

**ALTERING WETTABILITY IN GAS CONDENSATE SANDSTONE
RESERVOIRS FOR GAS MOBILITY IMPROVEMENT**

A Thesis

by

RUTH GABRIELA FERNANDEZ MARTINEZ

Submitted to the Office of Graduate Studies of
Texas A&M University
in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

May 2011

Major Subject: Petroleum Engineering

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Approved by:

Co-Chairs of Committee,	Mashhad Fahes
	Christine Ehlig-Economides
Committee Member,	Maria Barrufet
Head of Department,	Steve Holditch

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ABSTRACT

Altering Wettability in Gas Condensate Sandstone Reservoirs

for Gas Mobility Improvement. (May 2011)

Ruth Gabriela Fernandez Martinez, B.S., Texas A&M University

Co-Chairs of Advisory Committee: Dr. Mashhad Fahes
Dr. Christine Ehlig-Economides

In gas-condensate reservoirs, production rate starts to decrease when retrograde condensation occurs. As the bottomhole pressure drops below the dewpoint, gas-condensate and water buildup impede flow of gas to the surface. To stop the impairment of the well, many publications suggest wettability alteration to gas-wetting as a permanent solution to the problem. Previous simulation work suggests an “optimum wetting state” to exist where maximum gas condensate well productivity is reached. This work has direct application in gas-condensate reservoirs, especially in identifying the most effective stimulation treatment which can be designed to provide the optimum wetting conditions in the near-wellbore region.

This thesis presents an extensive experimental study on Berea sandstone rocks treated with a fluorinated polymer. Various concentrations of the polymer are investigated to obtain the optimum alteration in wettability to intermediate gas-wet.. This wetting condition is achieved with an 8% polymer solution treatment, which yields maximum gas mobility, ultimately increasing the relative permeability curves and allowing enhanced recovery from gas-condensate wells. The treatments are performed mainly at room conditions, and also under high pressure and high temperature, simulating the natural environment of a reservoir. Several experimental techniques are implemented to examine the effect of treatments on wettability. These include flow displacement tests

and oil imbibitions. The experimental work took place in the Wettability Research Lab in Texas A&M University at Qatar in Doha, Qatar.

The studies in this area are important to improve the productivity of gas-condensate reservoirs where liquid accumulates, decreasing production of the well. Efficiency in the extraction of natural gas is important for the economic and environmental considerations of the oil and gas industry. Wettability alteration is one of the newest stimulation methods proposed by researchers, and shows great potential for future research and field applications.

DEDICATION

*to my parents Carlos G. and Ruth,
for their loving support every step of the way*

*to my grandmother, mi Abue Olguita,
for sharing her energy and motivation,
being a role model of strength and wisdom*

Thank you.

I love you all very much.

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I would also like to thank Dr. Ehlig-Economides, for the academic advice and guidance since early in my career. I greatly appreciate the opportunities I have been given. It has been a pleasure working with you.

NOMENCLATURE

A	cross sectional area	q_g	gas volumetric flow rate
$\frac{dp}{dl}$	pressure gradient	r	interface radius
g	gravitational acceleration	R	gas constant
k	permeability	S_l	liquid saturation
k_{abs}	absolute permeability	t	time
k_e	effective permeability	T	temperature
k_g	gas effective permeability	v	fluid velocity
k_r	relative permeability	V_b	bulk volume
k_{rg}	gas relative permeability	V_d	dead volume
L	length	V_m	matrix volume
M	atomic mass	V_p	pore volume
N_c	capillary number	V_s	spacers volume
P_c	capillary pressure	V_1	porosimeter chamber volume
P_{nw}	non-wetting phase pressure	W_a	apparent weight
P_w	wetting phase pressure	W_{af}	final apparent weight
P_1	inlet pressure	W_{ai}	initial apparent weight
P_2	outlet pressure	W_{rf}	final real weight
q	volumetric flow rate	W_{ri}	initial real weight

β	high velocity coefficient
φ	porosity
μ	fluid viscosity
μ_g	gas viscosity
σ	interfacial tension
ρ	fluid density
θ	contact angle

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1. INTRODUCTION AND LITERATURE REVIEW

Condensate banking has been reported extensively in the industry's literature as a problem that affects primarily gas-condensate wells. As the bottomhole pressure drops below the dewpoint, retrograde condensation and water buildup impede flow of gas to the surface and deliverability starts to decrease. This section offers an introduction to the condensate banking problem, as well as some field examples where production has been affected. An overview of current solutions to this problem are included, with an emphasis in the background of wettability alterations, which is the main subject of this research work.

1.1. Condensate Banking

In most gas-condensate reservoirs, production rates are affected when the pressure near the wellbore region starts to drop. Commonly these wells produce gas with a small yield of condensate at the surface, approximately 10 STB/MMscf in lean gas reservoirs, and up to 300 STB/MMscf in rich gas reservoirs (Kamath 2007). As the pressure near the wellbore decreases, droplets of liquid from the heavier hydrocarbons start to form when pressures below the dewpoint are reached. The term retrograde gas is often used to call this liquid accumulation in gas wells. The phase diagram in Fig. 1 illustrates this process. As gas is being extracted, the bottomhole pressure drops isothermally along the vertical line and enters the two-phase region where condensate is formed. The liquid dropout can be from 2% to 20% of the production, depending on the composition of the hydrocarbons.

This thesis follows the style of *SPE Journal*.

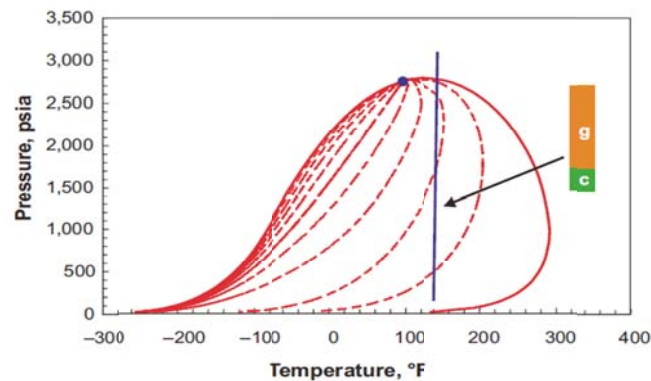


Fig. 1-Gas-condensate phase diagram, illustrating isothermal decrease in pressure where condensate starts to form. Adapted from Kamath (2007).

Fig. 2 shows the condensate bank formed vertically along the well. The liquid saturation blocks the near-wellbore region, decreasing productivity up to 50% in some cases (Kamath 2007). Typically, the condensate bank can reach tens of feet in radius, but even more in extreme cases, depending on the formation. In the illustration below we can see how the saturation of condensate decreases as the radial distance increases. Condensate banking affects mainly the near-wellbore region, making the mobility in this area the focus of our study.

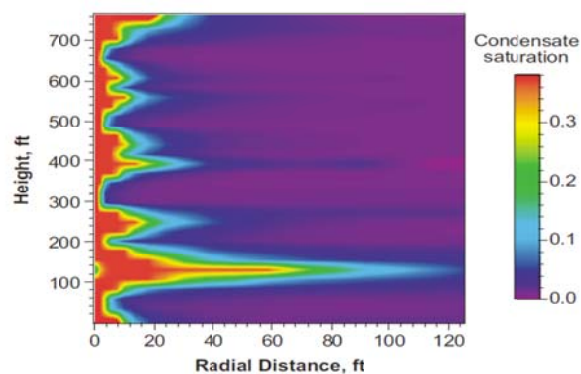


Fig. 2-Condensate buildup near the well, decreasing saturation with incremental radial distance from the well. Adapted from Kamath (2007).

The reduction in mobility in the near wellbore area is a consequence of liquid trapped in the pores of the rock, when the pressure difference between the non-wetting and the wetting phase is large. Capillary pressure is defined below (Anderson, W.G. 1987),

$$P_c = P_{nw} - P_w, \dots \dots \dots (1)$$

where P_c is capillary pressure, P_{nw} represents the pressure of the gas phase and P_w represents the pressure of the liquid phase in gas-condensate systems.

As the condensate bank is formed, the capillary forces start to overcome the viscous forces of the gas, causing trapping in the pores. This liquid buildup has direct negative effect on the gas mobility, sinking the gas relative permeability values. The relative permeabilities give us a measure of the conduction of fluids in porous media when two phases are present (Anderson, W. 1987). These are defined by the ratio of the effective oil or gas permeabilities k_e to the absolute permeability k_{abs} of the rock.

$$k_r = \frac{k_e}{k_{abs}}, \dots \dots \dots (2)$$

Many models have tried to characterize the condensate bank and it has been found that the relative permeability curves in a two-phase system are a function of the capillary number (N_c) (Bozorgzadeh and Gringarten 2006). The equation below defines N_c ,

$$N_c = \frac{v \mu}{\sigma}, \dots \dots \dots (3)$$

where the viscous forces are represented by the fluid velocity v and the fluid viscosity μ , and the capillary forces are represented by the interfacial tension σ .

Wettability and interfacial tension are related to capillary pressure proportionally through the equation below (Anderson, W.G. 1987),

$$P_c = \frac{2\sigma\cos\theta}{r}, \dots\dots\dots(4)$$

where θ is the wetting angle, σ is the interfacial tension and r is the radius of the interface.

As capillary number increases, the wetting and non-wetting relative permeabilities increase, given that the fluid viscous forces overcome the capillary forces, decreasing trapping of liquids (Fulcher et al. 1985). At the bottomhole and in high permeability reservoirs we deal with high velocity at the wellbore, which lessen the trapped oil saturation. However, with liquid accumulation in the wellbore area, velocity of the fluids decrease, affecting the relative permeability values and impairing the production. In the fields there is not much control on the velocity at which fluids are being produced given the various production constraints, but altering the wettability of the rock can greatly reduce residual liquid saturation and improve the mobility of the phases.

Studies have shown that with N_c ranging from 10^{-8} to 10^{-6} , residual saturations are not a strong function of capillary number (Mohanty 2010). In gas-oil systems the critical capillary number for mobilization of gas (10^{-8}) is smaller than to mobilize oil (10^{-5}) (M. Ding and Kantzas 2007). The flow experiments in the lab have to be conducted at a pressure gradient that results in a similar value of capillary number as that present in the region of interest around the wellbore. We decided to conduct our experiments at a pressure gradient between 0.1 and 0.3 psi/cm based on our communication with gas companies.

1.1.1. Field Cases

Several cases of condensate banking have been reported in the oil and gas literature. Loss in productivity of gas wells has been widely seen and analyzed around the world. Well testing procedures have helped predict the production from gas wells, trying to characterize the behavior of the liquid accumulation around the well. This issue is well known to the industry and unfortunately the solutions proposed to remediate condensate

blockage are not permanent. Treatments performed offer a temporary remediation, allowing liquid to build up again near the wellbore after a period of time. In this section some examples of real fields are presented. All of these have been affected by retrograde gas condensation.

Cal Canal Field, California (Engineer 1985) – Cal Canal Field is located 30 miles west of Bakersfield, California. The field was discovered in 1977 with an initial reservoir pressure of 7,343 psig and a dewpoint pressure of 5,835 psig. The reservoir temperature is 271°F. Producing from the Stevens sand, at 11,500 ft deep on average, the reservoir is very tight and abnormally pressured. Its average porosity is 12% and its permeability varies from 0.01 to 0.1 md. The irreducible water saturation is around 59%. The GIP was estimated to be 103.3 Bcf, including 85 Bscf of dry gas and 26.86 MMSTB of condensate. Average production from 16 wells is 541 Mscf/D of gas and 198 bbl/D of condensate. Production decline is observed in Fig. 3 below. There was an estimate that only 10% of the OGIP could be recovered, even with the reservoir pressure still above the dewpoint pressure. Fracturing and acidizing treatments were not successful. This is one of the extreme cases where more than 90% of the well productivity was lost because of condensate blocking.

