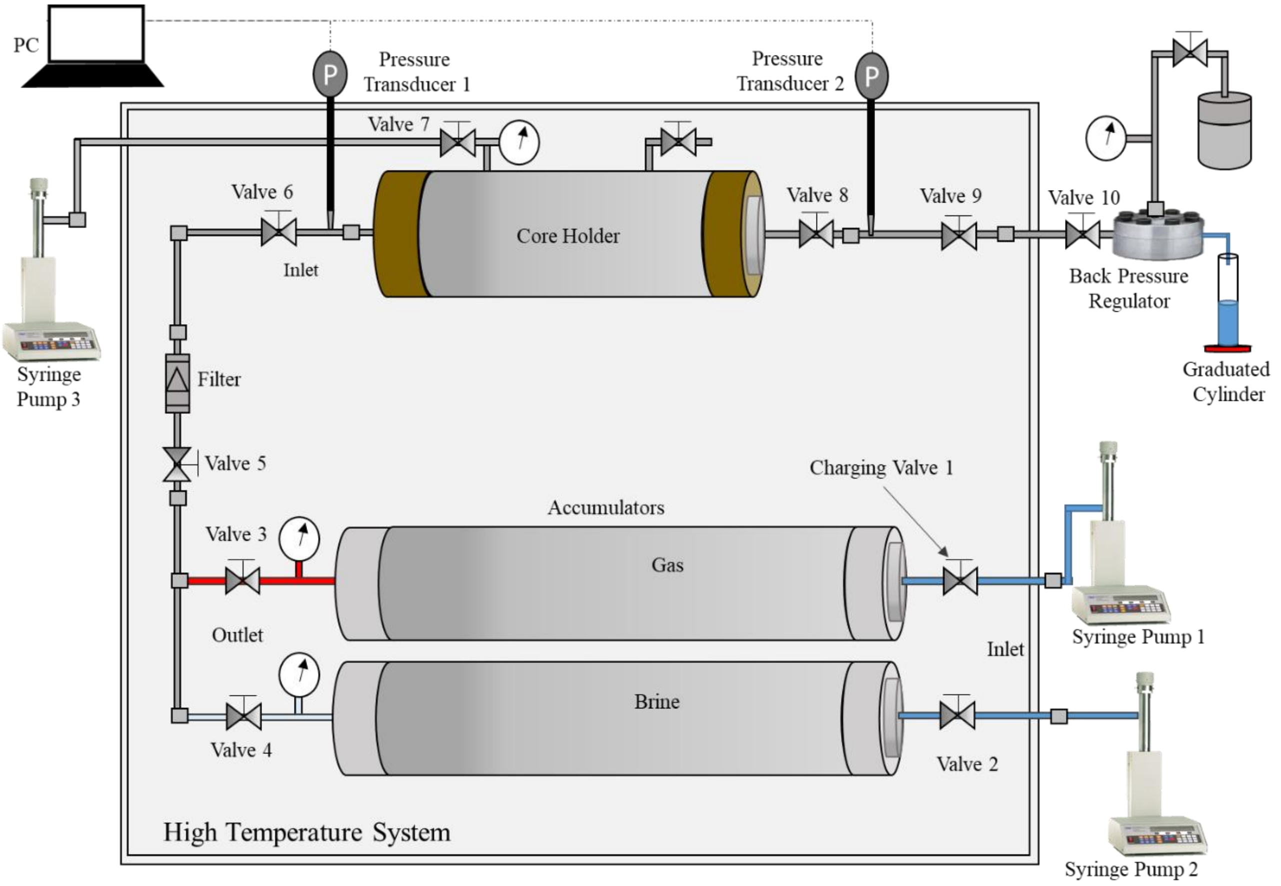


Figure 3.2. A schematic of the core-flooding setup used in this research.

The system consists of a core holder, two fluid accumulators, a back pressure regulator, a high-temperature oven, pressure transducers, syringe pumps, tubing, fittings, and valves. The main function of the core holder is to replicate the condition of the reservoir by allowing the phases to flow through the rock sample. In addition, the core holder makes it possible to increase the pore and confining pressure to up to 100 MPa. The core holder is divided into three parts: the inlet, the main body, and the outlet. The inlet consists of a threaded end cap that seals the holder and connects the 1/8" size tubing with the pressure gauge and inlet valve (Figure 3.3.). In the main body, there is an end plug with a nozzle connected to the threaded end cap that forms the flow system through the rock sample. The rock sample is contained in a rubber sleeve that connects the rock sample to the flow system and isolates the sample from the confining liquid in the annulus surrounding it. The outlet of the core holder has a floating spacer that is pushed against the sample outlet and seals the system. It also has a threaded end cap that seals the system from the outside and allows the injection fluids to flow through a tube in its centre that is connected to the pressure gauge and the corresponding outlet valve.

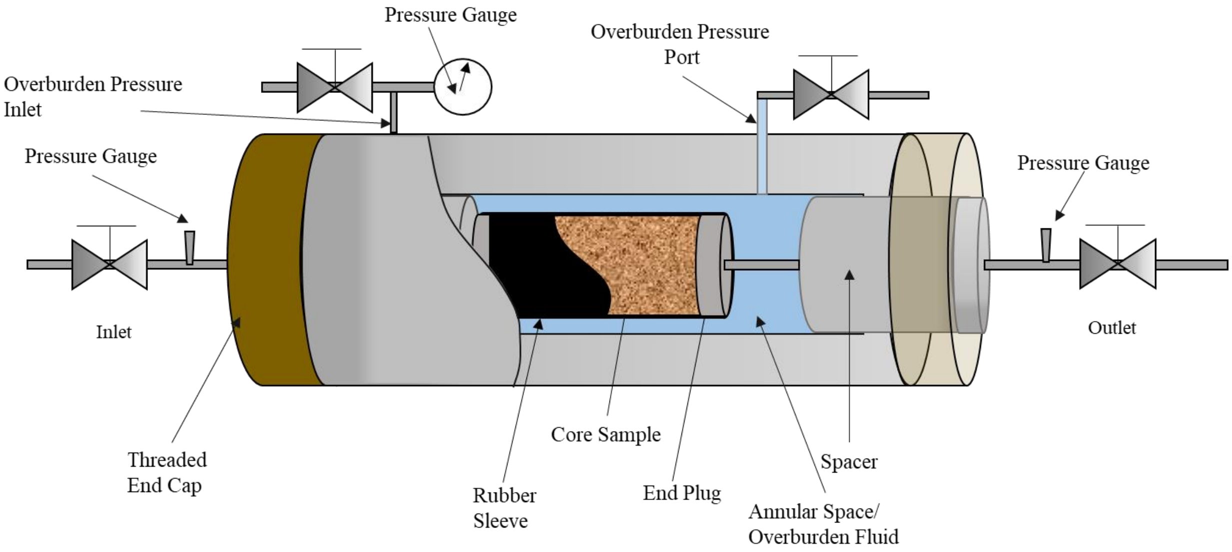


Figure 3.3. A schematic of the coreholder assembly used in this research.

Two fluid accumulators, each with a maximum capacity of one litre, were used to store gas and liquid phases to simulate the multiphase flow process when gas and brine are introduced into the system under high pressure. Similar to the core holder, each accumulator has an inlet and outlet cap (Figure 3.4). Inside the accumulator, a piston separates the fluid that is injected into the core holder to saturate the rock sample and the fluid that displaces the piston. Its main function is to regulate the pressure and flow conditions of the system. Syringe pumps thus control the flow by setting a constant pressure or flow rate during the injection process.

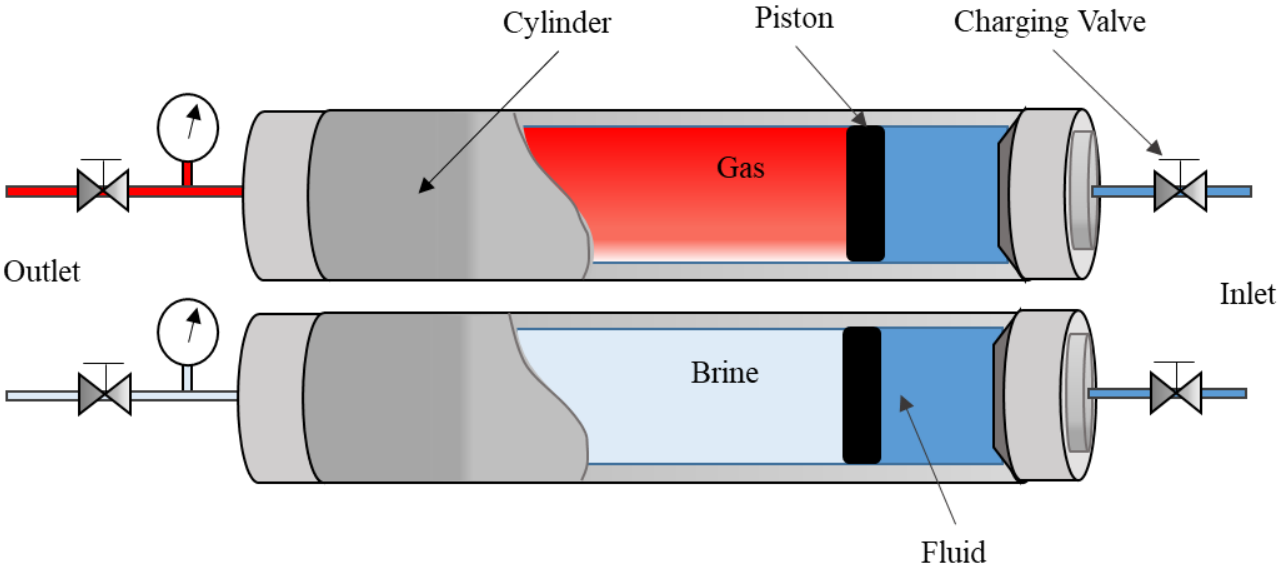
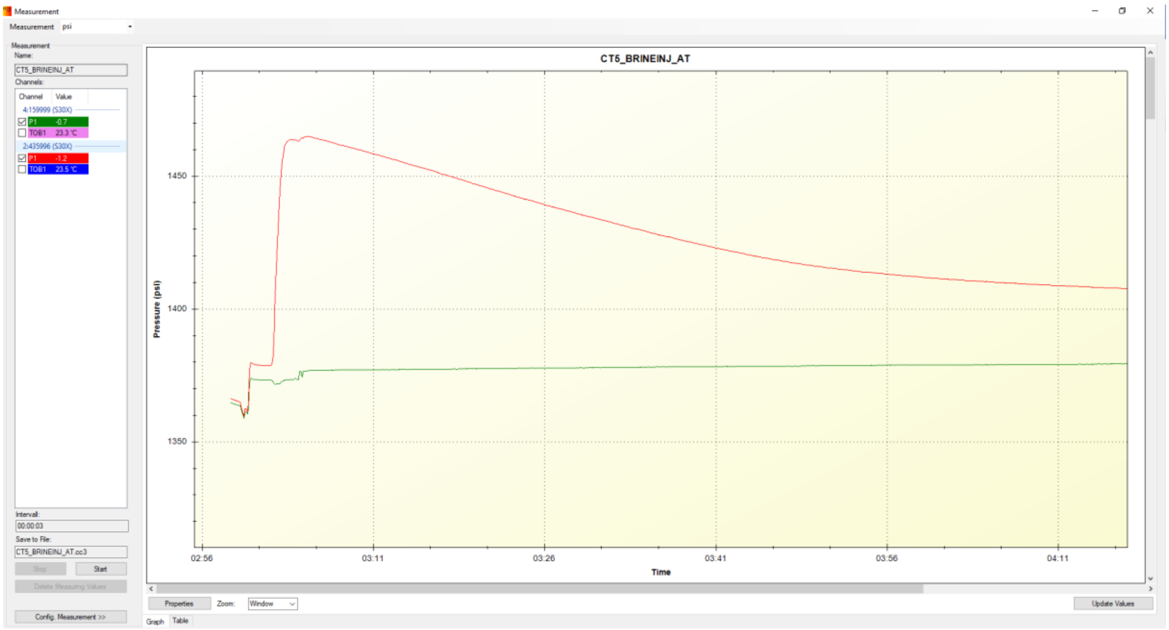


Figure 3.4. A schematic of the fluid accumulators used in this research.

The core holder was placed inside the high-temperature oven and connected to the syringe pump 3 (Figure 3.2) to simulate the confining pressure. Another flow line carries the fluids stored in the accumulators to the core holder, using a 1/8" tubing. The backpressure regulator located at the outlet end of the system maintains a constant pore pressure in the coreholder assembly. The dome-loaded backpressure regulator (BPR) has been set to 10 MPa by a sensitive diaphragm inside it, which regulates the flow of the two phases by an external pressure that keeps the system closed when the pressure is equal to or lower than 10 MPa. When the pressure exceeds 10 MPa during an experiment, the displaced liquid flows through the BPR and reaches a measuring cylinder to measure the volume of recovered brine.

Two accumulators filled with gas and brine were placed in the same high-temperature system and interconnected by a 1/16” flexible tube. Syringe pumps (1 and 2) were used to pressurise the accumulators and inject the desired fluid phase through the core sample as necessary. A series of valves were placed at various points in the system, as shown in Figure 3.3, to control fluid flow and isolate certain sections of the system in the event of leakage and ensure complete control over the system to minimise any potential hazards.

The pressure data were measured with encapsulated piezoresistive transducers. In these devices, the input signal of mechanical tension is converted into an electrical output signal. Most piezoresistive pressure transducers offer a measurement range of 5kPa to 200 MPa. The electrical signal was then digitised and recorded every three seconds using Control Center Series 30 software, which was also used to visualize the measured data in real time (Figure 3.5).



Measurement: psi

Measurement Name: CT5_BRINEINJ_AT

Channel	Value
4:159999 (S30X)	
☑ P1	-0.7
☐ TOB1	23.3 °C
2:435996 (S30X)	
☑ P1	-1.2
☐ TOB1	23.5 °C

Interval: 00:00:03

Save to File: CT5_BRINEINJ_AT.cc3

Zoom: Window

Figure 3.5. An example of the visualization of pressure recorded by transducers.

3.1.5. Numerical Simulation Software

An academic license of the commercial software t-Navigator (Rock Flow Dynamics) was used to develop the water blockage before and after rock treatment at the wellbore scale. This numerical reservoir simulation tool includes the Geology, Model Designer, and Simulation modules. The different modules allow the user to initialize a 3D reservoir model from scratch by creating a Cartesian grid, local grid refinement, rock property interpolation and dynamic data generation using PVT fluid information, relative permeability, and capillary pressure to model the dynamic conditions of a reservoir (Figure 3.6).

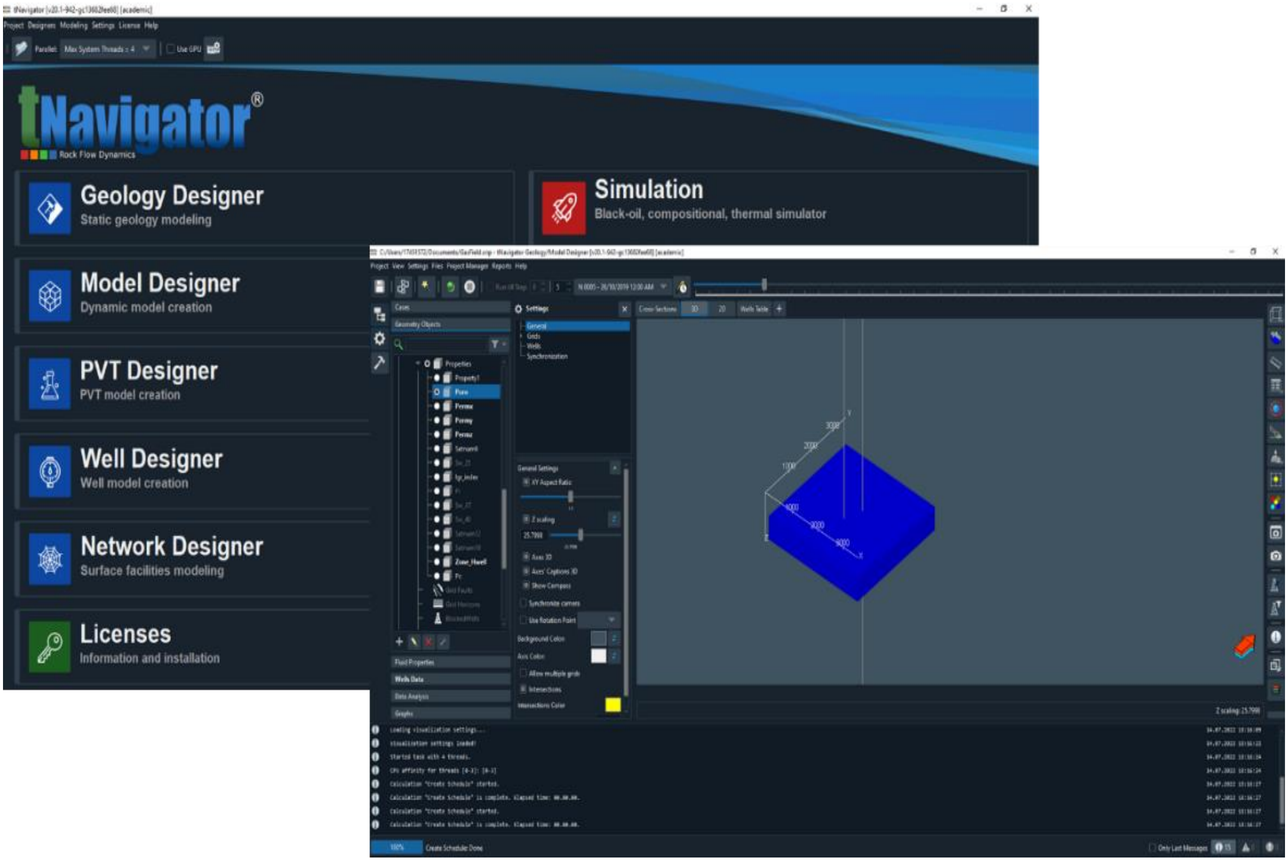


Figure 3.6. The visualization of the tNavigator software used for wellbore scale modelling.

The t-Navigator software incorporates the multiphase black oil model, where the differential equation has the following form:

$$\frac{\partial}{\partial t}(\emptyset N_c) = div\ \sum_{P=O,W,G} x_{c}, P\varepsilon_P\left(k\frac{k_{rP}}{\mu_P}\left(\nabla_{P_P} - \gamma_P \nabla D\right)\right) + q_c, \qquad c = 1,2,\ldots,n_c$$

$$p_O - p_G = P_{cOG},$$

$$p_O - p_W = P_{cOW},$$

$$S_W + S_O + S_G = 1$$

N_c = overall molar density of any component.

S_p = saturation of the phase P, P=O,W,G

p_W=water phase pressure ; pO = oil phase pressure ; pG = gas phase pressure

xc,P = molar fraction of component c in phase P.

ε_P = phase molar density

k= permeability tensor

k_{rP} = phase relative permeability

μ_P = phase viscosity

D = vertical depth vector

P_{cOW} = oil-water capillary pressure

P_{cOG} = oil-gas capillary pressure

3.2. Materials

3.2.1. Chemical Selection

The methodology for selecting a suitable wettability modifier started with a general screening to eventually find a specific set of non-fluorinated chemical alternatives. In the first step, the literature describing the fluorinated compounds that have successfully modified the wettability of rocks was reviewed, while in a later stage, particular cases of non-fluorinated surface treatments on cotton, wood or glass were studied as well. The screening process was done in three stages: initially, a list of fluorinated chemicals commonly used to modify rock surfaces was compiled (Table 3.1). The main objective of this stage was to understand the mechanism and chemical structure of the fluorinated compounds that might have a similarity to another type of polymer, especially oil-repellent substances. From the list, the short-chain fluorinated chemicals (FAS9 and FAS3) were selected due to their short structure and the presence of a coupling agent in their structure to perform contact angle tests to achieve oleophobicity. In addition, these chemicals are used to treat the rock sample and perform a comparative analysis with the results obtained with the benzoxazine monomer.

Table 3.1 Fluorinated compounds used during the wettability alteration.

Year	Name	Author
2012	Nonafluorohydroxyltriethoxy silane (FAS9)	Mousavi,2012
2012	1H,1H,2H,2H-Perfluorodecyltriethoxysilane (FAS)	Sharifzadeh, 2012
2012	Trimethoxy (3,3,3-trifluoropropyl)silane (FAS3)	Park,2012
2013	Fluoroacrylate (C=6; F=13)	Jiang, 2013
2014	Zonyl 8740 Fluoroacrylate	Zhang, 2014
2015	PTFE,PFOS	Esmailzadeh, 2015
2015	Zonyl UR Fluoroacrylate	Karandish, 2015
2017	Perfluorosylane	Sayed, 2017
2017	1H,1H,2H,2H-perfluorooctyltriethoxysilane (HFOTES)+silica nanoparticles	Saboori, 2017
2018	N-ethyl-N-hydroxyethyl perfluorooctanoamide	Li,2018

In the second stage of the chemical selection, a list of non-fluorinated compounds primarily constituted by silane and benzoxazine resin was analysed (Table 3.2). The former chemical is widely used in the silylation process to alter rock wettability using liquid solvents or gases as the carrier, therefore, it is a process extensively studied by others (Arjomand, Myers, et al. 2020). The benzoxazine resin, on the contrary, is a new type of resin used widely in other industries due to its favourable properties but not as a rock wettability modifier.

Table 3.2. Screening of non-fluorinated components to alter surface properties.

REFERENCE	CHEMICAL
(Wang, Su, et al. 2006)	**2,2-bis(3-phenyl-3,4-dihydro-2H-1,3-benzoxazinyl propane (BA-a)** 2-bis(3-methyl-3,4-dihydro-2H-1,3-benzoxazinyl)propane (BA-m)
(Liu et al. 2013)	3-(trimethoxysilyl)-n-propyl-3,4-dihydro2H-1,3-benzoxazine (P-tmos) **3-(trimethoxysilyl)-n-propyl-3,4dihydro-6-methyl-2H-1,3-benzoxazine (MP-tmos)** 3-(trimethoxysilyl)-n-propyl-3,4-dihydro-6-tert-butyl-2H-1,3-benzoxazine (PTBP-tmos)
(Gogoi et al. 2014)	2,2-bis(3-methyl-3,4-dihydro-2H-1,3-benzoxazinyl) propane (Benz-b) 3-tert-butyl-3,4-dihydro-8-allyl-2H-1,3-benzoxazine (Benz-m)

(Tang, Hess and Breedveld 2015)	Hydrolysed Methyltrimetoxysilane (HMTMS)

As mentioned in the previous chapter, researchers have obtained low surface-free energy values when applying these chemicals to glass surface (Figure 3.7). The published results indicate that the amine component used in the synthesis affects the contact angle when a glass surface material is treated with the monomer. Therefore, BA-a and MP-tmos, were selected for the initial screening due to the highest contact angle values reported (Wang, Su, et al. 2006; Liu et al. 2013).

