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A Sensitivity Study on Modified Salinity Waterflooding and Its Hybrid Processes

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A Sensitivity Study on Modified Salinity Waterflooding and Its Hybrid Processes

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Dedication

To my deeply respected uncle Abat Kadimovich, beloved parents Aigali and Mnira, my lovely daughter Rabiya, brother Azamat, sister Gulzhan, relatives, and friends who always supported me.

Менің білім шыңына деген алғашқы қадамыма демеуші болған әрі өмірлік мақсатыма жол ашқызған жездеме, Абат Қадемұлы, және оның отбасына мың да бір алғысымды білдіріп осы еңбегімді сол кісілерге арнаймын.

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Abstract

A Sensitivity Study on Modified Salinity Waterflooding and Its Hybrid Processes

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Waterflood is one of the most widely used techniques in enhanced oil recovery. In 1990s researchers came to conclusion that the chemistry of the injected water can be important in improving oil recovery. The low salinity water injection (LoSal^{®1}) has become one of the promising topics in the oil industry. It is believed that the main mechanism for incremental oil recovery in low salinity flooding is wettability alteration. Several papers discussed that the wettability alteration from oil-wet to mixed- or waterwet takes place due to clay swelling and expanding of double layer in sandstones and calcite dissolution along with rock surface reactions in carbonates. However, there is no consensus on a single main mechanism for the low salinity effect on oil recovery.

The main objective of this research is to conduct sensitivity analysis on main parameters in low salinity waterflooding and its hybrid processes affecting oil recovery in carbonates. We compare results by using coupled reservoir simulator UTCOMP-IPhreeqc. UTCOMP is the compositional reservoir simulator developed at the Center for

¹ LoSal® is the registered trademark of BP p.l.c

Petroleum and Geosystems Engineering in The University of Texas at Austin. IPhreeqc is the module-based version of the PHREEQC geochemical package, a state-of-the-art geochemical package developed by the United States Geological Survey (USGS).

We investigate the effect of low salinity water and carbon dioxide on oil recovery from carbonates by modeling the processes through the UTCOMP-IPhreeqc simulator. We perform sensitivity analysis on continuous gas injection (CGI), water-alternating-gas (WAG) flooding, and polymer-water-alternate-water (PWAG) flooding. We study the significance of reservoir parameters, such as reservoir heterogeneity (Dykstra-Parsons coefficient, V_{dp} , and crossflow, k_v/k_h), the salinity of injected water, the composition of gas, and polymer concentration in polymer-water solution on cumulative oil recovery. Moreover, we study the importance of inclusion of the hydrocarbon CO₂ impact on the aqueous-rock geochemistry by comparing two scenarios where in one scenario the hydrocarbon CO₂ effect is included in UTCOMP-IPhreeqc whereas in the other one the effect is neglected.

Finally, we perform sensitivity analysis on PWAG flooding for most influential design parameters using Design of Expert software. The reservoir parameters, such as average reservoir permeability, reservoir heterogeneity, and crossflow and injected polymer-water solution parameters, such as polymer concentration and salinity of injected water are optimization parameters in this study.

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CHAPTER 1: INTRODUCTION

1.1 Problem Statement

It is only 30 years since adjustment of geochemistry of injected water started to be taken into account as an important option for incremental oil recovery. Later on, researchers realized that geochemistry of the injected water plays an important role in different types of EOR processes. This thesis describes the effect of salinity change in the injected water on different types of EOR techniques, such as waterflooding, wateralternate-gas (WAG) flooding, and polymer-water-alternate-gas (PWAG) flooding oil recovery (EOR) processes of oil industry.

1.2 Research Objectives

The purpose of this research is to examine the effect of modified salinity waterflooding combined with other EOR processes. In accordance with several laboratory experiments and observations, it is believed that the main mechanism for additional oil recovery in low salinity waterflooding is wettability alteration. Combining waterflooding with CO₂ gives oil swelling and viscosity reduction, which leads to the reduction of mobility ratio. Addition of polymer is also responsible for reduction of the mobility ratio by increasing the viscosity of injected water; we add polymer to CO₂-WAG in order to study its effect for incremental oil recovery. We applied the integrated tool UTCOMP-IPhreeqc, The University of Texas at Austin in house 3D compositional simulator, coupled with the United States Geological Survey (USGS) geochemical package IPhreeqc, to model low-salinity waterflooding. This entails the hydrocarbon phase components (e.g., CO₂, CH₄, and acidic/basic) that create a buffering effect on the

aqueous-rock geochemistry. Tracer capabilities are also included in UTCOMP-IPhreeqc; polymer flood capability is added as an extension of the tracer option.

The objectives are as follows: first, we run a sensitivity analysis on the modified salinity effect on waterflooding. This includes simulation and numerical modeling of the low salinity effect using a synthetic 3-D model with measured reservoir rock and fluid data. The salinity of injected water is diluted two, five, and ten times.

Second, we model the combined effect of waterflooding and carbon dioxide (CO₂-WAG) in oil recovery. In order to compare CO₂-WAG flooding to Continuous Gas Injection (CGI), we also provide sensitivity analysis on CGI. Furthermore, we included polymer in water alternate gas flooding (PWAG) to study if it enhances the effect of gravity segregation reduction.

Third, we considered modified salinity effect on all above mentioned EOR processes.

Finally, Design Expert package was used for optimization. This study identifies the most significant components that affect incremental oil recovery.

1.3 BRIEF DESCRIPTION OF CHAPTERS

This thesis consists of six chapters: Chapter 1 presents the general information and the purpose of this study. Chapter 2 provides a literature review about the effect of low salinity on different types of rocks, and low-salinity related hybrid processes such as low-salinity polymer floods, low-salinity surfactant flood, low-salinity dilute surfactant flood, low-salinity water alternate gas flooding, and carbonated water flood. Chapter 3 introduces UTCOMP, The University of Texas at Austin in-house 3-D compositional simulator developed at the Center for Petroleum and Geosystems Engineering. Geochemical packages, such as IPhreeqc and EQBATCH are also introduced in this chapter. In Chapter 4, a sensitivity analysis was performed for low salinity effect on waterflooding, on water alternate gas flooding, and polymer water alternate gas floods. The sensitivity analysis was based on a 3D synthetic model with 100x100x3 gridblocks. In Chapter 5, Design of Experiment (DoE) method used to identify most influential reservoir and injected solution parameters for additional oil recovery in polymer-water-alternate-gas injection (PWAG). In addition, the response surface methodology (RSM) was used to optimize the cumulative oil recovery at field-scale where a response surface was built using different influential operational and uncertain design parameters. The final chapter describes the summary and conclusions and provides recommendations for future work.

CHAPTER 2: LITERATURE REVIEW

We review the most influential technical documents and articles regarding the injected water geochemistry effect on different types of EOR in this chapter. EOR is the implementation of different techniques to increase the absolute oil recovery from oil and gas reservoirs.

2.1 LOW-SALINITY WATER FLOODING

This section is mainly the summary in the area of low-salinity water injection. It includes the effect of low-salinity water injection on sandstone and carbonate rock reservoirs. Low-salinity waterflooding is an emerging EOR technique where the geochemistry of the injected water helps to improve oil recovery.

2.1.1 EFFECT OF LOW-SALINITY WATER INJECTION ON SANDSTONE ROCKS

In this section we review the literature related to low-salinity water flooding in sandstone reservoirs. Many mechanisms related to low-salinity have been proposed in the literature and the primary mechanisms and the conditions necessary for increasing oil recovery are still far from being understood adequately. Mechanisms that lead to improvement in oil recovery can be divided for two groups. First group includes all mechanisms that lead to wettability alteration and the second group does not involve wettability alteration. First group mechanisms discussed in oil industry are:

- Fines migration (debatable)
- Double layer expansion
- Multi-component Ionic Exchange (MIE)
- Limited release of mixed-wet particles
- Wettability alteration
- End effects

• Salinity shock

Second group where the wettability alteration is not involved proposes

- Increased pH and IFT reduction similar to alkaline flooding in-situ surfactant generation (saponification)
- Cement material dissolution
- Fines migration (debatable)
- Salt-in effect
- Osmotic pressure
- Viscosity ratio
- Particle-stabilized interfaces

These mechanisms are briefly discussed below.

Fines migration

Tang and Morrow (1999) conducted several corefloods where single clashash sandstone (CS) reservoir core was taken from the formation at a depth 2118.58 ft. CS reservoir brine was used for the entire CS core tests. During the first test the core was flooded with CS RB (Reservoir Brine) to obtain the base case where breakthrough and final recovery were 56 and 63.6% of OOIP respectively. The injection brine then changed to 10% of CS RB and production of fines was observed. The oil recovery increased linearly and additional oil recovery after 8.9 PV was 5.8%. Then, injection brine was switched to 10% CS RB-Ca (presence of calcium in the brine) where the oil flow was curtailed. Then, after re-establishing initial water saturation the sequence of floods repeated two times using the same brine. Both following tests show breakthrough and final oil recovery higher than in the first test but oil production was not linear. Fines production were observed for the first 3-5 PV of 10% CS RB flood where the amount of

fines produced decreased with each consecutive cycle. X-ray showed that effluent clay particles were mainly kaolinite. Tang and Morrow (1999) proposes fine migration (mainly kaolinite) as the primary mechanism for incremental oil recovery.

Double-layer expansion

This mechanism was first proposed by Ligthelm et al. (2009). The mechanism of double-layer expansion due to reduced salinity brine is well illustrated in Lee et al. (2010). According to their study, the reduction of salinity in injected water can provoke expansion of the diffuse layer (Figure 2.1) where divalent cations are exchanged for monovalent cations. The water layer adjacent to surface of the pore is expanded as the total ionic strength decreases, which leads to release of adsorbed oil from the clay surfaces.



Figure 2.1: Impact of salinity on Electrical Double Layer (Lee et al., 2010).

Multi-Component Ionic Exchange

Lager et al. (2008a) performed two corefloods on North Slope sandstone plugs 3" long and 1.5" in diameter. First coreflood was performed at 25°C at which oil recovery by high salinity brine, which consisted only NaCl ions, reached 42% OOIP followed by

low salinity flood; the total recovery resulted 48% OOIP, which is an additional 5% OOIP due to high salinity flooding. Second coreflood was performed at 102°C where high salinity flood gave 35% OOIP. After that the core was flushed with high salinity brine containing only NaCl until Ca^{2+} and Mg^{2+} was fully eluted from pore surface. Initial water saturation was reestablished and sample was aged in crude oil. High salinity flood was performed and oil recovery resulted 48% OOIP. It was followed subsequently by low salinity floods without and with Ca^{2+} and Mg^{2+} respectively and no additional oil was recovered in the first case and poor recovery was observed in the second one. Authors conclude that multi-component ionic exchange (MIE) is the main mechanism for additional oil recovery. Lager et al. (2008a) believed that divalent cations such as Ca^{+2} and Mg^{+2} of connate water create ionic bridges between negative oil components and negative sandstone rock surface. During low salinity water, containing lower divalent concentrations, monovalents such as Na^+ are exchanged with original divalents bridges. This is how oil components are released from the rock surface and rock surface becomes water-wet through multi-component ionic exchange.

Limited Release of Mixed-wet Particles

Buckley and Morrow (2010) performed high and low salinity corefloods on four Berea sandstones with absolute permeability on the range 60 to 500 md where all samples contain clay mixtures of kaolinite, illite, and chlorite. The crude oil was used from the Minnelusa formation and brines, high salinity corresponding to 38650 ppm of Minnelusa formation brine and 100-fold low salinity brine. Floods were imaged with a fieldemission SEM and X-ray μ -CT. Small mobilization of loosely bound particles was observed in one-phase aqueous experiments while the presence of oil increased mobilization considerably. Authors concluded that net increase in oil recovery contributed from migration of mixed-wet particles.

Wettability alteration

Berg et al. (2010) performed coreflooding in sandstone and obtained 5-15% increased recovery as demonstrated by Zhang and Morrow (2006). The majority of the experiments have been conducted with Montmorillonite clay and low salinity brine of 2 g/l NaCl. When flooding with low salinity water, some droplets are detached, which is recorded with a CDD camera. According to the experiment, 87% of the crude oil was released from the surface of the clay layer. It is evident that low salinity brine caused droplets of almost all sizes to detach from the surface. It is also reported that a substantial amount of clay swelling and de-flocculation is observed. Figure 2.2 shows snapshots of oil droplets on clay surface at the start and at the end of the experiment. Berg et al. (2010) concluded that main microscopic mechanism that brings an increase in oil recovery is the wettability modification of the clay surfaces.



Figure 2.2: Snapshots at the start and at the end of an experiment with low salinity brine (Berg et al., 2010).

<u>In-Situ Saponification</u>

McGuire et al. (2005) based on the study of Tang and Morrow (1999) low-salinity core floods on Berea sandstone, Prudhoe Bay Kuparuk Sand, Prudhoe Bay Northwest Eileen Area Ivishak Sand, Prudhoe Bay Main Field Ivishak Sand, and Endicott Kekiktuk Sand single well chemical tracer tests (SWCTT) concluded that the main mechanisms for increase in oil recovery are similar to those of alkaline flooding. They explained that the pH increase leads to the increase in oil recovery and the main mechanisms are generation of surfactants, wettability alteration, and interfacial tension (IFT) reduction.

Salt-in Effect

RezaeiDoust et al. (2009) mentioned that the solubility of organic material in water can be significantly decreased by adding salts and opposite the increase in solubility by removing salts from the solution, which is mentioned in the literature as the salt-in and salt-out effect respectively. Salt-in effect is a decrease in salinity below a critical ionic strength where divalent ions play crucial role on the solubility of organic material in the aqueous phase. It is in agreement with experimental works where low salinity effects on additional oil recovery have been observed at salinities in the range of 2000-3000ppm. Author proposed that some organic material will be desorbed from the clay surface by salt-in effect and in this way contribute to absolute oil recovery.

Increased pH and IFT reduction similar to alkaline flooding

Mohan et al. (1993) conducted corefloods on sandstone cores containing swelling and non- swelling clays where the cores were distracted from 7039ft from Stevens Sands in Elk Hills Field. Reference Berea sandstone was also observed for further comparison. High salinity water solution was switching to deionized water where after rapid reduction of salinity sharp increase in pH (up to 10.5) was observed. pH increase caused the detachment of kaolinites from the pore surface, migration and blocking the pore throats and reducing the permeability.

Osmotic pressure

Sandengen and Arntzen (2013) proposed osmosis as the underlying mechanism where oil acts as a semipermeable membrane that transports water, but not ions. In their experiment two oil droplets were placed into the glass tubes (5-10cm long and 1mm inner diameter), such that they separated high salinity water (5M NaCl) from a low salinity(distilled) water. Reference tubes also prepared where distilled water have been placed between oil droplets (no osmotic gradient). After 12 days of observance, oil droplets moved away from each other with saline water between oil droplets while in reference tube where distilled water was between oil droplets movement of droplets wasn't observed.

Low-Salinity Waterflooding at Lab Scales

Increase in recovery of crude oil with decrease in salinity has been observed for numerous laboratory waterfloods. All of these experiments confirm that waterflood performance is highly dependent on salinity of injected water. Some of these reports are discussed:

Tang and Morrow (1997) conducted imbibition and waterflood tests on Berea sandstone to see the effect of salinity, temperature and oil composition on oil recovery. The core permeabilities ranged from 487 to 614 md and the porosities were close to 23%. Three different types of crude oil and synthetic brine were used in this study. Laboratory experiments show that water wetness and oil recovery by waterflooding and spontaneous imbibition increase with decreasing the salinity of injected brine. They also pointed out

that the increase in temperature during the process of flooding can lead to wettability alteration towards water wetness. Figure 2.3 depicts the oil recovery from both processes.



