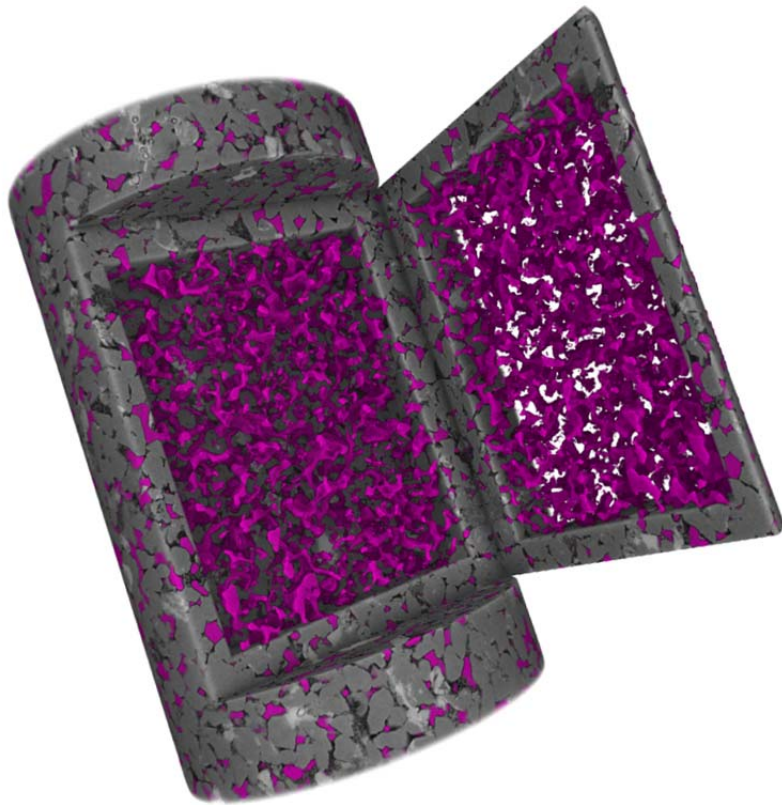




Australian
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University

Pore-scale Analysis of Residual Oil in Sandstones and its
Dependence on Waterflood Salinity, Analysed by
Tomography and Microscopy



Mehdi Shabaninejad

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Preface

This is an account of research carried out at the Department of Applied Mathematics, Research School of Physics and Engineering, within the Australian National University.

The thesis represents my original work; however some aspects were undertaken in collaboration with colleagues at the Australian National University (ANU) and FEI. All work in this thesis was performed under the supervision of Dr. Andrew Fogden.

Andrew Fogden and Rohini Marathe (ANU) assisted me in performing the experiments in Chapters 2-4. Jill Middleton (ANU) helped with the image analysis protocol used in this thesis, and Alessio Arena (FEI) assisted with mineral segmentation of the dry-state tomogram in Chapter 5. Carley Goodwin and Silvano Sommacal (FEI) assisted with parts of the sample preparation, acquisition and processing of the QEMSCAN mineral maps in Chapter 5.

This thesis does not contain material that has been accepted for the award of any other degree or diploma at any university. To the best of my knowledge, it includes no material previously published or written by another person, except where due reference or acknowledgement is made in the text.



Mehdi Shabaninejad

31 January 2017

To my beautiful Mehrsa

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Abstract

Understanding of the pore scale phenomena in porous media is a crucial step towards designing a more efficient enhanced oil recovery techniques in large scale oil reservoirs. Three dimensional (3D) x-ray micro CT imaging and recent advanced in 3D image analysis are primary tools that provide unprecedented level of detailed pore scale information of complex rock structures. Combining this technology with laboratory EOR experiments provides valuable insights into the mechanisms behind the oil recovery process. Low salinity water flooding is a relatively convenient and efficient tertiary recovery method which is applicable to the most of the reservoir types. However, its performance prediction is uncertain because this technique is not fully understood. Fundamental understanding of underlying mechanisms of low salinity water flooding, at the pore-scale, by direct visualization and image analysis is the aim of this thesis. In this thesis a technique to quantify fluids and rocks using series of images is developed and applied to 3D images of mini-plugs that underwent Spontaneous imbibition of high and low salinity brine or flooded by high or low salinity brine. Further, oil/rock and oil//brine interfacial areas, oil/brine interfacial mean curvature and oil saturation configuration in each pore was determined for each mini-plug. The image analysis and data interpretation demonstrate that small incremental oil recovery by low salinity brine corresponded to a slight shift towards water-wet in clay-rich outcrop sandstones. Further, the influence of oil composition in the low salinity brine flooding of reservoir sandstones was investigated. Two crude oil which are mainly distinctive in their total acid number (TAN) were used in spontaneous imbibition experiments. All mini-plugs shows strongly oil wet state after spontaneous imbibition of high and low salinity brine. The low salinity effect was observed in mini plug with high TAN oil while the mini-plugs with low TAN oil exhibited much less tertiary recovery. The analysis of mini-plug with high TAN oil shows that the salinity-induced wettability shift was sufficient to displace oil from locations that were already more water-wet in the state after spontaneous imbibition of high salinity brine, but was insufficient to cause oil movement from more oil-wet locations. Pore scale study of core flooded mini-plug shows that the low salinity brine redistributed oil blobs by displacing them from smaller to the larger pores and disconnecting oil. Microscopy studies of mini-plugs after spontaneous imbibition or core flooding provided further insight to the low salinity oil recovery mechanism at local minerals or wettability of pore walls.

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Nomenclature

Micro-CT: X-ray micro-tomography

SI: Spontaneous imbibition

SIH: spontaneous imbibition of high salinity brine

SIL: spontaneous imbibition of low salinity brine

SILL: very low salinity brine

SEM: scanning electron microscopy

SEM-EDS: energy dispersive x-ray spectroscopy

LSW: low salinity water flooding

MRB: Minnelusa reservoir brine

OOIP: original oil in place

MICP: Mercury injection capillary pressure

Sor: residual oil saturation

Soi: initial oil saturation

Swi: initial water saturation

PV: pore volume

BV: bulk volume

BB: brine-filled in SIH and SIL

OO: oil-filled in SIH and SIL

OB: oil-filled in SIH but brine-filled in SIL

BO: brine-filled in SIH but oil-filled in SIL

SO(SIH): residual oil saturation at high salinity spontaneous imbibition state

SO(SIL): residual oil saturation at low salinity spontaneous imbibition state

TAN: total acid number

TBN: total base number

BSEM: Back-Scattered Electron Microscopy

FESEM: field emission scanning electron microscope

FW: formation water

HS: high salinity

LS: low salinity

Std dev.: standard deviation

Std error: standard error

p.u.: per unit

H: mean curvature

IFT: interfacial tension

Pc: capillary pressure

1 Introduction

1.1 Introduction

A substantial fraction of oil in place in a reservoir will remain after primary and secondary recovery, for example by water flooding. Numerous enhanced oil recovery (EOR) techniques have been developed to target this residual oil after secondary recovery; reservoir engineers are tasked with choosing the optimal EOR strategy based on the type of reservoir, operational conditions and economic considerations. The choice and optimization of the approach is usually guided by laboratory experiments on restored core plugs, combined with simulations. Utilization of EOR is often restricted by the cost of the chemical formulations and their delivery and maintenance. In this respect, the relatively new and inexpensive tertiary EOR technique of low salinity water flooding (LSW) of sandstone reservoirs, in which the ionic composition of the conventional injected brine is lowered or modified, is an appealing alternative and has drawn much attention from research groups over the past decade. Laboratory and field data has demonstrated the potential of LSW in clay-containing sandstones; however, the fraction of incremental recovery is highly, and sometimes irreproducibly, variable (1,2).

This thesis utilizes a digital rock analysis approach to provide additional insight into LSW of sandstones. Small samples of outcrop and reservoir sandstones are imaged in 3D by X-ray micro-computed tomography (micro-CT) in a sequence of laboratory-prepared states before and after LSW. The images (tomograms) are registered into perfect alignment, so that changes in the distribution of oil and brine in the same rock pores throughout the process can be quantitatively analyzed. These micro-scale changes in oil volumes, areas and curvatures are also directly compared to the local mineralogy, with the overall goal of improving understanding of LSW from the bottom-up, as input to further optimization of reservoir recovery strategies.

1.2 Low Salinity Water Flooding Studies

Much research effort has been devoted in recent years to identifying the underlying mechanism(s) of the low salinity effect (3). Almost all of the proposed mechanisms relate back in some way to salinity-induced changes in the electrostatic intermolecular interactions of crude oil and rock across brine that lead to the wettability state of the

system becoming more water-wet. Early studies showed that the presence of clay, especially kaolinite, and crude oil and brine in the restored state are all necessary for additional oil recovery by LSW. It was first suggested that low salinity brine increased the electrostatic repulsion between kaolinite fines and grains, thus liberating the fines and the oil adhering to them (4). However, later studies demonstrated a low salinity effect in kaolinite-free sandstones (5,6). Further, in the majority of core plug LSW experiments, fines production or formation damage have not been observed. LSW of core plugs is frequently seen to be associated with an increase in pH, presumably resulting from cation exchange on the clay surfaces. Increase in pH generally leads to lowering of oil-brine interfacial tension (IFT) - as a milder version of oil saponification in alkaline flooding - and increased oil-rock repulsion, and was thus proposed as a mechanism for additional oil recovery by LSW (7).

Other researchers proposed alternative electrostatics-based mechanisms, such as multicomponent ion exchange or more generally, double layer expansion. In multicomponent ion exchange, cation exchange (eg Ca^{+2} and Mg^{+2}) between the mineral surface and the injected brine is thought to be the major mechanism behind low salinity water flooding(8). Decrease in salinity expands the electrostatic double layers (9) at the opposing oil/brine and brine/rock interfaces to thus increase the range of their electrostatic interactions. If repulsion is prevalent, this expansion causes the intervening brine film to increase in stability and thickness, which can shift the rock to being more water-wet and favor oil release and recovery. Other researchers have proposed that, based on the so-called salting-in effect (10), the solubility of organic material in water can be increased by removing salt from water, and therefore decrease in brine salinity below a critical ionic strength can lead to desorption of organic material from clays and its dissolution in the aqueous phase, to also favor a water-wet state and oil release. A multitude of other, related or unrelated mechanisms have also been hypothesized, including pH-induced desorption of organic material and mineral dissolution. The first one proposed that crude oil polar component becomes more soluble in water during low salinity water flooding and increases the pH locally in the vicinity clays and causes the detachment of organic materials from clays surfaces(11,12). In mineral dissolution, some minerals like anhydride can be dissolved during low salinity water flooding and will increase pH of solution which in turn changes the wettability of rock to more water wet (13).

Further, an osmotic pressure mechanism was also introduced recently, in which oil acts as a semi-permeable membrane. Pockets of high and low salinity brine either side of the oil can thus exert pressure to mobilize the oil and open new pathways (14). In summary, while it is generally accepted that oil/brine/rock interactions play a key role in the low salinity effect, the exact mechanism(s) are still debated (15). This partly stems from the difficulties in distinguishing causes and consequences in results from core plug flooding experiments. Some of these proposed mechanisms may only be side effect of the true mechanism.

1.3 Wettability

Wettability in general is defined as the tendency of one fluid, e.g. crude oil, to spread on or adhere to a solid surface, e.g. rock surface, in presence of another immiscible fluid, e.g. connate brine (16). When oil migrates from the source rock under gravity to form the reservoir, the capillary pressure suffices to displace brine from the center of larger pores, while smaller pores remain brine-filled. If the oil/brine/rock interactions are locally attractive, the brine films lining pore walls destabilize and become thinner, allowing local adsorption and deposition of the most polar components of the crude oil, namely its asphaltenes. In this way, these exposed surfaces of the rock become more oil-wet, while other surfaces protected by brine retain their native water-wetness, resulting in the so-called state of mixed wettability. Accurate characterization of the wettability state of the reservoir is paramount, since it has a significant effect on the amount, rate and efficiency of oil recovery by water flooding and subsequently by EOR techniques (17).

Wettability is characterized in the laboratory, usually using the Amott and/or USBM methods. These methods determine the overall saturation of oil and brine in restored core plugs during imbibition and drainage cycles. They thus characterize the core plug in terms of one or two indexes, which average the contributions from differing rock types or pore types within the plug and give no insight into the pore-scale distribution of the liquids. Alternatively, wettability can be more directly assessed via measurement of the advancing and receding contact angles of an oil droplet in brine on a (model) rock surface, although the scope of suitable surfaces is limited and the effects of roughness and heterogeneity are difficult to capture (18). The role of wettability in LSW has been investigated in many studies using these or related techniques (3,19-26), on the basis of which a shift towards a more water-wet state has often been inferred (27-32).

1.4 Digital Rock Analysis

Visualization and analysis of the pore-scale microscopic displacement due to LSW can help to improve understanding of its underlying mechanism(s) (33). Digital rock analysis uses a combination of powerful imaging tools, in particular micro-CT, scanning electron microscopy (SEM) and SEM with energy dispersive X-ray spectroscopy (SEM-EDS), to acquire 3D images of small rock samples at resolutions down to 1 μm , and 2D images of their sections at even higher resolution and with identification of the spatial distribution of minerals. Further, X-ray contrast techniques such as use of X-ray dense dopants have been developed to distinguish in micro-CT the distribution of immiscible fluids such as oil and brine in rock pores (34). Further, image processing techniques facilitate spatial registration of the tomograms of the same rock sample before and after each step in a sequence of laboratory-prepared states, such as saturation, drainage and imbibition experiments. Registration similarly allows the 2D SEM and SEM-EDS images of the subsequently cleaned sample to be aligned with the corresponding virtual section through the 3D tomograms for multi-modal image correlation. An extensive set of image analysis techniques have also been established for tomogram segmentation, to identify X-ray distinct phases of interest, e.g. rock grains or residual oil, and to partition and compute pore and fluid volumes, interfacial areas and curvatures, and other metrics (35,36). In addition, the insight gained from this pore-scale investigation of LSW can be extended towards nanometer scales using ultra-high resolution images from field emission SEM (FESEM) of asphaltenic residues of oil on mineral surfaces, the presence and extent of which dictate wettability alteration and change.

These capabilities of digital rock technology also introduce some constraints beyond those of traditional core flooding experiments. Resolution of pores by micro-CT in typical reservoir sandstones requires the use of miniaturized plugs, referred to as mini-plugs, of 3-5 mm diameter. One central challenge in digital rock analysis of LSW is thus to design and conduct the workflow of experiments and imaging on these mini-plugs to provide pore-scale insight while simultaneously minimizing the introduction of artifacts due to coring damage, brine doping and exposure to X-rays. Most of the studies in this thesis are of oil recovery by spontaneous imbibition of high and low salinity brine, since the experiments are simpler and the responses provide a more direct connection to salinity-induced wettability changes. However mini-plug LSW studies were also performed for comparison to spontaneous imbibition and to core plug LSW.

1.5 Thesis Outline

Chapter 2 is a micro-CT study of the recovery of crude oil by spontaneous imbibition of high and low salinity brine in mini-plugs of outcrop Berea sandstones. There the main workflow of the thesis is developed, involving the acquisition of tomograms of each mini-plug in a sequence of states, their registration and their segmentation for quantitative analysis of the distribution of residual oil (including resolved and sub-resolution contributions) and its salinity-induced changes.

Chapter 3 applies and extends the techniques developed in Chapter 2 to a micro-CT study of spontaneous imbibition of high and low salinity brine in mini-plugs of a North Sea reservoir sandstone, which is the main focus of this thesis. In particular, two crude oils, primarily differing in their acid number, were investigated for their low salinity response. The micro-CT imaging and analysis was complemented by FESEM imaging of asphaltene residues of these two oils on mineral surfaces.

Chapter 4 extends the spontaneous imbibition study of Chapter 3 to water flooding experiments performed by injection of high and low salinity brines into mini-plugs of the reservoir sandstone in a mini-holder/flow cell. Further, the analysis of Chapter 3 is extended by analyzing regions of interest within the mini-plug to decouple the true LSW response from the artificial contribution to recovery from the strong capillary end effect.

Chapter 5 complements the micro-CT-based studies of the reservoir sandstone in Chapters 3-4 by preparing polished sections of these same mini-plugs on which SEM and SEM-EDS are acquired and registered into the tomogram series. In this way the residual oil distributions from micro-CT are overlain onto the SEM-EDS mineral maps for spatial correlation of local oil detachment by low salinity to the underlying local mineralogy.

2 Spontaneous Imbibition in Outcrop Sandstones

2.1 Introduction

Laboratory and field data shows that oil recovery from clay-containing sandstones can increase by reduction of injected brine salinity. However the amount of EOR achieved is very variable and difficult to systematically optimize, due to insufficient understanding of this process (1,2,37,38,39).

