



## Review article

## Literature review of low salinity waterflooding from a length and time scale perspective

W.-B. Bartels<sup>a,b,\*</sup>, H. Mahani<sup>b</sup>, S. Berg<sup>b</sup>, S.M. Hassanizadeh<sup>a</sup><sup>a</sup> Utrecht University, P.O. Box 80.021, Utrecht, The Netherlands<sup>b</sup> Shell Global Solutions International B.V., Grasweg 31, 1031 HW, Amsterdam, The Netherlands

## ARTICLE INFO

## Keywords:

low salinity waterflooding  
 length and time scale consistency  
 EOR  
 SCAL  
 micro-CT  
 micro-model

## ABSTRACT

In recent years, research activity on the recovery technique known as low salinity waterflooding has sharply increased. The main motivation for field application of low salinity waterflooding is the improvement of oil recovery by acceleration of production ('oil faster') compared to conventional high salinity brine injection. Up to now, most research has focused on the core scale by conducting coreflooding and spontaneous imbibition experiments. These tests serve as the main proof that low salinity waterflooding can lead to additional oil recovery. Usually, it is argued that if the flooding experiments show a positive shift in relative permeability curves, field application is justified provided the economic considerations are also favorable. In addition, together with field pilots, these tests resulted in several suggested trends and underlying mechanisms related to low salinity water injections that potentially explain the additional recovery.

While for field application one can rely on the core scale laboratory tests which can provide the brine composition dependent saturation functions such as relative permeability, they are costly, time consuming and challenging. It is desirable to develop predictive capability such that new candidates can be screened effectively or prioritized. This has not been yet achieved and would require under-pinning the underlying mechanism(s) of the low salinity response.

Recently, research has intensified on smaller length scales i.e. the sub-pore scale. This coincides with a shift in thinking. In field and core scale tests the main goal was to correlate bulk properties of rock and fluids to the amount of oil recovered. Yet in the tests on the sub-pore scale the focus is on ruling out irrelevant mechanisms and understanding the physics of the processes leading to a response to low salinity water. Ultimately this should lead to predictive capability that allows to pre-select potential field candidates based on easily obtained properties, without the need of running time and cost intensive tests.

However, low salinity waterflooding is a cooperative process in which multiple mechanisms acting on different length and time scales aid the detachment, coalescence, transport, banking, and eventual recovery of oil. This means investigating only one particular length scale is insufficient. If the physics behind individual mechanisms and their interplay does not transmit through the length scales, or does not explain the observed fast and slow phenomena, no additional oil may be recovered at core or field scale.

Therefore, the mechanisms are not discussed in detail in this review, but placed in a framework on a higher level of abstraction which is 'consistency across the scales'. In doing so, the likelihood and contribution of an individual mechanism to the additional recovery of oil can be assessed. This framework shows that the main uncertainty lies in how results from sub-pore scale experiments connect to core scale results, which happens on the length scale in between: the pore-network scale.

On the pore-network scale two different types low salinity responses can be found: responses of the liquid-liquid or the solid-liquid interfaces. The categorization is supported by the time scale differences of the (optimal) response between liquid-liquid and solid-liquid interfaces. Differences in time scale are also observed between flow regimes in water-wet and mixed-wet systems. These findings point to the direction of what physics should be carried from sub-pore to core scale, which may aid in gaining predictive capability and screening tool development. Alternatively, a more holistic approach of the problems in low salinity waterflooding is suggested.

\* Corresponding author at: Utrecht University, P.O. Box 80.115, 350TC, Utrecht, The Netherlands.

E-mail address: [W.Bartels@uu.nl](mailto:W.Bartels@uu.nl) (W.-B. Bartels).<https://doi.org/10.1016/j.fuel.2018.09.018>

Received 25 February 2018; Received in revised form 1 September 2018; Accepted 5 September 2018

Available online 13 September 2018

0016-2361/ © 2018 The Authors. Published by Elsevier Ltd. This is an open access article under the CC BY license

[\(http://creativecommons.org/licenses/by/4.0/\)](http://creativecommons.org/licenses/by/4.0/).

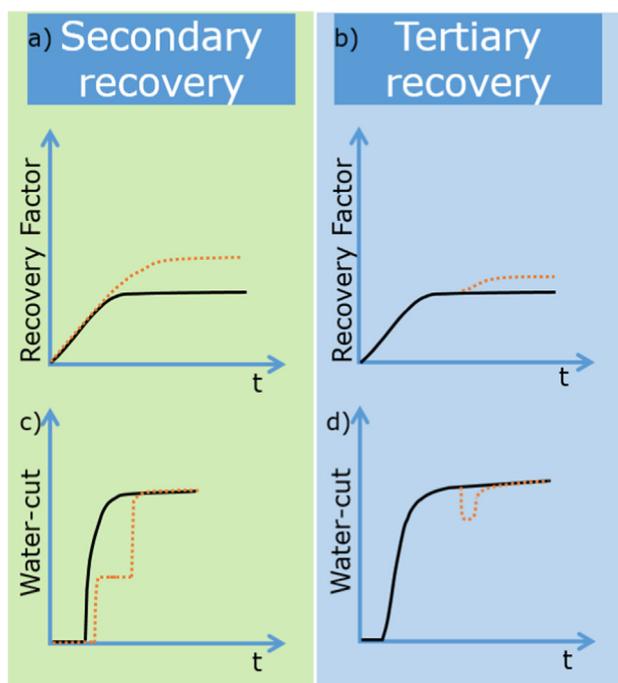


Fig. 1. Cartoon of secondary and tertiary low salinity waterflooding. The low salinity schemes are shown as orange dashed lines. The increase in recovery factor in a) and b), the dual-step water-cut in c), and the decrease in water-cut in d) are all manifestations of a response to low salinity waterflooding.

### 1. Low salinity waterflooding and predictive capability

#### 1.1. Definition and motivation of low salinity waterflooding

Recovery techniques commonly described as low salinity waterflooding aim at improving recovery by reducing and/or modifying the ionic content of injected brines [1–9]. The same group of recovery techniques have been described by other terms such as Smart waterflooding [10–13], LoSal [14,15], Advanced Ion Management [16,17], or Ion Tuning [18,19]. A cartoon of a successful application of this technique is shown in Fig. 1, in which the effect of low salinity water

injection is indicated as a dashed orange line.

Throughout this paper, the terms microscopic displacement efficiency, microscopic sweep efficiency, and macroscopic sweep efficiency are used. Microscopic displacement efficiency and microscopic sweep efficiency are used interchangeably. Both refer to the fraction of oil that has been recovered from (a) pore(s) that has/have been swept. Macroscopic sweep efficiency is standard reservoir engineering terminology and related to areal and volumetric sweep, which therefore is related to the overall result of the oil recovery process (including the effect of e.g. well patterns, thief zones etc.). These definitions follow the Schlumberger Oilfield Glossary [20].

Therefore we formulate the main motivation for field application of low salinity waterflooding as the acceleration of oil recovery, i.e. getting oil out by injecting less volumes of water due to improvement in microscopic sweep efficiency. From a commercial perspective reducing the residual oil saturation is of secondary importance [21,22]. The acceleration and/or residual oil reduction can be achieved by injecting low salinity water directly after primary depletion (secondary mode) or after a secondary high salinity brine waterflood (tertiary mode). Both scenarios are depicted in Fig. 1.

#### 1.2. Development of low salinity waterflooding research

Over the past fifty years, particularly since 1990, the activity around this group of techniques has increased, which is reflected in the number of publications related to the topic displayed in Fig. 2. Prediction of the future trend is difficult, and can be influenced significantly by the uptake and actual field deployment of the technology by the industry.

The first studies on intentional use of low salinity water to improve recovery were published by Reiter [24] and Bernard [25], although studies related to the role of salinity in clay swelling, and consequently on recovery efficiency in waterflooding, have been around longer [26,27]. In parallel to the development of literature revolving around low salinity waterflooding, the literature on wettability and wettability alteration in a more general context has evolved, but a detailed review thereof is beyond the scope of this work. The reader is referred to Anderson [28–34].

Despite the significant interest in the topic of low salinity waterflooding and the progress made over the past decades, it cannot be predicted reliably which crude oil, brine, rock (COBR) system is responsive to low salinity waterflooding, what the amount of additional

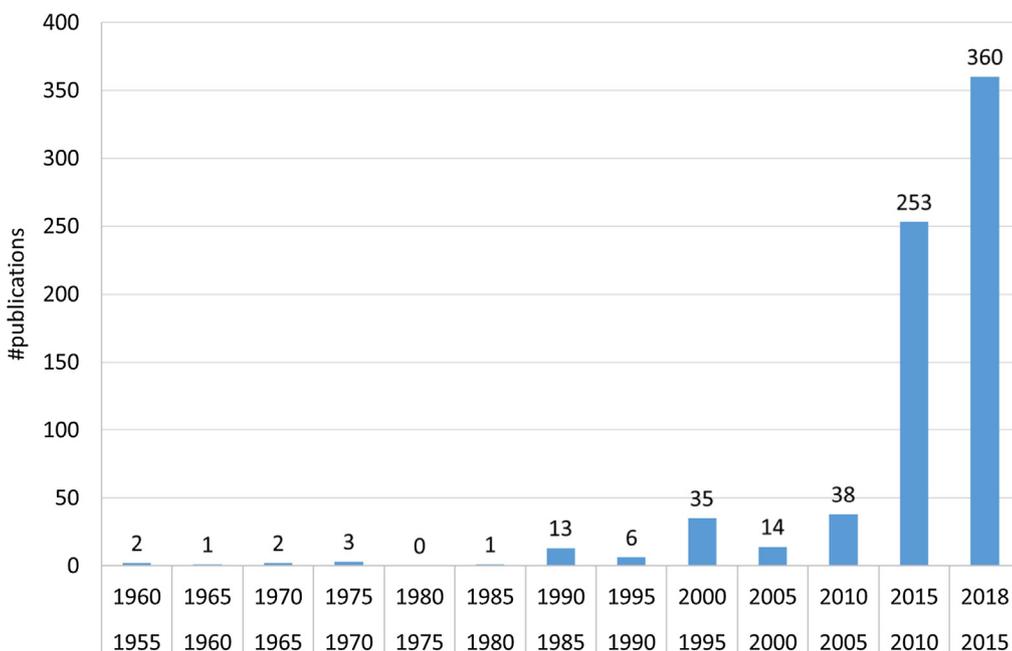
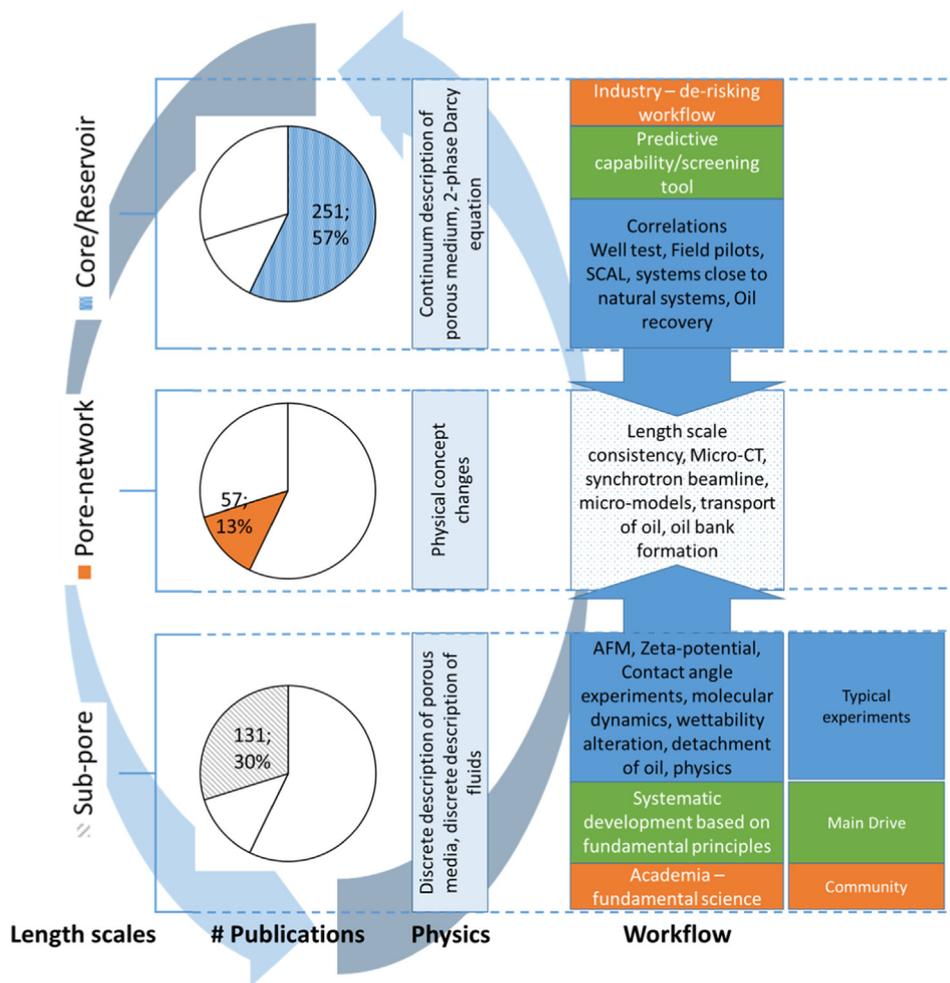


Fig. 2. The increase in number of publications since the mid 50's. The graph was created combining query data from Publish or Perish [23], Query: low salinity oil brine ion water flood NOT surfactant polymer coast plant bio, with the references in this paper, and a manual search on low salinity waterflooding. Each bin represents papers published in the interval including the lower boundary up to the upper boundary (e.g. 1955 ≤ publication year < 1960).



**Fig. 3.** Different approaches to low salinity waterflooding research are shown in the central column, including typical tools used by industry and academia. The industry often uses a top-down approach, with the main goal gaining predictive capability on oil recovery of natural systems. Academia uses generally a bottom-up approach, with as main driver scientific interest and as goal understanding the influence of salinity on wettability and fluid flow. Both have not yet achieved predictive capability, but combining the efforts on the intermediate length scale the pore-network scale may provide insight. The pie charts indicate the number of publications in each length scale. The number of publications related to the pore-network scale experiments is significantly less than the number of publications on sub-pore and core/reservoir scale experiments.

oil would be, and in what time the (additional) oil can be recovered. It is possible to demonstrate effective individual mechanisms in model systems that lead to a response, and it is possible to upscale Special Core Analysis (SCAL) experiments to the field scale for fields that are known to be responsive. However, based on the literature cited in this review, the contribution of individual mechanisms on short length scales to core scale additional oil recovery, has not been quantified yet in a consistent way. It may be that this is an ambitious goal to reach in the short term due to intrinsic complexity of the process and the different approaches followed to research the topic.