Figure 2.3: Oil recovery during spontaneous imbibition and waterflooding (Tang and Morrow, 1997).

Alotaibi et al. (2010) performed coreflood and contact angle experiments on Berea sandstone outcrop rocks. Scioto samples with permeability 0.01 to 0.1 md from Ohio outcrop rock used only for contact angle measurements. The porosity and permeability of Berea sandstone ranges 18-20% volumetric and 144 to 198 md, respectively. Formation brine, seawater, and aquifer water with wide ranges of salinity was used in the experiments. ZetaPALS (Phase Analysis Light Scattering) and Drop Shape analysis System (DSA) was used to measure contact angle, interfacial tension, and zeta potential for brines-clays-rock systems. Based on 4 coreflood tests authors concluded that salinity of injected water played a significant role on secondary and tertiary recovery at raised temperatures and that higher concentration of Mg in effluent is a prove of cation exchange between clays in the rock and brines. Authors summarized that the rock mineralogy plays key role in determining low salinity effect on contact angle.

Pu et al. (2010) conducted corefloods and spontaneous imbibitions tests on the anhydrite and dolomite rich cores from oil and water zones of Tensleep (T), Minnelusa (M) sandstone, and Phosphoria (P) dolomite formations. Filtered crude oil from T, M, P were used and brines were prepared from distilled water. Effluent analysis of all tests showed increased production of sulfates. Additional oil recovery by low salinity flooding was observed in corefloods on Tensleep cores recovered from oil zones while no reduction of residual oil saturation was observed in corefloods on cores from Tensleep water zone. Imbibition tests showed weakly to strongly wet conditions of the cores. The difference in behavior where improved oil recovery by low salinity flooding achieved is explained by authors as the shift from weakly to water wet condition due to anhydrate dissolution and release of dolomite crystals. For Minnelusa reservoir core the increase is ascribed to release of fines and partial blocking of pore throats. For Phosphoria dolomite reservoir core switch to injection of diluted reservoir brine resulted in increase in oil recovery. Rise of sulfate content in effluent prove the anhydrite dissolution.

Rivet et al. (2010) performed coreflooding to study effect of low salinity waterflooding on oil recovery, residual oil saturation, and relative permeability. Several outcrop Berea and oil reservoir cores were used for parallel and serial watefloods. Three types of crudes and nine brines with different ion concentration were used as the injection and in-situ fluids. The results of the experiment indicate that the improvement in oil recovery due to low salinity flooding is a result of wettability alteration from mixed-wet to water-wet condition. Authors indicated that low salinity brine improve ultimate oil

recovery only in mixed-wet systems. One of the corefloods with low-salinity brine where the sample was the most water-wet due to low clay content has no effect on additional oil recovery. None of the tertiary low-salinity floods gave additional oil recovery over secondary low-salinity flood.

Nasralla et al. (2011) pointed out that water chemistry plays a significant role in oil recovery. It was mentioned that the exchange of certain cations is the primary reason for higher oil recovery. In their study, they performed several corefloods on Berea sandstone at temperature 212 °F with two different types of crude oils. Solutions of NaCl, CaCl₂ and MgCl₂ of different concentrations were injected to test the effect of cation type, and cation concentration on oil recovery. Based on their experiments, they concluded that injecting CaCl₂ suppressed the oil recovery, while NaCl and MgCl₂ are beneficial for improving oil recovery. Figure 2.4 shows the comparison of oil recovery of different solutions at 5 wt%.



Figure 2.4: Comparison of oil recovery for experiments with different injected solutions (Nasralla et al., 2011).

Robbana et al. (2012) performed floods on cores from Main Field and Ridge Areas where the temperature and pressure carried out as in reservoir conditions. For the secondary recovery the samples were flooded with low salinity brine (1500ppm) at 4cc/hour. Authors reported additional oil recovery in both cases: secondary recovery from Main Field Area core (25md) was 9% whereas secondary recovery from Ridge Area core (100md) consisted 13.1% over high salinity coreflood.

Winoto et al. (2012) conducted corefloods on 17 sandstone and 6 carbonate outcrop samples to see the low-salinity effect in tertiary mode. The cores initially were saturated with seawater and pressurized up to 1000 psi to saturate the core. The initial water saturation was established by injection of crude oil at ambient temperature or 60°C for low permeability cores. Then, the cores were aged in crude oil for 30 days at 60°C to establish initial oil saturation. The cores were injected with seawater for the first 10PV followed by low salinity flood. After restoration the cores were flooded with 20 times diluted seawater for tertiary mode. Reduction in residual oil saturation in tertiary mode for 17 sandstone outcrops varied from 0 to 6% and the average oil recovery for low salinity effect at residual oil saturation was much lower than that is observed in reservoir rock and oil recovery from carbonates (6 outcrops and 8 reservoir cores) showed sufficient oil recovery in tertiary modes.

Fjelde et al. (2013) conducted coreflooding at 80°C using rock and stock tank oil from sandstone oil reservoir in North Sea. The experiments were performed on cores with clay content 13% of the bulk volume. The injected water was synthetic formation water (FW), 100-times FW diluted water (LSW1), 1000-times FW diluted water (LSW2), and only KCl present in water (LSW3). Experiments consisted of 4 corefloods:

- a) 10 PV of FW followed by 10PV of SW followed by 10PV of LSW1, and followed by 10PV of LSW2 were injected
- b) 4 steps of 10 PV of LSW2 flooded with 1 week aging after each flooding step
- c) 42 PV of LSW2 were injected
- d) 18 PV followed by 8 PV at higher rate LSW3 were injected.

Analysis of effluent and cation concentration shows the increase of pH in all 4 experiments which authors attribute to calcite dissolution of the rock. Authors pointed out that the reduction of divalent cations to the clay surfaces are important criteria for LSWF and lower brine salinity is not necessary lead to additional oil recovery

Shehata et al. (2014) conducted eight two-phase coreflood experiments using Grey Berea, Buff Berea, Bandera, and Parker sandstone cores to determine the effect of the clay content on low-salinity flooding on secondary and tertiary recovery modes. The experiments performed at 185°F, back flow pressure of 500 psi, and overburden pressure of 1800 psi. One of the Buff Berea cores were flooded with low-salinity brine (5000ppm) with different injection rate 0.5, 1, and 2ml/min. The final oil recovery was 60.91% OOIP where 53.29% was occurred after 7.71PV at 0.5ml/min. For the second Buff Berea coreflood formation water injection resulted in 44.7% OOIP oil recovery and low-salinity flood in secondary and tertiary modes did not give additional oil recovery. Both experiments on Grey Berea Sandstones showed similar behavior as the Buff Berea sandstones and additional oil recovery during low-salinity flood was about 13.32% OOIP over conventional flooding. Corefloods on Bandera sandstone cores with highest clay content revealed the highest oil recovery for low-salinity flooding and consists 10% for tertiary mode. Parker Sandstone corefloods show no response for low-salinity flood. Overall for all corefloods oil recovery from conventional waterfloods ranged from 24.6 to 44.7% OOIP. The additional oil recovery due to low-salinity flood in secondary mode ranged from 4-17% OOIP. None of three sandstone rocks showed response except Bandera sandstone rock (6.9% OOIP) in tertiary mode. Authors didn't find direct relation between oil recovery and clay content in the rocks.

Suijkerbuijk et al. (2014) conducted corefloods and imbibitions tests on 13 coreplugs from West Salym oil field with porosity and permeability in range of 18.6 to19.4% and 18 to 34.5 md, respectively. The crude oil and formation and 8 times dilutions of formation water from West Salym oil field was used in the experiments. The cores were initially flooded with injection rate 0.03cc/min by switching to 0.15cc/min and 1cc/min after oil production ceased. All corefloods demonstrated a positive effect from low-salinity floods. Author assigned the accelerated oil production to change of relative permeabilities and reduction of residual oil saturation. According to authors, no

increase in pressure drop across the cores during corefloods indicates that formation damage not occurred.

Low-Salinity Waterflooding at Field Scales

Increase in absolute oil recovery with decreasing the salinity is also reported in successful field applications.

Webb et al. (2004) conducted log-inject-log field test to identify if the additional oil recovery due to wettability change in low-salinity corefloods at laboratory scale can be observed in the reservoir environment. A production well was chosen carefully and the interval where the test was performed was the major producing interval in a giant clastic reservoir with the thickness around 150 ft. Porosity and the permeability of the reservoir vary 20-30% and 200-700 mD, respectively. Average water saturation is 23% and the average salinity of the connate water is 250,000 ppm. In order to measure residual oil saturation three different types of the brines with salinity 220,000, 120,000, and 3,000 ppm were prepared. The test was performed over 4 days and included PLT/PNC logs, injection of high-, intermediate-, and low salinity brines. The test results show significant reduction of oil saturation due to low salinity flooding; however it varies from top perforated interval (50% reduction) to middle and bottom intervals (10-20% reduction) in remaining oil. Author concluded that the results previously demonstrated at laboratory scale can be applicable to near well bore zone.

McGuire et al. (2005) performed four sets of single well chemical tracer tests (SWCTT) in sandstone reservoir in Alaska. The purpose of the test was to extensively evaluate the effect of EOR processes at field scale. The results of the test showed that low salinity water-flooding can successfully be applied at field scale. The incremental oil recovery due to low-salinity flooding ranged from 6 to 12% OOIP As discussed

previously, authors pointed out that the main mechanisms for additional oil recovery are similar to alkaline flooding: generation of surfactants, reduction in IFT, and wettability alteration.

Lager et al. (2008b) reported reduction of residual oil saturation for 10 saturation units from 0.30 to 0.20 when high salinity water (16,640 ppm of total dissolved solids TDS) was changed to a low salinity brine (2,600 ppm of TDS) in single well tracer test that was performed in an Alaskan reservoir. Authors indicate that the production rate was doubled for 12 months of production and water-oil ratio (WOR) decreased. Authors pointed out that those phenomena, such as clay swelling or fine migration, hadn't been detected. The effluent analysis of magnesium ion showed that the main mechanism responsible for additional oil recovery is the multi-component ionic exchange.

Seccombe et al. (2010) demonstrated comprehensive inter-well field trial of lowsalinity EOR in Endicott Field (Alaska). Field trial was designed to evaluate whether mixing or other mechanisms prevent additional oil recovery and whether the adverse mobility ratio between injected water and oil bank causes viscous fingering. They reported that pilot test of additional oil recovery is in good agreement with corefloods. This inter-well test consists of one injector and one producer with 1040 feet apart from each other. The incremental oil recovery from pilot was 10% of the total pore volume swept and was in good agreement with coreflood. The pilot test demonstrated that the low salinity waterflooding works equally at inter-well distances as it does in corefloods and single well tests.

Vledder et al. (2010) conducted extensive observation in the Omar field located in Syria. The analysis contained spontaneous imbibitions tests, SCAL, NMR, and single well Log-Inject-Log test in analogous field. The Omar field is evenly splited between marine Lower Rutbah and coastal Mulussa formations. The viscosity of the oil is 0.3 cp and formation water salinity is around 90000mg/l with 5000 mg/l bivalent cations. The rock contain 0.5-4% of clays -95-100% of which are kaolinites. The field was discovered in 1987 and after reservoir pressure during production declined rapidly the wells were closed. In January 1991 in order to revive the production water injection was implemented where the only source was the water from Euphrates River with salinity 500mg/l and bivalent cations less than 100mg/l. A total of 21 observations showed the wettability change with shift in wettability index from 0.8-1.0 to 0.05-0.45. The final incremental oil recovery due to low-salinity flooding of the Omar Field was 10-15% of the STOOIP and the main mechanism was the wettability change to more water-wet.

2.1.2 EFFECT OF LOW SALINITY WATER INJECTION ON CARBONATE ROCKS

There are different types of carbonate rocks, such as limestone, dolomite and chalk, which have different characteristics. Due to the absence or very little clay content in carbonates, low salinity flooding in carbonate rock may not behave in the same way as in sandstones. Due to complexity and digenetic variety of carbonate rocks, understanding of main mechanisms in modified salinity flooding in carbonate rock is not as mature as in sandstone.

Several mechanisms have been proposed to be the primary means for improving oil recovery via low-salinity waterflood in carbonate rocks.

- 1. Rock Dissolution
- 2. Surface Ion Exchange
- 3. In-situ Surfactant Formation (needs a high pH)

Some of the proposed mechanisms are explained below.

<u>Rock Dissolution</u>

Hiorth et al. (2010) used a chemical model that couples bulk solution and surface chemistry to analyze the behavior of a solid surface of carbonate. All the experiments were summarized used Stevns Klint outcrop chalk (mainly calcite carbonate) from Denmark with porosity 45-50% and permeability 2-5 mD. The analysis show that the dissolution of calcite could increase water wetness and the amount of calcite dissolved appears sufficient to incremental oil recovery, especially if to take into account that the calcite is preferentially dissolved where the oil wets the calcite. Based on the preliminary analysis author concluded that mineral dissolution is the main controlling factor responsible for incremental oil recovery. Figure 2.5 shows the schematic model for wettability alteration due to calcite dissolution.



a) A section of the pore space before any dissolution reaction



b) The dissolution of the chalk surface and new water-wet surface has been created
Figure 2.5: Schematic model for wettability alteration: a) before calcite dissolution, b)
after calcite dissolution (Hiorth et al., 2010).
Surface Ion Exchange

Zhang et al. (2007) investigated the effect of divalent cations Ca^{2+} and Mg^{2+} in the presence of SO_4^{2-} on wettability alteration; consequently on improved oil recovery. They performed several imbibition tests on chalk cores where they changed the mole fractions of ions Ca^{2+} , Mg^{2+} , and SO_4^{2-} ions at the temperatures in the range of 40-130°C in the injected brine. For instance, one of the imbibition tests was performed at 70°C. First, oil recovery was 10% when seawater was injected without Ca²⁺ and Mg²⁺ ions but with concentration of SO_4^{2-} ranging from 0 to 4 times higher than in seawater. Then the temperature was raised to 100°C but only a small increase in oil recovery was detected due to fluid expansion. When Ca²⁺(0.013mol/l) and Mg²⁺(0.045mol/l) were added to respective imbibing fluids, the increase in oil recovery was noticed and it was strongly related to SO_4^{2-} content in the fluid. Based on the experiments, the following conclusions were made: Improvement in oil recovery can be obtained in moderate water-wet chalk when Ca^{2+} and Mg^{2+} cations are present in injected water and only in the presence of SO4²⁻. Authors proposed a chemical mechanism for wettability alteration from oil or mixed-wet to more water-wet: as the sulfate adsorbs to the positive chalk surface it reduces the positive charge of the surface and the calcium ion by getting close enough to the surface reacts with the carboxylic groups adsorbed to the surface and liberates them from the surface. At higher temperatures, Mg^{2+} can substitute Ca^{2+} from the rock surface which is also will lead to wettability alteration and incremental oil recovery. Mechanism for wettability alteration and release of carboxylic material from the rock surface are shown in Figure 2.6.



Figure 2.6: Schematic model for wettability alteration (Zhang et al., 2007).