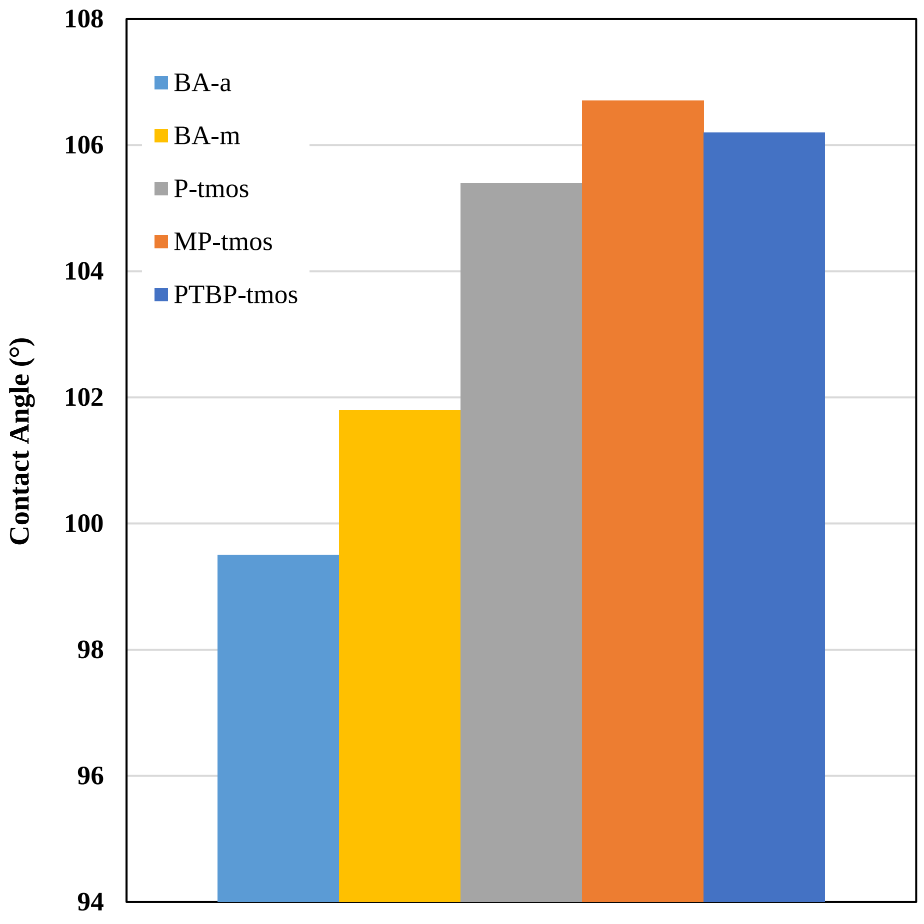


Figure 3.7. The contact angle of a glass surface treated with different benzoxazine monomers (Modified from Liu et al. 2011 and Wang et al. 2006) .

To synthesize the proposed benzoxazine monomer, p-cresol (4-methylphenol 99%), paraformaldehyde (crystalline form), and 3-aminopropyltrimethoxysilane (97%) (APTMS), chloroform (≥99%) with calcium hydride (95%) were purchased from Sigma-Aldrich. The procedure reported in the literature was followed to synthesize the benzoxazine monomer (BZ). (Liu et al. 2013) (Table 3.3).

Table 3.3. Chemical materials used during the synthesis of the benzoxazine monomer.

PRODUCT	Quantity (g)	Cost (AUD)	Provider	Cost (AUD/g)
4-Methylphenol	100	92	SA-Merk	0.920
3-APTMOS (mL)	100	102	SA-Merk	1.020
Paraformaldehyde	100	58	SA-Merk	0.580
Chloroform (mL)	1000	116	SA-Merk	0.116
Calcium hydride	100	148	SA-Merk	1.480
Tetrahydrofuran (mL)	1000	176	SA-Merk	0.176

In the synthesis, about 12.24 grams of paraformaldehyde were gradually dissolved in 200 ml of chloroform. Calcium hydride (28 grams) was added to the solution and heated to 65°C. Immediately, 35.8 grams of 3-APTMOS were added to the mixture while the temperature was raised to 85°C. Finally, 21.6 grams of p-cresol dissolved in 80 ml of chloroform were subtly incorporated into the system. After three hours of reaction, the chemical mixture was cooled for about ten minutes and filtered to remove residual solids. The resulting benzoxazine monomer was distilled for about thirty minutes and dried for two days (Figure 3.8).

A ^{1}H-NMR analysis was performed to confirm the efficacy of the benzoxazine monomer synthesis and qualitatively assess the purity of the resulting monomer. The chemical obtained showed similar high-field ^{1}H-NMR results compared with previously published results. (Liu et al. 2013) Figure 3.9 shows the presence of the trimethoxysilane coupling agent (black colour), benzene (blue colour), and oxazine rings (green colour) in the monomer structure. Finally, the monomer was dissolved in acetone or tetrahydrofuran (THF) for rock treatment (i.e., silylation initially to bind the monomer to the rock surface and subsequent thermal polymerisation to form a coating on the rock surface).

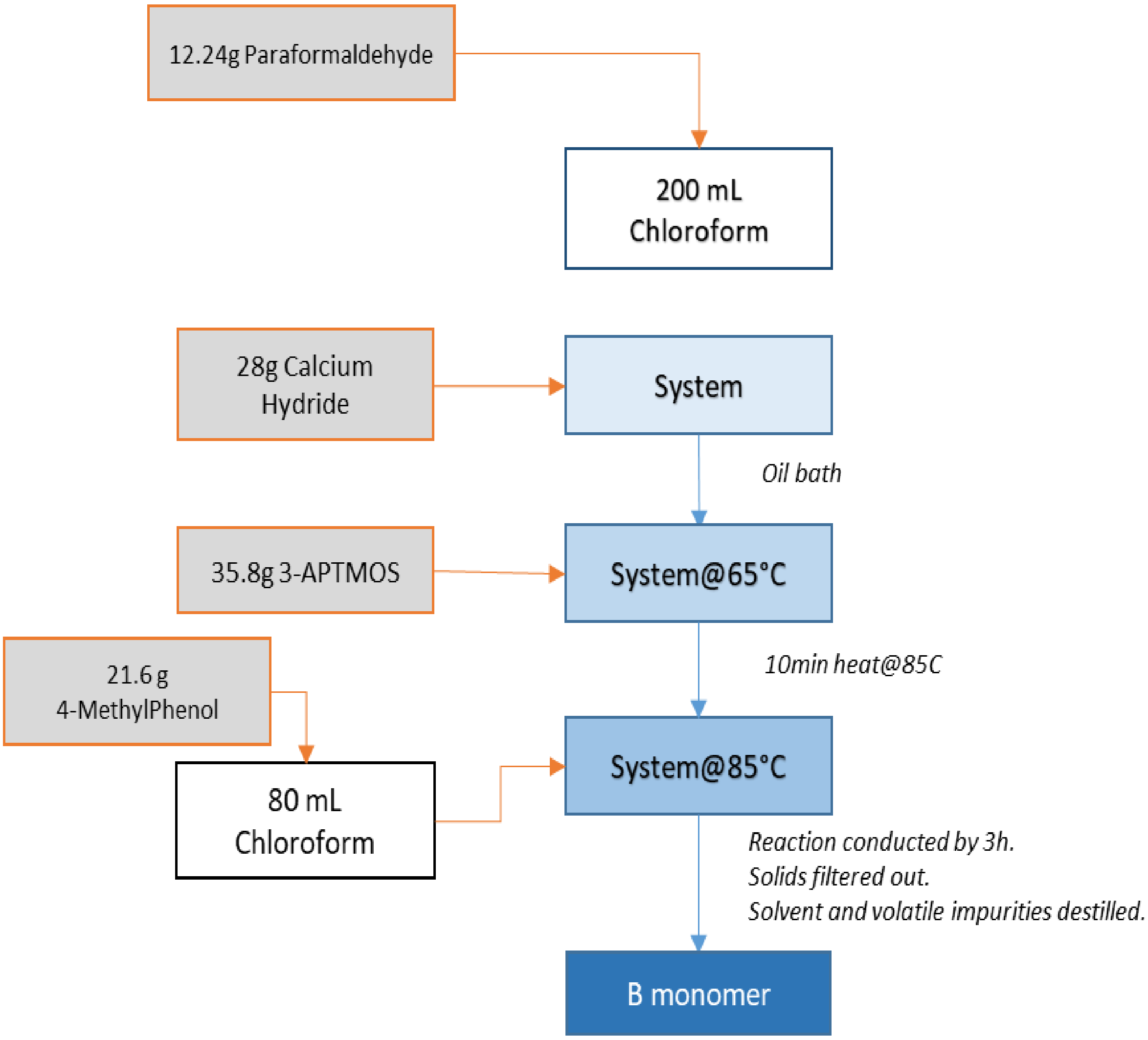


Figure 3.8. The synthesis process of a benzoxazine resin (Modified from Liu,2013).

A second aniline-based benzoxazine monomer was synthesised using Bisphenol A (97%), Pentafluoroaniline (98%), and Paraformaldehyde (crystalline). They were all used without any purification and were obtained from Sigma-Aldrich. Liu proposed a synthesis process to obtain a fluorinated benzoxazine monomer, which we will refer to PFA. Similar, to the previous benzoxazine monomer, ^{1}H-NMR analysis was performed to confirm that the chemical was synthesized correctly.

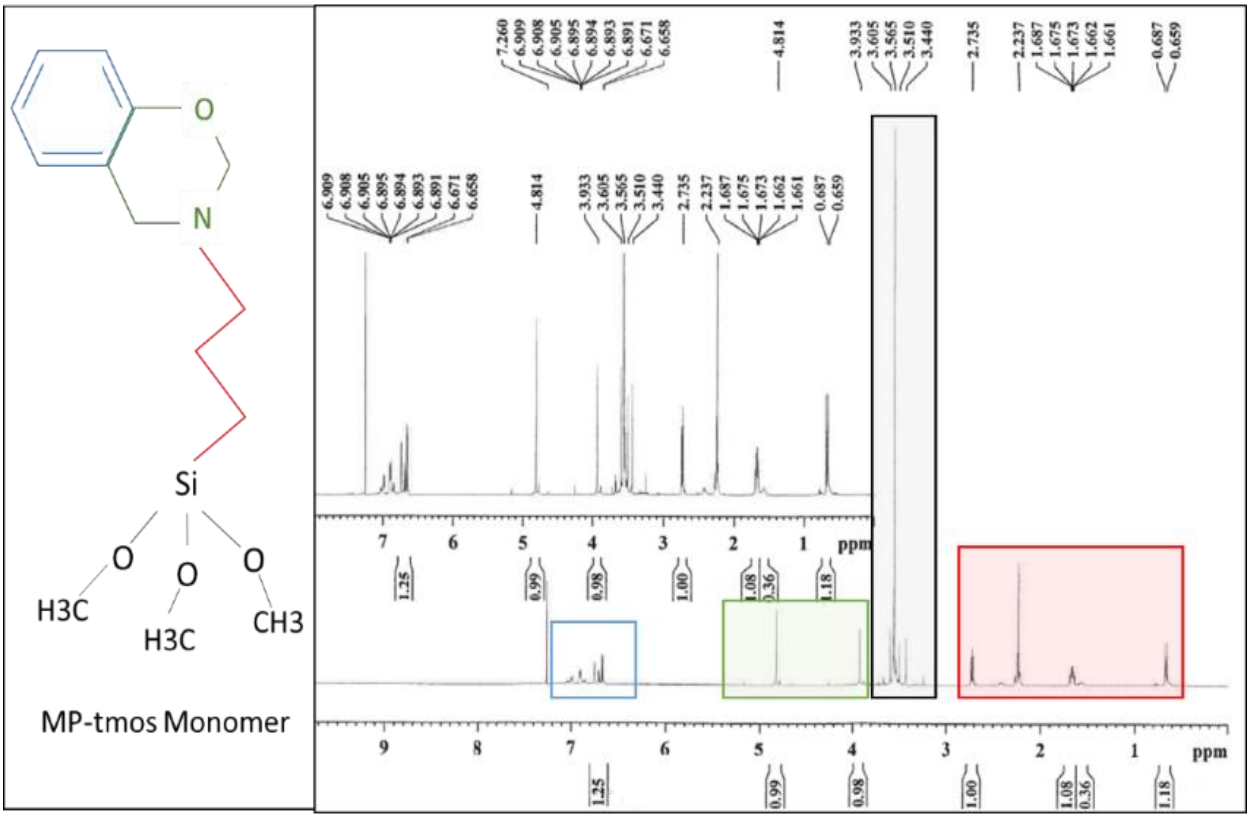


Figure 3.9. H-NMR –benzoxazine monomer.

3.2.2. Rock Samples

Low permeability reservoirs are not, in general, well-defined in the literature; most authors define low permeability reservoirs as those below 100 mD. To support this statement, researchers have analysed data for 9312 sandstone samples to obtain 662 unbiased reservoir values for porosity and permeability (Omatsone et al. 2010; Delamaide, Tabary and Rousseau 2014; Das et al. 2016). In addition, studies by the Bureau of Mines in the United States have shown that water blockage drastically affect affects reservoirs with permeabilities between 0.1 and 100 mD (Eakin, Miller and Eckard 1965).

In their quest to achieve hydrophobic conditions using fluorinated components, researchers pioneered the modification of wettability in a gas-liquid system using Berea Sandstone samples with permeabilities between 500 and 710 mD (Li and Firoozabadi 2000; Tang and Firoozabadi 2002; Fahes and Firoozabadi 2005; Wu and Firoozabadi 2010a, 2010b). Later, the researchers realised that it might be more appropriate to use rock samples with low permeability after the initial results of chemical treatment were satisfactory. For example, the authors used Berea Sandstone rock samples with permeabilities between 60 and 175 mD (Panga et al. 2007; Wang et al. 2015). Finally, recent studies have demonstrated the use of fluorinated and non-fluorinated chemicals on rock samples with permeabilities of less than 40 mD, as shown in Figure 3.10 (Thomas, Clouse and Longo 1993; Kumar, Pope and Sharma 2006; Al-Anazi et al. 2007; Panga et al. 2007; Noh and Firoozabadi 2008a; Wu and Firoozabadi 2010b; Zhang et al. 2014; Franco-Aguirre et al. 2018).

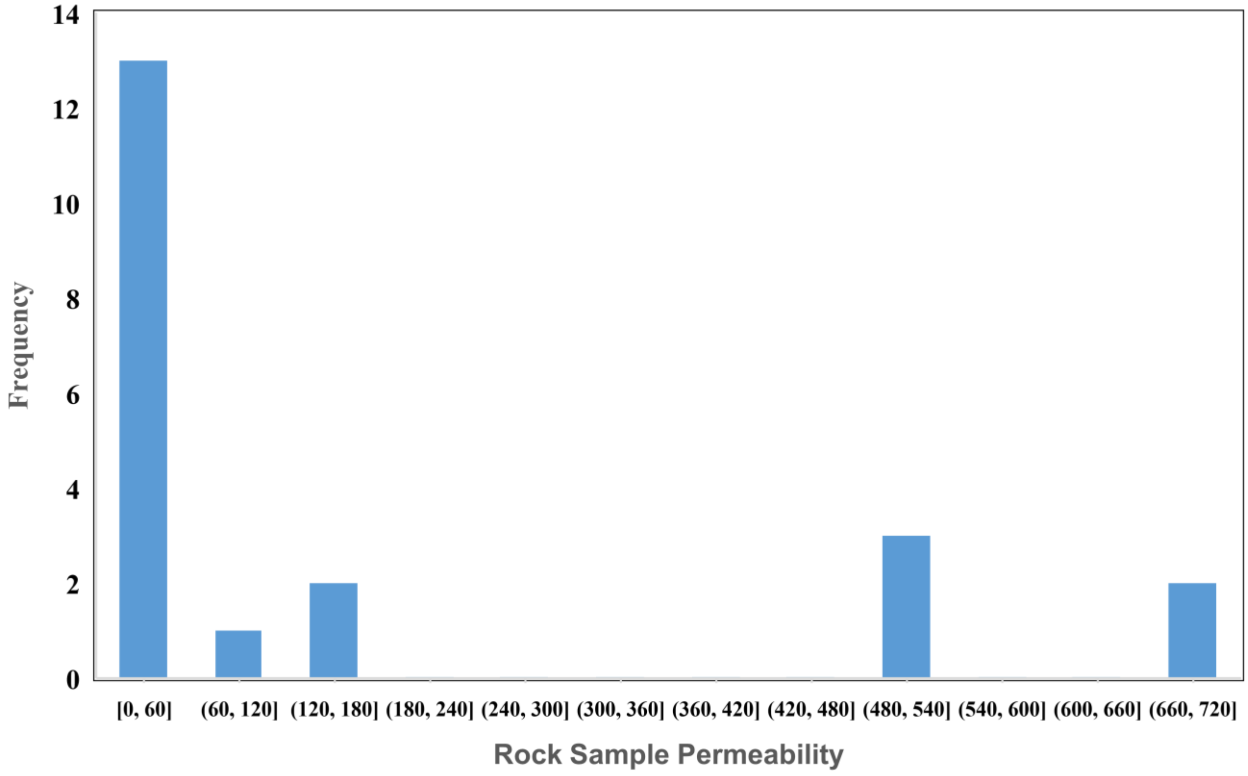


Figure 3.10. Rock sample permeability selected by other researchers to assess wettability alteration by chemical treatment.

In this PhD research, to test the performance of the benzoxazine resin to alter rock wettability, quartz-rich sandstone samples were selected for contact angle, spontaneous imbibition, and core-flooding experiments (Figure 3.11). To examine the effectiveness of chemicals in diminishing water blockage, rock samples with permeability in the range of 100 to 200 mD were selected because, as demonstrated by the earlier discussed literature review and detailed discussion presented in Chapter 2, the water blockage effect would be negligible for higher permeability reservoirs (Eakin, Miller and Eckard 1965).

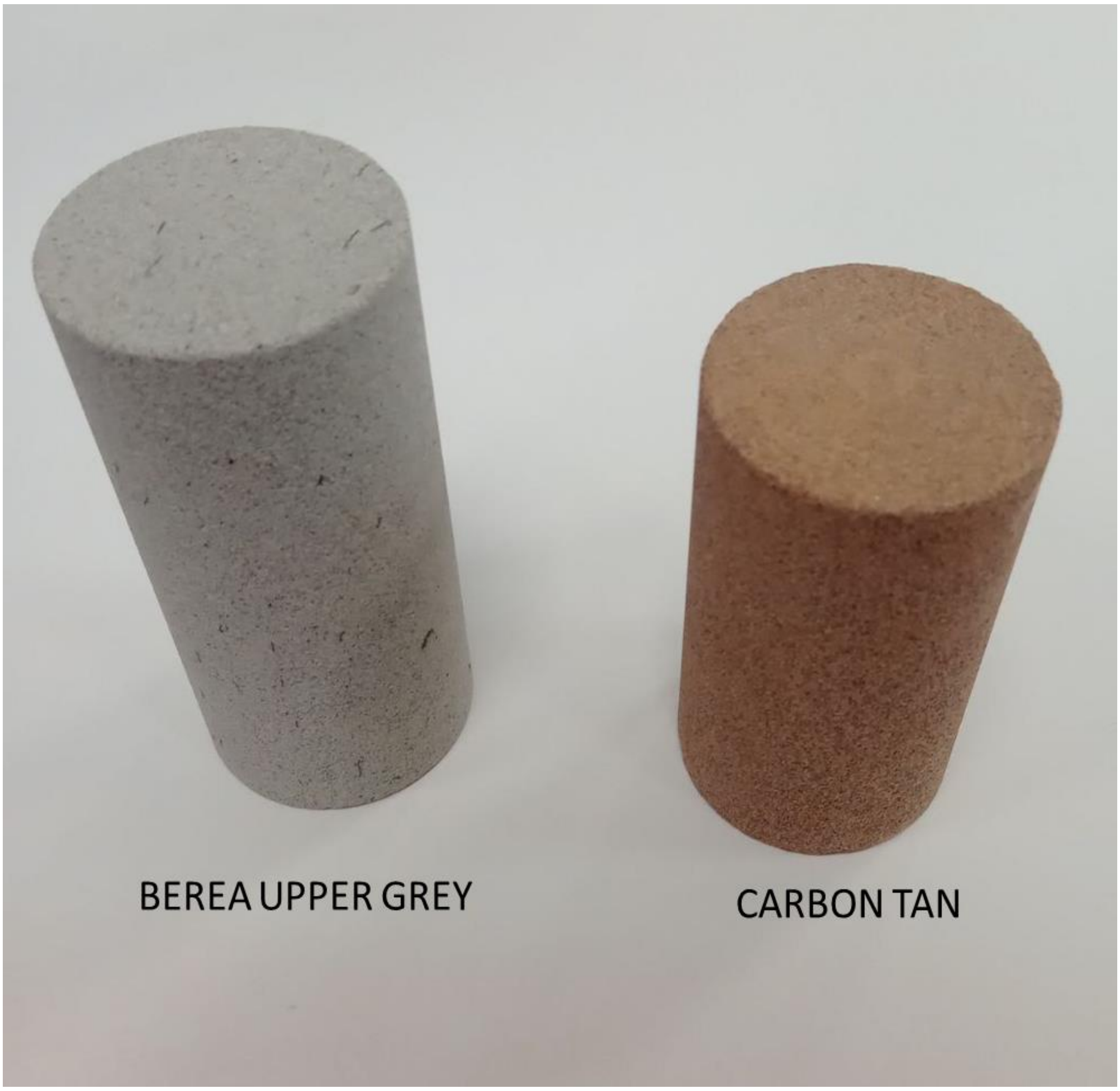


Figure 3.11. Rock samples used in the research analysis – Berea Upper Grey (k≈130 mD) and Carbon Tan (k≈6.8 to 21.3 mD).

The selected Berea Upper Gray (BUG) and Berea Sandstone samples contain more than 80% silica, with the remaining content being a combination of mostly clay materials and low levels of carbonates (XRD used to obtain composition) (Table 3.4) (Alshajalee et al. 2019; Arjomand, Easton, et al. 2020). The lower permeability Carbon Tan samples contain a lower quartz content and have much lower permeability compared to their BUG and Berea counterparts. The mineral composition of the samples used in this research, along with their basic petrophysical properties, are provided in Table 3.4.

Table 3.4. Petrophysical Properties and mineral composition of the selected Berea, Berea Upper Grey (BUG), and Carbon Tan (CT) samples.

SAMPLE	BEREA	BUG1	BUG2	CT1	CT2	CT3	CT4	CT5
PETROPHYSICAL PROPERTIES								
Diameter, cm	3.81	3.81	3.81	3.8	3.79	3.79	3.8	3.85
Length, cm	7	7	7	7.63	7.62	7.64	7.65	7.61
Gas Permeability, mD	224	129	130	21.1	18.4	21.3	17.5	6.8
Porosity, %	19.60	18.20	19.10	14.56	13.7	14.5	13.68	
Homogeneous	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes
MINERAL COMPOSITION (%)								
Quartz	81.2	89.3		64 (*)				
Kaolin	5.70	2.20		-				
Illite/Muscovite	4.50	1.60		-				
Albite	3.00	1.50		-				
Dolomite	0.50	-		11 (*)				
Calcite	0.30	-		10 (*)				
Chlorite	-	0.40		-				
K-Feldspar	4.80-	5.10-		15 (*)				

**(Cavé et al. 2010)*

3.2.3. Fluids

Deionised water induces stronger hydrophilicity than brine due to the formation of highly negatively charged surfaces and a thicker water film (Xie et al. 2016). In other words, the water contact angle slightly increases when using brine instead of deionised water. For this reason, we used deionised water to aid with the contact angle measurements as this better helps to examine the performance of the wettability alteration caused by the chemical treatments. However, the core-flooding experiments were performed using a synthetic brine (1 wt.% KCl) and nitrogen to simulate more representative in-situ conditions. The nitrogen-brine system has been widely used as a gas-liquid system to assess flow displacement showing representative results (Li and Firoozabadi 2000; Tang and Firoozabadi 2002; Noh and Firoozabadi 2008b; Wu and Firoozabadi 2010a; Zhang et al. 2014) while providing a safe environment for research.

3.3. Experimental Procedures

3.3.1. Sample Preparation

For the contact angle measurements, small chips of sandstone samples were cut, polished, and washed with methanol. The chips were polished to reduce any surface roughness effect on contact angle results; although, some researchers have reported that not having a completely smooth surface would have an insignificant effect on the results sought by the measurements (Fauziah et al. 2019). Pre-cut cylindrical core samples ($L \approx 7$cm and $D=3.81$cm) were also cleaned with methanol and dried in an oven for 24 hours to be used for spontaneous imbibition and core-flooding experiments. As indicated earlier in this chapter, the samples were cleaned in a temperature-controlled Dean-Stark set up with methanol to remove any possible contaminants present in their pore space and then dried in an oven at 70 °C for 24 hours. It is worth noting that the rock samples were sourced from a commercial distributor (Kocurek Industries, USA) who would cut them from quarried blocks.