Papers referred to in this review show that in industry a risk-driven workflow is used, usually following a route from the application side down to the smallest required level of detail, to assess feasibility for field deployment. This is a sharp contrast with a more fundamental-science driven workflow in academia, where starting from a more detailed picture mechanisms are systematically building on top of each other, approaching the application side. This issue is illustrated in Fig. 3. The fact that there is not a clearly formulated motivation and problem statement contributes to the difficulty of taking meaningful steps: it means that the problem(s) is/are not clearly defined enough to progress to solving complex cases and attempt modelling of the complete problem set.

### 1.3. Conventional reservoir engineering workflow and correlations

As will be described in more detail in the next paragraph, feasibility of low salinity waterflooding for a field/reservoir is assessed by following the conventional reservoir engineering workflow [35–38], leading to reservoir modelling with two-phase flow equations.

These reservoir models are used to assess the risk of recovery strategies, especially regarding the rate and amount of recovery. Therefore, reservoir models nowadays use a stochastic approach to assess the influence of variations of input parameters to the overall output of the reservoir (see e.g. [39]).

The models are statistically populated with parameters obtained from well logs, production history, correlations between rock and fluid properties and recovery, routine and SCAL laboratory workflows, where the focus of SCAL is on obtaining rock capillary pressure and relative permeability curves. Based on this input, forward predictions and uncertainty assessments are made on production rate and oil recovery factor.

Although the SCAL workflow varies significantly between institutions, in general the low salinity effect is represented through (salinity dependent) flow parameters like relative permeability-saturation and capillary pressure-saturation functions. These are typically experimentally determined in the laboratory through predominantly SCAL techniques, such as corefloods, centrifuge experiments, and porous plate tests. If these tests show a shift in relative permeability curves to a higher relative permeability for the oil phase and/or a lower relative permeability for the water phase, field application is justified from the experimental side (see e.g. [40,41]). Subsequently, the reservoir is further subjected to economic evaluation.

Implicitly the assumption is that the flow in laboratory samples (cm-m) is representative for the flow in the reservoir (up to km). This is justified, as the conceptual description of flow is the same, i.e. two-phase Darcy equation with relative permeability and capillary pressure curves. The major difference is the level of heterogeneity. Therefore, the laboratory results in turn are presumed to be suited for

(heterogeneity) upscaling. However, uncertainty in the geological structure, geological heterogeneities, and natural variability in experimental outcomes may reduce the representativeness; hence the stochastic approach taken in modelling.

In addition, the shift in relative permeability curves for the tested COBR system may not be the optimal shift that can be achieved. This is true even for fields that are known to be susceptible to low salinity waterflooding, for which the conventional approach detailed above provides sufficient information to start field implementation. However, to optimize the injection brine, a large number of SCAL experiments should be conducted, which is not feasible because of constraints in time and availability of rock samples [42,36].

Therefore, it is often attempted to link the response of a system to parameters of the rock and fluids that are more accessible and are routinely taken, such as salinity, ionic strength, divalent cation content, mineralogy (e.g. clay content), porosity, permeability, initial water saturation, ageing time, total acid number, total base number, and interfacial tension (e.g. [43–45]).

Some of the aforementioned parameters find their origin on sub-pore or pore scale, but try to complement core scale data. For instance, local mineralogy is a property which is pore or sub-pore scale. Unfortunately, including these extra parameters did not change the result of the multivariate statistics applied to the wider body of literature, which has not yielded clear favorable rock and fluid parameters. An example of this can be found in Fig. 4 and Aladasani et al. [44] for sandstone rocks, and Sohal et al. [45] for carbonate rocks, although Suijkerbuijk et al. [43] found that initial wettability and the presence of divalent cations in formation water influences the effectiveness of low salinity waterflooding.

Lack of correlation is somewhat expected, because even for normal waterflooding such a correlation does not exist, let alone for low salinity waterflooding which is undoubtedly a more complex process. There are multiple possible reasons for that. It simply might be that there are important parameters that have not been considered. An additional issue may be the implicit selection of the length and time scales in the experiments, by following the standard reservoir workflow. Alternatively, the scatter may be an effect of the different standards, methods or samples used as data basis for the statistics from the literature. It may also point to an inconsistency between the core scale effects, such as shifts in relative permeability and additional recovery, and the predominantly sub-core scale parameters that are monitored, such as local mineralogy, pH, and acid numbers. Since the description

of effects below the core scale follows different physical concepts (Navier-Stokes flow with interface dynamics, surface forces, electrochemistry, etc. compared to the two-phase Darcy equation), this is not too surprising. Another possible reason is a mismatch in time scales between core scale observations and natural time scales of the sub-pore level effects [8,46].

## 2. Necessity for length scale consistency

### 2.1. Recent trends in low salinity waterflooding experiments

Some recent experiments in the low salinity space on smaller length scales than the core scale, see Section 2.2, are believed to be more relevant for understanding the underlying mechanisms of low salinity waterflooding. In other words, these experiments deviate from the standard workflows which mainly conduct core scale experiments. This trend has exposed many disciplines predominantly situated in academia to petroleum industry workflows. These disciplines include for instance surface science, colloid science, chemistry, and molecular dynamics, see Fig. 3. On one hand this gives much more information, on the other hand it may also reduce focus and create possibilities for confusion. In the end, to address the predictability issue in low salinity waterflooding, information on smaller length scales should be used to gain insight in reservoir behavior. Especially, in helping to gain the ability to predict beforehand which reservoirs are responsive and how much additional oil can be recovered. This is a departure from the common risk reduction workflow of the industry which is based on easy accessible parameters and properties, see Section 1.3.

However, the increase in number of publications, which was shown in Fig. 2, has only led to partial solutions of the problems. There are still gaps in understanding to fill and consolidation steps to take. To improve clarity and avoid confusion, we will refine the definition of what is termed ‘low salinity effect’ in published literature. This refinement is particularly necessary when considering the length scale at which low salinity waterflooding is investigated. After all, an increase of recovery when reducing salinity is only valid for length scales at which recovery can be measured; recovery is not relevant when conducting, for instance, atomic force microscopy measurements. Therefore, ‘low salinity effect’ as used in literature is subdivided in a low salinity effect (LSE) and low salinity recovery (LSR).

To clarify these terms further, consider that a LSE can be different for each length scale and mainly reflects the response of a system upon

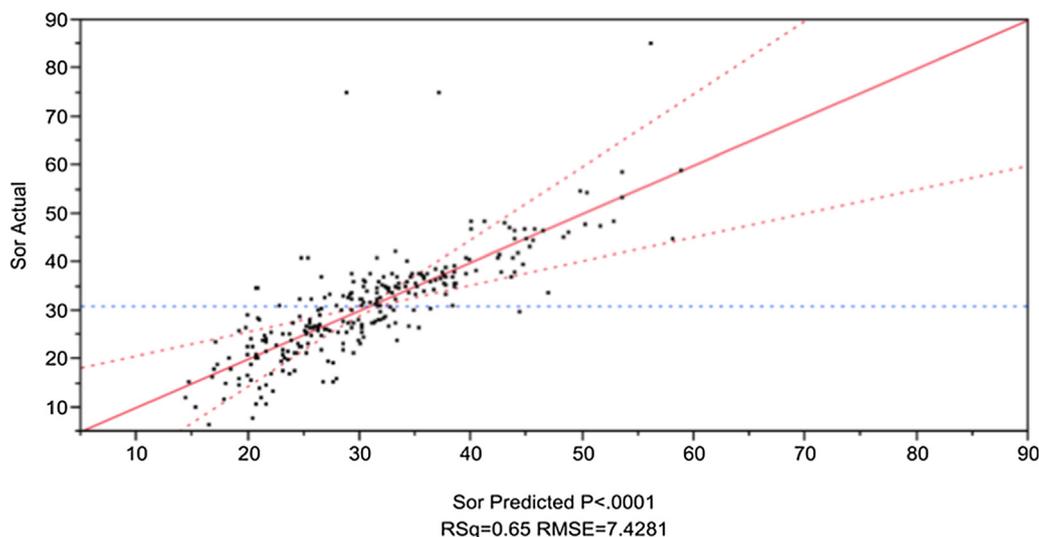
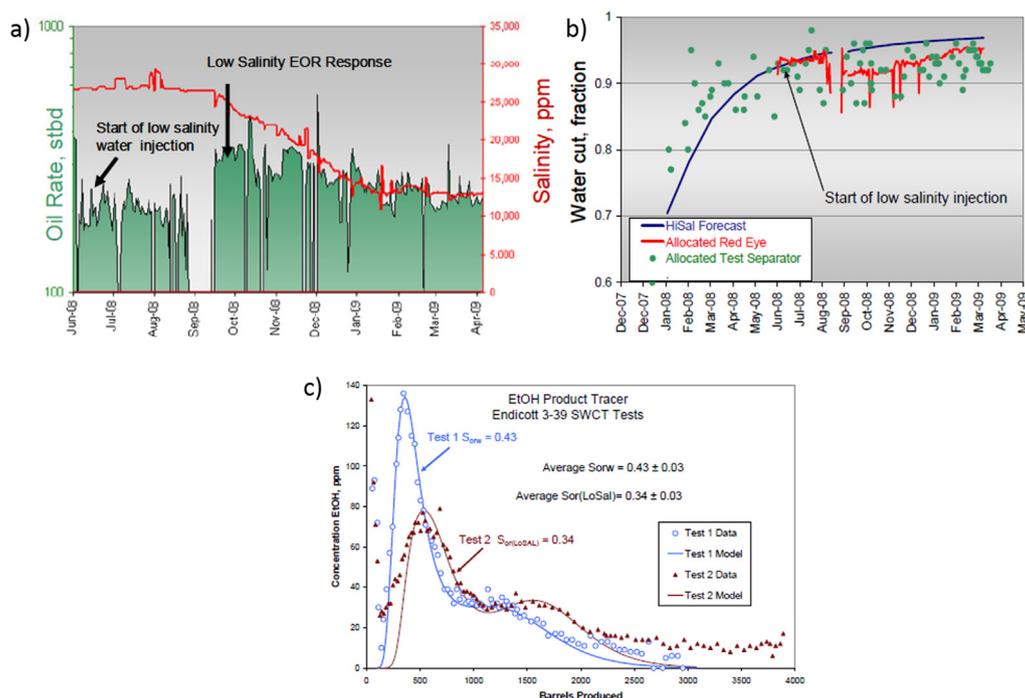


Fig. 4. An example of residual oil ( $S_{or}$ ) correlations computed by multivariate statistics on sandstones by Aladasani et al. [44]. They found a weak correlation of 65% between the experimental and predicted residual oil saturations. The solid line indicates the multi-variable regression curve, the red dashed lines show the confidence level.



**Fig. 5.** Example of successful field result in the Endicott field in Alaska. a) shows the increase in oil production rate accompanied by the decreasing water-cut in b) [72] whereas c) shows the decrease in remaining oil saturation [84].

exposure to low salinity water. There are many such effects, that often relate in some way to the Debye screening length, which is salinity dependent. In research involving atomic force microscopy, consider the change of adhesion forces and desorption of crude oil components from a solid. In micro-models, changes in, for instance, contact angles and interface curvatures can be considered as LSE. In 3D porous media visualized by X-ray tomography, the alteration of oil clusters (break-up and coalescence) by LS water is a manifestation of the LSE. Note that whilst all these effects are likely to occur when changing salinity, it does not mean that on core and field scale more/faster oil will be recovered, which is in the end the main goal of low salinity research. In other words, LSE does not mean LSR will be observed, and a LSR is the macroscopic concept that is of economic interest.

In light of the workflows in Fig. 3, this means that most of the literature starts approaching the whole LSR problem, which is at field and core scale and therefore of main interest, by making it an LSE problem (according to the top-down approach). Once LSE is found at a length scale below core or field scale, this is immediately assumed to be equal to seeing LSR at those larger length scales. In other words, a cause-effect relation is assumed between the two length scales, which is, as demonstrated in the previous paragraphs, not necessarily true. A bottom-up approach, which considers each length scale between sub-pore and core or field scale, is needed to confirm an LSR.

In the following sections, the LSE found using different sub-pore scale techniques is addressed, followed by a discussion about systems that potentially show additional recovery (LSR) on core scale systems and larger. Additionally, emphasis is placed on the protocols of SCAL experiments.

## 2.2. Oil adhesion and detachment from solid surfaces: the sub-pore scale

The dependence of oil adhesion/detachment to mineral surfaces on brine chemistry has been reported repeatedly. Contact angle measurements on (model) surfaces [47–57,8], zeta-potential measurements [58,52–54,57,7,59,22], and Atomic Force Microscopy measurements [60,47,61,49,62–67] show for systems responsive to altering salinity a change towards oil release, i.e. more water-wet contact angles, a larger

difference in solid-liquid zeta potentials between high and low salinity systems, and a reduction of adhesion forces.

The results show a strong dependence on the initial wettability state of the systems and that a response to low salinity waterflooding could be found in most COBR systems. However, it is unclear whether the response (LSE) will lead to additional recovery (LSR), since the systems under investigation are all below representative elementary volume [68]. Therefore, these experiments inherently cannot explain why responses on the core scale and larger sometimes do not occur. After all, there might be effects on the scale of multiple pores and/or related to the connectivity of the oil phase that are not observed in these small scale experiments.

## 2.3. Production of oil from rock: the core and reservoir scale

### 2.3.1. Reservoir tests: observations and results

Depending on the mode of low salinity injection (secondary or tertiary mode), the response of the reservoir could have different signatures or profiles. This can be modelled theoretically using Buckley-Leverett analysis [69,70]. In secondary mode low salinity waterflooding, the breakthrough time is delayed compared to high salinity waterflooding, and the water-cut at the producer follows a dual-step profile similar to that in Fig. 1c. The dual-step characteristic is related to the oil production originating from the reduction of remaining oil behind the displacement front, i.e. microscopic displacement efficiency improvement. In tertiary mode, the low salinity effect reverses the water-cut profile as additional oil is produced. This is shown in Figs. 1d and 4b.

Observations on the field scale show that the timing of oil bank production coincides with low salinity water breakthrough [71–73], as can be seen from the inter-well pilot test done by BP in the Endicott field in Alaska shown in Fig. 5.