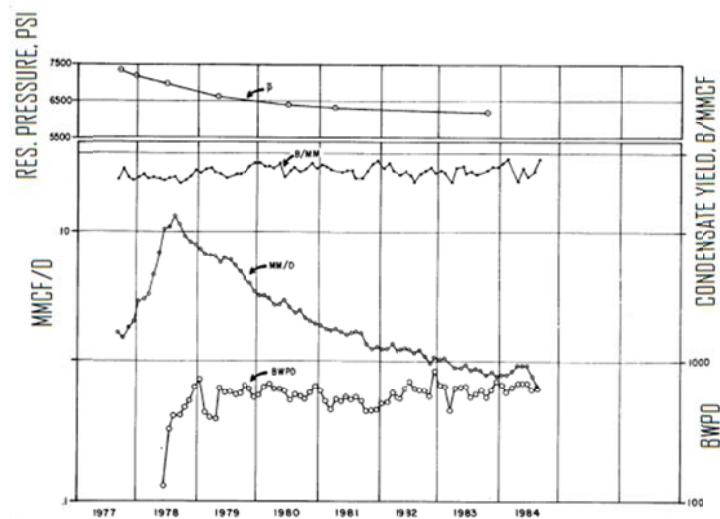


Fig. 3-Production data from Cal Canal Field, California, where only 10% recovery was predicted due to condensate banking. Adapted from Engineer (1985).

Kurunda Field, Australia (Hueni and Hillyer 1991) Kurunda Field is a lean gas-condensate reservoir from Tiirrawarra sandstone in the south of Australia. The formation is about 170 ft thick with 13% porosity and mostly low permeability around 5 md. The irreducible water saturation is approximately 30%. The GIP is 63.3 Bcf. Two producing wells yield 11MMcf/D and 3MMcf/D. The first one, well #3L is slightly below the laboratory dewpoint of 3,616 psi, with bottomhole pressure of 3,592 psi. Its production is relatively constant, as seen in Fig. 4. The second well, #1L is below the dewpoint pressure of 3,505 psi, with a bottomhole pressure of 3,150 psi, indicating a decrease in rate seen in Fig. 5.

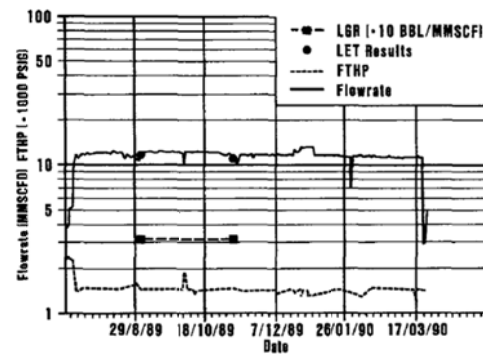


Fig. 4-Karunda #3L constant production data with pressure still above the dewpoint (Hueni and Hillyer 1991).

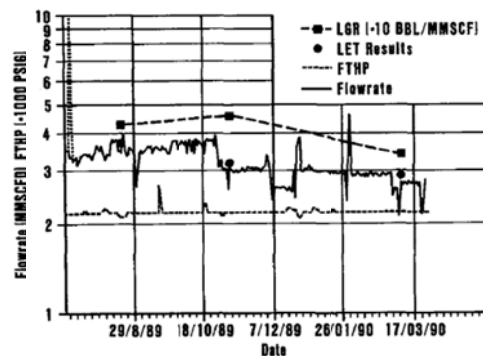


Fig. 5-Kurunda #1L production data, showing a decrease with pressure below the dewpoint (Hueni and Hillyer 1991).

Arun Field, Indonesia (Afidick et al. 1994) Arun Field is located on the North of Sumatra, Indonesia. Production began in 1977 at a reservoir pressure of 7,100 psia and a temperature of 352°F at 10,050 ft deep. It is a limestone formation with thickness of

more than 1,000 ft. The field produces 3.4 Bscf/D from 78 producers. The average pressure is 2,250 psi, which is below the dew point pressure of 4,400 psi. The Productivity Index plot in Fig. 6 below shows the decrease in deliverability of the well as the reservoir pressure drops. About 25% of the gas produced is injected to sweep rich gas condensate towards the producers.

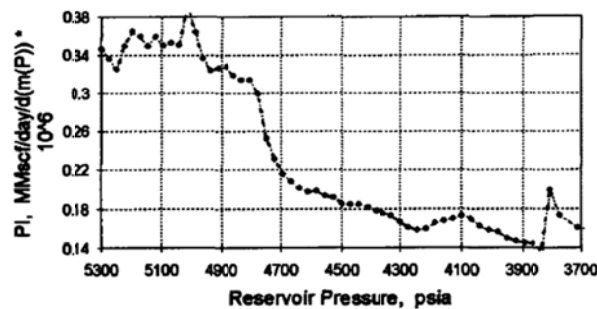


Fig. 6-Productivity Index (PI) vs. reservoir pressure of the Arun Field, showing a sharp drop with decreasing pressure. (Afidick et al. 1994).

Britannia Field, UK (Goktas et al. 2010) Britannia Field is located in the North Sea, approximately 209 km from the UK coast. It was discovered in 1975 and it started producing in 1998. It is a sandstone formation with permeabilities ranging from 0.01 to 200 md. The deepest gas liquid contact is at 13,170 ft deep. Initial reservoir pressure was 6,000 psi. GIP is estimated to 4.2 tcf. The reservoir pressure ranges from 1,000 to 3,500 psi, largely below the dewpoint pressure of 5,600 psi. There are 46 producing wells, from which the average productivity loss is 50% to 60%. Fig. 7 shows the decrease in pressure that has caused impairment of the well and Fig. 8 shows the liquid dropout as the wellbore pressure decreases.

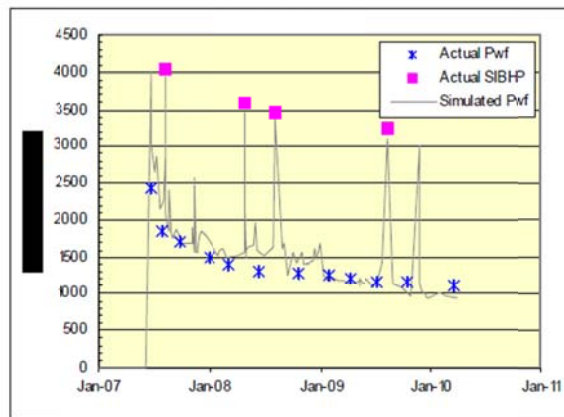


Fig. 7-BX1 pressure drop vs. time in Britannia Field, where the average productivity loss is 50% to 60% (Goktas et al. 2010).

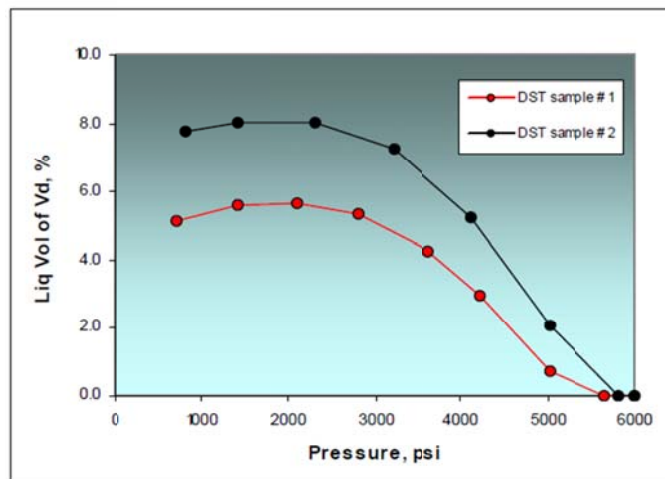


Fig. 8-Liquid condensation curve, showing increase in liquid dropout as BHP decreases (Goktas et al. 2010).

1.2. Current Methods for Reducing Condensate Banking Effect

In this section, methods to solve condensate blockage around the wellbore are presented. These methods are currently used in industry and each of them has different applicability depending on the formation and on the regulations of the region. Hydraulic fracturing is presented shortly as a solution for condensate banking, although it is an extensive subject area more known to be used in producing from low permeability reservoirs and unconventional oil and gas resources. Solvent injection is also described in this section with the purpose to illustrate increase in production due to a decrease in interfacial tension. Finally, a literature review on wettability alteration will serve as an introduction to this new area of research. In this case the approach taken alters the interaction of fluids with the surface of the rock, modifying the contact angle to reach an intermediate wetting condition.

1.2.1. Hydraulic Fracturing

Hydraulic Fracturing is a procedure that has been around since the 1940's. This stimulation process allows maximization of oil and gas extraction in low permeability formations and from unconventional resources. The treatment fluids are usually composed of water and sand with chemical additives. These are pumped into the formation at high pressure, inducing long fractures. The fractures allow better flow of oil and gas from the formation to the well. Great development of treatment design has allowed the industry to produce 600 Tcf of gas and 7 Bbbl of oil only in the United States (American Petroleum Institute 2010). Still to these days hydraulic fracturing is a delicate procedure that involves many considerations. The effectiveness and cost are influenced by many factors such as the selection of fluids, volumes to be injected, injection rates, etc. Most importantly, the total net revenue will define the correct treatment to be applied. Fracturing a well can be a large part of the total well cost (Veatch 1983). Depending on where the treatment would be performed, environmental

considerations are also present and in some regions there are more strict regulations than in the United States. Hydraulic fracturing has not been implemented worldwide. Environmental impact studies are still being done to determine the feasibility of this procedure in fragile surroundings. It is considered in this thesis as a solution to condensate banking, but it is by itself a large subject area, not in the scope of this study.

When applied in gas-condensate reservoirs to overcome the condensate banking problem, hydraulic fracturing could result in solving the problem by inducing a new pressure profile in the reservoir that minimizes condensate dropout. However, this is not always the case. In low pressure reservoirs, it has been shown that condensate accumulation around the fracture face could still result in significant productivity loss. In addition, there are cases of reservoir temperature and pressure conditions where it is challenging to find a suitable fracturing fluid.

1.2.2. Solvent Injection

Studies have shown that the relative permeability curves are a function of the liquid saturation and are influenced by the interfacial tension (IFT) and capillary number (N_c) (Ali et al. 1993; Mohanty 2010). As the IFT decreases, mobility of the liquids increases. Therefore to reduce liquid blockage around the wellbore, a solution is to decrease the IFT. Previous experimental work has been conducted to study the effect of IFT on liquid mobility, and it has been shown that recovery increases with low IFT values (Ali et al. 1993). To achieve a reduction in IFT gas can be injected to decrease the composition of heavier components in the condensate, and try to vaporize some of the liquid accumulation. However, the vaporization may not occur because the light components tend to accumulate at the vapor phase, and these are the first fluids to be produced.

Injection of solvents has also been studied and even proven in a real field, as was the case of Hatter's Pond field in Alabama (Al-Anazi et al. 2003). Hatter's Pond field was discovered in 1974. Production comes from two formations, the Smackover, a shallow

marine dolomite, and from the Norphlet sandstone formation. The field has 15 producing wells. Well 3-6 was producing from the Norphlet formation, where the thickness is 126 ft, the permeability is 1.25 md and the porosity 11.7%. Productivity decreased over time from 33 MMscf/D of gas and 4,700 bbl/D of condensate to 0.25 MMscf/D and 87 bbl/D. The well was treated with 1,000 bbl of methanol after performing laboratory tests to investigate the sensitivity of the reservoir cores to the substance. The treatment was immediately effective, increasing productivity to 0.5 MMscf/D of gas and 157 bbl/D of condensate. Nonetheless, production started decreasing after 4 months after the treatment. Fig. 9 below shows the production history before and after treatment.

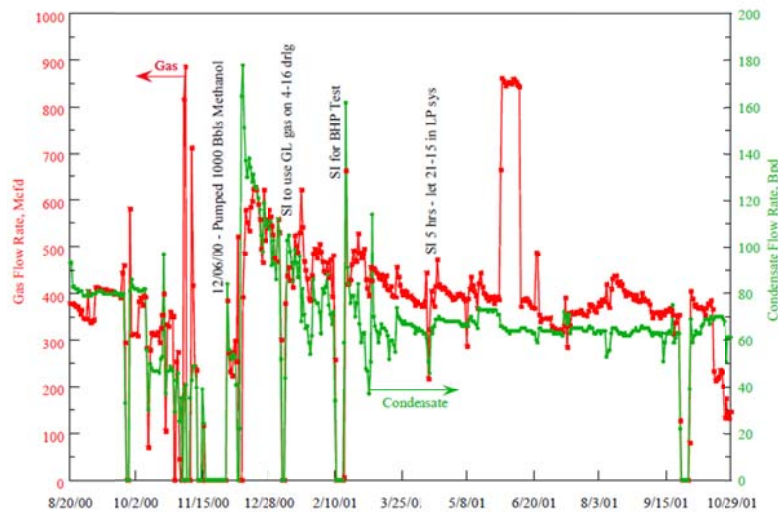


Fig. 9-Production data from well 3-6 in Hatter's Pond Field, where an increase in flow rate is observed after a methanol treatment, but the effects persist for only four months, disappearing afterwards (Al-Anazi et al. 2003).