3.3.2. Chemical Treatment

A sample saturator was used to saturate the rock sample with the chemical solution. Initially, inlet valve 2 was closed while the system was connected to a vacuum pump to remove any remaining air (Figure 3.12). Later, the system was connected to an accumulator filled with the appropriate chemical solution at a certain concentration. The chemical was injected into the porous space of the rock sample inside the sample saturator. The chemical solution was injected with a syringe pump by slowly increasing the injection pressure to 10.5 MPa. Once the selected pressure condition was reached, it was maintained for 24 hours to allow the chemical concentration to cover most of the pores entirely and for the chemical to interact with the surface of the rock.

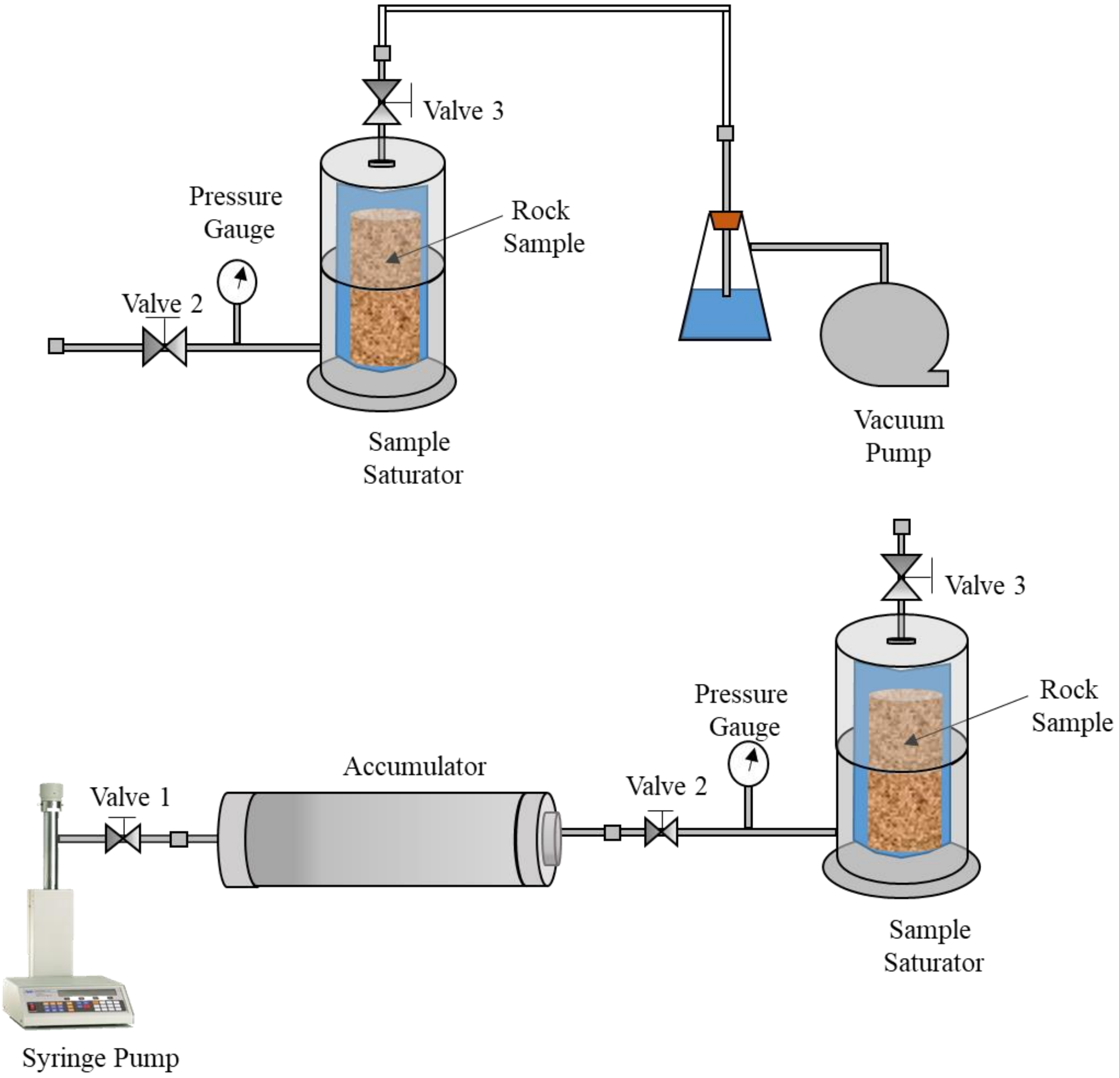


Figure 3.12. A schematic of the saturation system used in this research.

3.3.3. Benzoxazine-sandstone interaction during treatment

When a rock sample is immersed in the chemical solution during treatment, the silane that is part of the structure of the benzoxazine monomer (BZ) creates a bond (benzoxazine-Si-O-Si) with the sandstone rock surface, as shown in Figure 3.13. This process is followed by a thermal ring-opening polymerisation at 180°C (Figure 3.13b) that alters the surface wettability without involving any other reagents or catalysts, which is in contrast to other methods. (Qu and Xin 2011; Park et al. 2013; Sharifzadeh et al. 2015) The properties of the resulting polymer are discussed in detail in the upcoming chapter that will cover the experimental results and relevant discussions.

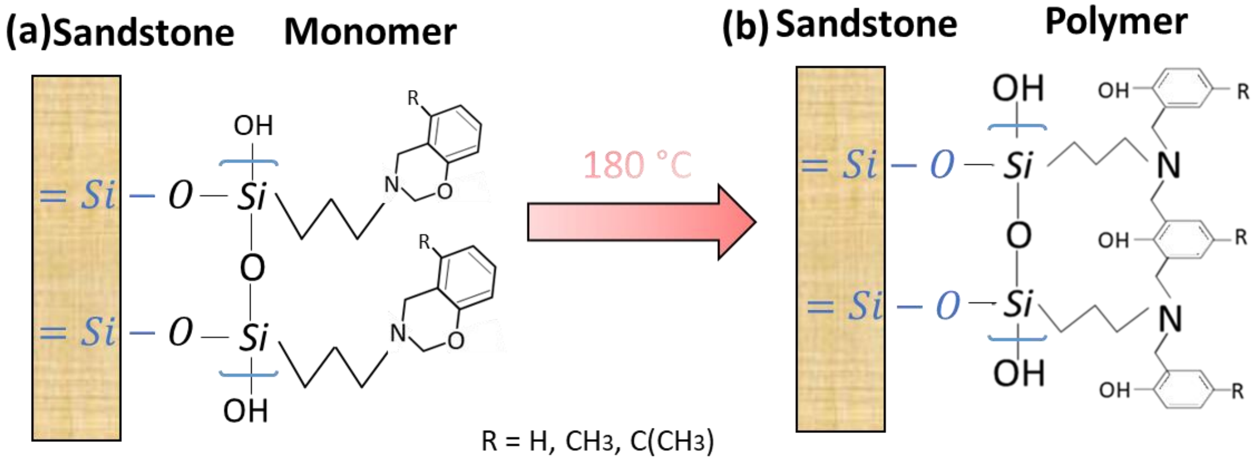


Figure 3.13. Interaction between the polymer and sandstone rock surface.

The proper assessment of the chemical-rock surface reaction is not a simple task when treating samples with a benzoxazine resin. In this research, the reaction of the benzoxazine monomer (BZ) with the rock surface was compared with that of another benzoxazine resin (fluorinated benzoxazine (FBZ)) that does not have the incorporated silane coupling agent in its chemical structure. This fluorinated benzoxazine monomer (FBZ) was synthesised and ^{1}H-NMR performed on it as stated in the available literature to confirm its structure (Ishida 2002). To perform the above-mentioned comparison, two different solutions were prepared by dissolving BZ and FBZ in acetone, each at a 5 wt.% concentration. These solutions were then used to spin-coat the surface of different glass slides. To complete the polymerisation process, the coated slides were subsequently cured at 180°C for 1 hour (for BZ) and 24 hours (for FBZ). After polymerisation, a thin coloured layer could be observed over the glass slides. To assess the chemical reaction of the benzoxazine resin with the treated surface, the glass samples were sequentially washed with acetone, methanol, and toluene. It was clearly observed that the coloured FBZ polymer layer could be easily removed by the above solvents, while the BZ polymer layer remained intact over the glass surface, suggesting that unlike BZ, the FBZ could not create a covalent bond with the surface. Similar results have been observed by other researchers who have concluded that a rock surface reacts with the benzoxazine structure when the amine type, which is often used in the synthesis of the benzoxazine resins, is replaced by APTMS (3-aminopropyltrimethoxysilane) (Qu and Xin 2011; Liu et al. 2013). The same effect as the above was observed after treating and washing the Berea sandstone samples with different solvents.

3.3.4. Contact Angle Measurements

To assess the impact of the chemical treatment on the wettability characteristics of the rock samples and to optimise the chemical formulation, the water contact angle was measured in the presence of air on the rock surfaces before and after the benzoxazine polymerisation. For this purpose, a goniometry setup composed of a high-resolution digital camera, a needle and a light source was used (Figure 4). Initially, a drop of water was placed with a needle over the surface of the untreated rock sample and the shape of the liquid-rock surface interaction was recorded to measure the contact angle.(Park and Seo 2011) Later, the rock samples were immersed in the BZ solution to form the silane bond between the monomer and the rock surface. Then the samples were cured at 180°C for 1 hour to induce thermal polymerisation on the rock surface. Subsequently, the above-outlined water contact angle measurement was repeated on the treated sample surface. For each of these, the contact angle was measured 10 times on different portions of the sample, and the average value is reported.

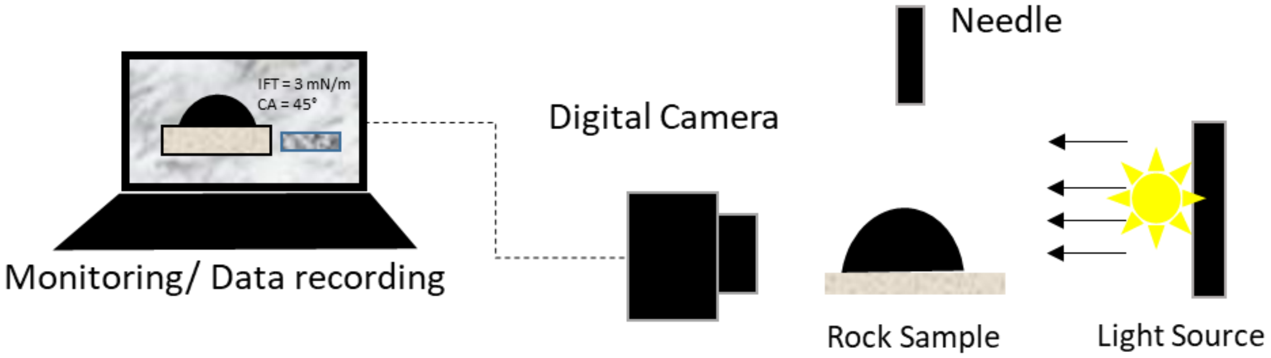


Figure 3.14. A schematic of the Contact Angle Test setup.

To obtain an optimum chemical formulation and application methodology, different treatment conditions (i.e., solvent type, chemical concentration, and sandstone type) were assessed using contact angle measurements. For example, the BZ monomer can be dissolved in acetone for injection into the rock pore space. In the literature, researchers have also diluted different types of benzoxazine in tetrahydrofuran (THF), obtaining repellence on glass surfaces (Wang, Chang and Kuo 2011; Qu and Xin 2011; Liu et al. 2013; Kim and Ishida 2002; Gogoi et al. 2014). Hence, a concentration of the chemical was diluted in both of these solvents (THF and acetone) to compare their efficacy against each other in treating rock samples. Moreover, sandstone samples were treated with different BZ monomer concentrations (2, 3, 5, 10 and 13 wt. %) dissolved in a solvent to determine the optimum value for further analyses. Those samples were washed with methanol and toluene to remove any remaining excess polymer in their pore space. Finally, the contact angle was measured over both

Berea and BUG sandstone samples to assess any differences in the wettability alteration effects between these two quartz-rich samples.

Additionally, the average surface free energy of the sandstone samples was calculated before and after treatment using water-air and diiodomethane-air as fluid systems of interest. The contact angle between each of these fluids and sandstone was also recorded experimentally in the presence of air. The calculation was performed using Owen's two liquids (equations 1-3) to obtain an approximate of the surface free energy of the functionalised sandstone samples after BZ treatment (Park and Seo 2011).

$$\gamma_S = \gamma_S^d + \gamma_S^p \qquad \textit{Equation 1}$$

where, γ_S is the surface free energy of the rock surface, γ_S^d and γ_S^p are the dispersion and polar components of the rock surface as calculated using the following equations.

$$\gamma_1(1+\cos\theta_1) = 2\left(\gamma_S^d\gamma_1^d\right)^{\frac{1}{2}} + 2\left(\gamma_S^p\gamma_1^p\right)^{1/2} \qquad \textit{Equation 2}$$

$$\gamma_2(1+\cos\theta_2) = 2\left(\gamma_S^d\gamma_2^d\right)^{\frac{1}{2}} + 2\left(\gamma_S^p\gamma_2^p\right)^{1/2} \qquad \textit{Equation 3}$$

where, $\gamma_1\ and\ \gamma_2$ are the surface energy of the liquids (water and diiodomethane while γ_1^d, γ_2^d are the dispersive components of the liquid surface energy and γ_1^p, γ_2^p are the polar components.

3.3.5. Spontaneous Imbibition Tests

Although the contact angle measurements are very insightful in assessing the localised wettability state of small substrates, to assess the effects of wettability change at a larger scale, spontaneous imbibition measurements were conducted on core samples before and after the chemical treatment. For these tests, two Berea Upper Gray samples (BUG1 and BUG2) were initially cleaned with methanol and then dried in an oven for 24 hours. Spontaneous imbibition tests were carried out on these samples using a high-accuracy balance connected to a string whose other end was attached to a core sample immersed in a container filled with water. The balance recorded the fractional mass of the water spontaneously imbibed by the pore space of the rock sample over time (Figure 3.15). Subsequently, the same rock sample was cleaned, treated with the BZ monomer and finally tested using the same procedure as above to determine possible changes in the spontaneous imbibition behaviour as caused by the induced wettability alteration. For effective evaluation of the wettability alteration, every test was conducted for at least 200 minutes. Based on the end results obtained from these tests, this timing was found to be adequate in reaching dynamic capillary equilibrium signalling the end of an experiment.

These tests were also used to compare the effect of concentration on performance when rock samples were treated with different concentrations of benzoxazine resin for the contact angle analysis. For example, one of the above-mentioned rock samples was treated in 5 wt.% and another in 10 wt.% BZ solution for 8 hours and then thermally polymerized at 180°C for 1 hour.

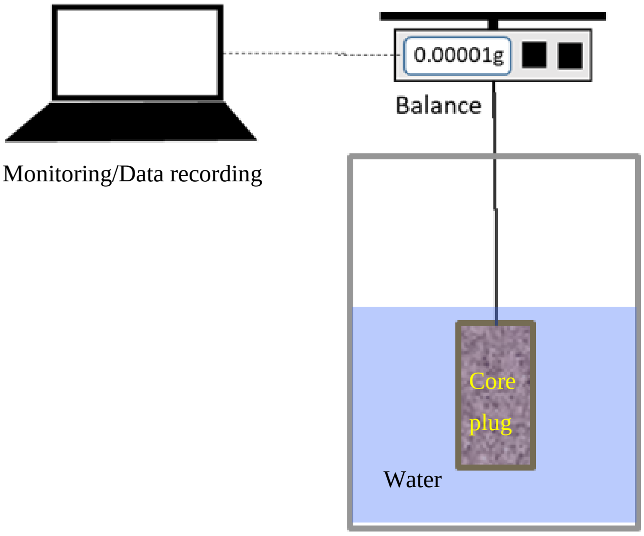


Figure 3.15. A schematic of the spontaneous imbibition test setup.

3.3.6. Coreflooding Experiments

During the spontaneous imbibition tests, 10 wt.% BZ in THF chemical treatment showed the best performance (the rationale for this is explained in more detail later in the results/discussion section) resulting in the greatest post-treatment change in the imbibed water volume. That result depicted a stronger wettability alteration of the rock pore surfaces to a less water-wet state reducing the ability of water to invade the pore space of a sample spontaneously. Coreflooding experiments were conducted using these optimized conditions to confirm the success of the treatment to alter the rock wettability to less water-wet at high pressure/high temperature conditions. Such experiments also provided the ability to evaluate the effect of the induced wettability alteration on critical dynamic multiphase flow properties such as relative permeabilities and residual saturations. Two core-flooding experiments were performed on BUG2 before and after the chemical treatment at 60 °C with confining and pore pressures of 17.24 MPa and 10.35 MPa, respectively. The pressure and temperature conditions were selected based on representative gas reservoir conditions for characterising the water blockage problem (Bennion et al. 1994). A detailed description of the coreflooding equipment was presented in earlier sections of this chapter (Figure 3.4).

The coreflooding experiments were conducted primarily to evaluate the impact of the benzoxazine treatment on the transport properties of gas/water in the core sample, and the procedure is summarised here. Firstly, the untreated sample (BUG2) was placed in the core holder under a minimum confining pressure, and the system was placed under vacuum for one day. Next, synthetic brine (i.e. 1% KCl solution) was injected into the system at a gradual pressure increment until the proposed pore pressure (i.e. 10.35 MPa) was reached. At the same time, the confining pressure (to 17.24 MPa) and system temperature (i.e. 60 °C) were gradually increased until reaching their respective final values. The system was left under such conditions for one day to completely saturate the rock sample and establish pressure and temperature equilibrium. (Arjomand, Myers, et al. 2020) Then, the absolute permeability of the sample was calculated using the Darcy equation (based on the slope resulting from linear regression) with the pressure drop values obtained by injecting water at several flow rates. Finally, a constant flow rate of 2 cc/min of nitrogen was injected into the system to displace the water phase from the saturated rock sample. The water volume displaced by the gas phase was collected and measured carefully to ascertain the water recovery profile. The pressures at the inlet and outlet of the system were also recorded to obtain the differential pressure during gas injection. At the conclusion of the experiment, the sample was unloaded, cleaned and chemically treated with a 10 wt.% solution BZ monomer in acetone and then cured at 180°C for 1 hour. Subsequently, an identical flooding procedure as above was applied to the treated rock sample. The recorded differential pressure and water recovery profiles resulted from the above two experiments were assessed together to determine the effects of the chemical treatment on the multiphase flow properties of the sample.

3.4. Core-scale numerical simulations

At the core scale, a 1D numerical model was built for each core sample with 100 grid cells along its axis, having overall dimensions of 0.076 m (length) by 0.038 m (diameter). In this grid system, a drainage process was then simulated in which nitrogen gas displaced the fully brine-saturated core. Once initialised, a water production and differential pressure history matching was performed on the experimentally measured data using a rigorous iterative procedure available in Sendra v2018.1 (Prores AS). The iterative procedure follows the equations and rules set in various analytical relative permeability models (e.g. models proposed by Corey, Sigmund & McCaffery). To ascertain the effects of the benzoxazine treatment on the relative permeability characteristics, history matching was conducted on the differential pressure and water recovery data from the drainage core-flooding experiment (from cores before and after chemical treatment). We have also incorporated the data from our previous study (Mauricio Ceron Lopez et al. 2021), which examined the effects of benzoxazine treatment on higher permeability samples (i.e., BUG samples of approximately 130 mD) to allow comparison with the results of this study which focuses on low permeability cores. In our case and under both sample conditions, the Sigmund & McCaffery model provided a very close fit generating the relative permeability curves as the output. This data was then extended into the numerical reservoir simulator to build the box model that allowed us to assess the effect of wettability alteration treatment on gas deliverability at a wellbore scale.

3.5. Wellbore-scale numerical simulations

A homogeneous box model with overall dimensions of 1219 × 1219 × 26 meters (in x, y, and z directions, respectively) representing the initial wellbore conditions (with the effects of water blockage) was created using a commercial numerical reservoir simulator (T-Navigator v20.1). A grid of 100 × 100 × 8 cells (in x, y, and z directions, respectively) was generated to populate with different rock and fluid properties (e.g., porosity, permeability, initial water saturation). Moreover, local grid refinement was applied around the well trajectory to better model the fluid characteristics and pressure drawdown around the wellbore (Table 3.5).

Table 3.5. Box Model - Grid Dimensions.

Direction	Length (m)	No. of cells	No. of Local Grid
X	1219	100	6
Y	1219	100	6
Z	26	8	1
TOTAL		**80000**	**288**

The in-situ conditions of the Paddy sandstone member, a relatively low permeability member (<100mD) of the Peace River Formation in the north-western part of Alberta – Canada, were selected for this case study. Principally due to the very close similarity with the mineralogy of the Carbon Tan rock sample, which is mainly composed of around 64% of quartz and its relatively low permeability (Diana 2013). The Paddy member is a quartz arenite sandstone rock composed of more than 40% quartz, formed by transported and deposited sediments in an estuarine bay complex (Leckie 1994). Average porosity, depth, reservoir thickness, and pressure from the Paddy formation were considered during the laboratory analysis to reproduce the sensitivity of this formation for aqueous fluid invasion (Bennion et al. 1994; Cimolai et al. 1993). The mentioned parameters were adopted to generate the initial conditions in a vertically homogeneous and radially symmetric wellbore model, as shown in Table 3.6.

Table 3.6. Reservoir - Wellbore Parameters.