Additionally, log-inject-log tests show that in the near-wellbore zone the residual oil saturation is reduced after the injection of low salinity water [71,74]. Single-well-chemical tracer test pilots by Yousef et al. [11] showed that the low salinity effect observed in the laboratory can be reproduced in the field. Skrettingland et al. [75] reported that

lack of response may be caused by an initially water-wet system. Furthermore, some historical field evidence can be found in Robertson [76]. These results show a change in the fractional flow when low salinity water breaks through, in line with the expectations from Buckley-Leverett theory. Furthermore, it shows oil remaining after high salinity brine injection is not true residual oil, since it can be further reduced by injecting low salinity water.

Lager et al. [14,77] showed changes in the ionic composition and pH of the effluent coinciding with the breakthrough of low salinity water, suggesting ion exchange mechanisms may be driving the LSE. This mechanism was unlikely to be dominant as suggested by Suijkerbuijk et al. [78], because cation stripping due to ion exchange can delay the low salinity effect, requiring additional pore volumes (PV). Yet, in the field case shown in Fig. 5a, the additional oil came at the time of the breakthrough of low salinity water.

Another mechanism that got traction is fines migration. Zeinijahromi et al. [79] successfully history matched production data of the Zichebashkoe reservoir assuming a fines migration regime. However, fines migration is generally considered unfavorable since the formation damage is irreversible and may lead to production loss [80,81].

2.3.2. Core scale tests: observations and results

Both corefloods and spontaneous imbibition experiments are

conducted in secondary and/or in tertiary mode. Figs. 6 and 7 show typical results of successful tests. If those tests are conducted on responsive COBR systems, an increase in recovery factor is observed given the same pore volumes injected (PVI), or at a fixed water-cut (typically ranging between 0.95–0.98, [22]). As already mentioned before, the recovery can be related to a change in production rate (i.e. production acceleration), as well as reduction of residual oil saturation as shown for coreflooding in the curves of Fig. 6a. In all those tests, if there is a low salinity effect it is usually produced within several PVI (e.g. [82,83,38]) an observation discussed in more detail in Section 4.2.

This does not mean that at the reservoir scale the same PVI is required. Firstly, the region near the wellbore sees many PVs. Secondly, as discussed in Section 1.3, the coreflooding experiments are mainly used to extract relative permeability functions based on numerical simulation of experimental data (oil production curve, pressure drop over core, in situ saturation profiles versus PVI). Thus the laboratory results cannot be directly applied to the field. The proper approach to translate laboratory data to the field is to use the relative permeability curves (inferred from the coreflooding) in the reservoir simulation model to perform field evaluation and design.

For proper quantification of low salinity additional oil, it is essential to conduct both secondary and tertiary low salinity waterflooding to extract high salinity and low salinity relative permeability functions [38,40,21]. To account for the capillary-end effect [85,86], which is a

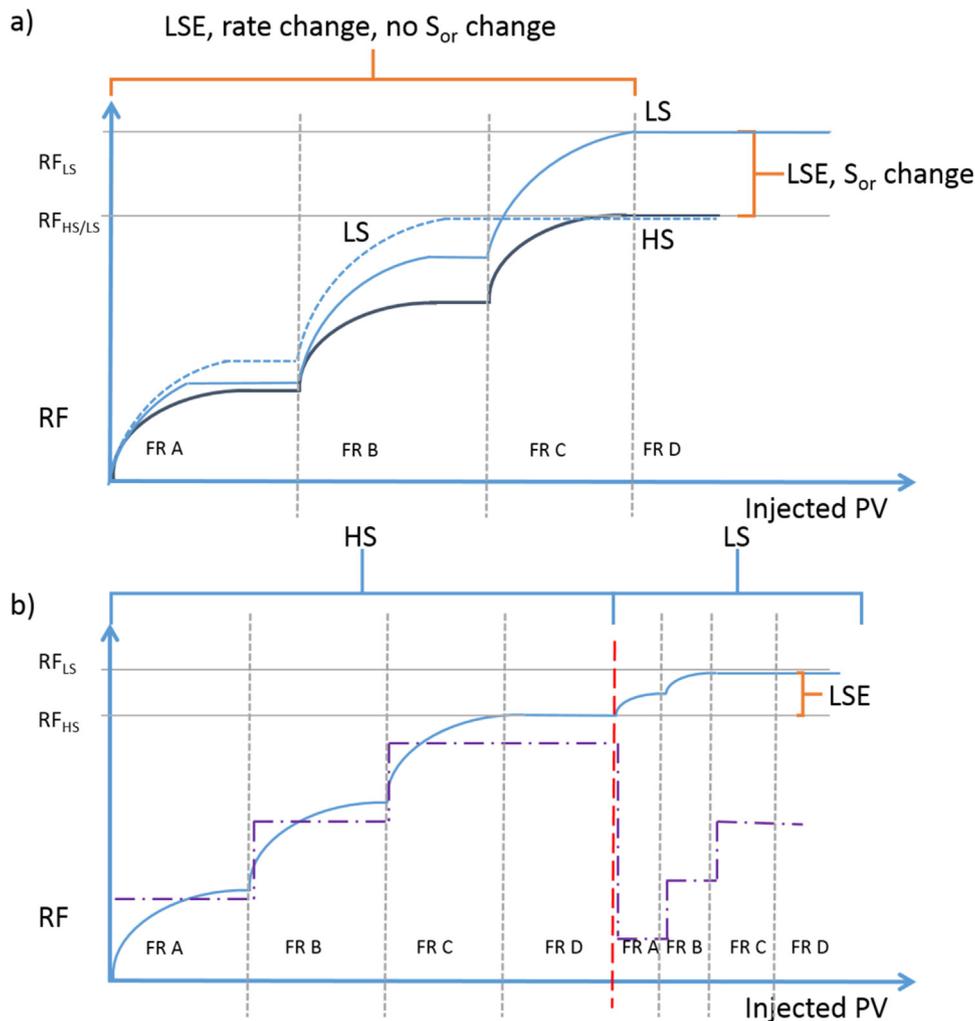


Fig. 6. Cartoon showing the recovery factor, RF, versus injected pore volume, PV, in coreflood experiments in secondary (a) and tertiary mode (b) at increasing flow rates, FR A-D. In a) the LSE/R with (light blue line) and without (dashed line)  $S_{or}$  change are shown compared to a standard high salinity waterflood. In b) the production curve with a LSE in tertiary waterflooding is shown, together with the expected pressure drop (dash-dot line). Pressure drops that are higher for low salinity water than for high salinity brine for the same flow rate imply formation damage.

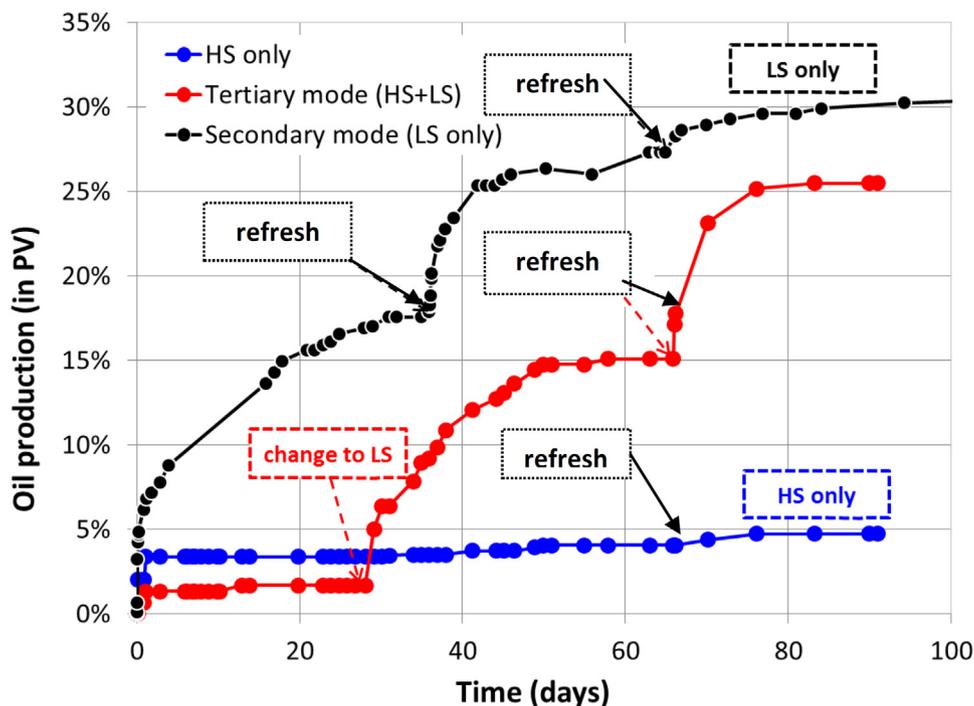


Fig. 7. Spontaneous imbibition test of a system responsive to low salinity water in secondary and tertiary low salinity modes, compared to a base line study of high salinity brine only [40]. “Refresh” indicates points where the liquid surrounding the sample was exchanged. When refreshing the water does not lead to additional production from the sample, it is assumed the maximum production is reached.

laboratory scale artifact, multi-rate injection beyond 1 ft/day and in situ saturation monitoring, as indicated in Fig. 6, are necessary to reduce the uncertainty in the relative permeability measurements.

In Fig. 7, all-faces-open spontaneous imbibition tests (Amott tests) from Sorop et al. [40] are shown. In these additional tests, the production rate and total production is measured whilst the sample is submerged in high salinity brine. When no additional oil is produced, the surrounding brine is switched to low salinity water. The magnitude of the response is a measure for the change in wetting state and a qualitative indicator if a COBR system is responsive to low salinity water. Other groups have also conducted these tests, see works of e.g. Zhang and Morrow [82], Ashraf et al. [3] and Yildiz and Morrow [87].

Usually, it is found that the additional recovery for low salinity waterflooding is larger in secondary mode than in tertiary mode corefloods [88,38,86,45]. A potential reason for this is that mobile oil saturation is less in tertiary mode than in secondary mode.

Additionally, during tertiary mode experiments, the low salinity water may mix with the high salinity brine already present, which may lead to a smoother salinity gradient near the front [89–91]. This may potentially reduce its effectiveness. Finally, it may be that in tertiary mode processes with a longer-time scale play a more important role. The last reason will be expanded in Section 4.2.

General observations from SCAL experiments In addition to the findings directly related to low salinity waterflooding, there are four important general observations regarding protocols of SCAL experiments. Variations in these protocols may influence the outcome of low salinity waterflooding experiments and therefore should be carefully considered:

- Globally, experimental protocols are not standardized. Different groups use different protocols, which makes it difficult to compare results of different studies directly and find commonalities. For instance, the core initialization procedure and the ageing time may vary. Another example is the use of initial oil permeability at connate water saturation to normalize relative permeability curves, whereas other groups use the brine permeability for this. This is related to the debate whether experiments on cores with preserved or restored wettability provide more accurate representations of the reservoir. The groups using preserved cores use the normalization

procedure with initial oil permeability.

- The capillary-end effect is often not considered or not reported even though it can be present in many core scale tests. Oil produced from the capillary-end effect can be a significant volume fraction in coreflooding experiments. This is of importance in mixed- to oil-wet cores, where the imbibition capillary pressure has an extended negative part. The mixed- to oil-wet rocks are seen as more important prospects for low salinity, because mixed- to oil-wet reservoirs usually make up a larger part of the reservoir portfolios of oil and gas companies. Additionally, non-water-wet systems tend to have higher remaining oil saturations, which means they have a higher fraction of oil that may be targeted by low salinity water. So, considering the capillary-end effect is important in a low salinity study. When a significant capillary-end effect exists (related to the area it covers around the core end), the oil production that occurs in corefloods may be partially related to the injection of low salinity water. Thus, the amount of oil coming from the end effect may significantly influence the estimated response of a system. To identify and quantify capillary-end effects in corefloods, usually X-ray saturation monitoring is needed to get saturation profiles in the core and assess the extent of the end effect. Sometimes, bump rates are used to reduce the end effect as discussed in Fig. 6.
- From experiments conducted on core and reservoir scales, mechanisms are usually inferred by an inverse problem. The inversion is in most cases based on pressure drops and injection and production into/from the core (e.g. effluent analysis for fines and pH, and oil and brine production), while details in the core remain hidden or inaccessible. Whereas this method can explain responses, it cannot be used to explain a lack of response, because direct observations are necessary for that. Also, the framework of interpretation (e.g. two-phase Darcy equation) limits the level of insight that can be gained.
- The modest additional oil that is recovered in responsive systems requires more precision and rigor in both protocols and equipment. For instance, as mentioned above, a significant capillary-end effect may adversely affect the results. In addition to that, the additional parameters that must be monitored (pH, salinity, fines content of the effluent etc.) make the tests more difficult to conduct to begin with. This stresses the importance of standardized protocols to allow

direct comparison between studies.

### 3. Suggested mechanisms of low salinity waterflooding

The mechanisms, both inferred/postulated from indirect measurements and directly observed, from sub-pore scale on one hand and the core and reservoir scales on the other hand, include fines migration [92–94,53,95,79], pH change effect [84,2,96,97], multi component ion exchange [98–100], surface-charge-change and double layer expansion [101,57,100,7,8,22]), formation of micro-dispersions [102,97], variations in interface viscoelasticity ([103–107], and references therein), and osmosis [108,109], mineral dissolution [110] or slight variations and combination of those.

For a more detailed overview and discussion on the mechanisms and instruments, the reader is referred to Rezaeidoust et al. [10], Sheng [111], Mugele et al. [112], Myint and Firoozabadi [113], Hamon [114], Jackson et al. [115] and Ayirala et al. [116]. Due to the nature of these mechanisms, which involve solid-liquid and liquid-liquid interaction, most of them can be relevant to both carbonate and sandstone rocks, even though mineralogy of the two rock types are different. However, the most accepted effect of low salinity is that wettability changes from a more oil-wet to a more water-wet state, but to what degree the above listed mechanisms contribute individually is not yet agreed upon.

In Fig. 8, the proposed mechanisms can be categorized into processes which pertain to the solid-liquid interface or the liquid-liquid interface. Logically, these two categories encompass the complete range of physics and chemistry that may be involved in causing a low salinity effect. What remains is combining academic and industry approaches in the length scale consistent framework described in Fig. 3. This may lead to an understanding what physics should be transferred through the length scales to come to predictive capability and eventually a screening tool.