1.2.3. Wettability Alteration

As discussed earlier, capillary pressure is one of the most influential parameters that contribute towards condensate blocking through its effect on the immobile condensate saturation. Wettability alteration towards reduced liquid-wetting aims at reducing the value of capillary pressure resulting in enhanced liquid mobility and less liquid accumulation.

Li and Firoozabadi (2000) proposed to alter wettability and conducted experiments on Berea sandstone cores injecting chemicals at room temperature. They reported increase of relative permeability and improvement in productivity rates. Tang and Firoozabadi (2002) followed up with imbibition tests at temperatures up to 90°C. They used fluoropolymers, showing increase in the mobility of the liquid-phase. Fahes and Firoozabadi (2005) continued the work of Tang with temperatures up to 140°C. They used nine polymers with water as a solvent and only one polymer resulted in permanent alteration of wettability at that temperature. Kumar et al. (2006) performed core flooding experiments with fluorinated surfactants and concluded that these were not stable at high temperatures. The surfactant Novec FC4430 yielded favorable results when mixed with methanol and water. The gas and condensate relative permeabilities increased by a factor of 2 with a water concentration of up to 10%. These experiments were performed at reservoir conditions.

Liu et al. (2006) did not specify the chemical or solvent used. However, the results they reported showed potential. The chemical WS12 is thermally stable and the relative permeability of gas increased by a factor of 2. This treatment has been applied to a real field as reported in Li and Liu (2008). They conducted a field application of the WS12 chemical in the Dongpu gas condensate reservoir in China. The results show that an enormous increase in production, but it declined after about four days. Just some of the relative permeability increase settled after the treatment. This application had positive results; nevertheless, the lack of previous production information from that well, makes it hard to have a real comparison of the effect of the chemical treatment.

Al-Anazi et al. (2007) show that fluorosurfactants are ineffective for wettability alterations in carbonate cores. An experiment with water, acetic acid, and ethyl alcohol showed the same results as a mixture adding the fluorosurfactant. They also showed that results were better for cores with a higher permeability. Tests with silane solved in desulfurized naphtha showed good results increasing the productivity index. Even though it does not appear to be much change, a factor of 2 is a significant increase. These tests were also performed at reservoir conditions. Bang et al. (2008) conducted experiments at reservoir temperature and pressure with a different set of mixtures. L19945 was mixed with 2-butoxyethanol (EGMBE) and ethanol, which showed an increase in oil and gas relative permeability of a factor of more than 2. These mixtures had surfactant concentrations from 0.1% to 2%. Similar results were obtained for L19973 in a mixture of propylene glycol (DPGME) and isopropanol (IPA), where the increase was almost by a factor of 2. Another advantage of these chemical mixtures was that the chemicals did not damage the rock.

Previous work has shown how it is possible to alter wettability of rocks to improve oil and gas mobility. Many substances have proved to be effective, and based on these findings we are able to contribute with a study that proves an optimum state of wettability that can be achieved. A simulation study by Zoghbi et al. (2010) showed results for an optimum state of wettability. This work is based on the analysis that the interaction of the fluids with the rock surface reaches a point that maximizes mobility. The treatments with a fluorinated surfactant show shifts in the relative permeability, yielding an optimum concentration that will maximize recovery. This study is important for economic considerations of field production, where stimulation treatments may be needed.

2. EXPERIMENTAL SET UP AND PROCEDURE

2.1. Materials Used: Cores, Fluids and Chemicals

The materials used in this study were carefully selected to obtain accurate results applicable specifically to gas-condensate reservoirs. They also simplify the experimental procedure without compromising the validity of the results. Since the changes we consider are due to wettability, we eliminate any other possible influence on mobility changes such as IFT and N_c effects.

2.1.1. Berea Sandstone Cores

Berea sandstone cores have been used extensively in laboratory experiments to investigate the flow behavior of fluids in the oil and gas industry. They are obtained in Cuyahoga County, Ohio, and commercialized for construction, industry and research around the globe. It is considered from the Late Devonian age. Berea is fine-grained and its grains are angular (Ohio Historical Central 2007). In this study we use cores that are approximately 1 inch in diameter and 3 to 6 inches in length. Their porosity is around 20% and their absolute permeability varies approximately from 170 to 260 md. The specifications of the cores are summarized in Table 1 . A picture can be seen in Fig. 10.

Table 1-Properties of Berea sandstone cores used for experimental procedures.

Core	Length (in)	Diameter (in)	Dry Weight (g)	Porosity ϕ (%)	Permeability (md)
B_RM14	2.745	1.006	75.6	21.4	178.34
BR1	3.008	0.999	80.78	21.5	236.06
BR2	2.95	0.999	78.93	22.8	233.9
BR3	5.945	0.998	158.6	22.03	264.74
BR4	6.006	1.018	172.17	19.5	186.53
BR5	5.951	1.018	170.6	19.4	187.71
BR6	6.036	1.019	173.27	19.5	173.66
BR7	5.936	1.018	171.2	NA	NA
BR8	6.03	1.019	172.96	19.4	186.92
BR9	5.94	1.018	169.84	19.4	198.78

**Fig. 10-Berea sandstone cores.**

2.1.2. Gas and Liquid Phases

The selection of synthetic fluids is very important in experimental procedures. For our purpose, the system needs to be simple to assure the dependency of gas mobility on the wettability of the rock and accurately measure the changes. Compressed air and nitrogen (N_2) were used as the gas phases. Nitrogen is of 99.9% purity and has a viscosity of 0.01787 cp. It is an inert gas, abundant in the atmosphere and easy to obtain in compressed form. It is also safe to work in the laboratory. N-decane ($C_{10}H_{22}$) was used as the liquid phase. N-decane has a viscosity of 0.92 cp and a density of 0.7288 g/cc at room temperature. N-decane was chosen because it is a hydrocarbon that can very well simulate reservoir fluid blockage along the wellbore region and the fluid behavior for the purpose of our study. It is also easy to handle with moderate safety considerations in experimental procedures at room conditions as well as at high temperatures and pressures. Air and n-decane were employed in the liquid imbibitions. For the core displacement tests nitrogen and n-decane were used. Note that the fluids and conditions are maintained the same throughout the experiments, avoiding changes in mobility due to interfacial tension IFT (Ali et al. 1993).

2.1.3. Fluorinated Surfactant and Solvent

The polymer used is Zonyl 8740. This DuPont product is an aqueous fluorochemical that provides water and oil repellency on porous mineral surfaces. It has an average molecular weight of 1,000. It is soluble in water and methanol, while it chemically bonds to the surface of the rock, allowing durable results. At room temperature it has a density of 1.095 g/cc and a viscosity of less than 250 cp.

The solvents used for the experiments are distilled water (H_2O) and methanol (CH_3OH). Methanol has a viscosity of 0.59 cp at 20°C, and a density of 0.7918 g/cc.

2.2. Equipment and Experimental Setup

The experimental setup can be seen in Fig. 11. It includes a core holder connected at the inlet to a valve to regulate the injection pressure of fluids. The fluids are received from the gas supply, and a liquid accumulator attached to a pump for liquid injection. At the outlet the core holder is connected to valves to control fluid flow, a vacuum pump to remove air for initial liquid saturation, a backpressure regulator to adjust outlet pressure, a separator to recover the fluids, a balance and a gas flow meter to record data. Pressure transducers are placed at the inlet and outlet to record the pressure drop in the system. An oven is used separately from the system to dry the rock after all the procedures.

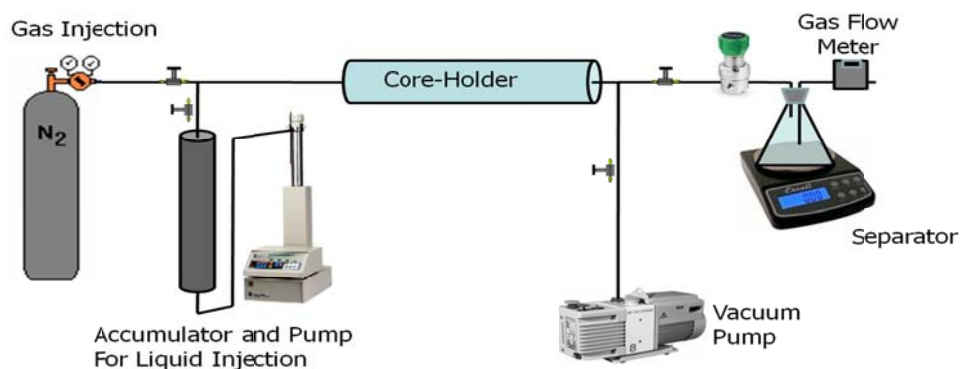


Fig. 11-Experimental Setup.

Specifications of the equipment can be seen in Table 2 in the next page. Given that the laboratories in Texas A&M at Qatar are fairly new, all the equipment is less than three

years old and it is kept in good condition. The experimental procedures are described in detail in the next section.

Table 2- Equipment specifications.

Item	Brand	Model	Specifications
Oven	Binder	FD 53	Up to 572° C
Balance	Mettler Toledo	X54035	Max 410 grams
Gas Regulator	Swagelok	KCYIERH412A20000	HP 3600 psig, LP 0 - 50 psig
Back Pressure Regulator	Swagelok	KBPIGOA4A60000	Inlet 0 - 250 psig
Transducer	Swagelok	S-Model Transducer	0 - 300 psig
Pumps	Teledyne Isco	500D	Syringe Pump
Accumulator	Phoenix Instruments		Working Pressure 5000 psi, Working Temperature 300°C
Core Holder	Phoenix Instruments	Triaxial Core Holder	Working Pressure 5000 psi, Working Temperature 150°C

2.3. Experimental Procedures

Below is a description of each of the procedures to obtain data from the cores before and after treatment. These experimental procedures are considered standard for core analysis in the oil and gas industry. Excel spreadsheets were used for calculations and analysis of the data obtained.

2.3.1. Dimensions

The dimensions of each one of the cores are measured with a caliper. The measurements are registered in inches and then converted to centimeters in the spreadsheet calculations.

2.3.2. Porosity Measurements

The porosity of the core samples is measured using a helium porosimeter. Helium is widely used for porosity measurements because it is an inert gas that has low absorption and high diffusivity. It also is also available in compressed form. The porosimeter was calibrated before the measurements were taken. With the pressure readings ($P_{1,2}$), the volumes of the chamber (V_1), the dead volume in the sample cell (V_d) and the volume of the spacers outside the sample cell (V_s) we obtain the matrix volume (V_m) from the equation below.

$$P_1 V_1 = P_2 (V_1 + V_d + V_s - V_m) \dots \dots \dots (5)$$

Then the porosity can be calculated from the ratio of the void volume and the bulk volume (V_b) of the rock as seen in Eq. 6.

$$\varphi = \frac{V_b - V_m}{V_b} \dots \dots \dots (6)$$

2.3.3. Absolute Permeability Measurements

The capacity of a porous medium to transport fluids is called absolute permeability. It is a property of the core, independently from the fluid used. This property can be measured during single-phase flow, using Darcy Law:

$$v = -\frac{k}{\mu} \frac{dp}{dl} \dots \dots \dots (7)$$

where k is the absolute permeability of the medium, $\frac{dp}{dl}$ is the pressure gradient, v is the velocity and μ is the viscosity of the fluid.

This relationship is not valid at high velocities of the flowing fluid, especially for gases. In this case we use Forchheimer's equation to represent the high velocity flow parameters:

$$-\frac{dp}{dl} = \frac{v\mu}{k} + \beta\rho v^2 \dots\dots\dots(8)$$

where k is the absolute permeability, and the added parameters are the high velocity coefficient β , and the density of the flowing fluid ρ .

The integration of Eq. 8 results in the following equation for compressible gas flow:

$$\frac{(P_1^2 - P_2^2)A}{2Lq} = \frac{\mu}{k} + \left(\frac{q}{A}\right) \frac{\beta M}{RT} \dots\dots\dots(9)$$

where P_1 is the pressure at the inlet, P_2 is the pressure at the outlet, M is the atomic mass of the gas, R is the gas constant, T is the temperature, L is the length of the core, q is the volumetric flow rate of the gas at standard conditions and A is the cross sectional area.