In recent years, many researchers have attempted to determine the mechanism(s) behind additional oil recovery by low salinity flooding, referred to as the low salinity effect. Early studies pointed out that an initial water saturation and clay mineral, especially kaolinite, are necessary for the low salinity effect, and suggested that fines migration was likely responsible for displacing oil adhering to these fines (4). However, the low salinity effect was also observed in kaolinite-free rocks and in the absence of formation damage (5,6). pH increase is often reported during low salinity water flooding and was considered as an alternative explanation for the low salinity effect (7). Other researchers proposed that multicomponent ion exchange (8) or double layer electrostatic repulsion (9) was responsible for the oil release. While it is widely accepted that oil/brine/rock interactions play a central role in the low salinity effect, the specific mechanism(s) remain debated (15). An osmotic pressure mechanism was also introduced recently, based on oil acting as a semipermeable membrane (for water but not ions), to provide the driving force to move oil droplets and open new pathways (14).

One of main complications in understanding the low salinity effect is unscrambling the difference between cause and effect in observed results. Some of the above-mentioned proposed mechanisms may only be a side effect rather than a root cause. Wettability shift toward water-wetting has been inferred in most low salinity core flooding studies (27-32), and results from a switch in oil/brine/rock electrostatic interactions to favor repulsion of oil from mineral across brine. In spontaneous imbibition experiments, these interactions between liquids and rock drive recovery without imposition of any external force. Spontaneous imbibition is thus a suitable mode, and perhaps a better operative condition compared to core flooding, to focus on rock wettability changes and their link to pore-scale displacements and the low salinity effect.

Visualization and quantitative analysis of the microscopic displacement during high and low salinity water flooding would clearly help to improve our understanding of

underlying mechanism(s). X-ray micro CT is a powerful tool that provides non-destructive 3D imaging down to micron resolution, combined with subsequent computational analysis of the distribution of oil and brine in rock samples and their changes (19). However, resolution of pore-scale details such as shapes of menisci generally requires that the micro-CT imaging be performed on small plugs, called mini-plugs. Further, an X-ray dense agent must be added to oil or brine to selectively increase its attenuation and so provide contrast between these two liquid phases. The challenge is thus to analyze the pore-scale changes of the low salinity effect without introducing artifacts or nullifying the effect due to these imaging requirements and related perturbations, including effects of X-ray exposure and heightened sensitivity to rock damage, air bubbles and other contaminants.

In this Chapter, the low salinity effect in clay-rich outcrop sandstones is probed by micro-CT imaging and analysis. A set of eight Berea sandstone mini-plugs underwent primary drainage and aging in crude oil to a mixed-wet state, followed by spontaneous imbibition of high and low salinity brines and imaging of this sequence of prepared starting and endpoint states. Tomogram registration and analysis were used to determine the salinity-induced changes in oil volume, oil/rock and oil/brine interfacial areas, and oil/brine interfacial mean curvature. Pore-scale statistics were extracted to explore any local correlation between the low salinity effect and pore geometry/topology. The qualitative observations and quantitative analyses demonstrated that the small oil recovery by the low salinity effect corresponded to a slight shift towards water-wet.

2.2 Materials and Methods

2.2.1 Materials

Three Berea outcrop sandstone samples labeled A, B and C were used in this study. Samples A and B had air permeability of ~ 60 mD and porosity of 18.3% and 17.9%, respectively, from MICP, while sample C had air permeability of ~ 500 mD and porosity of 19.5% from MICP. The crude oil used was from the Minnelusa formation, with density and viscosity of 0.9062 gcm^{-3} and 77.2 mPa.s at 20°C . It has n-C₇ asphaltene content of 9.0 wt % and acid and base numbers of 0.17 and 2.29 mg KOH/g oil, respectively. The initial (connate) and high salinity brine corresponded to Minnelusa reservoir brine (MRB), while the tested low salinity brines were 20- or 100-

fold dilutions of the high salinity brine (0.05MRB or 0.01MRB). The rock, oil and brine thus match those used in the plug-scale study of the low salinity effect by the group of Morrow (40).

For micro-CT imaging, the Berea samples were cored to 3 or 5 mm diameter mini-plugs using a manually-fed drill press with air as lubricant, and then cut using a diamond-blade saw to a length of 12.5 mm. Further, X-ray attenuation contrast was introduced via a so-called contrast brine, prepared by substituting 0.3 M NaCl for 0.3 M NaI (sodium iodide) in the high salinity brine recipe. The compositions of the MRB and Contrast brine are given in Table 2.1. All brines were vacuum degassed and adjusted with NaOH or HCl to pH 6.1-6.3 prior to use.

The rock samples were additionally characterized for spatial mineralogy and pore throat radius. For mineralogy, sister mini-plugs of 5 mm diameter were embedded in epoxy resin, cut crosswise for Berea samples A and B and lengthwise for sample C, and polished. 2D mineral maps of these polished sections were generated using automated SEM-EDS acquisition and analysis by QEMSCAN (FEI) acquired at 3 μm step size on a Quanta 650-FEG (FEI) microscope. Table 2.2 list the modal minerology obtained per area of each of these three Berea samples, while Figure 2.1(a-c) present their corresponding distributions. Strong similarities between the three are evident, although sample A possesses less quartz, compensated by more of most of the other minerals. Of the average of 4.5% clay present per sample, the main clay mineral is kaolinite, although muscovite/illite, biotite and chlorite also occur in significant fractions. The MICP curves in Figure 2.1(d) show that samples A and B are very similar, while C has somewhat larger pore throats, as expected from its higher permeability.

Table 2.1 Minnelusa Reservoir brine and Contrast brine recipe (mmol/l) and compositions (ppm).

Brine recipe	NaCl mmol/l	CaCl₂.2H₂O mmol/l	MgCl₂.6H₂O mmol/l	Na₂SO₄ mmol/l	NaI mmol/l	Ionic strength mmol/l	TDS g/l
Minnelusa	496.0	19.0	7.0	48.6	0	719.5	38.6
Contrast	196.0	19.0	7.0	48.6	300.0	719.5	66.09
Brine Composition	Na⁺ (ppm)	Ca²⁺ (ppm)	Mg²⁺ (ppm)	SO₄²⁻ (ppm)	Cl⁻ (ppm)	TDS (ppm)	
Minnelusa	13635	760	170	4664	19424	38653	

Table 2.2 Modal mineralogy from QEMSCAN of the three Berea sandstones.

	Berea A, Area %	Berea B, Area %	Berea C, Area %
Quartz	82.65	88.31	89.41
Alkali Feldspar	5.47	2.94	3.22
Plagioclase	1.83	1.22	0.75
Muscovite/Illite	0.90	0.59	0.63
Biotite	0.83	0.50	0.46
Kaolinite	3.14	2.95	2.52
Chlorite	0.43	0.29	0.28
Calcite	0.02	0.16	0.00
Dolomite/Ankerite	1.24	0.56	0.64
Siderite	0.24	0.25	0.04
Apatite	0.00	0.00	0.02
Pyrite	0.01	0.02	0.02
Rutile	0.12	0.12	0.06
Zircon	0.08	0.06	0.03
Unclassified/traces	3.07	2.06	1.96

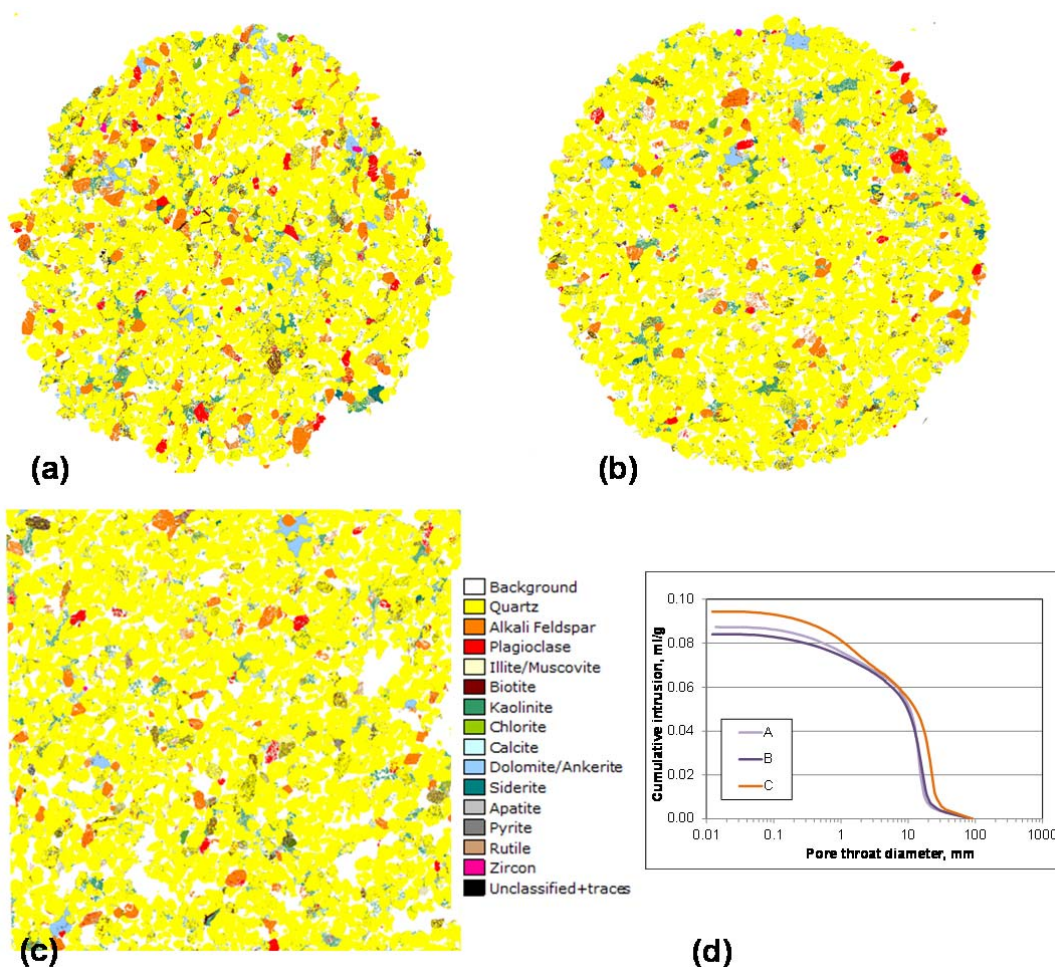


Figure 2.1 Mineral maps from QEMSCAN of mini-plug sections of Berea sandstone samples (a) A, (b) B, and (c) C; (d) Cumulative mercury intrusions for all three Berea samples.

2.2.2 Experimental Methods

2.2.2.1 Micro-CT Scanning

All imaging was performed at the ANU micro-CT facility. Each mini-plug was mounted in its sealed aluminum-tube holder for scanning, first in its dry state and then after oil recovery by spontaneous imbibition of high and low salinity brine, and in some cases again after imbibition of even lower salinity brine. Most mini-plugs were scanned over their middle section using a standard circular trajectory, although one mini-plug was scanned over a greater height and at higher fidelity using a helical trajectory on a HeliScan instrument (41).

2.2.2.2 Treatment of Mini-plugs

After micro-CT scanning in its dry state, each mini-plug was saturated with Minnelusa reservoir brine (MRB) by evacuation and vacuum infiltration for 3-4 hours. It was then transferred to a glass vial filled with crude oil and with 1 g of sand bed at the bottom. The mini-plug in its vial was centrifuged at the chosen speed (capillary pressure) for 20 min in each direction to uniformize the irreducible brine saturation profile. The mini-plug was then transferred to a second glass vial prefilled with crude oil and with its lid sealed by epoxy, and aged in an oven at 75 °C for 14 days. The first vial, with its oil and sand bed containing the drained brine, was used to measure the average initial water saturation of the mini-plug from the difference in brine mass between that originally saturating the mini-plug and that drained during centrifugation. The former was determined gravimetrically from the weight difference between the brine-saturated and dry state of the mini-plug. The latter was inferred from titration, by pipetting off the oil above the sand bed and homogenizing the remaining oil and brine in the sand by adding 1.9 g of dichloromethane (DCM) and 0.7 g of methanol, from which the blend's water content was determined by Karl Fischer titration.

Spontaneous imbibition (SI) was performed by transferring the aged plug to a vial containing 2.5 ml of brine (usually MRB) for secondary recovery at 75 °C for 7 days. Following this high salinity recovery step, the plug was transferred to another vial containing 2.5 ml of Contrast brine (see Table 2.1) at room temperature for 3 days, to allow diffusional exchange of MRB for Contrast brine (i.e. diffusion of Cl^- out and I^- in). This exchange step, to heighten the X-ray attenuation of the brine phase above that of oil, was conducted at room temperature to prevent or minimize any extraneous oil

production or movement. The mini-plug after this first spontaneous imbibition and exchange was then micro-CT scanned while immersed in this Contrast brine. The scanned mini-plug was then transferred back to a vial containing 2.5 ml of the un-doped brine (usually MRB) at room temperature for 3 days to allow diffusional re-exchange of Contrast brine for un-doped brine.

A second spontaneous imbibition was then performed by immersing the mini-plug in 2.5 ml of a second brine (usually diluted MRB) at 75 °C for 7 days. After this low salinity recovery step in tertiary mode, the above-mentioned transfer to Contrast brine was repeated for imaging of this second imbibed and exchanged state. Care was taken during all steps to avoid air entering the pore space.

2.2.3 Image Processing and Analysis

The 3D tomograms of each mini-plug in its dry state and after spontaneous imbibition of high salinity brine (SIH) and in turn low salinity brine (SIL) or very low salinity brine (SILL) were reconstructed and then post-processed and analyzed using Mango (42-44) software. After masking to exclude the plug holder walls, the tomograms of the spontaneously imbibed states were registered into perfect alignment with the dry-state tomogram. Segmentation was then performed using a converging active contours algorithm (42) to distinguish the oil and brine phases for calculation of residual oil saturation and metrics of its distribution.

Figure 2.2 displays a central longitudinal slice of the tomogram of a 5 mm mini-plug of Berea sample C in its SIH contrasted state in its aluminum sample holder. Oil is the darkest phase since it has lowest X-ray attenuation, while the aqueous phase is of uniform intermediate brightness due to its doping with NaI. The brighter grayscales are the rock, ranging from lower density minerals such as quartz and kaolinite to high density minerals (brightest) such as zircon. Guided by the mineral identification from the QEMSCAN map of a polished section, and its overlay onto the corresponding virtual section through the tomogram, groups of minerals can be separately distinguished according to their X-ray attenuation interval. In particular, Figure 2.2 shows examples of quartz, kaolinite, alkali (potassium) feldspar, muscovite/illite, dolomite/ankerite, and zircon, circled using their respective colors in the QEMSCAN legend of Figure 2.1(a-c).

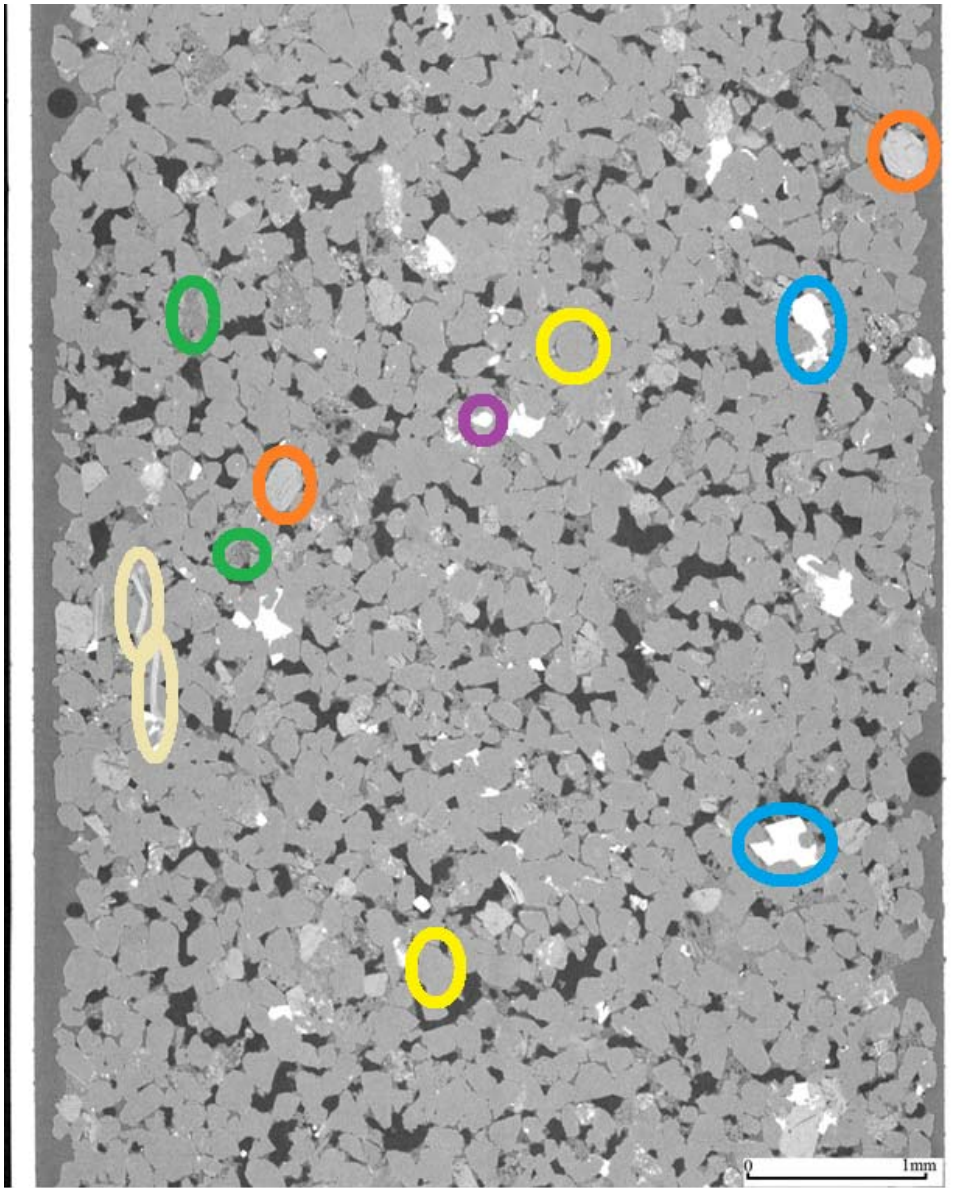


Figure 2.2 Central longitudinal slice of a 5 mm mini-plug of Berea C in its state of residual oil (dark blobs) after spontaneous imbibition of MRB (intermediate gray within and surrounding the mini-plug), with scale bar of 1 mm. Circles of yellow, orange and purple show grains of quartz, alkali feldspar and zircon, blue shows dolomite/ankerite cement, while green and light yellow show kaolinite and muscovite/illite, respectively.