### 4. Length and time scales of core and sub-pore scale processes

As suggested in the sections above, a single mechanism cannot explain all results. Therefore, low salinity waterflooding entails or invokes cooperative physical and chemical processes in which mechanisms cause detachment of crude oil, a more efficient transport (more efficient microscopic sweep and/or different trapping criteria), the (re-) formation of an oil bank, and eventual recovery of oil. The necessity of oil bank formation to production is well known [118]. The effectiveness of these processes seems to be dependent on the initial wettability state

[119,120,43], and the change of that state towards more water-wet conditions see also Section 3.

This leads to a paradox regarding the reduction of residual oil. The first part of the argument is that based on the definition of the capillary number, and the capillary desaturation curves for systems at constant wettability shown in Fig. 9a, a low salinity effect reducing  $S_{or}$  based on capillary desaturation can be ruled out. The reason is that most studies cited here show only small interfacial tension and viscosity changes with changing salinity, so an order of magnitude change of the capillary number cannot be achieved.

The second part of the argument is that the  $S_{or}$  can be changed by wettability alteration and perhaps reduction of trapping, rather than through changing the capillary number. This was discussed in Section 3 and shown in Fig. 8d, e. The paradox lies in Fig. 9b, which shows that moving toward more water-wet states increases the residual oil, whilst spontaneous imbibition tests, and sub-pore scale tests cited before in this paper, indicate increases in recovery and detachment of oil from solids. The detachment was discussed in Section 2.2. The apparent contradiction has been discussed in Masalmeh et al. [86] by considering the difference between the waterflood of a water-wet sample and making the sample more water-wet during a waterflood, and will be repeated in short here.

Based on Fig. 9b, a flood in a mixed-wet sample leads to lower  $S_{or}$  compared to a water-wet sample. When considering tertiary low salinity waterflooding, after the high salinity flood, the lower  $S_{or}$  for the original (mixed-wet) system is reached. Hereafter, the sample is brought in contact with low salinity water. Therefore, the wettability is altered only after mixed-wet  $S_{or}$  was already reached. So, no  $S_{or}$  increase can be observed at most  $S_{or}$  stays constant.

In secondary low salinity experiments, the same logic holds i.e. wettability alteration is only possible for the part of the sample that is in contact with low salinity water, which is at the back of the oil front in this case. The front itself moves through the rock which has the initial mixed-wet state. The low salinity water may cause additional detachment of the crude oil from pore walls or affect interface viscoelasticity which may affect trapping, both discussed in Section 3 and references therein, leading to a reduced  $S_{or}$  compared to a flood in a purely water-wet system.

Also, as explained in previous sections, there is a plethora of studies that downscale from the core scale to smaller length scales, and especially on smaller length scales a response can often be found or demonstrated. The question is, do these responses on small length scales, which often relate to wettability alteration, translate to production on

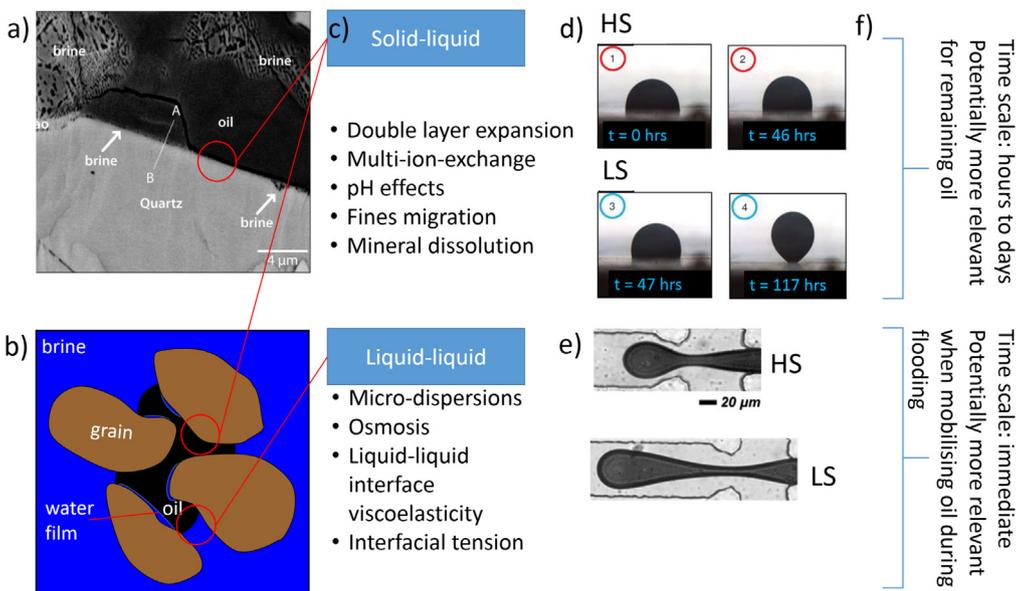


Fig. 8. a) [117] showing what solid-liquid interfaces look like. A thin water film is separating oil from quartz. b) Cartoon depicting solid-liquid interfaces based on Schmatz et al. and liquid-liquid interfaces. c) Mechanisms categorized based on the interface they are thought to work on. d) Examples of solid-liquid and liquid-liquid mechanisms from Mahani et al. [8] and e) Morin et al. [106]. f) Time scales ascribed to mechanisms acting on solid-liquid and liquid-liquid interfaces.

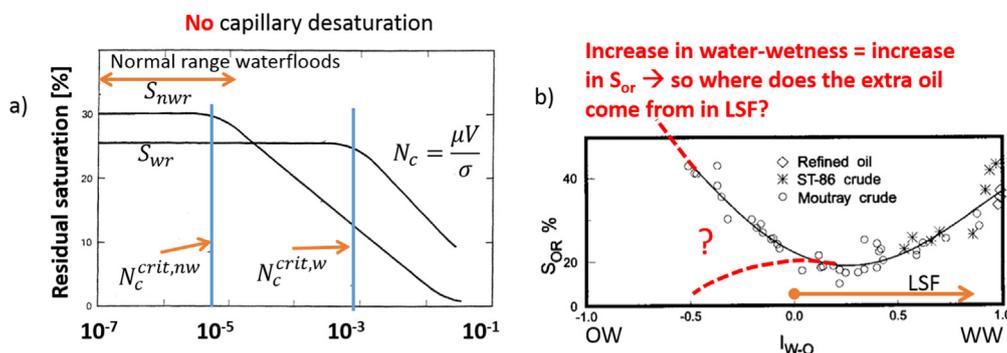


Fig. 9. a) Capillary desaturation curve from Lake [118]. It is well established in literature that additional oil/detachment after exposure to low salinity water is not related to capillary desaturation. Changing brine salinity usually does not have a strong effect on any of the parameters in the capillary number  $N_c$  (viscosity  $\mu$ , flow velocity  $V$  and interfacial tension  $\sigma$ ). Note that the assumption of constant wettability is made for capillary desaturation curves. b) Often additional recovery is observed when moving to more water-wetting conditions in low salinity waterflooding. But  $S_{or}$  increases for water-wet systems as is shown in this figure based on Jadhunandan and Morrow [121]. Recently, Christensen and Tanino [122] have questioned this as well.

large scales or is improvement of connectivity, reduction of trapping, or improvement of microscopic displacement efficiency leading to additional recovery? By considering the intrinsic length and time scales of the mechanisms proposed, the relevance of certain mechanisms may be discarded in the field. For instance, some of these mechanisms require a special level of salinity to occur, such as fines migration (clay deflocculation), which can be avoided by designing the brine composition/salinity [123–125].

Another example is mineral dissolution such as calcite or anhydrite ([110]), which may not occur in all rocks due to the mineralogy type. If it occurs, the brine can become equilibrated/buffered as it moves away from the injector.

Therefore, mineral dissolution loses relevance at field scale, while it may be to some degree important in the laboratory. Hence, small-scale success is not enough and carbonate dissolution can be excluded as primary driving mechanism ([41]).

A suggestion of compatible mechanisms and cooperative physics is shown in Fig. 10 where a combination of wettability alteration by double layer effects a) on a time scale of hours/days is combined with liquid-liquid mechanisms of interface viscoelasticity and ganglion dynamics b) to come to the creation of a more efficient oil bank compared to high salinity c), d). This is an example of two independent cooperative mechanisms that survive the consistency across the scales approach.

#### 4.1. Coalescence, reconnection and transport of oil: the pore-network scale

Adhesion and detachment of oil from solid/rock surfaces upon changing ionic composition of the adjacent fluid is relatively well researched, see 2.2. Production that is consistent with this, is sometimes observed on larger length scales, i.e. core scale or above. However, there is very limited understanding of how these two are connected. In other words, length scales on which collective phenomena and cooperative processes lead to the transport and coalescence of oil and oil bank formation are insufficiently studied. Based on the cited literature, this holds true for mixed-wet flow in general and for low salinity waterflooding in particular which adds chemical processes as additional mechanisms to consider. This is at least part of the reason low salinity waterflooding is not understood: the problem has not been solved on the more general level of flow in mixed-wet systems, yet a more complex specific case is being examined in detail.

Recently, micro-models and (fast) micro-CT scanning techniques have been used to study transport and coalescence of crude oil in both artificial and natural systems. The aim was to find the intrinsic length and time scales of flow in systems with mixed wettability, and the mechanisms involved in low salinity waterflooding that could lead to production. These tools offer valuable additions to core scale

experiments, such as coreflooding and spontaneous imbibition experiments. The main benefit is the addition of pore scale information to the ex-situ parameters that are usually monitored in those experiments, such as pressure, saturation, and production. Based on their temporal and spatial resolutions, micro-model set-ups, benchtop micro-CT systems, and synchrotron beamlines have been used for different types of studies that often address very complex systems. However, to understand low salinity waterflooding on the pore-network scale, it is suggested here that a workflow of increasing complexity should be followed.

This means first the dynamics of flow in water-wet systems on the pore-network scale needs to be understood, followed by flow in mixed-wet systems on the same length scale, and finally chemical processes relevant to low salinity waterflooding can be added.

##### 4.1.1. Flow in water-wet systems

Flow in water-wet systems has been investigated on the pore-network scale for both (quasi-) static [128–134] and dynamic cases [135–139,126]. A key finding from those works, was the identification of a ganglion dynamics flow regime, in which connectivity of individual oil ganglia to connected pathways could be (re-) established by capillary waves generated during snap-off events [126,127]. This is shown in Fig. 10b. It means that even when oil is broken up, there is still the possibility that a connected path is created that mobilizes the oil.

##### 4.1.2. Flow in mixed-wet systems

The next step is investigating the flow dynamics in mixed-wet systems instead of water-wet systems. These works [140,141] showed that the time scale of pore filling events is much longer in mixed-wet systems than in water-wet systems; pore filling in water-wet systems often occurred through Haines jumps. Additionally, besides water filling events also oil filling events can occur in systems of mixed-wettability. The reason is that besides water films also oil films occur [142], which could potentially increase or preserve the connectivity of the oil phase. Therefore, the graph depicted in Fig. 9b should show lower residual oil saturations for more oil wet rock, since the oil will stay connected through oil films. The reason experiments do not find this result may be because recovering oil through oil films takes much longer than the typical duration of flow experiments.

##### 4.1.3. Chemistry and parameters influencing low salinity waterflooding

The final step in understanding low salinity waterflooding on the pore-network scale is to show the response of a mixed-wet system to low salinity water and identify other parameters that influence the response.

To investigate this interplay of processes and parameters influencing the LSE, micro-models have been used. The representativeness of

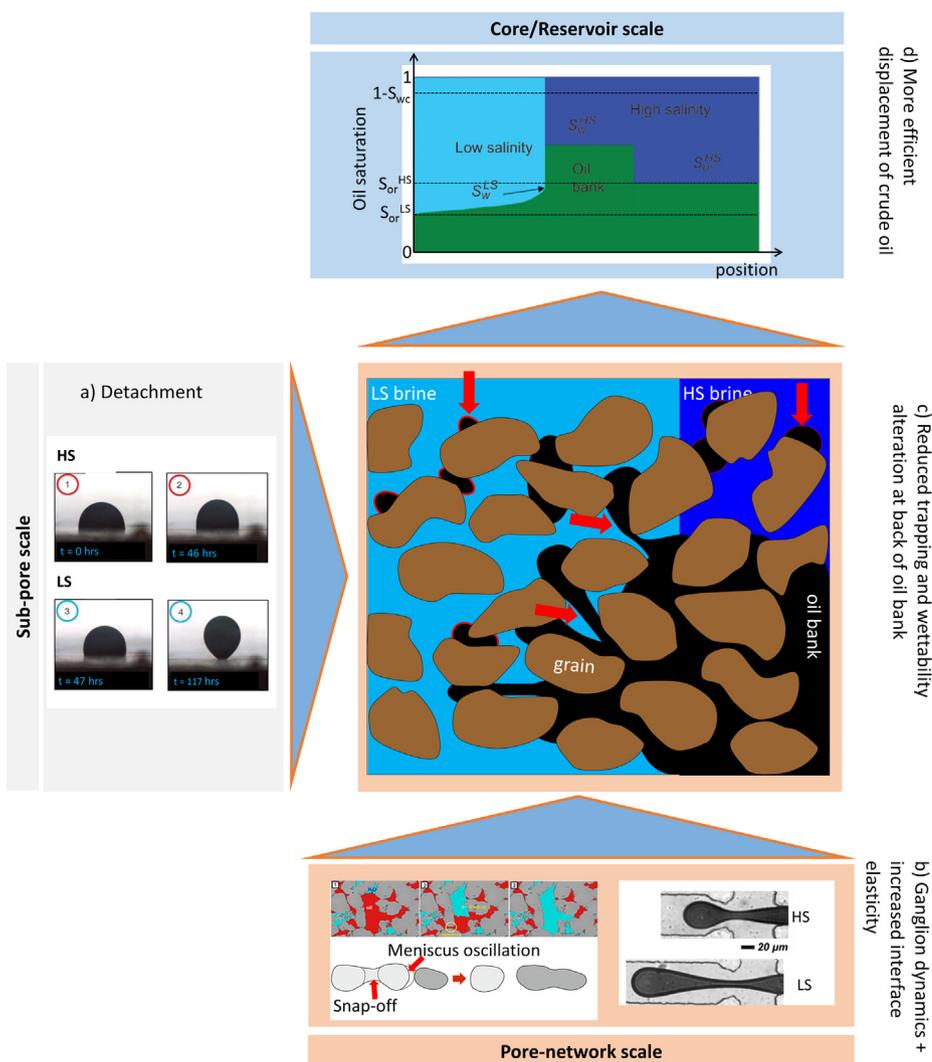


Fig. 10. Illustration how wettability alteration and detachment on the sub-pore scale [8] a), via ganglion dynamics [126] and interface viscoelasticity [106] on the pore-network scale b) may lead to a more efficient back of the oil bank at the pore-network scale c) shown here as elongated necks in oil blobs and contact angle changes (in red) for remaining oil drops – and consequently to a more efficient displacement on the core/reservoir scale [70] in d). While individual mechanisms have been proven, the connection across length scales and contribution to additional recovery at core scale are not. Liu et al. [127] have shown that connectivity is one of the most important factors in relative permeability. Therefore, suppression of snap-off via the mechanisms in b) are likely to support oil bank formation. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