Low-Salinity Waterflooding at Lab Scales

Increase in recovery of crude oil with decrease in salinity has been observed for numerous laboratory waterfloods. Most of these experiments confirm that waterflood performance is highly dependent on salinity of injected water. Some of these reports are discussed:

Hognesen et al. (2005) performed spontaneous imbibitions test on oil-wet carbonate rocks. Two different types of oil and three types of brine (seawater, seawater without sulfates, and seawater with 3 times the sulfate concentration) were used in this study. Outcrop Chalk from Stevns Klint and two limestone cores from Middle East were used in this study. The results of the test show that the oil recovery by spontaneous

imbibitions of oil-wet carbonate cores increases as the concentration of sulfates in injected water and the temperature increases.

Gupta et al. (2011) conducted corefloods on sandstone and dolomite cores from Middle East and West Texas reservoirs respectively where limestone cores consisted of 99% calcite while dolomite cores were 82% dolomitized. Oil from Middle Eastern reservoir was used in all experiments. Different types of synthetic brine with omitting or increasing different types of ions were used in the experiment. The typical injection rate during corefloods was kept 0.1cc/min, which is about 1-2 ft/day displacement rate. The sequence of floods was as follows: after injection of formation brine, the base brine was switched to modified brine. Figure 2.7 shows incremental oil recovery 5-9% OOIP was obtained when seawater contained sulfate ions was followed after formation water injection. Incremental oil recovery 7-9% OOIP were obtained when reduced hardness seawater was followed after formation water injection. Authors concluded the potential to significantly increase oil recovery compared to waterflood using formation water by addition of certain salts and softening the water.



Figure 2.7: Oil recovery and pressure drop for core D2 (Gupta et al., 2011).

Yousef et al. (2011) in their laboratory experiments show that altering the salinity and the ionic content of the injection water has significant impact on the wettability alteration of the carbonate rock surface. It is pointed out that the key mechanism for substantial oil recovery is the wettability alteration. Authors provided several laboratory experiments on the cores of one of Saudi Arabian carbonate reservoirs. Various diluted slugs of regular seawater have been used as the injection water and the additional oil recovery has been recovered. Twice diluted seawater gave additional 7- 8.5% oil recovery(TDS 28,835 ppm), 9-10% oil recovery with ten times diluted seawater, and 1-6% with twenty times diluted seawater. Figure 2.8 shows the cumulative oil recovery obtained with the wide range of diluted seawater injected.



Figure 2.8: Oil Recovery Curve from carbonate coreflooding. (Yousef et al., 2011).

Laboratory experiments were provided with interfacial tension, contact angle, and NMR measurements. The interfacial measurements show the trend of increasing oil/water IFT with reducing salinity of injected water. The contact angle measurements show the tendency of the rock to be more water-wet state with the reduction of salinity of injected water. NMR measurements show the alteration of charges of the surface of the rock leading to more interactions with water molecules. Results of the experiments show that a substantial oil recovery in carbonate cores was attained due to wettability alteration, as was indicated by NMR and contact angle measurements.

Romanuka et al. (2012) proposed two mechanisms for additional oil recovery from coreflooding experiments. Two approaches, such as increasing concentration of sulfates (SO₄), borates (BO₃), and phosphates (PO₄) in the injection brine and lowering total ionic strength, are considered for the wettability modification of carbonate rocks. Several spontaneous imbibition experiments have been performed on different types of carbonate cores. Formation brine injection was followed by low salinity coreflooding. 5-10% of additional oil recoveries have been observed when the low salinity brine with hiked (19-99 mM) sulfate concentration was injected subsequently after formation water. Also, an increase in oil recovery from 3-4 % to 8.7-14.5% had been observed when the temperature was raised from 70°C to 120°C in low salinity coreflooding of limestone cores. The range of recoveries 5-18% OOIP in dolomite cores during low salinity flooding is explained by different contents of anhydrites in the cores.

Al-Attar et al. (2013a; 2013b) conducted corefloodings on the carbonate samples from Bu Hasa field. The objective of this job was to study the effects of salinity and ion composition of the injected brine on rock/brine/oil systems to identify the mechanisms contributed for incremental oil recovery. Sea water, field injector waters with salinity 197,584 ppm and 224,987 ppm and dilutions of 5000 and 1000 ppm were used in the experiments. Contact angle and interfacial tension measurements were performed during the floods. Results of the test show 21.5% OOIP the additional oil recovery due to low salinity flood when high-salinity brine flood (197,362 ppm) was switched to low-salinity (5000 ppm) and final recovery was 84.5% of OOIP. Authors indicated that sulfate concentration play a crucial role on the flooding process such that increase of the sulfate concentration beyond 47 ppm has negative effect for flooding process. The wettability alteration as the main mechanism for improved oil recovery due to low-salinity flooding was proposed by the authors.

Alameri et al. (2014) performed seawater floods in carbonate cores followed by low salinity flooding. They reported 8 % incremental oil recovery when NaCl was removed from seawater in a relatively homogeneous core in one of the corefloods. However, in one of the sets, no incremental oil recovery was obtained due to vugdomination in the core. The ionic effluent concentrations showed decrease in Ca, Mg, Cl, and SO₄ in one of the sets. Authors assigned the electrical double layer (EDL) as the contributor for incremental oil recovery. One of the sets resulted in 6 and 1.1%incremental oil recovery, respectively when seawater was sequentially diluted for two and four times. They measured interfacial tension and contact angle and reported increasing of oil/brine IFT and changing of wettability for more water-wetness with lowering of the salinity of the brine.

Mahani et al. (2015) investigated the different wettability alteration mechanisms, such as calcite dissolution and surface charge change. In this study, limestone material originating from Middle-Eastern carbonate reservoir and Silurian dolomite were used for experiments. The carbonate patches with oil droplets were placed in glass windowed cell, where it was exposed to brines of different salinity (formation brine, sea water, 25 times diluted sea water, and 25 times diluted seawater equilibrated with sandstone particles). Zeta-potential, IFT, and contact angle were measured during the experiments. Based on their experiments, authors conclude that the wettability alteration become more water-wet state even with absence of calcite dissolution. Change in contact angle was consistent with zeta-potential measurements. Authors proposed the surface-charge-change as the primary mechanism for wettability alteration and consequently for additional oil recovery.

2.1.3 EFFECT OF INJECTION WATER CHEMISTRY ON HYBRID LOW-SALINITY IOR/EOR PROCESSES

Injection water chemistry plays an important role in several major enhanced oil recovery processes. These EOR processes include polymer flooding (PF), alkaline-surfactant-polymer flooding (ASP), surfactant flooding (SF), dilute-surfactant flooding for carbonates (DSF), miscible CO₂ water-alternating-gas flooding (WAG), and carbonated waterflooding. Figure 2.9 summarizes the importance of injection-water chemistry in different IOR/EOR processes.



Figure 2.9: Summary of injection-water chemistry in different EOR/IOR processes. (Ayirala et al., 2015).

2.1.3.1 LOW-SALINITY POLYMER FLOODING

Polymer flooding is a mature enhanced oil recovery process where the main driving mechanism is the use of viscosified water to achieve suitable mobility control. Optimized mobility control gives better microscopic sweep efficiency and mobilizes oil from previously unswept zones which are benefited for additional oil recovery. Hydrolyzed polyacrylamides (HPAM) is a commercial polymer widely used in oil industry; most of commercial successes in polymer flooding at field-scale are related to HPAM. Another type of polymers, which is not as popular as HPAM, is xanthan gum. Xanthan gums are biopolymers and the main disadvantage of xanthan is its proneness to bacterial degradation too quickly, bringing to lose the mobility control (Bragg et al., 1983).

Polyacrylamides are synthetic polymers that are anionic in nature, induced by negatively charged carboxylic groups in polymer chain. As a result, polyacrylamides are sensitive to salt ions present in the injection water because positively charged cation in the water bind tightly to negatively charged carboxylic acid groups in the polymer chain to render a "coiled state" for polymer molecules and, consequently to weaken their viscosifying characteristics. On the other hand, in low salinity water, there will be a strong repulsion between charges in the polymer chain, and, as a result, polymer molecules are in "swelled or elongated state" to yield higher viscosities for the same polymer concentration. Figure 2.10 indicates the effect of NaCl concentration on polymer viscosity. It is seen that a decrease in salinity, results in a significant increase in polymer viscosity.



Figure 2.10: Effect of salinity on HPAM (Koh et al., 2015).

Mohammadi and Jerauld (2012) provided mechanistic modeling to show the benefits of combining polymer with low salinity water. The summary of the case studies shows that only one third of the polymer is required with low salinity water compared to high salinity brine. At high oil viscosities, combined low salinity water with polymer gives the same incremental oil recovery as the sum of each technique individually. A 5-times reduction in chemical cost per barrel of oil recovered can be expected.

Even if there is no additional oil recovery using low-salinity make-up brine for polymer flooding, the project economics could improve due to the fact that the required polymer decreases by factor of two or four (Vermolen et al., 2014).

Kozaki (2012) set up laboratory experiments at The University of Texas at Austin and performed low salinity polymer coreflooding in tertiary mode on a Berea sandstone. The core was flooded with oil, aged for 30 days at 90°C, oil flood repeated, then core was flooded in secondary mode with 4.5 PV high salinity water, finally 4.6 PV of low salinity polymer was injected in tertiary mode. Incremental 8% of oil recovery and reduction of S_{or} by 6.7% were reported to be due to low salinity polymer flooding. Figure 2.11 shows oil recovery, oil cut, and average oil saturation.



Figure 2.11. High Salinity Water followed by Low Salinity Polymer Flood Oil Recovery (Kozaki, 2012).

2.1.3.2 COMBINED LOW-SALINITY WITH MISCIBLE CARBON DIOXIDE WATER-ALTERNATE-GAS FLOODING

Water-alternate-gas flooding is another technique, which isolates one of the disadvantages in continuous gas injection (CGI), such as gravity segregation between injected gas and reservoir. The main idea of miscible carbon dioxide water-alternate-gas flooding is improving gas flooding performance by controlling the gas mobility (Dang et al., 2014; Jiang et al., 2010). It is believed that three main mechanisms that contribute to additional oil recovery in CO_2 -WAG are zero gas/oil interfacial tension, oil-viscosity

reduction, and increased oil swelling. However, oil recovery in CO_2 -WAG flooding is affected by several factors, such as rock wettability, reservoir heterogeneity, and fluid properties (Jiang et al., 2010).

Particularly, Kulkarni and Rao (2005) conducted miscible CO_2 -WAG coreflooding in Berea sandstone. A 12% reduction in oil recovery was reported when the salinity of injected water in CO₂-WAG flooding was decreased. Reduction in oil recovery was explained by higher solubility of CO_2 in multivalent than in monovalent brines.

Jiang et al. (2010) performed corefloods in Berea sandstone in order to see the effect of salinity of the injection brine in Berea sandstone on CO₂-WAG performance. The corefloods were conducted at 60°C, miscible condition, and 20% above the minimum miscible pressure (MMP). Waterflood with different salinities was injected in secondary mode followed by CO₂-WAG in tertiary mode. Decrease in oil recovery with increasing injected brine salinity in waterflooding in secondary mode and slight increase in oil recovery with increase in oil recovery with increase in oil recovery mode have been reported.

Zolfaghari et al. (2013) conducted several high and low salinity CO₂-WAG corefloods in Berea sandstone. A 92% of ultimate oil recovery was reached when low salinity brine was used, which is up to 18% more than CO₂-WAG flooding based on high salinity brine. Figure 2.12 compares oil recoveries of CO₂-WAG floods with low and high salinity brines.



Figure 2.12: Effect of reduced salinity on oil recovery (Zolfaghari et al., 2013).

Dang et al. (2014) performed simulation study at field-scale (sandstone reservoir), where CO₂-WAG floods with low salinity brine showed 4.5-9% more incremental oil recovery than CO₂-WAG with high salinity. Authors mention that the success of low salinity CO₂-WAG flooding depends on different criteria; such as type and quantity of clay in reservoir, initial reservoir wettability condition, reservoir heterogeneity, mineralogy of the reservoir, composition of formation water and injection brine, reservoir pressure and temperature, and WAG parameters.

2.1.3.3 COMBINING LOW-SALINITY AND CARBONATED WATERFLOODING

In carbonated waterflooding, CO_2 is fully saturated in injection brine and this mixture CO_2 dissolved in water is injected from the surface into reservoir. At reservoir temperature and pressure, CO_2 diffuses from water into reservoir oil due to its solubility,

which is 3-7 times higher (Dong et al., 2011). The main mechanism for improved oil recovery in carbonated waterflooding is suitable mobility ratio due to oil viscosity reduction and swelling. It is reported that carbonated water flooding also reduces water oil interfacial tension (Yang et al., 2005). Two main advantages of carbonated waterflooding over conventional CO_2 and WAG flooding are the limitation of injected CO_2 due to injected water chemistry and gravity segregation reduction (Ayirala et al., 2014). There is no experimental work in literature on low salinity brine effect on carbonated waterflooding.

However, Zhang et al. (2013) performed a simulation study on the possible impact of reservoir brine salinity during different types of CO_2 injection. Authors performed analysis on brine salinity effect on water (WI), continuous CO_2 (CCI) and carbonated water injection (CWI). A 10% additional oil recovery was reported when the salinity of the injected brine was reduced in CWI from 250 kppm to 100 kppm.

2.1.3.4 HYBRID OF LOW SALINITY AND SURFACTANT FLOODING

Surfactants reduce the oil and water interfacial tension, which increase capillary number significantly and mobilize residual oil (Stegemeier et al., 1977; Healy et al., 1977). Surfactant flooding can be benefited from lower ionic strength, which makes possible to use the large variety of surfactants which are not applicable at higher salinities. At lower ionic strength, surfactant retention by adsorption decreases and this reduces the need for alkaline (Nourani et al., 2014; Alagic and Skauge 2010).

The benefit of combining low salinity injection water with surfactant flooding in sandstones was reported by Alagic and Skauge (2010).

Alagic and Skauge (2010) performed coreflood experiments on outcrop sandstone cores. Low salinity waterflooding was used in secondary mode followed by surfactant flooding in tertiary mode. Ultimate oil recovery more than 90% of original oil in place was reported. Authors attribute high oil recovery to synergy of destabilization of oil layers caused by change in brine salinity and simultaneous mobilization of the residual oil at low interfacial tension.

2.1.3.5 COMBINING LOW SALINITY WATER FLOODING AND DILUTE-SURFACTANT FLOODING

Reduction of surfactant amount in surfactant flooding from conventional 1-2wt% to less than 0.1wt% can be identified as dilute-surfactant flooding. The main advantage of using dilute-surfactant to conventional surfactant flooding is the cost efficiency. It is believed that wettability alteration induced by low cost surfactant at dilute concentration is the main mechanism for additional oil recovery (Spinler et al., 2000).

Al-Yousef et al. (2013) reported 15.5% of incremental oil recovery by combining low salinity water flooding in secondary followed by dilute surfactant flooding in tertiary mode. Core plugs (1-inch in diameter, and 1.5-inch in length) with average porosity of 25% and liquid permeability of 2.4 Darcy from a carbonate reservoir in Saudi Arabia were selected for experiment. Figure 2.13 shows the incremental oil recoveries.



Figure 2.13: Oil recovery from diluted seawater flood/diluted surfactant flood (Al-Yousef et al., 2013).