To measure the permeability and the high velocity coefficient, the core sample is packed in the core holder and overburden pressure is applied to 1,500 psi at room temperature. Then gas is injected at various differential pressures. The volumetric flow rate of the gas is measured at the outlet. The average pressure is kept over 60 psia to avoid gas slippage effects.

The left-hand side of Eq. 9, $\frac{(P_1^2 - P_2^2)A}{2Lq}$ is plotted on a y-axis vs. $\left(\frac{q}{A}\right)$, forming a linear relationship. The y-intercept is the free constant and equal to $\frac{\mu}{k}$. The absolute permeability is then obtained dividing μ by y-intercept.

2.3.4. Imbibitions

The imbibition procedure measures the amount of liquid imbibing in the core sample with time. An air-saturated core is suspended with a nylon thread from the bottom of a balance, where the weight will be recorded. The sample is then immersed in a container with n-decane. The liquid saturation in the core is calculated from the difference between the apparent weight of the dry core and the apparent weight of the core at each time step. The apparent weight of the dry core is calculated at the end of the experiment with the formula:

$$W_{ai} = W_{af} - (W_{rf} - W_{ri}) \dots \dots \dots (10)$$

where W_{ai} is the initial apparent weight of the dry core, W_{af} is the final apparent weight of the core at the end of the imbibition experiment, W_{rf} is the real weight of the dry core at the end of the experiment, and W_{ri} is the real weight of the dry core at the beginning of the experiment. Then the n-decane saturation is calculated at every time step t during the experiment as the fraction of liquid imbibed over the pore volume of the core. In this calculation we use the formula:

$$S_l(t) = \frac{W_a(t) - W_{ai}}{g\rho V_p} \dots \dots \dots (11)$$

where $S_l(t)$ is the liquid saturation at time t , $W_a(t)$ is the apparent weight of the core sample at time t , g is the gravitational acceleration, ρ is the density of the liquid and V_p is the pore volume of the sample.

Imbibition tests are a measure of wettability of the core because it is driven by capillary forces. The capillary pressure is defined as the difference between the non-wetting phase (air) and the wetting phase (n-decane). When liquid acts as the wetting phase, its pressure is lower than the gas phase, maintaining a capillary pressure that stops the complete imbibitions of the wetting phase in the core. An untreated core can reach a liquid saturation of more than 60% after an hour. The treatment of the core decreases the liquid saturation in the core sample even after several hours of imbibition.

2.3.5. Core Flooding Procedure

The dry rock is placed inside the core holder and an overburden pressure of 1,500 psi is applied. Then liquid is injected at a constant rate at the inlet, while the outlet pressure is atmospheric. The inlet pressure increases rapidly until breakthrough of the liquid in the outlet. Steady-state is achieved usually after six pore volumes of oil have been injected. The pressure is measured at every time step until steady state is reached. The difference in pressure drop is noted throughout this experiment in the treated and untreated rocks. In the untreated core the pressure gradient is higher than the pressure gradient in the treated core. This is an indication of increase in liquid mobility, and the increase in liquid mobility is a sign of the alteration in wettability. The pressure drop at steady state is a function of the relative permeability of the rock.

2.3.6. Relative Permeability Measurements

Measurements of relative permeability are hard to obtain. The reproduction of the relative permeability curves in oil and gas systems require a laborious and time-consuming procedure. In our study we obtain the endpoints of the relative permeability curves, where alterations in wettability are easier to notice. The procedure is described below.

Berea sandstone cores are saturated in the core holder or in a saturation cell, where more than one core can be saturated at the same time. When the core is placed inside either one of these chambers, air is taken out with the vacuum pump and left there for about an hour, making sure that complete vacuum has been created inside. Then injection of liquid can start to fill the vacuumed pores of the rock. The accumulator is filled with liquid in advance to start injecting at this point and is adjusted to inject at a high rate until the pressure in the chamber reaches 200 psi, where the core is left overnight. When the chamber is opened the next day, the weight of the saturated core is measured to

determine the percentage of saturation. In our experiments it is usual to obtain 95% to 99% saturation of the rocks.

Once the core is saturated in liquid, injection of gas starts at a constant pressure, usually from 2 psi to 3.5 psi, depending on the length of the rock to obtain pressure gradients from 0.1 psi/cm to 0.3 psi/cm. Measurements of the gas rate are obtained from the outlet all throughout the experiment and they increase until steady state is reached.

At low velocity Darcy's law applies and we can calculate the effective permeability of gas k_g from the equation below where q_g is the volumetric flow rate, A is the cross-sectional area of the core sample, $P_{1,2}$ are the pressures at the inlet and the outlet, μ_g is the viscosity of the gas and L is the length of the core.

$$\frac{q_g}{A} = \frac{k_g (P_1 - P_2)}{\mu_g L}, \dots \dots \dots (12)$$

The gas relative permeability is defined as the ratio of the effective permeability to the absolute permeability.

$$k_{rg} = \frac{k_g}{k_{abs}}, \dots \dots \dots (13)$$

Then the endpoint of the gas relative permeability curve is obtained from the measurement of gas relative permeability at steady-state plotted vs. the residual oil saturation calculated from the weight of the core immediately after it is unpacked from the core holder.

The relative permeability curves are influenced by interfacial tension and by capillary number effects (Ali et al. 1993; Fulcher et al. 1985). To determine that the change in the relative permeability endpoint is solely caused by the alteration in wettability, the gas and liquid phases are maintained for all of the experiments at the same conditions of temperature and pressure for the pre-treatment experiment, making sure that changes in IFT are not influential. Also the injection of gas is performed at the critical capillary number to mobilize gas. This value is 10^{-8} and was obtained in studies by M. Ding and

Kantzas (2007) in the references. Capillary number has a significant influence at high flow rates, but its effects are negligible at low injection rates (Mohanty 2010).

Fig. 12 below was taken from a simulation study that compared different wettability systems (Zoghbi et al. 2010). We observe the endpoint of the relative permeability curve for the intermediate-wet system to be the highest of all three. Even though there is more reduction of residual oil saturation for the gas-wet system, the gas relative permeability is lower, which indicates a decrease in mobility. The endpoints of the gas relative permeability curves are circled. These are the points we measure in our experiments.

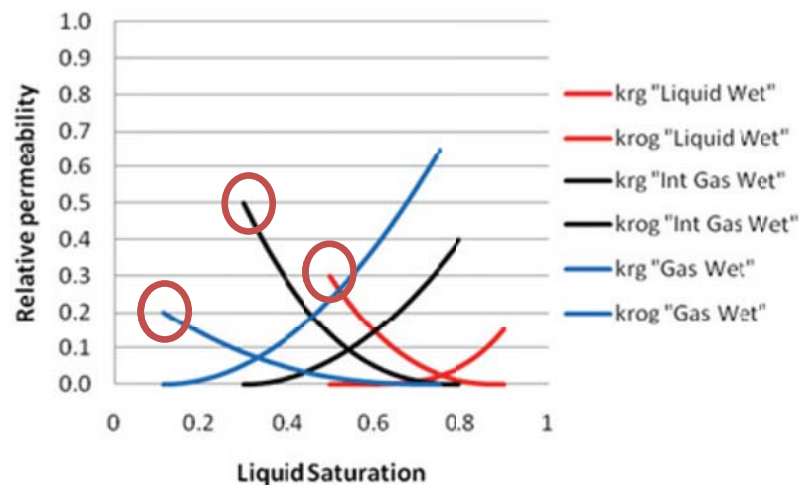


Fig. 12-Relative permeability curves in three different wettability systems. Intermediate-wet system yields maximum mobility (Zoghbi et al. 2010).

2.3.7. Chemical Treatment

The treatment solution is prepared by mixing Zonyl with water or with methanol. The amount of mass to be mixed is calculated with the density of the solvent to assure accuracy. The solution is stirred in a beaker in order to assure complete solution of the

polymer in the solvent. Then the mixture is placed in the accumulator for injection and sealed to avoid evaporation of the liquids.

The dry core is placed in the core holder with an overburden pressure of 1,500 psi. The mixture is ready to be injected in the accumulator. The injection starts at a rate of 2 cc/min until 5 pore volumes have gone through the core. Samples of the treatment mixture are collected at the outlet. When enough solution has gone through the core, the injection is stopped and inlet and outlet are sealed to avoid evaporation of the mixture as the treatment takes effect. The aging time is 3 hours for water and 12 for methanol. Water treatments may swollen the sandstone clay particles and decrease the absolute permeability of the rock. 3 hours of aging were considered enough time for the polymer to be absorbed without damaging the rock. However, we did encountered decrease in absolute permeability of the cores treated with water. Then methanol was chosen as solvent. Methanol experiments did not damage the rock considerably. 12 hours of aging time allows the polymer to bond to the surface of the rock.

After the aging period, the core is flushed with the solvent to avoid excess of the polymer that can block the pores. Once 5 pore volumes have gone through the core, nitrogen is injected at a pressure of about 10 psi for about 30 minutes. The core is then taken out to be put to dry in the oven.

3. RESULTS

This section details the results obtained from the chemical treatments on Berea sandstone at different concentrations of a fluorochemical. The properties of the rocks are measured before treatment to obtain the reference values and ranges of gas relative permeability and residual oil saturation at different pressure gradients. After the treatment, the same measurements are taken to see the changes with the absorption of polymer in the rock. The results show the process of determining what treatment is appropriate after another; the analysis after each treatment helped us establish the conditions for the treatments to come.

3.1. Rock Properties

Berea sandstone cores are used for this experimental work. All of the rocks used should fall into the same ranges of properties in order to obtain an accurate comparison after treatment. Their permeability varies approximately from 170 to 260 md and their porosity is around 20%. All the cores have a diameter of roughly 1 inch and they are 3 inches or 6 inches in length. Table 1 summarized the rock properties. Table 3 indicates the treatment performed on each one of them.

Table 3-Treatment information for each core sample.

Core	Information
B_RM14	Treated 3% in Water at Room Temperature
BR1	Treated 2% in Water at High Temperature
BR2	Treated 3% in Methanol at Room Temperature
BR3	Untreated
BR4	Untreated
BR5	Treated 2% in Methanol at Room Temperature
BR6	Treated 4% in Methanol at Room Temperature
BR7	Untreated
BR8	Treated 8% in Methanol at Room Temperature
BR9	Treated 12% in Methanol at Room Temperature

3.2. Liquid-Wet Berea

In our study we refer to gas-condensate systems, where the wettability of Berea sandstone rocks is strong-liquid wet. Condensate is the wetting phase with a contact angle ranging from 0 to 75°. Our intent is to modify this angle to transform the wettability of the system to intermediate gas-wet. In Fig. 13 below we can visually appreciate the change in wettability of the rock. The droplets of water and decane form a very small contact angle with the surface in the untreated rock. The decane droplet is not even visible because it is absorbed by the pores. In the treated rock the droplets form a much larger angle with the surface as we can see in Fig. 14.

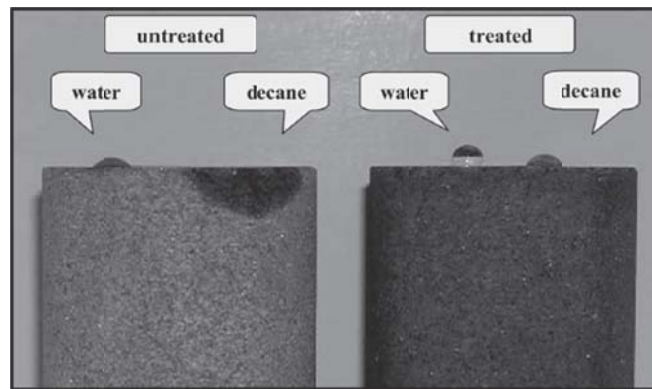


Fig. 13-Untreated and treated Berea sandstone. Adapted from Fahes and Firoozabadi, (2005).