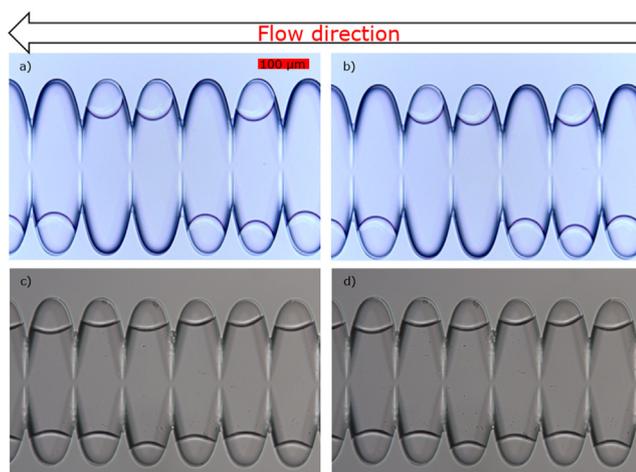


Fig. 11. Micro-model results from Bartels et al. [145] showing no response in systems with model oil (a-d), regardless of the presence of clays (c-d). Response is defined in these small scale experiments as changes in contact angles or interface curvatures, detachment of crude oil from the pore wall and clustering or mobilization of crude oil.

micro-models has been improved by taking SEM images of rocks and etching them into glass to mimic rock pore space geometry closely. Also, the material representativeness for micro-models resembling

sandstones has been improved by Bondino et al. [143], Song and Kovscek [144], Bartels et al. [145] who deposited clay minerals in the models to mimic the composition of sandstone rocks as shown in Fig. 11c, d and Fig. 13.

While Bondino et al. [143] concluded that low salinity water-flooding did not show any improvement in recovery, Song and Kovscek [144] found a significant additional recovery of 14% in tertiary mode. However, it should be noted that the field of view of the micro-model experiment was too small to link this LSE to a LSR on the core scale. Although the tests show that low salinity does cause oil to mobilize, clay migration and formation damage was also observed in their experiment due to the type and salinity of brines used. The field of view issue is similar for pore scale models (which are on millimeter scale) attempting to predict oil recovery, because the flow regimes are not representative for the core scale.

Bartels et al. [145] studied the sensitivity of the LSE to clay content, ageing, and presence of crude oil by means of a clay-coated single channel glass micro-model. They found that all systems were responsive when crude oil was used, as is shown in Figs. 11 and 12. The response consisted of contact angle changes to more water-wet states, and in some cases mobilization. This result underlines that oil polarity and electrical interactions between oil and solid are important, which may occur with crude oil but not with mineral oil, which lacks polar hydrocarbon groups that are responsible for the charged crude oil interfaces. Moreover, the study showed that wettability alteration is not always sufficient to increase oil production.

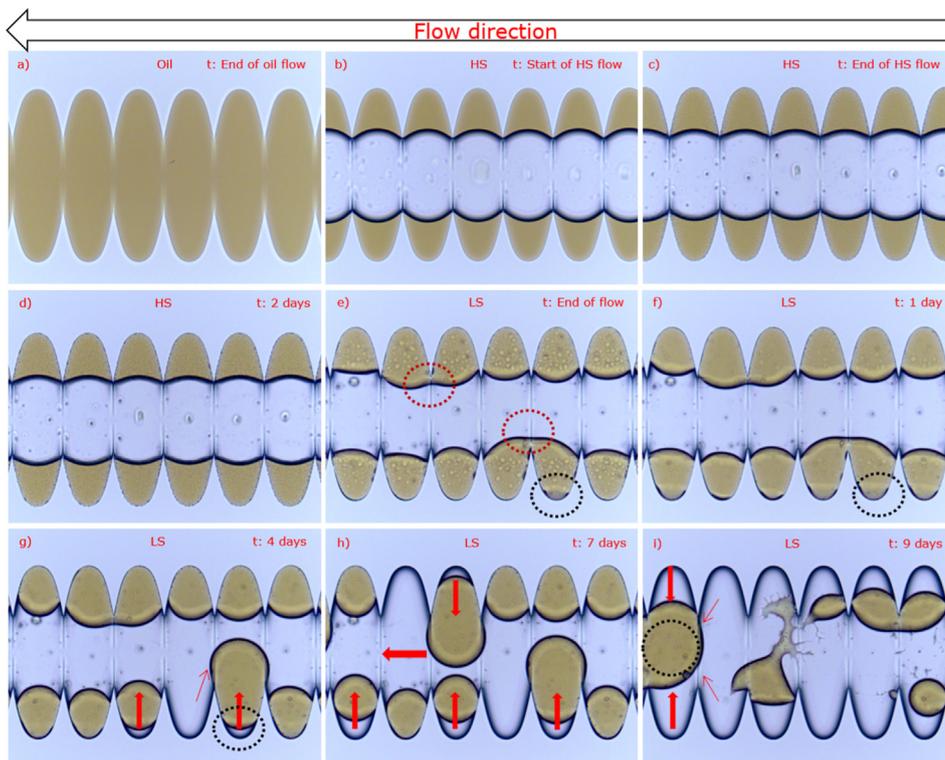


Fig. 12. Improved connectivity on long time scales. Crude oil without clays in the micro-model after a high salinity and after a low salinity waterflood after ageing. (ai) represent the various stages during the experiment. Please note that stable contact angle configurations are reached in high salinity after 2 days. In (d), changing to low salinity water shows contact angle change and mobilization of crude oil, even without flow E (e-i). This experiment also shows that for sandstones clay is not a prerequisite to see a low salinity response.

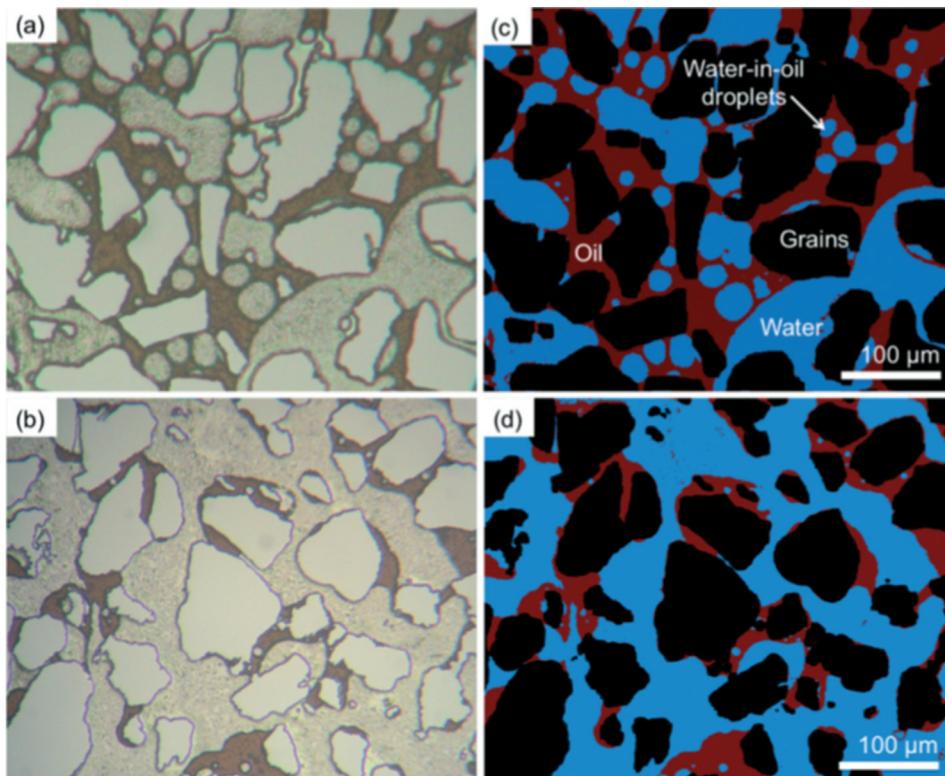


Fig. 13. Results from Song and Kovscek [144] showing improved recovery on short time scales. The images show water (blue), oil (red), and grains (black) and clay is present in the micro-model. a) shows the end of a high salinity (synthetic formation brine) flood and b) shows the result of a low salinity (deionized water) flood. c) and d) show the segmented counterparts of a) and b). The residual oil saturation values following the high salinity and low salinity waterfloods at the pore-network scale were  $S_{or} = 36\%$  and  $22\%$  respectively, indicating a 14% increase in oil recovery using deionized water. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

This highlights that low salinity waterflooding is a multi-length scale process and directly shows that wettability alteration at mineral surfaces (without oil release and/or coalescence) may not lead to more oil at core scale or beyond. In addition, the experiments of Song and Kovscek [144] on one hand and Bartels et al. [145] on the other hand, differ in the time scale of the effect. [144] find an immediate increase of recovery, whereas [145] find the response to increase over the course of

days. However, in [144] de-ionized water was used which is in the formation damage regime.

Open questions for micro-models would be to visualize the potential change in ganglion dynamics, flow paths and thus try to move from microscopic displacement efficiency to macroscopic sweep efficiency when changing brine salinity by using more complex networks. However, studies in 2D micro-models will always be limited by the lack

of long range connectivity of the wetting phase [146].

The next step in the suggested workflow of increasing complexity would be to conduct static and dynamic experiments in 3D using X-ray microtomography. Micro-CT has greatly contributed to two-phase flow studies and the parameters and factors important therein [147,148,136,149,139,150]. Yet, there are only a few studies focusing on (dynamic) enhanced oil recovery processes, in surfactant flooding [149,139] and low salinity waterflooding [151,109,140,152].

X-ray studies that aspire to look low salinity waterflooding, need to capture the dynamics of wettability alteration, which leads to some specific challenges as described below.

Firstly, there is no established way to characterize wettability on the pore-network scale that is addressed in micro-CT work. For (sub-) pore scale systems, contact angles express wettability states. For core scale systems, wettability is implicitly accounted for through capillary pressure saturation and relative permeability saturation curves. Attempts for pore-network scale wettability characterization have been made by Al-Raoush [128], Iglauer et al. [133], Andrew et al. [153], Herring et al. [154], Bartels et al. [145] and Khishvand et al. [152].

In particular, [153] used a distribution of contact angles, [128,133] use cluster size distributions and morphology, and [145,152] use the pore size distribution and the fluid distribution in them to describe the change of the wettability state. The discussion on which method is most appropriate is still ongoing.

Secondly, addition of X-ray contrast agents (dopants), which is deemed necessary for proper imaging, may influence or alter wettability. In the aqueous phase, often potassium/sodium iodide or cesium chloride are used. In the oleic phase, often iododecane and bromodecane are added to distinguish between phases using X-rays in adsorption contrast imaging. Furthermore, the authors found that in particular the dopants for the oleic phase have limited thermal and chemical stability, which inhibits sustaining the contrast between oil and brine during experiments. One solution would be to use phase contrast imaging (e.g. [155,156]), which makes the use of dopants unnecessary.

Moreover, ionizing radiation, especially in beamlines, may inadvertently alter wettability [157,158]. However, this has been reported so far only for chemically pure systems and may not be relevant for COBR systems which have a large degree of natural wettability variation.

Finally, the experimental control of wettability appears to be very difficult. As discussed in previous sections, low salinity waterflooding may depend in part on wettability alteration, which means the wettability state needs to be known in both the initial and final states. The creation of an initial wettability state is better controlled and/or more accurately quantified, using (model) systems in which the desired wettability state is created by chemicals e.g. silanization [128–130,132,131,159,134,154,109].

These artificial wettability states have the downside that they lack representativeness, even though they are well defined, and therefore the link to the original problem is not clear. The studies that control wettability by using the more natural process of ageing ([160] cf. [140,161]) do so in a more qualitative way: they state that one rock is more oil-wet than the other rock depending on ageing time. This makes it difficult to compare the results between different studies.

Despite the experimental challenges outlined above, there are several micro-CT studies that have looked at low salinity waterflooding. These works usually only show that a response to low salinity water is possible, without or with very careful statements how their results will translate to larger length scales. For instance, Shabaninejad et al. [151] show that oil is preferentially released from clays in sandstones and Sandengen et al. [109] combine micro-models and micro-CT to make a case for osmosis as a contributor to the LSE. Recently, Bartels et al. [140] performed dynamic low salinity waterflooding experiments. They showed that pore occupancy changes with change of salinity and the change in trapped oil between carbonate and sandstone samples was very different. Khishvand et al. [152] show a shift in the contact angle

distribution during low salinity waterflooding to reflect more water-wet states. However, translation of these findings to larger length scales has not been attempted.

Summarizing this section, there are quite a few studies describing dynamics of multi-phase flow in water-wet systems and cluster statistics as function of wettability in quasi-static experiments. The first studies investigating multi-phase flow in mixed-wet systems both in micro-models and micro-CT systems have emerged. Some of the work discussed here also succeeded in showing the pore-network scale low salinity response. However, the main open questions are: what does the LSE look like in dynamic 3D experiments, what sample size is needed to observe representative LSR, if and how a new oil bank forms in tertiary low salinity waterflooding, if in secondary low salinity waterflooding the trapping efficiency at the back of the oil bank is reduced, and in the end, what physics should be included from the sub-pore and pore-network scale to give a valid description and/or gain predictive capability of low salinity waterflooding at the core scale? To address the last question, hereunder the different time scales that emerged from different experiments (see Sections 2.2 and 2.3) are discussed.

#### 4.2. Time scales

Just as all mechanisms and process discussed above have their own intrinsic length scale, they also have an intrinsic time scale. Time scales are important for saturation change and link to the physical and chemical mechanisms underlying pore scale displacement. The time scales related to processes in fluid flow such as Haines jumps in water-wet systems (1 ms – 2 s, Mohanty et al. [146], DiCarlo et al. [162], Armstrong et al. [137]), are an order of magnitude faster compared to pore filling events in mixed-wet systems (up to several minutes, Bartels et al. [140], Rucker et al. [141]). This range of time scales can also be found in low salinity waterflooding research.

