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TITLE:

SMART WATER EOR POTENTIAL IN BRAZILIAN OIL FIELDS

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SUMMARY

The fact that the petroleum industry still invest a lot of money on different oil recovery techniques indicates that there is an increasing demand for oil that needs to be met. Water flooding is a common secondary oil recovery method that involves the injection of water to maintain reservoir pressure and sweep oil to the producer. Studies have proven that the efficiency of a water flood depends on many factors, wettability being one of them. Injection of smart water can help alter wettability of reservoir making it favourable to overcome capillary forces that trap oil in the reservoir. In the research, we investigate the potential of smart water in the Brazilian pre-salt fields. Due to lack of significant literature for fluids and rocks from the Brazilian pre-salts, we consider the potential of smart water for oil recovery done on studies with rocks similar to the Brazilian pre-salts. The results from these studies will answer if there is at potential for smart water in the Brazilian pre-salt oil fields. A review of the historical stages and production magnitudes will be carried out to determine the current state of the oil industry within Brazil. It will be established that Brazil has numerous oilfields that are distributed mainly in offshore oil reservoirs. The presence of large areas of carbonate rock reservoirs in the country is seen to be one of the determining factors for the availability of oil in the country. Also will be discussed the challenges such as: long distances of pre-salt oilfields, CO_2 separation due to its high concentration in the reservoirs and low reservoir temperatures.

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LIST OF ABBREVIATIONS AND NOMENCLATURE

API	American Petroleum Institute, an association which represents natural gas and petroleum industries in all aspects of business. API was founded in 1919 as a national standards organization but has since expanded influence to cover aspects of international oil and gas trade. One of API's stated missions is to promote safety across the industry, globally.
API Gravity (or API °)	API gravity is the Petroleum industry measure of specific gravity, applied to petroleum liquids at a standard temperature of 60°F ($15.\overline{555}°C$). Formula: $\mathrm{API}° = \frac{141.5}{\mathrm{Sp.Gr.}} - 131.5$; $°API = \left\| \begin{array}{c} light\ crude > 32° \\ medium\ crude \approx (22° - 32°) \\ heavy\ crude < 22° \end{array} \right.$
CBR	**Crude oil/Brine/Rock** three phase *physicochemical* system; describes the oil-bearing formation in terms of its three major components. Often refers to the contact interfaces and interactions between them that impact ability to recover oil from the reservoir.

FPSO vessel — FPSO: Floating Production Storage and Off-loading. A floating vessel that is kept near an off-shore oil field, used to process and store crude until it can be transferred to a tanker for transport to a refining facility.

Oil Recovery (OR) — Also known as oil extraction, this describes the process by which oil is extracted from the subsurface for processing. Three stages of recovery listed, below.

Primary OR (POR) — In primary stage recovery, artificial lift is supplied by pumping, or pressure in the subsurface to push oil to the surface for collection. Typical extraction rates range from 5 – 15% total fluids.

Secondary OR (SOR) — A phase of oil extraction where, as production begins to fall off via natural mechanisms, technology is used (such as fluid flooding, for example) to increase subsurface pressures high enough to resume or improve oil extraction rates. Additional fluid yields may increase by a range of 20 – 30% above Primary oil recovery extraction rates.

Enhanced Oil Recovery (EOR)

Enhanced Oil Recovery; sometimes called tertiary oil recovery (TOR): a set of techniques used to extract otherwise inaccessible petroleum fluids from the sub-surface. Additional fluid yields can be as much as an

	additional 40%. These methods are costly, so are only feasible when crude prices are high enough to recover operating costs.
Improved OR (IOR)	A term used to describe a variety of advanced extraction methods, which includes EOR and which can be used to improve crude oil recovery efficiency in the field, after primary and secondary methods have been applied and are no longer effective. It also includes several novel recovery techniques which are sometimes designated as quaternary OR.
Sour	Describes a crude oil containing more than 0.5% sulphur. Sour crude is more difficult to transport and refine (corrosion, adverse health effects, pollution issues), thus more expensive to process.
Specific Gravity (Sp Gr)	measure of the density of a material relative to the density of water at a specific temperature. $Sp.Gr. = \frac{density\ of\ a\ given\ material}{density\ of\ water}$
Sweet	Describes a crude oil containing less than 0.5% sulphur. Sweet crude is a premium fluid (non-corrosive; low viscosity; easy to extract, process) which often sells for $20 more than a sour crude.
Smart Water (SW)	Smart water, a type of “smart fluid”.
SW-EOR	Smart water EOR technique

Viscosity	Fluid resistance to flow; in the subsurface this depends on porosity, permeability, and wettability of formation matrix.
Deep water	Used here to describe depths where oil deposits are found, at depths up to 3,000 metres. Technologies used to produce fluids from these wells are quite mature, and EOR can range from chemical, thermal, or technical, to some combination of these.
Ultradeep water	Used here to describe depths at which pre-salt oil deposits are found. For example, it is said that pre-salt depths off the coast of Brazil are thought to lie at an average depth of 7,000 metres (between 2000 and 300 m sea water, 2000 m or so of post-salt sediments, to reach about 2000 m of oil-bearing pre-salt formation, thought to be a thick layer of rocks and salt).
Pre-Salt layer	Pre-salt layers are thick layers of rock and salt, which formed on the continental shelves of South Atlantic Ocean basins that formed after the Gondwana super-continent breakup (estimated to have occurred during the Jurassic era, ca. 0.180 billion years ago). The lacustrine layers underneath the salt layers often carry large amounts of petroleum, which formed from the fresh-water sediments deposited on the continental shelves (Petrobras, 2019).

Lacustrine	Refers to sedimentary rock deposits which formed from materials which originally lay at the bottom of ancient lakes, seas, playas, or other ancient water basins. The materials were transported there by streams or rivers, or by rain or snow melt run-off. Flows into these bodies were typically slow, and the particle sizes, porosity, and packing of grains in these formations
Sweep	a term used to define the degree to which petroleum is pushed, or swept, from the formation rock, vs. how much is left behind, adsorbed on rock surfaces or trapped in hard-to-access pores in the matrix.

Reserves-to-Production Ratio (RPR or R/P or R/PR)

Refers to non-renewable resources, such as fossil fuel (oil, natural gas, coal). It describes the estimated quantity of oil, gas, or coal in a formation, as a function of time. The expression for calculation of RPR is:

$$RPR = \frac{known\ quantity\ of\ the\ resource\ in\ a\ given\ area\ of\ study}{amount\ recovered\ or\ removed, per\ year}$$

Wettability	Refers to the degree to which a fluid is able to wet a solid surface. The key parameter describing wettability is the contact angle between the fluid and the surface. Low contact angles correspond to a higher degree of wettability.
Imbibition	Diffusion that occurs when water is absorbed by a material, which causes a large increase in volume and pressure due to the resulting concentration gradient. This occurs when a

	wetting fluid displaces a non-wetting fluid, a mechanism that is exploited by EOR methods using smart water, for example.
Brine	water in an oil reservoir which contains a significant concentration of salts. It may also contain dissolved solids.
Oil-wet	Surface chemical condition of reservoir rocks, where the wettability of the solid by oil is higher than that of water.
Water-wet	Surface chemical condition of reservoir rocks where the wettability of the solid surface by water is greater than that of petroleum.
Porosity	a property of porous materials, such as reservoir rocks, which describes the percentage of void space in the material. Void space may be empty or filled. In a reservoir rock, void space can contain oil, water, or both.
Permeability	a fluid mechanics property of soils or rocks which quantifies how well rocks or soils can pass fluid. Permeability is a function of porosity, pore size distribution, and pore shape and/or tortuosity.
Fingering	describes a phenomenon sometimes observed in a porous medium containing two fluids with different viscosities, one pushing the other. If the fluid interface is stable, the displacement front is somewhat uniform. If the interface becomes unstable, the displacement front develops break-through patterns resembling fingers, leaving behind some of the fluid to be displaced.

OOIP	original oil in place
bopd	Abbreviation for barrels of oil per day, a common unit of measurement for volume of crude oil. The volume of a barrel is equivalent to 42 US gallons. (https://www.glossary.oilfield.slb.com/en/Terms/b/bopd.aspx)
TDS	Total dissolved solids.
DSW	Desulfated injection water
SI	Spontaneous imbibition
SW	Synthetic seawater
SW0T	Synthetic seawater without SO4
SW0NaCl	Seawater depleted in NaCl
SW0NaCl–4SO_4^{2-}	Seawater depleted in NaCl with 4 times the concentration of SO_4^{2-}
SW0NaCl–4Ca^{2+}	Seawater depleted in NaCl with 4 times the concentration of Ca^{2+}

ACKNOWLEDGEMENTS

Despite the cold weather, homesickness, cultural difference, non-Brazilian food and all the challenges that I have experienced and that I will still go through because of my choice in taking this course, I can say that it was worth.

Thanks to my supervisors, Tina and Skule, it was truly an honor to work with you. From the beginning, I was able to follow the lessons of these excellent teachers and so I chose them as my supervisors.

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I would like to thank all my colleagues and friend for their wonderful cooperation. You supported me and were willing to help me.

Thank you God for everything.

Chapter 1: INTRODUCTION

The objective of this research is to present, via case studies, an analysis of some experiments with a characterization similar to that fields lying off the Brazilian coastline. These fields lie within deep-water formations. At the end of this study will be discussed if the technique of Smart water can be or not applied as method of oil recovery. Possible candidates for future application of the smart water technique may be the following: Campos Basin (Jubarte or Baleia Azul pre-salt fields, for example) and Santos Basin (i.e., Lula, Iracema, and Lapa/Carioca pre-salt fields, on-stream between 2013 and 2018).

The estimated proven amounts of crude oil reserves from Brazil's conventional and pre-salt fields has been estimated at about 12.63 billion barrels (12.64 BB-BBL) as of 2018 (ANP, 2018). The geology features, and fossil fuel reserves of Brazil will be reviewed later in this section. From that data, candidates for the case studies will be chosen and evaluated for suitability of using Smart Water – Enhanced Oil Recovery techniques to fully produce fluids in the sub-sea formations.

1.1 BACKGROUND

Conventional wisdom suggests that 'money makes the world go'. In practice, energy is what really makes it go, and currently, the bulk of it is obtained from consumption of fossil fuels (oil, gas, or coal). A nation which can produce enough oil to meet its energy needs gains economic stability and extra oil can be exported to improve that nation's fortunes. Estimates suggest that South America contains as much as 322.2 billion barrels of *proven reserves* (more than 20% of the total global underground oil reserves, currently). Of these, 15% belong to Brazil, based on 2017 data (Eni World Oil Review ,2018).

The pre-salt Brazilian oil reserves lie in offshore (deep and ultra-deep waters) basins such as, the Campos, Espírito Santo and Santos. The bulk of crudes recovered from these fields are of medium-heavy to heavy ° API, but recent finds have included light, sweet crude fractions as shown in table 1.1 (low sulphur, API gravity ~ 33°) (https://www.eni.com/docs/en_IT/enicom/company/fuel-cafe/WORLD-OIL-EVIEW-2018-Volume-1.pdf).

Table 1. 1 Quality levels: API gravity and sulphur content (Eni World Oil Review ,2018).

Ultra Light	API level equal to or greater than 50° low sulphur content
Light & Sweet	API level equal to or greater than 35° less than 50°, sulphur content less 0.5%
Light & Medium Sour	API level equal to or greater than 35° and less than 50° sulphur content equal to or greater than 0.5% and less than 1%
Light & Sour	API level equal to or greater than 35° and less than 50° sulphur content equal to or greater than 1%
Medium & Sweet	API level equal to or greater than 26° and less than 35° sulphur content less 0.5%
Medium & Medium Sour	API level equal to or greater than 26° and less than 35° sulphur content equal to or greater than 0.5% and less than 1%
Medium & Sour	API level equal to or greater than 26° and less than 35° sulphur content equal to or greater than 1%
Heavy & Sweet	API level equal to or greater than 10° and less than 26° sulphur content less 0.5%
Heavy & Medium Sour	API level equal to or greater than 10° and less than 26° sulphur content equal to or greater than 0.5% and less than 1%
Heavy & Sour	API level equal to or greater than 10° and less than 26° sulphur content equal to or greater than 1%

The geology of these fields is complex, pre-salt and other structures, produced by the break-up and separation of South America from Africa during the Gondwandan break-up, as shown in Figure 1.1 http://www.drillingcontractor.org/industry-eager-for-repeat-of-brazil-pre-salt-boom-offshore-angola-30574). As a result, thick, deep-water salt deposits were formed which appear to contain large amounts of untapped petroleum reserves within them, at depths of up to 6,000 m.

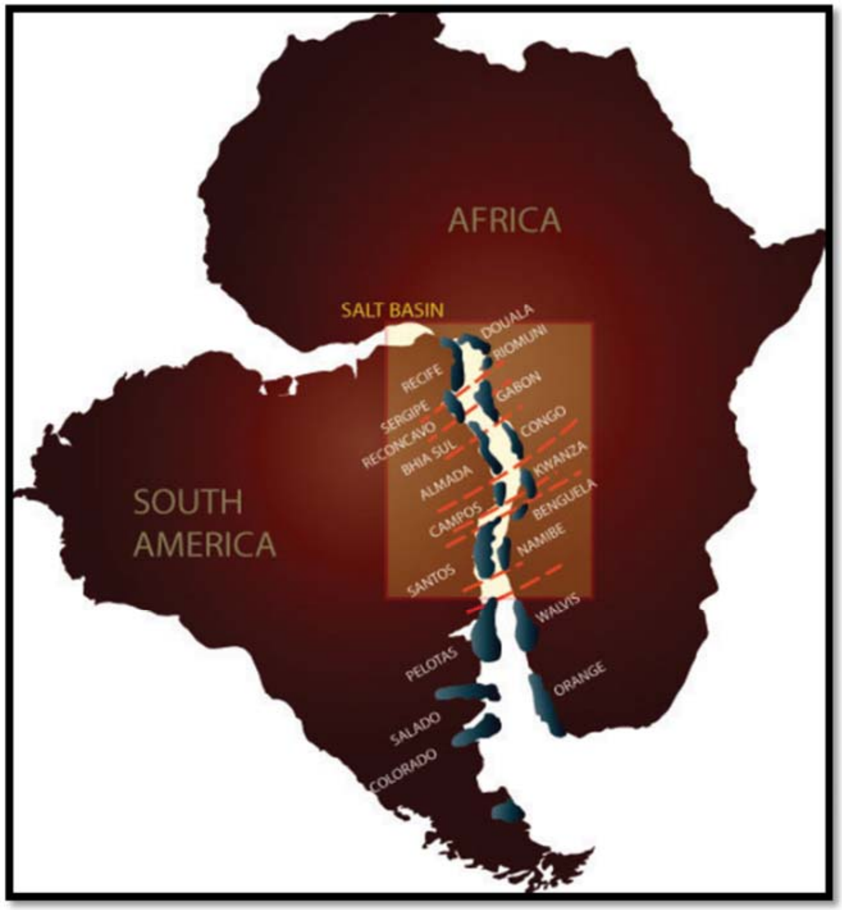

Figure 1. 1 separation of South America from Africa

Increasing production of crude oils in the pre-salt regions result in liquids characterized as medium-heavy crudes with an average API gravity of 22°, and lighter crudes with API gravity > 31.1°, as shown in table1.2.

Table 1. 2 Pre-salt Crudes, selected characteristics (Petrobras, 2007)

Buzios (P-74)	medium heavy crude; sulphur content is around 0.31% $\boldsymbol{API\ gravity\ \approx 28.4°}$
Campos	Crudes contain a medium amount of sulphates API varies from 19.6° to 42.1° (http://www.oilfieldwiki.com/wiki/List_of_crude_oil_products)
Libra/Mero field	Pre-salt production zone API ~ 27°
Lula/Tupi field	Pre-salt production zone; sweetish crude API ~ 28

Figure 1.2 below maps the estimates of global petroleum proven reserves, by continent/area(https://en.wikipedia.org/wiki/List_of_countries_by_proven_oil_reserves). Even though the focus of this work is on Brazilian reserves, this figure serves to illustrate the potential for increasing production output in the coming years, which might be good candidates for application of various enhanced techniques, such as smart water-EOR.

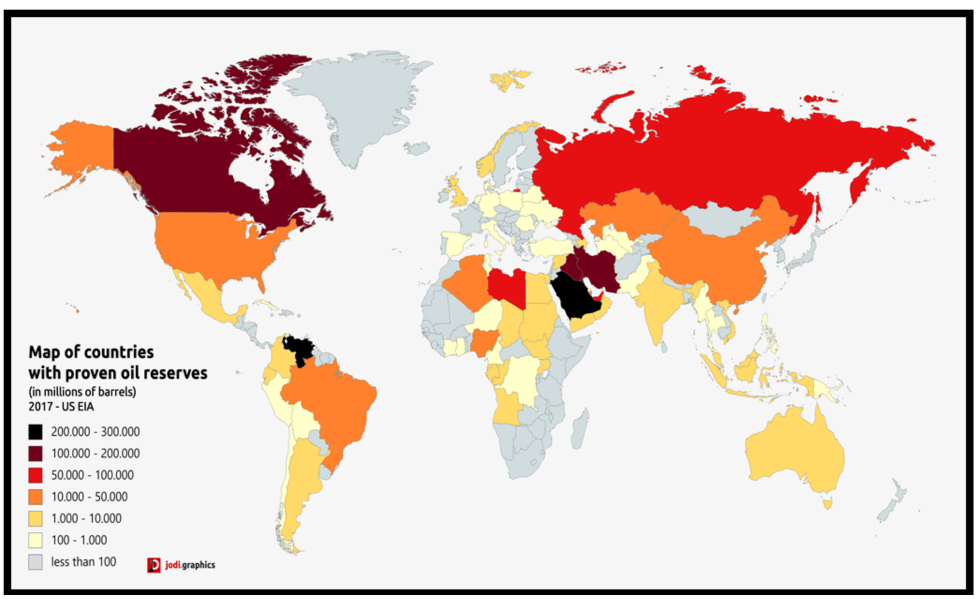

Figure 1. 2 Proven, recoverable, and unconventional oil reserves, by region, in billions of barrels.

1.2 PURPOSE

The purpose of this research is to conduct some case studies into the potential and potential effectiveness of using Smart Water EOR in oil recovery efforts from off-shore deep-water petroleum-bearing basins such as the Campos, and Santos. Each study will focus what specific Smart Water techniques could apply and potential improvement on % recovery of subsurface petroleum volumes and potential problems. Case studies will combine data obtained in the lab experiments and literatures. Data from the literature or obtained from commercial sources, such as Petrobras, or elsewhere, can be evaluated using insight developed from this work.Goals will include looking for predictors, relative or absolute, which could be used to develop a tool for developing production plan estimates, assessing risks, and calculating costs.

1.3 THESIS OUTLINE

To present the work, the text of the thesis was structured in five chapters.

- Chapter 01 will develop the rationale for this research and describe its approach.
- Chapter 02 contains the theoretical framework to describe EOR concepts, Geology for both Sandstone and Carbonates rocks, Wettability fundamentals and Smart water theories.
- Chapter 03 contains an evaluation of Brazilian oil sector and characteristics of the Brazilian pre-salt oilfields.
- Chapter 4 Contains case studies and debates
- Chapter 5 Discussion
- Chapter 6 contains the final remarks and recommendations for future works.