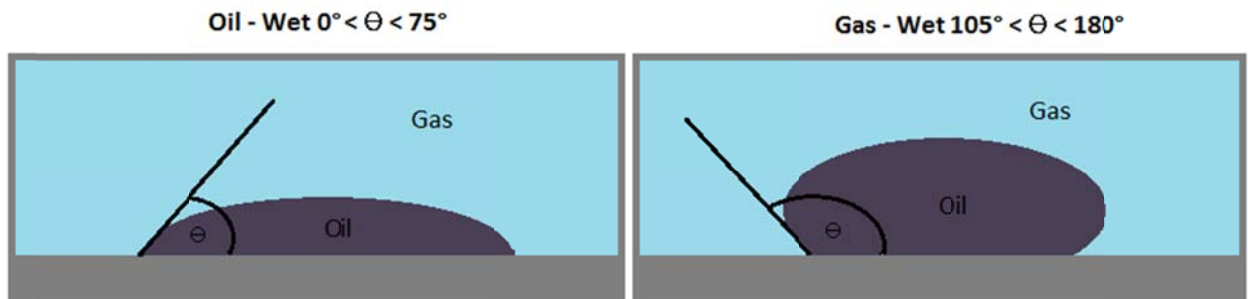


Fig. 14-Gas-Condensate wettability.

Fig. 15 shows the decane spontaneous imbibitions run before the treatment of the rocks. The core is initially saturated with gas (air) and it is immersed in decane while the change in weight is being recorded. The results show the absorption of liquid in the pore spaces with time. The data is reproduced for each core before treatment. The imbibitions for the shorter rocks BR1 and BR2 resulted in higher liquid saturation for the same amount of time. This is only because of the length. In longer rocks more time is needed

to obtain the same amount of saturation. In addition, there is more trapping of gas in the longer rocks because of the process of counter-current flow that the gas has to go through during this experiment. In the figure we appreciate the similar behavior for all of the rocks, which is important for the comparison of the results after treatment. More details on the pattern seen in these results are shown in APPENDIX A.

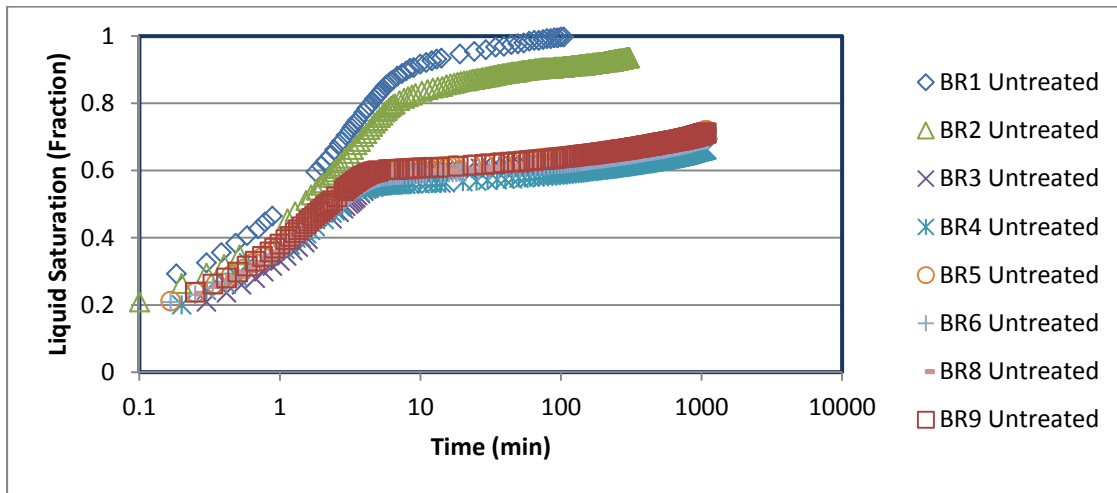


Fig. 15-Decane imbibitions for untreated Berea sandstone cores.

Before the treatments the gas relative permeability of the rocks are measured at the endpoints of the relative permeability curves. Fig. 16 shows the similar trend of measurements for all of the cores. We target a pressure gradient from 0.1 to 0.2 psi/cm, injecting nitrogen at a pressure of 1 psi to 1.5 psi for the 3-inch rocks, and 1.5 to 3 for the 6-inch rocks. After determining some of the preliminary results, we decided to use 6-inch rocks for the treatments. Information from the longer cores is much easier to obtain due to greater stability of the flow inside and all along the length in addition to reduced capillary end effect.

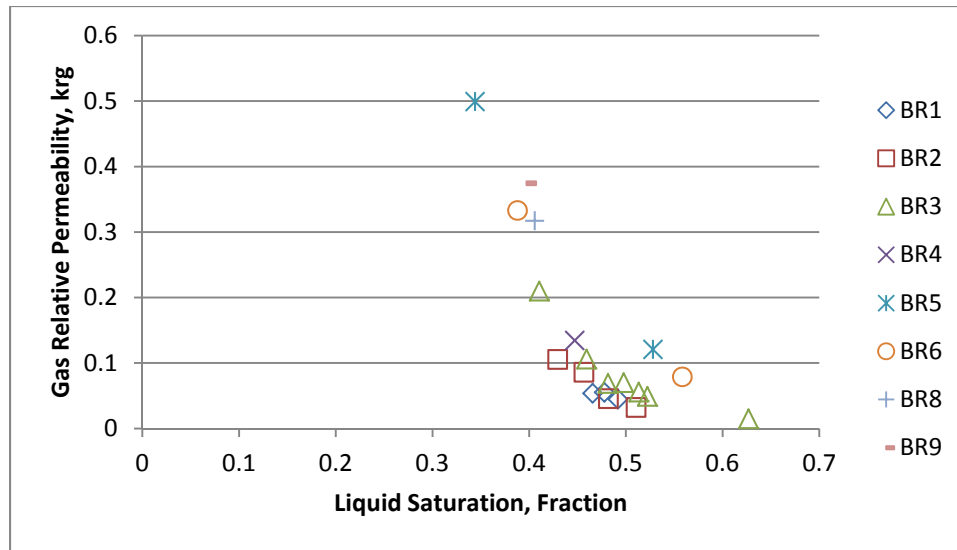


Fig. 16-Gas relative permeability of untreated rocks at the endpoints.

3.3. Treatment Results

After obtaining and analyzing the untreated information from the Berea cores, we determine the treatment to be performed. Initially one treatment was conducted at high temperature and high pressure. However, given the objective of this project to obtain an optimum wettability state, we decided to do treatments at room temperature that are less delicate and less time consuming. For our intent, room temperature treatments will deliver sufficient information. We may consider high temperature treatments for later stages of the research.

Table 4 shows a summary of the treatment results. A description for each one of the treatments follows below. Notice the reported values of polymer adsorption which increases from 0.4 mg/g to 1 mg/g as the concentration of the polymer is increased. The effect on absolute permeability in the successful treatments is negligible, in the order of 1%.

Table 4- Summary of treatment results.

High Temperature						
Core and Treatment	History	Absolute Permeability (md)	Dry Weight (g)	Polymer absorbed (g)	Polymer absorbed (mg/g)	Decrease in absolute permeability
BR1 T2% in Water	Untreated	236.06	80.78			
	Treated	197.24	80.91	0.13	1.6067	16%
Room Temperature						
Core and Treatment	History	Absolute Permeability (md)	Dry Weight (g)	Polymer absorbed (g)	Polymer absorbed (mg/g)	Decrease in absolute permeability
B_RM14 T3% in Water	Untreated	178.34	75.6			
	Treated	160.27	75.58	-0.02	-0.2646	10%
BR2 T3% in Methanol	Untreated	233.9	78.92			
	Treated	215.82	78.94	0.02	0.2534	8%
BR5 T2% in Methanol	Untreated	187.71	170.49			
	Treated	185.76	170.56	0.07	0.4104	1%
BR6 T4% in Methanol	Untreated	173.66	173.21			
	Treated	171.33	173.34	0.13	0.7500	1%
BR8 T8% in Methanol	Untreated	186.92	170.2			
	Treated	181.42	170.39	0.19	1.1151	3%
BR9 T12% in Methanol	Untreated	198.78	169.79			
	Treated	194.66	169.96	0.17	1.0002	2%

3.3.1. Treatment 2% in Water at High Temperature

BR1 was treated with a mixture of 2% Zonyl in water at 100°C. The absorption of polymer was 1.6 mg/g. A summary of the treatment results is in Table 4. In the figure below we observe the change in the imbibitions from untreated to treated. The end liquid saturation decreased greatly from 100% to less than 20% for the same amount of time. However, the absolute permeability decreased from 236.06 md to 197.24 md after treatment. This is a 16% decrease in absolute permeability. We believe the decrease in permeability could have been caused by (1) blockage of the pores due to the absorption of the polymer even though the polymer was flushed with the solvent immediately after treatment, or (2) by the water used as solvent, which is known to cause decrease of permeability in sandstone. Fig. 17 shows the results of this experiment.

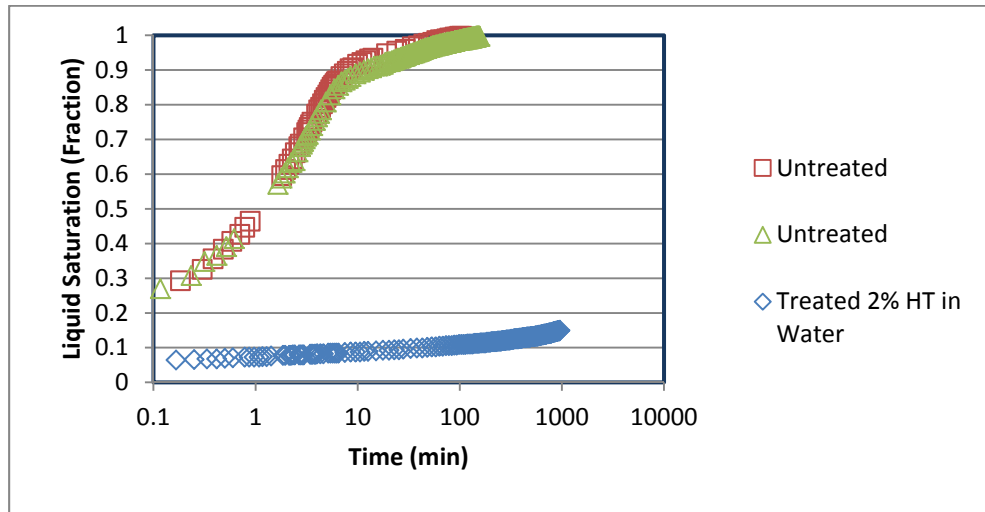


Fig. 17-BR1 Liquid Imbibitions.

3.3.2. Treatment 3% in Water at Room Temperature

B_RM14 was treated at room temperature with a mixture of 3% Zonyl in water. The liquid imbibitions in decane did not show a great decrease in liquid saturation after treatment. Even though the decane being absorbed is less initially, the end saturation was

higher for the treated rock with 80% of liquid saturation from 70% for the untreated rock as seen in Fig. 18. The change in weight of the rock shows that there was no absorption of the polymer as seen in Table 4. However, there was a decrease in absolute permeability of 10%, from 178.34 md to 160.27 md. From these results we decided to change the solvent given that water was altering the absolute permeability of the cores.

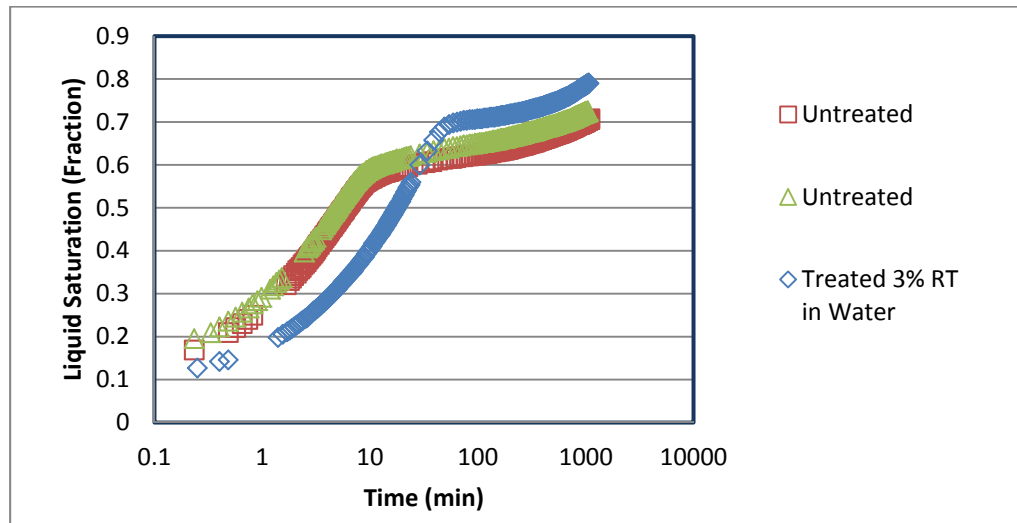


Fig. 18-B_RM14 Imbibitions.