Reservoir Parameters	Value	Unit
Depth	1700	m
Reservoir Pressure	10.4	MPa
Formation Thickness	25	m
Average Porosity	15	%
Permeability Range	15 - 170	mD
Formation Temperature	60	°C

Water injection was simulated at the early stage of production, intending to reproduce the condition created by the invasion of the water phase into the wellbore region. For sensitivity analysis, three invasion radii of 4, 10, and 16 meters were considered while using Equation 3.1 to calculate the amount of chemical solution to be injected (V_{wb}). This volume is directly proportional to the square difference of the invasion diameter (d_{inv}) and wellbore diameter (d_{well}) at a determined reservoir thickness (Z). For every simulation scenario, the invasion radius defines the region or area over which the relative permeability properties are altered while the rest of the reservoir would maintain its initial value. This arrangement reflects the fact that water blockage occurs only in the vicinity of the wellbore. Therefore, three relative permeability cases and water saturation levels were created to represent the initial condition of the reservoir and the altered zone region effect of water blockage (Appendix A). Figure 3.16 shows the water saturation model principally characterizing the area around the wellbore with a water saturation value of 80% (S_{wc}), while the rest of the reservoir has an initial water saturation of 40% (S_{wi}), which is a typical irreducible water saturation as reported in the literature (Bennion, Thomas and Ma 2000a).

$$V_{wb} = \frac{\pi \times (d_{inv} - d_{well})^2}{4} \times Z \qquad \text{(Equation 3.1)}$$

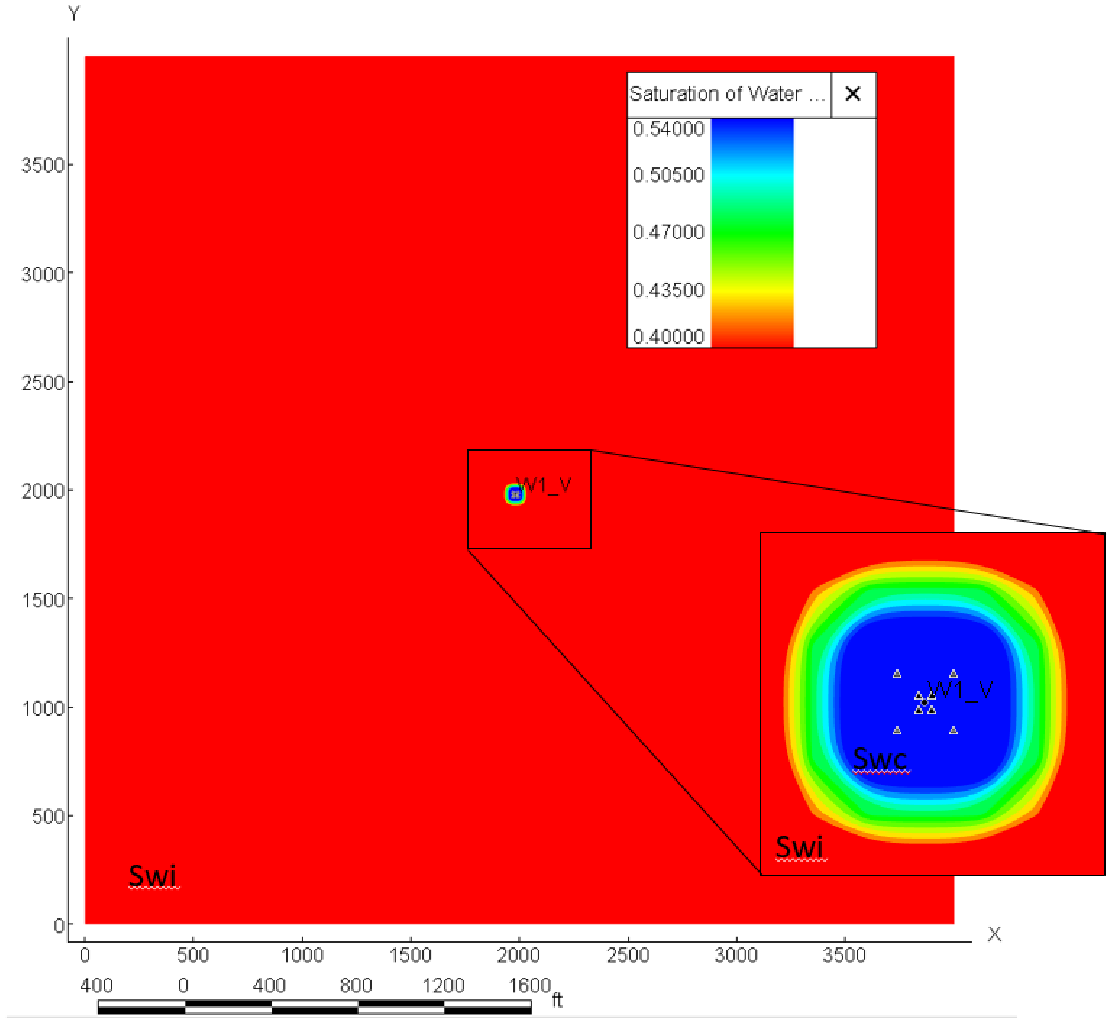


Figure 3.16. Water saturation model – initial conditions – area around the well with water blockage effect (blue coloured) and beyond wellbore region with no water blockage (red colour).

After the well setup, different production simulation scenarios were established at a constant flow rate of 1500 Mscf/day for thirty months. The minimum bottom-hole flowing pressure was set at 10 MPa. The entire reservoir interval (25 m) was considered open to flow. Broadly categorized, we considered two sets of scenarios in our box model simulation runs, one with and one without the water blockage effect, with details of each set presented below:

INITIAL RESERVOIR SCENARIO. - This is an ideal scenario representing the initial conditions of the reservoir with no water blockage effect considered. Accurately measuring initial water saturation is a complex challenge requiring special coring techniques using hydrocarbon-based mud or water-based mud with some chemical tracers. Bennion defined a permeability and initial water saturation relationship with the aqueous phase trap index (APT), which mainly defines the trapping sensitivity effect. An APT between 0.8 to 1 is a zone of potential damage; therefore, a value of 1 is assumed for initial water saturation (S_{wi}) (Equation 3.2) and relative permeability to gas (kr_g) (Equation 3.3)(Bennion et al. 1996b).

$$Sw_i = \frac{APT - 0.25\ Log_{10}(k_{abs})}{2.2} \qquad \text{(Equation 3.2)}$$

$$kr_g(S_w) = kr_g{}' \times (S_e)^x \qquad \text{(Equation 3.3)}$$

$$S_n = \frac{Sw_{max} - Sw}{Sw_{max} - Sw_{min}} \qquad \text{(Equation 3.4)}$$

Where krg' is the relative permeability endpoint of the non-wetting phase, which is assumed to be double the relative permeability endpoint measured in the lab before the rock treatment (Bennion, Thomas and Ma 2000a; Bennion et al. 1996b; Bennion, Thomas and Ma 2000b). This was done by simply extrapolating the relative permeability to gas before treatment as determined experimentally. The m value represents the relative permeability shape factor, which is typically a value higher than 1. The Sn value represents the normalized water saturation, Sw_{max} is the maximum water saturation value, and Sw_{min} is the minimum water saturation. Additionally, when modeling the low permeability scenario, the calculated initial water saturation has been increased by 25% to simulate a pessimistic scenario, which will prevent us from overestimating the final result (Appendix A).

WATER INVASION SCENARIOS.- Three well production scenarios examining the water blockage effect with different benzoxazine treatment radii (of 4, 10, and 16 meters) were simulated with identical initial saturation conditions. Figure 3.17 shows a schematic of the different scenarios with the corresponding water saturation conditions. Similar scenario setups were then used to illustrate the enhanced productivity effect of the wettability alteration caused by benzoxazine treatment. The main input data in simulating the above scenarios were the relative permeability curves obtained from the 1D core-scale analysis to upscale the experimental core-flooding results to the wellbore box model.

It is worth noting that different permeability values of 15 mD (this study) and 130 mD (our previous study (Mauricio Ceron Lopez et al. 2021)) were used in separate models to investigate the effect of absolute permeability on the achievable productivity enhancement resulting from wettability alteration.

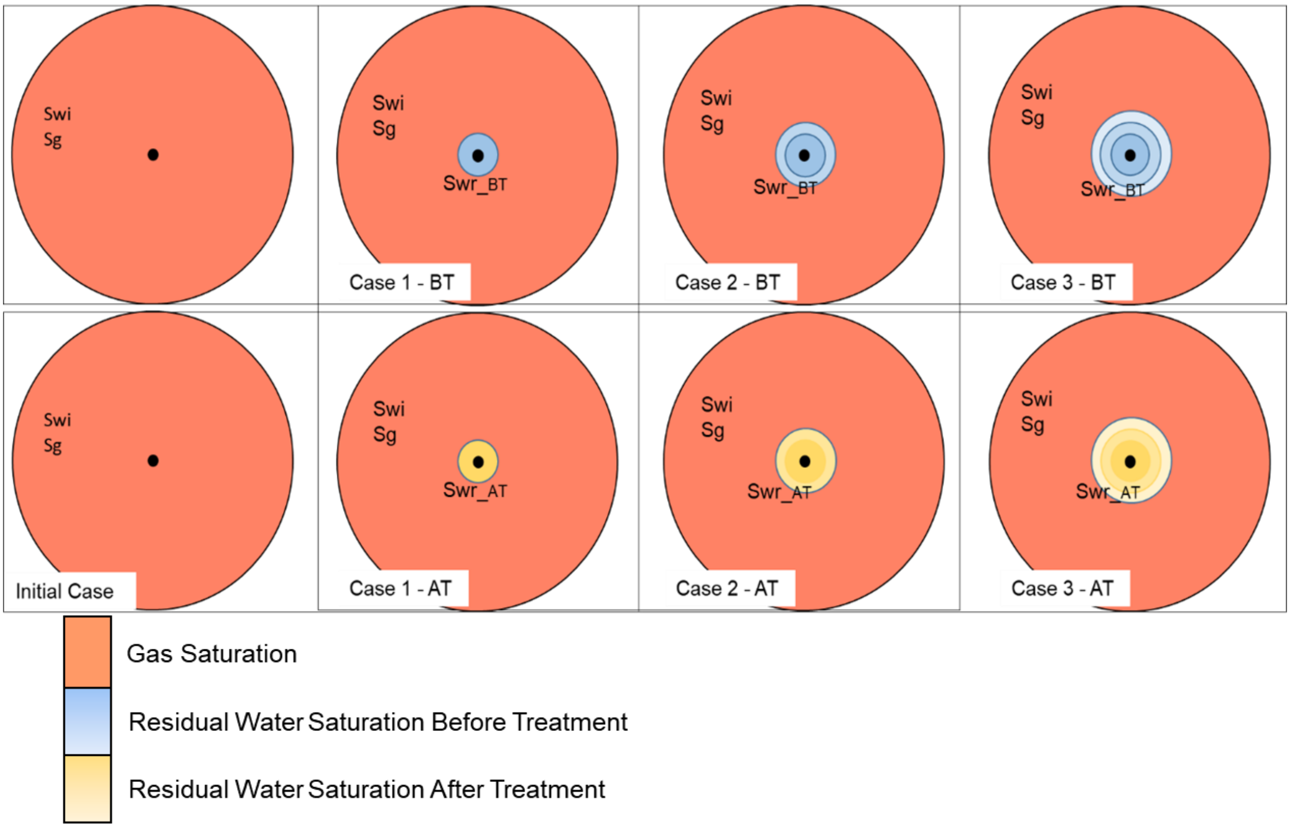


Figure 3.17 Schematic diagram of the initial water saturation (Swi), residual water saturation before treatment (Swr_BT), and residual water saturation after treatment (Swr_AT) for three different water invasion scenarios.

CHAPTER 4 EXPERIMENTAL RESULTS, INTERPRETATION AND DISCUSSION

As indicated and described in detail in Chapter 3, a combination set of experimental and numerical simulation techniques were used to achieve the objectives set for this PhD research. The current chapter aims to present and discuss the results from the above investigations. The chapter will review and interpret the experimental results first before discussion their implications at larger scale based on the outputs generated by wellbore scale simulations.

4.1. Initial assessment on wettability alteration

4.1.1. Polybenzoxazine surface energy characteristics

When sandstone samples are treated with the BZ monomer (i.e. a monolayer forms on the rock surface through the reaction of the silane moiety in the BZ compound and the silicates present on the surface of the sandstone), the surface free energy does not reflect any immediate improvement in wettability alteration. However, after curing the rock sample with simple heating in an oven at 180°C for 1 hour, the monomer undergoes ring-opening polymerization of the oxazine ring present in the benzoxazine molecule. The above takes place due to the ring-opening forming a cationic initiator that then promotes the surface polymerization (Ishida 2011). This process is accompanied by a complex combination of intramolecular and intermolecular interactions between O-H and N-H bonds resulting from the polymerization.(Kim and Ishida 2011) Intramolecular interactions increase with temperature while intermolecular interactions increase with the increment of the curing time. After the curing process, the surface is coated with the polymer resulting in a substantial decrease in the surface free energy of the treated rock sample. Such a change would then increase the water contact angle, resulting in a significantly more hydrophobic substrate (Wang, Su, et al. 2006; Qu and Xin 2011; Wang, Chang and Kuo 2011; Liu et al. 2013).

Figure 3.13 shows the structure of the chemical before and after polymerization. It depicts the polybenzoxazine after thermal polymerization and the complex interaction of both intramolecular and intermolecular forces between the hydrogen-nitrogen and hydrogen-oxygen atoms of the benzoxazine structure, respectively. It is these interactions that give rise to the wettability change that is observed.

4.1.2. Contact Angle Measurements

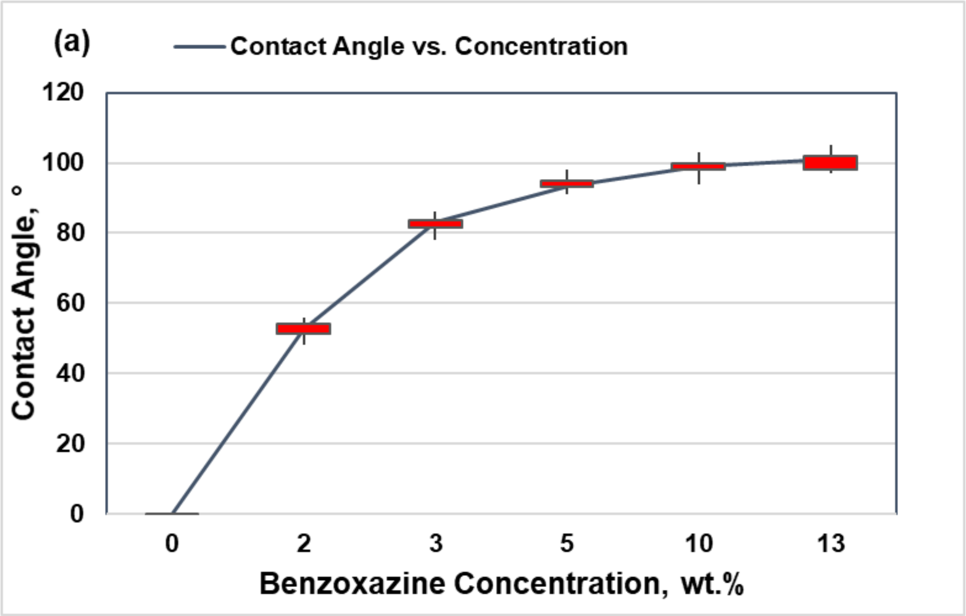
As indicated earlier, the contact angle measurements were conducted on rock substrates to assess the extent of any possible wettability alteration caused by the BZ treatment and also optimize the treatment process with respect to the solvent type, BZ concentration and to some extent the rock sample type. To ascertain the effects of solvent type, Berea sandstone was treated using a 10 wt. %

solution in THF and cured at 180°C for 1 hour. Such a treatment shifted the contact angle of the water-air-rock system from 0° to 101°. Another treatment conducted on the same rock type and under the same conditions using a similar solution prepared in acetone shifted the contact angle from 0 to 99° (Table 4.1). It is evident from these results that using acetone as the solvent results in a similar or slightly lower contact angles. For subsequent experiments, we decided to use THF as a solvent.

Table 4.1. Contact angle measurements on Berea sandstone before and after treatment with a 10 wt.% BZ solution as prepared using acetone and THF solvents.

Concentration	Solvent	Average Contact Angle (°)
Before Treatment	Acetone	0
After Treatment	Acetone	99
Before Treatment	Tetrahydrofuran	0
After Treatment	Tetrahydrofuran	101

The data measured under varying BZ concentrations (2, 3, 5, 10 and 13 wt.%) indicate that the water contact angle increases with increasing concentration (after 1 hour of curing at 180°C), suggesting an improvement in the hydrophobic condition of the rock (Figure 4.1a). For example as can be seen from 4.1a, treating sandstone surface with 5 and 10 wt.% BZ, increases the contact angle from 0° to 90° and 100°, respectively. While the primary objective of this work is to achieve a less water-wet condition, a negligible contact angle increment seems to be achieved for concentrations higher than 10 wt.% (Figure 4.1b). Furthermore, there is the possibility at higher concentrations that the polymer might begin to impede permeability if some of the monomer is no longer attached directly to the surface during polymerisation. A similar trend in contact angle change has been reported for other chemical treatments by other researchers. Fahes et al. (Fahes and Firoozabadi 2005). treated Berea sandstone cores with 2 and 8 wt.% fluoroaliphatic silyl ether concentrations to obtain water contact angles of 135° and 150°, respectively. Likewise, Wang et al. (Wang et al. 2015) increased the water contact angle when treating sandstone samples with a fluorinated chemical with concentrations ranging from 0.1 to 0.8 wt.%. They observed that at a higher concentration of 0.6 wt.% the water contact angle could increase to around 140°. Our results show that using a concentration between 5 and 10 wt.% of BZ the most hydrophobic condition could be achieved. 4.1b depicts the change in water droplet shape and contact angle over the rock sample treated with 5 wt.% BZ for different exposure times (i.e. 5, 25 and 45 minutes). As can be seen, although the contact angle value decreases with time, the chemical is still able to offer good level of water repellency delaying the water absorption in the pore space of the rock substrate. Given the above favourable contact angle results as well as the straightforward synthesis process and the availability of the chemicals for reaction, BZ monomer can be considered as a cost-effective alternative for such rock treatments, which is also relatively environmentally friendly.



(b) Post- Treatment Water Contact Angle

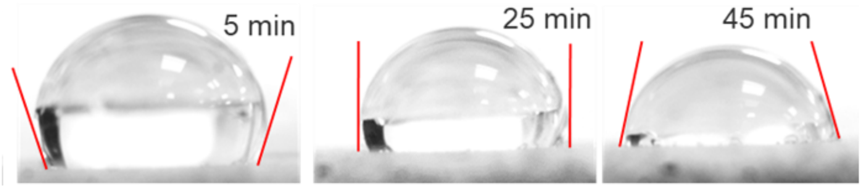


Figure 4.1. Contact angle measurements: (a) Change in water contact angle on Berea sandstone sample with change in chemical concentration in acetone (b) Time dependency of water droplet shape on Berea sandstone treated with 5wt.% BZ in acetone.

Despite the above positive results, contact angle measurements may be considered a highly localised technique conducted on a small substrate and are only indicative of results on a larger scale. Therefore, it is essential to use other more robust and reliable techniques to evaluate the effect of the chemical concentration on dynamic multiphase flow characteristics of the fluid-rock system e.g. the relative permeability and residual saturations. Spontaneous imbibition tests and, most importantly, coreflooding experiments, whose results will be presented and discussed in upcoming sections of this chapter are considered much more insightful with respect to the above.

Using a 5 wt.% BZ solution in acetone and curing for 60 minutes at 180°C, both sandstone rock types used in this work were treated. Under this treatment, the contact angle for the Berea sample increased from 0 to 95° while for BUG2 increased from 0 to 89° demonstrating that a slightly less water-wet condition could be achieved in the latter sample (Table 4.2). Such a difference can be attributed to a combination of possible experimental factors such as variation in rock mineralogy, surface roughness differences, etc.

Table 4.2. Contact angle measurements on Berea and BUG2 before and after treatment with 5 wt.% BZ monomer.

	Rock Sample	Contact Angle (°)
Before Treatment	Berea	0
After Treatment	Berea	95
Before Treatment	BUG2	0
After Treatment	BUG2	89

Initially, when water is brought in contact with an untreated sandstone rock surface, the basic components of quartz interact with the polar components of water. Therefore, the liquid phase rapidly spreads over the rock surface. At that point, the surface free energy of quartz is around 76 mJ/m2 (Fowkes 1968), while water surface tension is around 72 mJ/m^2 (Zdziennicka, Szymczyk and Jańczuk 2009). In 2000, Jin et al. (Jin et al. 2016) decreased the surface free energy of sandstone samples to less than 20 mJ/m^2 using a fluorinated solution as the surface treatment agent. Other researchers, such as Wu et al. (Wu and Firoozabadi 2010b) have used fluoropolymers to increase the water contact angle from 0 to 110° by lowering the surface free energy. Similarly, Firozabadi et al. (Li and Firoozabadi 2000) used a commercial fluorocarbon polymer to treat a sandstone sample and the contact angle increased from 0° to 125°. Those results indicate that the surface free energy decreases resulting in an increase in the water contact angle with increase fluorine content in the polymers. In our case however, in samples with high quartz content (more than 80%) and intermediate permeability values (between 120 to 230 mD), the treated rock surface reaches hydrophobic conditions by altering the surface free energy of the rock sample using a non-fluorinated compound.

The BZ monomer polymerisation or curing time affects the resultant rock surface tension when curing at an adequate curing temperature such as 180°C used in this work. For instance, our surface free energy calculations done using equations 1-3 show an average value of around 34 mJ/m^2 over the curing times of 60 to 180 minutes for a 10 wt.% solution, while the surface energy value increases with longer curing times (Figure 4.2). A similar trend was observed among the contact angle data measured under varying curing times, showing an increase over curing times of 60 to 180 minutes but a decrease with longer curing times (Figure 4.2). Other researchers found that the curing time during thermally accelerated polymerisation of benzoxazine resins has a significant influence over contact angle value as well as surface free energy (Selvi et al. 2014; Jin et al. 2016). For example, Liu et al. showed that the surface free energy of treated glass with a benzoxazine resin at a curing temperature of 180 °C reaches its lowest value during the first 120 minutes and then increases when the curing time is continued for 1200 minutes (Liu et al. 2013; Qu and Xin 2011). In our case, the best hydrophobic condition (i.e. minimising the surface tension of the rock sample and increasing the water contact angle) could be achieved by heating the treated sample at 180°C for only 60 minutes. The ideal curing temperature to increase hydrophobicity is 180°C, nevertheless, when polymerising the chemical at lower temperatures, the curing time should be increased to obtain adequately low surface free energy values (Liu et al. 2013; Gogoi et al. 2014).

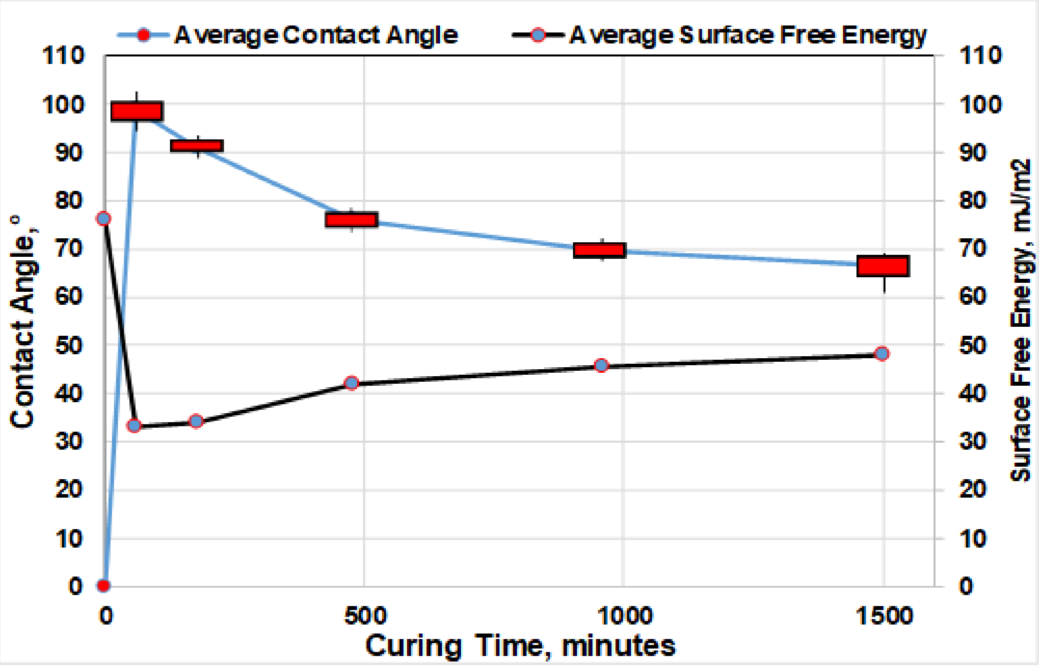


Figure 4.2. Water contact angle and surface tension of Berea sandstone at different curing times at 180°C.

4.1.3. Spontaneous Imbibition Tests

The amount of water spontaneously imbibed into a water-wet rock sample depends on its degree of water wetness. In fact, based on the Young-Laplace definition(Causserand and Aimar 2010), the capillary force that encourages the invasion of the wetting phase into a porous medium is inversely proportional to the contact angle value. Therefore, any wettability alteration generated by a chemical treatment that modifies the surface properties of an originally water-wet porous rock may be reflected by the volume of water spontaneously imbibed into the rock.