CHAPTER 3: INTRODUCTION TO UTCOMP-IPHREEQC

The purpose of this chapter is to introduce the simulator that makes it possible to perform all sensitivity analyses described in Chapter 4. UTCOMP-IPhreeqc is a coupled multi-phase reactive-transport simulator developed in The University of Texas at Austin. This package combines the geochemical modeling power of IPhreeqc (Charlton and Parkhurst, 2011), developed by the United States Geological Survey (USGS) with The University of Texas at Austin in-house compositional reservoir simulator UTCOMP.

3.1 UTCOMP RESERVOIR SIMULATOR

UTCOMP is The University of Texas at Austin in-house non-isothermal, threedimensional, equation-of-state (EOS) implicit pressure and explicit phase saturations and compositions (IMPES) compositional reservoir simulator, UTCOMP has been designed for variety of enhanced oil recovery processes, such as immiscible and miscible gas flooding (Chang, 1990; Khan, 1992; Xiao, 1994; Cheng *et al.*, 2000; Vikas, 2002; Ghasemi Doroh, 2012; Li, 2012; Darabi, 2014; Korrani, 2014; Mohebbinia *et al.*, 2013; Mohebbinia, 2013; Shirdel, 2013; Rezaveisi *et al.*, 2014a; 2014b; Shakiba, 2014; Abouie, 2015; Cavalcante Filho et al., 2015; UTCOMP Technical Documentation, 2011). Four-phase flow behavior, such as aqueous, oil, gas, and second non-aqueous liquid phases, can be modeled using this simulator (Chang 1990).

The main up-to-date features of the simulator are:

- Three-dimensional EOS IMPES compositional
- Rigorous and simplified flash calculations (including three phase flash calculation capability)
- K-value method for phase behavior calculations

- Higher-order total variation diminishing (TVD) finite-difference method
- Full physical-dispersion tensor
- Variable-width cross-section option
- Vertical or horizontal well capability
- Tracer-flood capability
- Polymer-flood capability
- Dilute-surfactant option with both equilibrium and non-equilibrium mass transfer
- Gas-foam-flood capability (capillary pressure model and table-look-up approach)
- Black-oil model
- Asphaltene precipitation model
- CO₂ sequestration in aquifers

A simplified computational scheme of UTCOMP is shown in Figure 3.1 where prior to simulation in the initialization step, all gridblock pressures are corrected for gridblock depth; initial overall hydrocarbon mole fractions have to be provided by operator in order to perform phase behavior calculations, and constant terms of transmissibilites are calculated. Simulation starts at time t, after the initialization step is performed where pressure equation is solved implicitly. Once the gridblock pressures are updated, mass conservation equation is solved explicitly (Chang, 1990). Next step is the determination the number of hydrocarbon phases and their amounts and phase compositions using the flash calculation. Peng-Robinson and Modified Redlich-Kwong cubic equation of states are used in UTCOMP. Stability analysis is performed prior to flash calculation, which determines the number of equilibrium phases evolving from the mixture at given temperature, pressure and fluid compositions. Once flash calculations are performed, molar and mass densities are evaluated and consequently phase saturations are calculated. Next, the phase saturations are used to calculate relative permeability and capillary pressure of phases. Once relative permeability and capillary pressure are calculated, the energy balance equation is solved to compute gridblock temperatures. Finally, reservoir rock and fluid properties are updated for the new component compositions, pressure and temperature. This algorithm will be continued till the end of the simulation. A detailed description of UTCOMP can be found in Chang (1990) and UTCOMP Technical Documentation (2011).



Figure 3.1: A simplified UTCOMP computational flowchart (Korrani, 2014).

3.1.1 PRESSURE EQUATION IN UTCOMP

Gridblock pressures are solved implicitly and the pressure equation is derived with the condition that pore volume is completely filled with fluid.

$$V_t(P,\vec{N}) = V_P(P), \tag{3-1}$$

where

- V_t = total fluid volume (ft³)
- $V_p =$ pore volume (ft³)
- P = pressure (psi)
- \vec{N} = component moles

This equation is derived based on the fact that total pore volume should be completely filled by fluid volume (Chang, 1990), and pore volume is a function of pressure while the in situ fluids are functions of pressure and total number of moles of each component. The final pressure equation in UTCOMP is as follows:

$$\begin{pmatrix} V_p^0 c_f - \frac{\partial V_t}{\partial P} \end{pmatrix} \left(\frac{\partial P}{\partial t} \right) - 0.006328 V_b \sum_{i=1}^{n_c+1} \overline{V}_{ii} \vec{\nabla} \cdot \sum_{j=1}^{n_p} \vec{k} \lambda_{ij} \xi_j x_{ij} \nabla P$$

$$= 0.006328 V_b \sum_{i=1}^{n_c+1} \overline{V}_{ii} \vec{\nabla} \cdot \sum_{j=1}^{n_p} \vec{k} \lambda_{ij} \xi_j x_{ij} \left(\nabla P_{c2j} - \gamma_j \nabla D \right)$$

$$+ V_b \sum_{i=1}^{n_c+1} \overline{V}_{ii} \vec{\nabla} \cdot \sum_{j=1}^{n_p} \phi \xi_j S_j \vec{K} \nabla x_{ij} + \sum_{i=1}^{n_c+1} \overline{V}_{ii} q_i,$$

$$(3-2)$$

where

- $V_p^0 =$ pore volume at reference pressure (ft³)
- $c_f =$ formation compressibility (psi⁻¹)
- V_t = total fluid volume (ft³)
- P = pressure (psi)
- t = time (day)
- $V_b =$ bulk volume (ft³)

 $n_c =$ number of components

 \overline{V}_{ii} = the partial derivative of total fluid volume with respect to component *i* (ft³/lbmole)

 $n_p =$ number of phases

$$\vec{k}$$
 = absolute permeability diagonal tensor (md)

$$\lambda_{rj}$$
 = relative mobility of phase *j* (cp⁻¹)

$$\zeta_i$$
 = molar density of phase *j* (lbmoles/ft³)

$$x_{ij}$$
 = mole fraction of component *i* in phase *j*

$$P_{c2j}$$
 = capillary pressure of phase 2 and phase *j* (psi)

$$\gamma_j =$$
 specific weight of phase *j* (psi/ft)

$$D =$$
 depth from the datum plane (ft)

$$\phi = \text{porosity (fraction)}$$

$$\vec{\vec{K}}$$
 = dispersion tensor (ft²/day)

$$S_j =$$
 saturation of phase *j*

 $q_i =$ molar flowrate of component *i* (lbmoles/day)

Equation (3-2) is solved for pressure at a given time t and the rest of the physical quantities are taken from previous time level.

3.1.2 MASS CONSERVATION EQUATION IN UTCOMP

Once the gridblock pressure are updated, mass conservation is solved explicitly to calculate the total moles of hydrocarbon components. Mass conservation equation for each component in UTCOMP is as follows (Chang, 1990):

$$\frac{\partial N_i}{\partial t} - V_b \vec{\nabla} \cdot \left[\sum_{j=1}^{n_p} 0.006328 \zeta_j \vec{k} \lambda_{j} x_{ij} \left(\nabla P_j - \gamma_j \nabla D \right) + \phi \zeta_j S_j \vec{k}_{ij} \nabla x_{ij} \right] - q_i = 0$$

$$for \, i = 1, 2, ..., n_c, n_{c+1},$$
(3-3)

where

$$N_i$$
 = number of moles of component *i* (lbmoles)

t = time (day)

 $V_b =$ bulk volume (ft³)

 $n_p =$ number of phases

$$\zeta_j = \text{molar density of phase } j \text{ (lbmoles/ft}^3)$$

$$\vec{k}$$
 = absolute permeability diagonal tensor (md)

$$\lambda_{rj}$$
 = relative mobility of phase j (cp⁻¹)

$$x_{ij}$$
 = mole fraction of component *i* in phase *j* (lbmoles/lbmoles)

$$P =$$
 pressure (psi)

$$\gamma_j =$$
 specific weight of phase *j* (psi/ft)

$$D =$$
 depth from the datum plane (ft)

$$\phi = \text{porosity (fraction)}$$

$$S_j =$$
saturation of phase *j*

$$\vec{\vec{K}}$$
 = dispersion tensor (ft²/day)

$$q_i =$$
 molar flowrate of component *i* (lbmoles/day)

The mass conservation equation is discretized and then solved explicitly in UTCOMP. The detailed explanation of discretization can be found in Chang (1990).

3.2 UTCOMP GEOCHEMISTRY MODULES

3.2.1 EQBATCH

EQBATCH is a geochemical package developed in The University of Texas at Austin by Bhuyan (1989). The main function of EQBATCH was performing batch reaction equilibrium calculations. EQBATCH is a preprocessor batch program which originally was linked to another The University of Texas at Austin in-house simulator UTCHEM (Delshad et al. 1996). EQBATCH was responsible for calculation of all equilibrium concentrations for all the flow and solid species based on the chemical reactions considered in UTCHEM. It is assumed that all fluids dissolve in the water phase and the initial pH of the reservoir and the makeup water can be adjusted by EQBATCH (UTCHEM Technical Documentation, 2000; Bhuyan, 1989). The output of EQBATCH can be used in UTCHEM input file as the geochemical input data. The originally EQBATCH was designed for modeling ASP floods taking into account geochemical reactions, such as soap generation, alkali precipitation, and alkaline consumption in ion exchange reactions. Korrani (2014) coupled EQBATCH with the UTCOMP compositional simulator for mechanistic modeling of low salinity waterflooding. The structure of geochemistry of UTCOMP-EQBATCH is very close to that of UTCHEM-EQBATCH except to the fact that oil-component/alkaline agent reactions are excluded from UTCOMP-EQBATCH because no surfactant phase behavior is applied in UTCOMP (Korrani et al. 2016). However, EQBATCH is not a robust geochemical module and has several limitations (e.g., lack of surface complexation and kinetic reactions); hence, Korrani (2014) coupled IPhreeqc of the USGS with UTCOMP to overcome the limitations inherent in EQBATCH. Next section describes the IPhreeqc geochemical package and the coupled UTCOMP-IPhreeqc simulator.

3.2.2 IPhreeqc

IPhreeqc is the open-source package based on PHREEQC geochemical package (Pakhurst and Appelo 2013; 1999) for use in scripting and programming languages integrated into C++, C, and FORTRAN programs (Charlton and Parkhurst 2011). All PHREEQC properties are functional in IPhreeqc; in fact "T" in IPhreeqc stands for "Interface" (Korrani, 2014). Hence, IPhreeqc provides an interface to all equilibria calculations in PHREEQC geochemical package. PHREEQC which is **pH-RE**dox-**EQ**uilibrium in **C** language is a very flexible, free, open-source geochemical package. It is capable of simulating a large variety of equilibrium reactions between water and minerals, ion exchangers, surface complexes, solid solutions, and gases. General kinetic formulation of the package allows simulating non-equilibrium mineral dissolution and precipitation, microbial reactions, decomposition of organic compounds, and other kinetic reactions (Charlton and Parkhurst, 2011). This USGS tool has several types of aqueous activity models, such as (Parkhurst and Appelo, 2013):

- 1) Lawrence Livermore National ion-association aqueous model;
- 2) WATEQ4F ion-association aqueous model;
- Pitzer specific-ion-interaction aqueous model the Pitzer aqueous model can be applied for high-salinity waters that are out of range of calculation by Debye-Hückel theory;
- 4) Specific ion Interaction Theory (SIT) aqueous model;

PHREEQC can handle wide range of geochemical calculations, such as

- a) speciation and saturation index calculations;
- b) batch reaction and one-dimensional transport calculations with reversible and irreversible reactions, which include aqueous, mineral, gas, solid-solution,

surface-complexation, and ion-exchange equilibria, and specified mole transfers of reactants, kinetically controlled reactions, mixing of solutions, and pressure and temperature changes;

c) Inverse modeling, which finds sets of mineral and gas mole transfers that account for differences in composition between waters within specified compositional uncertainty limits.

It is worth noting that Peng-Robinson equation of state can be applied in PHREEQC to calculate fugacity of gas components in contact with the aqueous phase and subsequently evaluate gas component solubilities in the aqueous phase (Parkhurst and Appelo, 2013).

We apply UTCOMP-IPhreeqc in our simulations because IPhreeqc is a complete geochemical package (has identical capabilities as PHREEQC) that overcomes the constraints related to the comprehensive reactive-transport modeling present in EQBATCH.

3.3 UTCOMP-IPhreeqc

As mentioned in the previous section, IPhreeqc provides an interface through which UTCOMP can communicate with the PHREEQC package. Two types of coupling of PHREEQC to client programs are available. Soft coupling is the reading and writing of files by the client and server. The disadvantage of this type of coupling is the time consumption because it takes time to read and write files and perform calculations at each time step. Another type of coupling - hard - is modifying the source codes to add routines that transfer data between client and server. Hard coupling is most likely to be difficult due to complicated data structures in PHREEQC. That is why the USGS has released IPhreeqc to tackle the issues with hard and soft coupling. Coupling with IPhreeqc is a hybrid between soft and hard coupling approaches (Korrani, 2014). Coupling reservoir simulator (UTCOMP in our case) with IPhreeqc runs the simulation faster than soft coupling with PHREEQC for the following reasons (Korrani, 2014; Abouie et al., 2016):

- 1) IPhreeqc skips reading and writing files;
- 2) IPhreeqc loads database only once for entire simulation;
- IPhreeqc performs solution speciation only once at the first step and modifies it in the following steps whereas in soft coupling with PHREEQC solution speciation is performed at each time step;

Figure 3.2 shows flowchart where calculations for aqueous and hydrocarbon phases are independent. It is appropriate for compositions for single or two-phase cases with dead oil, where the effect of the hydrocarbon to aqueous phase and rock geochemistry is neglected (Korrani, 2014).



Figure 3.2: Simplified UTCOMP-IPhreeqc flowchart where the impact of soluble hydrocarbon components on aqueous-rock geochemistry is neglected (Korrani, 2014).

However, to take into account hydrocarbon phase effect on aqueous/rock geochemistry new model was written (Figure 3.3). In this computation after solving the mass conservation equation for hydrocarbon and geochemical elements the total moles of geochemical elements of aqueous phase are updated (Korrani 2014). Then, the fugacities and the total moles of hydrocarbon components in contact with the aqueous phase are updated. Then IPhreeqc is run to find the new equilibrium. According to assigned fugacities, some hydrocarbon phase components dissolve into aqueous phase or move from aqueous phase into hydrocarbon phase. Then the total number of hydrocarbon phase components is updated in UTCOMP. New flash calculation for hydrocarbon phase is then performed and new fugacities of hydrocarbon phase are compared with the previous fugacities. If the difference is large the iteration loop is followed until the desired convergence is achieved. After convergence on the phase composition calculation module, hydrocarbon phase compositions are evaluated and phase saturations are calculated.



Figure 3.3: UTCOMP-IPhreeqc flowchart where the impact of soluble hydro--carbon components on aqueous-rock geochemistry is included (Korrani, 2014).

The calcite dissolution proposed by Hiorth et al. (2010) (Figure 2.5), where during modifying salinity waterflooding in carbonate reservoirs the calcite from the surface of the rock dissolves and releases the adsorbed oil and thus more water-wet surface is created, is applied in UTCOMP-IPhreeqc as the main wettability alteration mechanism for carbonate reservoirs. Research at The University of Texas at Austin is ongoing to improve the model (Sanaei, 2016).