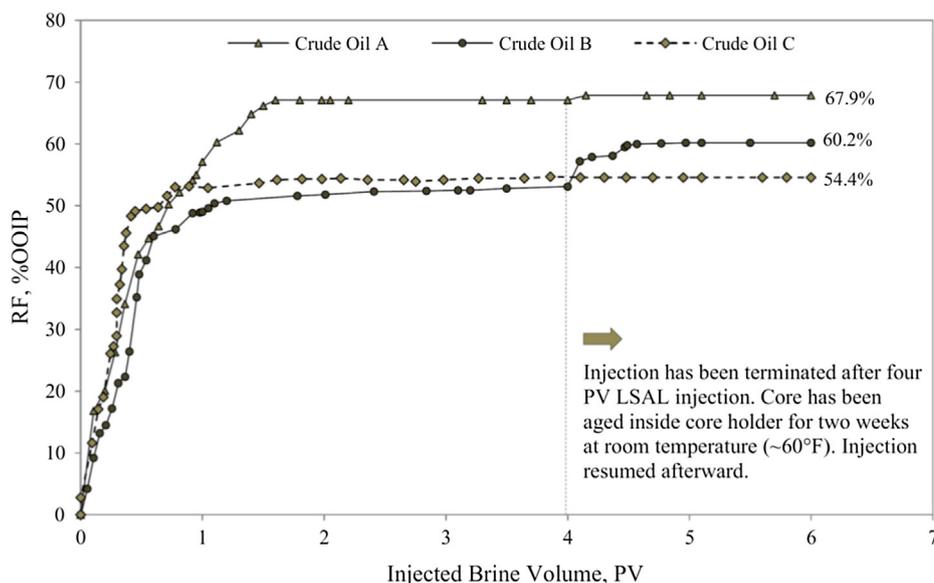
Recent works by Mahani et al. [7,8], Bartels et al. [145] have shown that contact angle change of oil droplets or wettability alteration in the micro-model by low salinity has a time scale of hours to days. In addition, McMillan et al. [163] reported additional oil recovery ca. 7.6% in corefloods after shut-in for two weeks, shown in Fig. 14).

As already mentioned in Figs. 8 and 10, this response may be explained by low salinity water accessing pores that are inaccessible to high salinity brine, or by an increase in liquid-liquid interface viscoelasticity [103–106] and references therein) that reduces trapping at the back of the oil bank.

These observations open a debate at what time scales proposed mechanisms are most efficient, in addition to the discussion on the importance of individual mechanisms in general. Moreover, this means equilibration times during sample preparation and experiments should be adapted to the processes under investigation. An additional consideration is what part of a porous medium is in geochemical equilibrium. Given different transport rates (convective or diffusive for instance), it may be possible for large parts of a pore network to be in local equilibrium, or, in contrast, in a dynamic state.

The longer time scale seems to be related to the solid-liquid interface and wettability alteration. The magnitude of time scales found in the droplet experiments of Mahani et al. [8], shows that Fickian diffusion in the water film is several orders of magnitude faster compared to the experimental observations. Incorporating electro-chemical diffusion into the models (to account for the effect of oil and rock surface change on ion transport in and out of the film) brings the time scales in agreement with experimental data [46].

Of course, it is conceivable that other factors may influence the time scale as well. For instance, surface roughness, charge heterogeneities on both solid and liquid surfaces, and drop and cluster sizes add complexities besides electro-chemical potential and the initial conditions in terms of film thickness and initial wettability in general. Because the time scales are associated with phenomenon in water films, rather than the physical size and scale of porous media, it is plausible that the



**Fig. 14.** Figure taken from McMillan et al. [163]. Effect of crude oil exposure (no flow) with low-salinity brine (10,000 ppm) in Berea sandstone cores. Crude oils A and C did not show any additional recovery after a shut in of two weeks. The system with crude oil B shows 7.6% OOIP additional recovery. This effect ties into the time scales discussed in Fig. 8 and the cooperative mechanisms in Fig. 10.

magnitude is not changed when moving to systems on larger length scales.

Therefore, in the laboratory the time effect would not be of the same relevance as it is at field scale (where the operation is in order of months-years). In the laboratory, the time scale of wettability alteration can be similar to the duration of experiment. This raises the question whether the increased oil recovery observed in low salinity water-flooding experiments is related to wettability alteration (solid-liquid interactions) or other mechanisms, as outlined before.

## 5. Free energy surfaces and kinetics

So far, this review has illustrated the complexity of investigating processes involved in LSE and LSR, which mainly arises from the combination of multiphase flow in mixed-wet systems and chemical processes related to wettability alteration. Most proposed mechanisms, processes and driving forces have been found to contribute to LSE for a specific COBR system on a specific time scale, albeit the results are not always consistent. One open issue is the length scale consistency i.e. which processes on smaller length scales contribute to LSR on the core and reservoir scale. In addition, the question is on what time scale recovery (rate) can be maximized: is it necessary to rely on the solid-liquid interfaces to respond or is the effect more related to the liquid-liquid interface. This is predominantly important for laboratory tests (experiments take hours - days), whereas in the field the exposure time of COBR to low salinity water is months years, spanning all time scales for the processes discussed in this review. When trying to unify all these different processes on all the different length and time scales in one framework, energy landscapes, kinetics, and thermodynamics could potentially be helpful.

### 5.1. Energy landscapes and thermodynamic framework in porous media

The concept of energy landscapes is a concept which is used in other fields such as glass formation or protein folding [164,165] and is making its way into porous media research [166,167]. The local minima and global minimum of the free energy surface as shown in Fig. 15a, represent different fluid topologies and saturations. The energy barriers to go to a lower minimum can be overcome or circumvented (in the  $n$ -th dimension) by different processes which take a different amount of time to complete. These processes are the driving forces for the suggested low salinity waterflooding mechanisms. A cartoon of this idea is shown in Fig. 15a,b. An implicit simplified form

of this idea can be found in papers by Buckley et al. [168], Liu and Buckley [48], Drummond and Israelachvili [169,62], Didier et al. [13] and Fig. 15c, where salinity-pH diagrams ('wettability maps') are drawn indicating either adhesion forces or contact angles.

The cartoons and map in Fig. 15 clearly indicate why initial wettability state is important for the overall result and can easily be thought of as 2D cross sections of an  $n$ -dimensional surface.

Note that adding more parameters to a system increases the number of possible dimensions. Adding more complexity may further increase the number of local minima, possible driving forces, and the number of time scales involved. This could also lead to more possible pathways. Since all available processes in the direction of equilibrium start at the same moment in time, it is not possible to separate them from each other. Whether a certain process has a significant contribution to the response is therefore a very difficult question to answer.

From a scientific point of view, the framework is a very interesting idea. However, energy landscapes are very difficult to obtain and in the end the interest is in finding a practical screening tool for low salinity waterflooding candidate reservoirs i.e. showing an LSR, not just an LSE. So far, it is not clear how this framework may provide that, but this may be an area for future research.

## 6. Summary and possibilities for future research

In summary, the main difficulties in low salinity waterflooding research are the multi-length- and time scale nature of the problem, and the lack of a unifying framework that explains main experimental observations. Consequently, there is currently no robust predictive capability whether a particular COBR system is responsive to low salinity water, in the sense that on field scale an additional recovery can be expected at an economically meaningful extent.

For fields that are known to be susceptible to low salinity waterflooding, modified SCAL workflows can be applied for successful field implementation. Still, the optimal composition of injection brine is not known and cannot be predicted in these cases.

The experiments conducted so far have focused mostly on the core scale. Efforts trying to correlate additional recovery to bulk properties of oil, brine, and rock, with no sub-core scale information where at least some of the underlying processes occur. This has not led to predictive capability. More advanced experiments have monitored additional parameters such as ion and fines content, which have led to many inferred mechanisms. Lack of predictive capability also inhibits effective screening or prioritization of candidate fields.

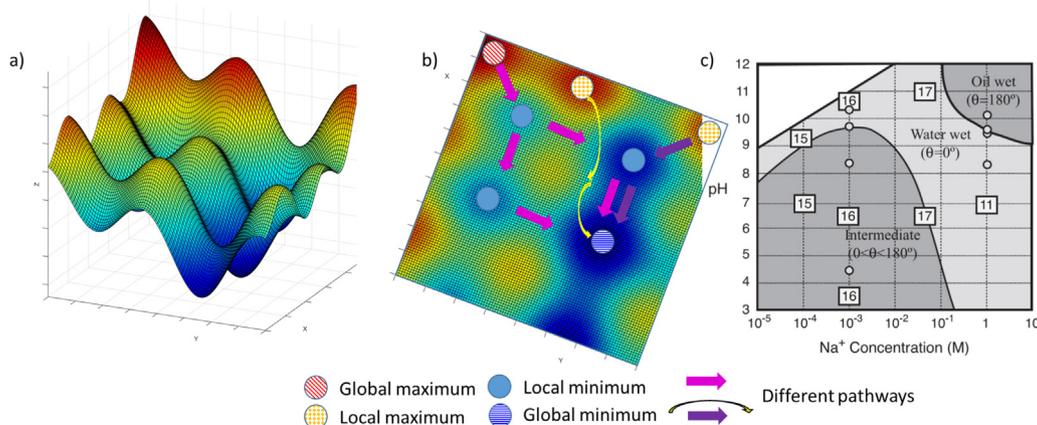


Fig. 15. Cartoon of a complex energy landscape b) xy-planar view of the same energy landscape with maxima and minima indicated and different routes that can be followed to reduce the free energy. Energy barriers have to be overcome c) wettability map from [62].

Dedicated experiments focused on directly observing the response of a system to low salinity water, find that proposed mechanisms almost always occur on the investigated length scale, but depend strongly on the initial wettability state. Whether those mechanisms regardless of the length scale on which they have been observed in the end contribute to formation of an oil bank and ultimately production remains unclear.

One reason is because the translation of physics observed on the sub-pore scale to the core scale i.e. the pore-network scale is not as well investigated. This leads to a gap in understanding how detached oil (re-) connects to or forms an oil bank. Studies dedicated to closing this gap, should focus on the fundamental description of flow in water-wet and mixed-wet systems, before adding the (geo) chemistry part necessary for understanding low salinity waterflooding.

Currently, the first results regarding the dynamics of mixed-wet flow and quasi-static low salinity waterflooding experiments are being analyzed and published. This opens the door for pore scale modelling which may lead to better understanding of what physics should be carried from sub-pore via pore-network to core and reservoir scale. In the end, this may help in gaining predictive capability and the development of a screening tool for field candidates for low salinity waterflooding.

## Acknowledgements

The authors thank Ali Fadili and Axel Makurat for the internal review of this work. Funding: This work was carried out as part of a PhD project at Utrecht University, sponsored by Shell Global Solutions International B.V.

## References

- [1] Loahardjo N, Xie X, Yin P, Morrow N, Low salinity waterflooding of a reservoir rock. In: Presented at the International Symposium of the Society of Core Analysts held in Calgary, Canada, 10–12 September 29; 2007.
- [2] Austad T, Rezaeidoust A, Puntervold T. Chemical mechanism of low salinity water flooding in sandstone reservoirs. SPE Improved Oil Recovery Symposium 2010.
- [3] Ashraf A, Hadia N, Torsaeter O, Tweheyo M. Laboratory investigation of low salinity waterflooding as secondary recovery process: effect of wettability. SPE Oil and Gas India Conference and Exhibition 2010.
- [4] Morrow N, Buckley J. Improved oil recovery by low-salinity waterflooding. J Pet Technol 2011;63:106–12.
- [5] Fjelde I, Asen S, Omekeh A. Low salinity water flooding experiments and interpretation by simulations; 2012.
- [6] Sandengen K, Arntzen O. Osmosis during low salinity water flooding. In: IOR 2013–17th European Symposium on Improved Oil Recovery; 2013.
- [7] Mahani H, Keya A, Berg S, Bartels W-B, Nasralla R, Rossen W. Insights into the mechanism of wettability alteration by low-salinity flooding (lsf) in carbonates. Energy Fuels 2015;29:1352–67.
- [8] Mahani H, Berg S, Ilic D, Bartels W-B, Joekar-Niasar V. Kinetics of low-salinity-flooding effect. SPE J 2015;20:8–20.
- [9] Vasconez N, Sabyrgali Y, Mackay E. Core flood modelling of ion-exchange during low salinity waterflooding. In: AAPG Latin America & Caribbean Region, Geoscience Technology Workshop; 2016.
- [10] Rezaeidoust A, Puntervold T, Strand S, Austad T. Smart water as wettability modifier in carbonate and sandstone: a discussion of similarities/differences in the chemical mechanisms. Energy Fuels 2009;23:4479–85.
- [11] Yousef A, Al-Saleh S, Al-Jawfi M. Smart waterflooding for carbonate reservoirs: Salinity and role of ions. SPE Middle East Oil and Gas Show and Conference 2011.
- [12] Awolayo A, Sarma H, AlSumaiti A. A laboratory study of ionic effect of smart water for enhancing oil recovery in carbonate reservoirs. SPE EOR Conference at Oil and Gas West Asia 2014.
- [13] Didier M, Chaumont A, Joubert T, Bondino I, Hamon G. Contradictory trends for smart water injection method: role of pH and salinity from sand/oil/brine adhesion maps, SCA2015-005; 2015.
- [14] Lager A, Webb K, Collins I, Richmond D. Losal enhanced oil recovery: Evidence of enhanced oil recovery at the reservoir scale. SPE Symposium on Improved Oil Recovery 2008.
- [15] Webb K, Lager A, Black C. Comparison of high/low salinity water/oil relative permeability. In: Presented at the International Symposium of the Society of Core Analysts held in Abu Dhabi, UAE, 29 October–2 November 29 (2008).
- [16] Gupta R, Smith G, Hu L, Willingham T, Lo Cascio M, Shyeh J, et al. Enhanced waterflood for carbonate reservoirs-impact of injection water composition. SPE Middle East Oil and Gas Show and Conference 2011.
- [17] Vo L, Gupta R, Hehmeyer O. Ion chromatography analysis of advanced ion management carbonate coreflood experiments. In: Abu Dhabi International Petroleum Conference and Exhibition; 2012.
- [18] Xie Q, Ma D, Liu Q, Lv W. Ion tuning waterflooding in low permeability sandstone: Coreflooding experiments and interpretation by thermodynamics and simulation. In: Presented at the International Symposium of the Society of Core Analysts held in St. John's Newfoundland and Labrador, Canada, 16–21 August; 2015.
- [19] Xu S, Wu J, Lv W, Wang J, Liu Q. Experimental study on the wettability alteration mechanism of ion tuning waterflooding. Special Topics Rev Porous Media: Int J 2016;7.
- [20] The schlumberger oilfield glossary, 2018.
- [21] Nasralla RA, van der Linde HA, Marcellis FH, Mahani H, Masalmeh SK, Sergienko E, et al., Low salinity waterflooding for a carbonate reservoir experimental evaluation and numerical interpretation. In: Abu Dhabi International Petroleum Exhibition & Conference; 2016.
- [22] Mahani H, Menezes R, Berg S, Fadili A, Nasralla R, Voskov D, Joekar-Niasar V. Insights into the impact of temperature on the wettability alteration by low salinity in carbonate rocks. Energy Fuels 2017;31:7839–53.
- [23] Harzing A, Publish or perish; 2007.
- [24] Reiter P. A water-sensitive sandstone flood using low salinity water. University of Oklahoma; 1961. [Ph.D. thesis].
- [25] Bernard G. Effect of floodwater salinity on recovery of oil from cores containing clays. In: SPE California Regional Meeting; 1967.
- [26] Hughes R, Pfister R. Advantages of brines in secondary recovery of petroleum by water-flooding. Trans AIME 1947;170:187–201.
- [27] Martin J. The effects of clay on the displacement of heavy oil by water. In: Venezuelan Annual Meeting; 1959.
- [28] Anderson W. Wettability literature survey-part 1: rock/oil/brine interactions and the effects of core handling on wettability. J Pet Technol 1986;38:1–125.
- [29] Anderson W. Wettability literature survey-part 2: wettability measurement. J Pet Technol 1986;38:1246–62.
- [30] Anderson W. Wettability literature survey-part 3: the effects of wettability on the electrical properties of porous media. J Pet Technol 1986;38:1–371.
- [31] Anderson W. Wettability literature survey-part 4: effects of wettability on capillary pressure. J Pet Technol 1987;39:1283–300.
- [32] Anderson W. Wettability literature survey part 5: the effects of wettability on relative permeability. J Pet Technol 1987;39:1–453.
- [33] Anderson W. Wettability literature survey-part 6: the effects of wettability on