In the current work, spontaneous imbibition tests were conducted on two BUG core plugs (BUG1 and BUG2) to evaluate the effectiveness of the BZ treatment in improving water repellency in sandstone rocks. However, before these tests, an evaluation was done into the possible impact of the BZ treatment on the absolute permeability of the core plugs. Our investigations revealed that treating the core plugs with 5 and 10 wt.% BZ in acetone cured at 180°C for 1 hour would not have a considerable effect on their gas permeability. Table .3 indicates a maximum reduction of 6% in the gas permeability of the samples while their weights increased by 1.56 and 3.65 mg/g after the chemical treatment of BUG1 and BUG2 with 5 and 10 wt.% BZ, respectively. Wu et al. reported 9 to 27% gas permeability reduction when treating rock samples with 0.25 to 3 wt.% fluorinated chemicals, while the weight gain increment for their treated samples was around 1 mg/g.(Wu and Firoozabadi 2010b) Moreover, Karandish et al. measured the amount of chemical adsorption to be around 2.5 mg/g when treating rock samples with a fluorinated chemical (Karandish et al. 2015). The permeability measurements reported in Table .3 depict an acceptable reduction after rock treatment which does not compromise the gas flow in a treated rock formation. The weight gain increments for our samples (less than 3.7 mg/g) seem to be higher than those reported by other researchers. Such a difference may be attributed to the presence of polymer residues (i.e. without creating a bond through the silane moiety in BZ with the rock sample) in the pore space of the samples. After the above observations and subsequent to the gas permeability measures reported in Table .3, any unreacted polymer was removed by washing the rock samples using methanol and toluene in consecutive cleaning cycles over 24 hours. These cleaned samples were then used for the subsequent spontaneous imbibition and coreflooding experiments.

Table 4.3. The effect of BZ treatment on the gas permeability and dry weight of BUG1 and BUG2 core plugs.

Rock Sample	**Concentration (%)**	**Gas Permeability, (mD)**		**Weight Difference (mg/g)**
		Before Treatment	**After Treatment**	
BUG1	5	129	121	+1.56
BUG2	10	130	127	+3.65

The results of the spontaneous imbibition tests show a favourable reduction of water uptake into treated rock samples from 68% to less than 30% of their pore volume (PV) over approximately 200 minutes (Figure 4.3). These tests were also used to evaluate the effect of BZ concentration used for treatment and the extent of the wettability alteration as judged by the level of water imbibed into the treated samples. As apparent from Figure 4.3, doubling the BZ concentration from 5 to 10 wt.% resulted in 6% PV (from 28% PV to 22% PV) reduction in the water uptake into the BUG sandstone. Wu et al. (Wu and Firoozabadi 2010b) performed similar spontaneous imbibition tests on sandstone samples showing a reduction of water uptake from 60% PV to around 13% PV with a fluorinated compound treatment. Similarly with a different a fluorinated chemical, Karandish et al.(Karandish et al. 2015) demonstrated a water imbibition reduction from 60% PV to less than 10% PV. In both cases, the use of fluorinated chemicals can decrease the water imbibition by approximately 50% PV.

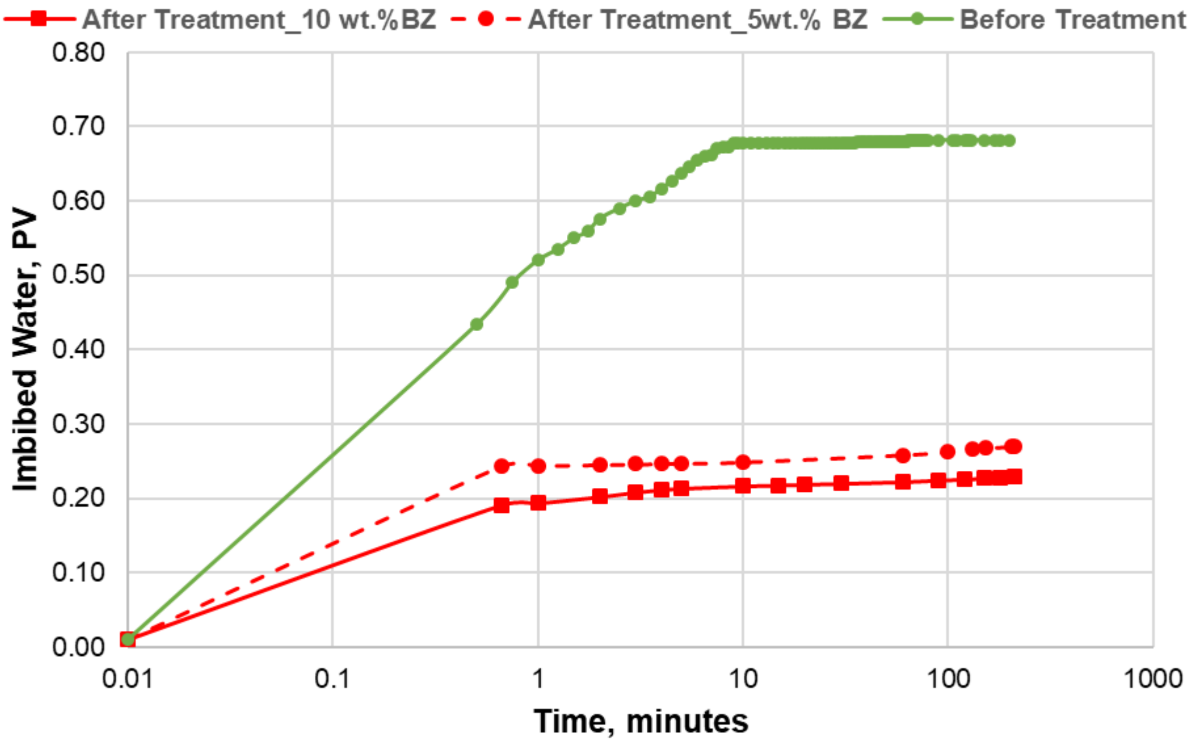


Figure 4.3. Spontaneous water imbibition profiles – BUG2 sample without chemical treatment (green line), BUG1 sample treated with 5 wt.% BZ (red broken line) and BUG2 sample treated with 10 wt.% BZ monomer (red solid line).

4.1.4. Core-flooding Experiments

As mentioned earlier, altering the wettability of a near wellbore rock formation from a strongly water-wet state to an intermediate gas-wet condition could help with reducing any pre-existing excessive residual water saturation in this region. This change could then improve the effective permeability to gas and alleviate the potential severe restriction put on the gas flow. Such a desirable outcome can be observed from the data obtained from our core-flooding experiments. Figure 4.4 presents the differential pressure data recorded across BUG2 core plug during gas injection into this sample at 10.35 MPa and 60°C before and after chemical treatment (10 wt.% BZ in acetone cured at 180°C for 1 hour). As evident from the plotted data, lower differential pressures were recorded for much of the duration of the gas flooding conducted on the treated plug yielding a higher end point effective permeability to gas in this sample. The data presented in Table 4.4 reveals a 10% reduction in the residual water saturation and an almost 22% improvement in the end point gas relative permeability in the treated sample. As demonstrated by both contact angle and spontaneous imbibition tests, the BZ polymer coating on the rock pore surfaces increases the hydrophobicity that would then improve water removal during the gas injection, which would, in turn, reduce the pressure differential during gas flooding, implying a higher effective permeability to gas. A similar behaviour has been reported by other researchers who conducted core-flooding experiments at elevated pressure and temperature. For example, Fahes et al.(2005) observed a decrease in the pressure drop during brine injection into core plugs after treating the rock sample with a fluorinated chemical (Fahes and Firoozabadi 2005).

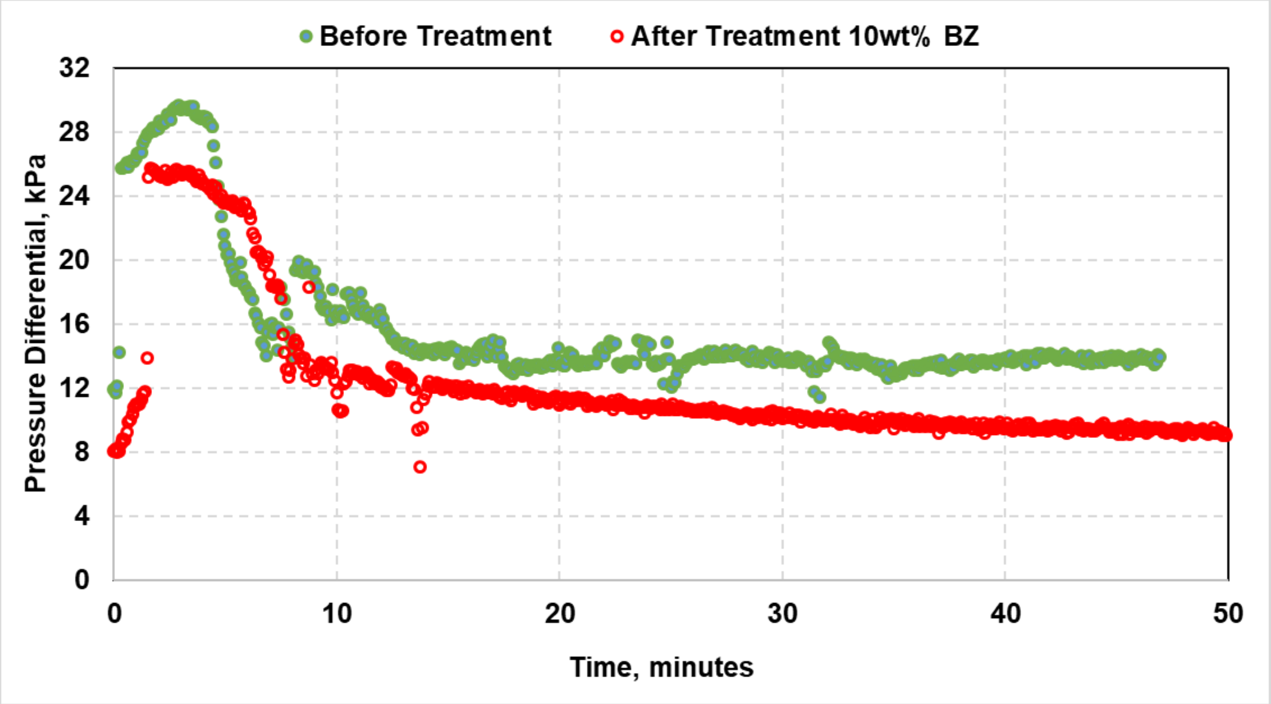


Figure 4.4. Pressure differential profiles recorded during gas injection before and after 10 wt.%. BZ treatment – BUG2 sandstone.

Table 4.4. Residual water saturation and end point relative permeability results before and after chemical treatment - BUG2.

CASE	S_{wr} (%)	End point K_{rg} (fraction)
BEFORE TREATMENT	59.6	0.060
AFTER TREATMENT	53.8	0.073

The positive effect of our BZ treatment on water recovery is further confirmed with the water production profiles plotted in Figure 4.5. As can be seen from this figure, the gas breakthrough is postponed in the treated sample resulting in a pronounced difference between the two profiles. Li et al.(Li et al. 2011) demonstrated an increase of around 16% in the final water recovery in a low permeability (less than 10 mD) sandstone sample treated with a fluorinated solution as measured using a core-flooding test. The higher water recovery increment achieved by Li et al. may be attributed to the higher degree of hydrophobicity achieved using fluorinated compounds and that the water blockage is expected to be more severe in low permeability samples. Regardless of these conditions, the water increment during core-flooding suggests clear evidence of rock wettability alteration from strongly water-wet to less water-wet.

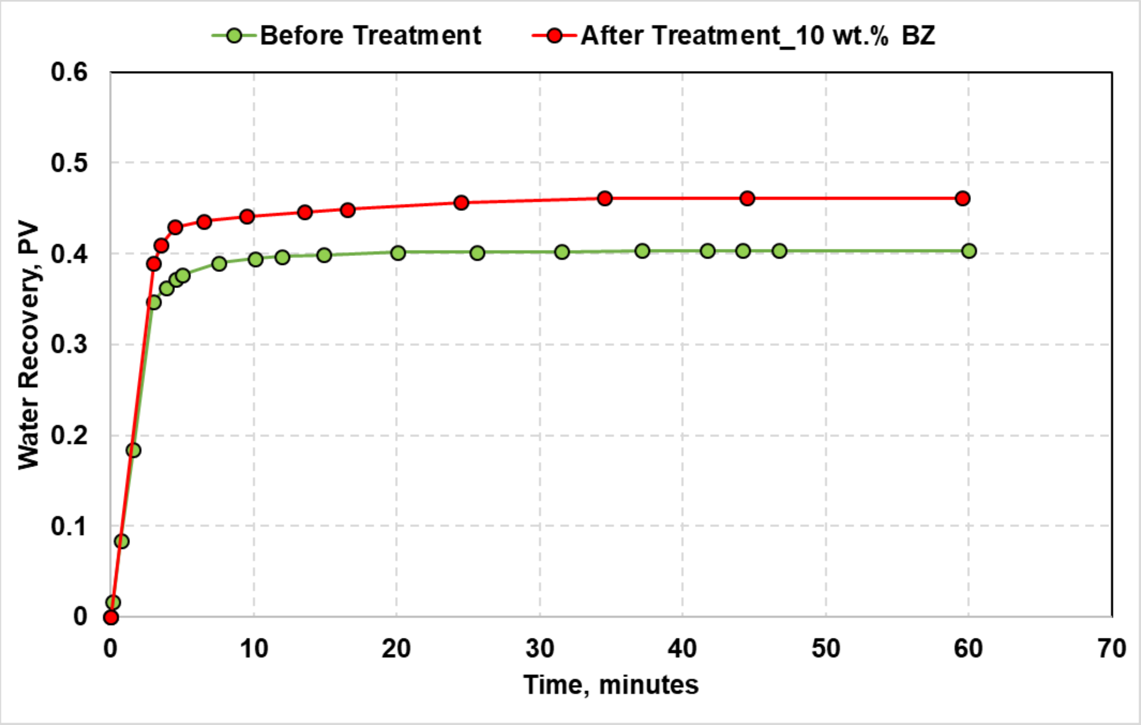


Figure 4.5. A comparison between the water recovery during gas injection conducted before and after BZ treatment (10 wt.%)- BUG2 plug.

4.2. Complementary Screening in Low permeability rock samples

This section describes the most relevant characteristics of the benzoxazine treatment at different static and dynamic conditions. Initially, the chemical polymerization temperature was tested between 120 to 180 C, ° and ambient condition contact angle measurements were conducted to optimize the curing temperature/monomer concentration. Spontaneous imbibition experiments were also conducted to evaluate these effects as well on rock samples with initial permeability values less than 20 mD. Following this, core flooding experiments using realistic reservoir conditions (e.g., low permeability, low chemical concentration) were conducted at elevated pressure/temperature values. Following this, a wellbore model was built to assess the effect of the chemical treatment around the wellbore area at different treatment conditions, such as invasion radius and rock permeability. The effect of chemical concentration on rock permeability was also evaluated.

In our previous study (Mauricio Ceron Lopez et al. 2021), which used moderate permeability BUG sandstone (~130 mD), a 10 wt.% solution of benzoxazine resin monomer was applied using a curing temperature of 180 °C. Given the reasonable permeability of these samples, there was less concern around permeability loss due to treatment. As reported, our investigation revealed only a very subtle (on average ~5%) decrease in sample permeabilities after treatment. However, given the low permeability of CT samples used in the current study, there was a genuine concern about the significant effect of treatment on sample permeabilities if the same high concentration was used here. Therefore, it was deemed necessary to optimize the chemical concentration so we would strike a balance between adequate surface coverage to induce necessary wettability alteration and the negative effect on permeability.

A detailed description of how our novel benzoxazine would work was provided in our previous work (Mauricio Ceron Lopez et al. 2021). However, in brief, at an elevated temperature (i.e., 180 °C or lower, as examined later in this manuscript), the benzoxazine monomer structure undergoes ring-opening polymerization leading to the formation of intramolecular forces between polymer chains, thus decreasing the surface energy of the rock and the associated capillary strength of the pores. This effect can be manifested in a reduction in the rock's spontaneous brine imbibition rate, as discussed in more detail in our previous study. Therefore, a decision was made first to perform a preliminary investigation into the effectiveness of a reduced benzoxazine concentration (i.e., 2.5 wt.%) in changing spontaneous imbibition characteristics of the CT sandstone when compared with that of a much higher concentration (i.e., 8%). Spontaneous imbibition experiments were conducted over a longer period of time relative to the contact angle measurements (time duration 30 minutes to 1 hour). In doing the above evaluation because, as discussed in our previous work (Mauricio Ceron Lopez et al. 2021), the former technique is done at the larger core scale as compared with contact angles that may be considered highly localised property of a surface conducted over a very small surface portion of a substrate. Furthermore, the spontaneous imbibition process can also be considered much more insightful in relating to the dynamics of the rock-fluid system as they are impacted by the pore network and wide pore size distribution in a core sample.

Initially, samples CT1 and CT4 were treated with 8 and 2.5 wt.% monomer concentrations, respectively, while curing conditions remained similar (180 °C for 1 hour). The purpose of using this considerable difference in benzoxazine concentration was first to compare the effect of a high benzoxazine concentration value (closely similar to the concentration used in our previous research analysis, as well as other researchers' chemical concentration used for rock sample treatment) versus a low concentration, which can avoid a possible pore diameter reduction due to chemical adsorption and presence in the porous space. As evident from the data plotted in Figure 4.6, both samples behaved similarly regarding the rate and eventual level of water that spontaneously imbibed into their pore spaces before treatment. However, as expected, the treated sample CT1 exhibited a considerably larger reduction in brine imbibition rate in comparison to CT4. Furthermore, when the samples reached equilibrium, CT4 had imbibed four times more water than CT1 (see Figure 4.6). These results suggest that the degree of wettability alteration is directly proportional to the chemical concentration present in the solution. Nevertheless, the result obtained for sample CT4 was still considered positively significant, as will be demonstrated further by the results of the core flooding experiments discussed later. Therefore, our attention was shifted to the effect of the chemical concentration on the pore network and the absolute permeability of CT sandstone.

With the positive effects of the chemical treatment on the spontaneous imbibition results being evident at the proposed chemical concentrations, we evaluated the permeability loss associated with both concentrations in samples CT1 and CT4. As evident from data presented in Table 4.5, 8 wt.% concentration reduced CT1 permeability from 21.1 mD to 16.2 mD, translated to 22.2 % of its initial permeability, which is a considerably unacceptable amount for an already low permeability rock. The significance of the above reduction may become more apparent, knowing that in our previous work, a 10 wt.% concentration tried with moderate permeability rocks (~130 mD) only induced a 2.3 - 6.2% permeability reduction. In comparison, the 2.5 wt.% concentration caused only a 10.7 % reduction in the permeability of sample CT4, which shows negligible results of permeability reduction that would not mean a drastic alteration of the pore diameter in size reduction/ increment as previously analysed by other researchers (Fahes and Firoozabadi 2005; Noh and Firoozabadi 2008b). They found a maximum absolute permeability reduction of around 8 to 19 % in rock samples with absolute gas permeabilities between 2 to 10 mD after chemical treatment with a fluorinated concentration range between 4 and 8 wt.%. Fahes et al., 2005 discarded samples treated with 8% fluorinated chemical solution due to a drastic permeability reduction of around 80%. The high amount of the chemical present in the pore system could drastically alter the flowing conditions through the rock sample. Furthermore, Noh et al 2008 discarded rock samples treated with 2 to 4 wt.% fluorinated chemical due to a more than 22% absolute permeability reduction after rock treatment. Therefore, in this study, the most suitable benzoxazine concentration during rock treatment was established as 2.5 wt.% to maintain a lower than 10% permeability reduction, to minimize the effect of chemical polymerization in the pore system by any possible blockage of the pore throat or reduction of the pore diameter in Carbon Tan rock samples between 10 to 20 mD. After thermal polymerization, rock samples were washed with a solvent (e.g., methanol) followed by a substantial water displacement at high pressure of 10.35 MPa, to minimize the presence of the remaining polymer that did not create a covalent bond with the surface of the rock.

Table 4.5 Physical characteristics of Carbon Tan sandstone samples, the treatment conditions and permeability variation before and after treatment.

Sample ID	Diameter (m)	Length (m)	Resin conc. (wt.%)	Curing Temp. (°C)	Curing Time (hrs)	Gas Permeability (mD)		Gas Permeability Reduction (%)
						Before treat.	After treat.	
CT1	0.038	0.0763	8	180	2	21.1	16.2	22.2
CT2	0.0379	0.0762	2.5	125	2	18.4	16.5	10.3
CT3	0.0379	0.0764	2.5	150	2	21.3	20.2	6.1
CT4	0.038	0.0765	2.5	180	2	17.5	15.8	10.7
CT5	0.0385	0.0761	2.5	110	48	6.8	6.5	3

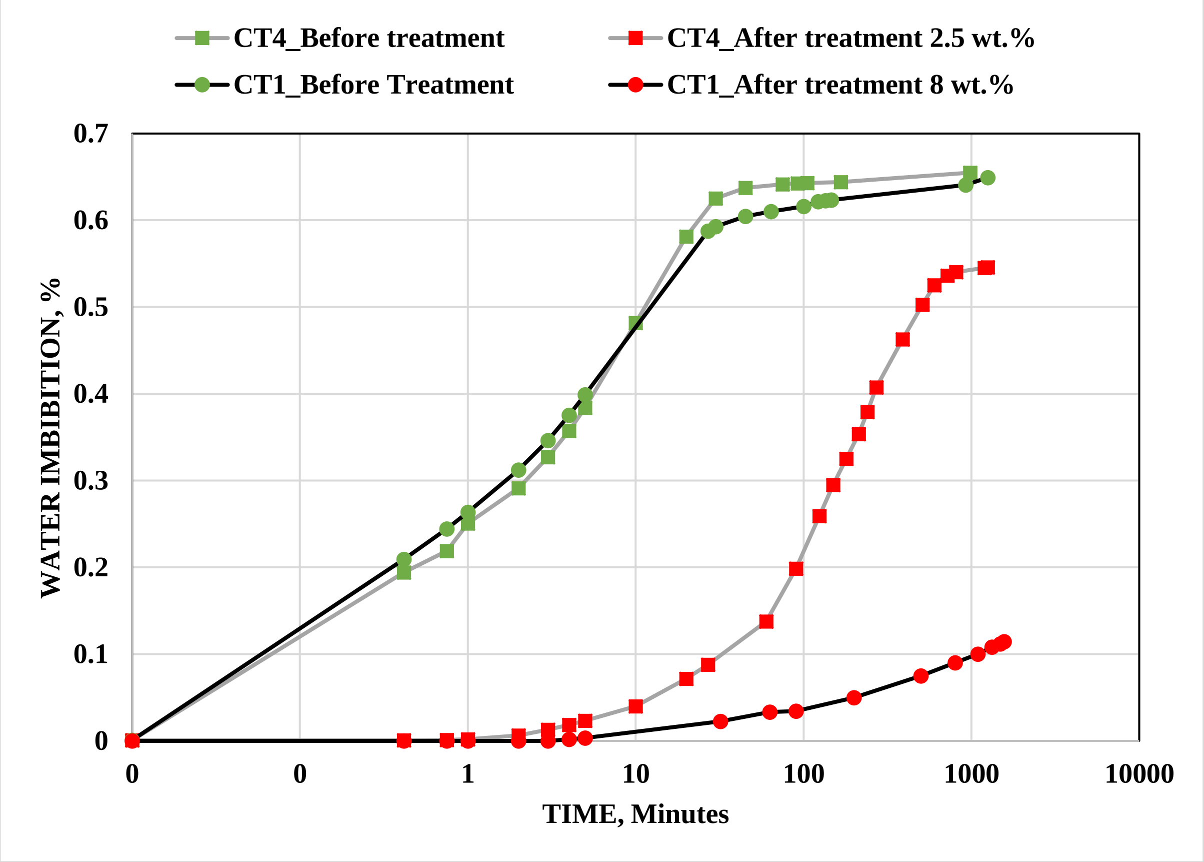


Figure 4.6. Spontaneous brine imbibition results of CT4 (2.5 wt.% benzoxazine concentration) and CT1 (8 wt.% benzoxazine concentration) both thermally polymerized at 180 °C (BT: Before treatment, AT: After treatment).