2.3 Results and Discussion

2.3.1 Image Analysis of Residual Oil

Table 2.3 lists all experiments performed on the eight samples and their key details and results. Each row corresponds to an imaged state, the naming of which in the first column follows the formula: mini-plug number (1-8), Berea sample (A-C), imbibition

experiment number (1-3), and imbibing brine (H = MRB, L = 0.05MRB, LL = 0.01MRB). For example, the state in the first row **1_A_1_H** is the first mini-plug studied, taken from Berea sample A, imaged after its first spontaneous imbibition (secondary recovery), of high salinity brine MRB. Columns 2-7 of Table 2.3 list the experimental details, namely the mini-plug diameter, the porosity from MICP on the sister sample of Berea A-C from Figure 2.1(d), the centrifuge spin speed used in primary drainage, equivalent capillary pressure imposed on mini-plugs by centrifuge, the initial brine saturation determined from gravimetric and titration measurements as described above, and the brine used in subsequent spontaneous imbibition. Columns 8-11 list the results from segmentation of residual oil in the tomogram corresponding to this imbibition step (SIH, SIL or SILL). In particular, two-phase segmentation of each such imaged state was performed to distinguish the residual oil resolved at the tomogram voxel size of approximately 2 or 3 μm for the 3 or 5 mm diameter mini-plugs, respectively. Figure 2.3 displays an example of the result of this segmentation. The remainder of space comprises the grains and clay minerals and brine occupying the rest of the resolved pores (referred to as macro-pores) and filling the sub-resolution microporosity. Instances of oil in micro-pores were comparatively rare and were not considered in this simplest segmentation, but will be analyzed in the next sub-section.

Table 2.3 Experimental details of Berea mini-plugs and residual oil segmentation results.

Sample Name	Diameter (mm)	Φ (MICP) (%)	Spin speed (rpm)	P_c (psi)	S_{wi} (%PV)	Flood Brine	Oil volume Fraction (%BV)	S_{or} (%PV)	RF (%OOIP)	ARF (%OOIP)
1_A_1_H	3	18.3	2250	2.47	36.0	MRB	9.0	49.0	23.4	
1_A_2_L	3	18.3	2250	2.47	36.0	0.05MRB	7.9	43.4	32.3	8.9
2_A_1_H	3	18.3	3500	5.97	9.3	MRB	7.1	38.9	57.1	
2_A_2_LL	3	18.3	3500	5.97	9.3	0.01MRB	7.0	38.2	57.9	0.8
3_A_1_L	3	18.3	3500	5.97	6.6	0.05MRB	7.0	38.4	58.9	
3_A_2_LL	3	18.3	3500	5.97	6.6	0.01MRB	6.9	37.8	59.6	0.7
4_B_1_H	3	17.9	3500	5.97	12.4	MRB	7.1	39.4	55.0	
5_B_1_L	3	17.9	3500	5.97	16.3	0.05MRB	6.9	38.8	53.6	
6_C_1_H	3	19.5	2250	2.47	39.1	MRB	5.6	28.9	52.5	
7_C_1_H	5	19.5	3000	4.39	18.2	MRB	10.6	54.6	33.3	
7_C_2_L	5	19.5	3000	4.39	18.2	0.05MRB	10.1	52.1	36.3	3.0
8_C_1_L	5	19.5	3000	4.39	18.2	0.05MRB	10.6	54.5	33.4	
8_C_2_H	5	19.5	3000	4.39	18.2	MRB	10.5	54.1	33.8	0.4
8_C_3_LL	5	19.5	3000	4.39	18.2	0.01MRB	10.3	52.7	35.6	1.8

Column 8 in Table 2.3 lists the volume fraction of segmented residual oil relative to the overall bulk volume of the tomogram field of view within the mini-plug, while column 9 converts this to average residual oil saturation after division by MICP porosity in column 3. Oil recovery factor RF was calculated as a percentage of original oil in place (OOIP) in column 9 as:

$$RF(\%OOIP) = \frac{S_{oi} - S_{or}}{S_{oi}} \times 100 \quad (1)$$

where $S_{oi} = 1 - S_{wi}$ is initial oil saturation from column 6 and $S_{or}(\%PV)$ is from column 9. Enhanced oil recovery, ΔRF , shown in the last column of Table 2.3, is the increment in RF from one state of spontaneous imbibition (e.g. SIH) to the next (e.g. SIL).

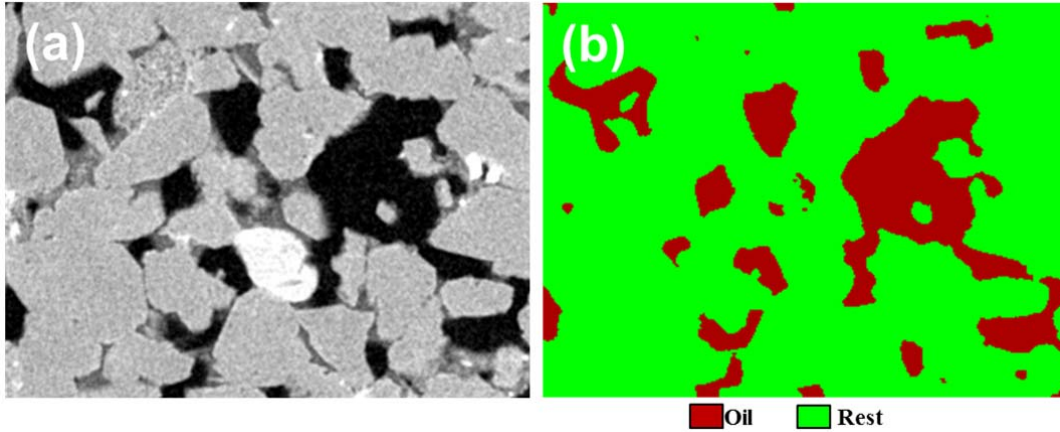


Figure 2.3 Tomogram subarea (1.1 mm × 0.8 mm) of sample 7_C after (a) SIH and (b) its two-phase segmentation into oil and the remainder.

The matrix of experiments investigated the effects of varying initial brine saturation and the subsequent sequence of SIH, SIL and SILL. The first two mini-plugs studied, 1_A and 6_C, were primary drained to relatively low capillary pressure, yielding very high S_{wi} (36.0% and 39.1%, respectively). Centrifuge spin speed was increased to achieve lower S_{wi} in the subsequent six mini-plugs. The 3 mm diameter mini-plugs of Berea A remained intact through the planned pair of imaged states of spontaneous imbibition in Table 2.3. Those of Berea B and C broke on handling after their first imaged state, so no evaluation of incremental recovery in tertiary mode was possible. Owing to their delicacy, and to the higher permeability of Berea C, later experiments on this sample

used mini-plugs (7_C and 8_C) of 5 mm diameter, which remained intact through their planned imaging sequences.

The Contrast brine used for exchange after the first spontaneous imbibition of the first mini-plug tested (state 1_A_1_H) contained 0.15 M NaI rather than the 0.3 M NaI in Table 2.1. This low concentration of dopant was used to minimize perturbation of the imbibed state during the ion exchange step. However, the resulting X-ray attenuation contrast between oil and brine was so weak that segmentation of oil in the tomogram became difficult and ambiguous. The concentration of NaI in the Contrast brine was thus increased to 0.3 M in all subsequent imaged states. Figure 2.4 shows a longitudinal slice of the tomogram sequence of mini-plug 1_A registered between its dry state and after SIH and after SIL. The increase in brightness of the aqueous phase from SIH to SIL, and the consequent increase in oil/brine contrast for segmentation, is apparent.

The incremental recovery factor of 8.9% due to low salinity in this first mini-plug 1_A in Table 2.3 is much greater than in all other subsequently tested mini-plugs. In Figure 2.4, the distribution and shape of residual oil after SIH is suggestive of a mixed-wet state. Oil recovery by low salinity brine, via release from surfaces of grains and clay aggregates bounding larger pores, appears to be substantial. On the other hand, oil in smaller pores between pore-filling kaolinite booklets (near the top of the zoom-in in Figure 2.4(e-f)) does not appear to have been displaced. Some local movement of fines also occurs in association with the additional oil displacement. The high incremental recovery may stem in part from the low secondary recovery factor (lowest of all mini-plugs) and in part from the above-mentioned uncertainty in oil segmentation of the SIH tomogram, and thus the results for mini-plug 1_A in Table 2.3 should best be regarded as an outlier.

Figure 2.5 displays similar registered views of the tomograms of mini-plug 2_A, which underwent SIH in secondary mode and SILL in tertiary mode. Compared to 1_A, this mini-plug was drained to lower S_{wi} (9.3%), and yet the resolved oil blob shapes after SIH are now more suggestive of a weakly water-wet state with relatively small brine-advancing contact angles. Occurrence of oil within kaolinite aggregates is also rarer than in 1_A. These observations are consistent with the much higher recovery factor (57.1%) by spontaneous imbibition. Incremental recovery from 2_A by (very-) low salinity brine was the least of all mini-plugs in Table 2.3, possibly owing to this water-wet state after SIH allowing little scope for extra recovery in SILL by further shift to

more water-wet. The differences between mini-plugs 1_A and 2_A emphasize the variability in experiments on such small sub-samples. The large matrix in Table 2.3 was thus tested to reduce this variability and obtain clearer overall indications of the low salinity effect.

Mini-plug 3_A in Table 2.3 was drained down to an initial brine saturation of 6.6%, similar to 2_A, but then underwent SIL (rather than SIH) in secondary recovery mode, followed by SILL in tertiary mode. Residual oil saturation and recovery factor of SIL and SILL for 3_A were very similar to the corresponding values of SIH and SIL for 2_A. This implies that the low salinity effect is largely absent in both secondary and tertiary mode. A representative slice from this sequence of registered tomograms for mini-plug 3_A is shown in Figure 2.6. The distribution of residual oil is qualitatively similar to that in 2_A and is consistent with a weakly water-wet state in which the adhesion of oil to rock only appears to be strong in certain locations. The switch from SIL to SILL results in occasional detachment of oil and withdrawal of the terminal meniscus, but usually to an insufficient extent to lead to overall recovery.

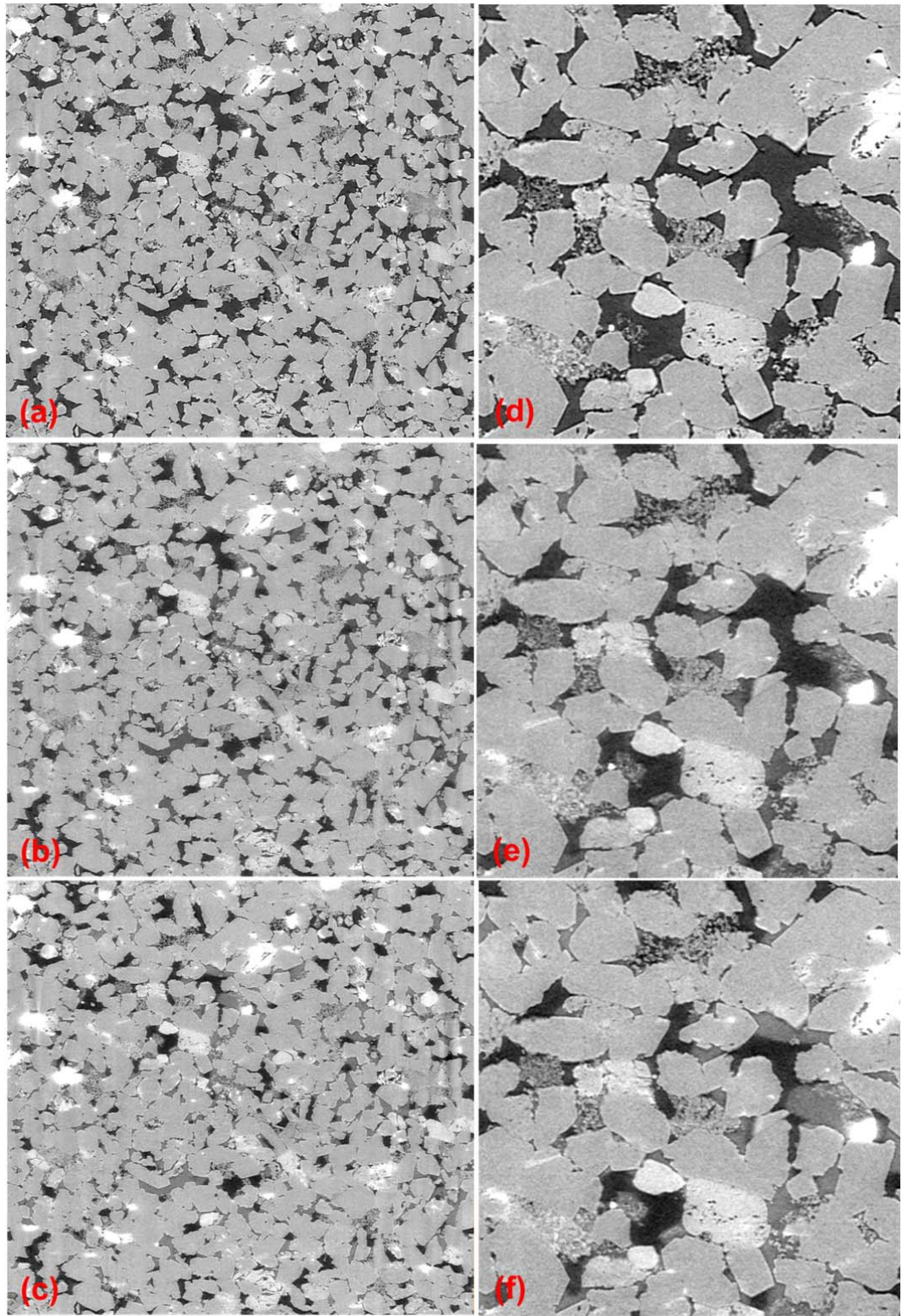


Figure 2.4 Tomogram longitudinal slice of 3 mm diameter mini-plug 1_A, masked to 2.9 mm $\times$ 2.7 mm, and registered between the (a) dry state, and the states after (b) SIH followed by (c) SIL. (d-f) Zoom-in of a sub area of 1.0 mm $\times$ 1.1 mm from the slice at left.