Chapter 2: THEORY FRAMEWORK

The ideas, techniques, and protocols behind the use of "smart water" for enhanced oil recovery are based on the premise that more efficient recovery of petroleum fluids can be achieved by addressing the crude oil – brine – rock (CBR) system surficial properties, and altering them to improve sweep efficiency, increase petroleum flow, alter petroleum-rock wettability to make formation prefer to be water-wet; in short, the goal is to manage the overall amount of water, salt, and other materials added to the sub-surface to minimize environmental impacts, reservoir damage, and maximize extraction. Before addressing smart water in detail, it would be useful to cover some oil extraction basics, so in this section, EOR will be more precisely defined and a few of the most-widely used processes described. The off-shore basins and stratigraphy in one or more producing basins off the eastern coast of Brazil will be discussed in terms of mineralogy, basic petroleum fluid characteristics, historical production numbers, formation surface chemistry (where known), and, specifically, the phenomenon of wettability, which will be defined in terms of the Crude Oil/Brine/Rock (CBR) three-phase system.

The Brazilian offshore formations consist of oil-bearing strata lying in pre-salt, salt, and post-salt formations, with complex geology. The rifting resulting from the break-up of the Gondwandan supercontinent produced the basement rocks on which the pre-salt, post-salt, and salt layers which make up the basin, lie. The basin lies partially on-shore, with the major portion offshore (The Campos basin is one of offshore fields lying off the coast of Brazil.), in deep waters (up to 2,000 m deep). The formation contains pre-salt, salt, and post-salt zones, all of which can produce, and each of which has distinct properties, which influence the ease of oil extraction. As well, the quality of oil obtained from each zone is unique and should be discussed briefly; each has experienced different degrees of weathering, fluid migration, exposure to and flow of water that will influence how smart water EOR might be applied.

2.1 OIL RECOVERY AND EOR METHODS

The production of oil employs a vast array of methods that can be used to tap oil that is present in deep underground reservoirs as well as offshore sites. At the core of oil production, the process of extraction is comprised of three different phases: primary, secondary and tertiary/Enhanced Oil Recovery (EOR) phases, as shown in the following Figure 2.1 (https://worldoceanreview.com/en/wor-3/oil-and-gas/where-and-how-extraction-proceeds/3/).

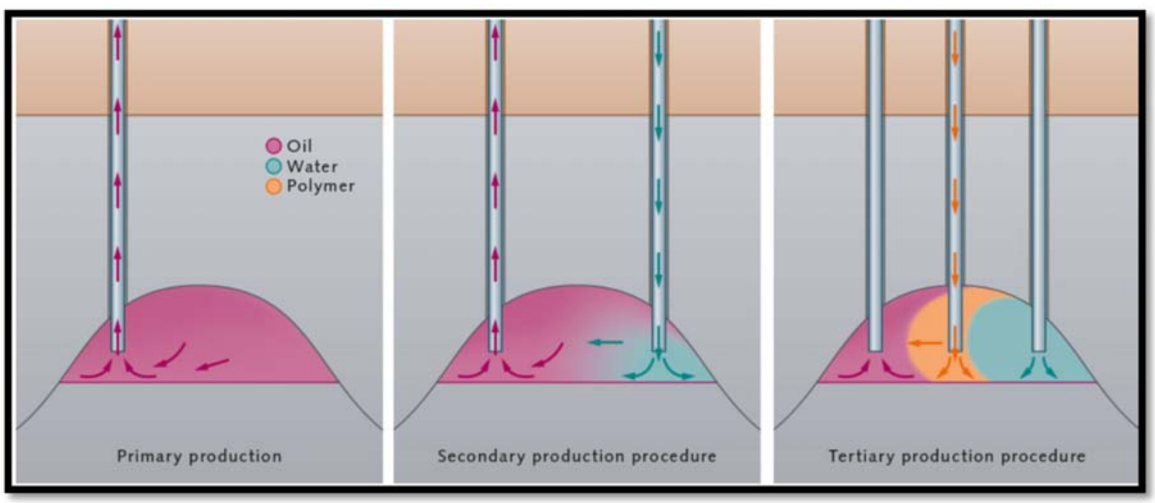

Figure 2. 1 Oil production here broken down into three phases: primary production, secondary phase and the tertiary production phase.

2.1.1 Primary recovery

Primary recovery refers to oil extraction from a formation, which is achieved using the natural forces present in the well and subsurface. Force driving the oil into the well may include exploiting the well's natural pressure (gas or water), gravitational flow of liquid in the formation, or original surface-chemical properties of the CBR to obtain production. Mechanisms by which this occurs are simple: if the well contains gas, for example, the gas will expand as it moves towards the surface. This can drive well flows and to maintain steady production throughout the primary recovery phase. The same is true of water drive. In a case where well pressures are not high enough to obtain decent, steady flow, artificial lift can be supplied via submersible pumps, to achieve flows – this may still be considered a primary recovery method. The key feature is that no external water, chemicals, foams, or polymers have been added to the well, and it hasn't been pumped full of materials to fracture the oil-bearing formation (Salino et al., 2013).

2.1.2 Secondary recovery

Secondary recovery is initiated on a well when natural drive mechanisms can no longer maintain the rates of fluid flow to the well's surface. As this slow-down occurs, fluid recovery slows, wellhead pressures drop, the ratio of water and/or gas to petroleum increases, or it becomes necessary to supply artificial lift to continue to bring fluids to the surface. When this occurs, more artificial lift may be added to the well, or pressures may be boosted by pumping water or gas into the well, to restore fluid drivers and increase volumes of non-petroleum well fluid. Provided the well is not over-pressured, adding fluid to the well to increase pressures has been very effective in this phase of production. Recall that Primary Recovery uses the natural drivers in the well to produce fluids – no external fluids or significant artificial lift is supplied. In secondary recovery, external drive mechanisms maintain fluid recovery from the well. In some cases, it is possible to supply thermal energy to the formation to supply additional drive to the well, but this is more expensive (Al-Hadhrami & Blunt, 2007).

2.1.3 Definition of EOR

Enhanced Oil recovery is a term used to describe several different techniques used by the petroleum industry to restore or improve the extraction of oil from a reservoir formation. This goal can be achieved in several ways. EOR is sometimes called *tertiary* recovery, especially in older papers, texts, and working papers, and has traditionally been used, when economically feasible, to extract oil from reservoir rocks that are otherwise difficult to produce after primary and secondary methods have begun to fall off. The reasons oil-bearing rocks might be difficult to extract vary: the type, size, and distribution of pores in the formation rocks might restrict oil and/or water flow; the formation rocks may be preferentially oil-wet in the presence of formation water, or oil may be strongly adsorbed onto the rocks (often the case in carbonate reservoirs). As well, in the case of off-shore basins, water-depth and ocean floor geology pose unique challenges that require custom solutions, especially where the off-shore field lies off the continental shelf in deep water (Eni World Oil Review ,2018).

Because of the very great potential in the long term for oil production from Brazil's off-shore basins, the quality of oil obtainable from both pre-salt and post-salt-formation, given the current favourable oil prices, it makes sense to invest in development and application of EOR (such as smart water) to Brazil's deep and ultra-deep wells.

2.1.3.1 EOR processes and Application

EOR processes can vary widely within the three categories (Primary, secondary and EOR), but in general, they all proceed via a similar mechanism by modifying selected properties of the system: chemical (wettability, pH, viscosity), mechanical (pressure, sweep), or thermal processes (viscosity, subsurface multi-component thermodynamics). The Petroleum Engineer's handbook includes this definition: "An enhanced recovery process that goes beyond water or gas flooding. It may involve steam, fire, chemicals, miscible gases, bacteria or other techniques (SPE Contributors, 2019). Figure 2.2 shows some EOR Processes and figure 2.3 shows Smart water EOr Process (Saeed Rashida et al., 2015).

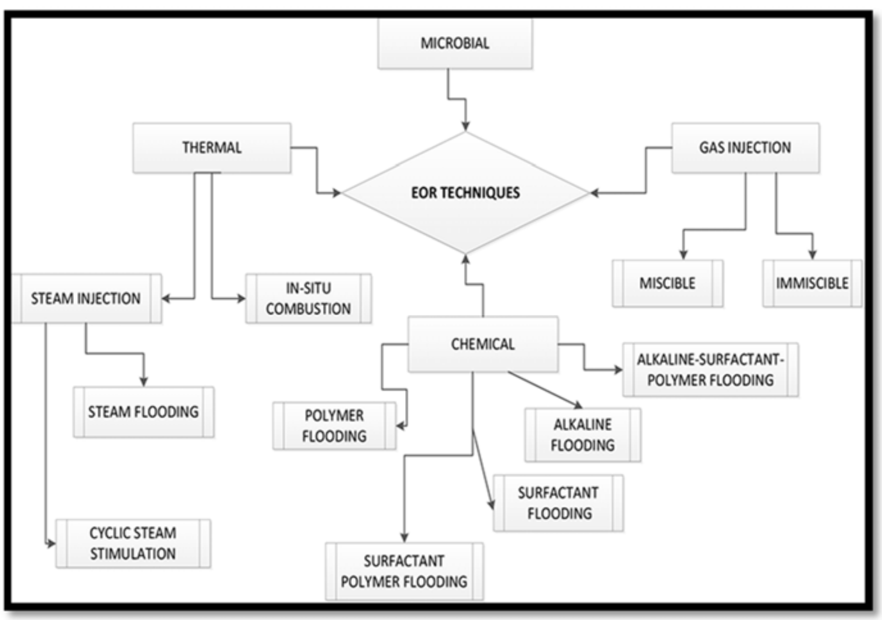

Figure 2. 2 Classification of some EOR techniques

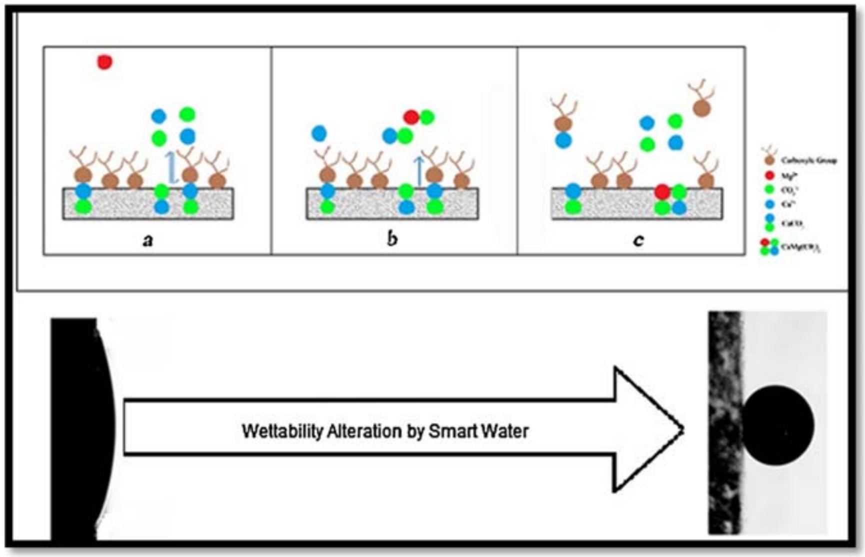

Figure 2. 3 The Smart Water process shows the result where Mg^{2+} alone changes the surface wettability and SO_4^{2-} plays a catalytic role during wettability alteration process by Mg^{2+}.

Table 2.1 below is showing the historic of Petrobras` EOR processes in the Brazilian basins (ANP, 2018).

Table 2. 1 EOR History of Petrobras

Technology	**# Applications**	**Success**
thermal		
Steam	Large Scale	Yes
In-situ combustion	2 pilots	No
Chemicals		
Polymer	4 pilots	No
Water production control	Large scale	Yes
Miscible		
CO_2	3 pilots	In 1 of the pilots
WAG	Large scale pre-salt BS	In progress
Microbiological		
MEOR	10 wells and 1 full field	In 7/10 wells: Yes full field: No
Others		
Electromagnetic heating	3 pilots	No
Pulsed water injection	full field	Yes

Figure 2.4 intends to demonstrate the active and successful EOR projects in the world (Oil &Gas Journal, 2016).

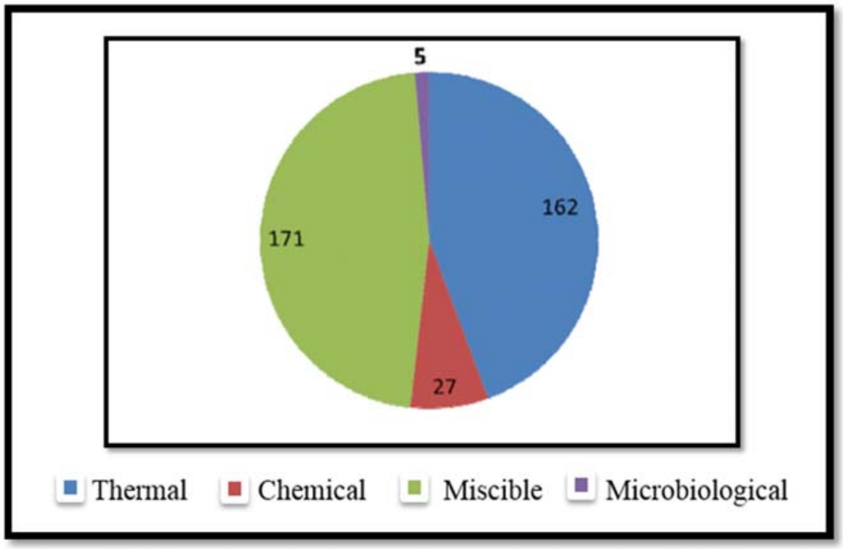

Figure 2. 4 the active and successful EOR projects in the world.

It can be said that that PETROBRAS 'main EOR experiences are related to the application of thermal and miscible methods, also observed when analysing the experiences of other operators in the world. As observed by Rosa A et. al. (2019) the main challenges and conclusions for applying EOR in the current Brazilian scenario may be listed below:

- Most of the reservoirs have a good response to water injection, not justifying investments for a small increase in production from EOR. In addition, many wells in these reservoirs currently produce high water cut, which delays the return of additional oil gain from EOR methods;
- large well spacing in an offshore scenario that generates large return times of chemical injection, in addition to the need for larger volumes, which impairs the economic viability of EOR projects;
- Lack of experience of the oil industry in the application of EOR methods in offshore environment, especially in deep water depth, indicating its implementation challenge. Even in the onshore environment, EOR

methods, such as chemical and microbiological, are still not widely applied in the world;

- the use of seawater, captured for injection in an offshore environment, with high salinity greatly reduces the efficiency of the chemicals used in EOR projects;
- Finally, in cases where there is a technical feasibility for implementing EOR methods, the main barrier is the lack of economic attractiveness due to the high costs involved, due to both the facilities and equipment required as to the products and their supply logistics.

2.2 GEOLOGY OF SANDSTONE (SANDSTONE RESERVES)

Sandstones reservoir are a Clastic sedimentary rocks which consisting of mineral grains and rock fragments. Sedimentary particles are derivative from weathered and fragmented older rocks, igneous, metamorphic or sedimentary, typically with some chemical changes. Sandstone reservoirs are generally poised of stable minerals (e.g., quartz, feldspar and rock fragments), accessory minerals and pores saturated with fluids. Figure 2.5 shows the geographic distributions of sandstone reservoirs (Ehrenberg et al., (2005)).

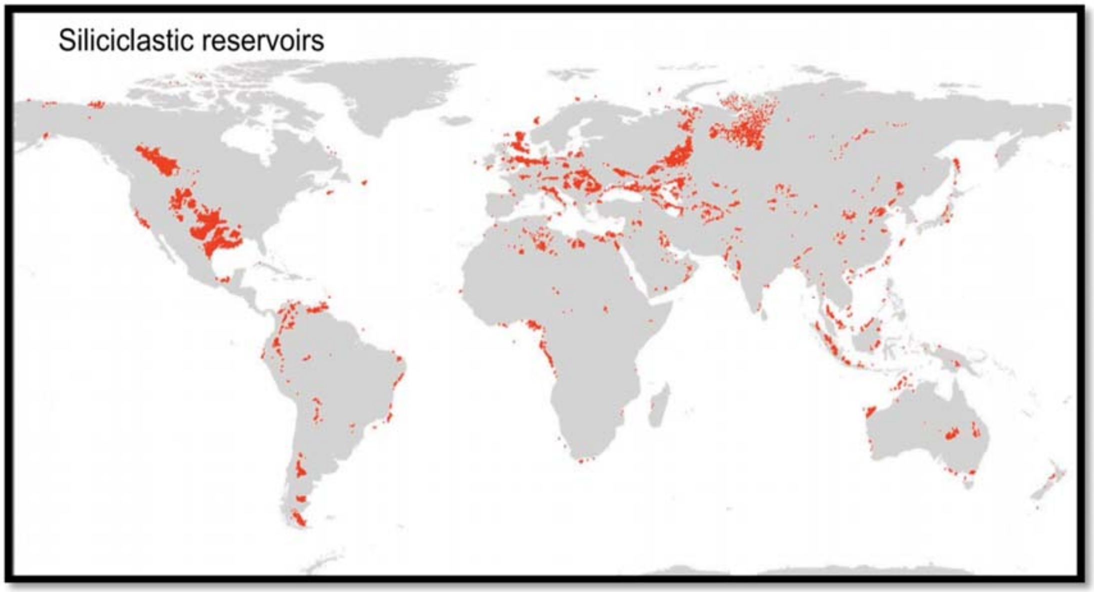

Figure 2. 5 Geographic distributions of sandstone reservoir.

Below the table 2.2 shows the main characteristics between Sandstone and Carbonate reservoir.

Table 2. 2 Comparing Carbonates vs Sandstone characteristics

Aspect	Sandstone	Carbonates
Heterogeneity	Fairly homogeneous as the sediment may travel up to hundreds of kilometers before deposition which gives in general good sorting.	Highly heterogeneous due to local deposition (poor sorting) and the nature itself of the diverse marine organisms, which form the sediments.
Amount if primary porosity in sediments	Around 22% in the youngest deposits and decreasing over time.	Around 15% in the youngest deposits. Due to early calcite cementation.
Influence of Diagenesis	Diagenetic processes once the sandstone is formed normally decrease the porosity due to quartz cementation.	Dissolution of calcite by acidic water can create a fairly high amount of vugs which could increase the total K, but also stylolite structures can create horizontal flow barre.
Permeability-Porosity	Medium to high porosity but low/medium permeability (assuming consolidated sandstone).	Low porosity but high permeability, the difference is even more acute if it exists secondary porosity in the form of fractures.

2.2.1 Sandstone Reserves in Brazil

According to Petrobras (2011), Around 88% of the proved reserves and more than 80% of the 2 million boe daily production come from Cretaceous and Tertiary deep-water sandstones in Campos Basin, until recently understood as turbiditic depositional systems. Figure 2.6 shows the schematic on this depositional system.