In Fig. 19 below we have the results for decane injection in the B_RM14 core before and after treatment. This figure confirms what we determined from the imbibitions graph. The initial inlet pressure slope is lower for the treated rock, allowing the liquid to flow in the rock with less pressure. Nevertheless, as steady-state condition is reached, the pressure is higher than the untreated result. This agrees with the reduction in the absolute permeability of the rock. The pattern in the liquid injection curves is discussed in APPENDIX B.

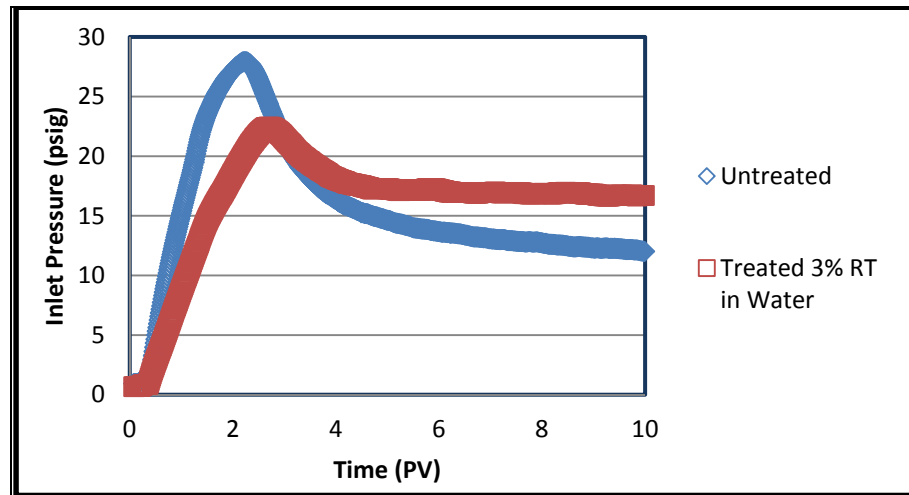


Fig. 19-B_RM14 Liquid Injection.

3.3.3. Treatment 3% in Methanol at Room Temperature

BR2 was treated at room temperature with a mixture of 3% Zonyl in Methanol. 0.25 mg/g were absorbed in the core. The treatment decreased the maximum saturation of decane from almost 100% in the untreated rock to about 70% in the treated rock. Fig. 20 shows the liquid imbibition results for this treatment. The absolute permeability decreased only from 233.9 md to 215.82 md, which is only a 8% decrease that may have been caused by the accumulation of the polymer in the pores possibly due to inefficient displacement of excess polymer at the end of the treatment. This permeability reduction was successfully avoided in later treatments.

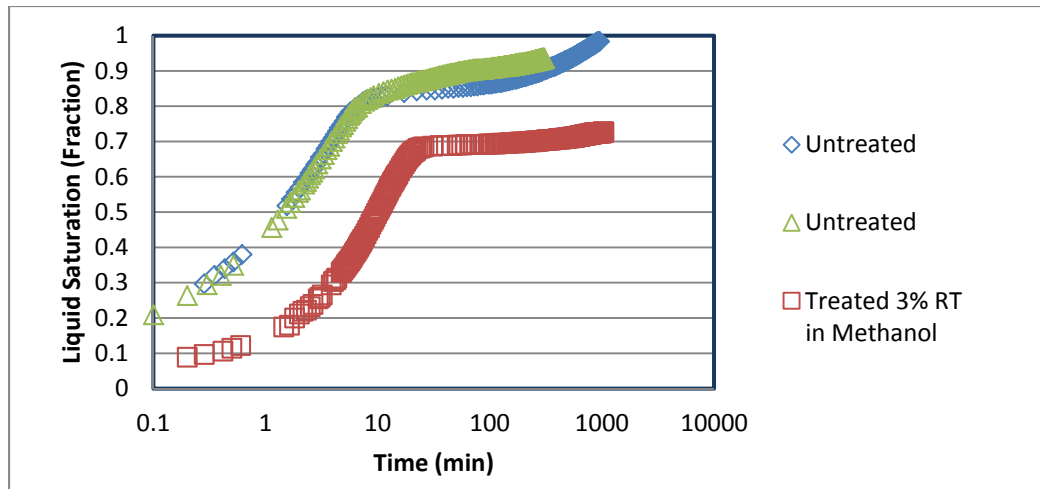


Fig. 20-BR2 Liquid Imbibitions.

Fig. 21 below shows the change in gas relative permeability endpoint. The blue dots were measured before the treatment at different pressure gradients denoted to the right of each data point. The red and blue dots are measurements after treatment. At a pressure gradient of 0.17 psi/cm, the irreducible oil saturation went from 0.42 to 0.4, which already shows a shift to the left that results in an increase in gas relative permeability.

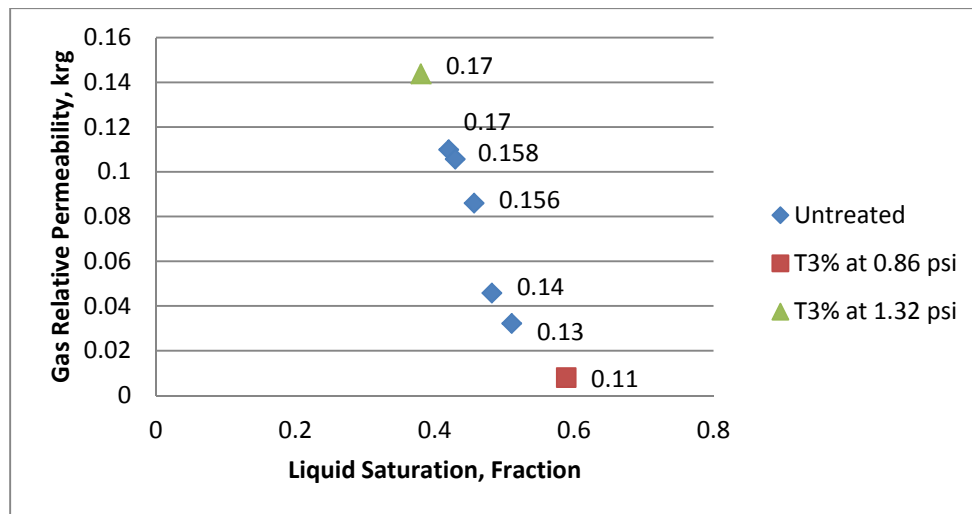


Fig. 21-BR2 Gas relative permeability endpoints for treated and untreated at denoted pressure gradients.

This treatment defined the prototype for the following treatments, varying the concentration of Zonyl in a Methanol mixture. This combination alters the wettability of sandstone and it does not decrease the absolute permeability of the rock considerably. Cores of 6 inches in length are used for the following treatments.

3.3.4. Treatment 2% in Methanol at Room Temperature

BR5, a 6-inch core was treated with a mixture of 2% Zonyl in Methanol. The absorption of the polymer was 0.41 mg/g. The permeability decrease only 1% from 187.71 md to 185.76 md. The liquid imbibitions results in Fig. 22 don't show much change in the decane saturation of the treated rock, just a slight decrease in initial saturation and an increase in the final saturation.

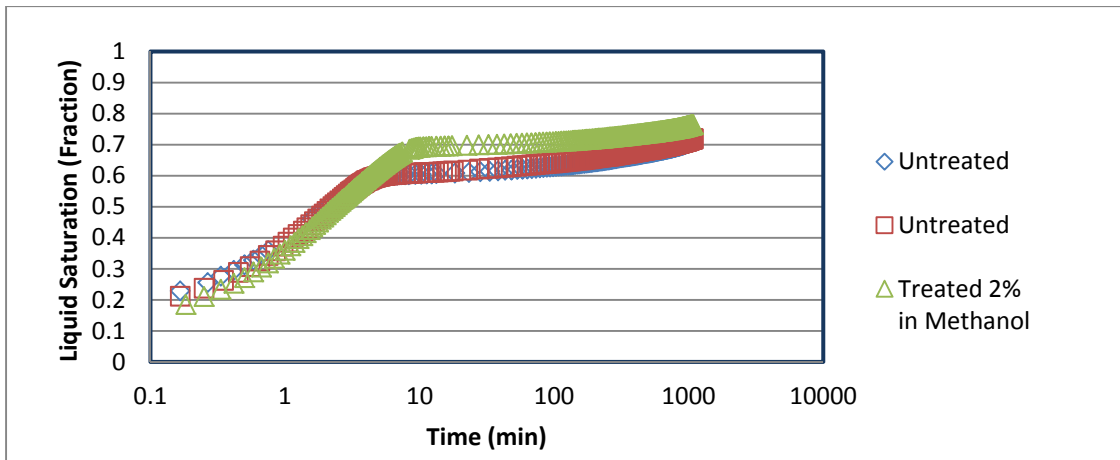


Fig. 22-BR5 Liquid imbibitions.

The change in gas relative permeability was also very light. In Fig. 23 we observe the endpoints for the untreated rock in red at different pressure gradients. At the same pressure gradients the treated endpoints moved very slightly to the left, decreasing the irreducible oil saturation only about 0.01. From these results we determine to increase the saturation of the polymer to 4%.

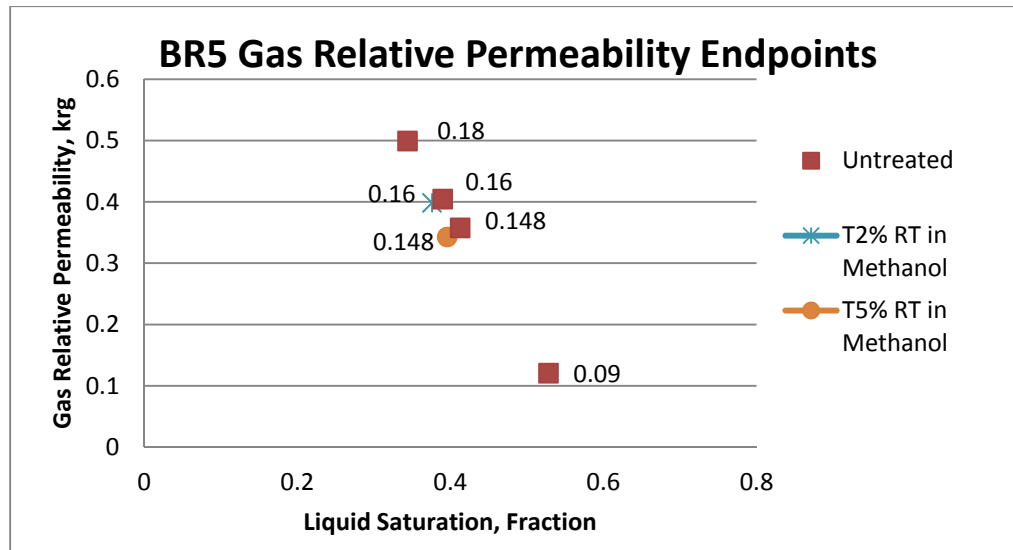


Fig. 23-BR5 Gas relative permeability endpoints.

3.3.5. Treatment 4% in Methanol at Room Temperature

BR6 was treated at room temperature with a mixture of 4% Zonyl in Methanol. The polymer absorbed was 0.75 mg/g. The permeability only decreased 1% from 173.66 md to 171.33 md. The liquid imbibitions in Fig. 24 shows more change than the 2%. However, not much difference is appreciated yet with this concentration. The gas relative permeability graph shows a slight increase in irreducible oil saturation and a decrease in gas relative permeability, considering the same pressure gradient of 0.13 psi/cm for the untreated and the treated rock. Nevertheless, this change is not significant and can hardly be appreciated. The change in gas relative permeability in Fig. 25 is also very light. The next step to obtain results will be to treat a rock at 8%.