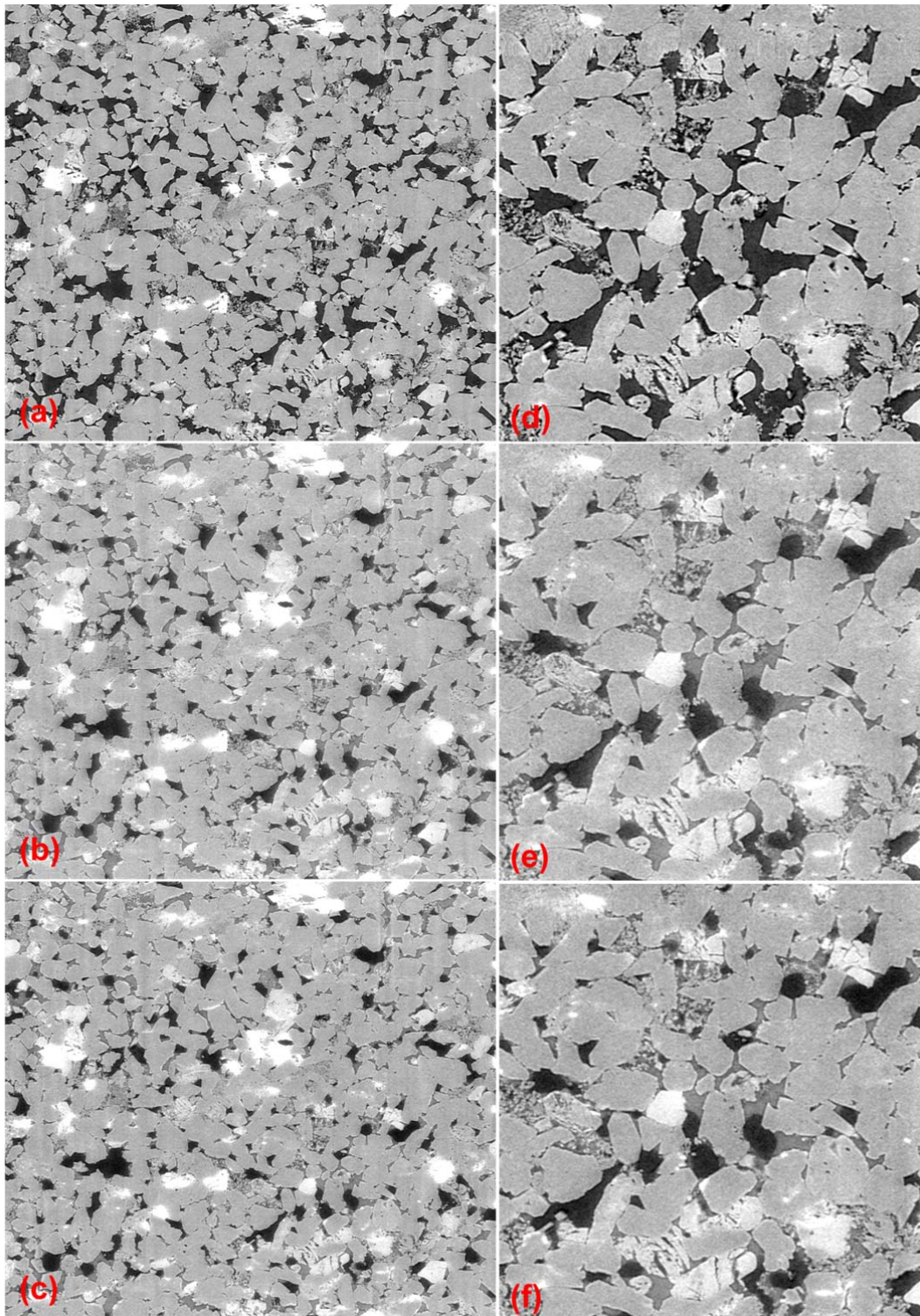


Figure 2.5 Tomogram longitudinal slice of 3 mm diameter mini-plug 2_A, masked to $3.0 \text{ mm} \times 2.7 \text{ mm}$, and registered between the (a) dry state, and the states after (b) SIH followed by (c) SILL. (d-f) Zoom-in of a sub area of $1.2 \text{ mm} \times 1.2 \text{ mm}$ at left.

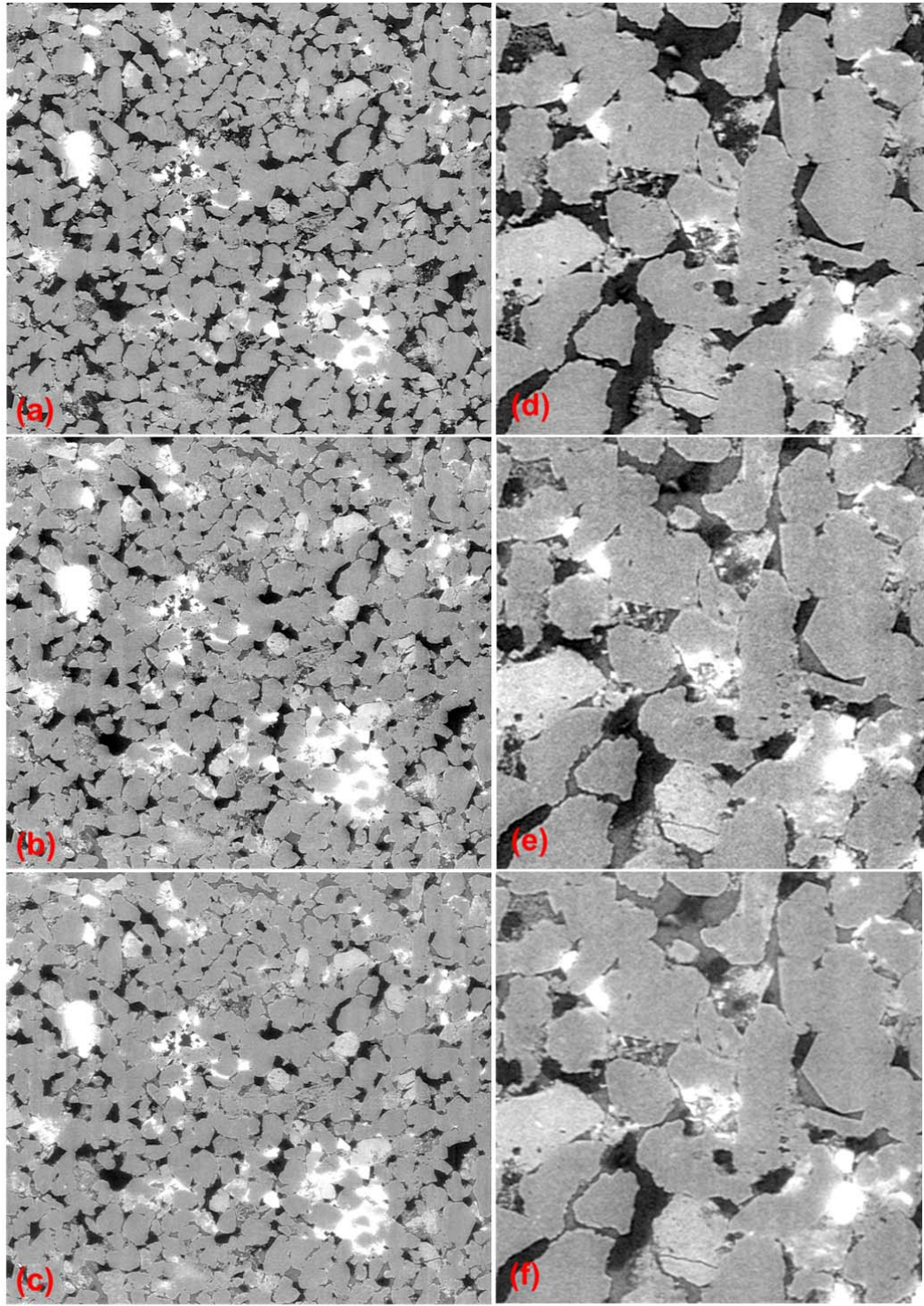


Figure 2.6 Tomogram longitudinal slice of 3 mm diameter mini-plug 3_A, masked to $2.5 \text{ mm} \times 2.2 \text{ mm}$, and registered between the (a) dry state, and the states after (b) SIL followed by (c) SILL. (d-f) Zoom-in of a sub area of $1.3 \text{ mm} \times 1.4 \text{ mm}$ at left.

Formation of water emulsions in the bulk oil during low salinity water flooding has been reported in several studies (14, 45) and has been hypothesized as an additional mechanism for oil recovery. Stable droplets of brine in oil were also observed in the Berea A mini-plugs of this study, with the highest amount in 1_A, occasional occurrence in 3_A, and only very rare instances in 2_A. Figures 2.7 and 2.8 show registered tomogram slices and subareas from 1_A and 3_A after their sequence of two imbibition states. Cyan circles show examples of oil displacement by detachment and meniscus movement, as described above, during SIL in tertiary mode in 1_A. On the other hand, green circles show emulsified brine droplets that form during tertiary mode imbibition (SIL for 1_A and less commonly for SILL in 3_A).

These stable droplets generally form within larger pores that are completely oil-filled and that lie near the mini-plug periphery. The mechanism for their formation and stabilization is not fully understood. One possible explanation is that they form due to shearing of the oil during insertion of the mini-plug into its holder for imaging; however this would not seem to explain their preference for the SIL state. Another explanation is that they form by osmotic pressure, which acts to pump water molecules from the surrounding low salinity brine through the semi-permeable membrane of oil to hydrate pockets of high-salinity connate brine that have been disconnected and isolated by the pore-filling oil. In this case the hydration driving force that swells these locally isolated connate pockets to droplets must also reconnect them, since subsequent ion exchange of Cl^- for I^- in the Contrast brine (which cannot pass through oil) accesses and brightens the droplets in the tomogram.

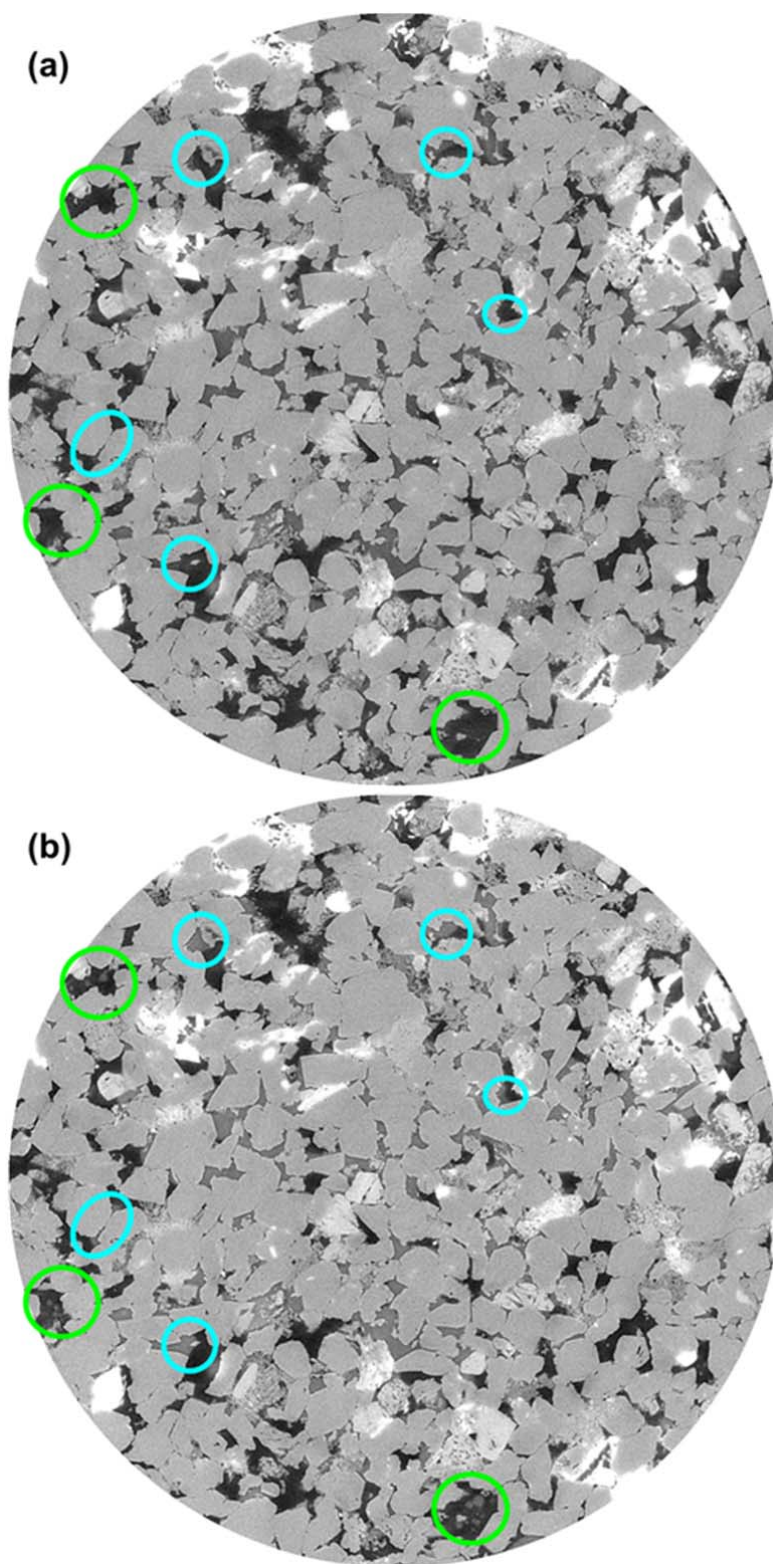


Figure 2.7 Tomogram cross-sectional slice of 3 mm diameter mini-plug 1_A, masked to 2.7 mm $\times$ 2.7 mm, and registered between (a) SIH and (b) SIL, with circles showing low salinity brine displacing oil (cyan) and emulsified brine (green).

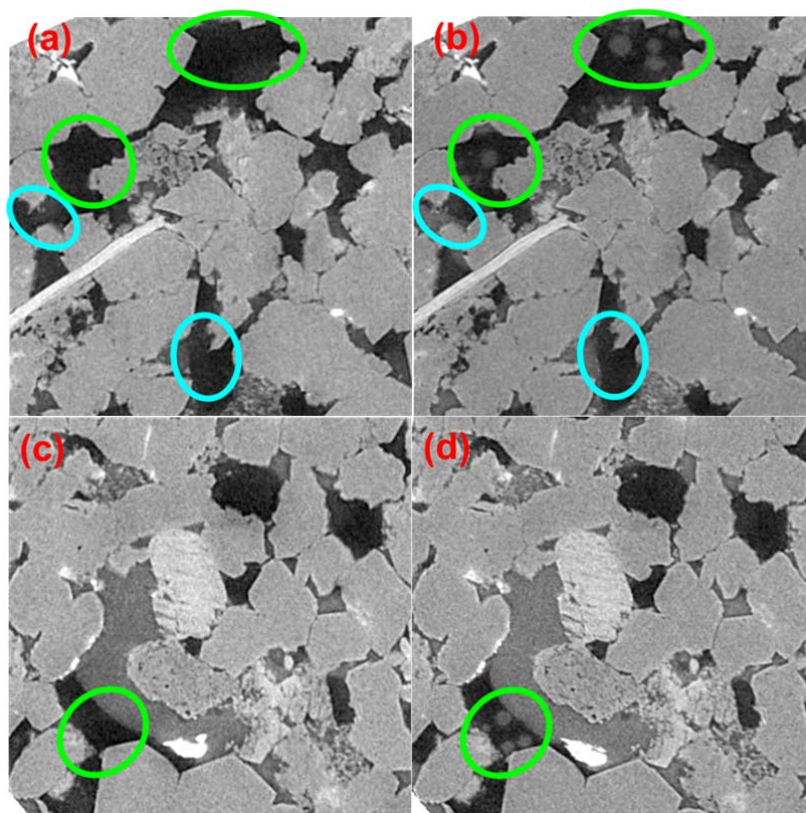


Figure 2.8 Subarea ($0.66 \text{ mm} \times 0.66 \text{ mm}$) of tomogram cross-sectional slice of 3 mm diameter mini-plug 1_A, and registered between (a) SIH and (b) SIL, and similarly for 3 mm diameter mini-plug 3_A of the same sized subarea for (c) SIL and (d) SILL. Circles show low salinity brine displacing oil (cyan) and emulsified brine (green).

For the two mini-plugs 4_B and 5_B of 3 mm diameter cored from Berea B, in which only one state of spontaneous imbibition was imaged in Table 2.3, the results are qualitatively similar to those for 2_A and 3_A. The measured initial brine saturation is again fairly low and secondary recovery factor from segmentation of either SIH or SIL is around 55%, so no low salinity effect is apparent. Representative cross-sectional slices of their tomograms, registered between the dry and imbibed states, are given in Figures 2.9 and 2.10. The oil distributions are again similar in nature to those for 2_A and 3_A, and are suggestive of a weakly water-wet or weakly mixed-wet state, in which partial recovery is associated with some local snap-off in water-wet locations, while the residual oil remains adhered to or pinned at locally more oil-wet locations on grains and on the extremities of pore-filling clay aggregates.