Turbidites are deposits resulting from turbidity currents and are deposited when the current loses its energy. Turbidites was first described by Arnold H. Bouma (1962) studying deepwater sedimentation. Turbidites are special deposits which help to host important economic resources such as hydrocarbon and most recent success in Deep water exploration has been linked with them, for instance 90% of deepwater reserves have been found in turbidites (Henry Pettingill, 1989).

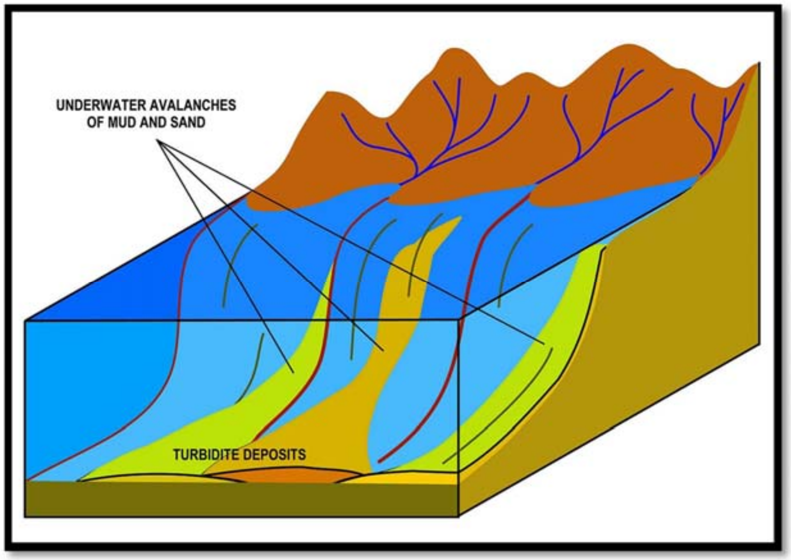

Figure 2. 6 turbiditic depositional systems.

The mainly offshore areas are Sergipe-Alagoas, Espirito Santo, Campos, Santos and Pelotas. Figure 2.7 shows two main plays producing in Brazil (http://www.anp.gov.br/images/Palestras/15_cisbgf/DG_ABERTURA_SBGf_Publicacao.pdf).

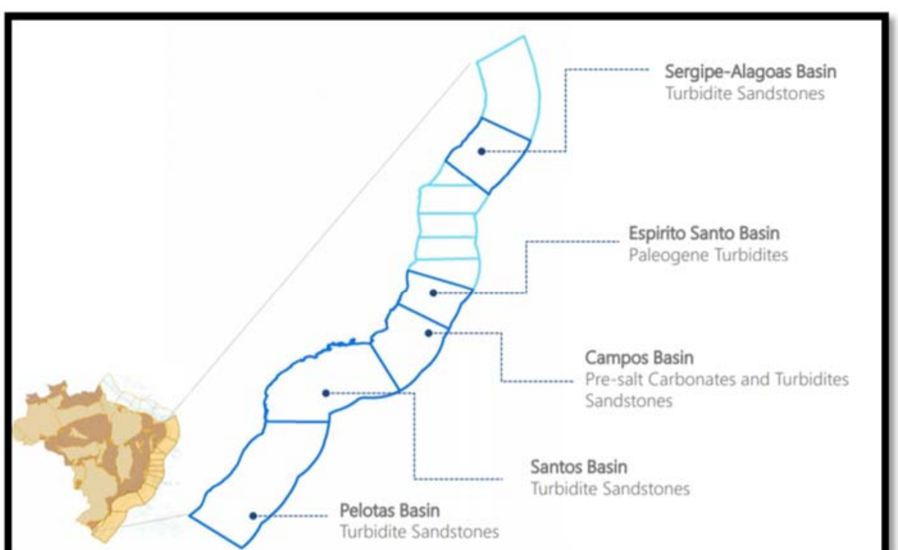

Figure 2. 7 two main plays producing in Brazil are Turbidite Sandstone and Pre-salt Carbonates.

The Namorado reservoir (Campos basin) is typical turbidite sand interbedded with marls and shales deposited during the Cenomanian/Turonian. Porosity varies from 20 to 30% and permeability is up to 1 darcy. Younger reservoirs mostly are large-scale sandstone turbidites, ranging in age from Santonian to Miocene, and represent the main accumulations, up to now, in the Marlim, Albacora, Roncador, Mexilhão, Jubarte, Cachalote, and Golfinho fields. Porosities in these fields are up to 30% (Source:www.offshore-mag.com/geosciences/article/16761140/subsalt-seen-as-promising-exploration-frontier-for-brazil).

2.3 GEOLOGY OF CARBONATES (CARBONATE RESERVES)

According to Guardado et al. (1989), carbonate reserves contain approximately 60% of the world's total oil reserves. Additionally, 40% the world's natural gas is held within carbonate reserves. On a global perspective, major oil producers in the world such as Saudi Arabia have large oil fields in carbonate reserves. Figure 2.8 shows conventional Petroleum Reserves in Carbonates Reservoirs (www.slb.com/~/media/Files/industry_challenges/carbonates/brochures/cb_carbonate_reservoirs_07os003.pdf).

Carbonate reserves have a number of properties that set them different from silicates. Sediments of carbonates are formed and deposited in situ. Carbonate rocks are characterized by vast quantities of calcareous matter that arise from the death, decomposition and disintegration of animal and plant matter. Most carbonate sediments depict a varying diversity in grain size and carbonate shapes as compared to carbonate deposits. Carbonate rocks typically occur as brittle rocks with numerous fractures. The presence of fractures on carbonate rocks is major indicator of the reserve performance. Fractures within the carbonate reservoirs are instrumental in creating permeability and connectivity within the rock reservoirs. Carbonate oil reservoirs usually present major challenges in development due to a number of reasons. To begin with, carbonate reserves present poorer recoveries compared to their siliciclastic counterparts. Lower primary recoveries can be experienced owing to limited connections of carbonate volumes to large aquifers. Due to these challenges, prediction of performance of carbonate reservoirs may be difficult to establish. In addition, management of carbonate reservoirs may prove to be a difficult task due to inaccuracy in targeting the appropriate injection and production wells.

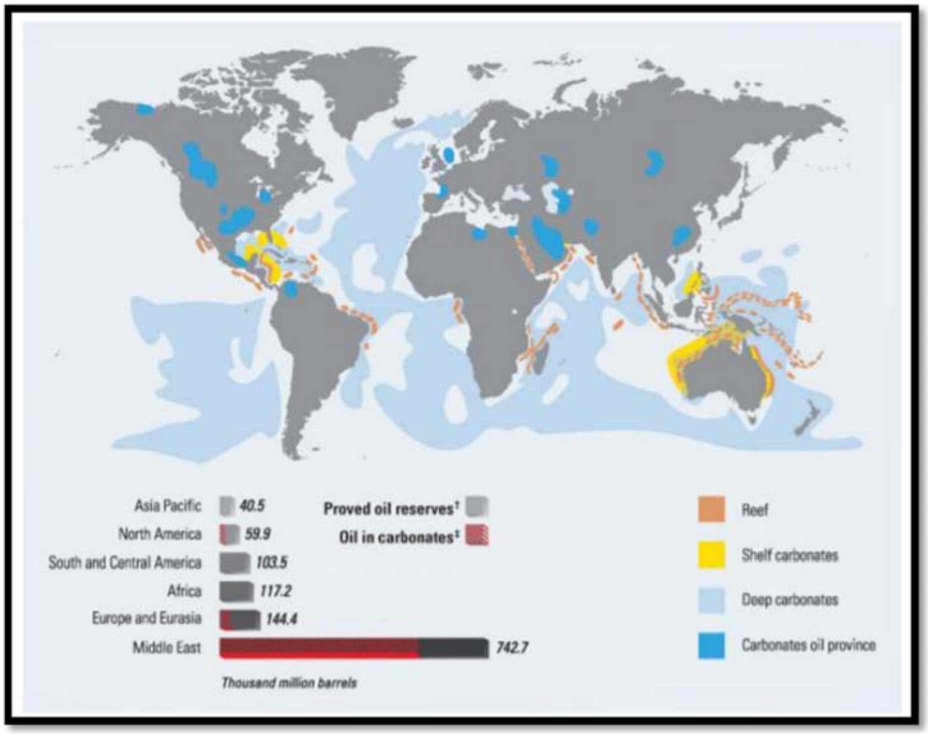

Figure 2. 8 world Distribution of Carbonate Reserves.

Carbonates naturally exhibit varying characteristics such as permeability and porosity (Guardado et al., 1989). These properties are usually characterized on smaller proportions hence complicating the overall process of characterizing the carbonate rock reservoirs. The heterogeneous nature of the carbonate rocks is fundamental in developing a comprehensive understanding of the flow and fluid properties of the carbonate rocks. Sizes of pores also vary in carbonate reserves. The pore size is crucial in determining the oil-carrying capacity of the carbonates. Carbonates with large cavities have the capacity to store large quantities of oil. For large unconnected cavities, the oil-carrying capacity is reduced and hence low flow rates are exhibited. The uncertainty in managing carbonate reservoirs is attributed by a number of factors including: water saturation of the rocks, the net pay, rock permeability and rock porosity. Carbonates have typical tendencies of exhibiting oil-wet features. Due to such characteristics, early water breakthroughs are commonly experienced in carbonate reserves. Additionally, they have thick zones of transition in rock reservoirs that exhibit reduced permeability.

Carbonate rock deposits contain various types of rocks. In geology, their types as opposed to their lithofacies usually characterize rocks. Various carbonate rock type's rock reserves different settings. Typical settings in which carbonate rock deposits may be found include: chalk, karst, organic build-ups such as reefs, leached zones, subtidal complexes and grain stone shoals. Across the various carbonate rock deposits, the primary texture of the rock will often be overlaid post deposited material arising from the processes of cementation.

2.3.1 Carbonate Reserves in Brazil

Brazil's onshore and offshore basins span a huge sedimentary block estimated to be an area of more than six million square miles (Guardado et al., 1989). Across this stretch, there are rich deposits of carbonate rocks that exhibit widespread distribution in terms of the age of formation. The carbonate rocks that are present in the Brazilian onshore and offshore basins range from Precambrian rocks to more recently formed carbonate reservoirs. Despite the large deposits of carbonate rocks in Brazil, only 4% of hydrocarbon reserves are seated in the carbonate deposits. Recent oil exploration techniques carried out in Brazil have shown promising results of potential higher deposits of hydrocarbons in the carbonate deposits.

The vast deposits of carbonate rocks in Brazil are distributed in different areas of oil fields in Brazil. Intra-cratonic regions such as the Basin of Sao Francisco have abundant layers of carbonate rocks that were formed during the Precambrian era. These rocks are mainly formed of microbial facies. These oil fields have registered limited quantities of gas in fewer oil wells. Another type of carbonate rock called the Paleozoic carbonates are dominant in the regions of Amazonas and Solimoes basins. These carbonate deposits have not registered any significant commercial explorations to date. The eastern marginal basins and the Campos basin contain large deposits of the Aptian carbonate rocks. The Aptian carbonate reserves have registered significant oil reserves in the basins of Santos and Campos. Peloids are contained within the Marine carbonates. These carbonate deposits have proven to be economically viable registering daily oil reserve capacity estimated at about six billion barrels. So far, these reservoirs have produced over 600 million barrels of oil. The carbonate reserves found in this region have been witnessed to exhibit varying degrees of porosities and permeabilities (Guardado et al., 1989). Microbialite and coquina facies have been reported from the Brazilian Pre-Salt carbonate play. These reservoir types are infrequent and poorly defined in terms of reservoir characterization (P.W.M. Corbett et al., 2014). These reservoirs are mostly composed of limestone, dolomite and silica. (Facanha et al., 2016).

The coquinas are generally heterogeneous in their porosity and permeability, but like other lacustrine carbonates, they are rarely reservoirs (Corbett et al. (2015)).

Fgure 2.9 shows Coquina reservoir at Campos Basin, as it occurs in seismic line (top right) with detail image with GR log and hand sample from core drilling (Jahnert, Ricardo et al. 2016).

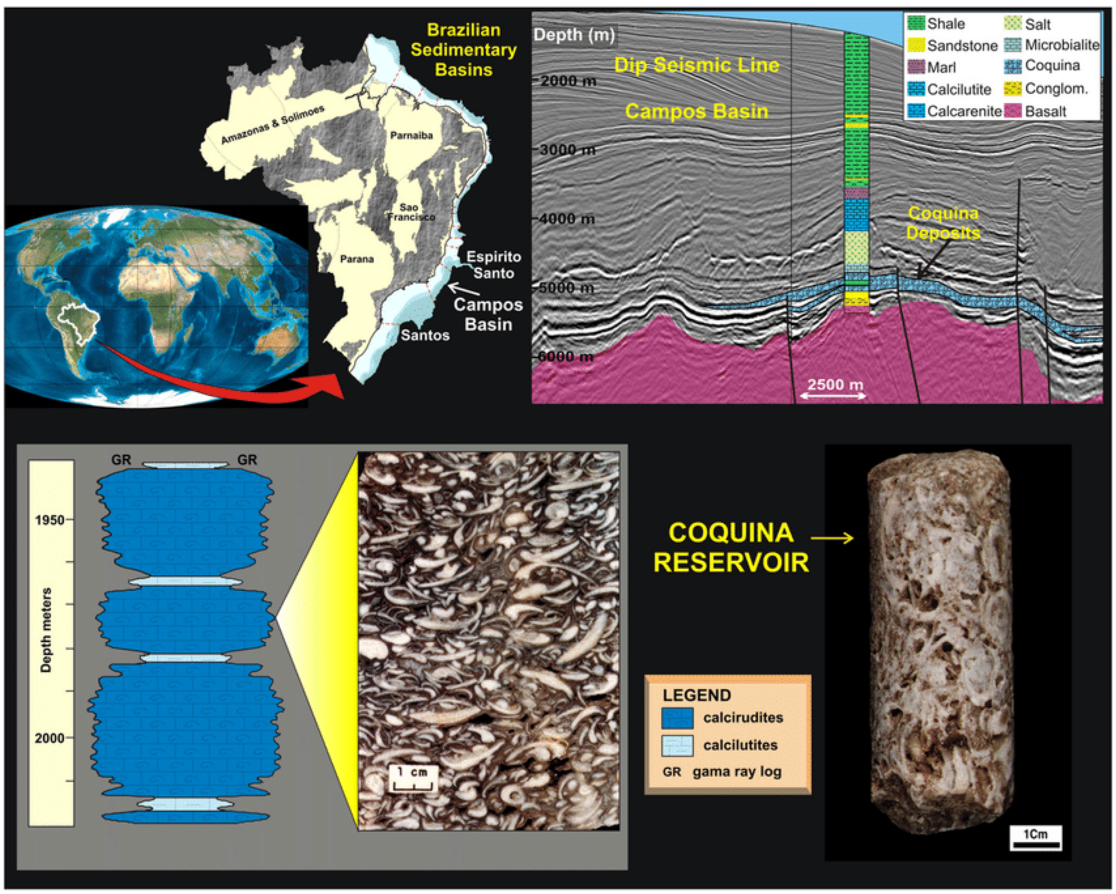

Figure 2. 9 Coquina reservoir at Campos Basin.

2.4 WETTABILITY FUNDAMENTALS

Wettability in oil exploration and mining is referred to as the tendency of two fluids to adhere to the surface of a solid material. Wettability is concerned with the elative adhesion of any two fluids towards the surface of a given solid material. For a porous medium, wettability concerns itself with the measure of individual fluids to spread the surface of a solid material. The wettability of a given material regulates the flow, position and channeling of fluids within the reservoir. Wettability can also be termed as a measure of the preference of the rock to two given fluids (water or oil for the case of oil reserves). The presence of two fluids adhering to the rock surface implies two different possibilities: an oil-wet rock and a water-wet rock. In the case of a water-wet rock, water tends to reside in the small pores and hence adhere to the large portion of the surface of the rock. An oil-wet rock implies a preferential contact of the oil to the rock. In this case, the oil dwells on the small pores on the surface of the rock and hence contact a larger portion of the surface of the rock (RezaeiDoust et al., 2009).

The wettability of the surface of a solid rock may be dependent on a number of factors. One crucial factor on which wettability depends is the thickness of water film existing between the crude oil and the surface of the rock. The water film has unique properties that directly influence wettability. First, a thick water film results into a stable system with a water-wet set-up. An unstable system leads to the breakage of the water film which causes the adsorption of polar elements into the rock. Finally, the stability of the water film is dependent on the degree of pressure that causes disjointing forces. This may result into intermolecular and other ionic force formations within the rock-water-oil system.

According to RezaeiDoust et al. (2009), the degree of wettability may vary from strongly water-wet conditions to strongly oil-wet conditions depending on the interactions between the brine, rock and oil. A neutral wettability results when there is no clear depiction of preference to either oil or water by the rock surface. In this condition, both fluids present in the rock set have an equal adherence to the surface of the rock. Mixed wettability is experienced in instances where larger pores are subjected to oil-wet conditions while the smaller pores are subjected to water-wet conditions.

2.4.1 Initial Wettability

The carbonates reservoir, which can be distributed into limestone, chalk, and dolomite, has a large portion of the known petroleum trapped.Carbonates are on average oil-wet (Cuiec 1984). These reservoirs usually have high salinity in their formation water and a high concentration of calcium (Ca^{2+}). Generally, according to tests and studies, the oil recovery from carbonates is well below 30% due to low water wetness, natural fractures, low permeability, and inhomogeneous rock properties. At pertinent reservoir conditions, the carbonate surface is positively charged. The carboxylic material in crude oil, as determined by the acid number, AN (mg KOH/g), is the most important wetting parameter for carbonate CBR systems (Austad,Tor 2013).

Crude oil components containing the carboxyl group, -COOH, are mostly found in the heavy end fraction of crude oils, i.e., in the resin and asphaltene fraction (Speight, 1999). The bond between the negatively charged carboxylic group, -COO- , and the positively charged sites on carbonate surface is very strong, and the large molecules will cover the carbonate surface. Temperature is also important in carbonate reservoirs. There is a trend that shows more water-wet states as the temperature of the reservoir increases. This is due to that carboxylic material content decreases by decarboxylation, as the reservoir temperature increases, and $CaCO_3$ presence catalyzes this sort of reaction, which becomes only significant during geological time (Shimoyama and Johns 1972).

Opposite to carbonates, a sandstone is composed of many minerals. Minerals of the silica type are negatively charged at the relevant pH range of the formation water. It is, however, the clay minerals that are most strongly adsorbed by polar component negative charges and the clays therefore act as cation exchangers. The relative affinity of cations toward the clay surface is regarded to be:

$Li^+ < Na^+ < K^+ < Mg^{2+} < Ca^+ < H^+$

It ought to be observed, that the proton H^+, is the most reactive cation toward the clay. While the concentration of H^+ is very low in the pH range between 6 and 8, it will still play an important role in cation exchange reactions at low salinities (Austad,Tor 2013).In competition with cations, both basic and acidic material can absorb on the clay surface and make the clay preferential oil-wet. The adsorption of both basic and acidic material onto the clay is very sensitive to the pH, and it can change dramatically within the pH range: $5 < pH < 8$ (RezaeidDoust et al., 2011).