According to Korrani et al. (2015), an interpolating technique is applied in UTCOMP-IPhreeqc for the wettability alteration due to calcite dissolution in carbonate rocks. At each time step after equilibrating data for all gridblocks by IPhreeqc, UTCOMP calculates the interpolating parameter for each gridblock using the following equation:

$$\theta = \frac{\xi_{\max} - \xi(x,t)}{\xi_{\max} - \xi_{\min}},\tag{3-4}$$

where, $\zeta(\mathbf{x}, \mathbf{t})$ is the amount of calcite in each gridblock, ζ_{max} is the amount of calcite above which no wettability alteration occurs. ζ_{min} is the value below which the rock is totally water-wet. Maximum and minimum thresholds in equation are the matching parameters. Noteworthy, the interpolating parameter is equal to 1.0 when the calculated value is greater than 1.0 and is equal to 0.0 when the calculated value is less than zero.

The θ parameter is then used to interpolate between the two relative permeability and capillary pressure sets as follows:

$$k_{rl}^{altered} = (1 - \theta)k_{rl}^{oil-wet} + \theta k_{rl}^{water-wet}$$
(3-5)

where

 $k_{rl}^{oil-wet}$ - relative permeability at complete oil-wet condition $k_{rl}^{water-wet}$ - relative permeability at complete water-wet condition

$$P_c^{altered} = (1 - \theta) P_c^{oil-wet} + \theta P_c^{water-wet}$$
(3-6)

where

 $P_c^{oil-wet}$ - capillary pressure at complete oil-wet condition $P_c^{water-wet}$ - capillary pressure at complete water-wet condition

In addition to low salinity water injection, UTCOMP-IPhreeqc is capable of modeling other processes such as formation damage as a result of water-rock interactions (Korrani, 2014; Sanaei et al., 2016).

CHAPTER 4: SIMULATION CASE STUDIES (SENSITIVITY ANALYSIS)

4.1 Introduction

This chapter presents the description of case studies, including problem statement, simulation process, input data for numerical analysis, and the schematic of the reservoir and well locations. These case studies are three-dimensional compressible and incompressible flows, quarter five-spot well pattern, three dimensional waterflooding, miscible WAG and PWAG displacement. The effect of heterogeneity, geochemistry of injected fluid, configuration of injected slugs is on reservoir performance is investigated in case studies. The initial geochemistry of reservoir water is taken from Chandrasekhar (2013). The following studies are considered in this chapter:

- (1) Effect of gridding on simulation results
- (2) Waterflooding
 - (a) Effect of heterogeneity
 - (b) Effect of geochemistry of injected water
 - (c) Effect of different combinations of high and modified salinity flooding
- (3) Continuous gas injection
 - (a) Effect of heterogeneity
 - (b) Effect of composition of injected gas on oil recovery
- (4) Water-alternate-gas flooding
 - (a) Effect of heterogeneity
 - (b) Effect of geochemistry of injected water
 - (c) Effect of different combinations of high and modified salinity flooding
 - (d) Effect of composition of injected gas on oil recovery

- (e) Effect of slug sizes on oil recovery
- (5) Polymer-water-alternate-gas flooding
 - (a) Effect of heterogeneity
 - (b) Effect of geochemistry of injected water
 - (c) Effect of different combinations of high and modified salinity flooding
 - (d) Effect of composition of injected gas on oil recovery
 - (e) Effect of polymer concentration
 - (f) Effect of slug sizes on oil recovery
- (6) Comparison of simulation results for waterflooding/WAG/PWAG

The purpose of this chapter is to investigate the results of the sensitivity analysis on waterflooding/WAG/PWAG at different reservoir conditions and geochemistry of injected water.

4.2 Model Description

The UTCOMP-IPhreeqc simulator is used to simulate the quarter 5-spot 3D synthetic model with injection well (Well_2) in grid 10 in x and y-direction and perforated in 3 layers, and production well (Well_1) in grid 1 in x and y-direction and perforated in all layers in z-direction, for all cases. Figure 4.1 depicts a schematic view of the reservoir model with injector and producer well configurations. The geometrical and petrophysical properties of the simulation model are presented in Tables 4.1 and 4.2, respectively.



Figure 4.1: Schematic view of quarter 5-spot synthetic simulation model.

Parameter	Value	Comments	
Number of Gridblocks	300	3D (10 x 10 x 3)	
Gridblock Sizes (dx, dy, dz), ft	dx is 350ft dy is 350ft dz is 20,30,50 ft	Constant grid size in the x and y-directions, and variable grid size in z directions.	
Reservoir Model Dimensions, ft	3500 ft x 3500 ft x 100 ft	Length x Width x Thickness	

 Table 4.1: Geometrical properties of a quarter 5-spot pattern

Parameter	Value		
Porosity	0.3		
Average permeability (md), x-direction	300		
Average permeability (md), y-direction	300		
Average permeability (md), z-direction	30		
Rock compressibility (psi ⁻¹)	5.0×10 ⁻⁶		
Water compressibility (psi ⁻¹)	3.30×10 ⁻⁶		
Initial Water saturation	0.24		
Irreducible water saturation	0.2		
Reservoir temperature (°F)	160.0		
Initial pressure (psi)	4000.0		
Reservoir depth (ft)	975		
Water viscosity (cp)	0.7		
Oil viscosity (cp)	4		
Number of wells	2 1 injector 1 producer		
Simulation time(days)	6570		

Table 4.2: Petrophysical properties of a quarter 5-spot pattern

UTCOMP-IPhreeqc has capability to build 7 sets of permeability curves:

- (1) Baker's model
- (2) Modified Stone's model
- (3) Pope's model
- (4) Corey's model
- (5) Modified Corey's model
- (6) Look up table
- (7) Corey's number with trapping number effect

In this study Corey type of equations for relative permeability is used (equation 1). A set of relative permeability curves for oil and water-wet condition is shown in Figure 4.2 where solid red and blue curves are the initial set of relative permeability curves and dashed red and blue curves are the oil and water relative permeability curves after low-salinity flooding.

$$k_{ro} = k_{ro}^{o} \left(\frac{S_o - S_{or}}{1 - S_{or} - S_{wr} - S_{gr}} \right)^{e_o}$$
(4-1)

where $S_{or} = f(S_g, S_w)$



Figure 4.2: Initial and adjusted oil and water relative permeability curves before and after modified salinity flooding.

Hydrocarbon compositions and critical properties are shown in Table 4.3 where P_c – critical pressure; T_c – critical temperature; V_c – critical volume; W_t – molecular weight; OM –acentric factor; PARACH – Parachor; VSP – volume shift parameter. Initial reservoir water geochemistry properties were taken from Chandrasekhar (2013).

Reservoir and modified injected (seawater (SW), 10, 5, 2-times diluted) water geochemistry are presented in Table 4.4. It is worth mentioning that the initial chloride concentration reported in Chandrasekhar (2013) is 111810 ppm but produced chlorides are about 17143 ppm (Korrani et. al 2015). We assume 17143 ppm for the chloride concentration in our simulations.

component	Composition (mole fraction)	PC (psia)	TC (°R)	VC (ft ³ /lbmole)	WT (lb/lbmole)	ОМ	PARACH	VSP
CO_2	0.005	1071.6	547.57	0.416	44.0100	0.2250	0.0	0.0
C_1	0.495	667.8	343.1	1.6019	16.043	0.0130	0.0	0.0
C ₃	0.03	616.3	665.6	3.2183	44.100	0.1524	0.0	0.0
C_6	0.07	436.9	913.3	5.9358	86.180	0.3007	0.0	0.0
C ₁₀	0.2	304.0	1111.9	10.1075	142.290	0.4882	0.0	0.0
C ₁₅	0.15	200.0	1270.1	16.7303	206.000	0.6500	0.0	0.0
C ₂₀	0.05	161.9	1380.1	21.5281	282.000	0.8500	0.0	0.0

Table 4.3: Reservoir fluid composition and critical properties of the reservoir fluid

Table 4.4: Geochemistry of the reservoir and injected water

	Concentration ppm					
Ions	reservoir	Seawater(SW)	10-times diluted	5-times diluted	2-times diluted	
Na	49933	13700	4993	9987	24967	
Mg	3248	1620	324	650	1624	
Ca	14501	521	1450	2900	7251	
Cl	17143	24468	1714	3429	8572	
S	234	3310	23	47	117	
TDS(mg/l)	85059	43619	8504	17013	42531	

4.3 Sensitivity Analysis on Conventional Waterflooding

This study introduces the sensitivity analysis on conventional waterflooding in carbonate reservoirs. We first study the impact of numerical dispersion on simulation results and then investigate the effect of other properties, such as heterogeneity of the reservoir, geochemistry of injected water, and different combinations of injected fluid on reservoir performance.

4.3.1 Effect of Gridding on Simulation Results

In this case we study the effect of gridding (i.e., numerical dispersion) on oil recovery for conventional waterflooding in carbonate reservoirs. Four cases with different grid sizes are designed in UTCOMP-IPhreeqc in Table 4.5. Average permeability in x and y directions are 300md, and in z-direction is 30md. The purpose of this study is to see the effect of numerical dispersion while mixing two different waters with different salinities, so the injection water is 10-times diluted as of reservoir water. Figure 4.3 shows the comparison of oil recovery using different grid sizes. As can be seen from this figure there is no considerable difference in oil recovery due to the gridding. For the sake of computational time the grid size of 350 feet (i.e., $10 \times 10 \times 3$) with less number of gridblocks is used in all other simulation studies in this chapter.

Case	parameter	grid size in x and y direction, ft
1	10x10x3	350
2	20x20x3	175
3	35x35x3	100
4	50x50x3	70

Table 4.5: Cases with different griddings


Figure 4.3: Effect of grid size on cumulative oil recovery.

4.3.2 Effect of Heterogeneity on Absolute Oil Recovery

This case introduces the effect of heterogeneity on conventional waterflooding in carbonate reservoirs. To imitate the heterogeneity where average permeability is 300md, Dykstra-Parson coefficient (V_{dp}) varies between 0.6-0.8 in this study and ratio between vertical and horizontal permeability (k_v/k_h) varies between 0.1-1.0. In this study four cases, as presented in Table 4.6, are compared to see the effect of heterogeneity on absolute oil recovery. The carbonate reservoir is flooded for 6570 days (1.2 PV) with

conventional 10-times diluted low-salinity waterflooding. The geochemistry of injected water is 10-times diluted and given in Table 1.5. The injection rate is kept constant at 12000 STB/day. Figures 4.4 and 4.5 show the permeability distribution for cases with $V_{dp} = 0.6$, $k_v/k_h = 0.1$ and $V_{dp} = 0.8$, $k_v/k_h = 0.1$, respectively.

Case	parameter
1	Vdp = 0.6; Kv/Kh = 0.1
2	Vdp = 0.6; Kv/Kh = 1.0
3	Vdp = 0.8; Kv/Kh = 0.1
4	Vdp = 0.8; Kv/Kh = 1.0

Table 4.6: Cases with different heterogeneity properties



Figure 4.4: Permeability distribution for $V_{dp} = 0.6$, $k_v/k_h = 0.1$.



Figure 4.5: Permeability distribution for $V_{dp} = 0.8$, $k_v/k_h = 0.1$.

Figure 4.6 shows the UTCOMP-IPhreeqc simulated oil recovery results at different V_{dp} and k_v/k_h . The highest oil recovery of 65% is obtained when V_{dp} is equal to 0.6 (i.e., better areal sweep efficiency) with k_v/k_h of 1.0 (i.e., better vertical sweep efficiency). The lowest recovery of 59% is observed when V_{dp} is equal to 0.8 (i.e., lower areal sweep efficiency) and k_v/k_h is equal to 0.1 (i.e., lower vertical sweep efficiency). As can be seen from the simulation results, more oil can be recovered when the reservoir is less heterogeneous. This study shows 6% difference in final absolute oil recovery between least and most heterogeneous cases.



Figure 4.6: Effect of heterogeneity on oil recovery.

4.3.3 Effect of Geochemistry of Injected Water on Absolute Oil Recovery

This section investigates the impact of the injected water composition on absolute oil recovery. Calcite and dolomite are assumed to be minerals contained in the matrix. The pitzer.dat database of IPhreeqc/PHREEQC is chosen for geochemical calculations. The pitzer activity model is suitable at high salinities and temperatures (Parkhurst and Appelo, 2013). Surface complexation (Korrani et al., 2015) is included in the model. The impact of hydrocarbon (CO₂) solubility on the aqueous-rock geochemistry is also included in our simulations. Five types of injected water are considered in this study: 2, 5, 10-times diluted, seawater, and high salinity water where the salinity of injected water is similar to reservoir water and shown in Table 4.4. Overall 16 cases are run in this study (cases with high salinity, seawater, 2, 5, and 10-times diluted floods – shown in Table 4.7).

di	diluted)		
Case			
1	Vdp = 0.6; $Kv/Kh = 0.1$; high salinity water injected for 1.2PV		
2	Vdp = 0.6; $Kv/Kh = 1.0$; high salinity water injected for 1.2PV		
3	Vdp = 0.8; $Kv/Kh = 0.1$; high salinity water injected for 1.2PV		
4	Vdp = 0.8; $Kv/Kh = 1.0$; high salinity water injected for 1.2PV		
5	Vdp=0.6; Kv/Kh = 0.1; high salinity water for 0.6PV,SW,2,5,10-times diluted for 0.6PV		
6	Vdp=0.6; Kv/Kh = 1.0; high salinity water for 0.6PV, SW, 2,5,10-times diluted for 0.6PV		
7	Vdp =0.8; Kv/Kh = 0.1; high salinity water for 0.6PV, SW,2,5,10-times diluted for 0.6PV		
8	Vdp=0.8; Kv/Kh = 1.0; high salinity water for 0.6PV, SW,2,5,10-times diluted for 0.6PV		
9	Vdp = 0.6; $Kv/Kh = 0.1$; SW, 2,5,10-times diluted water injected for 1.2PV		
10	Vdp = 0.6; $Kv/Kh = 1.0$; SW, 2,5,10-times diluted water injected for 1.2PV		
11	Vdp = 0.8; $Kv/Kh = 0.1$; SW, 2,5,10-times diluted water injected for 1.2PV		
12	Vdp = 0.8; $Kv/Kh = 1.0$; SW, 2,5,10-times diluted water injected for 1.2PV		
13	Vdp = 0.6; $Kv/Kh = 0.1$; SW , $2, 5, 10$ -times diluted for 0.6 PV, high salinity water for 0.6 PV		
14	Vdp = 0.6; $Kv/Kh = 1.0$; SW , $2, 5, 10$ -times diluted for 0.6 PV, high salinity water for 0.6 PV		
15	Vdp = 0.8; $Kv/Kh = 0.1$; SW , $2, 5, 10$ -times diluted for 0.6 PV, high salinity water for 0.6 PV		
16	Vdp = 0.8; $Kv/Kh = 1.0$; SW , $2, 5, 10$ -times diluted for 0.6 PV, high salinity water for 0.6 PV		

Table 4.7: Cases with the geochemistry of injected water (seawater, 2, 5, 10-times

First, we compare all the cases when high salinity, seawater, 2, 5, and 10-times diluted waters are involved. Figures 4.7, 4.8, 4.9, and 4.10 show the UTCOMP-IPhreeqc simulated oil recoveries at the combination of high-salinity (reservoir water) with

seawater flooding. In Figure 4.7 the solid red and blue lines represent continuous seawater injection and high salinity waterflooding (HSF), respectively. The dashed lines represent mixed floodings where 0.6 PV of high salinity water is chased by 1.8 PV of modified salinity water or vice versa. The highest oil recovery 61% is obtained when seawater was injected constantly for 2.4 PV. Figure 4.8 shows oil saturation in layer 1 when combinations of seawater and high-salinity water have been injected. Figure 4.9 shows pH distribution in layer 1 at the start and end of seawater flooding. The increase in pH from about 5.6 at the start of the flooding to about 6.4 at the end of the flooding can be explained by calcite dissolution. The initial low pH value is due to the buffering effect of the hydrocarbon CO₂ on the aqueous-rock geochemistry, which was included in our simulation. Figure 4.10 shows the wettability alteration interpolating parameter (θ) distribution at the start and end of the seawater waterflooding in layer 1 which is responsible for wettability alteration where 0 is fully oil-wet and 1 is fully water-wet condition. This figure shows that at the end of the flooding almost all of the porous media changed wettability from oil-wet to water-wet condition due to calcite dissolution. Noteworthy, as discussed in Korrani et al. (2015), the model implemented in UTCOMP-IPhreeqc for modified salinity waterflooding (MSF) in carbonates is function of both calcite dissolution and surface complexation. This model is an explicit function of calcite dissolution and an implicit function of surface complexation (Korrani et al., 2015). That is why calcite dissolution and hence wettability alteration is not a local effect and propagates throughout the reservoir. If the surface complexation is excluded from our simulation the wettability alteration due to modified salinity waterflooding is limited to couple of gridblocks near the injection well.