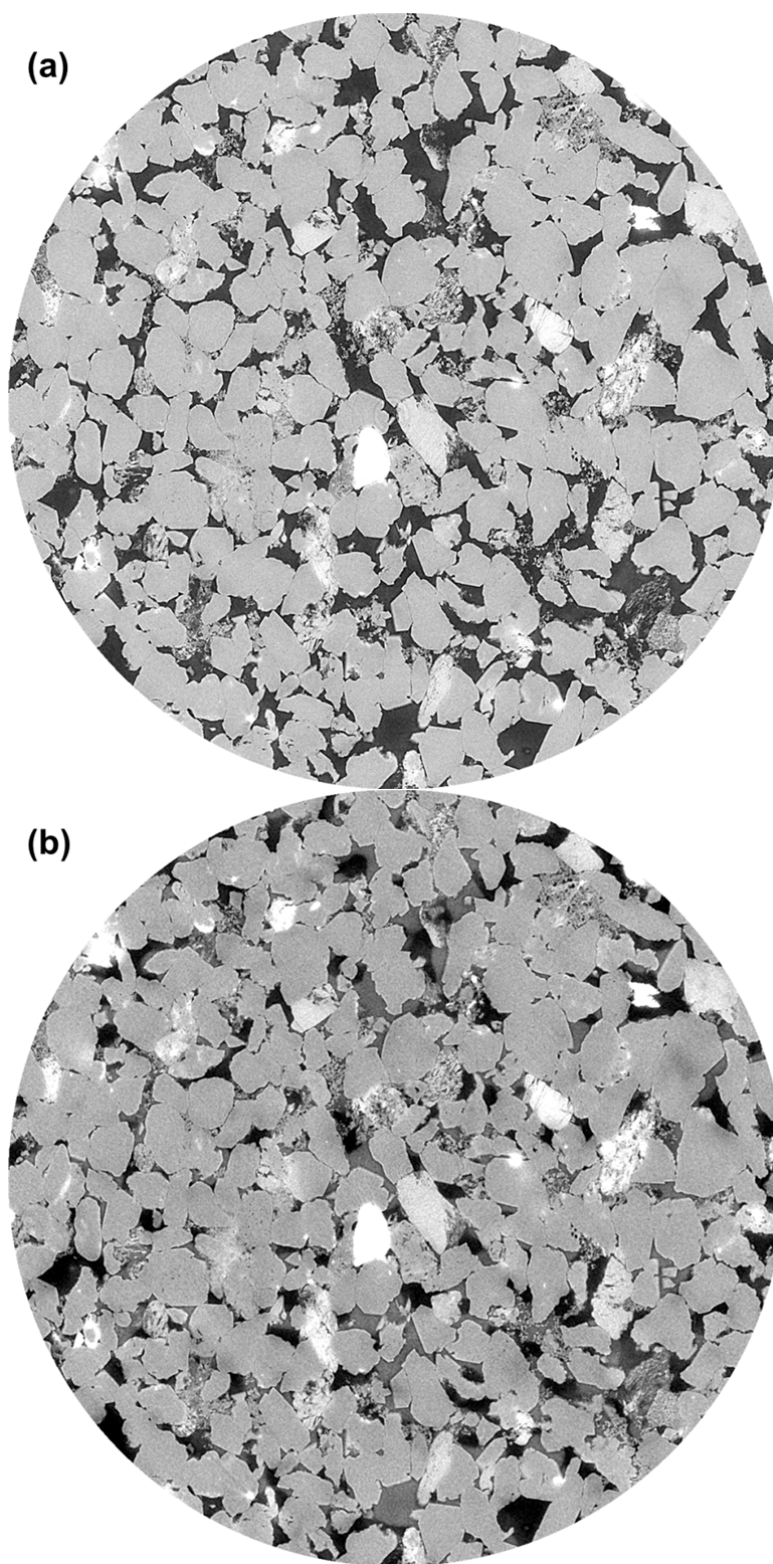


Figure 2.9 Tomogram cross-sectional slice of 3 mm diameter mini-plug 4_B, masked to $2.6 \text{ mm} \times 2.6 \text{ mm}$, and registered between the (a) dry and (b) SIH states.

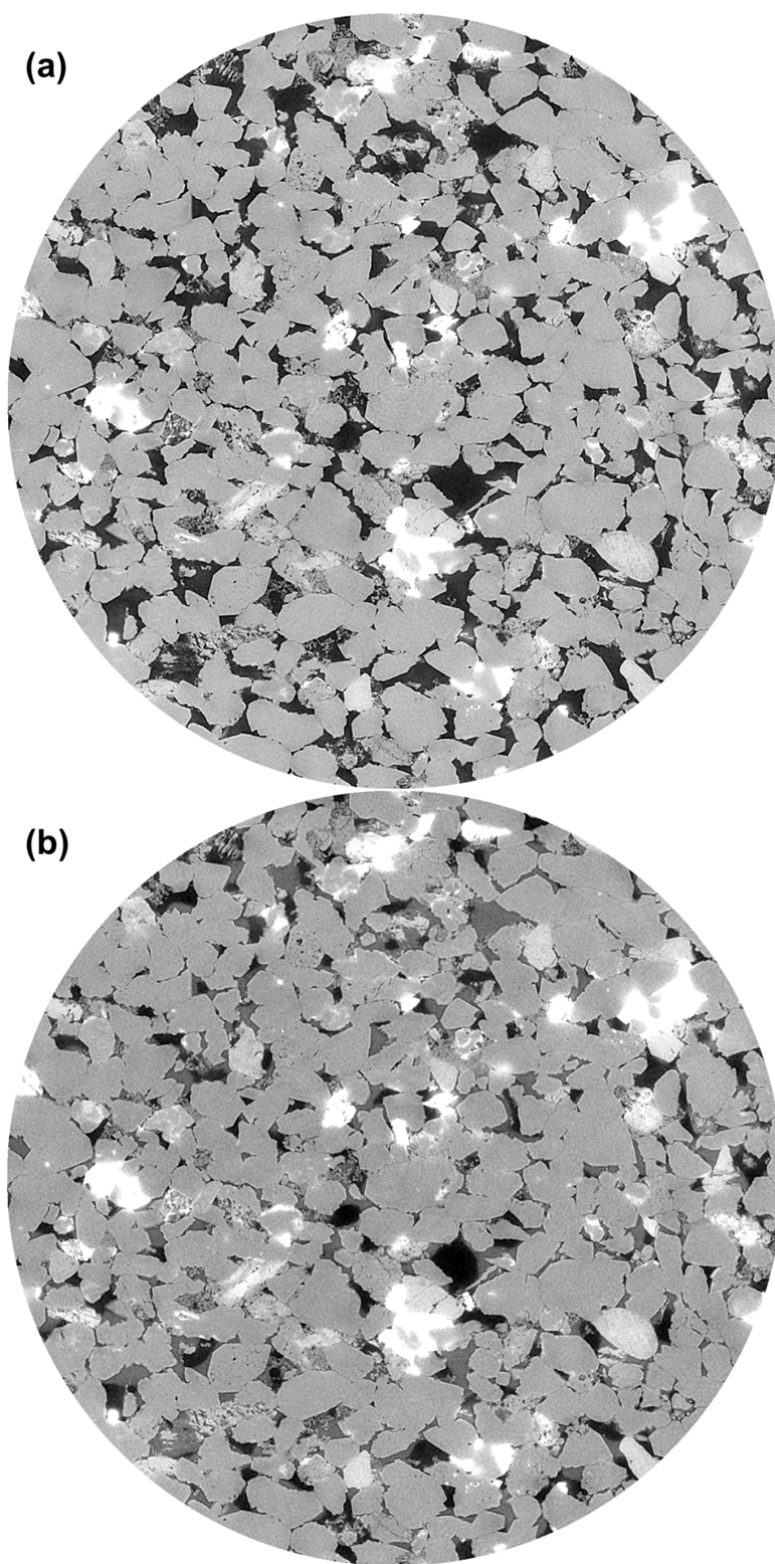


Figure 2.10 Tomogram cross-sectional slice of 3 mm diameter mini-plug 5_B, masked to $2.6\text{ mm} \times 2.6\text{ mm}$, and registered between the (a) dry and (b) SIL states.

Three mini-plugs were cored from the higher permeability Berea sample C, of 3 mm (6_C) and 5 mm (7_C and 8_C) diameter in Table 2.3. Mini-plug 6_C was drained at low capillary pressure, resulting in high initial water saturation of 39.1% similar to 1_A. However its secondary recovery factor for SIH was much higher than for 1_A and almost as high as for mini-plugs 2-5, further suggesting that the disparate results for 1_A are an outlier. As mentioned above, 6_C broke during subsequent handling, so tertiary recovery was not studied. A cross-sectional slice of the registered tomograms of its dry and SIH states is shown in Figure 2.11. The higher permeability of C relative to A and B is apparent from the substantially larger pores. The residual oil distribution is again suggestive of a weakly mixed-wet state, in which recovery and snap-off from water-wet locations has occurred, while in other locations the oil blobs remain anchored to hinder further recovery. These anchoring sites often correspond to pore-filling clay mineral, presumably kaolinite. Substantial mobilization of fines has taken place between the dry and SIH states, one example of which is circled in Figure 2.11. Some of these fines may have been created or liberated in the coring process and migrated further inwards, aided by the high permeability. This provided an additional reason for the switch from 3 to 5 mm diameter mini-plugs for the remainder of the Berea C studies.

For these subsequent two 5 mm diameter mini-plugs 7_C and 8_C in Table 2.3, primary drainage spin speed was increased to 3000 rpm ($P_c \sim 4.39$ psi), yielding a lower S_{wi} of 18.2%. These two mini-plugs of the more permeable Berea consistently gave higher S_{or} and lower recovery factor (in all modes) than the tighter mini-plugs 2-5. The imaging of mini-plug 7_C in its dry, secondary SIH and tertiary SIL states was performed using a helical trajectory on a HeliScan micro-CT scanner to image a greater height (of the middle section) and at higher fidelity than for the circular scans of all other mini-plugs. A central longitudinal slice of these three registered tomograms, together with a zoom-in, are shown in Figure 2.12. Most of the residual oil after SIH lies in the larger pores, while the smaller pores are mainly occupied by brine, and presumably were so throughout the restoration process. Again the overall impression is that the wettability state after SIH is weakly mixed-wet, with many menisci possessing low contact angles at their contacts with grains, while in other locations the oil lines the pore walls with high contact angle, or appears to be pinned to exhibit an intermediate angle.

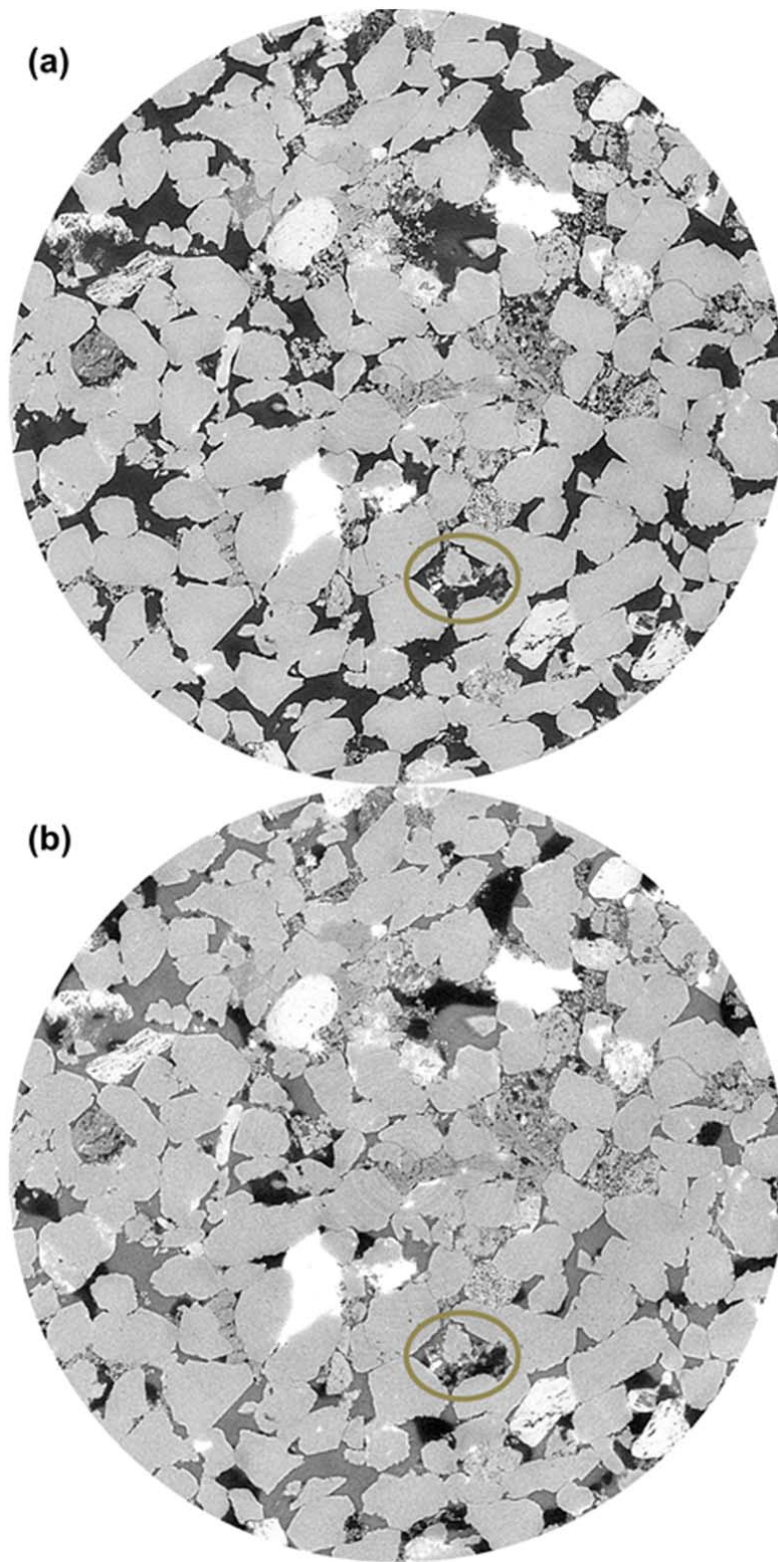


Figure 2.11 Tomogram cross-sectional slice of 3 mm diameter mini-plug 6_C, masked to 2.6 mm $\times$ 2.6 mm, registered between the (a) dry and (b) SIL states, with clay movement circled.

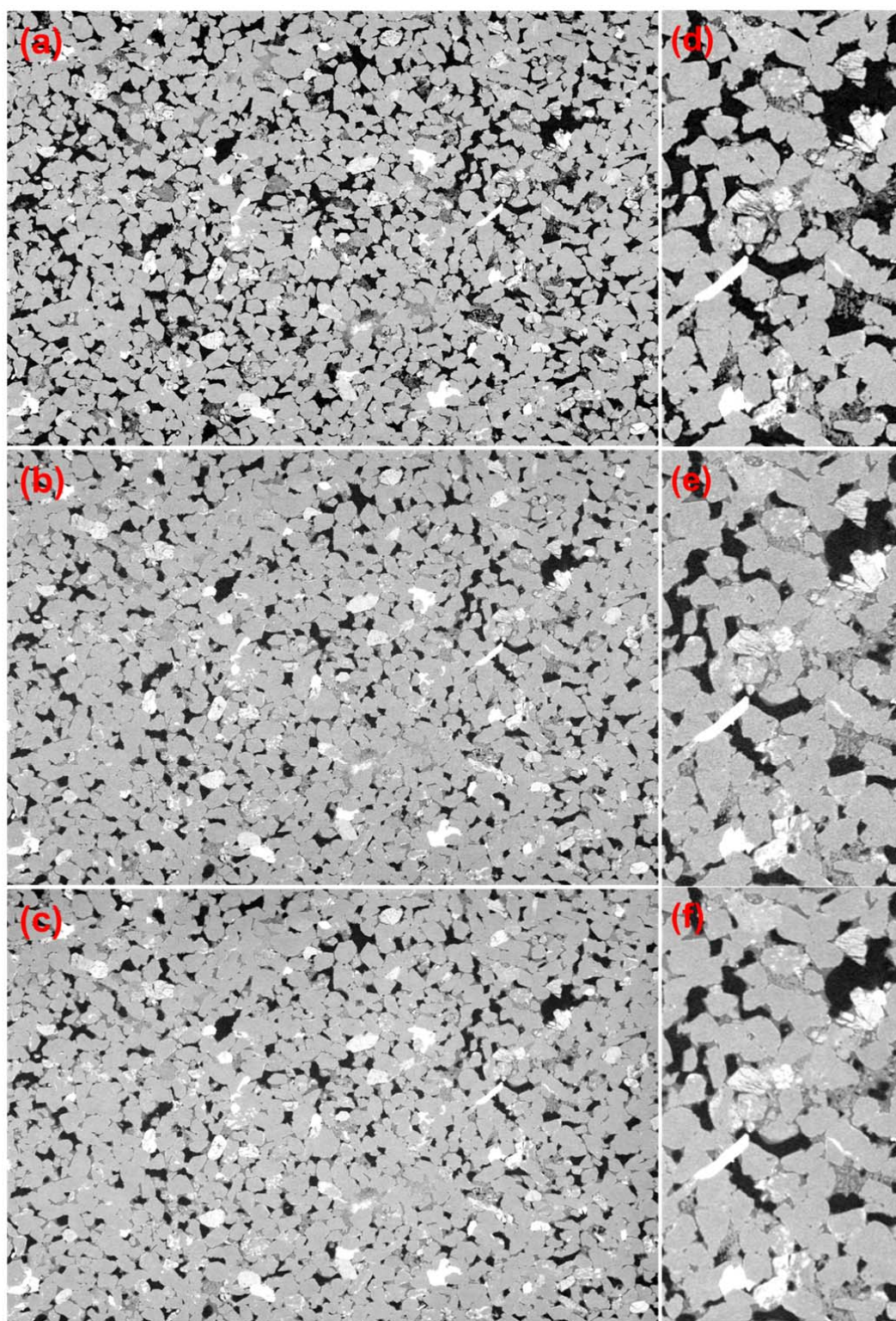


Figure 2.12 Tomogram longitudinal slice (rotated sideways) of 5 mm diameter mini-plug 7_C, masked to $4.4 \text{ mm} \times 6.7 \text{ mm}$, and registered between the (a) dry state, and the states after (b) SIH followed by (c) SIL. (d-f) Zoom-in of a sub area of $2.2 \text{ mm} \times 1.2 \text{ mm}$ at left.