The adsorption of both basic and acidic material from the crude oil appeared to increase as the pH decreased to about 5. Clays are generally not regularly distributed in an oil reservoir, and therefore, certain areas can be less water-wet than others are. These areas might be skipped in a water flood method, and both microscopic and macroscopic sweep efficiencies are reduced (Sheng J. 2013).

2.4.2 Wettability Alteration

Wettability alteration is used in the field of studies to describe the process of modifying the rock reservoirs to more water-wet conditions. The modification of wettability improves the process of oil recovery in oil-wet conditions and ultimately increases the efficiency of oil recovery.

Any process aimed at improving wettability demands activation energy for the chemical reaction processes that occur. The carbonate rock containing oil reserves has the capacity to adsorb carboxylic elements present in the oil. Due to this, wettability can be neutral, water-wet or preferential oil-wet. Without using surfactants, several studies have proven that seawater can act as a wettability modifier in carbonates at high temperatures by increasing the water-wetness of the targeted systems (Austad et al. 2008, Puntervold et al. 2009, Fathi et al. 2011). The mechanism of wettability alteration suggests that the potential determining ions, Ca^{2+}, Mg^{2+} and SO_4^{2-} are capable of influencing the surface And desorbing the crude oil components, thus changing the wettability of the rock. (Zhang et al. 2007).

In sandstones, the reversibility of the adsorption processes and the pH dependence are the basis of wettability alteration. Wettability changes in either direction, towards oil-wet or water-wet states can be explained by a variability of the main properties of a specific system (RezaeiDoust et al. 2011). The initial water wetness of a sandstone reservoir can be improved if any of the following changes occur: Increased concentration of Ca^{2+} in the FW, Increased pH of the brine and If Tres is raised.

The chapters about smart water will be addressed more on these mechanisms of wettability alteration for both types of rocks.

2.4.3 Wettability measurements - Contact Angle

This function exists between the relationships of solid to liquid or liquid-to-liquid interactions. The wettability of a reservoir is normally a function of temperature, carbonate heterogeneity, pressure and reservoir pressure. In wettability, the angle of contact is usually a function of solid roughness and rock heterogeneity. Consequently, the wettability of a rock surface can be classified in terms of their contact angles. For instance, a water-wet rock has a contact angle ranging between 0°–75° while an oil-wet rock has a contact angle ranging from 115°–180°, as shown in figure 2.10 (https://www.cscscientific.com/csc-cientific-blog/initiation-to-contact-angle). Contact angle measurements are carried out using a drop shape analyzer. This allows for the assessment of rock wettability in quantifiable portions of the crude oil that is present within the carbonate reserves (Zhang and Austad, 2006).

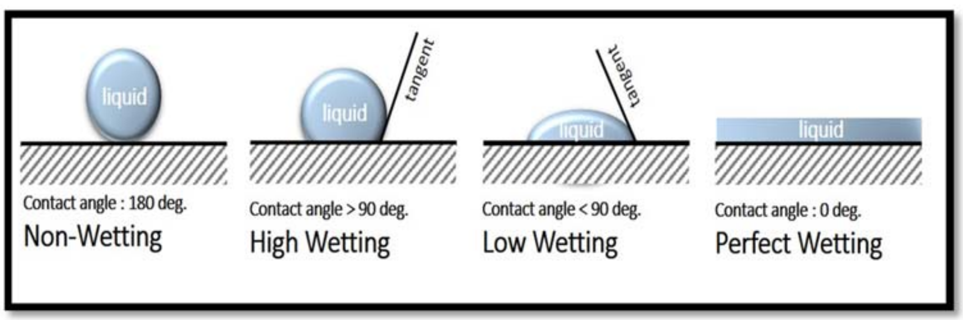

Figure 2. 10 A small angle (less than 90 degrees) means the surface is favorable for wetting. If the angle is larger than 90 degrees, the solid tends to be difficult to wet.

A smaller contact angle observed in carbonate rocks is indicative of carbon dioxide presence in the rocks which implies more water-wet conditions. This can be observed for calcite and coquinas deposits. The solubility of carbon dioxide in brine is increased with an increase in the pressure at the reservoir. This in turn causes and overall increase in water-wet surfaces for the rock samples present in the carbonate oil reservoirs.

It is usually very difficult to measure the wetting state of carbonate reservoirs in situ (Zhang et al., 2006). For this reason, typical wettability measurements are often carried out in the labs using large sample materials collected from the reservoirs. Spontaneous imbibition, the Amott method can particularly be used to assess wettability as well.

2.5 SMART WATER EOR

Smart Water is ion-modified water designed for wettability alteration and improved microscopic sweep efficiency. The Smart Water composition is generally based on either seawater or fresh water, and is thus environmentally friendly. The technique is economical, no expensive chemicals are added, and no injection problems. From an economical point of view, the smartest water should be injected from the start of the water flooding process.

For both carbonates and sandstone reservoirs, the oil recovery by injecting original formation water is usually different from the recovery obtained when injecting a water with a different composition from formation water. The oil recovery can both increase and decrease compared to formation water, which is in equilibrium with the CBR system. By using a “Smart Water,” the oil recovery can be increased significantly from both carbonates and sandstones (Austad,Tor 2013). This is demonstrated in Figure 2.11.

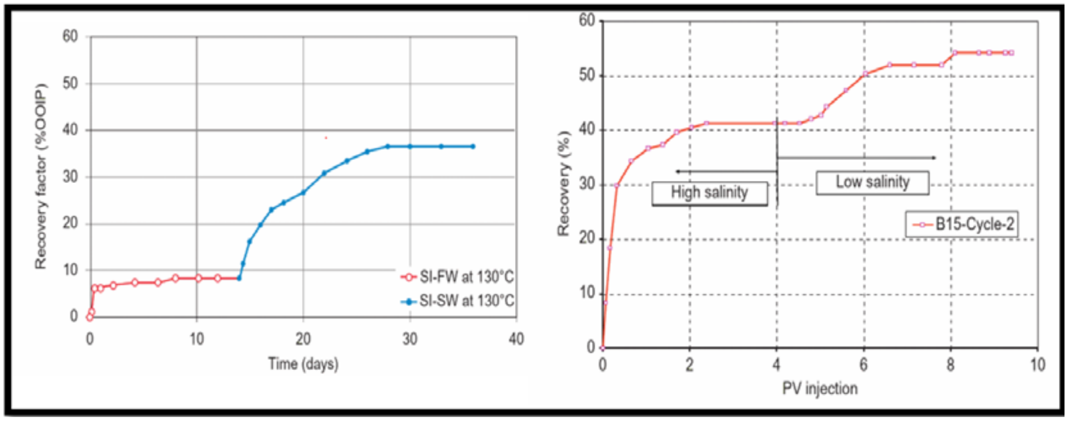

Figure 2. 11 First plot shows spontaneous imbibition of formation water, FW, and seawater, SW, into a reservoir limestone core 130 °C (Ravari et al, .2010) and second plot shows low salinity effects in Sandstone (Austad et al.,2010).

Extensive research has been executed in order to understand the chemical/physical mechanism for the wettability alteration process-taking place at the rock surface, and the mechanism is still under discussion in the available literature. The Smart Water EOR group at the University of Stavanger has worked with wettability modification in carbonates more than 20 years and in sandstones for about 11 years. (Austad,Tor 2013).

With the purpose of estimate the potential of using "Smart Water," the chemical mechanism must be understood in detail because "Smart Water" does not function in all types of oil reservoirs.

2.5.1 Smart Water EOR in Carbonates

According to studies and experiments over the years, is broadly recognized that wettability alteration is one of the main mechanisms for enhanced oil recovery as the trapping and fluids distribution would be affected by wettability (Strand et al. 2005).

Some requirements must be in order for SW mechanism(s) to occur such as, brine composition, crude oil type, connate water saturation and reservoir temperature. Another important requires is the properly categorize of initial wetting state of a carbonate system.

The acid number of a crude is then an important parameter regarding wetting (Fathi et al. 2011). All the way through geological time, crude oil can be vulnerable to change in the chemical composition that can create polar components with higher or lower affinity toward carbonate surfaces. One of the carbonate reservoirs features is to be naturally fractured, it is very challenging to recover the remaining oil in the matrix blocks, as water cannot be imbibed due to the negative capillary pressure effect. Therefore, early water production occurs and most of the reserved oil remained there, which becomes unrecovered (Austad et al. 2005). Since carbonate reservoirs are to be oil-wet, the wettability changes to more water-wet state would increase oil recovery.

Mechanism(s) of wettability alteration by smart water injection was studied (through experiments, researched.) and the conclusion of these studies show that $Ca^{2+,}$ Mg^{2+} and SO_4^{2-} alter the wettability of carbonate surface at different temperatures. It was also reported that SO_4^{2-} only has a catalytically role and reduces the positive surface charge (RezaeiDoust et al. 2009). Figure 2.12 shows a schematic model of the suggested mechanism for wettability alteration induced by seawater (Zhang et al. (2007)).

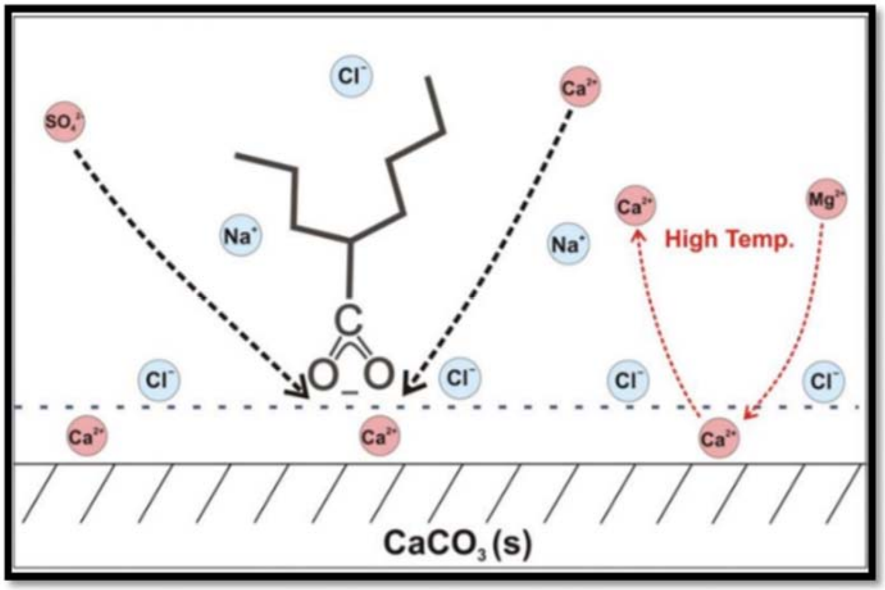

Figure 2. 12 Schematic model of the suggested mechanism for wettability alteration induced by seawater. First case proposed mechanism when Ca^{2+} and SO_4^{2-} are active species. Second case Mechanism when Mg^{2+}, Ca^{2+} and SO_4^{2-} are active species at higher temperature.

Understanding carbonates properties and the best Smart water composition and its effects of on fluid flow within a complex reservoir is crucial in estimating the producible reserves and determining production strategies to maximize recovery.

2.5.2 Smart Water EOR in Sandstone

Sandstones constitute around 15% of the sedimentary rocks. Their textures can record depositional setting, dispersal and transport mechanisms. They are also major reservoirs of ground water and hydrocarbons. They are mainly composed of quartz, feldspars, rock fragments, accessory minerals, micas and clay minerals (Piñerez Torrijos, Iván. 2017).

A great number of Laboratory tests for example by researchers at British Petroleum (BP) (Austad, 2013) have confirmed that EOR can be obtained when performing a low salinity water flood, with salinity range of 1000-2000ppm. Thus, a low salinity water may act as a smart EOR fluid in a sandstone oil reservoir.

The suggested chemical mechanism or EOR by low salinity water flood was based on three experimental observations:

i. Clay must be present in the sandstone.
ii. Polar components (acidic and or basic material) must be present in the crude oil.
iii. The formation water must contain active ions like Ca^{2+} .

Figure 2.13 demonstrated the suggested mechanism (Austad et al.,2010))

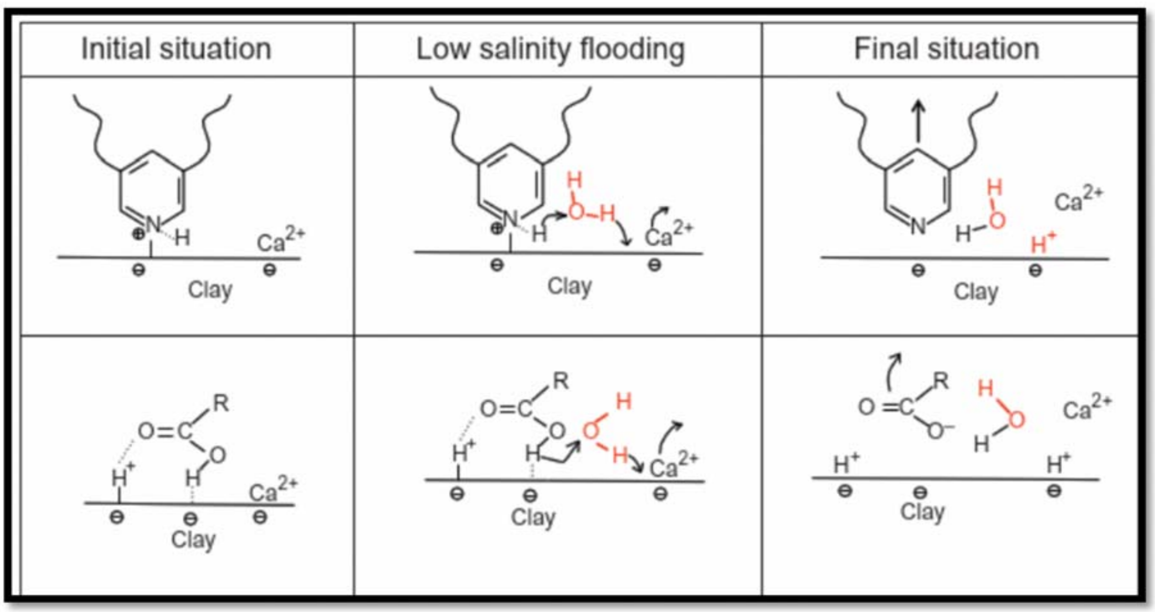

Figure 2. 13 Proposed mechanism for low salinity EOR effects. Upper: desorption of basic material. Lower: Desorption of acidic material. The initial pH at reservoir conditions may be in the range of 5.

As mentioned by Dr. Iván Darío Piñerez (2017), the reversibility of the adsorption processes and the pH dependence are the bases of wettability alteration in sandstones. See an example below in figure 2.14 when pH is increased (RezaeiDoust et.,2011). Here, Independent of the composition of the low salinity brine the low salinity EOR effects were comparable, and pH of the effluent increased as the fluid was switched from high to low salinity.

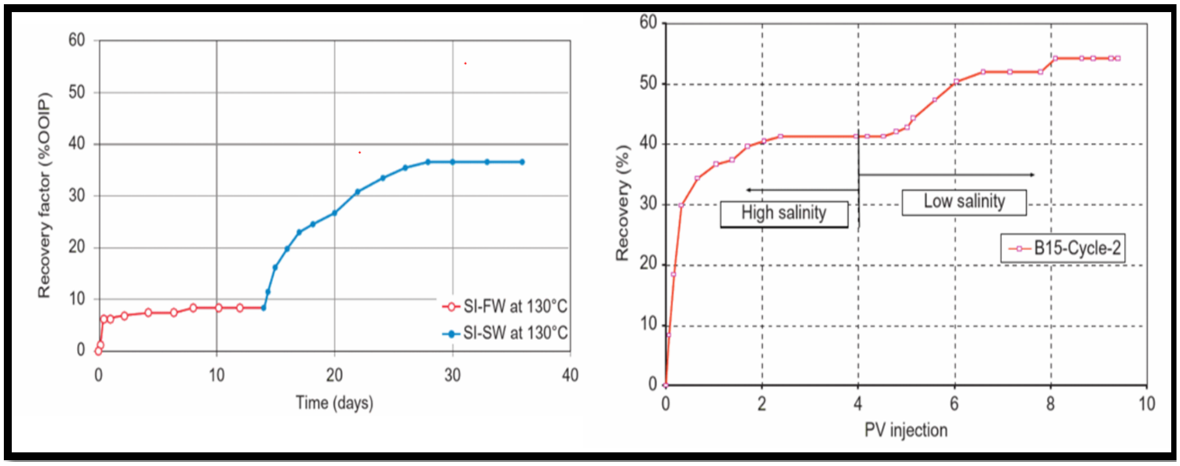

Figure 2. 14 First plot, pH change caused by different low salinity brines and second plot is the crude oil recovery (OOIP%) curve for brine composition tests.

2.1 SPONTANEOUS IMBIBITION

Spontaneous imbibition is the process caused by the capillary action where the wetting fluid phase is aspiring into a rock porous medium. Areal sweep can be affected by Imbibition process because it can advance or delay water movement in the reservoir. Spontaneous imbibition denotes to the process of absorption with no pressure driving the phase into the rock. It is possible through imbibition test to analyse the potential that the rock has to attract water or oil, since the rock can be imbibed by the two fluids. The wettability of the rock is defined by which phase imbibes more.The role of imbibition has been documented in abundant categories of recovery processes, including water flooding of heterogeneous reservoirs and alternate injection of water and gas (Norman RMorrow et al., 2001).

For low-permeability fractured reservoirs is essential to consider spontaneous imbibition as important oil recovery mechanism. However, for rock surface preferential oil-wet this mechanism will not occur (Dag Chun Standnes 2004).

For spontaneous imbibition measurements, the standard test equipment employs an Amott cell. It has a graduated section to determine imbibition volumes. Spontaneous imbibition can be performed on unconsolidated cores using a coreholder, graduated separator system and a pump in a closed circulating system as presented in figure 2.15 (Colin McPhee et al., 2015).

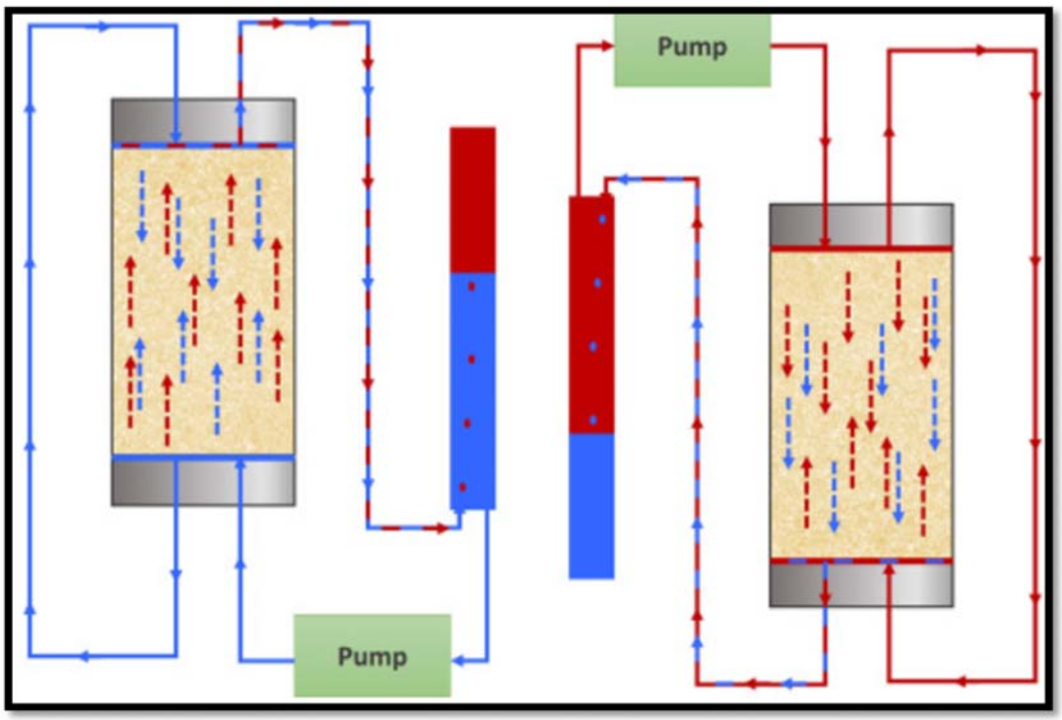

Figure 2. 15 Spontaneous imbibition schematic for unconsolidated material (using coreholder, separator and pump).