- waterflooding. *J Pet Technol* 1987;39:1–605.
- [34] Abdallah W, Buckley J, Carnegie A, Herold J, Graue A, Habashy T, et al. Fundamentals of wettability. *Oilfield Rev* 2007;19:44–61.
- [35] Ahmed T. 4 edition Reservoir Engineering Handbook Gulf Professional Publishing; 2010.
- [36] McPhee C, Reed J, Zubizarreta I. *Core Analysis: A Best Practice Guide* vol. 64. Elsevier; 2015.
- [37] Rotondi M, Callegaro C, Masserano F, Bartosek M, Low salinity water injection: Eni's experience. In: Abu Dhabi International Petroleum Exhibition and Conference; 2014.
- [38] Suijkerbuijk B, Sorop T, Parker A, Masalmeh S, Chmuzh I, Karpan V, et al., Low salinity waterflooding at west-salym: Laboratory experiments and field forecasts. *SPE Improved Oil Recovery Symposium* (2014).
- [39] Deutsch C, Srinivasan S, Improved reservoir management through ranking stochastic reservoir models. In: *SPE/DOE Improved Oil Recovery Symposium*; 1996.
- [40] Sorop T, Masalmeh S, Suijkerbuijk B, van der Linde H, Mahani H, Brussee N, et al., Relative permeability measurements to quantify the low salinity flooding effect at field scale. In: Abu Dhabi International Petroleum Exhibition and Conference; 2015.
- [41] Nasralla R, Sergienko E, Masalmeh S, van der Linde H, Brussee N, Mahani H, et al. Potential of low-salinity waterflood to improve oil recovery in carbonates: Demonstrating the effect by qualitative coreflood. *SPE J* 2016;17:2010.
- [42] Kennedy M. *Practical petrophysics* vol. 62. Elsevier; 2015.
- [43] Suijkerbuijk B, Hofman J, Ligthelm D, Romanuka J, Brussee N, van der Linde H, Marcelis F, Fundamental investigations into wettability and low salinity flooding by parameter isolation. In: *SPE Improved Oil Recovery Symposium*; 2012.
- [44] Aladasani A, Bai B, Wu Y-S, Salehi S. Studying low-salinity waterflooding recovery effects in sandstone reservoirs. *J Pet Sci Eng* 2014;120:39–51.
- [45] Sohal M, Kucheryavskiy S, Thyne G, Sgaard E. Study of ionically modified water performance in the carbonate reservoir system by multivariate data analysis. *Energy Fuels* 2017;31:2414–29.
- [46] Joekar-Niasar V, Mahani H. Nonmonotonic pressure field induced by ionic diffusion in charged thin films. *Ind Eng Chem Res* 2016;55:6227–35.
- [47] Buckley J, Liu Y, Cie X, Morrow N. Asphaltenes and crude oil wetting—the effect of oil composition. *SPE J* 1997;2.
- [48] Liu L, Buckley J. Alteration of wetting of mica surfaces. *J Pet Sci Eng* 1999;24:75–83.
- [49] Yang S-Y, Hirasaki G, Basu S, Vaidya R. Mechanisms for contact angle hysteresis and advancing contact angles. *J Pet Sci Eng* 1999;24:63–73.
- [50] Berg S, Cense A, Jansen E, Bakker K. Direct experimental evidence of wettability modification by low salinity. *Petrophysics* 2010;51.
- [51] Lebedeva E, Fogden A. Adhesion of oil to kaolinite in water. *Environ Sci Technol* 2010;44:9470–5.
- [52] Alotaibi M, Nasralla R, Nasr-El-Din H. Wettability studies using low-salinity water in sandstone reservoirs. *SPE Reservoir Eval Eng* 2011;14:713–25.
- [53] Fogden A, Lebedeva E, Changes in wettability state due to waterflooding. In: Presented at the International Symposium of the Society of Core Analysts held in Austin, Texas, USA 18–21 September; 2011.
- [54] Fogden A. Effect of water salinity and pH on the wettability of a model substrate. *Energy Fuels* 2011;25.
- [55] Lebedeva E, Fogden A. Wettability alteration of kaolinite exposed to crude oil in salt solutions. *Colloids Surf A* 2011;377:115–22.
- [56] Nasralla R, Bataweel M, Nasr-El-Din H. Investigation of wettability alteration by low salinity water in sandstone rock. In: *Offshore Europe Meeting*; 2011.
- [57] Nasralla R, Nasr-El-Din H. Double-layer expansion: is it a primary mechanism of improved oil recovery by low-salinity waterflooding? *SPE Reservoir Eval Eng* 2014;17:49–59.
- [58] Buckley J, Takamura K, Morrow N, Influence of electrical surface charges on the wetting properties of crude oils. In: *SPE Reservoir Engineering*; 1989.
- [59] Jackson M, Al-Mahrouqi D, Vinogradov J. Zeta potential in oil-water-carbonate systems and its impact on oil recovery during controlled salinity water-flooding. *Nat Sci Rep* 2016;6.
- [60] Basu S, Sharma M. Measurement of critical disjoining pressure for dewetting of solid surfaces. *J Colloid Interface Sci* 1996;181:443–55.
- [61] Basu S, Sharma M. Investigating the role of crude-oil components on wettability alteration using atomic force microscopy. *SPE J* 1999;4:443–55.
- [62] Drummond C, Israelachvili J. Fundamental studies of crude oil-surface water interactions and its relationship to reservoir wettability. *J Pet Sci Eng* 2004;45:61–81.
- [63] Hassenkam T, Pedersen C, Dalby K, Austad T, Stipp S. Pore scale observation of low salinity effects on outcrop and oil reservoir sandstone. *Colloids Surf A* 2011;390:85–97.
- [64] Hassenkam T, Mitchell A, Pedersen C, Skovbjerg L, Bovet N, Stipp S. The low salinity effect observed on sandstone model surfaces. *Colloids Surf A* 2012;403:79–86.
- [65] Matthiesen J, Bovet N, Hilner E, Andersson M, Schmidt D, Webb K, et al. How naturally adsorbed material on minerals affects low salinity enhanced oil recovery. *Energy Fuels* 2014;28:4849–58.
- [66] Hilner E, Andersson MP, Hassenkam T, Matthiesen J, Salino P, Stipp S. The effect of ionic strength on oil adhesion in sandstone—the search for the low salinity mechanism. *Nat Sci Rep* 2015;5. [srep09933].
- [67] Shi L, Olsson M, Hassenkam T, Stipp S. A ph-resolved view of the low salinity effect in sandstone reservoirs. *Energy Fuels* 2016;30:5346–54.
- [68] Bear J. *Dynamics of fluids in porous media*. Dover New York Google Scholar; 1972.
- [69] Buckley S, Leverett M. Mechanism of fluid displacement in sands. *Trans AIME* 1942;146:107–16.
- [70] Jerauld G, Webb K, Lin C, Seccombe J, Modeling low-salinity waterflooding. In: *SPE Annual Technical Conference and Exhibition*; 2006.
- [71] Vledder P, Gonzalez I, Carrera Fonseca J, Wells T, Ligthelm D, Low salinity water flooding: proof of wettability alteration on a field wide scale. In: *SPE Improved Oil Recovery Symposium*; 2010.
- [72] Seccombe J, Lager A, Jerauld G, Jhaveri B, Buikema T, Bassler S., et al., Demonstration of low-salinity eor at interwell scale, endicott field, alaska. In: *SPE Improved Oil Recovery Symposium*; 2010.
- [73] Mahani H, Sorop T, Ligthelm D, Brooks D, Vledder P, Mozahem F, Ali Y, Analysis of field responses to low-salinity waterflooding in secondary and tertiary mode in syria. In: *SPE EUROPEC/EAGE Annual Conference and Exhibition*, 2011.
- [74] Callegaro C, Bartosek M, Nobili M, Masserano F, Pollero M, Baz D, Kortam M, Design and implementation of low salinity waterflood in a north african brown field. In: Abu Dhabi International Petroleum Exhibition and Conference; 2015.
- [75] Skrettingland K, Holt T, Tweheyo M, Skjevraak I. Snorre low-salinity-water injection—coreflooding experiments and single-well field pilot. *SPE Reservoir Eval Eng* 2011;14:182–92.
- [76] Robertson E. *Low-salinity waterflooding to improve oil recovery—historical field evidence*. Idaho National Laboratory (INL); 2007. [Technical Report].
- [77] Lager A, Webb K, Seccombe J, Low salinity waterflood, endicott, alaska: Geochemical study & field evidence of multicomponent ion exchange. In: *IOR 2011–16th European Symposium on Improved Oil Recovery*; 2011.
- [78] Suijkerbuijk B, Kuipers H, Kruijsdijk van C, Berg S, van Winden J, Ligthelm D, et al., The development of a workflow to improve predictive capability of low salinity response. In: *International Petroleum Technology Conference IPTC held in Beijing, China, IPTC-17157-MS*; 2013.
- [79] Zeinijahromi A, Ahmetgareev V, Ibatullin R, Bedrikovetsky P. Sensitivity study of low salinity water injection in zichebashskoe oilfield. *J Pet Gas Eng* 2015;6:10–21.
- [80] Bennion D, Bennion D, Thomas F, Bietz R, et al. Injection water quality—a key factor to successful waterflooding. *J Canad Pet Technol* 1998;37.
- [81] Blume T, Weisbrod N, Selker J. Permeability changes in layered sediments: impact of particle release. *Groundwater* 2002;40:466–74.
- [82] Zhang Y, Morrow N, Comparison of secondary and tertiary recovery with change in injection brine composition for crude-oil/sandstone combinations. In: *SPE/DOE Improved Oil Recovery Symposium*; 2006.
- [83] Soraya B, Malick C, Philippe C, Bertin H, Hamon G, Oil recovery by low-salinity brine injection: laboratory results on outcrop and reservoir cores. In: *SPE Annual Technical Conference and Exhibition*, 2009.
- [84] McGuire P, Chatham J, Paskvan F, Sommer D, Carini F, Low salinity oil recovery: An exciting new eor opportunity for alaska's north slope. In: *SPE Western Regional Meeting*; 2005.
- [85] Huang D, Honarpour M. Capillary end effects in coreflood calculations. *J Pet Sci Eng* 1998;19:103–17.
- [86] Masalmeh S, Sorop T, Suijkerbuijk B, Vermolen E, Douma S, Van Der Linde H, Pieterse S, Low salinity flooding: Experimental evaluation and numerical interpretation. In: *IPTC 2014: International Petroleum Technology Conference*; 2014.
- [87] Yildiz H, Morrow N. Effect of brine composition on recovery of mourtray crude oil by waterflooding. *J Pet Sci Eng* 1996;14:159–68.
- [88] Thyne G, Gamage S, Hasanka P, Evaluation of the effect of low salinity waterflooding for 26 fields in wyoming. In: *SPE Annual Technical Conference and Exhibition*; 2011.
- [89] Graue A, Fern M. Water mixing during spontaneous imbibition at different boundary and wettability conditions. *J Pet Sci Eng* 2011;78:586–95.
- [90] Graue A, Fern M, Aspenes E, Needham R. Wettability effects on water mixing during waterflood oil recovery. *J Pet Sci Eng* 2012;94–95:89–99.
- [91] Graue A, Fern M, Moe R, Baldwin B, Needham R. Water mixing during waterflood oil recovery: the effect of initial water saturation. *SPE J* 2012;17:43–52.
- [92] Kia S, Fogler H, Reed M, Effect of salt composition on clay release in berea sandstones. In: *SPE International Symposium on Oilfield Chemistry*; 1987.
- [93] Morrow N, Tang G, Valat M, Xie X. Prospects of improved oil recovery related to wettability and brine composition. *J Pet Sci Eng* 1998;20:267–76.
- [94] Tang G, Morrow N. Influence of brine composition and fines migration on crude oil/brine/rock interactions and oil recovery. *J Pet Sci Eng* 1999;24:99–111.
- [95] Bedrikovetsky P, Zeinijahromi A, Siqueira F, Furtado C, de Souza A. Particle detachment under velocity alternation during suspension transport in porous media. *Transp Porous Media* 2012;91:173–97.
- [96] Aksulu H, Hams D, Strand S, Puntervold T, Austad T. Evaluation of low-salinity enhanced oil recovery effects in sandstone: Effects of the temperature and pH gradient. *Energy Fuels* 2012;26:3497–503.
- [97] Sohrabi M, Mahzari P, Farzaneh S, Mills J, Tsois P, Ireland S. Novel insight into mechanisms of oil recovery by low salinity water injection. *SPE J* 2015;17:2778.
- [98] Lager A, Webb K, Black C, Singleton M, Sorbie K. Low salinity oil recovery—an experimental investigation. *Petrophysics* 2008;49:28–35.
- [99] Lee S, Webb K, Collins I, Lager A, Clarke S, O'Sullivan M, Routh A, Low salinity oil recovery—increasing understanding of the underlying mechanisms of double layer expansion. In: *IOR 2011–16th European Symposium on Improved Oil Recovery*; 2010.
- [100] Kuznetsov D, Cotterill S, Giddins M, Blunt M, Low-salinity waterflood simulation: Mechanistic and phenomenological models. In: *SPE Asia Pacific Enhanced Oil Recovery Conference*; 2015.
- [101] Ligthelm D, Gronsveld J, Hofman J, Brussee N, Marcelis F, van der Linde H, Novel waterflooding strategy by manipulation of injection brine composition. In: *EUROPEC/EAGE Conference and Exhibition*; 2009.
- [102] Mahzari P, Sohrabi M, Crude oil/brine interactions and spontaneous formation of micro-dispersions in low salinity water injection. In: *SPE Improved Oil Recovery*