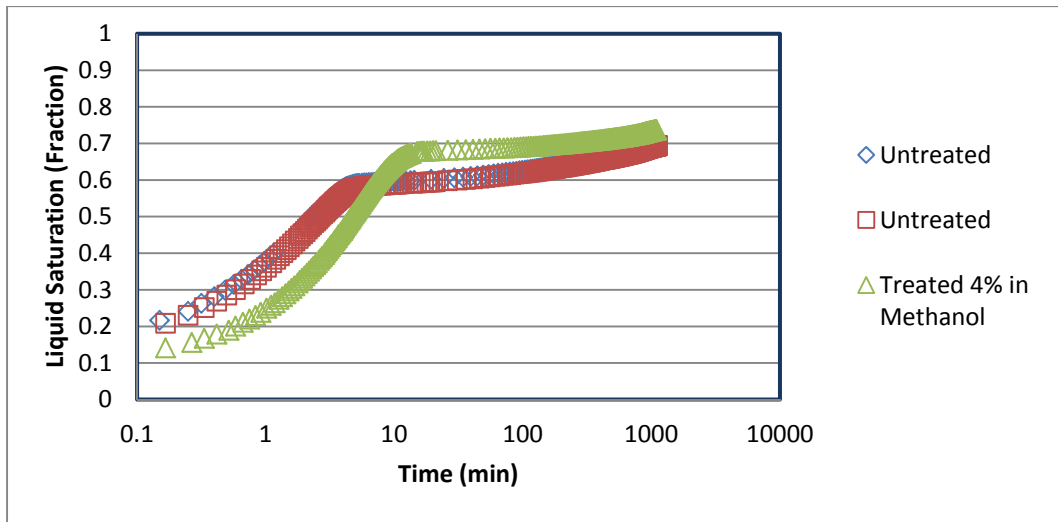


Fig. 24-BR6 Liquid Imbibitions.

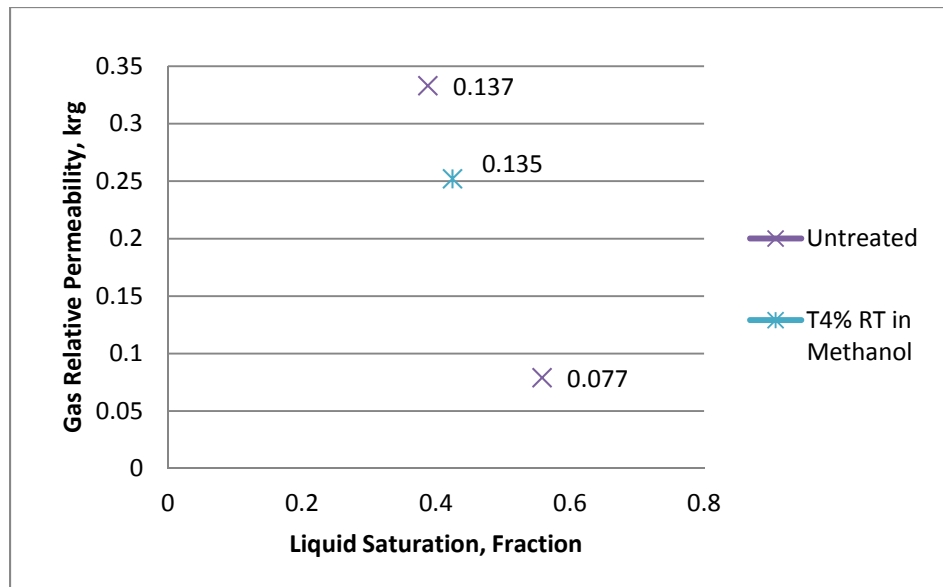


Fig. 25-BR6 Gas relative permeability endpoints.

3.3.6. Treatment 8% in Methanol at Room Temperature

BR8 was treated at room temperature with a concentration of 8% zonyl in methanol. The polymer absorbed was 1.12 mg/g. The permeability was reduced from 186.92 md to 181.42 md, a reduction of only 3%. The liquid imbibition results in less absorbed liquid the first stages of the experiment. In Fig. 26, we observe a slower rate of liquid imbibing inside the rock. About an hour in the experiment, the liquid in the treated rock surpasses the untreated rock saturation displacing more of the gas phase inside the pores, ending in a similar final saturation of about 70%. We can observe a significant increase in gas relative permeability at a pressure gradient of 0.15 psi/cm. The irreducible oil saturation is reduced from 40% to 30% as seen in Fig. 27. This treatment shows the highest increase in mobility.

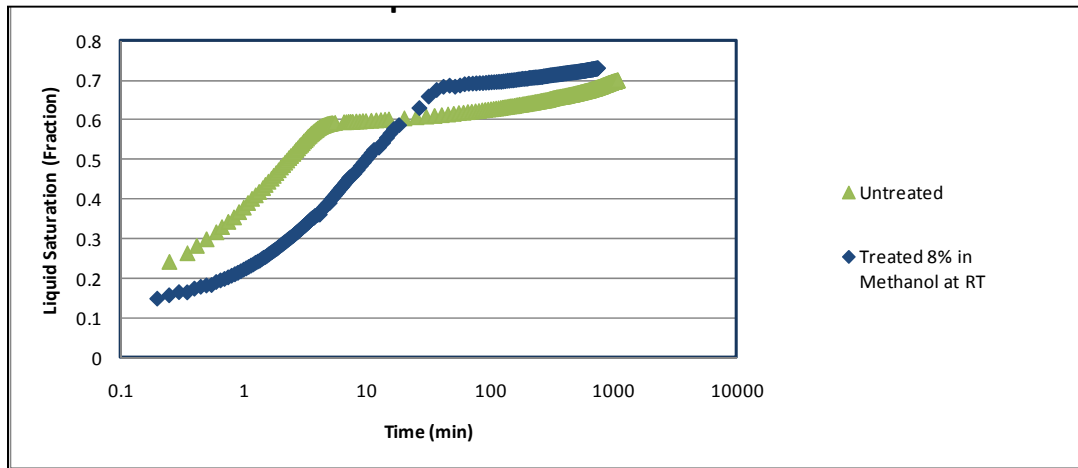


Fig. 26-BR8 Liquid Imbibitions.

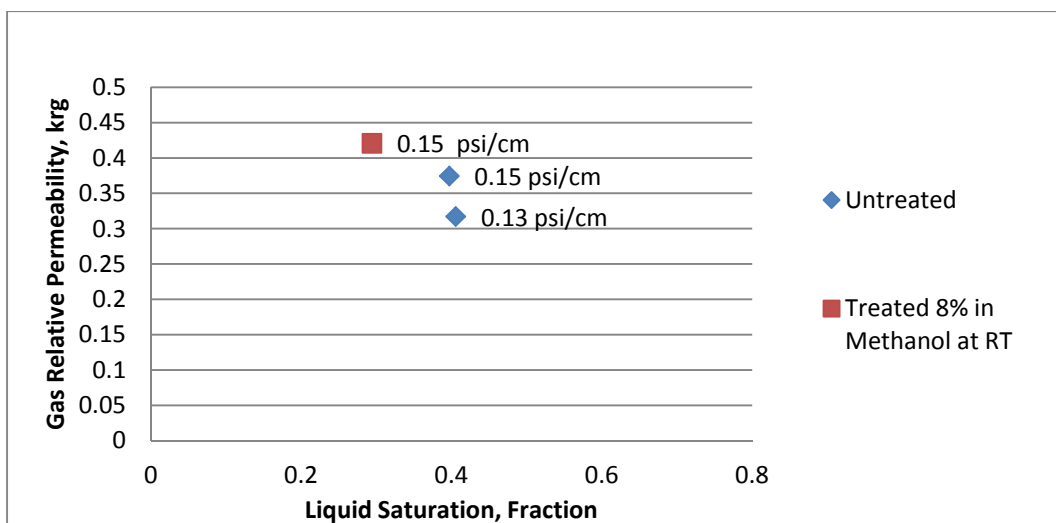


Fig. 27- BR8 gas relative permeability endpoints.

The improvement in liquid mobility is shown in the graph below, where the pressure gradient is lower for the treated core, while the untreated core has a much steeper slope. Fig. 28 shows the liquid injection results where this can clearly be seen. When steady-state is reached, the treated core is maintained at a higher pressure, which may be effect of the small reduction in permeability. Both liquid injections are at a rate of 2 cc/min.

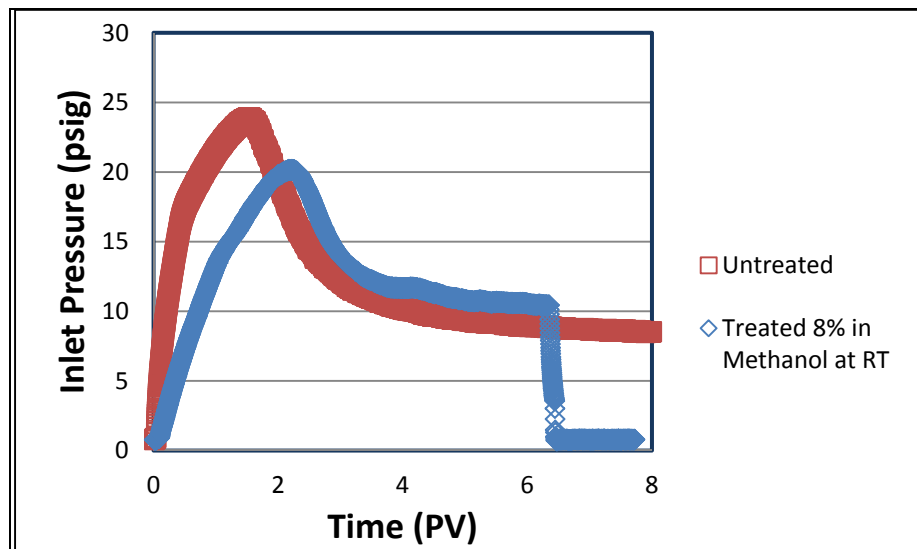


Fig. 28-BR8 liquid injection before and after an 8% treatment.

3.3.7. Treatment 12% in Methanol at Room Temperature

BR9 was treated with 12% concentration of zonyl at room temperature. In this treatment we start to see a turn in the wettability alteration of the treated rock. The imbibition in Fig. 29 shows higher liquid saturation than the 8% treatment. The permeability decreased only 2% from 198.78 md to 194.66 md. The polymer absorbed was 1 mg/g.

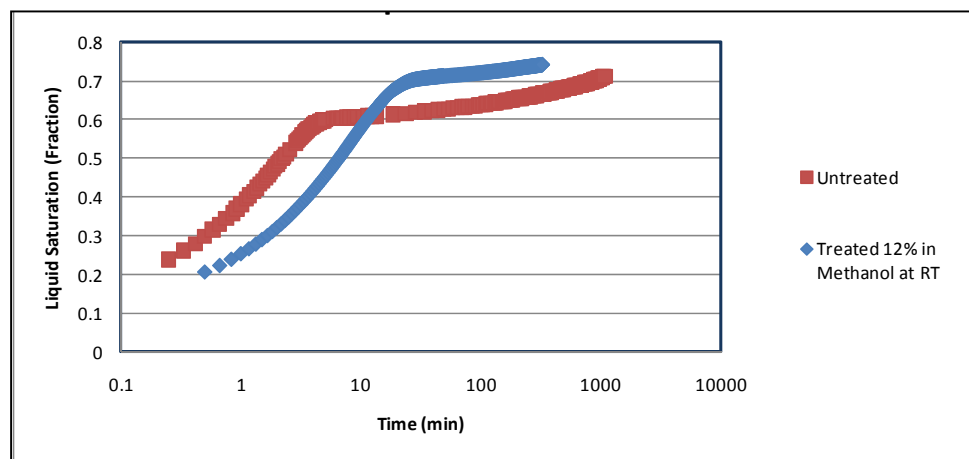


Fig. 29-BR9 liquid imbibitions.

The results from the gas relative permeability endpoint measurements show clearly the reach of an optimum at the 8% treatment. The red endpoints are the untreated core measurements, and the results in boxes are the treatments, where the 8% extends the furthest reducing liquid saturation at the same pressure gradient. In the 12% treatment we still see improvement from the untreated core, but not from the treatment at less concentration of Zonyl. These results are seen in Fig. 30.