Chapter 3: EVALUATION OF BRAZILIAN OIL SECTOR

3.1 HISTORY OF BRAZILIAN OILFIELDS

Until 1997, Petrobras, a state-owned petroleum company, had been exclusively been authorized to conduct upstream activities. With the approval of the Petroleum Law in 1997, Petrobras' 42-year monopoly in oil and gas exploration and production was brought to a halt (Guardado et al., 2000). Under a concession regime, petroleum exploration rights have been undergoing annual licensing by various regulatory agencies in the country. Following the end of Petrobras' monopoly, the National Petroleum Agency (ANP) was formulated for the purpose of contracting, regulating and supervising the operations of the petroleum industry within the country (Ali and Thomas, 1996).

The Petroleum Law cancelled the laws in which Petrobras was established for instance, under the new rules, Petrobras would involve in free market competition with other interested companies. Further, the government would be granted majority shares within Petrobras allowing it to be the controlling authority. Also, Petrobras continued to have privileges over assets available both on the downstream and upstream. After these changes, Petrobras experienced major structural changes to accommodate a vertical structure of operation. This way, the company was better positioned and act independently from other government agencies. In the following Figure 3.1 is possible to have an overview of Oil and gas sector in Brazil (ANP,2018).

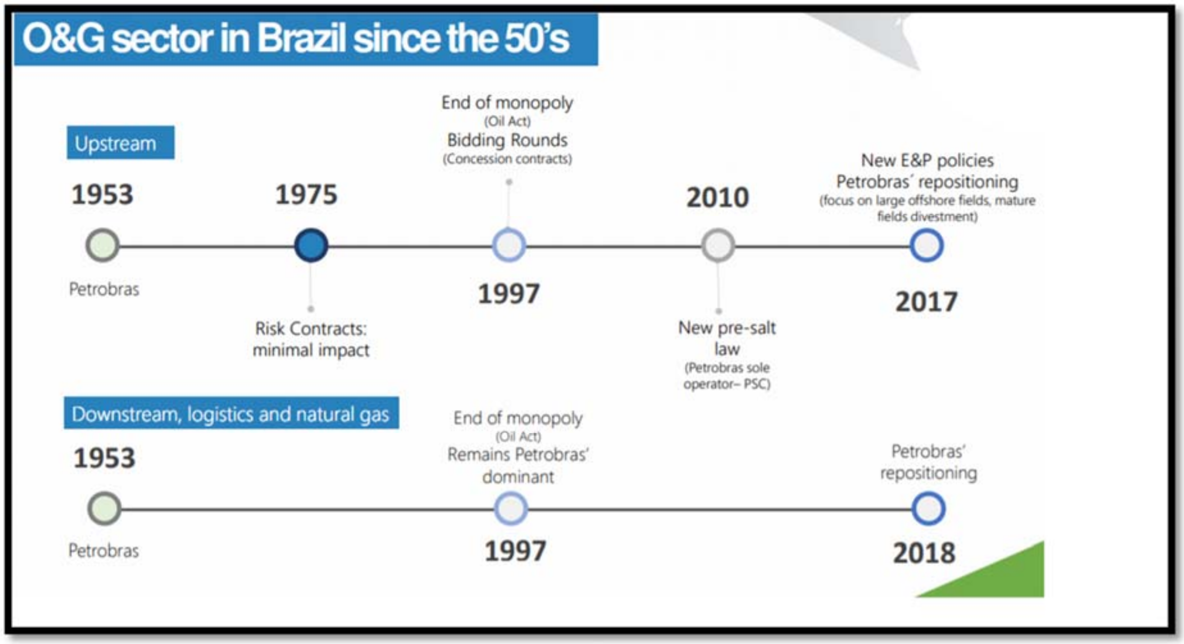

Figure 3.1 Progression of O&G sector in Brazil.

3.2 OVERVIEW OF BRAZILIAN OIL SECTOR

The Brazilian oil sector has been expanding in the industry from the time oil was first discovered in the country. In recent years, oil fields still being discovered in different places in Brazil. Figure 3.2 below shows recent discoveries (www.ANP.gov.br).

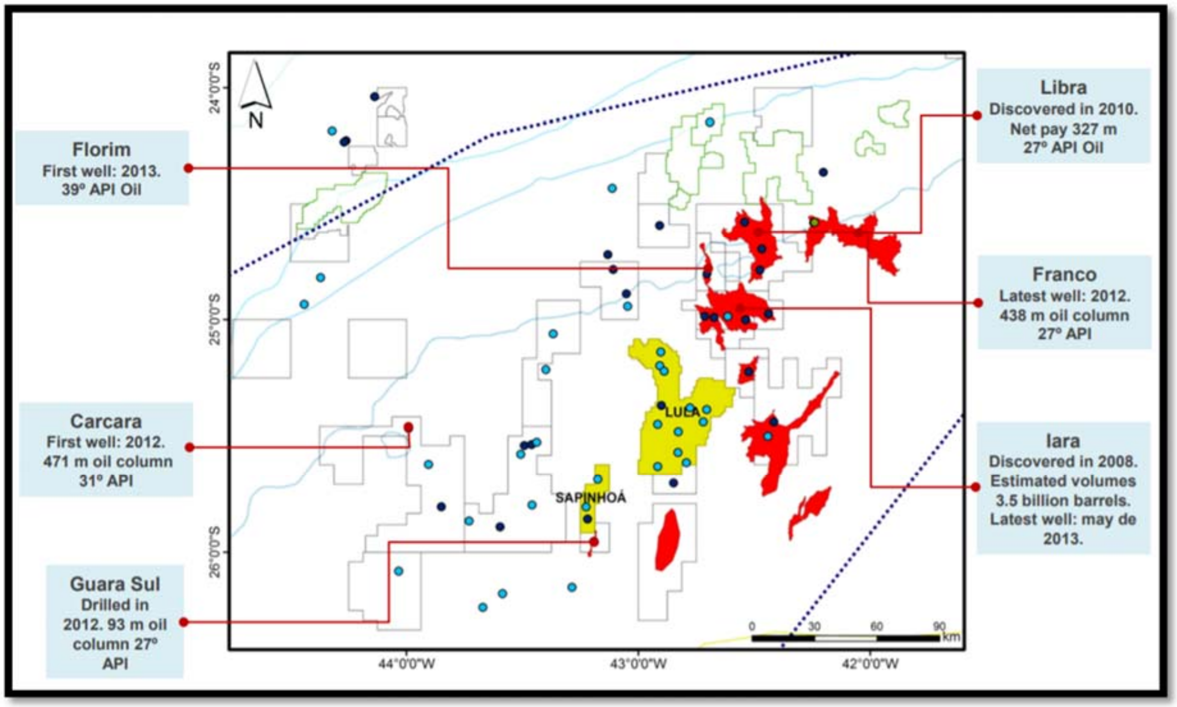

Figure 3.2 Recent discoveries

Today, Brazil stands as one of the largest producers of oil in South America. Additionally, it compares well against world's major oil producers such as Saudi Arabia and United Arab Emirates. The continued discovery oil new oil reserves coupled with the termination of the State's monopoly in oil exploration and mining opened a new era for the Petroleum industry in Brazil.

The Lula oil field region was discovered to contain the pre-salt oil reserve by Petrobras in 2006. Two years later, the first oil was first drawn from the Jubarte field on the same pre-salt reserve. In a series of consecutive explorations, the pre-salt oil reserve has proven to conceal larger quantities of oil reserves. The Pre-salt layer sits 5,000 meters below the Brazilian seabed. The Pre-Sal layer spans a distance of 795 km, connecting two different Brazilian states – Santa Catarina and Espirito Santo. Owing to its large-scale existence, the Pre-Sal layer is one of the largest oil fields discovered in the world within the last decade (source: ANP). The entire stretch of the oil field is estimated to contain approximately 1.6 trillion m^3 of gas and oil. This figure represents about six times the present oil reserves in the country. With appropriate mining methods and technologies, an appropriate investment plan can be formulated to yield higher production rates. The present use of some EOR methods such as water flooding and gas flooding in Brazilian oil fields puts it on the right technological track to achieving higher production levels of oil.

3.3 CHARACTERISTICS OF THE BRAZILIAN PRE-SALT OILFIELDS

According to ANP 2018 estimation of the oil production in Brazil is slightly more than 2.5 million barrels per day as presented in Figure 3.3 (source: www.ANP.gov.br). With the use of newer technologies, ANP 2018 claims that Brazil's daily production could hit 5.5 million barrels per day by the year 2026 as shown in Figure 3.4 (www.ANP.gov.br). That rapid growth in daily oil production is tightly linked to the discovery of the Pre-Sal layer.

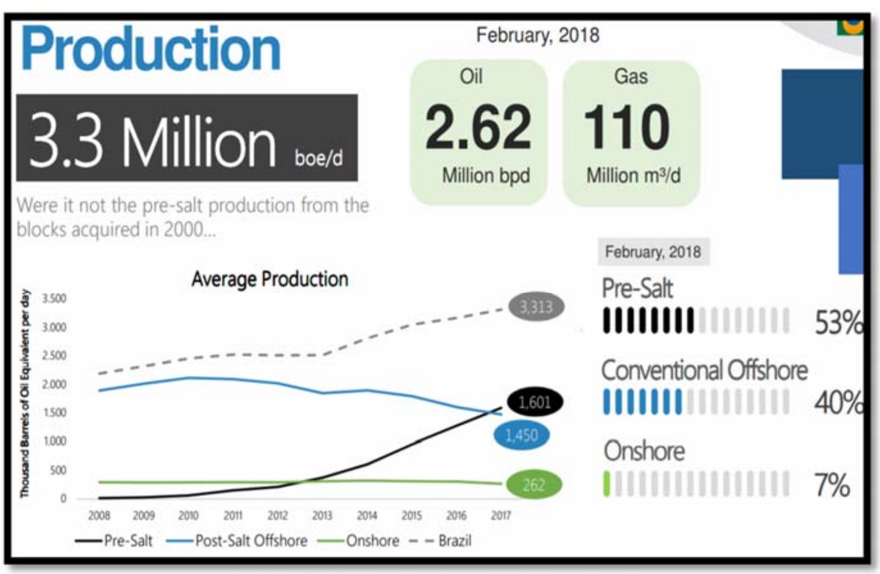

Figure 3. 3 Brazilian oilfields Production

Figure 3. 4 Potential investments and forecast production .

Both national and international literatures there are important descriptions about the characteristics of the Brazilian pre salt. The following are some of the main characteristics and challenges of pre salt over the last few years:

- The distance between the coast and the pre salt fields is a challenge for the area related to logistics and the environment. Distance can be approximately 300km from the coast.
- To separate CO_2 from the produced gas, Petrobras has adopted the membrane system (CEZAR et al., 2015), with the intention of injecting CO_2 for recovery (EOR- CO_2 injection and WAG). CO_2 gas due to environmental reasons can not be venting to the atmosphere.
- Pre-Salt carbonate reservoirs are mainly composited of two types of formations: the upper sag is characterized by microbial carbonates, and the lower sag is represented by the coquinas. It is known that

these formations are extremely heterogeneous with interbedded microbial and volcanic rocks that have been affected by different geological processes, such as hydrothermalism (MATIAS et al., 2015). Pepin et al. (2014) studied the coquinas formations and after performing laboratory tests had as a result that, the rock matrix in Pre-Salt reservoirs is a very heterogeneous carbonate. Values for the permeability ranged from 0,001 to 358 mD (millidarcy) and for porosity, the variation is from 2, 57% to 22, 5%.

- Water depth up to 2,250 meters.
- Medium to light oil with API gravity around 28°-30° and some fields contain high contents of CO_2, around 8-19%.
- The internal pressures in the Pre-Salt reservoirs are higher than the ones in conventional fields from the Campos basin. This is critical for injection wells and lines that operate at pressures at approximately 8000 psi (CEZAR et al., 2015).
- Low temperatures (between 60 and 70 °C) and the oil properties (high API and low viscosity) represent good conditions for gas-oil miscibility (Pizarro; Branco, 2012).
- Santiago G. Drexler et al., (2016) has mentioned in his studies that, the literature does not provide many wettability measurements for crude oil/brine/rock systems similar to that of the Brazilian Pre-Salt.
- The salt layer is a good heat conductor. Therefore, the reservoir temperatures are lower than expected for rocks at great depths but more critical for wax deposition and hydrate blockages (Petrobras)

(http://www.firstmagazine.com/DownloadSpecialistPublicationDetail.593.ashx).

- Thermodynamic simulations have forecast the possibility of calcium carbonate, barium and strontium sulphate precipitation. Low sulphate seawater injection is an option to prevent sulphate scale formation. Chemical treatments may be required to prevent calcite precipitation in the perforations and subsea equipment. To cope with this challenge, Petrobras' expertise in the Campos Basin, as well as support from international institutions, are being used to define the chemicals to be applied and investigate interaction that seawater or EOR methods may have with the reservoir rock. http://www.firstmagazine.com/DownloadSpecialistPublicationDetail.593.ashx

3.3.1 Campos Basin

The Campos basin is situated in the southeastern part of Brazil and is mostly located at the offshore of the Rio de Janeiro. The basin occupies an area of about 115,000 km^2 and lies side by side with the Espírito Santo.

These were the sand-rich tertiary succession Neocomian basalts was located. This was having a Precambrian metamorphic basement. Oil exploration in the Campos Basin began at the end of the in the 1950s, when Petrobras began a campaign to acquire two-dimensional seismic data in shallow waters in the Campos Basin (De Campos, B Bastos G (2015)).

Oil recovery in Campos basin first took place in 1974 when the Albian carbonate reservoir was first discovered underwater at a depth of 120 m. After this discovery, still in the 1970s several fields were discovered in the shallow waters of the Campos Basin in different exploratory plays, such as Badejo in coquinas of the lower Aptian (rifte stage), Enchova in sandstones of the Eocene and the first giant field of Brazil that was the field of Namorado discovered in turbidites of Cenomanian.

At the time of discovery, some of the oilfields could not be exploited due to the depth and some of the fields contained unconventional oil reservoirs, which by then still needed more technology for them to be exploited. Some of the oilfields along this region included the Barremian coquinas, Neocomian fractured basalts, late Albian to early Miocene siliciclastic turbidites and early Albian calcarenites.

By around 1984, Brazilians started to discover deep and ultra-deepwater giant fields such as Marlim Sul, Barracuda, Roncador, Albacora, Albacora Leste, and the most recent Jubarte and Cachalote. Figure 3.5 shows Location map and Main Reservoirs for the oilfields from the Campos Basin (Bruhn, 1998).

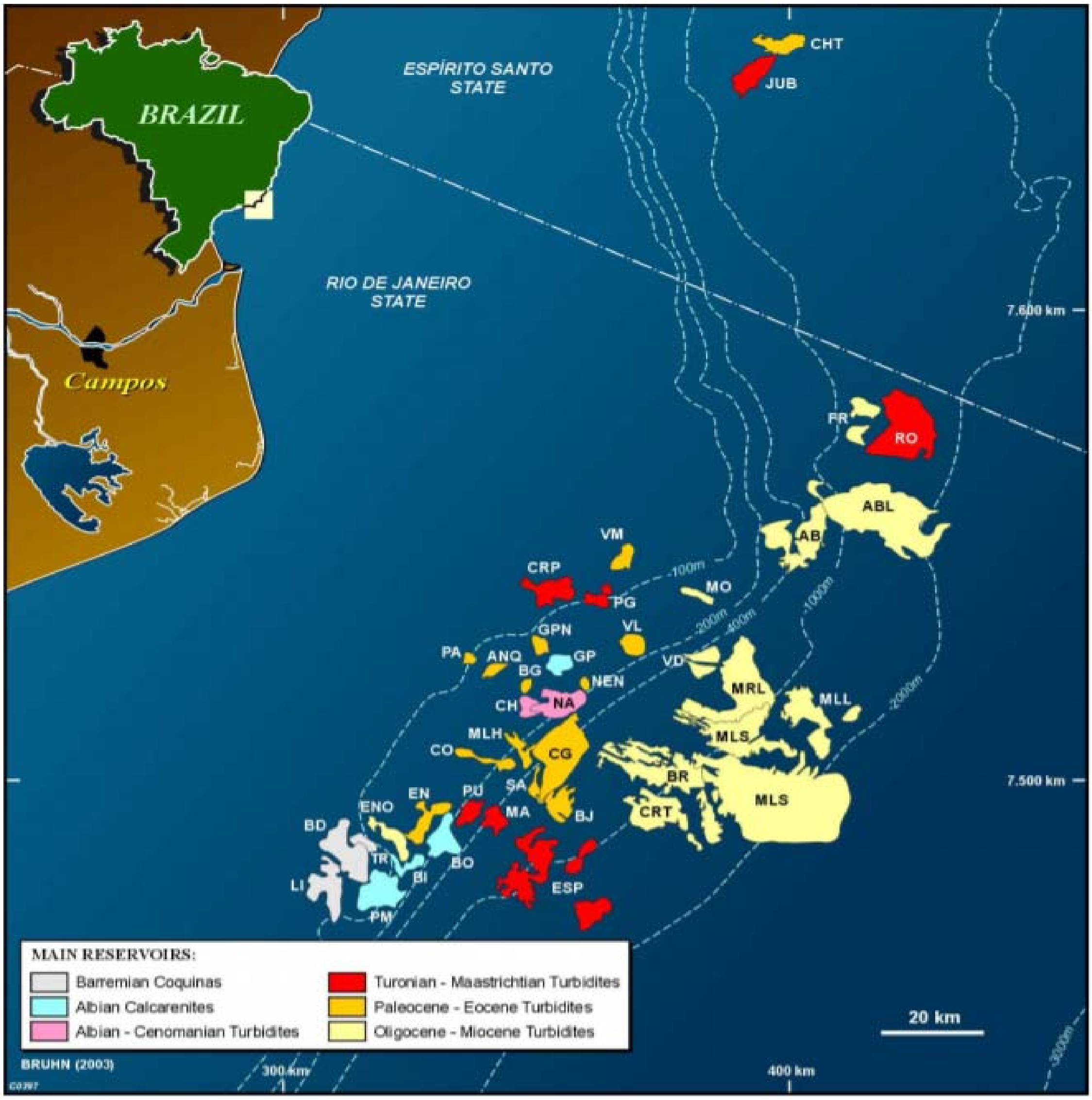

Figure 3. 5 Location map for the forty-one oilfields from the Campos Basin. Most of the fields contain reserves in more than one reservoir type;

There are 12 major turbidite systems in the Campos Basin:

Marine Transgressive Megasequence:

1. Late Albian – Namorado Sandstone;
2. Late Cenomanian - Namorado Sandstone;
3. Turonian/Coniacian - Espadarte Sandstone;
4. Santonian - Carapeba Sandstone;

5. Campanian/Maastrichtian - Roncador Sandstone;
6. Late Paleocene - Barracuda Sandstone;
7. Early Middle Eocene - Enchova Sandstone;

Marine Regressive Megasequence:

8. Late Middle Eocene - Corvina Sandstone;
9. Early Oligocene - Caratinga Sandstone;
10. Late Oligocene – Marlim Sandstone;
11. Late Oligocene/Early Miocene – Marlim Sandstone;
12. Early Miocene – Albacora Sandstone.