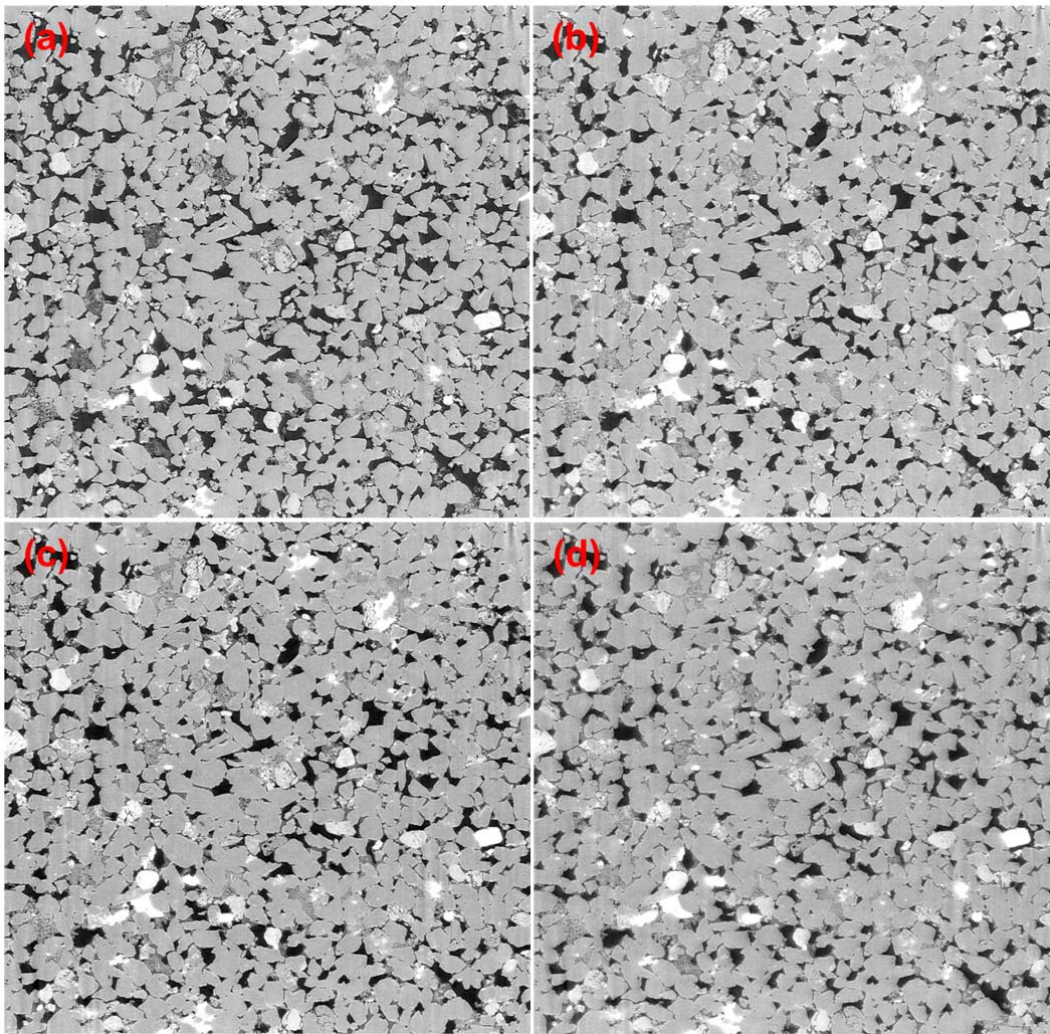


Figure 2.13 Tomogram longitudinal slice of 5 mm diameter mini-plug 8_C, masked to 4.6 mm $\times$ 4.5 mm, and registered between the (a) dry state, and the states after (b) SIL followed by (c) SIH and (d) SILL.

Mini-plug 7_C exhibits a small but significant incremental recovery of 3.0% OOIP during subsequent SIL. From Figure 2.12, the extra recovery is mainly due to detachment of pinned oil from some contact points in intermediate-large pores, leading either to release and withdrawal of the existing oil meniscus or to a snap-off event. Oil blobs for which the meniscus spanning neighboring grains recedes slightly during SIL may be directly driven by brine advance at these sites, or by detachment at another site which indirectly causes this meniscus movement. The impression is that wettability shifts somewhat towards water-wet, although the majority of the oil is too strongly adhering or pinned to be mobilized in SIL. This mini-plug will be the subject of further analysis in the next sub-section.

To investigate other combinations of high and low salinity imbibition, mini-plug 8_C in Table 2.3 underwent the sequence SIL followed by SIH followed by SILL. From oil segmentation, the secondary recovery by SIL was virtually identical to that by SIH in 7_C, suggesting that no low salinity effect is operative in secondary mode. Further, the lack of additional recovery in 8_C from SIL to SIH served to demonstrate that the sequence of experimental steps before and after immersion in the brine of interest, involving exchange with Contrast brine and mini-plug mounting and demounting, have little or no effect on oil recovery. This increases confidence that any changes are actually due to the spontaneous imbibition step itself, rather than to these associated preparation procedures. The final change from SIH to SILL resulted in additional recovery from 8_C of 1.8% OOIP, which is less than that in 7_C but more than from the preceding (salinity increasing) step for 8_C.

Figure 2.13 shows a representative slice from this sequence of registered tomograms for mini-plug 8_C. The oil distribution is qualitatively similar to that for 7_C, with most oil again found in larger pores while smaller pores between grains and even smaller ones within pore-filling clay aggregates remain brine-filled. The switch from SIL to SIH results in practically no pore-scale movement of oil, while the subsequent switch to SILL leads to some oil detachment and meniscus movement as for SIL in 7_C, although to a lesser extent.

2.3.2 Further Image Analysis of Residual Oil

The results of the preceding sub-section suggest that a limited low salinity effect is operative in tertiary mode in Berea sandstone. The overall incremental recovery is small and variable; further image analysis in the current sub-section aims to apply more advanced techniques to extract more sensitive pore-scale measures of these slight changes. This is performed on mini-plug 7_C, since its tomograms have the largest field of view and highest quality, and its additional recovery of 3.0% OOIP by low salinity is intermediate to the extremes of large and very small tertiary recovery from mini-plugs 1-8. For this purpose, a segmentation workflow was developed to include contributions from sub-resolution microporosity, such as in clay aggregates.

2.3.2.1 Additional Classification of Oil Occupancy and Changes

Based on the history of oil/brine occupancy and the oil movement from secondary SIH to tertiary SIL, such as in mini-plug 7_C, voxels in the resolved pore space (referred to as macro-pores) fall into one of the following four possible categories of occupancy (46):

- BB (macro-pore voxels which remain brine filled in the SIH and SIL states)
- OO (macro-pore voxels which remain oil filled in the SIH and SIL states)
- OB (macro-pore voxels which were oil filled in the SIH state but became brine filled in the SIL state, i.e. where oil is displaced by low salinity brine)
- BO (macro-pore voxels which were brine filled in the SIH state but became oil filled in the SIL state, i.e. where oil displaced by low salinity brine re-invades a brine-occupied pore).

Sub-resolution porosity (referred to as micro-porosity), which is mainly hosted by pore-filling clay mineral, is simply subdivided into the two complementary categories of:

- Micro-brine (micro-pore voxels occupied by brine)
- Micro-oil (micro-pore voxels occupied by oil).

Figure 2.14 shows a subarea of the registered tomogram series of mini-plug 7_C to illustrate with colored arrows examples of the macro- and micro-pore occupancy categories. The BB (blue) arrows indicate typical small resolved pores (dark in the dry tomogram) which are filled with brine in SIH and remain so after SIL. The OO (black) arrows show typical larger resolved pores that retain oil after both SIH and SIL processes. The OB (cyan) arrows show parts of resolved pores where residual oil after SIH was displaced by brine after SIL. One example of the rarest category of BO is shown by a red arrow, pointing to a small resolved pore (bounded by quartz grains and a weathered grain or pore-filling clay aggregate) which is filled with brine after SIH but is invaded by displaced oil after SIL.

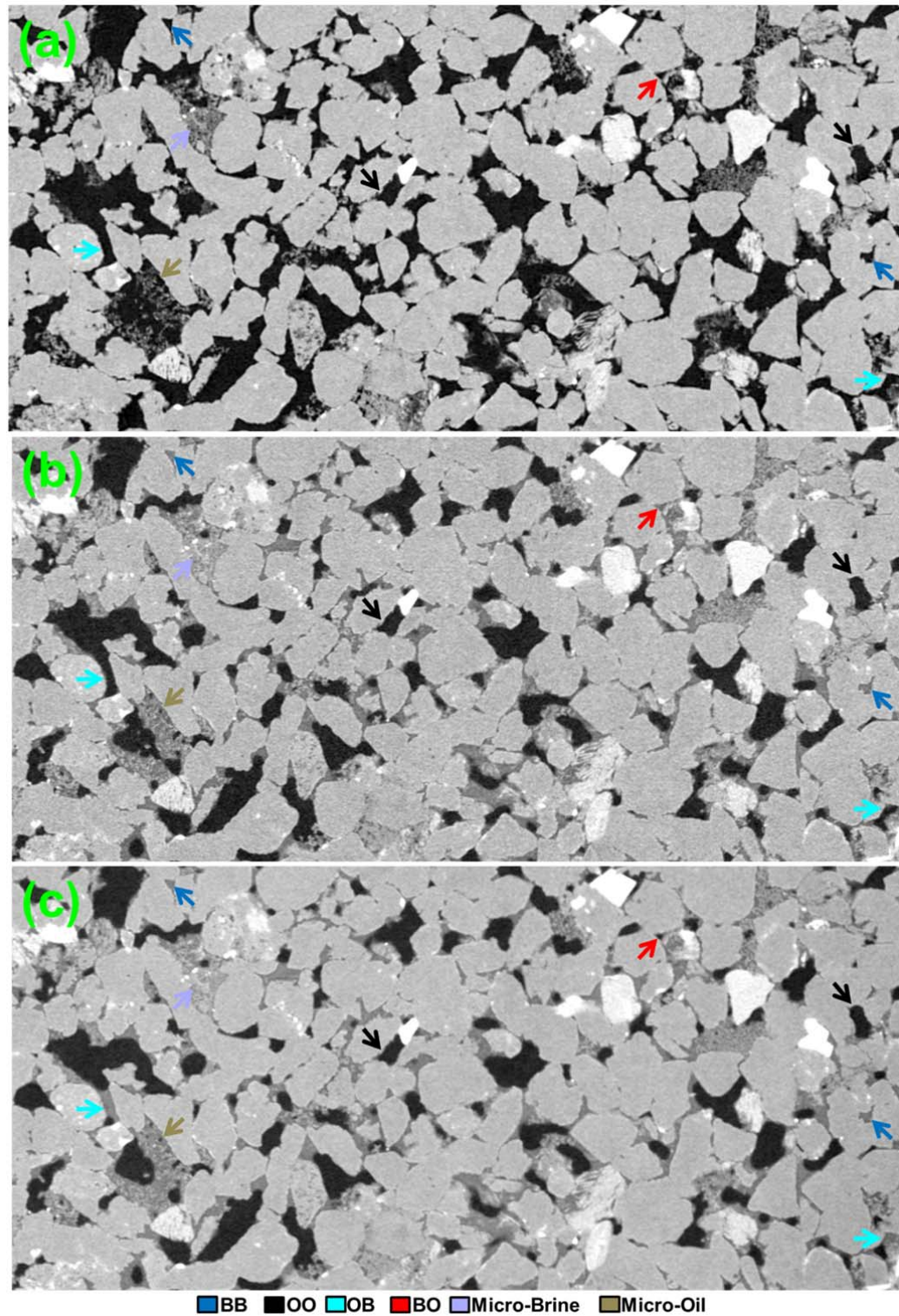


Figure 2.14 Subarea ($4.9 \text{ mm} \times 2.4 \text{ mm}$) of tomogram longitudinal slice of 5 mm diameter mini-plug 7_C, registered between the (a) dry state, and the states after (b) SIH followed by (c) SIL, showing the definitions of pore occupancy classes.

Micro-porous clay aggregates can be filled with brine or oil or a coexisting combination of both. The purple arrow in Figure 2.14 shows an example of the micro-brine category, in the form of a pore-filling microporous clay aggregate which is brine filled after SIH and SIL (and presumably was so throughout the restoration process). The olive arrow shows a clay aggregate which contains micro-brine and micro-oil (in both SIH and SIL). Note that the distinction between macro-oil and micro-oil is arbitrarily set by tomogram resolution; some of the small oil droplets in this clay aggregate are almost resolvable, while others fall below this limit and constitute true micro-oil.

2.3.2.2 Segmentation Workflow for Residual Oil

The segmentation in Section 2.3.1 only addressed oil in resolved pores in the mini-plug tomograms, and the estimation of oil saturation relied upon MICP for the value of total porosity. The extension of this simplest treatment to segmentation of total porosity and oil in sub-resolution micro-pores requires the acquisition and registration of one additional tomogram (here of the mini-plug 7_C), namely in its state after saturation with the Contrast brine. This tomogram was acquired after all imbibition steps and subsequent solvent cleaning, followed by re-saturation of the mini-plug.

Figure 2.15 shows a subarea of the registered tomograms for this sequence of states: (a) dry, (b) brine saturated, (c) after SIH, and (d) after SIL. From these, the following difference tomograms were calculated (by subtracting the normalized attenuation grayscale value of corresponding voxels): (e) brine-saturated minus dry, (f) SIH minus dry, (g) brine-saturated minus SIH, and (h) SIL minus SIH. These difference maps were then used to assist in segmenting the various components of interest within the mini-plug, shown by the colors in Figure 2.15(i-l) as explained in the following paragraphs.

The dry tomogram in (a) suffices to segment the three phases in (i), referred to there as Grain (solid mineral), Pore Space (macro-pores) and Clay (including its micro-pores). The difference tomogram in (e) cancels out all contributions from the solid fraction of minerals (which thus become dark) to leave only the signal from macro-pores (bright) and micro-pores (intermediate grayscales). In particular, segmentation of (e) then quantifies the micro-porosity value at each voxel within the Clay phase as a linear function of the intermediate grayscale value there, shown in (j) (36).

In this way the total macro-pore space and micro-pore space are identified, and thus once the fraction of these occupied by oil is determined, the remainder of each is the brine-occupied fraction. The resolved macro-oil after SIH (referred to as Oil in Figure 2.15) can be segmented directly from the SIH tomogram in (c) as the darkest phase, as was done in Section 2.3.1, or with greater sensitivity and consistency from the difference in (g) as the brightest phase. The difference in (f) or (g) within the Clay phase is then use to subdivide this intermediate phase into Brine-filled clay clusters (darker in (g)) and Oil-filled clay clusters (brighter in (g)). Figure 2.15(k) shows the resulting full subdivision of pore space into these four phases. The sub-resolution micro-oil after SIH is then obtained by applying the above-mentioned grayscale map of micro-porosity to the Oil-filled clay phase. The same procedure was also implemented for the corresponding tomogram and differences of the SIL state. The further categorization of resolved Oil and Brine phases into their four categories of occupancy history (BB, OO, OB and BO) is obtained from superposition of these segmentations of macro-oil and macro-brine in SIH and SIL. Alternatively, the tomogram difference between these two imbibed states in (h) can be used to identify OB and BO as the brightest and darkest phases (shown by cyan and red arrows, respectively), with the result given in (l).

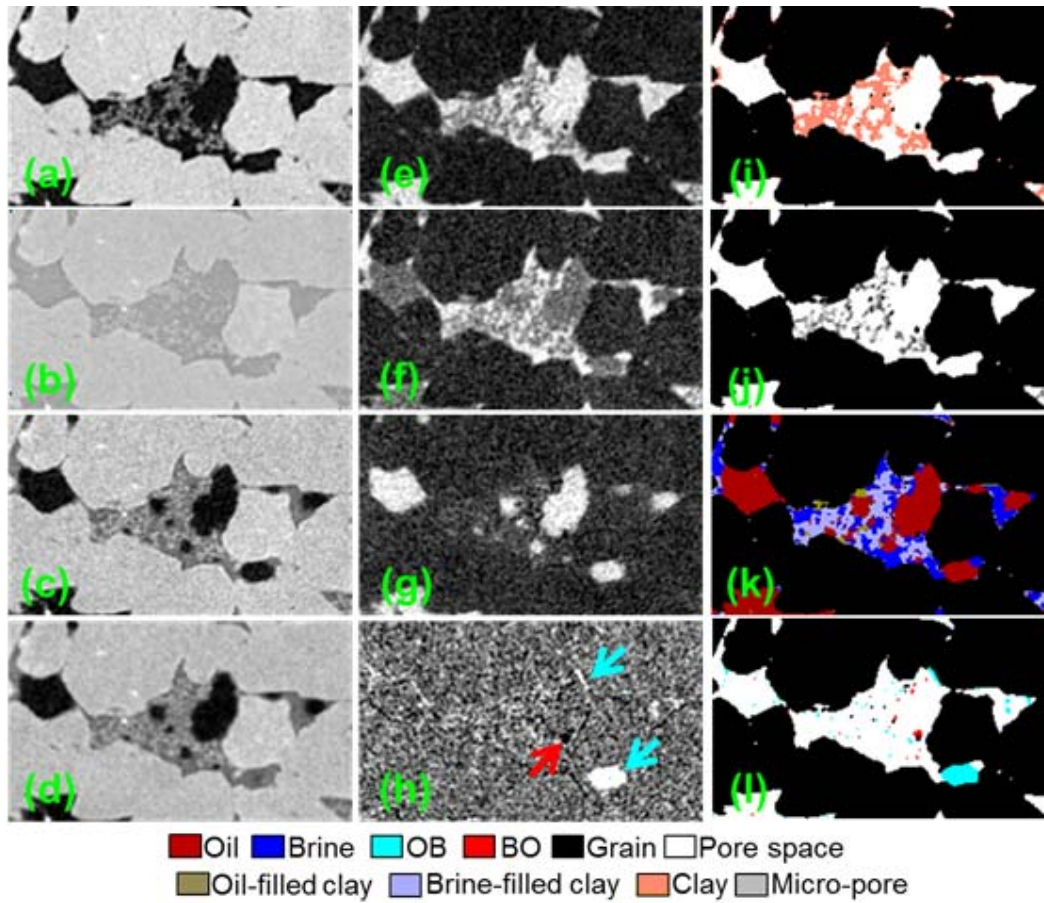


Figure 2.15 Subarea ($0.7 \text{ mm} \times 0.4 \text{ mm}$) of tomogram cross-sectional slice of 5 mm diameter mini-plug 7_C, registered between the states: (a) dry, (b) brine saturated, (c) SIH, and (d) SIL, and the resulting differences: (e) brine-saturated minus dry, (f) SIH minus dry, (g) brine-saturated minus SIH, and (h) SIL minus SIH, leading to the segmentations of all components in (i)-(l).