- Symposium; 2014.
- [103] Alvarado V, Moradi Bidhendi M, Garcia-Olvera G, Morin B, Oakey J, Interfacial visco-elasticity of crude oil-brine: an alternative eor mechanism in smart water-flooding. In: SPE Improved Oil Recovery Symposium; 2014.
- [104] Alves D, Carneiro J, Oliveira I, Façanha F, Santos A, Dariva C, et al. Influence of the salinity on the interfacial properties of a Brazilian crude oil-brine systems. *Fuel* 2014;118:21–6.
- [105] Chávez-Miyauchi T, Firoozabadi A, Fuller G. Nonmonotonic elasticity of the crude oil-brine interface in relation to improved oil recovery. *Langmuir* 2016;32:2192–8.
- [106] Morin B, Liu Y, Alvarado V, Oakey J. A microfluidic flow focusing platform to screen the evolution of crude oil-brine interfacial elasticity. *Lab Chip* 2016;16:3074–81.
- [107] Wang X, Alvarado V. Effects of low-salinity waterflooding on capillary pressure hysteresis. *Fuel* 2017;207:336–43.
- [108] Fredriksen S, Rognmo A, Fern M. Pore-scale mechanisms during low salinity waterflooding: Water diffusion and osmosis for oil mobilization SPE-180060-MS; 2016.
- [109] Sandengen K, Kristoffersen A, Melhuus K, Josang L. Osmosis as mechanism for low-salinity enhanced oil recovery. *SPE J* 2016;179741.
- [110] Pu H, Xie X, Yin P, Morrow N. Low-salinity waterflooding and mineral dissolution. In: SPE Annual Technical Conference and Exhibition; 2010.
- [111] Sheng J. Critical review of low-salinity waterflooding. *J Pet Sci Eng* 2014;120:216–24.
- [112] Mugele F, Bera B, Cavalli A, Sietanu I, Maestro A, Duits M, et al. Ion adsorption-induced wetting transition in oil-water-mineral systems. *Nat Sci Rep* 2015;5.
- [113] Myint P, Firoozabadi A. Thin liquid films in improved oil recovery from low-salinity brine. *Curr Opin Colloid Interface Sci* 2015;20:105–14.
- [114] Hamon G. Low-salinity waterflooding: facts, inconsistencies and the way forward. *Petrophysics* 2016;57:41–50.
- [115] Jackson M, Vinogradov J, Hamon G, Chameris M. Evidence, mechanisms and improved understanding of controlled salinity waterflooding part 1: sandstones. *Fuel* 2016;185:772–93.
- [116] Ayirala S, Al-Enezi S, Al-Yousef A. A state of the art review to develop novel workflow for microscopic scale understanding of advanced water flooding mechanisms in carbonates. *J Pet Sci Eng* 2017;157:530–46.
- [117] Schmatz J, Urai J, Berg S, Ott H. Nanoscale imaging of pore-scale fluid-fluid-solid contacts in sandstone. *Geophys Res Lett* 2015;42:2189–95.
- [118] Lake L. Enhanced oil recovery. Prentice Hall Inc.; 1989.
- [119] Tang G, Morrow N. Salinity, temperature, oil composition, and oil recovery by waterflooding. In: SPE Journal SPE-36680-PA; 1997.
- [120] Alagic E, Spildo K, Skauge A, Solbakken J. Effect of crude oil ageing on low salinity and low salinity surfactant flooding. *J Pet Sci Eng* 2011;78:220–7.
- [121] Jadhunandan P, Morrow N. Effect of wettability on waterflood recovery for crude-oil/brine/rock systems. *SPE Reservoir Eng* 1995;10:40–6.
- [122] Christensen M, Tanino Y. Residual oil saturation under mixed-wet conditions: Optimal wettability revisited. In: SCA18-040; 2018.
- [123] Clementz D. Clay stabilization in sandstones through adsorption of petroleum heavy ends. *J Pet Technol* 1977;29:1–061.
- [124] Scheuerman R, Bergersen B. Supplement to 'injection-water salinity, formation pretreatment, and well-operations fluid-selection guidelines'. *J Pet Technol* 1989.
- [125] Scheuerman R, Bergersen B. Injection-water salinity, formation pretreatment, and well-operations fluid-selection guidelines. *J Pet Technol* 1990;42:836–45.
- [126] Rücker M, Berg S, Armstrong R, Georgiadis A, Ott H, Simon L, et al., The fate of oil clusters during fractional flow: trajectories in the saturation-capillary number space. In: Presented at the International Symposium of the Society of Core Analysts held in St. John's Newfoundland and Labrador, Canada, 16–21 August; 2015.
- [127] Liu X, Herring A, Arns C, Berg S, Armstrong R. Pore-scale characterization of two-phase flow using integral geometry. *Transp Porous Media* 2017;118:99–117.
- [128] Al-Raouh RI. Impact of wettability on pore-scale characteristics of residual non-aqueous phase liquids. *Environ Sci Technol* 2009;43:4796–801.
- [129] Karpyn Z, Piri M, Singh G. Experimental investigation of trapped oil clusters in a water-wet bead pack using x-ray microtomography. *Water Resour Res* 2010;46.
- [130] Kumar M, Fogden A. Patterned wettability of oil and water in porous media. *Langmuir* 2010;26:4036–47.
- [131] Kumar M, Fogden A, Senden T, Knackstedt M. Investigation of pore-scale mixed wettability. *SPE J* 2012;17:20–30.
- [132] Landry C, Karpyn Z, Piri M. Pore-scale analysis of trapped immiscible fluid structures and fluid interfacial areas in oil-wet and water-wet bead packs. *Geofluids* 2011;11:209–27.
- [133] Iglauer S, Fern M, Shearing P, Blunt M. Comparison of residual oil cluster size distribution, morphology and saturation in oil-wet and water-wet sandstone. *J Colloid Interface Sci* 2012;375:187–92.
- [134] Celauro J, Torrealba V, Karpyn Z, Klise K, McKenna S. Pore-scale multiphase flow experiments in bead packs of variable wettability. *Geofluids* 2014;14:95–105.
- [135] Avraam D, Payatakes A. Flow regimes and relative permeabilities during steady-state two-phase flow in porous media. *J Fluid Mech* 1995;293:207–36.
- [136] Berg S, Ott H, Klapp S, Schwing A, Neitelner R, Brussee N, Makurat A, Leu L, Enzmann F, Schwarz J, Kersten M, Irvine S, Stampanoni M. Real-time 3d imaging of haines jumps in porous media flow. *Proc Nat Acad Sci* 2013;110:3755–9.
- [137] Armstrong R, Ott H, Georgiadis A, Rücker M, Schwing A, Berg S. Subsecond pore-scale displacement processes and relaxation dynamics in multiphase flow. *Water Resour Res* 2014;50:9162–76.
- [138] Berg S, Armstrong R, Ott H, Georgiadis A, Klapp S, Schwing A, et al. Multiphase flow in porous rock imaged under dynamic flow conditions with fast x-ray computed microtomography. *Petrophysics* 2014;55:304–12.
- [139] Youssef S, Rosenberg E, Deschamps H, Oughanem R, Maire E, Mokso R. Oil ganglia dynamics in natural porous media during surfactant flooding captured by ultra-fast x-ray microtomography. In: Presented at the International Symposium of the Society of Core Analysts held in Avignon, France, 8–11 September; 2014.
- [140] Bartels W-B, Rücker M, Berg S, Mahani H, Georgiadis A, Fadili A, et al. Fast X-ray micro-ct study of the impact of brine salinity on the pore-scale fluid distribution during waterflooding. *Petrophysics* 2017;58:36–47.
- [141] Rücker M, Bartels W-B, Berg S, Mahani H, Georgiadis A, Brussee N, et al. The effect of wettability on pore scale flow regimes, submitted to. *Geophys Res Lett* 2018.
- [142] Salathiel R. Oil recovery by surface film drainage in mixed-wettability rocks. *J Pet Technol* 1973:1216–24.
- [143] Bondino I, Doorwar S, Ellouz R, Hamon G. Visual microscopic investigations about the role of ph, salinity and clay on oil adhesion and recovery. In: Presented at the International Symposium of the Society of Core Analysts held in Napa Valley, California, 16–19 September (2013) 16–19.
- [144] Song W, Kovscek A. Functionalization of micro-models with kaolinite for investigation of low salinity oil-recovery processes. *Lab Chip* 2015.
- [145] Bartels W-B, Mahani Hassan, Berg Steffen, Menezes Robin, van der Hoeven JA, Fadili Ali. Oil configuration under high salinity and low salinity conditions at pore scale: a parametric investigation using a single-channel micro-model. *SPE J* 2017;22.
- [146] Mohanty K, Davis H, Scriven L. Physics of oil entrapment in water-wet rock. *SPE Reservoir Eng* 1987;2:113–28.
- [147] Andrew M, Bijeljic B, Blunt M. Pore-scale imaging of geological carbon dioxide storage under in situ conditions. *Geophys Res Lett* 2013;40:3915–8.
- [148] Armstrong R, Berg S. Interfacial velocities and capillary pressure gradients during haines jumps. *Phys Rev E* 2013;88:043010.
- [149] Youssef S, Deschamps H, Dautriat J, Rosenberg E, Oughanem R, Maire E, Mokso R. 4d imaging of fluid flow dynamics in natural porous media with ultra-fast X-ray microtomography. In: presented at the International Symposium of the Society of Core Analysts held in Napa Valley, California, USA, 16–19 September 176; 2013.
- [150] Bultreys T, De Boever W, Cnudde V. Imaging and image-based fluid transport modeling at the pore scale in geological materials: a practical introduction to the current state-of-the-art. *Earth-Sci Rev* 2016;155:93–128.
- [151] Shabaninejad M, Marathe R, Middleton J, Fogden A. Micro-ct pore-scale analysis of low salinity recovery from reservoir sandstones. In: 77th EAGE Conference and Exhibition 2015; 2015.
- [152] Khishvand M, Alizadeh A, Oraki Kohshour I, Piri M, Prasad R. In situ characterization of wettability alteration and displacement mechanisms governing recovery enhancement due to low-salinity waterflooding. *Water Resour Res* 2017.
- [153] Andrew M, Bijeljic B, Blunt M. Pore-scale contact angle measurements at reservoir conditions using x-ray microtomography. *Adv Water Resour* 2014;68:24–31.
- [154] Herring A, Sheppard A, Andersson L, Wildenschild D. Impact of wettability alteration on 3d nonwetting phase trapping and transport. *Int J Greenhouse Gas Control* 2016;46:175–86.
- [155] Pfeiffer F, Weitkamp T, Bunk O, David C. Phase retrieval and differential phase-contrast imaging with low-brilliance x-ray sources. *Nat Phys* 2006;2:258–61.
- [156] Als-Nielsen J, McMorrow D. Elements of modern X-ray physics. John Wiley & Sons; 2011.
- [157] Weon B, Je J, Hwu Y, Margaritondo G. Decreased surface tension of water by hard-x-ray irradiation. *Phys Rev Lett* 2008;100:217403.
- [158] Roth J, Eller J, Büchi F. Effects of synchrotron radiation on fuel cell materials. *J Electrochem Soc* 2012;159:F449–55.
- [159] Kumar N, Wang L, Siretanu I, Duits M, Mugele F. Salt dependent stability of stearic acid langmuir-blodgett films exposed to aqueous electrolytes. *Langmuir* 2013;29:5150–9.
- [160] Graue A, Viksund BG, Eilertsen T, Moe R. Systematic wettability alteration by aging sandstone and carbonate rock in crude oil. *J Pet Sci Eng* 1999;24:85–97.
- [161] Bartels W-B, Rücker M, Boone M, Bultreys T, Mahani H, Berg S, et al., Pore-scale displacement during fast imaging of spontaneous imbibition. In: Presented at the International Symposium of the Society of Core Analysts held in Vienna, Austria, 28 August-1 September; 2017.
- [162] DiCarlo DA, Cidoncha J, Hickey C. Acoustic measurements of pore-scale displacements. *Geophys Res Lett* 2003;30.
- [163] McMillan M, Rahnema H, Romiluy J, Kitty F. Effect of exposure time and crude oil composition on low-salinity water flooding. *Fuel* 2016;185:263–72.
- [164] Sastry S, Debenedetti P, Stillinger F. Signatures of distinct dynamical regimes in the energy landscape of a glass-forming liquid. *Nature* 1998;393:554.
- [165] Mallamace F, Corsaro C, Mallamace D, Vasi S, Vasi C, Baglioni P, et al. Energy landscape in protein folding and unfolding. *Proc Nat Acad Sci* 2016;113:3159–63.
- [166] Morrow N. Physics and thermodynamics of capillary action in porous media. *Ind Eng Chem* 1970;62:32–56.
- [167] Cueto-Felgueroso L, Juanes R. A discrete-domain description of multiphase flow in porous media: rugged energy landscapes and the origin of hysteresis. *Geophys Res Lett* 2016;43:1615–22.
- [168] Buckley J, Bousseau C, Liu Y. Visual microscopic investigations about the role of ph, salinity and clay on oil adhesion and recovery. *SPE J* 1996.
- [169] Drummond C, Israelachvili J. Surface forces and wettability. *J Pet Sci Eng* 2002;33:123–33.