An example of oilfield in the Campos basin is the field called Roncador , located in the northern area of the Campos Basin, about 125 km from the Cabo de São Tomé, was discovered in October 1996. Below table 3.1 shows characteristics of this field.

Table 3. 1 characteristics of Roncador field.

Water Depth (m)	1500 to 1900
Reservoir Area (km^2)	111
Major Reservoir Types	Turonian - Maastrichtian Turbidites
Net pay (m)	270
Oil Gravity (°API) Module 1A4 Module 2 Module 3 Module	 28 to 31 18 22 18
Temperature (°C)	60
Initial Reservoir Pressure (psi)	8250
Viscosity (cp)	~10
CO2 in sloution (%)	8~12
Presalt layer thickness (m)	2000

3.3.2 Santos Basin

The Santos Basin is under ultra-deep waters with a water depth of 1900 to 2400 meters (Formigli Filho et al. 2009). It is situated in the southeastern region of Brazil and approximately 290 km from the Rio de Janeiro coast. Santos basin database information is quite small due to recent discovery reasons (Significant discoveries since 2007). Around 200 wells were drilled to access the pre-salt reservoir in Santos basing (Maul et al., 2018b).

Figure 3.6 shows Santos basin oilfields (E. Schnitzler (Petrobras) et al.2015).

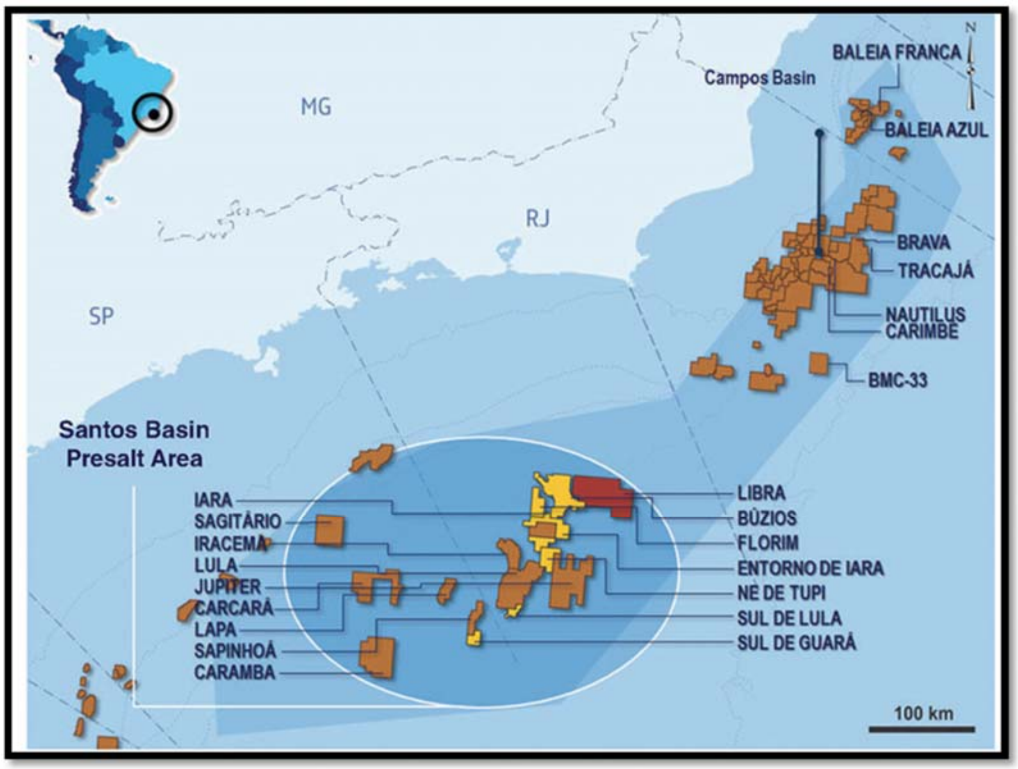

Figure 3. 6 Santos Basin pre-salt cluster

Hydrocarbon and reservoir types are listed below:

- Gas in Santonian turbidites -*1984 (4900 m)*
- Oil in Albian grainstones -*1988-2001 (4500 m)*
- Oil and gas in Santonian - Campanian turbidites -*1999-2005 (4200 m)*
- Oil and gas in Aptian carbonates - *2006-2012 (6000 m)*

Table 3.2 shows the main characteristics of Santos Basin.

Table 3. 2 Santos Basin main characteristics

Age Aptian	Microbial Carbonates
Age Upper Cretaceous	Turbidite Sandstones
Total Area (km^2)	~350000
Area on offer (km^2)	~5280
Cumulative Thickness (m)	23170
Top Depth (mMSL) (Mean sea level (MSL) Or sea Level)	1900-2400
Gas to Oil Ratio (m3/m3) (GOR)	
Oil Gravity (°API)	28-33
Average Porosity (%)	10-20
Average Permeability (mD)	~1

Lula oil field is one of the largest oil fields in Santos basin Brazil and it lies 250 kilometers off the coast of Rio de Janeiro. The Petrobras discovered the oil field in the period of 2006 and by then it was named Tupi in honor of Tupi people. By 2010, the oil field was then given the name Lula. According to Reuters (2010), the oil field is believed to have a potential of producing 8 billion barrels which was believed to potentially contribute in meeting the growing oil demand globally. In the viewpoint of the depth of the reservoir, it has been noted that this oil field lies 2000 meters of the water. Consequently, it has been articulated that this oil field lies approximately 5km of salt and sand rock which at times have also made it difficult to recover some of the economically viable oil from the field.

Marcelo Becher Rosa et al (2018) observed that slightly more than 10 years after the discovery of this oil field, it was considered the largest deep-water oil production in the world and this is the reason why it was considered to have the potential of largely contributing to the growing oil demand in the world.

Table 3.3 shows the main characteristics Lula field's reservoirs.

Table 3. 3 the main characteristics Lula field is reservoirs.

Water Depth (m)	**2200**
Top Depth (mMSL) (Mean sea level (MSL) Or sea Level)	5000 ~5500
Major Reservoir Type	Aptian Carbonates
Discovered (Year)	2006
Gas to Oil Ratio (m3/m3) (GOR)	220~240
Oil Gravity (°API)	28
Temperature (°C)	64
Initial Reservoir Pressure (psi)	8250
Viscosity (cp)	1.14
CO2 in sloution (%)	8~18
Presalt layer thickness (m)	2000

Chapter 4: CASE STUDIES

Before starting the case studies, a summary of the essential parameters for the smart water evolution will be presented for a better understanding. For the case studies, we will consider smart water only for carbonate rocks. Dependent on the chemistry-optimized seawater used in the injection the adsorption/interaction of keys ions can cause the wettability alteration and consequently, the rise of oil recovery. In carbonates, seawater is used as smart water to change wettability and reduce capillary trapping of oil. For this mechanism to occur it is necessary to have in the injected seawater the following ions: Sulfate, calcium and magnesium. However, it is crucial always to keep in mind that for application of smart water in carbonates must take into account the following maxims: Temperature, rock mineralogy and initial wettability (S.C.Ayirala and A.A. Yousef 2014). Another significant wetting parameter is the Acid number (AN) which has the function of determining the carboxylic material in crude oil. The imbibition rate and oil recovery decreased dramatically as the AN of the oil increased (Standnes and Austad, 2000a). Figure 4.1 shows the desired chemical injection water for Smart water in Carbonates (S.C.Ayirala and A.A. Yousef 2014).

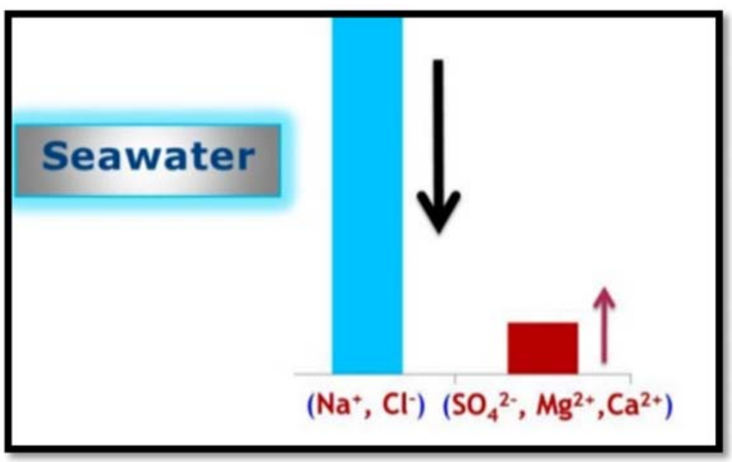

Figure 4. 1 desired injection water for Smart water in Carbonates. Considerable decline in Na^+ and Cl^- and slight increase in SO_4^{2-} , Mg^{2+} and Ca^{2+}. Process dependent on temperature, rock minerology and initial chemistry.

In this work, through case studies, the wettability-changing phenomenon of smart water will be studied considering water at different concentrations of seawater and formation water. The intention even though through case studies, is to show the evaluation of initial wettability and wettability alteration from carbonate reservoirs systems.

4.1 CASE STUDY 1

A study carried out by Ruidiaz et al. 2017 with the intention of studying the wettability alteration for both dolomite and limestone cores (corresponding Brazilian pre-salt reservoirs), and its effects on oil recovery percentage. Experiments were carried out using different brines (200,000 and 35,000 ppm salinities respectively) containing CO_2. The analysis of the experiment was done considering qualitative and quantitative evaluation (spontaneous imbibition and Amott–Harvey index).

4.1.1 Properties of the Samples

Dolomite and Limestone were the carbonate rocks used in the experiment.The dolomite cores were from the Silurian Devonian formation, Pennsylvania, USA and the limestone cores were from the Morro do Chaves formation (Sergipe-Alagoas Basin, Brazil). Both carbonate cores used in the experiments show characteristics similar to Brazilian Pre-salt. Rocks cores presented properties ranged between 7 and 21% for porosity and from 10 to 400 mD in absolute permeability. (Ruidiaz1 et al., 2017).

- **Crude oil**

  The researchers used in this study Crude oil from a Brazilian pre-salt reservoir. Table 4.1 shows the following crude oil properties:

Table 4. 1 Crude oil properties – Study case 2.

Description	Reservoir Temperature (°C)	API (°)	Viscosity (cp)	TAN (mg KOH/g.)
Oil	64	28	6.4	0.165

Also informed by the researchers that due to the observed interaction between the carbonate brine and the original crude, derived oil was prepared by des-asphalting (ASTM D6560-05) and dewaxing (ASTM D2007-11) the original oil for use in the displacement runs involving Carbonate water injection.

- **Brine Sample**

Brine used in this experiment was synthetic formation brine (FW) and seawater (SW), and their carbon dioxide saturated versions (carbonated seawater – CSW, carbonated formation water – CFW). The synthetic brines were prepared with 100% of NaCl dissolved in distilled and de-ionized water (Ruidiaz et al., 2017).

The following table 4.2 shows some of the test conditions.

Table 4. 2 properties of the different brines concentrations

Description	Equivalent concentration (ppm)	Temperature **(°C)**	Age (hours)
Seawater	35000	64	1000 and 2500
Formation Water	200000	64	1000 and 2500

For these experiments, Ruidiaz et al., 2017 considered CO_2 dissolved in both brines (CSW and CFW) at 2000 psi and the calculated solubilities for seawater and reservoir water are 0.7826 mol/kg s/n and 0.4880 mol/kg s/n, respectively.

4.1.2 Methodology

- **Seawater and Formation water**

Setup for Spontaneous imbibition experiments for Seawater and Formation water considered a low pressure for a standard Amott cell. During the tests, each Amott cell with SW and FW was placed with individual sample. In the course of the tests, production was monitored. The test started at the irreducible oil saturation condition (Sor) and was carried out in four steps in order to evaluate the Amott–Harvey wettability index: The steps correspond to the processes of natural imbibition in oil, forced displacement with oil, natural imbibition in brine and forced displacement with brine. At each step, the volumes were collected and measured to calculate the index . After the first round of evaluation (round 1), the rocks were subjected to a second full wettability index evaluation (round 2) using the switched brine. Finally, the rocks were again evaluated with the initial brine (round 3) (Ruidiaz et al., 2017).

The figure 4.2 below demonstrates the experimental setup (an unsteady-state oil recovery apparatus) (Ruidiaz et al., 2017).

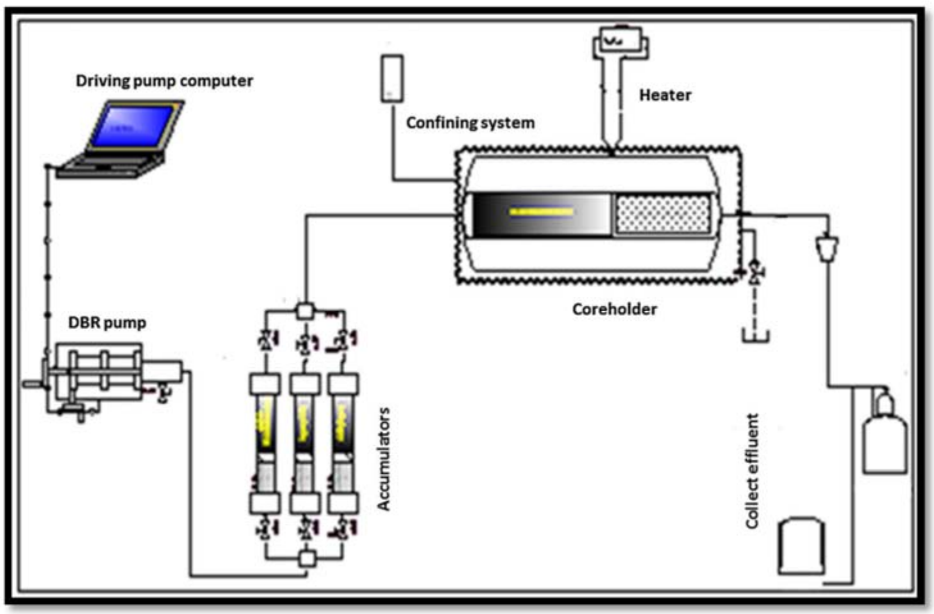

Figure 4. 2 Experimental workflow for the Amott–Harvey wettability tests (The setup consists of a positive displacement pump (by DBR) connected to a series of three pressurized vessels containing, respectively, oil, FW and SW, the coreholder and the collecting system).

- **Carbonated Seawater and Carbonated Formation water**

For carbonated seawater and carbonated formation water tests were performed at a high-pressure Amott cell. In addition, here for the evaluation of the Amott–Harvey index with carbonated water, the derived oil was used instead of the original crude. An adaptation of the coreholder was required in order to proceed with the spontaneous imbibition test under pressure. The adaptation consisted of placing an aluminum ring assembled inside the coreholder as shown in Fig. 4.3 (Ruidiaz et al., 2017). The ring provides volume to receive the fluid necessary to carry the imbibition test in the sequence. Fluid must remain pressurized to avoid desorption of CO_2 from the liquid phase. The remaining of the procedure for evaluating the wettability index was kept the same, including the rounds of changes in brine concentration (Ruidiaz et al., 2017).

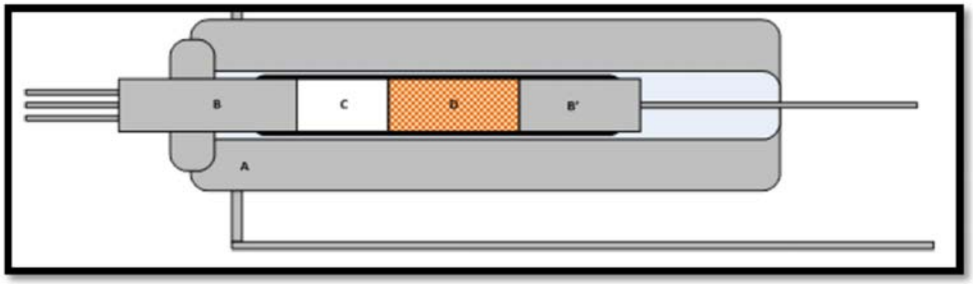

Figure 4. 3 Adaptation in the coreholder for Amott–Harvey test with carbonated water, where A casing coreholder, B input diffuser with three injection lines, B` output diffuser with a single line, C adaptation in coreholder, aluminum ring, D rock sample.

4.1.3 Results and evaluations

4.1.3.1 Seawater and Formation water

i. Analysis of Oil recovery by spontaneous imbibition

Oil recovery test was performed in samples aged 1000 and 2500 h using seawater and formation water as imbibition fluids. For dolomite and limestone samples, Figure 4.4 shows the volume of produced oil against time. For Limestone, the authors made the following observations: For the two aging conditions used in the experiment the volume of oil recovery reach a state of little or no change after 1000h time. Also for both brines concentration the result was similar, not having much change for oil recovery (Ruidiaz et al., 2017).

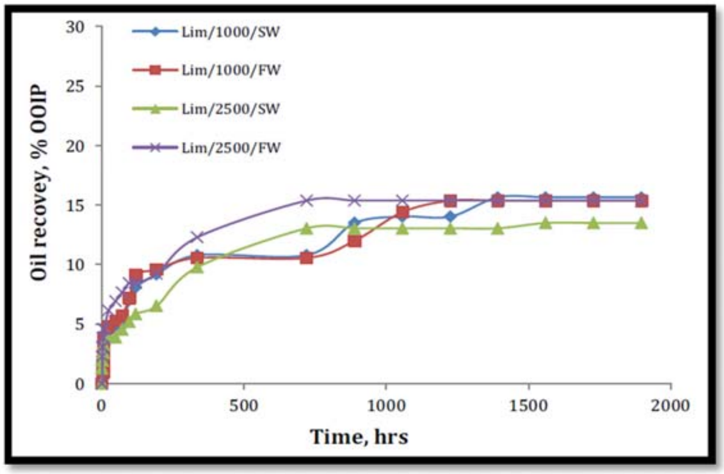

Figure 4. 4 Oil recovery by spontaneous imbibition with different waters, for Limestone sample.