Figure 2.16 shows the result of this segmentation workflow for a registered cross-sectional slice of mini-plug 7_C in its SIH and SIL states. The SIH tomogram is thus segmented into the five phases: grain, macro-oil, macro-brine, micro-oil and micro-brine. The SIL tomogram is segmented in the same way, and the resolved oil and brine phases can be further subdivided into the four pore occupancy categories (BB, OO, OB and BO). Note that macro-oil and macro-brine in SIL are $OO + BO$ and $BB + OB$, respectively, while macro-oil and macro-brine in SIH are $OO + OB$ and $BB + BO$, respectively.

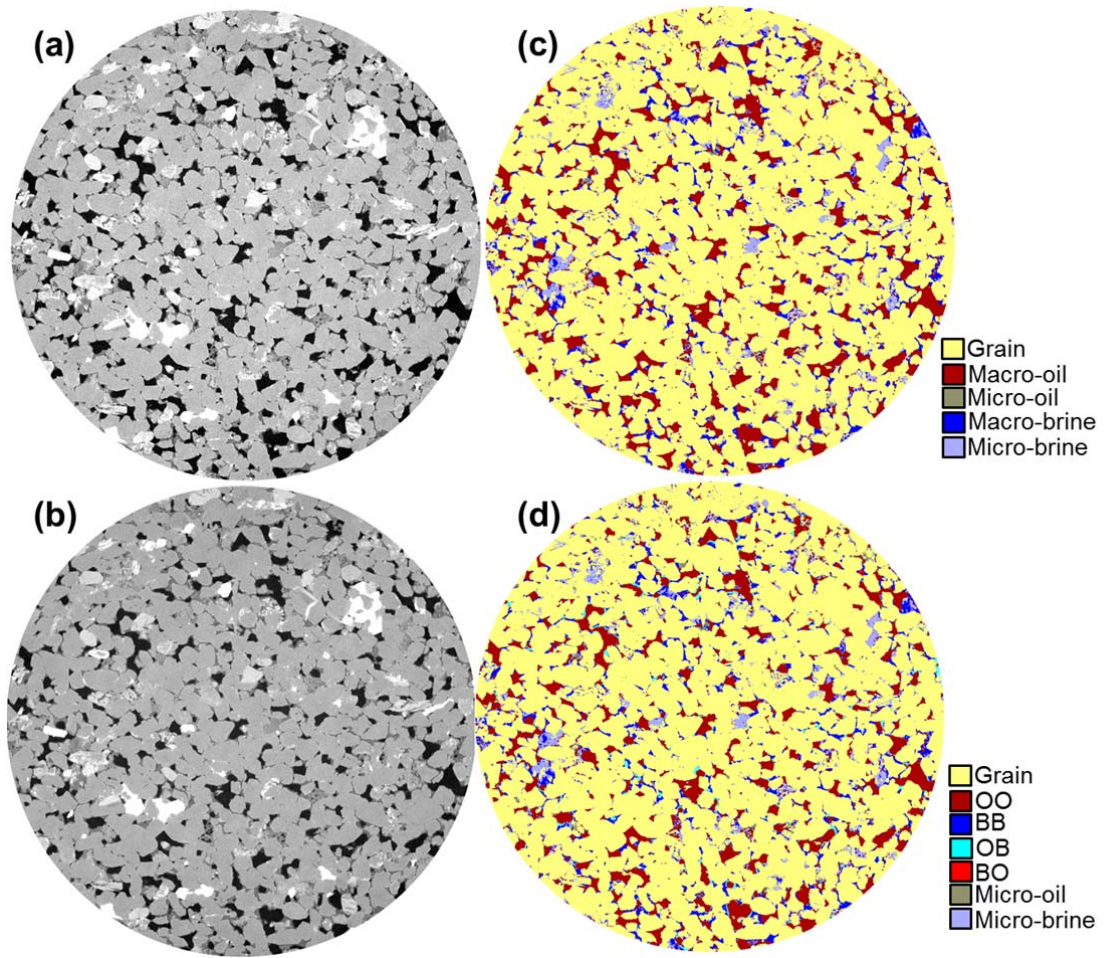


Figure 2.16 Tomogram cross-sectional slice of 5 mm diameter mini-plug 7_C masked to 4.5 mm × 4.5 mm, registered between the (a) SIH and (b) SIL states, and after (c) segmentation of SIH into grain and macro- and micro-liquid (oil and brine) phases, and (d) segmentation of SIL into grain and macro- and micro-liquid phases, with the macro-liquids further sub-divided according to pore occupancy history.

Table 2.4 lists the volume fractions of these segmented phases, averaged over the entire masked tomogram of mini-plug 7_C. The porosity segmentation gives macro- and micro-porosity of 17.2% and 3.9%, respectively, for this tomogram voxel size cut-off of 3 μm . The total of 21.1% is in reasonable agreement with the MICP value of 19.5% from sister material of Berea C. The resolved (macro-) oil fraction of this total pore volume is 57.8% and 54.1% in SIH and SIL, respectively. The discrepancy compared to the previous corresponding (macro-) estimates for S_{or} of 54.6% and 52.1%, respectively, in Table 2.3 is due to the differences in segmentation workflow (discussed further below) and in the segmented versus MICP porosity value used. The total (macro- plus micro-) oil recovery factor from Table 2.4 is 25.9 and 30.1%OOIP,

respectively, giving an EOR increment from SIH to SIL of 4.1% OOIP, compared to 3.0% OOIP estimated in Table 2.3.

The subdivision into macro- and micro-pores in Table 2.4 clearly shows that residual oil is strongly biased to residing in macro-pores, occupying 71% after SIH and 67% after SIL of total available macro-pore volume. The corresponding fractions for oil in micro-pores after SIH and SIL are only 15% and 17%, respectively, of micro-pore capacity, as expected from the tendency for tight pores to remain brine-filled throughout restoration. The low salinity effect is thus only operative in macro-pores; in fact oil occupancy of micro-pores slightly increases from SIH to SIL (although the difference lies within segmentation uncertainty – see the discussion below). This implies that if the low salinity effect involves oil release from clay minerals, it can only occur from the external surfaces of clay aggregates (not within them) bounding macro-pores in this sample. The subdivision of macro-pores into their four categories of occupancy in SIH and SIL in the bottom row of Table 2.4 shows that the volume of oil re-displacing brine (BO) in SIL is very small relative to the reverse (OB).

Regarding the discrepancies and small inconsistencies between the two methods of segmentation, the direct, single-segmentation approach for macro-oil in Section 2.3.1 is naturally limited by its neglect of micro-oil and its assumption that total porosity is represented by its MICP value. The use in the current Section 2.3.2 of the extra tomogram of the brine-saturated state, together with registration for segmentations from multiple combinations of tomogram differences, reveals far more detailed and in-depth information, although these details and high-order measures (further explored in subsequent sub-sections) are understandably more sensitive to artifacts and accumulated errors. The main sources of segmentation error, aside from operator subjectivity in choice of thresholds, are tomogram artifacts, particle movement, and limitations in signal/noise.

The main type of artifact is beam hardening, which is manifested in two forms. The cupped radial profile of attenuation, from the mini-plug periphery to its center, is readily corrected in tomogram reconstruction. On the other hand, streaks local to high density inclusions such as zircon (one example of which can be seen towards the upper left in Figure 2.4(a-c)) are less easily corrected for and introduce false segmentation features in the vicinity of each of these. Movement of fines and loosely bound grains or fragments between imaged states (e.g. from dry to SIH) was seen above to occasionally

occur in some mini-plugs. Such movement will obviously show up as changes, in the form of bright and dark features, in difference tomograms, which will in turn be falsely segmented as oil or brine movement unless they are locally masked out. While difference tomograms allow quantification of sub-resolution porosity and saturations within these tighter regions (e.g. clay aggregates), the signal there is naturally weaker than from macro-pores. Signal can be boosted by increasing the oil/brine attenuation contrast, e.g. by strongly doping the brine phase. However, in studies of salinity effects, the exchange of low salinity brine (e.g. 0.05MRB) for a high salinity NaI solution can induce changes in oil distribution during this experimental step. For this reason, a relatively low concentration (0.3 M) of NaI was used in the Contrast brine, with the consequence that identification of oil and brine within the clay phase is somewhat uncertain.

Table 2.4 Volume fractions of phases segmented from the entire masked volume of the sequence of registered tomograms of mini-plug 7_C. Solid mineral phase fractions and porosities are given as percentage of total bulk volume (BV), and liquid saturations as percentages of total pore volume (PV).

	Grain (%BV)	Clay (%BV)	Macro-porosity (%BV)				Micro-porosity (%BV)		Total Porosity (%BV)	
Dry	76.7	2.2	17.2				3.9		21.1	
			Oil (%PV)		Brine (%PV)		Oil (%PV)	Brine (%PV)	Oil (%PV)	Brine (%PV)
SIH			57.8		23.5		2.8	15.8	60.6	39.3
SIL			54.1		27.1		3.2	15.5	57.3	42.6
			OO (%PV)	BO (%PV)	OB (%PV)	BB (%PV)				
SIL/SIH difference			53.3	1.2	4.5	22.3				

2.3.2.3 Profiles of Residual Oil

The tomogram-averaged measures in Table 2.4 are investigated in greater detail in this and the following sub-sections. To begin with, 1D profiles of residual oil volume, either longitudinally down the mini-plug (in which each tomogram cross-sectional slice is averaged) or radially out from its axis (averaged over each successive annulus) serve to characterize any mini-plug-scale variations. The longitudinal profile of the volume fraction of each segmented phase in the SIH state is plotted against height from top to

bottom of the field of view of mini-plug 7_C in Figure 2.17(a). Macro- and micro-porosity have uniform profiles, indicating that this outcrop rock is homogenous over these scales. As expected, macro-porosity exhibits larger amplitude variations than micro-porosity. These same variations are mirrored in the profile of macro-oil, as it mainly resides in larger pores, while macro-brine resides in smaller resolved pores or the corners of larger ones, and thus exhibits a flatter profile, similar to that of micro-brine.

Longitudinal profiles of total oil volume fraction (summing macro- and micro-oil) after SIH and SIL, as well as OB, BO and oil change (the difference OB minus BO) are given in Figure 2.17(b). The total oil profiles, which can now be seen on this expanded vertical scale to rise slightly from mini-plug top to bottom, exhibit the same local variations in SIH and SIL. These peaks and troughs cancel out in the profile of oil change to yield a much flatter profile, reflecting the fact that most salinity-induced changes involve only a slight pore-scale rearrangement or movement of menisci. The weak trend to rising oil saturation towards the bottom coincides with a similar rise in porosity there. The oil change profile shows that the low salinity effect appears to exhibits a slight peak towards the middle of the mini-plug, and dips quite noticeably very close to the bottom of the field of view due to a rise in BO from its typically very low levels. As the bottom of the tomogram field of view is about 3 mm above the bottom of the mini-plug, it is likely that this rise in BO and dip in oil change are artifacts resulting from a slight non-uniformity in tomogram grayscale arising near the end of the acquisition.

The corresponding radial profiles out from the central axis of mini-plug 7_C are plotted in Figure 2.18. The volume fraction curves of all segmented phases (and their changes) settle down as the annulus volume increases with radius, to exhibit radially uniform distributions. The mini-plug outer periphery (at radial distance of 2.5 mm) is sufficiently masked to avoid any impact from coring damage (as would be apparent from a rise in porosity there) within the analyzed cylinder. The slight dip in the curves of phases with small volume fractions, such as micro-oil, OB and oil change, near the edge of this analyzed cylinder may be real or may be an artificial effect of slight residual beam hardening on segmentation of these more subtle phases.

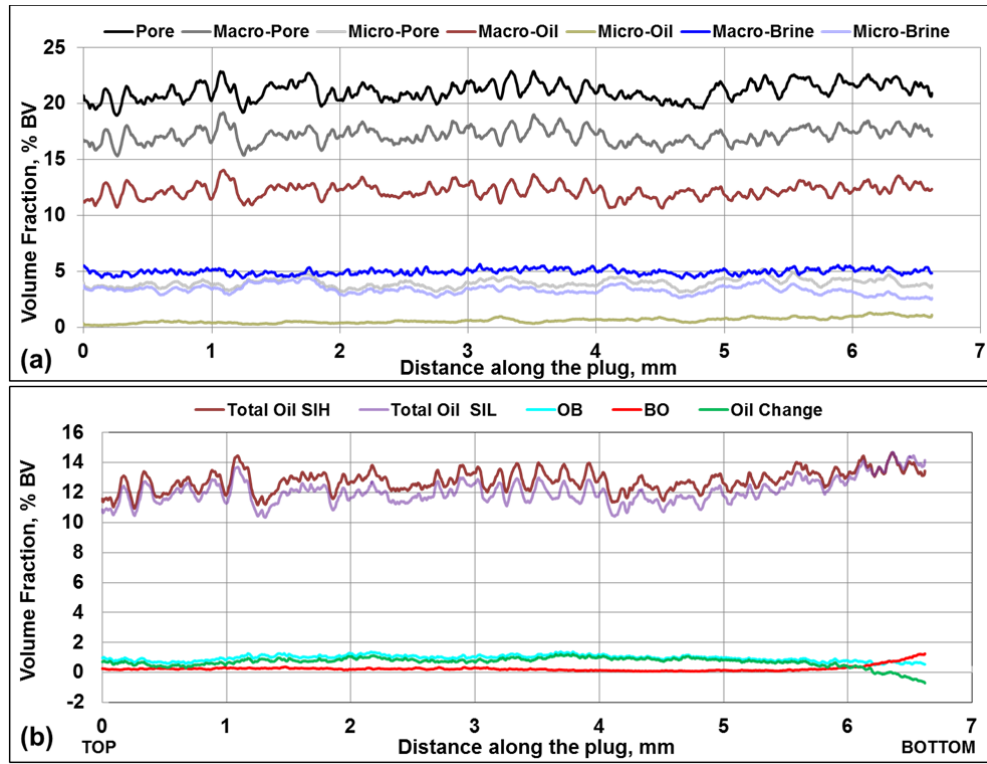


Figure 2.17 (a) Longitudinal profiles of volume fraction, as percentage of total bulk volume (BV), of all segmented phases of mini-plug 7_C in its SIH state, and (b) comparison of oil volume fractions and changes from SIH to SIL.

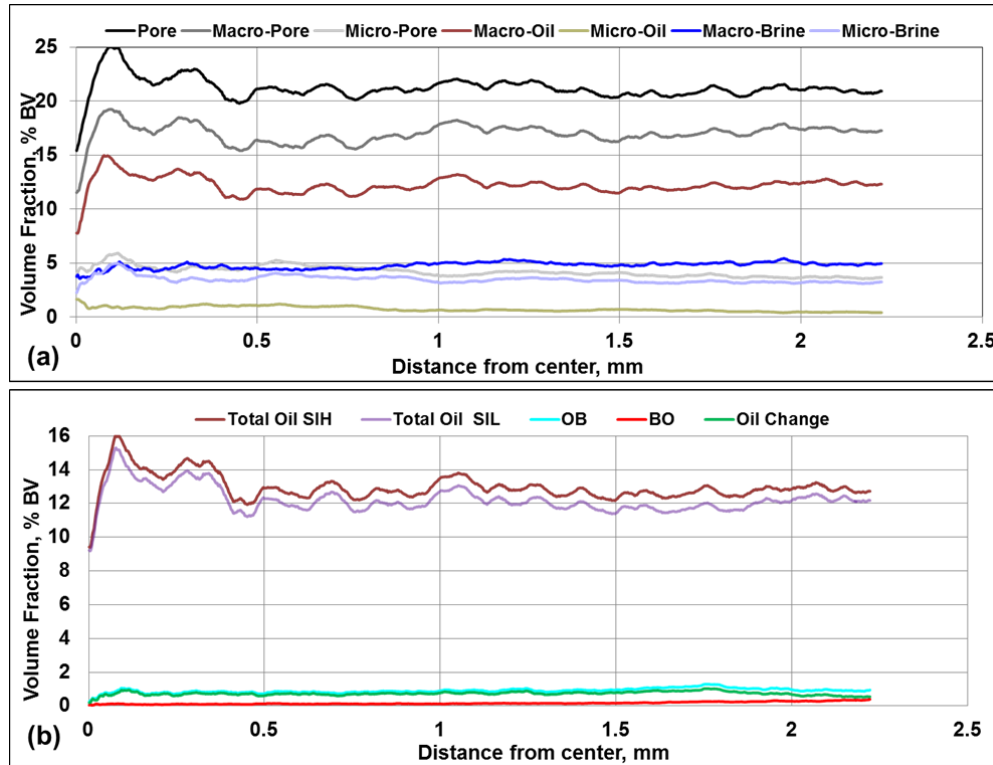


Figure 2.18 (a) Radial profiles of volume fraction, as percentage of total bulk volume (BV), of all segmented phases of mini-plug 7_C in its SIH state, and (b) comparison of oil volume fractions and changes from SIH to SIL.