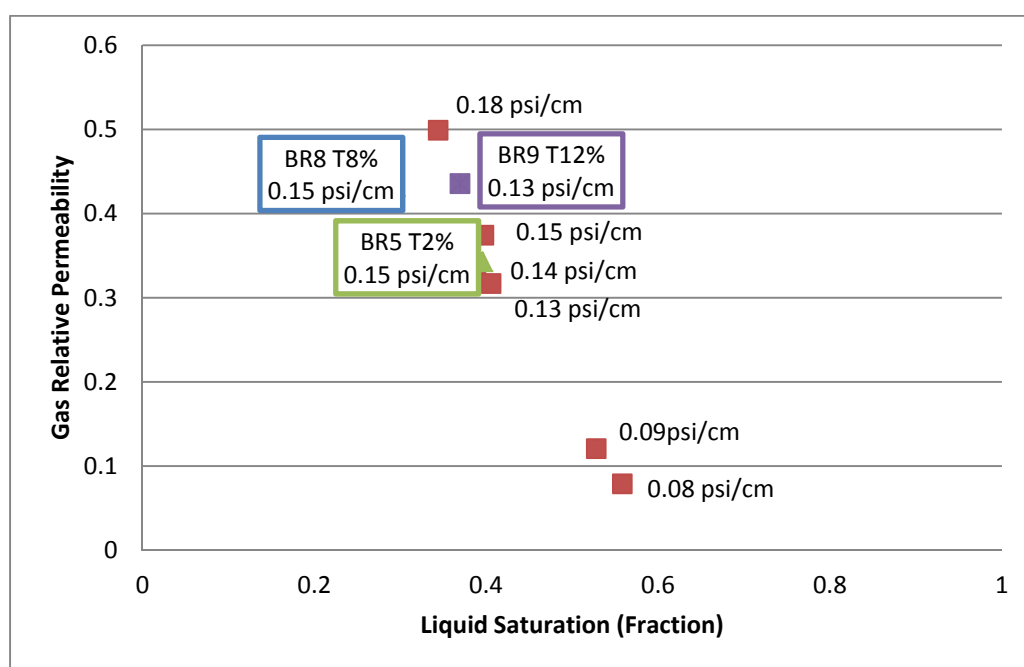


Fig. 30-Gas relative permeability endpoints.

Table 5 below summarized the results obtained, showing a maximum reduction of irreducible oil saturation (S_{oirr}) in the 8% treatment.

Table 5-Results comparison, showing improvement in gas relative permeability and decrease in irreducible oil saturation.

Core	Treatment		Pressure gradient (psi/cm)	Gas Relative Permeability krg0	Liquid Saturation (Fraction)	Increase in krg0	Decrease in Soirr
BR5	2%	Untreated	0.150	0.358	0.413	-4%	-4%
		Treated	0.150	0.343	0.396		
BR8	8%	Untreated	0.150	0.374	0.397	12%	-26%
		Treated	0.150	0.421	0.294		
BR9	12%	Untreated	0.134	0.317	0.406	37%	-9%
		Treated	0.133	0.436	0.370		

Wettability alteration is intended to be a permanent treatment that improves mobility of gas in wells affected by condensate banking. Further studies are recommended to test the durability of the polymer under reservoir conditions, and its sensitivity to temperature.

4. SUMMARY AND CONCLUSIONS

After the wellbore pressure has decreased below the dewpoint in gas-condensate reservoirs, deliverability of gas starts to decrease. To mitigate the effect of liquid accumulation, altering the wettability of the reservoir rock is presented as a durable solution. The impairment of gas wells can be observed and quantified in a decrease of the relative permeability curves. These curves are dependent on irreducible oil saturation, and are highly influenced by capillary forces. In this approach, instead of modifying the rate of injection or the interfacial tension of the liquids, we alter the interaction of the liquids with the surface of the rock. When the contact angle is modified to 90° , a strong liquid-wet system becomes intermediate gas-wet, improving the mobility of the phases.

Previous work has presented changes in wettability that improved flow of gas and liquid, but none of them has proven an optimum state that can be reached. Past experimental work has focused on finding substances to make the alteration permanent and resistant to reservoir conditions. Based on these findings, our work has successfully used Zonyl (fluorosurfactant) at several concentrations in a mixture of methanol to alter wettability of Berea sandstone rocks. The mixture used did not damage the rock, and it increased the gas relative permeability, decreasing the irreducible oil saturation.

The optimum concentration was found to be 8% of Zonyl. This treatment increased the gas relative permeability by 14% and decreased the residual oil saturation by 10% where a maximum gas and liquid mobility is proven.

Some conclusions can be drawn from this study:

1. Alteration in wettability is obtained treating Berea sandstone rock with a mixture of zonyl and methanol without damaging the rock.
2. An optimum state of wettability was reached with a treatment of 8% Zonyl in methanol.

3. Increase in gas relative permeability at the optimum polymer concentration is accompanied with reduction of irreducible saturation.
4. Changes in gas and liquid mobility start to be evident at a concentration of 3%.
5. The treatment is sensitive to temperature and its effects are still to be studied.

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APPENDIX A

IMBIBITION TESTS

Fig. 31 below shows the imbibition results of all the untreated core samples. We observe a similar pattern for all of them, where we can differentiate two slopes. The initial higher slope extends from the beginning of the experiment to about 8 minutes in the experiment for the 3-inch cores (BR1 and BR2), and until about 6 minutes for the 6-inch cores (BR3 to BR9). The second slope in the remaining of the experiment shows the saturation occurring at a lower rate. This phenomenon is explained in the conditions of the experiment. Because the core is under the pressure of the liquid from all its surroundings in an isolated system, some of the gas escapes immediately from the surface of the rock and bubbles are seen rising out to the surface. When 8 minutes (6 minutes for the longer cores) have passed, the gas that is deeper in the rock has to fight harder to leave the core and this phenomenon reduces the rate at which the core is being saturated. More studies are being performed to understand what the gas is going through inside the core and simulations will soon explain this trend.

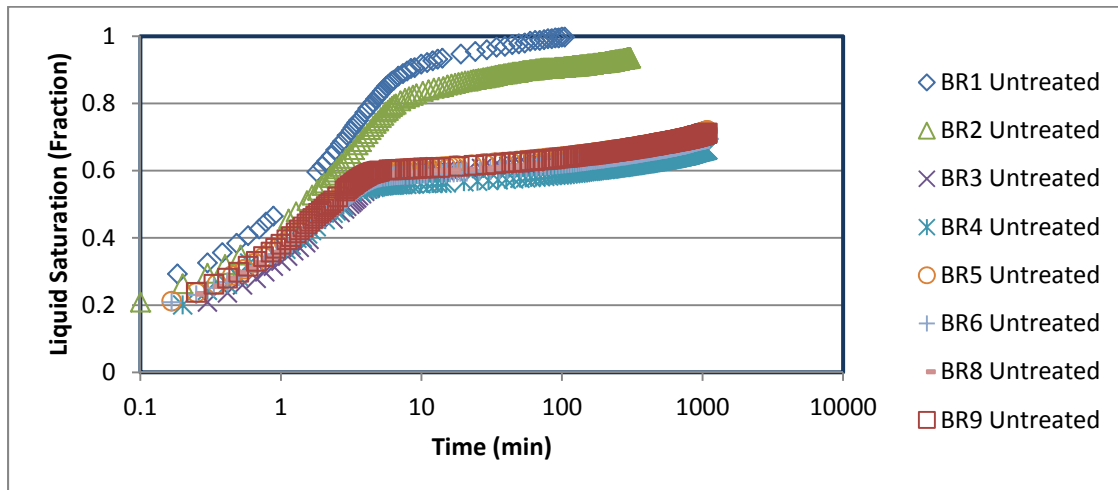


Fig. 31-Liquid imbibition for all the core samples.

Comparing results of a treatment in Fig. 32, we observe the change of slope much later in the experiment, being easier for the gas to exit from deeper in the rock until 70 minutes into the experiment. Also, the saturation of the core at this point is higher than the untreated core, which we believe indicates that more gas is being displaced by the liquid.

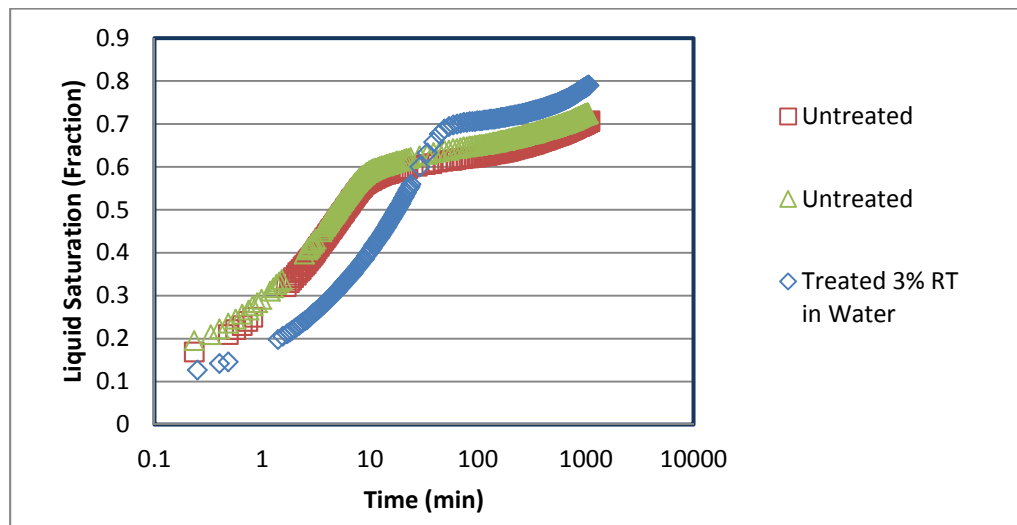


Fig. 32-B_RM14 imbibition comparison before and after a 3% treatment of Zonyl.

APPENDIX B

LIQUID INJECTION TESTS

Fig. 33 shows the liquid injection for the 8% treatment, where we can see the difference in slope for the treated and untreated core. This graph indicates an increase in liquid mobility obtained from the treatment. The pressure in these curves reaches an optimum after 1.5 pore volumes (PV) have been injected in the untreated core and after 2.25 PV in the treated core. It is interesting to observe that the liquid breakthrough happens at about 0.9 PV in the untreated core and about 0.8 PV in the treated core, but the pressure still rises after that. Breakthroughs are pointed out by the arrows in Fig. 33. A possibility is that even after breakthrough the gas in the pores is compressing and does not exit the core until it cannot compress further and it is pushed by the liquid to the outlet. The behavior of the gas and liquid in this experiment is not fully understood and more studies need to be done on this area to fully comprehend what is happening. What is relevant in our case is the pressure behavior before breakthrough where the reduction in slope represents an enhancement in oil mobility. Note that at the end of the experiment, the rock is almost fully saturated and the pressure value is mainly a function of absolute permeability instead of relative permeability.

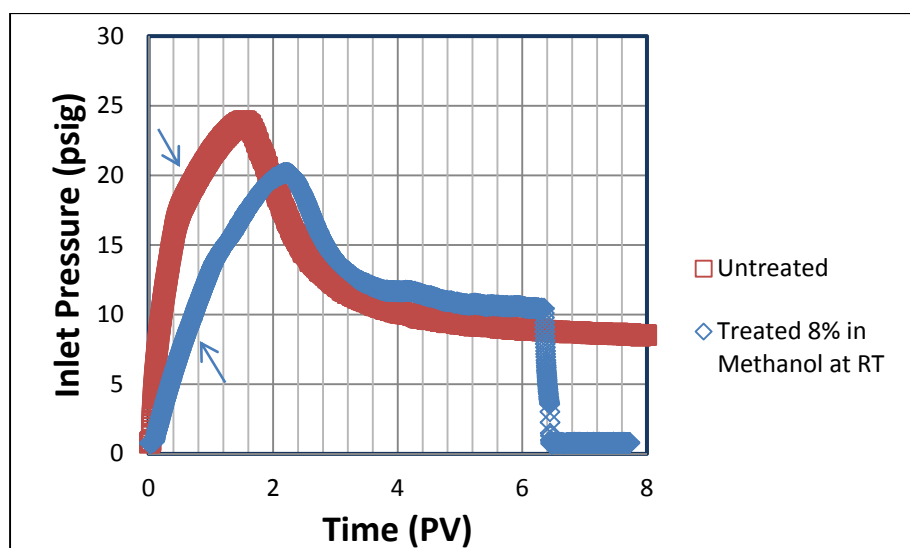


Fig. 33- Liquid injection for BR8 before and after an 8% treatment of Zonyl.

VITA

Name: Ruth Gabriela Fernandez Martinez

Address: c/o Dr. Christine Ehlig-Economides
Department of Petroleum Engineering
Texas A&M University
College Station, Tx 77843-3116

Email Address: ruth_gfm@yahoo.com

Education: B.S., Industrial Engineering, Texas A&M University, 2009
M.S., Petroleum Engineering, Texas A&M University, 2011