On the other hand, considering the same process used in the limestone, oil production decreased as time increased, this can be seen in the figure 4.5 (Ruidiaz et al., 2017). For 1000h aged cores the following results were observed: the percentage of recovery for seawater was 12.7% and for formation water the observed value was 16.6%. For the aged sample at 2500h, there was a decrease in the volume of recovered oil, 4.8 and 6.2%, in that order (Ruidiaz et al., 2017).

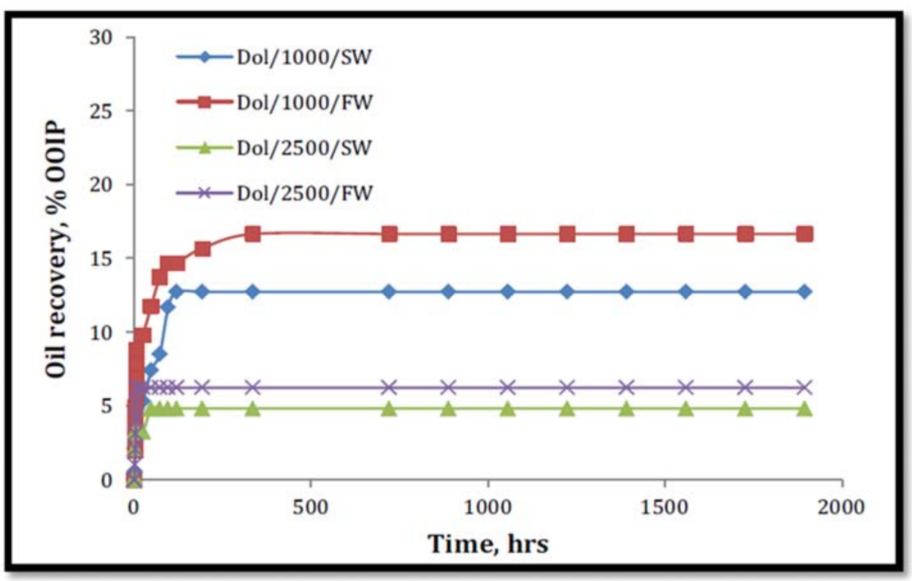

Figure 4. 5 Dolomite core sample oil recovery by spontaneous imbibition with different waters

One of the reasons for different results between limestone and dolomite rocks can be attributed to mineral composition. However, the rock composition was not reported in the paper. Ruidiaz et al., 2017 comment that high concentration of magnesium may influence the adsorption of the polar components that make the dolomite rock surface more oil-wet.

ii. Cumulative oil recovery by spontaneous imbibition

After the first round of evaluation (round 1), the rocks were subjected to a second full wettability index evaluation (round 2) using the switched brine. Finally, the rocks were again evaluated with the initial brine (round 3). Following the round according arrangement: for Seawater SW-FW-SW and for Formation water FW-SW-FW (Ruidiaz et al., 2017).

For the dolomite sample the result can be observed in the figure 4.6 (Ruidiaz et al., 2017). The production of oil increases with each new evaluation. It is notable that the increase volume of oil produced in all cores occurred independently of the brine concentration used as imbibition fluid. Perhaps this increase in recovery is associated with possible dissolutions (Zhang and Austad 2006).

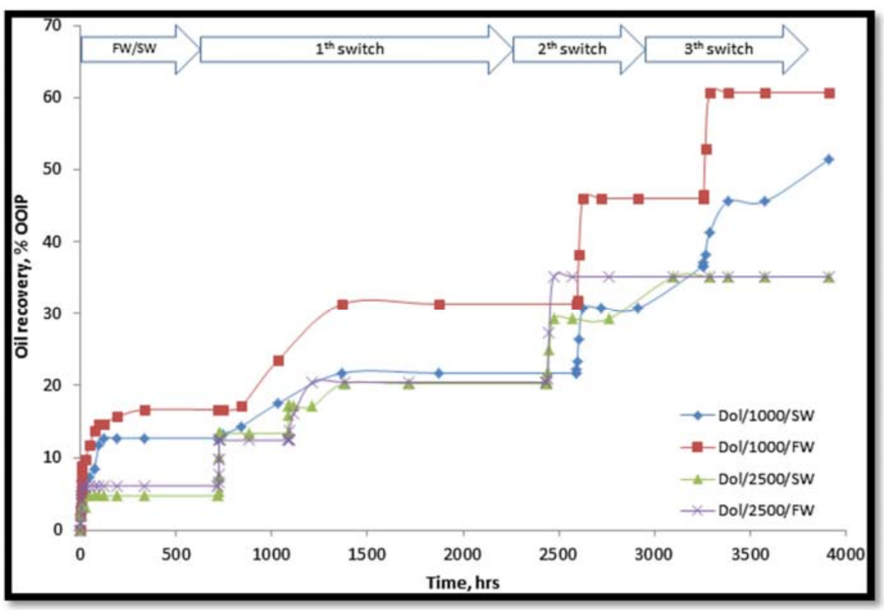

Figure 4. 6 Oil recovery in dolomite samples after switching brine concentrations

In the case of limestone, despite passing the same tests as dolomites, there was no change in the result, as shown in Figure 4.7 Ruidiaz et al., 2017 suspect that this result may be due to the difference in mineral composition between the two rocks studied.

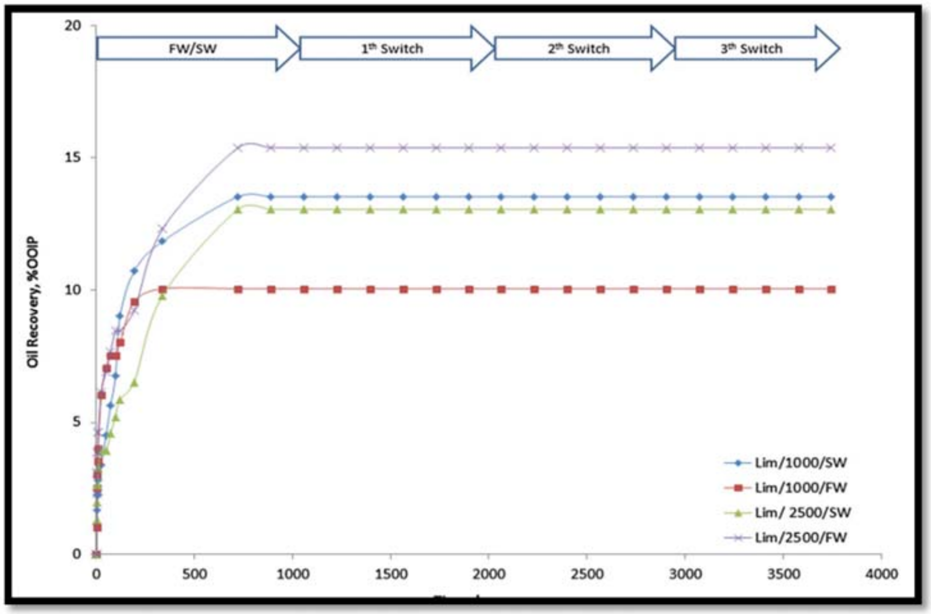

Figure 4. 7 Oil recovery in limestone samples after switching brine concentrations

iii. Wettability alteration by Amott–Harvey index (IA_H)

For Amott test a rock is defined as:

- Water wet when the Amott–Harvey index is between 0.3 and 1,
- Weakly water wet when the Amott–Harvey index is between 0 and 0.3,
- Weakly oil wet when the Amott–Harvey index is between -0.3 and 0,
- Oil wet when the Amott–Harvey index is between -1 and -0.3.

Figure 4.8 shows indexes results for limestone core at 2500h aged using SW and FW, and its corresponding brine switches(Ruidiaz et al., 2017).

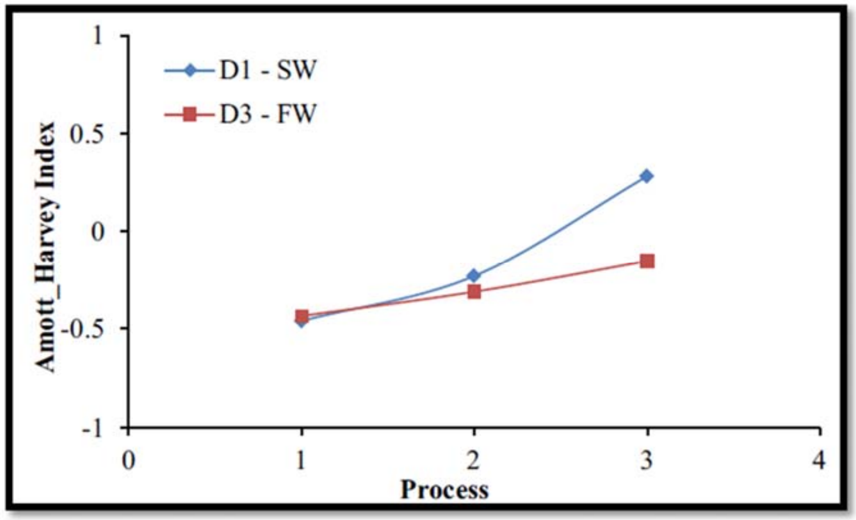

Figure 4. 8 Amott–Harvey wettability index for dolomites started with SW and FW.

Figure 4.9 shows indexes results for limestone core at 2500h aged using SW and FW, and its corresponding brine switches (Ruidiaz et al., 2017).

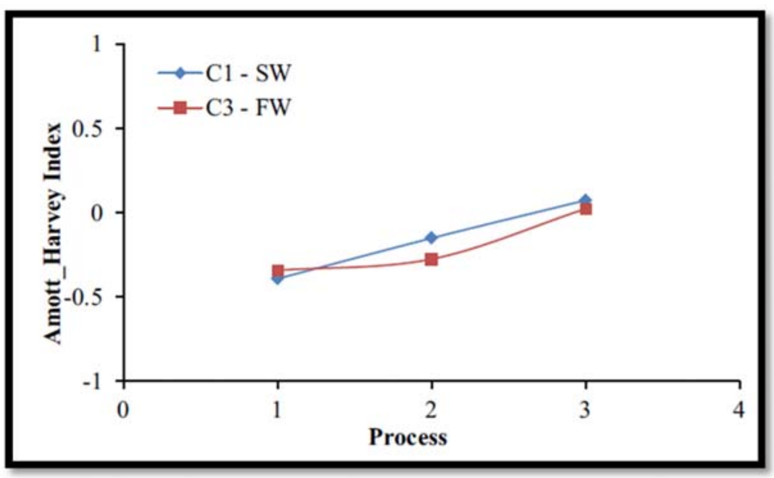

Figure 4. 9 Amott–Harvey wettability index for dolomites started with SW and FW.

When the test starts with seawater, for both types of rocks, it is possible to verify a clearer increase of the indexes if compared with when started with formation water. For both types of waters, there was an increase in the index in the direction of neutral-wetting zone and water-wetting zone (Ruidiaz et al., 2017).

4.1.3.2 Carbonated Seawater and Carbonated Formation water

i. **Analysis of Oil recovery by spontaneous imbibition**

For CSW and CFW tests, cores were aged at 2500h, temperature at 64 °C and containment pressure greater than 3,000 psi and fluid injection pressure above 2000 psi and maintaining the outlet pressure at 2000 psi (Ruidiaz et al., 2017).

Figure 4.10 figure shows the volume of oil recovered for CSW and CFW test, for limestone. For CSW Oil recovery reached 48% while CFW did not reach even 20% OOIP.

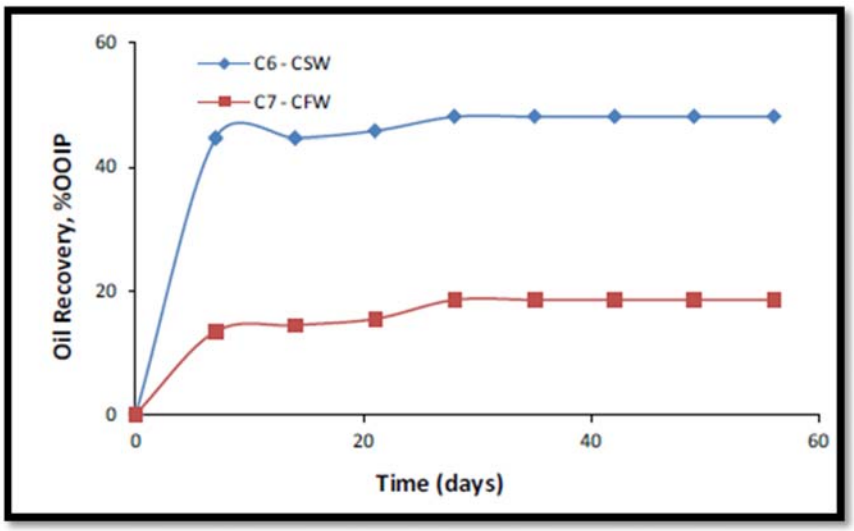

Figure 4. 10 Oil recovered from CSW AND CFW test for Limestone sample.

In figure, 4.11 can be observed the result obtained from the experiment for dolomite sample. The authors suggested that the volume of oil produced was not due to wettability alteration. The oil recovery was 20% for CFW and 25% for CSW.

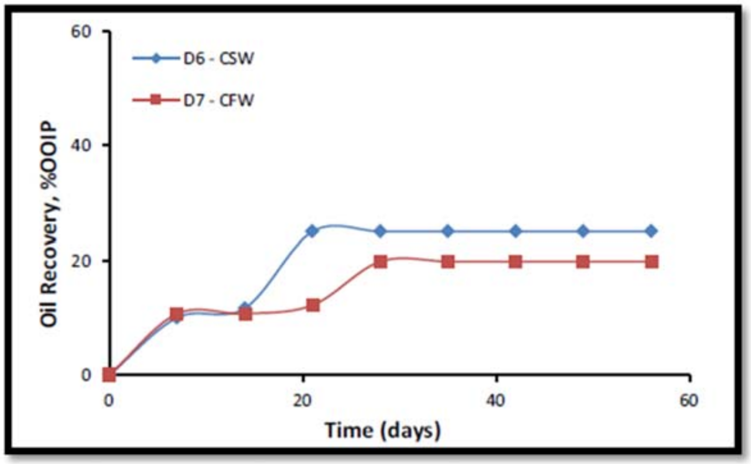

Figure 4. 11 Oil recovered from CSW AND CFW test for dolomite sample.

4.2 CASE STUDY 2

This second case study was performed by (Fathi et al, 2011) with the aim to investigated wettability alteration in carbonate reservoirs by modified seawater and its sensitivity to the ionic composition, concentration of the injected brine as well as the reservoir temperature. Although the properties of rock and fluids investigated in this study are different from those of the Brazilian pre-salt fields (case study 1), it provides a knowledgeable resource for understanding and predicting how ionic composition of fluids and temperature can influence the performance of smart water in carbonates. This knowledge can then be used to hypothesize the performance in Brazilian pre-salt fields. The main fluid and rock properties are presented below.

4.2.1 Properties of the Samples

- **Crude Oils**

The authors prepared different crude oils samples with different concentration as informed in table 4.3 that were used according to the need and purpose of the experiments. The following denotations are used to describe the oil properties: Oil A was made by diluting an acidic stabilized crude oil, base oil, with 40 vol % heptane. Oil B was prepared by adding oil A into a crude oil sample depleted in polar components (Fathi et al, 2011).

Table 4. 3 Description of Oil Properties at room temperature

oil type	density[a] (g/cm^3)	AN (mg of KOH/g)	BN (mg of KOH/g)	viscosity[a] (cP)
base oil	0.886	2.82	1.13	20.47
oil A	0.815	2.0	0.5	3.38
oil B	0.798	0.5	0.3	2.60
oil C	0.801	<0.01	<0.01	2.44

For the displacement studies at high temperatures, 100°C-120°C, the cores were saturated with oil A and aged for 8 weeks, while, for lower temperatures, 70°C-90°C, the cores were saturated with oil B and aged for 4 weeks.

- **Rock Materials**

The porous medium used gotten from outcrop Stevns Klint chalk from nearby Copenhagen, Denmark. The porosity and permeability of the chalk was in the range of ~45% and 1–2 mD, respectively. The properties of the cores are properly highlighted in table 4.4. The properties of this coccolithic material are quite similar to the North Sea chalk oil reservoirs (Fathi et al, 2011).

Table 4. 4 Core properties

core ID	Φ (%)	S_{wi} (%)	S_{oi} (%)	remarks	crude oil
SWK#1	48	10	90	SI by VB at 90 °C	cores saturated and aged with oil B (AN = 0.5 mg of KOH/g)
SWK#3	46	11	89	SI by SW0NaCl at 90 °C	
SWK#5	47	9	91	SI by SW0NaCl−4SO_4^{2-} at 90 °C	
SWK#6	46	9	91	SI by SW at 90 °C	
SWK#7	46	11	89	SI by SW0NaCl−4SO_4^{2-} at 70 °C	
SWK#8	44	11	89	SI by SW0NaCl at 70 °C	
SWK#9	44	10	90	SI by SW at 70 °C	
SK#1	46	9	91	SI by SW0NaCl at 100 °C	cores saturated and aged with oil A (AN = 2.0 mg of KOH/g)
SK#2	48	10	90	SI by SW0NaCl−4Ca^{2+} at 100 °C	
SK#3	47	10	90	SI by SW0NaCl−4SO_4^{2-} at 100 °C	
SK#4	45	10	90	SI by SW0NaCl at 120 °C	
SK#5	48	9	91	SI by SW0NaCl−4SO_4^{2-} at 120 °C	
SK#6	46	10	89	SI by SW0NaCl−4Ca^{2+} at 120 °C	
SWK#10	45			clean reference core for wettability test	

- **Brine properties**

Artificial formation water (VB) and synthetic seawater (SW) were used in the tests. Brine was displaced by Synthetic seawater. (Fathi et al, 2011 used Seawater (SW) changing the ionic composition and salinity and the following terminologies were used:

- SW0NaCl: SW depleted in NaCl
- SW0NaCl–4SO_4^{2-}: SW0NaCl with 4 x SO_4^{2-} compared to ordinary SW.
- SW0NaCl–4Ca^{2+}: SW0NaCl with 4 x Ca^{2+} compared to ordinary SW.

Table 4.5 shows the different brines composition used in the experiment.

Table 4. 5 Brine compositions (mol/L) (Fathi et al, 2011.

ions	VB (mol/L)	SW (mol/L)	SW0NaCl (mol/L)	SW0NaCl−4SO_4^{2-} (mol/L)	SW0NaCl−4Ca^{2+} (mol/L)	SW0T (mol/L)	SW1/2T (mol/L)
HCO_3^-	0.009	0.002	0.002	0.002	0.002	0.002	0.002
Cl^-	1.07	0.525	0.126	0.126	0.193	0.583	0.538
SO_4^{2-}	0.00	0.024	0.024	0.096	0.024	0.000	0.012
SCN^-	0.00	0.000	0.000	0.000	0.000	0.000	0.012
Mg^{2+}	0.008	0.045	0.045	0.045	0.045	0.045	0.045
Ca^{2+}	0.029	0.013	0.013	0.013	0.052	0.013	0.013
Na^+	1.00	0.450	0.050	0.194	0.050	0.460	0.427
K^+	0.005	0.010	0.010	0.010	0.010	0.010	0.022
Li^+	0	0.000	0.000	0.000	0.000	0.000	0.012
ionic strength	1.112	0.657	0.257	0.473	0.368	0.644	0.647
TDS (g/L)	62.80	33.39	10.01	16.79	11.43	33.39	33.39

4.2.2 Methodology

- **Spontaneous Imbibition.**

After the preparation and aging of the core samples. At specified temperatures with an interval between 70°C and 120°C and a with a back pressure of 10 bar to prevent boiling of the fluids, the test of spontaneous imbibition were executed. The produced oil was monitored and oil recovery (% OOIP) was measured against time (Fathi et al, 2011.