Figure 4.7: Oil recovery at different combinations of high salinity and sea waters where MSF and HSF refer to modified salinity waterflooding (i.e., sea water in this figure) and high salinity waterflooding, respectively.



Figure 4.8: Oil saturations at the end of seawater injection flooding (layer 1).



Figure 4.9: pH distribution (layer 1).



a) 1st day of seawater flooding b) End of seawater flooding

Figure 4.10: θ parameter distribution in layer 1 (wettability alteration interpolating parameter).

Figures 4.11, 4.12, 4.13, and 4.14 show the UTCOMP-IPhreeqc simulated results for the oil recovery at the combination of high-salinity with 2-times diluted reservoir water flooding. In Figure 4.11 the solid red and blue lines represent continuous 2-times diluted and high-salinity flooding respectively. The dashed lines represent mixed floodings where 0.6 PV of high salinity water is chased by 1.8 PV of modified salinity water or vice versa. The highest oil recovery 56% is obtained when 2-times diluted water was injected constantly for 2.4 PV. Figure 4.12 shows oil saturation in layer 1 when combinations of 2-times diluted and high-salinity water were injected. Swept area in this case is not as good as in case with seawater injection. Figure 4.13 shows pH distribution in layer 1 at the start and end of the 2-times diluted waterflooding. The increase in pH from about 5.6 at the start of the flooding to about 6.4 at the end of the flooding can be explained by calcite dissolution. Figure 4.14 shows the θ parameter distribution at the start and end of the waterflooding in layer 1 which is responsible for wettability alteration. This figure shows that similar to the seawater injection at the end of the flooding, wettability of almost all of the porous media has from oil-wet to water-wet condition due to calcite dissolution.



Figure 4.11: Oil recovery at different combinations of high salinity and 2-times diluted injected water where MSF and HSF refer to modified salinity waterflooding (i.e., 2-times diluted reservoir water in this figure) and high salinity waterflooding, respectively.





Figure 4.12: Oil saturations at the end of 2-times diluted reservoir water injection (layer 1).







Figure 4.14: θ parameter distribution in layer 1 (wettability alteration interpolating parameter).

Figures 4.15, 4.16, 4.17, and 4.18 show the UTCOMP-IPhreeqc simulated results for the oil recovery at the combination of high-salinity with 5-times diluted reservoir water flooding. In Figure 4.15 the solid red and blue lines represent continuous 5-times diluted and high-salinity flooding respectively. The dashed lines represent mixed floodings where 0.6 PV of high salinity water is chased by 1.8 PV of modified salinity water or vice versa. The highest oil recovery 61% is obtained when 5-times diluted water was injected constantly for 2.4 PV. Figure 4.16 shows oil saturation in layer 1 when combinations of 5-times diluted and high-salinity water were injected. Figure 4.17 shows pH distribution in layer 1 at the start and end of the 5-times diluted waterflooding. Figure 4.18 shows the θ parameter distribution at the start and end of the 5-times diluted waterflooding in layer 1.



Figure 4.15: Oil recovery at different combinations of high salinity and 5-times diluted injected water where MSF and HSF refer to modified salinity waterflooding (i.e., 5-times diluted reservoir water in this figure) and high salinity waterflooding, respectively.



Figure 4.16: Oil saturations at the end of 5-times diluted reservoir water injection (layer 1).



Figure 4.17: pH distribution (layer 1) at 5-times diluted waterflooding.



Figure 4.18: θ parameter distribution in layer 1 at 5-times diluted waterflooding (wettability alteration interpolating parameter).

Figures 4.19, 4.20, 4.21, and 4.22 show the UTCOMP-IPhreeqc simulated results for the oil recovery at the combination of high-salinity with 10-times diluted reservoir water flooding. In Figure 4.19 the solid red and blue lines represent continuous 10-times diluted and high-salinity flooding respectively. The dashed lines represent mixed floodings where 0.6 PV of high salinity water is chased by 1.8 PV of modified salinity water or vice versa. The highest oil recovery 62% is obtained when 10-times diluted water was injected constantly for 2.4 PV. Figure 4.20 shows oil saturation in layer 1 when combinations of 10-times diluted and high-salinity water were injected. Figure 4.21 shows pH distribution in layer 1 at the start and end of the 10-times diluted waterflooding. Figure 4.22 shows the θ parameter distribution at the start and end of the 10-times diluted waterflooding in layer 1.



Figure 4.19: Oil recovery at different combinations of high salinity and 10-times diluted injected water where MSF and HSF refer to modified salinity waterflooding (i.e., 10-times diluted water in this figure) and high salinity waterflooding.



Figure 4.20: Oil saturations at the end of 10-times diluted reservoir water injection (layer 1).



Figure 4.21: pH distribution at 10-times diluted reservoir waterflooding (layer 1).



Figure 4.22: θ parameter distribution in layer 1 at 10-times diluted reservoir waterflooding (wettability alteration interpolating parameter).

Figure 4.23 compares oil recoveries when the water with different geochemistry is injected. Oil recovery for the high salinity injection is included in this figure for comparison. Oil recovery curves at seawater, 10, 5, 2-times diluted, and high salinity injected water shows the oil recovery 61%, 62%, 61%, 56%, and 35% respectively, which means that 10-times dilution most gives the maximum final recovery.



Figure 4.23: Comparison of oil recoveries at different dilutions of injected water.

4.4 Continuous Gas Injection (CGI)

 CO_2 flooding is one of the promising gas injection EOR techniques that work on different types of the reservoir. Gas flooding can be miscible or immiscible and the difference is that there is interface between the displaced and displacing fluid during immiscible flooding while in the miscible flooding interface does not occur. Two mechanisms such as viscosity reduction and oil swelling are responsible for immiscible flooding while interfacial tension reduction is the main mechanism in miscible flooding (Stalkup et al., 1983).

4.4.1 Heterogeneity Effect on Oil Recovery during CGI

Similar to section 4.2, we investigate the effect of heterogeneity on continuous gas injection in carbonate reservoirs. Dykstra-Parson coefficient (V_{dp}) varies between 0.6-0.8 in this study and ratio between vertical and horizontal permeability (k_v/k_h) varies between 0.1-1.0. Four cases are compared to see the effect of heterogeneity on absolute oil recovery, as shown in Table 4.6. The carbonate reservoir was flooded with a gas comprising of 75% of CO₂ and 25% of CH₄ for 6570 days. The injection rate is kept constant 120 MMScf/day. Figure 4.24 compares cases with different V_{dp} and k_v/k_h when pure CO₂ is injected.

Figure 4.24 shows the UTCOMP-IPhreeqc simulated results for the oil recovery at different Vdp and kv/kh. The highest oil recovery 70% is obtained at Vdp equal to 0.6 and kv/kh proportion is not important because the vertical to horizontal permeability ratio is negligible during gas injection. 61% of oil recovery is obtained at Vdp equal to 0.8, while for less heterogeneous case (V_{dp} of 0.6), 9% more oil recovery is observed. Similar to waterflooding during continuous gas injection more oil can be recovered when the reservoir is less heterogeneous.



Figure 4.24: Effect of heterogeneity on oil recovery during continues CO₂ gas injection.

4.4.2 Sensitivity Study on Different Injected Gas Composition on Oil Recovery during CGI

Next study considers the reservoir behavior when different gas mixtures (Table 4.8) are injected to the reservoir. Table 4.3 shows seven components considered initially in reservoir. As shown in Table 4.8, CO_2 and CH_4 are only two components in different mixtures considered as the injection gas.

Case	concentration
1	${ m CO}_2=0.5;{ m CH}_4=0.5$
2	$CO_2 = 0.75; CH_4 = 0.25$
3	$CO_2 = 1; CH_4 = 0$

Table 4.8: Concentrations of injected gas

Figure 4.25 shows the effect of injected gas composition on oil recovery at V_{dp} of 0.6 and k_v/k_h of 0.1. The highest oil recovery 63% is obtained when CO₂ concentration is equal 50% of the injected gas. When CO₂ is the only injected gas component minimum oil recovery of 57% is seen.



Figure 4.25: Oil recovery vs time at different concentrations of injected gas.

4.5 Water Alternate Gas (WAG) Flooding

The main goal of water-alternate gas (WAG) flooding is to override the disadvantages of continuous gas injection, such as the gravity segregation due to severe density difference between displaced fluid and displacing gas. It is believed that additional oil recovery can be achieved by applying WAG and improving mobility control is the main controlling mechanism (Fjelde et al., 2010). This study includes the

effect of heterogeneity and composition of injected water and gas composition on reservoir performance during WAG flooding. This section also includes the study of CO_2 dissolution on the aqueous phase which was included in UTCOMP-IPhreeqc.

4.5.1 Effect of Heterogeneity on Oil Recovery during WAG Flooding

In this section we investigate the effect of heterogeneity on water-alternate gas flooding in carbonate reservoirs. Dykstra-Parson coefficient (V_{dp}) varies between 0.6-0.8 in this study and the ratio between vertical and horizontal permeability (k_v/k_h) is in range 0.1-1. Cases have been compared to see the effect of heterogeneity on absolute oil recovery. The carbonate reservoir has been injected with different composition of gas and water for 6570 days. In all WAG scenarios, we inject water for 365 days followed by gas injection for another 730 days, and this process is repeated to the end of 6570 days. The injected water is 10-times diluted. The gas injection rate is kept constant 12 MMScf/day. Figure 42 presents the comparison of cases with different V_{dp} and k_v/k_h when CO₂ concentration in injected gas is equal to 75% and CH₄ mole percent is 25%.

Figures 4.26 presents the UTCOMP-IPhreeqc simulated results for the wateralternate-gas flooding oil recoveries at different V_{dp} and k_v/k_h . The difference in k_v/k_h at V_{dp} equal to 0.8 make curves separate at 2000 days and oil recovery at kv/kh equal 1 is equal to 40% which is 6% higher when kv/kh is equal to 0.1. The highest oil recovery 53% is obtained at V_{dp} equal to 0.6 and k_v/k_h equal to 1.0. It can be inferred from the results that more oil can be recovered when the reservoir is less heterogeneous. The interesting observation is that compared with the continuous gas injection in which oil recovery was independent of the vertical to horizontal permeability ratios, in the case of

WAG, oil recovery increases as K_v/K_h increases. This clearly explains the advantage of WAG over CGI.



Figure 4.26: Effect of heterogeneity on WAG flooding.

4.5.2 Effect of Water Composition Combinations on Oil Recovery during WAG Flooding

This study introduces how the modification of the geochemistry of injected water can affect the absolute oil recovery in WAG flooding. We consider different combinations of water-alternate-gas flooding. The water-alternate-gas flooding is performed with different composition water for 6570 days and injection rate is kept constant 12000 STB/day. The injected gas is pure CO_2 and the injection rate has been kept constant 12 MMScf/day. Each of 6 slugs of different compositions of gas is injected for 730 days at constant injection rate 12 MMScf/day followed by water slug at constant rate 12000 STB/day, 365 days each and total WAG flooding time was 6570 days.

Figure 4.27 shows the UTCOMP-IPhreeqc simulated results for the WAG flooding oil recoveries at different dilutions of injected water. This figure demonstrates the impact of the geochemistry of injected water in the WAG process with seawater, 10times, 5-times, 2-times, and high salinity. All cases show water-gas breakthrough at about 1700 days. The WAG flood where the chemistry of the injected water is 10-times diluted shows the highest oil recovery 57%, which is 1%, 4%, 3%, and 8% more than in the case when the injected water is 5-times diluted, 2-times, seawater, and high salinity. The difference between oil recoveries of high salinity and low-salinity WAG floods is in fact the result of net effect of CO_2 solubility in the aqueous phase as well as the wettability alteration due to modified salinity injection, which are both functions of aqueous salinity. CO₂ solubility in the aqueous phase decreases as the aqueous salinity increases whereas more wettability alteration occurs by further lowering of the injected aqueous salinity. It appears from our simulation results that although by lowering the salinity of the injected water more CO₂ is dissolved in the aqueous phase, beneficial effect of lowering the injected aqueous salinity in terms of wettability alteration is higher. That is why oil recovery increases as the injected aqueous salinity decreases.



Figure 4.27: Oil recovery at different dilutions of injected water at $k_v/k_h = 0.1$ and $V_{dp} = 0.6$.

4.5.3 Effect of Gas Composition on Oil Recovery during WAG Flooding

Next, we consider the reservoir behavior when different compositions of gas during water-alternate-gas flooding are injected. CO_2 and CH_4 are only two gas components in different proportions are considered as the injection gas. CO_2 in concentration 100%, 75% and 50% and CH_4 in concentration 0%, 25% and 50% respectively are considered as the injection gas in this study. Injected water in WAG flooding consists of high salinity (reservoir water) and 10-times diluted reservoir water. Each of 6 slugs of different compositions of gas are injected for 730 days at constant injection rate 12 MMScf/day followed by water slug at constant rate 12000 STB/day, 365 days each and total WAG time was 6570 days.

Figure 4.28 presents the UTCOMP-IPhreeqc simulated results for the wateralternate-gas flooding oil recoveries for different injected gas compositions. Cyclic injection of high salinity water is followed by gas slug and modified salinity (10-times diluted). This figure shows that the compositions of gas has a negligible effect on oil recovery in WAG flooding. The main mechanisms for improving absolute oil recovery are wettability alteration and mobility control which mainly depends on properties of injected water, viscosity reduction and oil swelling due to miscible gas flooding.



Figure 4.28: Oil recovery at different compositions of injected gas at $k_v/k_h = 0.1$ and $V_{dp} = 0.6$.