4.2.1. Effect of curing temperature on contact angle and spontaneous imbibition results

After determining that a 2.5 wt.% treatment solution would produce acceptable wettability alteration without a significant adverse effect on rock permeability, our attention turned to the possibility of reducing the curing temperature, which would expand the application envelope of our novel benzoxazine treatment to a lower temperature (e.g., shallower) reservoirs. This section of the manuscript will present and discuss the results of the contact angle measurements and spontaneous imbibition tests performed in pursuing the above possibility.

Based on our previous study, contact angle values between 90 and 110° could be achieved, indicating intermediate wettability conditions and the ability to alleviate part of the damage associated with water blockage (Mauricio Ceron Lopez et al. 2021). Furthermore, values in this range are consistent with those obtained for the same resin cured on glass surfaces (Liu et al. 2013). Table 4.6 shows the average water contact angle measured under ambient conditions over substrates cut from rock samples CT2, CT3, and CT4 that were all treated using 2.5 wt.% concentration but at 125, 150, and 180 °C curing temperatures, respectively. As can be seen, the most favourable result obtained was 108° when the polymerization temperature reached 180 °C, while lower 89° and 99° were obtained at milder curing temperatures of 150 °C and 125 °C, respectively. Besides the above investigation, with sample CT5 we also explored the possibility of achieving acceptable results by reducing the curing temperature further to 110 °C but extending the curing time to 48 hours. As reported in Table 4.6, although this treatment managed to shift the wettability towards less water-wet conditions, the contact angle remained in the range of 50-60°, suggesting that at this highly reduced temperature, the monomer had very likely attached to the rock surface through the silane moiety. Extensive polymerization had not occurred; therefore, surface energy could not be reduced to the necessary low levels. Given this unsuccessful outcome, the treatment conducted on CT5 was excluded from subsequent evaluations to evaluate the benzoxazine treatment's performance at reduced curing temperatures. It is worth noting that the contact angle values reported in Table 4.6 are average values of 10 separate measurements conducted on a rock substrate at the experimental condition specified in the table.

Table 4.6. Contact angle results for 2.5 wt. % treated samples at different polymerization temperatures (PV: pore volume).

Rock Sample	Curing Temperature, (°C)	Curing time (hrs)	Resin Conc. (wt.%)	Contact Angle (°)		Brine Imbibed (PV)		Change Brine Imbibed (%)
				Before	After	Before	After	
CT2	125	2	2.50	0	99	0.65	0.58	10.90
CT3	150	2	2.50	0	89	0.65	0.53	18.50
CT4	180	2	2.50	0	108	0.66	0.55	16.60
CT5	110	48	2.50	0	50-60	-	-	-

Intermediate wettability conditions for the two-phase system are obtained when the water contact angle is in the range of 75 to 105°. (Anderson 1986; Wang et al. 2011) Based on this classification, researchers investigating the application of fluorinated chemicals to alter rock wettability have typically reached values between 112 to 150° under similar conditions. (Fahes and Firoozabadi 2005; Al-Anazi et al. 2007; Noh and Firoozabadi 2008b; Li et al. 2011; Mousavi, Hassanajili and Rahimpour 2013; Zhang et al. 2014; Franco-Aguirre et al. 2018) In comparison, our results clearly demonstrate that the benzoxazine monomer can alter the surface of the rock from strongly water-wet to intermediate gas-wet conditions at even reduced polymerization temperatures during the treatment process. While the contact angle results were promising, as mentioned earlier, the spontaneous imbibition tests could be more insightful in revealing the performance of the benzoxazine treatment at reduced curing temperatures. The impure compounds in the synthesis process also affect the feasibility of polymerizing the benzoxazine resins based on the ring-opening process. Researchers evidenced that a non-catalytic polymerization in some benzoxazine types can occur even at 30 to 40 °C due to the phenolic impurities present in the synthesis process (Han et al. 2017; Akkus, Kiskan and Yagci 2020).

For a monomer concentration of 2.5 wt. %, Figure 4.7 compares the pre- and post-treatment spontaneous brine imbibition results for samples CT2, CT3, and CT4 cured at 125, 150, and 180 °C, respectively. Overall, all three samples behaved similarly before treatment, reaching a plateau of about 65% spontaneously imbibed brine saturation at 16.7 hours (Figure 4.7). Although a similar data set looks more scattered for the three samples after treatment, the water uptake plateau decreased to an average value of about 55% at 16.7 hours mark. These results suggest that the reduced 2.5 wt. % monomer concentration can still alter the rock wettability, producing an effect in the porous space to reduce the capillary strength while having only a tiny impact on the absolute permeability.

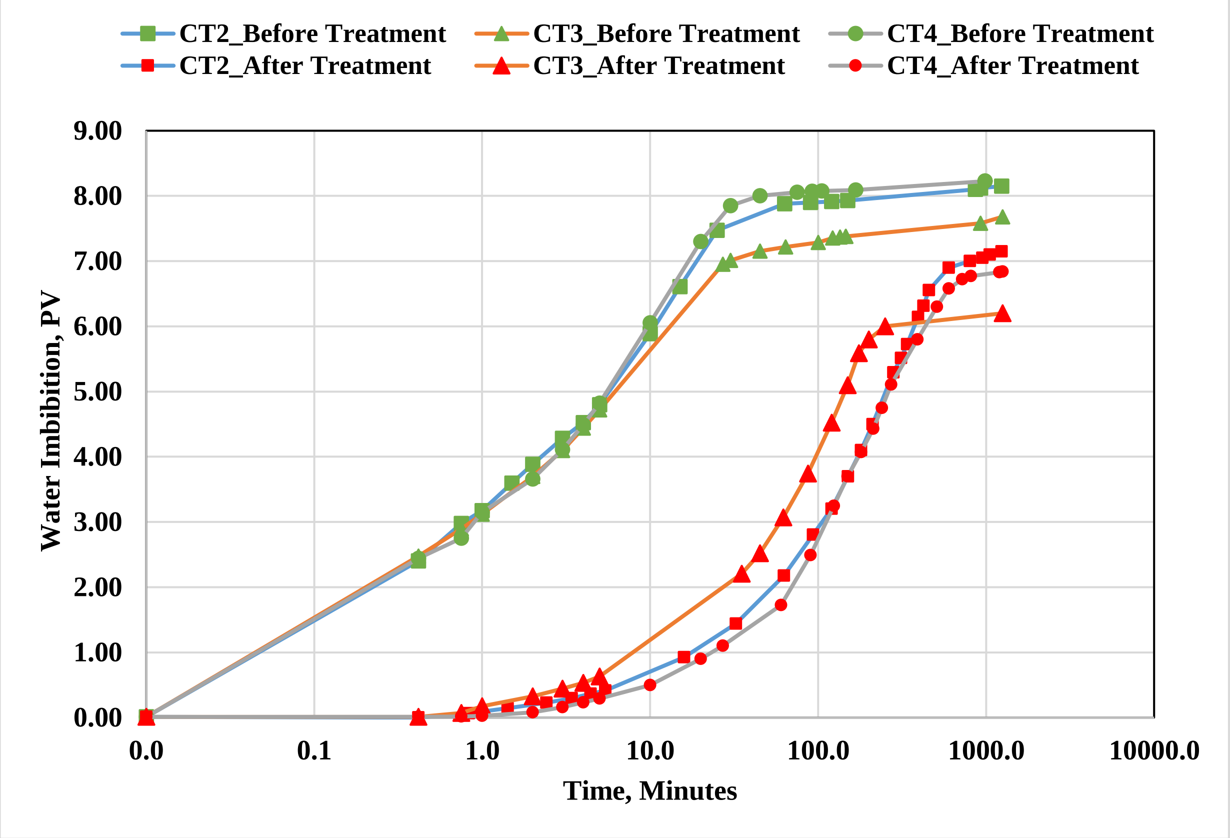


Figure 4.7. Spontaneous brine imbibition results for samples CT2, CT3, and CT4 before and after benzoxazine treatment (BT: before treatment, AT: after treatment).

The contact angle data recorded for all curing temperatures explored (Table 4.5) do not follow the expected decreasing trend with a reduction in the polymerization temperature of the benzoxazine monomer as suggested elsewhere (Liu et al. 2013). A similar unconformity is evident among the spontaneous brine imbibition results reported in Fig. 6, where one may expect that a water-wet rock's initial strength to imbibe water would be more preserved with a decrease in curing temperature. However, the above abnormal behaviour may not seem highly unexpected considering the difficulties associated with achieving desirable outcomes when treating natural porous rocks with complex pore networks and internal pore surface systems as opposed to the treatments done on highly ideal and uniform surfaces as that of glass (Liu et al. 2013).

4.2.2. Core flooding results

To further understand the implication of the induced wettability alteration, coreflooding experiments were conducted under elevated pressure and temperature before and after benzoxazine treatment on samples CT2, CT3 and CT4.

As a sample dataset, Figure 4.8 compares the pre and post-treatment differential pressure data (colored data points) recorded for the primary drainage floods conducted on CT3 during which gas displaced the initial brine-saturated sample. As can be seen, the treatment resulted in a reduction in the differential pressure data, which is more evident during post-breakthrough times. This reduction is attributed to improved gas relative permeability caused by enhanced brine removal from the sample's pore space. These effects are desirable outcomes of the induced wettability alteration, and they agree with the results published by other researchers who treated rock samples with wettability-altering fluorinated chemicals (Noh and Firoozabadi 2008b; Jiang, Li and Zhang 2013; Fahimpour, Jamiolahmady and Sohrabi 2012; Fahes and Firoozabadi 2005; Erfani Gahrooei and Ghazanfari 2017; Aminnaji et al. 2015). For example, Noh and Firoozabadi demonstrated a 24% reduction in differential pressure when applying a 4 wt.% concentration of a fluorinated chemical (Noh and Firoozabadi 2008b).

The above outcome is taken as further evidence that benzoxazine treatment can alter the wettability of sandstone rocks from strongly water-wet to intermediate gas-wetting resulting in improved gas mobility by alleviating water blockage in low permeability rocks. What is more, the above may be considered more significant than similar conclusions drawn from earlier discussed contact angle and spontaneous imbibition tests as the core flooding data (e.g., those reported in Figure 4.8) were measured under fully dynamic fluid flow and elevated pressure and temperature conditions.

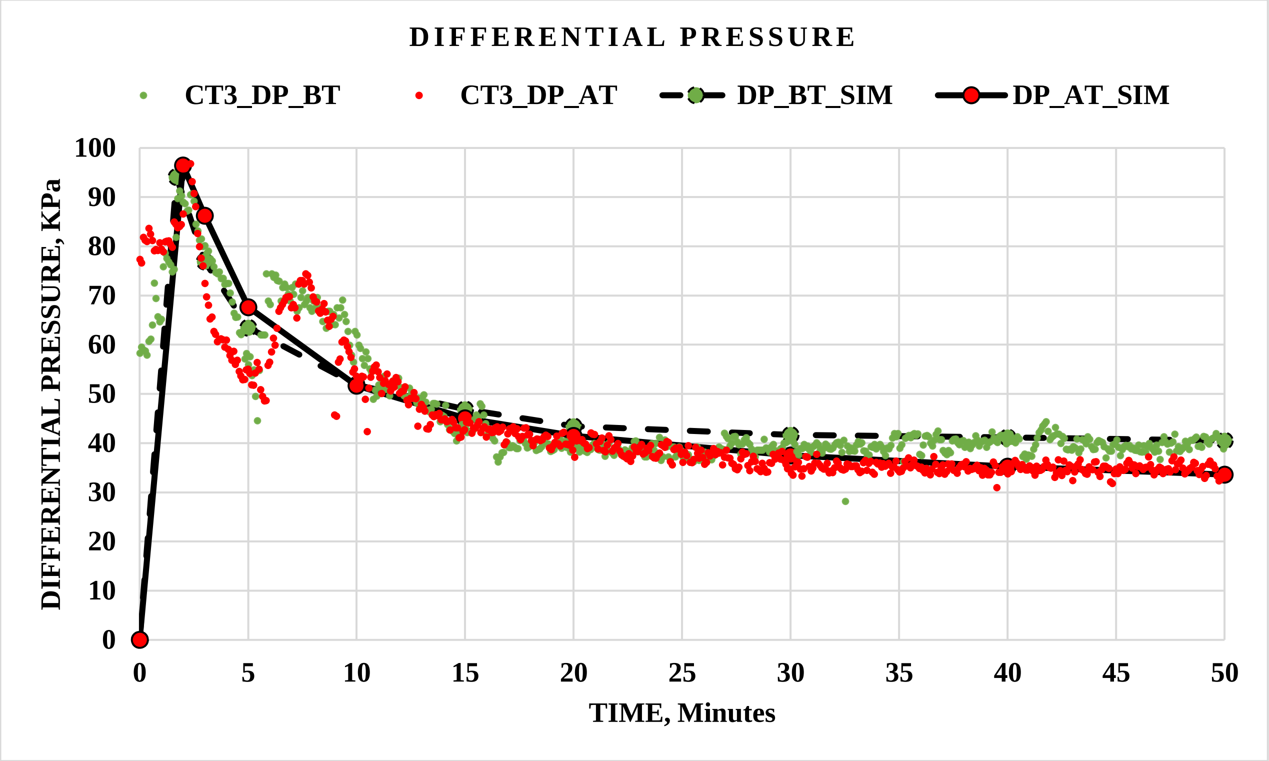


Figure 4.8. Differential pressure for primary drainage flood conducted on CT3 (DP: differential pressure, BT: before treatment, AT: after treatment, SIM: numerically simulated data during history matching procedure to derive relative permeability data).

The brine recovery data recorded during primary drainage floods (Figure 4.9 and Table 4.6) indicate that the benzoxazine treatment (across all curing temperatures explored) resulted in an average of 6.5% additional brine recovery. All these results align with the conclusions reported by Li et al.(Li et al. 2011) where they demonstrated that a fluorinated chemical could increase water recovery by around 15% during gas displacement in a sandstone rock. The observed enhancement in water recovery supports the earlier discussion presented around the shift in differential pressures (Figure 4.8) and is seen as added evidence that our treatment approach can result in promising outcomes under dynamic fluid flow conditions. This increase in water recovery combined with the decrease in differential pressure agrees with the benzoxazine treatment's wettability alteration mechanism we have proposed. The incremental brine recoveries obtained in this study are comparable with those reported in our previous study, in which we treated intermediate permeability samples with a much higher monomer concentration (10 wt.%) cured at 180 °C (Mauricio Ceron Lopez et al. 2021). This may demonstrate the outstanding effectiveness of the treatment in low permeability rocks, as achieving enhanced recovery is more challenging under low permeability conditions. Moreover, the additional brine recoveries obtained in the current work for either 125 or 150 °C curing temperatures are almost the same as that achieved for the optimal curing temperature of 180 °C (Figure 4.9 and Table 4.7), demonstrating that this approach can be successfully applied under temperatures as low as 125 °C. In other words, although it is known that during polymerization, an increase in temperature enhances the strength of the intramolecular forces resulting in a further decrease in the surface free energy (i.e. higher level of wettability alteration), adequate results can still be obtained at the lower end of the temperature range.

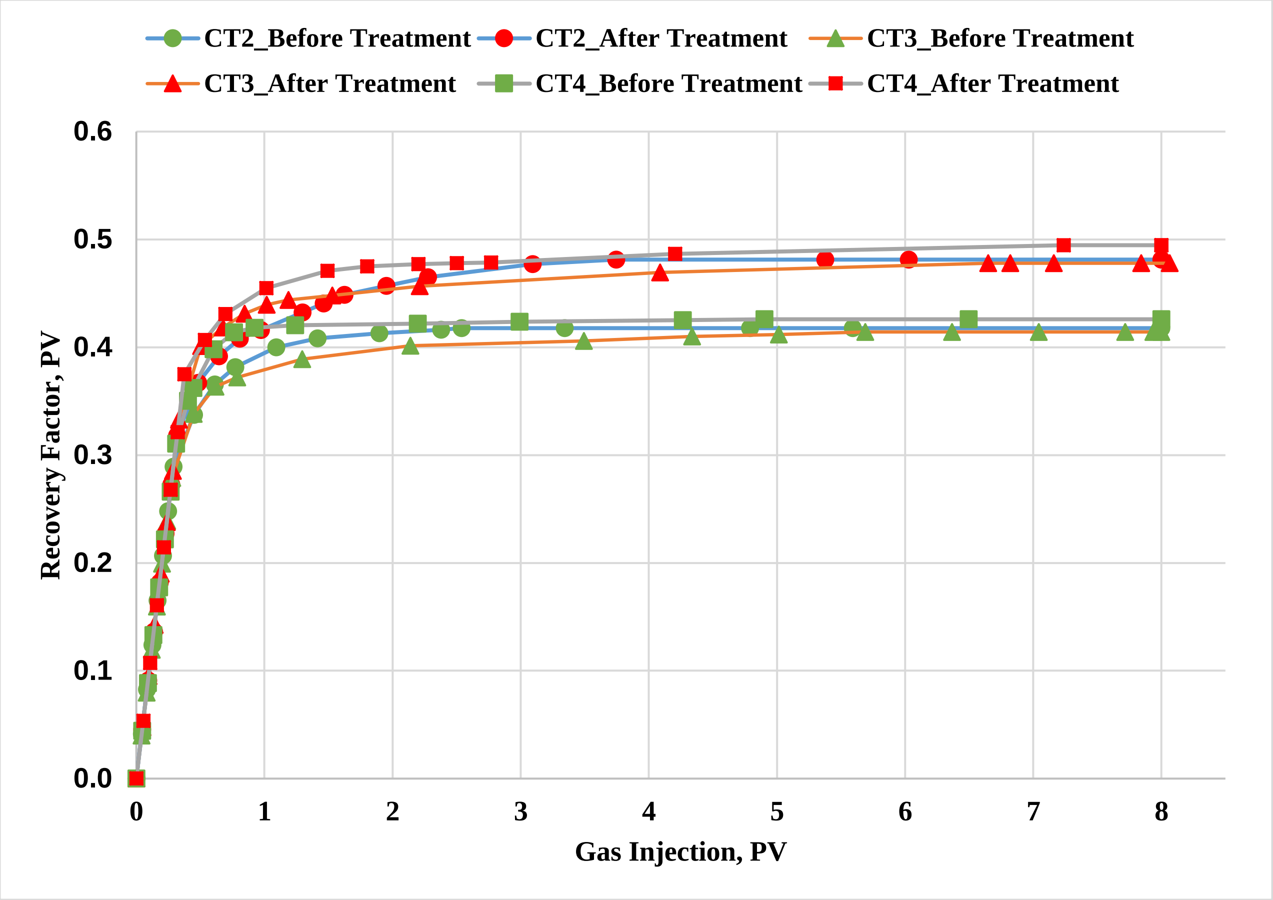


Figure 4.9. Comparison of water recovery during the primary drainage process conducted on samples CT2, CT3, and CT4 before and after chemical treatment (BT: before treatment, AT: after treatment).

Table 4.7. A summary of brine recovery results during the primary drainage flood conducted on samples CT2, CT3 and CT4.

Rock Sample	**Before Treatment**		**After Treatment**		**Increment**	
	Water Production	**Recovery Factor**	**Water Production**	**Recovery Factor**	**Water Production**	**Recovery Factor**
CT2 (125 °C)	5.2	0.42	5.9	0.48	13.5%	6.3%
CT3 (150 °C)	4.9	0.41	5.6	0.48	14.3%	6.4%
CT4 (180 °C)	5.4	0.43	6.2	0.50	15.9%	6.9%

To further elaborate on the alleviating effect that benzoxazine treatment can have on water blockage, Table 4.8 compares the end-point relative permeability values before and after treatment and the corresponding residual brine saturations for samples CT2, CT3 and CT4. As can be observed, CT4 (treated at 180 °C) exhibits a 20% improvement in the end-point relative permeability to gas and a 12% reduction in residual water saturation. While data reported for samples CT2 and CT3 reveal reductions in residual brine saturation (~11%) similar to that seen for CT4, their resultant enhancement in end-point gas relative permeability is similar (~7 %) but considerably less than for CT4. Two factors occur during polymerization at elevated temperatures (ring opening and cross-linkage (Liu et al. 2013)), making this process simple and dependent on the curing conditions (temperature and time). The curing time remained constant to assess curing temperature, obtaining slightly better results on the CT4 in terms of end-point relative permeability and recovery factor. At the selected temperatures, the silane moiety creates a linkage between the benzoxazine monomer and the rock surface, reaching suitable chemical adsorption, while the ring opening of the benzoxazine monomer provides a reduced surface tension at values closer to 180 °C. At lower temperatures, the efficiency of the ring-opening process decreases during polymerization, leading to less favourable surface tension conditions of the treated rock sample (Liu et al. 2006; Liu et al. 2013).

The above results may not be as significant as those reported in the literature for fluorinated chemical treatments. However, the observed trends are in line with those seen for these chemicals.(Noh and Firoozabadi 2008b; Li et al. 2011) As elaborated in our previous work (Mauricio Ceron Lopez et al. 2021), it is also important to highlight that benzoxazine resin is significantly cheaper and less harmful to the environment than fluorinated compounds.

Table 4.8 End-point relative permeability and residual water saturation core-flooding results.