- **Chromatographic Wettability Test.**

During different imbibing brines Fathi et al, 2011, used the chromatographic wettability test to determine the increase in the water-wet surface area after spontaneous imbibition. The wettability index is considered as completely oil-wet for a value of 0, neutral wettability for a value of 0.5 and completely water wet for a value of 1.

4.2.3 Results and evaluations

4.2.3.1 Evaluation considering oil B

i. **Spontaneous Imbibition Using Oil B**

To perform the test the samples were aged for 4 weeks, oil B was used and the temperatures applied during the tests were 70 °C and 90 °C. Figure 4.12 shows the results of the tests performed at 70°C, fluids with different salinities and ionic compositions (Fathi et al, 2011).

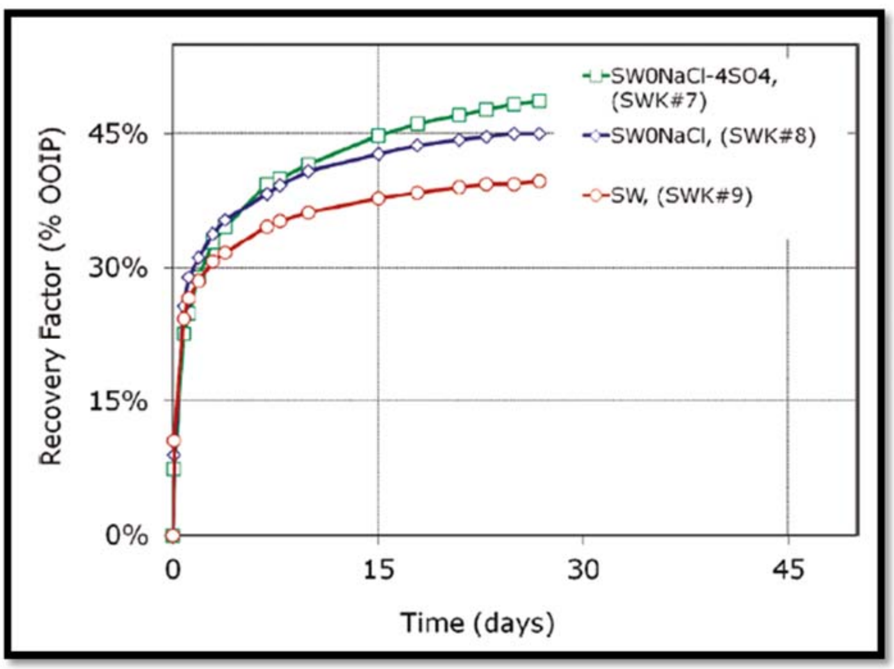

Figure 4. 12 Spontaneous imbibition into oil-saturated chalk cores using SW, SW0NaCl, and SW0NaCl-4$SO_4{}^{2-}$, Swi = 10% and AN = 0.5 mg of KOH/g.

The recovery was nearly 38, 45 and 50 % OOIP for SW, SW0NaCl, and SW0NaCl-4SO4 2-, respectively.

Figure 4.13 shows the results of the tests performed at 90°C, using formation water, seawater and modified seawater (Fathi et al, 2011).

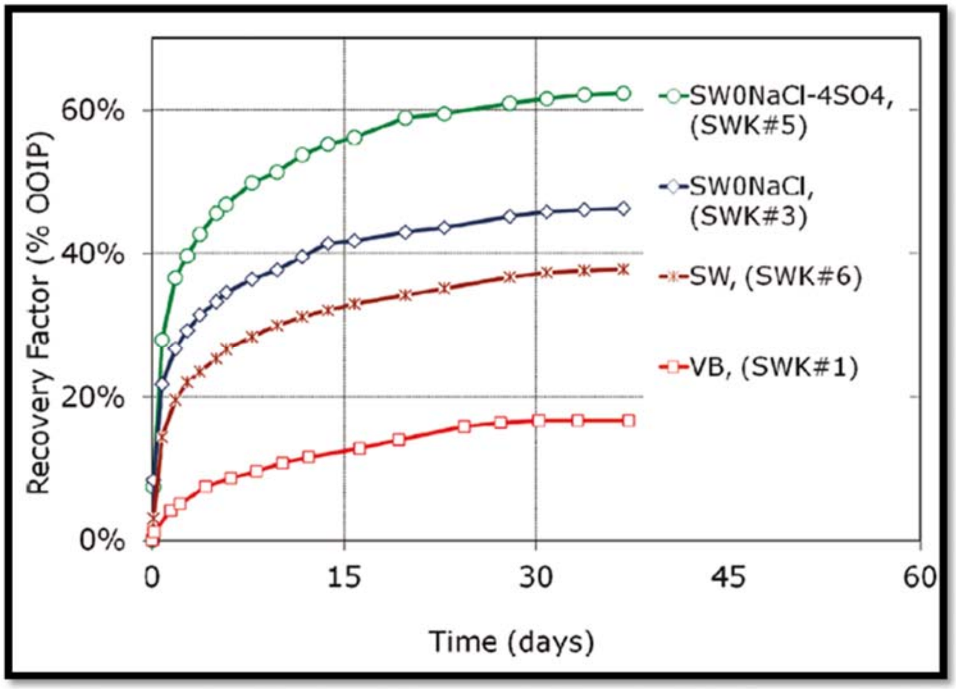

Figure 4. 13 Spontaneous imbibition into oil-saturated chalk cores using VB, SW, and modified seawater-, Swi = 10% and AN = 0.5 mg of KOH/g.

In this experiment, the results for SW, SW0NaCl and SW0NaCl-4SO_4^{2-} were 38%, 47% and 62% of OOIP, respectively.

The result for SW0NaCl-4SO_4^{2-} is a higher percentage of oil recovery if compared to SW, Fathi et al, 2011explained that the proportion of imbibition was upgraded when removing NaCl and spiking the fluid with sulfate.

ii. Chromatographic wettability test for oil B

Table 4.6 shows the test results performed after the imbibition of VB, SW and modified seawater fluids into the core at 90 °C, oil B with AN of 0.5 mg of KOH/g.

The water-wet fraction of the core after the imbibition by formation brine was calculated to be for example WI = 0.133/0.300 = 0.44 (Fathi et al, 2011).

Table 4. 6 Chromatographic Wettability results

imbibing fluid	A_{wet}	WI
VB	0.133	0.44
SW	0.155	0.52
SW0NaCl	0.67	0.56
SW0NaCl$-4SO_4^{2-}$	0.180	0.60
clean reference core	0.300	

Figure 4.14 the correlations of oil recoveries and water-wet fraction of the rock surface, as determined in table 4.6.

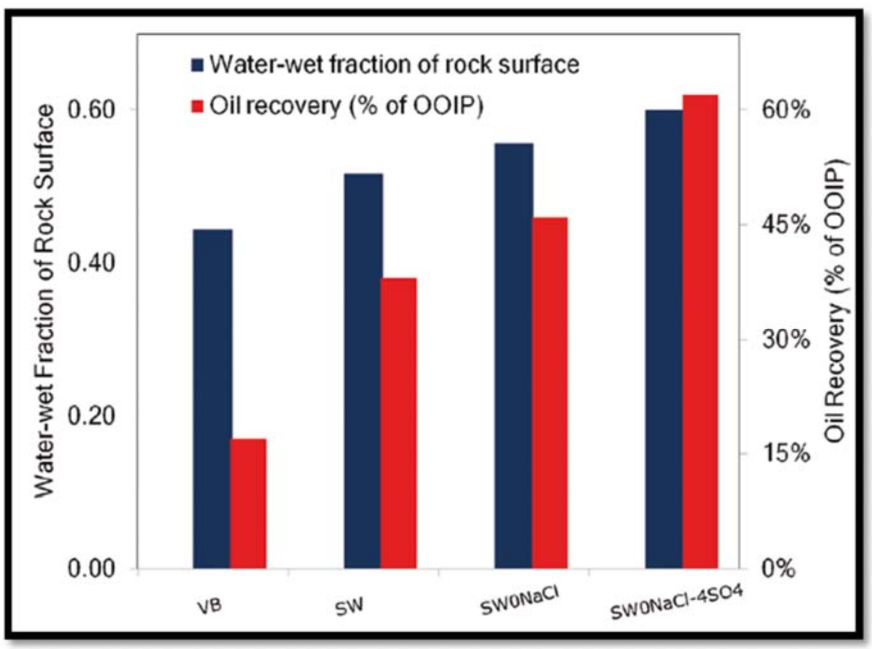

Figure 4. 14 Relationship between the oil recovery and water-wet fraction. As the water-wet fraction of the rock surface increases from 0.44 to 0.6, the oil recovery increases from 17 to 62% of OOIP

4.2.3.2 Evaluation considering oil A

➢ **Spontaneous Imbibition.**

To perform the test the samples were aged for 60 days, oil A with AN = 2.0 mg KOH/g was used and the temperatures applied during the tests were 100 °C and 120°C. Figure 4.15 shows the results of the tests performed at 100°C, fluids with different salinities and ionic compositions (Fathi et al, 2011).

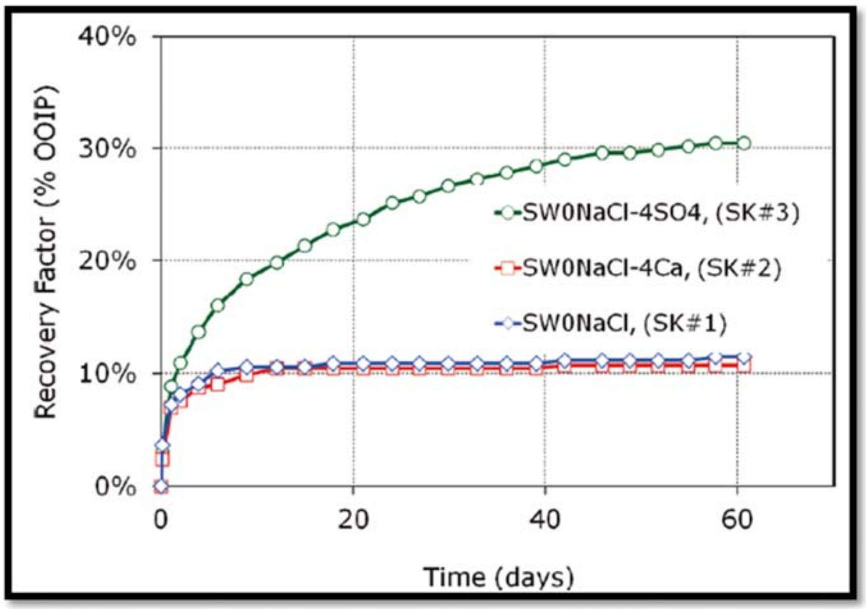

Figure 4. 15 Spontaneous imbibition into oil-saturated chalk cores C using different imbibing fluids with different salinities and ionic compositions: SW0NaCl, SW0NaCl-4SO_4^{2-}, and SW0NaCl-4Ca^{2+}. Swi = 10%, oil A, and AN = 2.0 mg of KOH/g.

The oil recovery results for spontaneous imbibition, at 100°C, showed the highest result for SW0NaCl-4SO_4^{2-} fluid and almost the same results for SW0NaCl or SW0NaCl-4Ca^{2+} fluids.

Figure 4.16 shows the results of the tests performed at 120°C, using different imbibing fluids with different salinities and ionic compositions (Fathi et al, 2011).

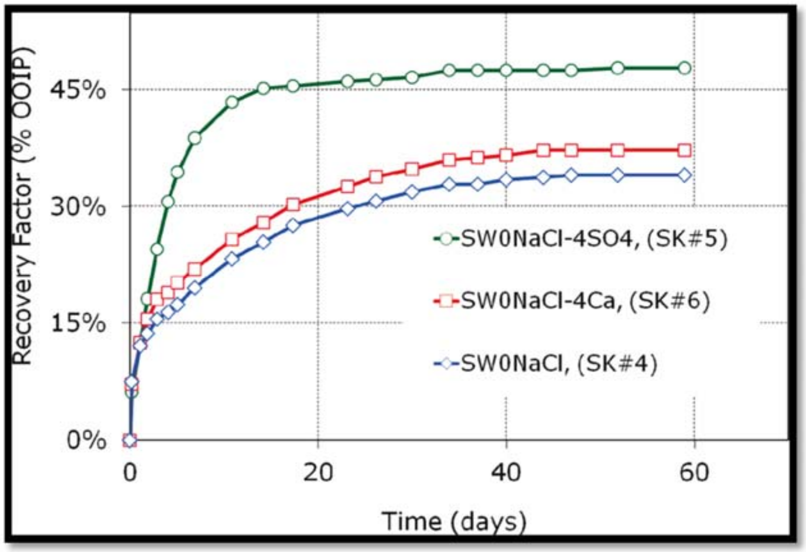

Figure 4. 16 Spontaneous imbibition into oil-saturated chalk cores at 120 °C using different imbibing fluids with different salinities and ionic compositions: SW0NaCl, SW0NaCl-4SO_4^{2-}, and SW0NaCl-4Ca2$^{+.}$ Swi = 10%, oil A, and AN = 2.0 mg of KOH/g

In this experiment at 120°C, the recovery results for SW0NaCl, SW0NaCl-4SO_4^{2-}, and SW0NaCl-4Ca^{2+} were 31%, 33% and 46% of OOIP, respectively.

Chapter 5: DISCUSSION

In the previous chapter, two study cases were presented and the effect of smart water on enhanced oil recovery was discussed. The results from both field cases suggest that Smart water can significantly alter the wettability of the Brazilian pre-salts field. In the first study case by (Ruidiaz et al. 2018), significant wettability alteration and increase in oil recovery was reported due to the injection of smart water in dolomite. Conversely, there was almost a non-perceptible change in the wettability index for limestone. This is suspected to be because of the lower reservoir temperature. Previous research by (Strand et al.2008) have reported a difficulty in observing significant EOR effects with the injection of seawater-based fluids at lower temperatures. They explain this effect because of the lower reactivity of the main ions responsible for the wettability alteration, Ca^{2+} and SO_4^{2} towards the surface of the rock at lower temperatures. Another study provides a lower limit temperature of 70°C for this process (Fathi et al, 2011). In a study carried out by Puntervold et al., (2015), it was verified that At 100 °C, the oil recovery was almost doubled when seawater was spiked with 4 times the SO_4^{2-} concentration of seawater. However, it is not advisable to spike the seawater with SO_4^{2-} at high temperatures because of anhydrite, $CaSO_4(s)$ precipitation. As the pre-salt reservoirs have the tendency of low temperatures, it can be said that the spiking sea water with increased SO_4^{2-} concentration in the injection brine could therefore compensate for lower temperature (Zhang and Austad, 2006).

In addition, results from study case two propose that ionic composition, concentration and temperature can have significant effect of the performance of SW. They reported a corresponding increase in oil recovery and water wet fraction in cores with an increase in SO_4^{2-} in the imbibing fluids. This implies that SW can further be optimized by increasing SO_4^{2-} concentration, depleting the NaCl concentration in SW. Furthermore, an increase in temperature can also enhance the performance of the modified SW, as higher oil recovery was reported at higher temperatures.

As seen throughout the process, the most suitable water for injection of Smart water into carbonate rocks is Seawater and preferably with sulfate. However, oil and gas companies are using for injection the so-called produced water, which comes along with petroleum, and which was separated and treated on the platform before being injected, with chemicals injected, together to prevent the growth and proliferation of bacteria that metabolize sulfate seawater and release H_2S. The need to use Nano filtration in the first place is to remove the sulfates and avoid inorganic deposits by reaction with the excess barium and strontium present in the wells. Removing the ions prevents the precipitations generated by the barium and strontium sulphates, highly fouling of wells and pipes, which in a first step reduces the productivity of oil and gas extraction and, in a second, can come to condemn the well or require expensive cleaning with appropriate vessels to clean pipes and other affected systems. . If gas formation occurs because of the proliferation of bacteria, the reservoir becomes acidic, causing acidification of the gas and oil, which causes them to lose value in refining (https://www.petroleoenergia.com.br/agua-de-injecao-membranas-de-nanofiltracao-removem-sulfato-da-agua-do-mar-para-melhorar-extracao-em-plataformas-offshore/5/).

Although seawater has a cheaper cost, many companies use produced water to reinject due to the high production of produced water. The reuse of such water in offshore platforms for injection operations is attractive, mainly when environmental regulations demand effective treatment of such water before releasing it to the sea.

Chapter 6: CONCLUSION

Development of the Pre-Salt holds great potential for the petroleum industry and for Brazil. However, studies in real fields related to smart water EOR still far from a good model. Existents, experiments are performed by respectable universities as such: University of Stavanger in Norway, UFRJ Rio de Janeiro and UNICAM Sao Paulo both in Brazil. With promising new projects under development in Brazil, it seems smart that oil and gas companies investing in a smart water EOR techniques.

So far, we know the main mechanisms to change wettability via smart water. As the pre salt is practically newly discovered, many analyzes still need to be identified to state whether or not the use of smart water has a great potential. Due to the oil and reservoir characteristic as well as the environmental scenario, the development of the pre- Salt Basins has challenges such as a better study or definition of pre-salt fields mineralogy, reservoir temperature are lower than expected for rocks at great depths and production of H_2S due to Sulfate injection. Also, challenge about pre-salt rocks studies to identify initial wettability.

The case studies were performed with outcropt or rocks similar to real reservoir and with systemic brines or similar to a real scenario. Thus, despite the positive results in the recovery of oil through the alteration of wettability by Smart water in the case studies, it can be said that a better study with samples of real rocks or even an experiment in a pilot well could provide a more promising result. Recalling that the injection of seawater with sulfate is not a regular practice in Brazil for several reasons, as seen in chapter 5, which implies that the current EOR process of oil recovery current in use is meeting the expectations of the operators.

Therefore, what was suggested at the beginning of the thesis was answered through the case studies. Satisfactory results were achieved with the application of smart water, even at low temperatures, being a good option for oil recovery in the pre-salt.

However, for future work related to this subject it may be expected a development related to:

- Pre-salt rock from a real field for a more elaborate study about mineralogy and properties;

- Evaluation and study of seawater injection to confirm the current problems reported in the literature for conventional oil fields;
- Improve the studies (using cores from real pre-salt oil field) related to application of smart water in rocks found in pre salt, such as coquinas;
- Experiments with temperatures greater than or less than the temperature used in the first case study (64°C);
- Comparative values related to seawater and produced water used in the injection water in offshore oil fields;
- Comparative values and check what is more advantageous if using sulfate water and have more oil production, or use water without sulfate and avoid problems related to it.

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