4.5.4 The Effect of CO₂ Dissolution Consideration in the UTCOMP-IPhreeqc Simulator

This study represents the sensitivity analysis and behavior of fluids in fresh and saline water during WAG flood when solubility of CO_2 in aqueous phase is disabled in the UTCOMP-IPhreeqc simulator. If the impact of the dissolution of CO_2 in the aqueous phase is neglected in our simulations, some of the results will significantly be affected, particularly at high reservoir pressure CO_2 dissolves in aqueous phase and carbonic acid is formed which affects the pH of the system. Moreover, insoluble carbonates can be formed by interaction of carbonate anions with cations presented in water. UTCOMP-IPhreeqc is capable of modeling the effects of soluble hydrocarbon and acidic/basic components. The sequential iterative approach takes into account the effect of the soluble hydrocarbon components in this coupled reservoir simulator. We are able to disable CO_2 dissolution in aqueous phase in UTCOMP-IPhreeqc and compare it with the cases in which CO_2 dissolution was taken into account.

Figure 4.29 presents the UTCOMP-IPhreeqc simulated results for the WAG flooding to see CO_2 dissolution effect in aqueous phase when high and low-salinity water geochemistry was considered. This figure shows that neglecting CO_2 dissolution in aqueous phase during high salinity flood gives small overestimation as when the effect has been taken into account. However, neglecting CO_2 dissolution during WAG flood where the low-salinity geochemistry of injected water is considered gives significant difference. The reason for this is the fact that the hydrocarbon CO_2 solubility in the aqueous phase is a function of aqueous salinity. The CO_2 solubility in the aqueous phase is higher at lower salinities. Oil recovery with no CO_2 dissolution gives 61% of OOIP, which is 4% more with the case where CO_2 dissolution has been taken into account.



Figure 4.29: Significance of the impact of hydrocarbon CO_2 on aqueous-rock geochemistry - Comparison of high salinity (reservoir connate water) and low salinity flooding (10-times diluted reservoir water) with and without CO_2 dissolution on aqueous phase.

4.6 Polymer Water Alternate Gas Flooding

The main goal of polymer-water-alternate gas (PWAG) flooding is a new combination method similar to water-alternate-gas flooding with one valuable difference. PWAG is the synergy of polymer flooding with CO₂ flood where the addition of polymers to water gives better volumetric sweep efficiency. In this study we discuss PWAG flooding based on the synthetic 3D model that is used in our previous sections.

Below is UTCOMP-IPhreeqc procedure for modifying the water viscosity as a function of shear rate, polymer concentration, and salinity. Meter's equation is applied to include the impact of the shear rate on the polymer viscosity (Meter and Bird, 1964).

$$\mu_{p} = \mu_{\infty} + \frac{\mu_{p}^{0} - \mu_{\infty}}{1 + \left(\frac{\dot{\gamma}}{\dot{\gamma}_{1/2}}\right)^{P_{\alpha} - 1}}$$

$$(4-2)$$

where

$$\gamma = \frac{\gamma_{\rm C} \left| \overline{\mathbf{u}}_{\rm W} \right|}{\sqrt{\overline{\mathbf{k}}\mathbf{k}_{\rm rW} \phi \mathbf{S}_{\rm W}}} \tag{4-3}$$

and

$$\bar{\mathbf{k}} = \left[\frac{1}{k_{x}} \left(\frac{\mathbf{u}_{x1}}{\mathbf{u}_{1}}\right)^{2} + \frac{1}{k_{y}} \left(\frac{\mathbf{u}_{y1}}{\mathbf{u}_{1}}\right)^{2} \frac{1}{k_{z}} \left(\frac{\mathbf{u}_{z1}}{\mathbf{u}_{1}}\right)^{2}\right]^{-1}$$
(4-4)

where

 μ_p is the apparent viscosity of polymer solution;

 γ is the shear rate;

 $\gamma_{1/2}, \gamma_c$, and P_a are input parameters;

 $\gamma_{1/2}$ is shear rate at which viscosity is the average of μ_p^0 , μ_{w} ;

 P_a is an empirical coefficient;

 γ_c is 3.97C sec⁻¹, where C is the shear rate coefficient used to explain deviation of the porous medium from the ideal capillary-bundle model;

 $\overline{\mathbf{k}}$ is the average permeability;

k_{rw} is the aqueous phase relative permeability;

S_w is the aqueous phase saturation;

 ϕ is the porosity;

u_w is the Darcy flux of the aqueous polymer solution;

 μ_{∞} the polymer viscosity at infinite shear rate, and it is approximately equal to water viscosity;

 μ_p^0 is the polymer viscosity at zero shear rate and it is calculated as the function of polymer concentration and salinity as follows:

$$\mu_{p}^{0} = \mu_{w} \left(1 + \left(A_{p1} C_{41} + A_{p2} C_{41}^{2} + A_{p3} C_{41}^{3} \right) C_{SEP}^{Sp} \right)$$
(4-5)

where μ_w is the water viscosity;

 A_{p1}, A_{p2}, A_{p3} are the fitting parameters obtained from laboratory data;

 C_{SEP}^{Sp} represents the dependence of polymer viscosity on salinity and hardness (see UTCOMP technical documentation for more details).

In UTCOMP-IPhreeqc we get divalent and monovalent concentrations from the IPhreeqc module and transfer them into UTCOMP to calculate polymer viscosity as a function of salinity. The effect of the following parameters for absolute oil recovery is considered in this study: heterogeneity of the reservoir, salinity of the injected water, and polymer concentration in the injected water. Previous section showed that the effect of gas composition is negligible in WAG flooding; hence, it is not considered in PWAG flooding. Tables 4.9 and 4.10 are showing the polymer concentrations in injected water and polymer solution viscosity parameters, respectively. Figure 4.30 shows the calculated polymer viscosity as a function of shear rate.

Table 4.9: Concentrations of polymer in injected solution

Case	Concentration, ppm
1	500
2	750
3	1000

Table 4.10: Parameters for calculating polymer solution viscosity

parameter	value
AP1	0.005
AP2	0.002
AP3	0
S slope	-0.3
B _{SE}	20



Figure 4.30: Polymer viscosity vs shear rate at different polymer concentrations.

4.6.1 Effect of Heterogeneity on Oil Recovery

This section introduces the effect of heterogeneity on PWAG flooding. Dykstra-Parson coefficient (V_{dp}) varies between 0.6-0.8 and the ratio between vertical and horizontal permeability (k_v/k_h) is in range 0.1-1. 4 different cases are designed to see the effect of heterogeneity on absolute oil recovery. The synthetic reservoir has been injected with composition of gas and polymer-water solution for 6570 days or 0.8PV. Figure 4.31 compares cases with different V_{dp} and k_v/k_h when CO₂ concentration in injected gas is equal to 75%, polymer concentration in water 500 ppm, and water is high-salinity reservoir water. Each of 6 slugs of compositions of gas is injected for 730 days at constant injection rate 12 MMScf/day followed by polymer-water slug at constant rate 12000 STB/day, 365 days each and total PWAG time is 6570 days. The wettability alteration option due to modified salinity waterflooding is included in this study.

Figure 4.31 shows the UTCOMP-IPhreeqc simulated results for the PWAG flooding oil recoveries at different V_{dp} and k_v/k_h . Before breakthrough there is no significant difference between the considered cases, however the difference in kv/k_h and V_{dp} makes curves separate at water breakthrough time after about 0.3 PV of PWAG flooding. The highest oil recovery 55% is obtained at V_{dp} equal to 0.6 and k_v/k_h equal to 1.0 which is higher the lowest case for 22% when V_{dp} is equal to 0.8 and k_v/k_h equal to 0.1. As can be seen from the results more oil can be recovered when the reservoir is less heterogeneous. It is worth noting that in PWAG flooding, aqueous salinity affects three key parameters determining the success of the process. These parameters are: polymer adsorption on the rock surface, CO₂ solubility in the aqueous phase, and wettability alteration due to modified salinity injection.



Figure 4.31: Effect of heterogeneity on PWAG flooding oil recovery where high-salinity water and 75% CO₂ concentration in gas is considered.

4.6.2 Effect of Water Composition Combinations on Oil Recovery during PWAG Flooding

This study introduces how the modification of the geochemistry of injected water can affect the absolute oil recovery in PWAG flooding. PWAG flooding is performed with different composition of water for 0.8 PV and polymer-water solution. The injected gas is the 75% CO₂ solution with injection rate of 12 MMScf/day. The polymer concentration in solution has been kept 1000 ppm during this study.

Figure 4.32 presents the UTCOMP-IPhreeqc simulated results for PWAG flooding oil recoveries at different dilutions of injected water. This figure shows the

comparison where the difference of injected water in PWAG flooding with seawater, 10times, 5-times, 2-times, and high salinity was considered. All cases show water-gas breakthrough at about 0.25PV. The PWAG flood where the chemistry of the injected water is 10-times diluted shows the highest oil recovery 60%, which is 2%, 9%, 3%, and 11% more than in the case when the chemistry of water was diluted 5, 2-times, seawater, and high salinity.



Figure 4.32: Oil recovery at different dilutions of injected water at $k_v/k_h = 0.1$ and $V_{dp} = 0.6$.
4.6.3 Effect of Polymer Concentration on Oil Recovery during PWAG Flooding

In this section we study the modification of the polymer concentration in injected water-polymer solution and its effect on performance of PWAG flooding. PWAG flooding is performed for 6570 days or 0.8PV and polymer-water solution injection rate is kept constant 12000STB/day. The injection gas is the 75% CO₂ solution and the injection rate has been kept constant 12 MMScf/day. 10-times diluted reservoir water is considered as the part of polymer-water injection solution in this study. Each of 6 slugs of compositions of gas have been injected for 730 days at constant injection rate 12 MMScf/day followed by polymer-water slug at constant rate 12000 STB/day, 365 days each and total PWAG time is 6570 days.

Figure 4.33 shows the UTCOMP-IPhreeqc simulated results for PWAG flooding oil recoveries at different concentration of polymer of 500 ppm, 750 ppm, and 1000 ppm in injected solution. PWAG flooding with the polymer concentration in injection solution of 1000 ppm shows slightly higher oil recovery of 60% which is approximately 1% more than in the case with polymer concentration in injection solution of 750 ppm and 500 ppm.



Figure 4.33: Oil recovery at different polymer concentrations in injected polymer-water solution and WAG at $k_v/k_h = 0.1$ and $V_{dp} = 0.6$.

4.7 Comparison of Different Types of Hybrid EOR Techniques

In this section we compare oil recoveries of different types of EOR techniques. Waterflooding, WAG, and PWAG flooding were performed for 6570 days where the injection rate is kept constant 12000STB/day. The injected gas composition is 75% CO₂ and 25% CH₄ and the injection gas rate is kept constant 12 MMScf/day. The polymer concentration in PWAG solution has been kept 1000 ppm and high-salinity (reservoir water) and low-salinity (10-times diluted reservoir water) were considered in this study. V_{dp} equal to 0.6 and k_v/k_h equal to 0.1. In case of high or low-salinity waterflooding the reservoir flooded continuously with high (reservoir water) or 10-times diluted reservoir water for 6570 days at constants rate 12000STB/day. In case of WAG and PWAG

flooding each of 6 slugs of compositions of gas have been injected for 730 days at constant injection rate 12 MMScf/day followed by water or polymer-water slug at constant rate 12000 STB/day, 365 days each and total PWAG time is 6570 days.

Figure 4.34 shows the UTCOMP-IPhreeqc simulated results for oil recoveries at different types of EOR techniques. This figure shows the adjusting water salinity of injected water is beneficial for all hybrid types of EOR. The PWAG flood where the chemistry of the injected water is 10-times diluted shows the highest oil recovery 60%, which is 30% more than that of the case when the continuous high-salinity waterflooding have been performed.



Figure 4.34: Oil recovery at different types of hybrid EOR techniques at $k_v/k_h = 0.1$ and $V_{dp} = 0.6$.

4.8 Conclusion

Sensitivity analysis on different types of EOR techniques have been studied in this chapter. Studies conducted in all sections showed that as we expect, the less heterogeneous reservoir is more suitable for additional oil recovery. Reducing the salinity of injected water brings to additional oil recovery in all EOR techniques. Section 4.3 showed that modification of the salinity of the injected water can lead to significant increase in ultimate oil recovery. The interpolating parameter distribution maps, which is responsible for wettability alteration show that wettability was changed from more oilwet to more water-wet condition during modified salinity waterflooding. pH increase in all waterflooding cases can be explained by calcite dissolution from the rock surface. Section 4.5 showed the benefit of combining water and gas injection over conventional waterflooding and Section 4.6 showed the benefits of adding polymer to overcome negative sides of mobility ratio and improving sweep efficiency. Section 4.5 also discussed the significance of including the effect of hydrocarbon CO₂ dissolution on the aqueous-rock geochemistry during WAG flooding. Our simulation results showed that neglecting the impact of hydrocarbon CO₂ dissolution on the aqueous-rock geochemistry during low-salinity flooding overestimates the ultimate oil recovery.

CHAPTER 5: HYBRID EOR FIELD CASE OPTIMIZATION

The concept of experimental design (DoE) and response surface methodology (RSM) is applied in this study to identify an optimal hybrid EOR design in terms of maximizing ultimate oil recovery. This study consists of four parts, first part describes Design of Experiment and Response Surface Methodology, second part is the chemical flooding optimization approach using DoE, RSM, and UTCOMP-IPhreeqc, third part is optimization and results itself, and the last part is conclusion.

5.1 Design of Experiment and Response Surface Methodology

Design of Experiment is the method developed by Sir R.A.Fisher in 1920s that is used to determine the relationship between different input variables affecting the output of the process (Ghomian, 2008, Ghorbani, 2008, Al-Shalabi, 2014). The input variables consist of state parameters and decision variables where state parameters uncertain or cannot be controlled and decision variables can be controlled. In this study two-level factorial design is used where each input variable has only maximum and minimum levels. Two-level factorial design is the method for analyzing the response variable where the effect of single variable or group of two variables on response variable is considered. There are two types of two-level factorial design, such as full or fractional. The number of simulations in fractional design is reduced. The half-normal probability plot and the effect plot are graphical methods for analyzing the data. The half-normal probability plot determines the factors that impact the objective function (output). Parameters not influencing the objective function in the plot are usually in straight line and influencing parameters tend to deviate from straight line. The effect plot identifies the parameters that impacts objective function and rank them in order from most significant to negligible. The effect plot also shows whether any parameter has positive or negative effect on the objective function.

Response surface methodology is a combination of statistical and mathematical techniques used to optimize the process where graphical response generated from empirical model obtained with observed data. The main function of response surface methodology is to get a representative function of the objective variable. Empirical model in RSM is built from multiple regression process which allows testing and modeling of multiple independent variables where first-order response surface model is called multiple linear regression models with k repressors and takes a form:

$$y = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \dots + \beta_k x_k + \varepsilon$$
 (5-1)

where

 β_j , j=0, 1, 2, ..., k are regression coefficients which estimated by the least squares method

The second-order response surface model is the most commonly used method as it contains the curvature on the built response surface and has the form (Myer and Montgomery, 2002; Prasanphanish, 2009):

$$y = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \dots + \beta_k x_k + \sum_{i < j} \sum_{i=2}^k \beta_{ij} x_i x_j + \sum_{i=1}^k \beta_{ii} x_i^2 + \varepsilon$$
(5-2)

5.2 Chemical Flooding Optimization Approach

DoE and RSM are widely used in enhanced oil recovery processes for reducing uncertainties. In this study we apply experimental design and response surface methodology for optimizing the low-salinity polymer-water-alternate gas (PWAG) flooding in carbonate reservoir. The optimization steps are as follows:

- Determine the minimum and maximum response and design variables (uncertain and decision variables).
- 2. Use Design of Experiment to generate simulation cases.
- 3. Run all simulation cases using the UTCOMP-IPhreeqc simulator.
- 4. Import the simulation results to DoE for screening out the significant parameters.
- Use response surface methodology to generate cases for significant design parameters.
- 6. Run all simulation cases using the UTCOMP-IPhreeqc simulator.
- 7. Import the simulation results to RSM to build the response surface model.
- 8. Perform numerical optimization using the created response surface and validate the results using the UTCOMP-IPhreeqc simulator.