Sample ID	**Curing Temp (°C)**	**Before Treatment**		**After Treatment**		**k_{rg}(@S_{wir}) Increase (%)**	**S_{wir} Reduction (%)**
		k_{rg}(@S_{wir})	**S_{wir} (frac.)**	**k_{rg}(@Swir)**	**S_{wir} (frac.)**		
CT2	125	0.099	0.582	0.106	0.519	7.1	-10.8
CT3	150	0.107	0.586	0.111	0.522	4.0	-10.9
CT4	180	0.110	0.574	0.132	0.505	20.0	-12.0

The earlier discussed shift in the post-treatment end-point gas relative permeability is evident across almost the entire relative permeability curves, as observed from the data in Figure 4.10. This figure compares pre- and post-treatment relative permeability curves for the drainage floods conducted on sample CT3. Generally, the relative permeability to gas is higher after treatment with the monomer for fixed water saturation. The Sigmund and McCaffery set of equations (Equation 4.1, Equation 4.2, and Equation 4.3) were used to perform the iterative process of history matching the pressure differential (Figure 4.8 – where DP_BT_SIM curve represents the differential pressure before treatment and the DP_AT_SIM represents the after treatment generated during the matching procedure) and brine recovery during the unsteady-state fluid displacement to finally determine the relative permeability of gas and brine based on the different procedures (Sigmund and McCaffery 1979; Saeedi et al. 2016). Compared with other models, such as Corey, the mentioned model seemed to capture better the complexity of the gas phase mobility, lower density, capillary-viscous ratio, and the shape of the relative permeability curves.

$$kr_w = \frac{kr_w'(S_e)^{N_w} + AS_e}{1+A} \qquad \text{(Equation 4.1)}$$

$$kr_g = \frac{kr_g'(S_e)^{N_g} + B(1-S_e)}{1+B} \qquad \text{(Equation 4.2)}$$

$$S_e = \frac{S_w - S_{wir}}{1 - S_{wir} - S_{gir}} \qquad \text{(Equation 4.3)}$$

The values kr_w and kr_g are the relative permeability values of the wetting and non-wetting phase, respectively. Se is the normalized water saturation value, while kr_w' and kr_g' represents the relative permeability end-points of the wetting and non-wetting phases. The empirical constants N_w, N_g, A, and B were iteratively determined by different trials for history matching the differential pressure and displaced brine recovery. The N_w and N_g are values that minimize the error function between the observed and calculated pressure differential and displaced fluid recovery. In this process, the model also incorporates the capillary pressure effect into the relative permeability calculation; leading to a more suitable relative permeability calculation for the wetting and non-wetting phase that could be used in further analysis at the wellbore scale. Finally, the capillary pressure term has been obtained during the core scale simulation modelling by the use of the commercial Sendra software by the use of equation 4.4 to, later on, use the corresponding capillary equation 4.5 to convert the capillary pressure values from laboratory conditions to a more real wellbore scale. These results were calculated before and after treatment to input the values in the wellbore model. The C_w, C_o, a_w, and a_o are constant and non-negative parameters, where C_w, C_o are expressed in units of pressure, while S_o represents the hydrocarbon phase saturation (Andersen et al. 2020).

$$P_C = \frac{C_w}{\left(\frac{S_w - S_{wir}}{1 - S_{wir}}\right)^{a_w}} - \frac{C_o}{\left(\frac{S_o - S_{or}}{1 - S_{or}}\right)^{a_o}} \qquad \text{(Equation 4.4)}$$

$$P_{C\,res} = \frac{(\sigma \cos\theta)_{res}}{(\sigma \cos\theta)_{lab}} P_{C\,lab} \qquad \text{(Equation 4.5)}$$

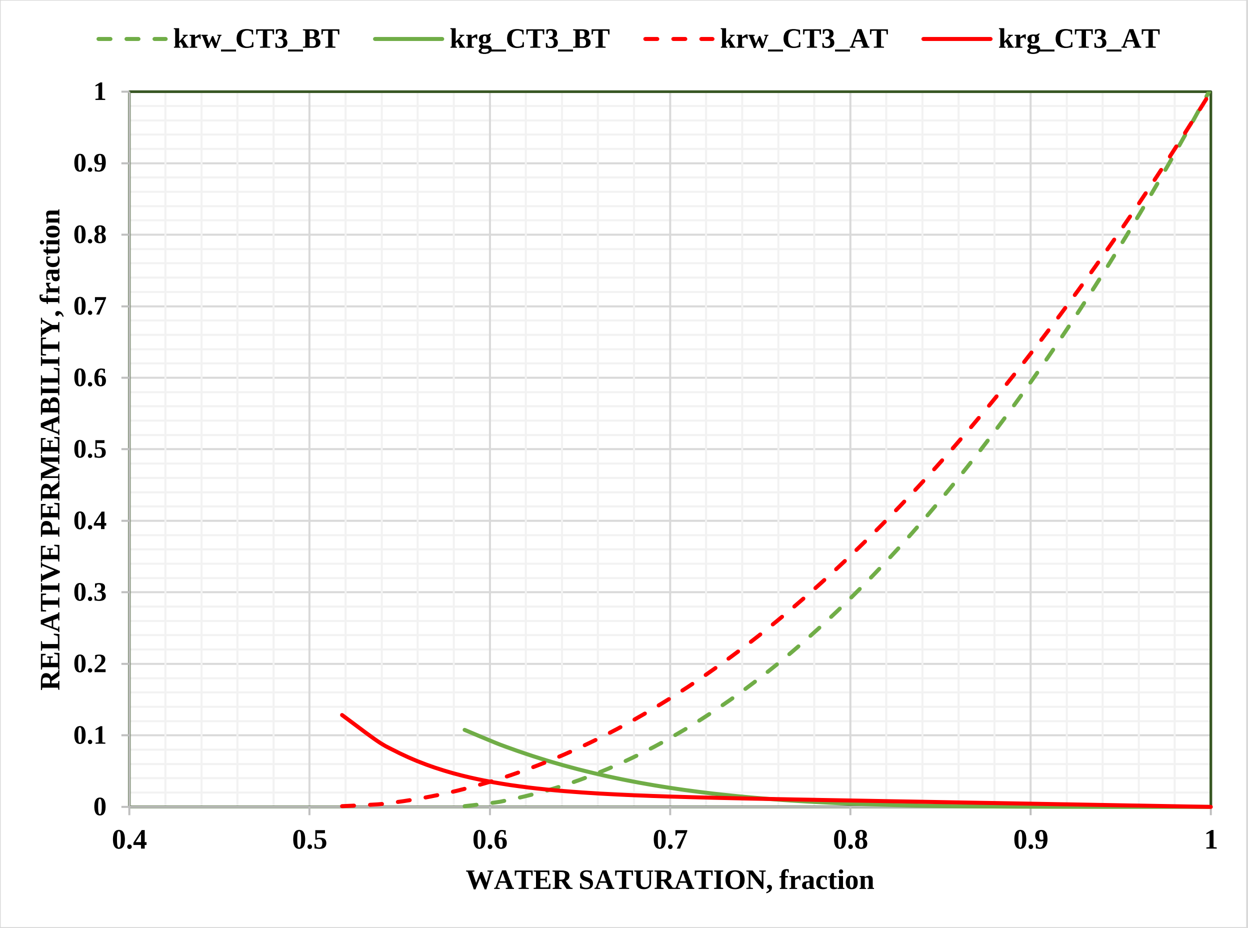


Figure 4.10. A sample relative permeability data derived by history matching the core flooding results before and after chemical treatment for sample CT3.

Overall, the experimental procedure of water imbibition and flow displacement depicted moderate improvements in water recovery and relative permeability to gas compared with other researchers' results using non-fluorinated and fluorinated chemicals. The flow displacement showed an increment of the end-point relative permeability values of 4 to 20%, while the residual water saturation decreased from 10 to 12 % when treating the samples with a 2.5% chemical solution. The improvement mainly relies on the polymerization conditions of the chemical (curing temperature and time) and the purity of the raw chemical materials during the synthesis process of the benzoxazine resin. On the other hand, there are limited studies providing results associated with using non-fluorinated compounds to alter wettability; for example, a non-fluorinated analysis proposed by Arjomand, 2020 proposed a non-fluorinated silylation procedure at 60 °C to alter the wettability of a CO2-brine-rock system (Arjomand, Myers, et al. 2020). This study showed that the chemical could increase 60% of the end-point CO2 relative permeability to obtain more than 25% water recovery. This procedure involved the use of CO2 as a solvent and carrier fluid. Our analysis focused on investigating an environmentally friendly chemical treatment that does not degrade or decrease its performance when increasing temperature; therefore, the hydrophobic characteristics increase, especially when reaching high polymerization temperatures such as 180 °C, which is the ideal curing temperature of the monomer.

On the other hand, extensive research has been conducted on applying fluorinated compounds to alter rock wettability. The results reveal that fluorinated compounds are the most effective alternative to alter wettability. For example, Noh, 2008 in his flow test analysis, obtained a 60 to 70 % increment in water mobility using fluorinated chemicals and a drastic reduction of 90% approximately in the volume imbibed by the treated rock sample (Noh and Firoozabadi 2008b). Those results surpass the effects of benzoxazine resin. When comparing the results of the benzoxazine resin with any of the fluorinated compounds, it is evident that the performance is not at the same level; the fluorinated compounds can lower the surface free energy of the rock considerably, reaching values lower than 5mJ/m2 when applying fluorinated nano-silica components (Erfani Gahrooei and Ghazanfari 2017). Those results were obtained due to the characteristic of the chemical solution to modify the surface roughness and lower the surface free energy of the sample.

Additional analysis on the change of wettability from oil-wet to less oil-wet has been performed using the benzoxazine monomer to treat sandstone and carbonate rock samples. Therefore, the same procedure proposed in our analysis was performed for a gas-condensate-rock system using decane and hexadecane as the fluid phase. Additionally, a solution composed of benzoxazine and FAS was assessed to demonstrate that using a short-chain fluoropolymer is not enough to reach oleophobic results. When assessing the solutions proposed, the contact angle could not reach more than 5° in less than a minute during contact angle measurement. During spontaneous imbibition, the chemical solutions were unable to reduce the imbibition rate to any extent. Finally, the flow test analysis, using sandstone and carbonate rock samples, did not show any further improvement during water and gas displacement over the treated samples. Therefore, the surface free energy of the treated surface is not enough to repeal the liquid phase, as the surface tension of the liquids (decane and hexadecane) are 24 and 28 mJ/m2, respectively (Zisman 1964). In our previous research, we showed an approximated surface free energy of 34 mJ/m2, which is not enough to modify the wettability of the rock from oil-wet to less oil-wet (Mauricio Ceron Lopez et al. 2021). Based on the work done by Lui et al., treated glass surface with benzoxazine resin to obtain less than 20 mJ/m2. This research demonstrates that oleophobic characteristics could alter wettability in glass surfaces (Liu et al. 2013). In our research, such conditions could not be achieved when treating glass and rock samples ranging from 10 to 130 mD. Curing time between 1 to 180 hours and curing temperatures up to 180 °C were assessed to obtain lower surface free energy values; nevertheless, results did not depict promising results compared with those obtained by Liu. During the synthesis process, the phenolic impurities could probably affect the ring opening during thermal polymerization, leading to a drastic increment of the surface free energy value. Nevertheless, reaching such surface conditions is considerably low, benzoxazine can be used for water blockage applications.

4.3. - The application of benzoxazine resin at lower temperatures.

A principal concern is the application of chemical treatment at lower temperatures, especially at temperatures below 120 °C. This condition is of importance in situations where the depth of the reservoir and the temperature are considerably low for applying benzoxazine treatment. For this purpose, an initial contact angle and spontaneous imbibition technique were assessed under different treatment conditions, such as chemical concentration, polymerization time, and temperature. Unfortunately, none of the obtained results were clear enough to observe a potential application of the treatment at lower temperatures. The principal reason was that the chemical was unable to polymerize at lower temperatures, thereby reducing its surface modification characteristics. To address this problem and find a feasible solution for further field application, it is essential to develop a complementary technique that could enhance the treatment while maintaining the conditions obtained when treating the rock surface at high temperatures.

In lower temperature formations which at the same time are not too deep, it is necessary to increment the temperature around the wellbore to 150 to 180 C to achieve proper thermal polymerization of the benzoxazine chemical solution. The laboratory analysis has established that a short one-hour exposure of the monomer to high temperatures is sufficient to polymerize the chemical solution over the surface of the rock. Therefore, the utilization of a downhole heating device could provide a functionalised alternative to obtain this objective. This type of heating device has been used for wellbore treatment to improve flowing conditions, especially in those oil reservoirs with high viscosity. Moreover, this tool has also been applied to remove waxes or for clay dehydration. With the application of a substantially less expensive chemical in comparison with other fluorinated chemicals, the use of a heating device in shallow depths could not drastically affect the economical outlook of the treatment (Appendix B). On the contrary, it provides a considerable improvement in polymerization as achieved by the direct control of the temperature at which the chemical is exposed underground.

4.4. Box model numerical simulation results

4.4.1. Effect of invasion radius around the wellbore.

Figure 4.11 compares the pre- and post-treatment numerically simulated gas production profiles (over seven years) for a 15 mD rock formation assuming different radii of water invasion (4, 10, and 16 m). For further comparison, this figure also includes an additional curve representing the unaffected productivity of the same formation (i.e., no water invasion or 'Initial Conditions'). As can be seen, the water invasion suppresses the gas productivity with a larger radius causing a more significant effect. The subsequent chemical treatment improves productivity across all cases explored, with its impact becoming more significant with an increase in the water invasion radius. The above comparison becomes more evident using the data included in Figure 4.12, which compares the effects of water blockage on final simulated gas recovery for the above three water invasion radii and then reveals how much improvement the benzoxazine treatment can make across all explored cases. The figure shows that productivity loss ranges from 12.4 to 23.6% as the water invasion radius increases from 4 to 16 meters, respectively. The chemical treatment then results in more remarkable incremental improvement for higher invasion radii increasing productivity between 2.9 to 10.6%.

4.4.2. Effect of absolute rock permeability.

To evaluate the effect of absolute rock permeability on the performance of benzoxazine treatment as revealed by the box model simulations, we have used the relative permeability curves for CT2 from the current work and similar data generated for a BUG sample (~130 mD) from our previous study (Mauricio Ceron Lopez et al. 2021) in two separate simulation models. For this investigation, we have considered the intermediate water invasion radius of 10 m. As noted earlier, when the reservoir permeability is low, given the higher capillary strength, the reservoir is prone to a more pronounced water blockage effect.

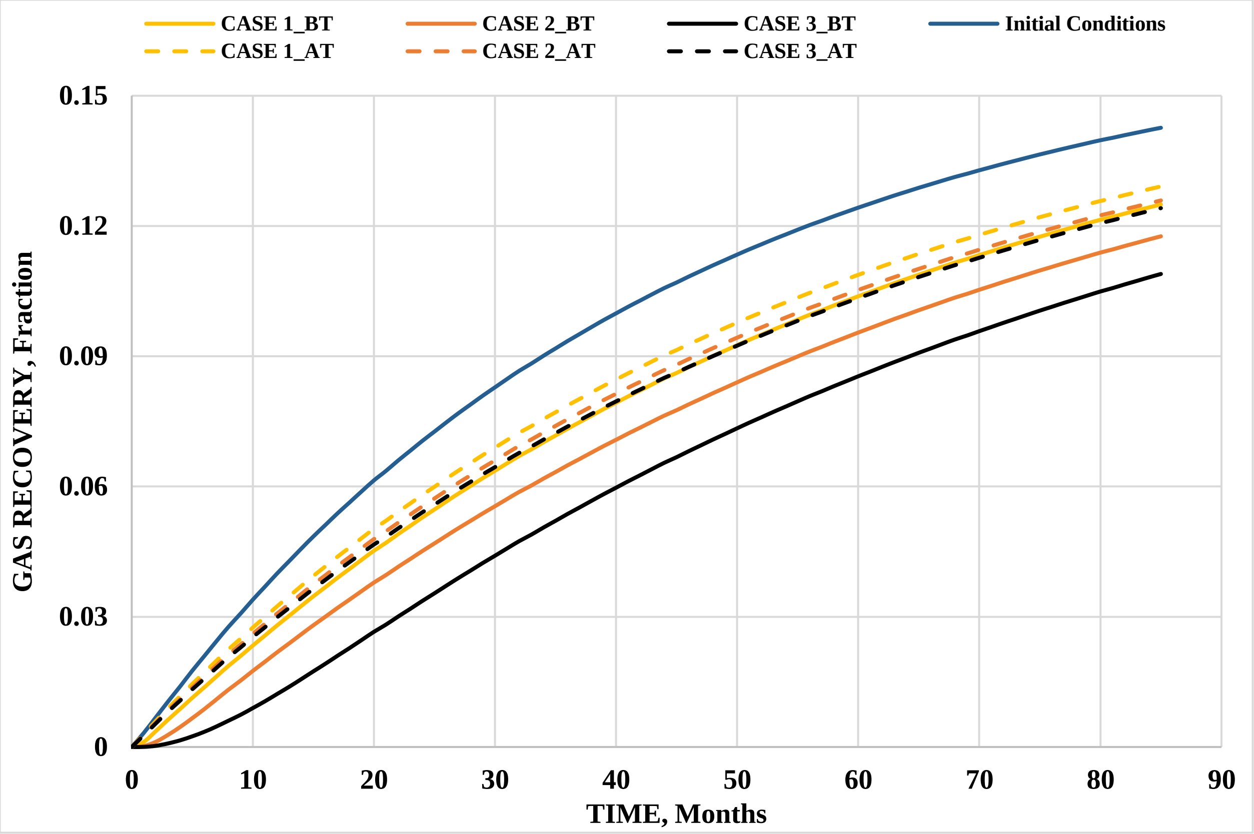


Figure 4.11. Gas recovery profiles for various scenarios, including initial conditions (i.e., no water invasion), different radii of water invasion (4 (Case 1), 10 (Case 2), and 16 m (Case 3)), and after chemical treatment as generated using box model numerical simulation under an absolute permeability of 15 mD (BT: before treatment, AT: after treatment).

The numerical simulation results in Figure 4.13 show that, as indicated above, the negative effect of water blockage diminishes from 17.5% to a mere 0.6% when permeability increases from 15 to 130 mD. The same figure also indicates that upon treating the two rock types with benzoxazine, a recovery enhancement of 5.8% may be expected for the case of low permeability rock compared with a negligible 0.1% effect for the case of higher permeability rock formation. This trend, resulting from the box model simulation, highlights that low permeability formations are more prone to water blockage, presenting a higher potential for water blockage removal using the wettability alteration technique such as that developed in this research.

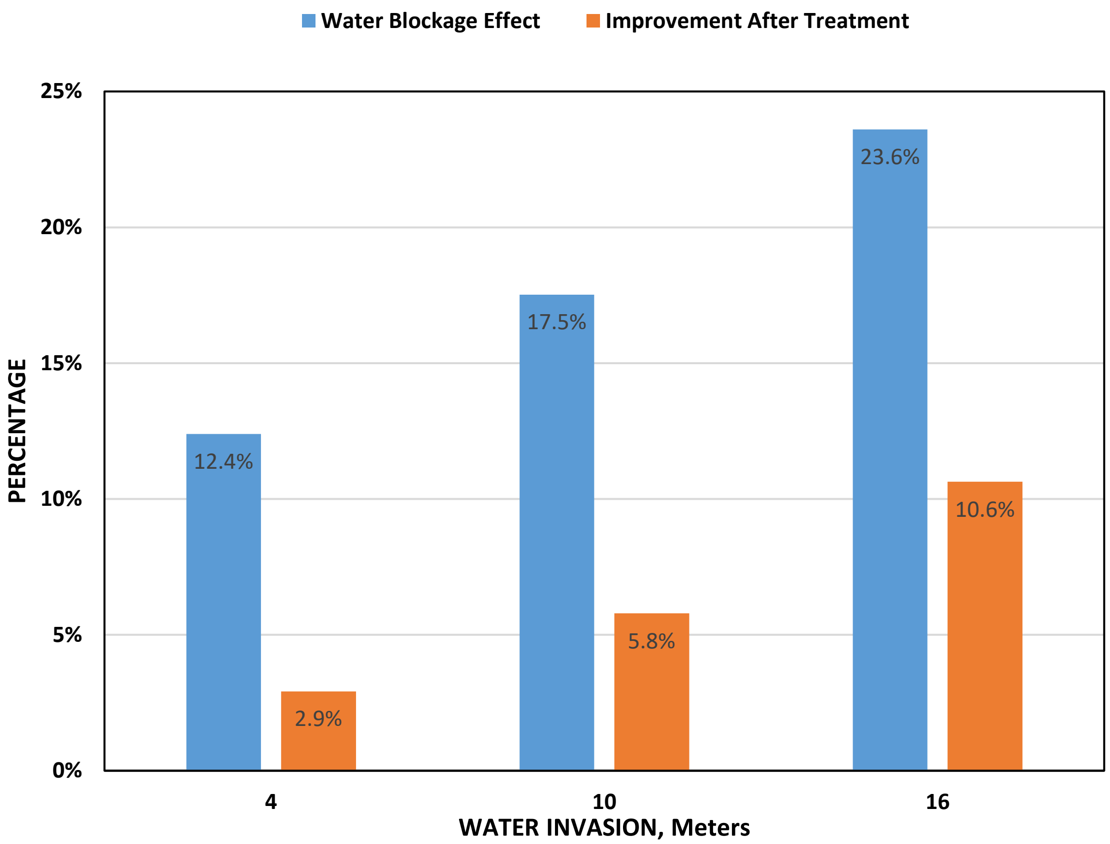


Figure 4.12. Percentage of recovery factor reduction due to water blockage at three cases of water invasion (4, 10, and 16 meters) (blue color) and subsequent incremental improvement in recovery for the same invasion radii as caused by benzoxazine treatment (orange color) – Box model simulation under an absolute permeability of 15 mD.

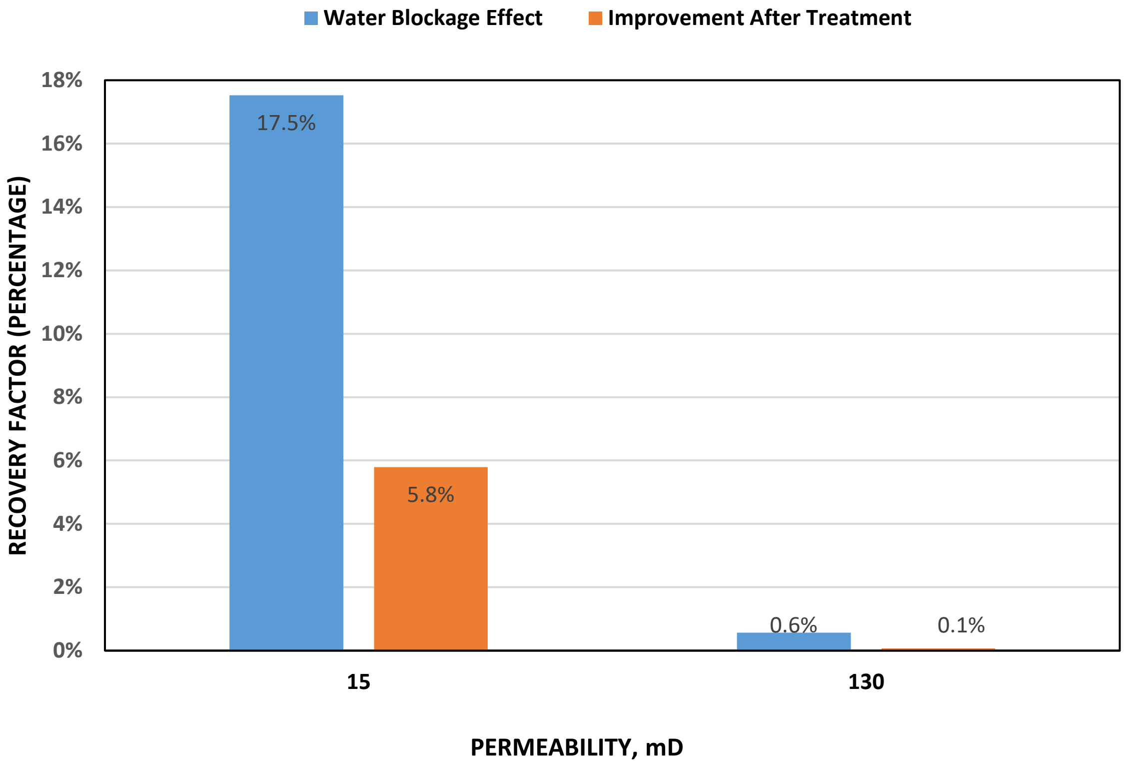


Figure 4.13. Percentage of recovery factor reduction due to water blockage at water invasion radius of 10 m for two absolute permeabilities of 15 and 130 mD (blue color) and subsequent incremental improvement in recovery for the same invasion radius and permeability values as caused by benzoxazine treatment (orange color) – results of box model numerical simulation.

CHAPTER 5 SUMMARY, CONCLUSIONS AND RECOMMENDATIONS

5.1 Summary and Conclusions

Water blockage in the near wellbore region as caused by the strong water-wet condition of a rock formation can drastically affect gas deliverability. Wettability alteration by functionalizing the rock pore surface is seen as a viable permanent solution that can reduce the severity of water blockage significantly and improve gas productivity in affected wells. Aligned with this objective, there have been several successful attempts to date using fluorinated chemicals to change the rock wettability from a liquid wet state to an intermediate gas wet condition. However, concerns over the cost and potential ecotoxicity have prevented the use of such chemicals at the field-scale. In an effort to find and test a feasible alternative, an environmentally friendly and cost-effective BZ monomer was synthesised and tested to determine whether it could adequately modify the wettability characteristics of representative sandstone rock samples. A combination of contact angle, spontaneous imbibition and core flooding tests were used to demonstrate the ability of this chemical to create a hydrophobic condition when applied to sandstone rock surfaces and, therefore, help to alleviate water blockage.

The results obtained in this research using coupled experimental and numerical techniques at two different scales (core vs. wellbore region) demonstrate the potential of this novel chemical treatment in effectively improving gas productivity under a wide range of application conditions.

When high quartz content rock samples were treated with 10 wt.% BZ monomer in acetone and polymerized at 180°C for 1 hour, the water contact angle increased from 0° to an average value of 99° in a water-air system. Moreover, spontaneous imbibition tests showed up to 45% reduction in the volume of water that could be imbibed into sandstone core plugs under ambient conditions. Finally, core-flooding experiments conducted at 10.35 MPa and 60°C showed more 10% reduction in the residual water saturation accompanied by a 22% improvement in the end point relative permeability to gas. The above results demonstrate the competence of this novel BZ treatment in addressing water blockage in moderate permeability sandstone rock formations.

The effect of water blockage on gas deliverability is a more significant concern in low-permeability reservoirs compared to their higher permeability counterparts. Therefore, the effectiveness of the developed chemical treatment was further tested using a set of lower permeability rocks. The results obtained demonstrate that the treatment can alter wettability in low-permeability reservoirs at polymerization temperatures lower than the optimal value of 180 ºC, expanding the application envelope of the treatment to lower-temperature reservoirs.

When treating a low-permeability sample with a concentration of 2.5 wt.% of the benzoxazine monomer, the absolute rock permeability decreased by 3–10 wt.% of its initial value at different polymerization temperatures (125–180 °C). But despite this subtle negative outcome, the spontaneous imbibition analysis demonstrated that the chemical could delay the water intake into the sample by decreasing the imbibition rate. Similarly, the contact angle after rock treatment increased from 0 to values between 89° and 108° at different polymerization temperatures. Therefore, the chemical solution was found to alter the surface free energy of the rock without drastically reducing the absolute gas permeability.

The core-flooding tests conducted on lower permeability rocks at elevated pressure and temperature further validated the promising results of other experimental techniques. The results of these dynamics experiments indicated residual water saturation reduction of 10.8–12% after treatment when brine-saturated samples were flooded with gas. Furthermore, improvements in end-point gas relative permeability of 4–20% were also achieved. These results demonstrate that the benzoxazine resin could be potentially used to treat reservoirs with temperatures between 125 and 150 °C, resulting in desirable outcomes.

Box model numerical simulations were used to upscale the results from core to wellbore scale. The simulation runs used the relative permeability data derived from core-flooding tests. The simulation results show that under low-permeability conditions (15 mD), productivity loss ranges from 12.4 to 23.6% as the water invasion radius increases from 4 to 16 m, respectively. The chemical treatment then resulted in greater incremental improvement for higher invasion radii increasing productivity between 2.9 and 10.6%. These results further confirm that low-permeability formations are more susceptible to water blockage, as demonstrated by gas recovery reductions of 17.5% to 0.6% obtained under 15 and 130 mD permeabilities (water invasion radius of 10 m), respectively. Therefore, such formations are more suitable for water blockage removal using the wettability alteration technique such as the one developed in this research. For example, our simulation results indicate a 5.8% post-treatment increase in gas recovery under 15 mD formation permeability compared with a mere 0.1% increase under 130 mD.

An important concern with wettability modifiers is thermal durability. Our proposed chemical solution has been thermally polymerized at an extreme condition of 180°C, demonstrating excellent performance at high temperatures. The treatment has been found to decrease the residual water saturation while increasing the gas relative permeability after water removal. Those outcomes are influenced by polymerization temperature during rock treatment, incrementing residual water saturation when the polymerization temperature increases, further improving the relative permeability to gas. Such results demonstrate that the benzoxazine resin could be potentially used to also treat reservoirs with temperatures between 125 and 150 °C.

5.2. Recommendations for further work

The overall result obtained using the benzoxazine monomer are of great importance in the attempt to find a non-fluorinated alternative to remediate water blockage that involves a gas-water fluid system. Nevertheless, there is a need to obtain treatment that can help dealing with condensate blockage around the wellbore that involves a hydrocarbon liquid-gas fluid system. There are numerous gas reservoirs globally facing condensate blockage/banking issues negatively impacting well productivity. This research program made an effort to investigate the application of the benzoxazine resin (even combined with fluorinated chemicals during synthesis process) to alter wettability in a gas-decane-rock system with unsuccessful outcomes. Therefore, further work could be done to improve the synthesis of the monomer to improve thermal polymerization while maintaining or improving its surface free energy characteristics. This could lead to a more promising application to remove condensate blockage, which is currently considered challenging without the application of fluorinated compounds. In this research, a range of solvents (i.e. acetone, tetrahydrofuran, hexane and ethanol) were used to dilute the benzoxazine monomer. If an improved benzoxazine resin is synthesised, a solvent screening process would also be essential for treating rock pore surfaces.

This research was initially performed using high quartz content (above 80% in moderate permeability samples and above 60% in low permeability samples). More heterogeneous rock samples with less than 50% quartz content or even carbonate samples could be tested in future investigations.

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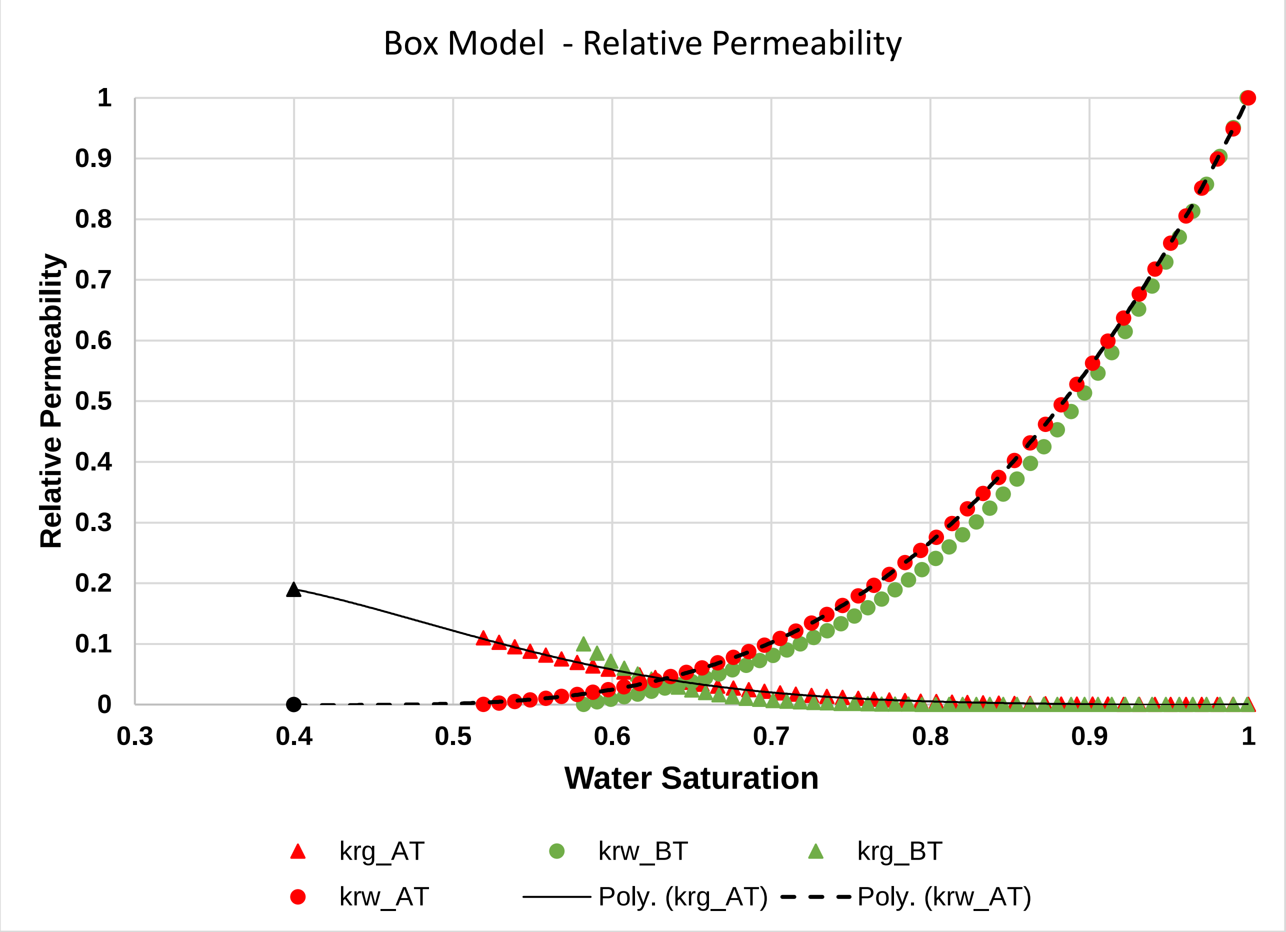
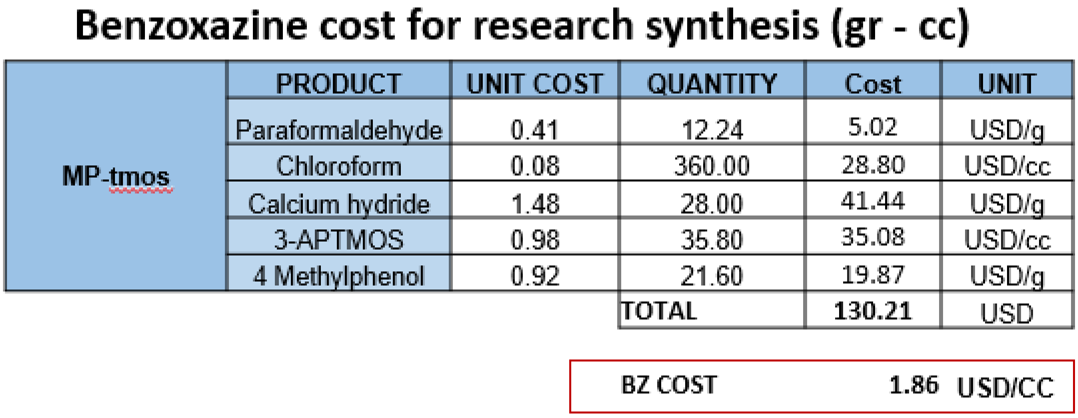
APPENDIX A Box Model Relative Permeability



APPENDIX B Benzoxazine Chemical cost

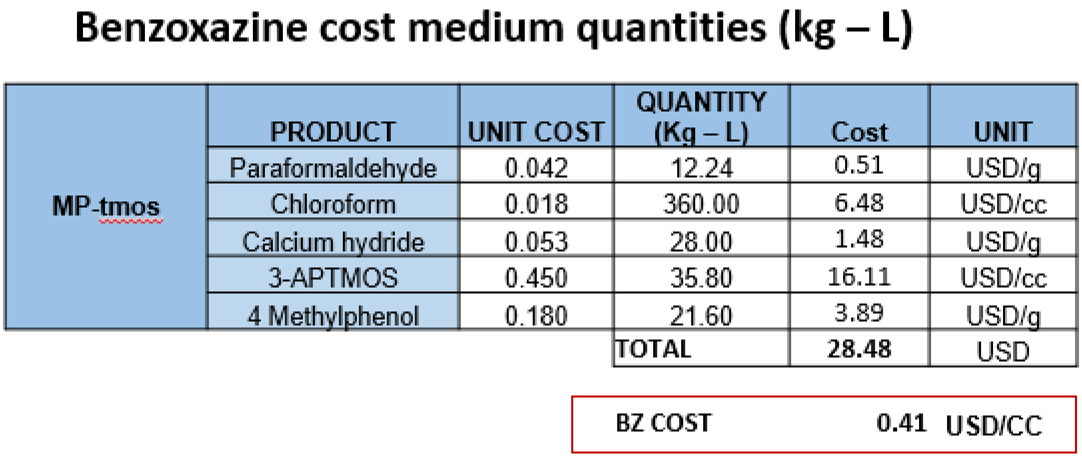
The cost of Benzonxazine resin as wettability modifier is approximately 40 % less or even more than using fluorinated chemicals. Moreover, at higher quantities the benzoxazine products for synthesis could decrease drastically up to 0.41 usd/cc approximately. All this data was obtained from providers such as Gelest and Sigma – Aldrich.



Benzoxazine cost for research synthesis (gr - cc)

	PRODUCT	UNIT COST	QUANTITY	Cost	UNIT
MP-tmos	Paraformaldehyde	0.41	12.24	5.02	USD/g
	Chloroform	0.08	360.00	28.80	USD/cc
	Calcium hydride	1.48	28.00	41.44	USD/g
	3-APTMOS	0.98	35.80	35.08	USD/cc
	4 Methylphenol	0.92	21.60	19.87	USD/g
			TOTAL	**130.21**	USD

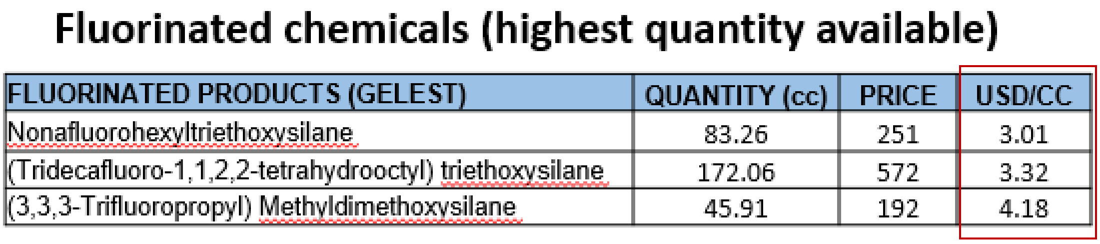
BZ COST **1.86** USD/CC



Benzoxazine cost medium quantities (kg – L)

	PRODUCT	UNIT COST	QUANTITY (Kg – L)	Cost	UNIT
MP-tmos	Paraformaldehyde	0.042	12.24	0.51	USD/g
	Chloroform	0.018	360.00	6.48	USD/cc
	Calcium hydride	0.053	28.00	1.48	USD/g
	3-APTMOS	0.450	35.80	16.11	USD/cc
	4 Methylphenol	0.180	21.60	3.89	USD/g
			TOTAL	**28.48**	USD

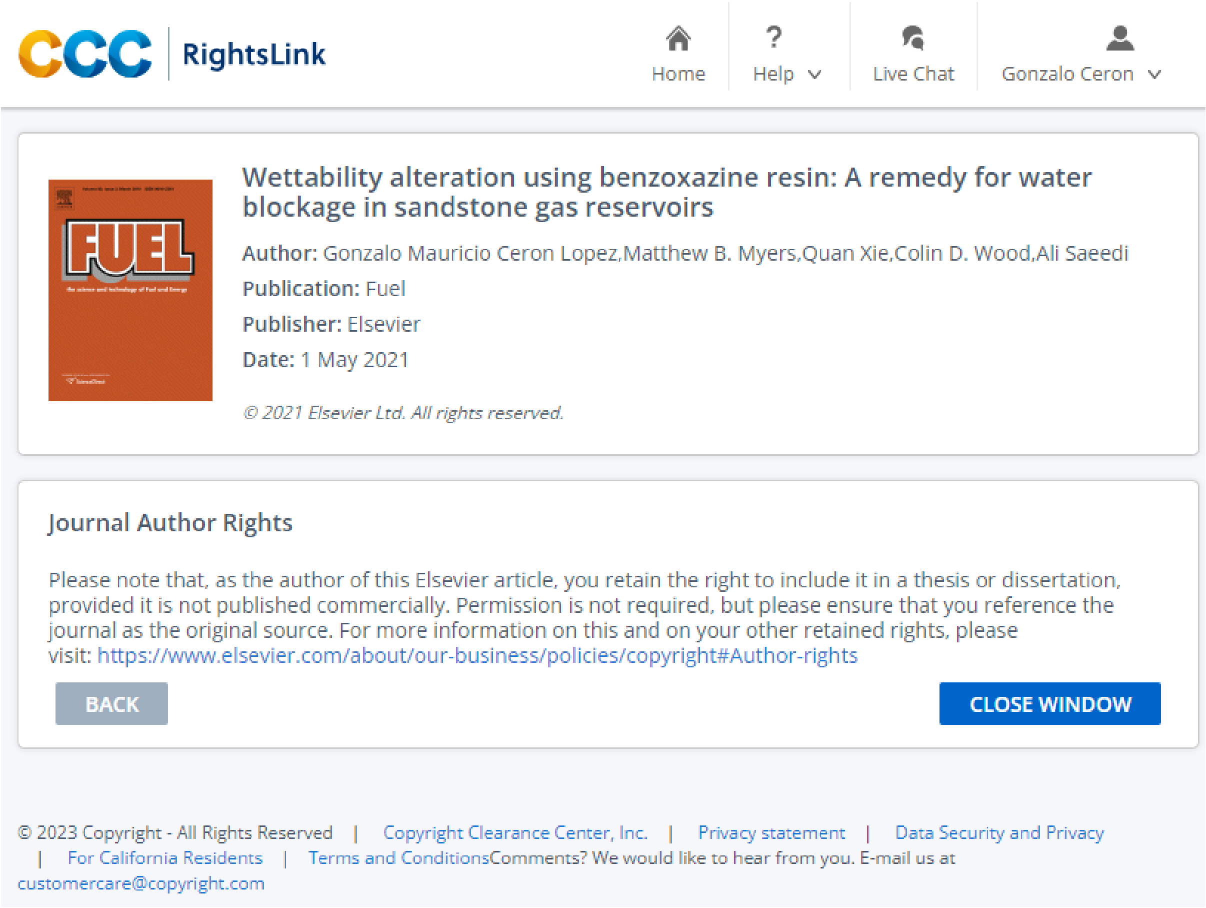
BZ COST **0.41** USD/CC



Fluorinated chemicals (highest quantity available)

FLUORINATED PRODUCTS (GELEST)	QUANTITY (cc)	PRICE	USD/CC
Nonafluorohexyltriethoxysilane	83.26	251	3.01
(Tridecafluoro-1,1,2,2-tetrahydrooctyl) triethoxysilane	172.06	572	3.32
(3,3,3-Trifluoropropyl) Methyldimethoxysilane	45.91	192	4.18

APPENDIX C Official Permissions and Copyright



Wettability alteration using benzoxazine resin: A remedy for water blockage in sandstone gas reservoirs

Author: Gonzalo Mauricio Ceron Lopez,Matthew B. Myers,Quan Xie,Colin D. Wood,Ali Saeedi

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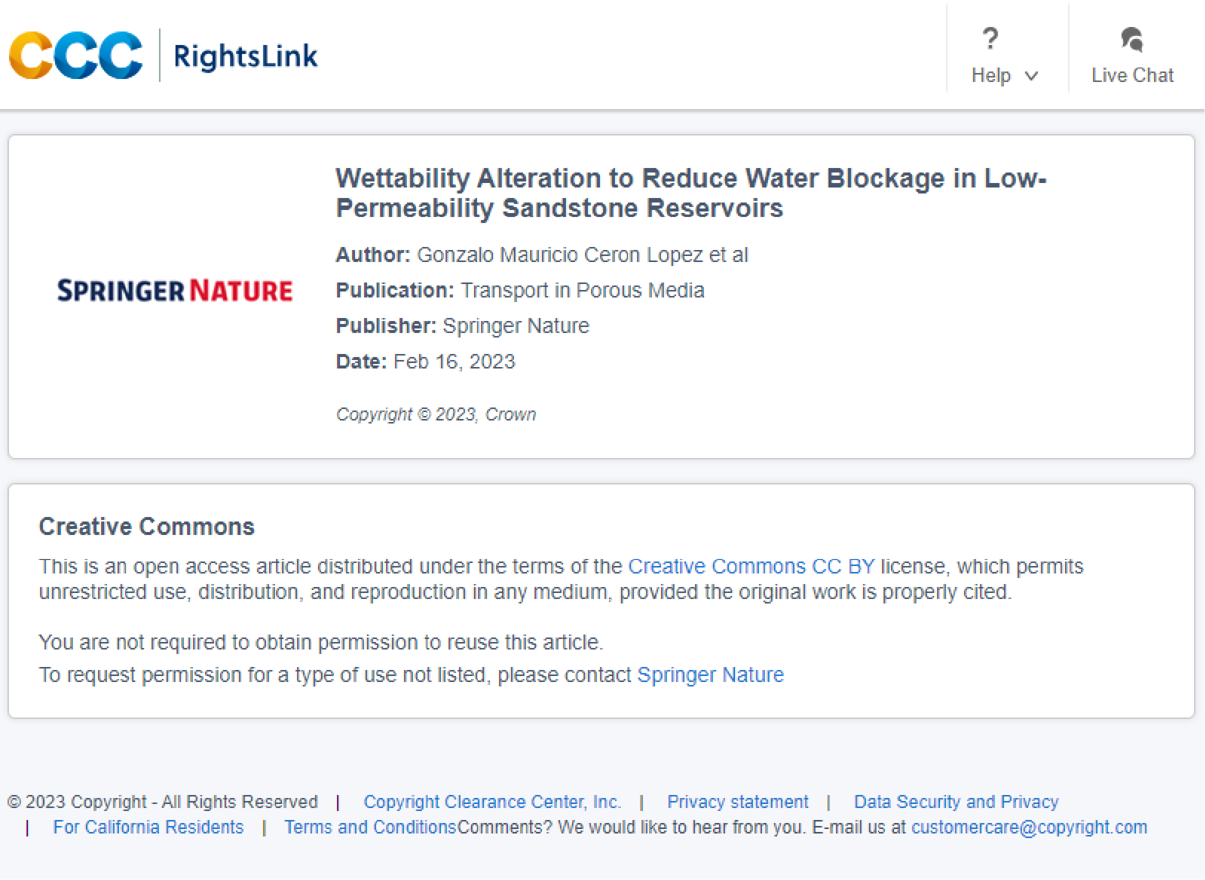

Wettability Alteration to Reduce Water Blockage in Low-Permeability Sandstone Reservoirs

Author: Gonzalo Mauricio Ceron Lopez et al
Publication: Transport in Porous Media
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APPENDIX D Attributions of Co-Authors

Journal Paper: Wettability Alteration Using Benzoxazine Resin: A Remedy for Water Blockage in Sandstone Gas Reservoirs

Gonzalo Mauricio Ceron Lopez[*,†], Matthew Myers[*,‡], Quan Xie[†], Colin D. Wood[*,†], and Ali Saeedi[*,†]

[†]Curtin University, Kensington, WA 6151, Australia
[‡]CSIRO, Australian Resources Research Centre, Kensington, WA 6151, Australia
[*]Corresponding authors

Name	**Conception and Design**	**Acquisition of Data and Method**	**Data Conditioning and Manipulation**	**Analysis and Statistical Method**	**Interpretation and Discussion**
Matthew Myers	X	X			X
I acknowledge that these present my contributions to the above research output and I have approved the final version Signed					
Quan Xie					X
I acknowledge that these present my contributions to the above research output and I have approved the final version Signed					
Colin D. Wood					X
I acknowledge that these present my contributions to the above research output and I have approved the final version Signed					
Ali Saeedi	X				X
I acknowledge that these present my contributions to the above research output and I have approved the final version Signed					

Journal Paper: Wettability Alteration to Reduce Water Blockage in Low Permeability Sandstone Reservoirs

Gonzalo Mauricio Ceron Lopez[1], Matthew B. Myers[2,3*], Quan Xie[1], Colin D. Wood[2,3], Duraid Al-Bayati[1,4], Ali Saeedi[1]

[1] Department of Petroleum Engineering, Curtin University, GPO Box U1987, Perth, WA, Australia 6102
[2] Curtin University Oil and Gas Innovation Centre (CUOGIC), Technology Park, Curtin University, Bentley, WA, Australia 6102
[3] Commonwealth Scientific and Industrial Research Organisation, Perth, WA, Australia 6151
[4] University of Kirkuk, College of Engineering, Petroleum Engineering Department, Kirkuk, 36001, Iraq

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<tr><th>Name</th><th>Conception and Design</th><th>Acquisition of Data and Method</th><th>Data Conditioning and Manipulation</th><th>Analysis and Statistical Method</th><th>Interpretation and Discussion</th></tr>
<tr><td>Matthew Myers</td><td>X</td><td>X</td><td></td><td></td><td>X</td></tr>
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<tr><td>Quan Xie</td><td></td><td></td><td></td><td></td><td>X</td></tr>
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<tr><td>Colin D. Wood</td><td></td><td></td><td></td><td></td><td>X</td></tr>
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<tr><td>Duraid Al-Bayati</td><td></td><td>X</td><td></td><td></td><td></td></tr>
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<tr><td>Ali Saeedi</td><td>X</td><td></td><td></td><td></td><td>X</td></tr>
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