5.3 DOE AND RSM RESULTS FOR THE CHEMICAL EOR OPTIMIZATION

Most data needed for simulation is obtained from Chapter 4. The quarter 5-spot 3-D Cartesian grid model with 10x10x3 gridblocks is used for this study. A heterogeneous model is considered by generating permeability distribution.

5.3.1 DESIGN OF EXPERIMENT

The cumulative oil recovery is chosen as the objective function. Five design variables including (3) uncertain and (2) decision variables are considered for sensitivity analysis. The uncertain design variables are reservoir permeability, heterogeneity (V_{dp}) and crossflow (k_v/k_h ratio). The decision design variables are polymer concentration in injected polymer-water slug (ppm) and the salinity of injected water (mg/l). Two-level fractional factorial design is applied for experiment. Table 5.1 shows five design parameters with the range of each variable. For simplification each parameter is assigned by letter. Table 5.2 shows simulation runs based on the two-level fractional factorial design. Based on the five selected design variables, 32 simulation runs are suggested by two level fractional factorial design.

	Variable	Symbol	minimum	maximum
Objective FunctionCumulative Oil Recovery (%)			-	-
Uncertain Variables	Reservoir Permeability (mD)	А	200	1000
	Reservoir Heterogeneity (V _{dp})	В	0.6	0.75
	kv/kh Ratio	С	0.1	1.0
Decision Variables	Polymer Concentration (ppm)	D	100	1000
Decision variables	Salinity of Injected Water(mg/l)	Е	8504	85059

Table 5.1: Two-level fractional factorial design variables

	Uncertain Variables			Decision Va	Response Variable	
Run	Reservoir Permeability (md)	Reservoir Heterogeneity (V _{DP})	k _v /k _h Ratio	Polymer Concentration (ppm)	Injected Water Salinity (mg/l)	Cumulative Oil Recovery (fraction)
1	200	0.6	1.0	100	8504	0.527
2	200	0.75	1.0	100	85059	0.335
3	200	0.6	1.0	100	85059	0.459
4	200	0.75	0.1	1000	85059	0.313
5	1000	0.6	1.0	100	8504	0.637
6	200	0.6	0.1	100	85059	0.389
7	1000	0.6	0.1	100	85059	0.563
8	1000	0.75	0.1	1000	85059	0.531
9	200	0.75	0.1	1000	8504	0.400
10	200	0.6	0.1	1000	8504	0.500
11	200	0.75	1.0	1000	85059	0.335
12	1000	0.6	1.0	1000	85059	0.607
13	200	0.75	1.0	100	8504	0.380
14	1000	0.75	0.1	1000	8504	0.638
15	1000	0.75	1.0	1000	85059	0.555
16	200	0.75	0.1	100	85059	0.260
17	1000	0.75	0.1	100	8504	0.601
18	1000	0.6	1.0	1000	8504	0.712
19	200	0.6	1.0	1000	8504	0.540
20	200	0.75	0.1	100	8504	0.290
21	1000	0.75	1.0	1000	8504	0.655
22	200	0.6	0.1	100	8504	0.456
23	1000	0.6	0.1	100	8504	0.613
24	1000	0.75	0.1	100	85059	0.536

 Table 5.2: Design of Experiment simulation runs based on the two-level fractional factorial design

25	1000	0.6	0.1	1000	85059	0.578
26	1000	0.75	1.0	100	85059	0.573
27	1000	0.6	0.1	1000	8504	0.700
28	200	0.75	1.0	1000	8504	0.440
29	200	0.6	0.1	1000	85059	0.402
30	1000	0.6	1.0	100	85059	0.580
31	200	0.6	1.0	1000	85059	0.449
32	1000	0.75	1.0	100	8504	0.638

Table 5.2: continued.

Based on the UTCOMP-IPhreeqc simulation runs, the sensitivity analysis is performed using DoE results are presented in the form of the half normal plot, Pareto chart, analysis of variance table (ANOVA) in order to identify the ranking of significant and insignificant design parameters affecting the cumulative oil recovery and screening out insignificant parameters.

Figure 5.1 is the half normal plot which identifies any parameter or the combination of parameters that deviate from straight line of normal distribution. The figure shows that parameter reservoir permeability has the largest deviation from straight line and the most significant parameter that affects cumulative oil recovery. The second and third parameters are the salinity of injected water and reservoir heterogeneity, respectively.



Standardized Effect

Figure 5.1: Half-Normal Plot (Sensitivity Analysis).

Figure 5.2 is the Pareto chart which shows the ranking of the five parameters and their effect on the cumulative oil recovery. The significance of any type of parameters is also determined in ANOVA table where a parameter (Prob>F) having a value less than 0.05 is counts as a significant parameter in column six of Table 5.3. where degree of freedom for the model is the number of model terms, including the intercept, minus one, mean square estimate of the model variance, calculated by the model sum of squares divided by model degrees of freedom, F value is the test for comparing model variance

with residual (error) variance, and P value is the probability of seeing the observed F value if the null hypothesis is true. Table 5.3 represents the ANOVA table where is clearly shown that parameters A, B, C, D, E, AB, AC, CD, DE, and ABD are significant model terms. Table 5.4 and Figure 5.3 show the effect of design parameters on response variable (cumulative oil recovery) where can be seen that reservoir permeability contributes 69.04%, injected water salinity 10.46%, reservoir heterogeneity 9.97%, crossflow 2.79%, and polymer concentration 1.76%.



Figure 5.2: Pareto Chart (Sensitivity Analysis).

Source	Sum of Squares	Degree of Freedom	Mean Square	F-value	P-value
Model	0.47	12	0.039	416.52	< 0.0001
A-reservoir permeability	0.33	1	0.33	3463.90	< 0.0001
B-reservoir heterogeneity	0.047	1	0.047	500.22	< 0.0001
C-crossflow	0.013	1	0.013	140.10	< 0.0001
D-polymer concentration	8.385E-003	1	8.385E-003	88.43	< 0.0001
E-salinity of injected water	0.050	1	0.050	524.88	< 0.0001
AB	0.016	1	0.016	164.27	< 0.0001
AC	2.080E-003	1	2.080E-003	21.94	0.0002
AD	7.200E-005	1	7.200E-005	0.76	0.3944
BD	3.125E-006	1	3.125E-006	0.033	0.8579
CD	1.128E-003	1	1.128E-003	11.90	0.0027
DE	4.232E-003	1	4.232E-003	44.63	< 0.0001
ABD	3.528E-003	1	3.528E-003	37.21	$< \overline{0.0001}$

Table 5.3: ANOVA table (Sensitivity Analysis)

Table 5.4: Effect of design parameters on response variable

Effect of Design Parameters on Response Variable				
Design Parameters	Contribution (%)			
Reservoir Permeability	69.04			
Reservoir Heterogeneity (V _{dp})	9.97			
Crossflow (k _v /k _h)	2.79			
Polymer Concentration	1.76			
Injected Water Salinity	10.46			



Figure 5.3: Effect of design parameters on response variable.

5.3.2 RESPONSE SURFACE METHODOLOGY

RSM diagnostic plots we use for the estimation are Box-Cox plot, Normal plot of Residuals, and Predicted vs. Actual plot. Figure 5.4 is the Box-Cox plot, which is a tool for determining the most appropriate power transformation where the lowest point represents the value of lambda that results in the minimum residual sum of squares in the transformed model. The potential for improvement is greatest when the range of the maximum to minimum response value is greater than 3 and in our case the lambda is 1 which means there is no need for transformation.



Figure 5.4: Box-Cox plot.

Figure 5.5 is the Normal Plot of Residuals, which shows the normally distributed residuals. This probability plot indicates whether the residuals follow a normal distribution, in which case the points in plot will follow a straight line.



Externally Studentized Residuals

Figure 5.5: Normal plot of residuals.

Figure 5.6 is the Predicted vs. Actual plot, which shows whether the generated equation of cumulative oil recovery of RSM match the actual cumulative oil recovery. If predicted vs. actual matching line is straight and slope is close to one the generated equation of surface response model predicts the cumulative oil recovery accurately.



Figure 5.6: Actual vs. Predicted plot.

The linear response surface equation for cumulative oil recovery is as follows: $Cumulative \ oil \ recovery = 1.12812 - 5.02656E - 004 \times A - 1.20616 \times B + 0.088279 \times C - 2.20418E - 004 \times D - 6.63104E - 007 * E + 1.16319E - 003 \times AB - 4.47917E - 0.005 \times AC + 5.16667E - 005 \times AD + 4.57407E - 004 \times BD - 2.93210E - 005 \times CD - 6.67639E - 010 \times DE - 7.77778E - 007 \times ABD$ (5-3)

where A is the average reservoir permeability (mD), B is the reservoir heterogeneity (V_{dp}) , C is the crossflow (k_v/k_h) , D is the polymer concentration in injected solution (ppm), and E is the salinity of injected water (mg/l). The combination of parameters is 109

represented by the product of letters and coefficient, for example in case of ABD, we multiply the coefficient with reservoir permeability, heterogeneity, and polymer concentration of injected solution. The performed optimization using DoE and RSM shows the scenario of the highest cumulative oil recovery in Table 5.1.

The results in Table 5.1 show that the maximum oil recovery can be obtained at reservoir permeability 1000 mD, reservoir heterogeneity 0.6, crossflow equal to 1, polymer concentration in injected polymer-water solution of 1000 ppm, and injected water salinity 8504 mg/l. Figure 5.7 shows the effect of two decision variables which are polymer concentration and injected water salinity on cumulative oil recovery. This figure shows the cumulative oil recovery increases with increasing polymer concentration and decreasing injected water salinity.



D: polymer concentration

Figure 5.7: Cumulative oil recovery based on decision variables.

A 3-D surface representation of the cumulative oil recovery as a function of polymer concentration and injected water salinity (both decision variables) is shown in Figure 5.8. This figure shows that increase in cumulative oil recovery is proportional to polymer concentration in polymer-water solution and inversely proportional to the salinity of injected water.



Figure 5.8: 3-D surface response of cumulative oil recovery at varied decision variables, such as polymer concentration (ppm) and injected water salinity (mg/l).

Finally, we validate the results obtained from RSM for the best scenario where the objective function is cumulative oil recovery with the UTCOMP-IPhreeqc simulator. Figure 5.9 shows the cumulative oil recovery at reservoir permeability 1000 mD, reservoir heterogeneity (V_{dp}) is equal to 0.6, crossflow (k_v/k_h) equal to 1, polymer concentration in injected solution equal to 1000 ppm, and salinity of injected water equal

to 8504 mg/l. The UTCOMP-IPhreeqc simulation results are in good agreements with RSM best scenario. The UTCOMP-IPhreeqc actual simulated results show 71.2% in cumulative oil recovery and RSM predicted is 70.7%.



Figure 5.9: Oil recovery at reservoir permeability 1000mD, reservoir heterogeneity equal to 0.6, crossflow equal to 1, polymer concentration in injected solution equal to 1000 ppm, and salinity of injected water equal to 8504 mg/l.

5.4 CONCLUSION.

DoE and RSM approaches were applied to optimize PWAG process. The best scenario is obtained by maximizing cumulative oil recovery where the effect of the five selected design parameters on cumulative oil recovery is shown in Table 5.4. Our simulation results show that the highest polymer concentration and lowest salinity of injected water are the optimum options for cumulative oil recovery in this study. Predicted RSM results are in good agreement with actual UTCOMP-IPhreeqc simulation results.

CHAPTER 6: SUMMARY, CONCLUSIONS, AND RECOMMENDATIONS

6.1 Summary and Conclusions

This thesis presented simulation work on case studies of sensitivity analysis using the UTCOMP-IPhreeqc simulator. This study was undertaken to investigate the effect of modified geochemistry of injected water on cumulative oil recovery in different types of EOR processes.

The following represents the summary for this research:

- 1. Chapter 1 provided the introduction which consists of problem statement, research objectives, and brief description of chapters.
- 2. Chapter 2 is the literature review where the different mechanisms for incremental oil recovery due to modified (or low) salinity waterflooding in sandstone and carbonate rocks proposed in the literature were discussed. Chapter 2 also included the literature review on different types of modified salinity hybrid EOR processes (e.g., modified salinity polymer flooding, modified salinity alternate gas) and application at laboratory and field scales.
- Chapter 3 introduced the UTCOMP-IPhreeqc simulator, The University of Texas at Austin in-house reactive-transport reservoir simulator. We explained in this chapter why UTCOMP-IPhreeqc is suitable for sensitivity analysis on modified salinity flooding on waterflooding,

continuous gas injection (CGI), water-alternate-gas flooding (WAG), and polymer-water-alternate-gas-flooding (PWAG).

- Chapter 4 presented the sensitivity analysis using UTCOMP-IPhreeqc on waterflooding, continuous gas injection, water-alternate-gas flooding, and polymer-water-alternate-gas-flooding.
- Chapter 5 included the optimization and prediction of actual results of cumulative oil recovery by using Design of Experiment (DoE) and Response Surface Methodology (RSM).
- 6. Chapter 6 is the summary and recommendation for future work.

The following represents the main conclusions from this research:

1. Wettability alteration is still believed to be the reason for the low-salinity effect on oil recovery from carbonates.

- 2. Modified-salinity geochemistry of injected water shows higher cumulative oil recovery than in the case with high-salinity in all types of EOR processes studied in this research.
- Increase of heterogeneity (V_{dp}) of the reservoir hinders the oil recovery. At higher reservoir heterogeneities the significance of including polymer becomes more pronounced.
- Increase in crossflow (k_v/k_h) is beneficial for incremental oil recovery. However, its impact becomes less important in the continuous gas injection process.
- For the cases studied, gas composition does not have any impacts on oil recovery during water-alternate-gas (WAG) injection.

 Neglecting the impact of CO₂ dissolution on the aqueous-rock geochemistry during modified salinity flooding overestimates cumulative oil recovery.

6.2 Recommendations for future work

The following represents the recommendations for future research:

- 1. Including the impact of temperature on different types of EOR processes studied in this research.
- Perform the sensitivity analysis on slug sizes and WAG ratios in processes such as WAG and PWAG flooding.
- 3. The model implemented in UTCOMP-IPhreeqc for modified salinity waterflooding in carbonates is based on calcite dissolution (explicit) and surface reactions (implicit). Although this model mimics some of the experimental observations, this model does not interpret some important aspects of modified salinity waterflooding in carbonates (e.g., the beneficial impact of enriching seawater with sulfate). Hence, this model needs to be improved to interpret more experimental observations.
- 4. In this work we did not study the hybrid process of modified salinity waterflooding and surfactant flooding. This work can be extended to study this hybrid process as well.

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