2.3.2.4 Pore-scale Distribution and Connectivity of Residual Oil

Having dealt with overall residual oil saturation and its mini-plug-scale distribution, the next step is analysis of the pore-scale distribution to get closer to the underlying mechanisms of oil recovery during SIL. For this purpose, the segmented macro-pore space was partitioned into labeled individual pore bodies using a watershed algorithm (36), onto which the segmented macro-oil after SIH and SIL was overlain to directly compare the oil saturation per pore. This results in the scatter plot of residual macro-oil saturation after SIH and SIL versus the volume of each individual pore as given in Figure 2.19. A moving average is also plotted to clarify the overall trend versus pore size, along with the corresponding volume-weighted distribution curve to show the contribution to overall residual oil saturation.

The tomogram images shown and discussed above demonstrated that the smallest resolved pores have high brine saturation, and that sub-resolution porosity extends this trend to even higher brine saturations. The upward trend in residual oil saturation towards the left end in Figure 2.19 is thus thought to be an artifact from the partitioning of these extremely small voxelated pores. The moving average increases as expected over pore volumes large enough to contribute significantly to overall saturation, although with considerable scatter around it; pores of size around 10^{-3} mm^3 commonly exhibit oil saturations ranging from 60 to 90%, and instances of much lower saturation are still common. The impression from Figure 2.19 is that the moving average is shifted downwards from SIH to SIL fairly uniformly over all pore sizes, while the decrease in the cumulative distribution is naturally skewed toward larger pores.

Greater insight into the effect of salinity can be obtained from the corresponding plot of the oil change ($S_{O(SIH)} - S_{O(SIL)}$) per individual pore, which is given in Figure 2.20. Based on the moving average, the low salinity effect exhibits a slight peak at pore volumes just below 10^{-3} mm^3 . This also corresponds to the sizes over which the scatter is greatest, mainly in OB (oil displacement by brine) but also in the slight counter-effect of BO (moved oil subsequently displacing brine). While the contribution of pores of this intermediate size to overall residual saturation in Figure 2.19 is much less than from larger pores, they provide the clearest hallmark of the slight shift toward a more water-wet state.

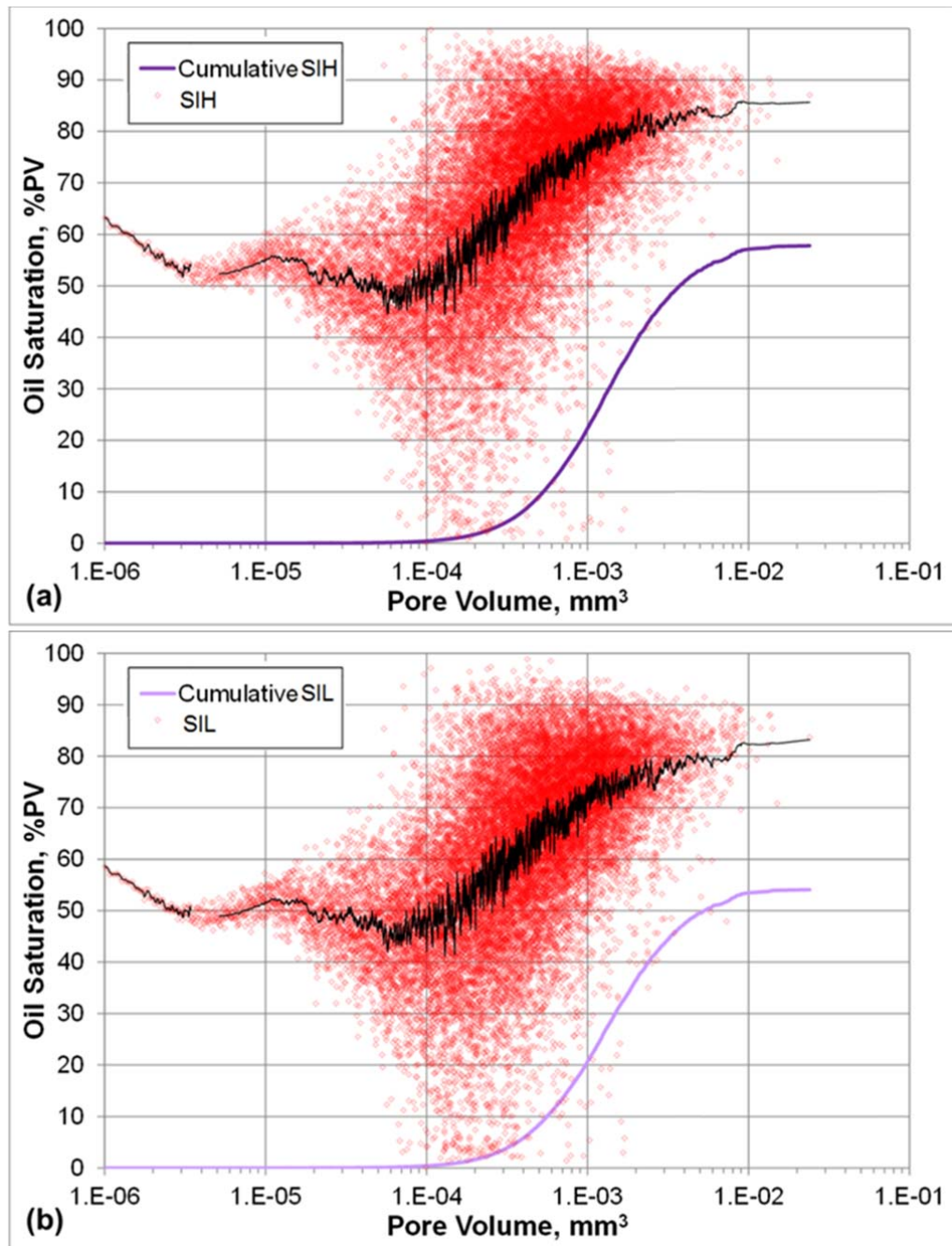


Figure 2.19 Scatter plot of residual oil saturation in each resolved pore body versus its individual volume (red points), also showing moving average (black line) and volume-weighted cumulative distribution (purple curve) after (a) SIH followed by (b) SIL, in mini-plug 7_C.

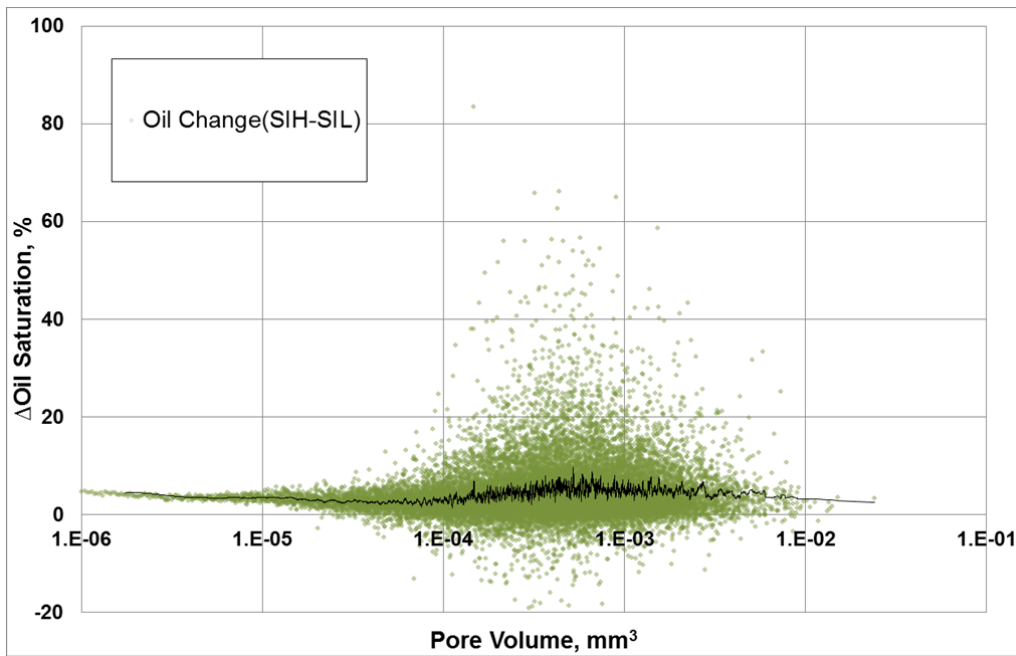


Figure 2.20 Scatter plot of change in residual oil saturation (SIH minus SIL) in each resolved pore body versus its individual volume (green points), also showing moving average (black line), for mini-plug 7_C.

In addition to analysis of pore-scale oil saturation, quantification of the connectivity of residual oil blobs in SIH and SIL can provide further insight into wettability shift, as oil is highly connected in oil-wet systems and is highly disconnected in strongly water-wet states. Connectivity was calculated by the GangliaCount algorithm (47, 48) in Mango, which tracks the number of adjoining pore bodies that each connected oil blob spans and occupies a substantial fraction of (with this oil saturation cut-off value taken here as 50%). The resulting volume-weighted distribution curves, normalized to 100% of the residual oil volume, are shown in Figure 2.21, in which a blob occupying 1 or 2 pores is a singlet or a doublet, and so on. After SIH, 60% of the residual oil volume remains connected throughout the masked tomogram as one giant cluster. The upward and leftward shift from SIH to SIL clearly demonstrates that oil is less connected after tertiary recovery. The frequency of smaller blobs is increased in SIL, and the largest blob now only comprises 20% of all oil volume. Oil connectivity thus provides a more sensitive indicator than oil saturation of the significant shift towards a water-wet state due to blob retraction and snap-off.

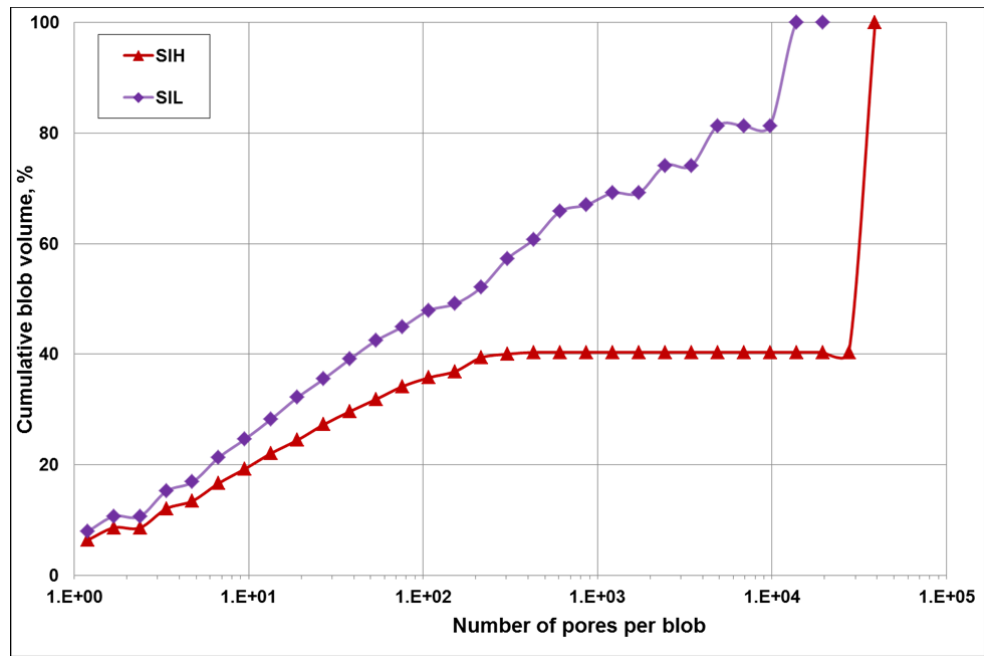


Figure 2.21 Cumulative distribution of residual oil volume in mini-plug 7_C after SIH and SIL, as a function of the number of connected pores spanned by each separate ganglion.

2.3.2.5 Interfacial Areas of Residual Oil

The resolved residual oil shares interfaces with brine, with grains and with external surfaces of clay aggregates. Calculation of these interfacial areas of macro-oil in the segmented tomograms after SIH and SIL and analysis of the changes provides further insight into the mechanism(s) of the low salinity effect. Area was calculated in Mango using an algorithm for smoothing of voxelated interfaces, and the average values over the masked tomogram are shown in Figure 2.22. Figure 2.22(a) shows the percentage breakdown of total area in the system into its contributions from all six possible interfaces between the four resolved, segmented phases. Oil recovery from SIH to SIL reduces the oil contact with grains (with a concomitant gain in brine-grain area) and increases the oil-brine interfacial area. However, the normalization to 100% is not conducive to fair comparison. Figure 2.22(b) focuses on the contribution from the three interfaces with oil, now with their area (in mm^2) scaled by the total volume of macro-oil (in mm^3) in the SIH or SIL state. In particular, this shows that oil-grain area decreases in proportion to the oil volume decrease, while oil-clay area exhibits a proportionally weaker decrease from SIH to SIL. According to this measure, low salinity exhibits a stronger preference for oil removal from grains than from external surfaces of clay aggregates.

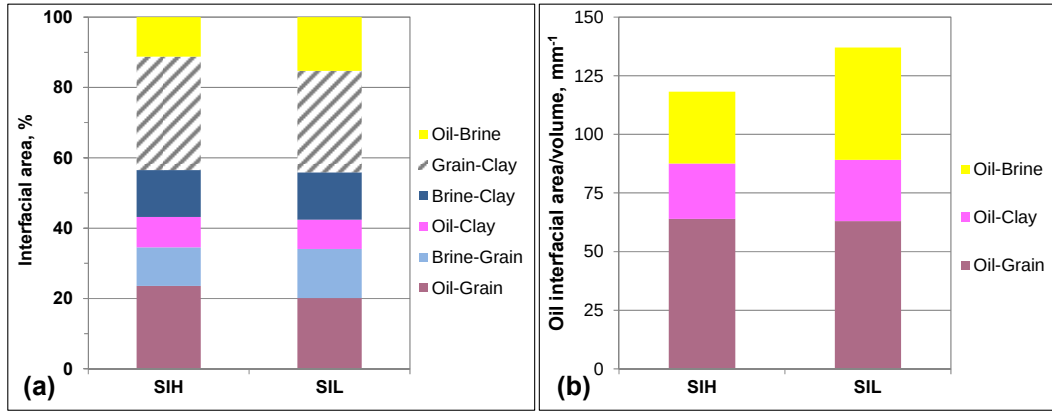


Figure 2.22 (a) Overall statistics of interfacial area for each resolved phase combination after SIH and SIL, normalized to 100%, and (b) oil contact area with grain, clay and brine relative to oil volume, in mini-plug 7_C.

Figure 2.23 presents other statistical measures of interfacial area and its changes within the resolved, segmented phases of mini-plug 7_C. Figure 2.23(a) shows that grains offer more surface area than external clay surfaces (at tomogram resolution, with smoothened voxels), and grains more commonly contact oil than brine while clays more commonly contact brine than oil. Accordingly, from Figure 2.23(b), the majority (around 70%) of oil contact with pore walls is with grains rather than clays, while the division of brine contact between grain and clay is closer to 50:50. Figure 2.23(c) shows that i) the decrease in oil contact area from SIH to SIL is greater for grain than clay when counted per total pore wall area (/Pore-rock), and that ii) this tendency becomes stronger when the count is more correctly weighted by the available area presented by grain or clay (/Pore-mineral), and that iii) this tendency becomes even stronger when the count is even more correctly weighted by the starting area of oil contacting grain or clay in the SIH state (/Oil-mineral). Figure 2.23(d) shows that oil-brine interfacial area is roughly one-quarter of pore wall area, and its increase from SIH to SIL is, as expected, primarily due to interfaces created by brine displacing oil (OB) rather than by oil re-displacing brine (BO). Further, from Figure 2.23(b), almost 70% of OB contact area release from rock is from grains, which exceeds the average of 60% of total pore area coming from grains. The conclusion consistently supported by these various measures is that tertiary recovery by low salinity brine in this case is due to preferential detachment of oil from grains, not clay external surfaces.

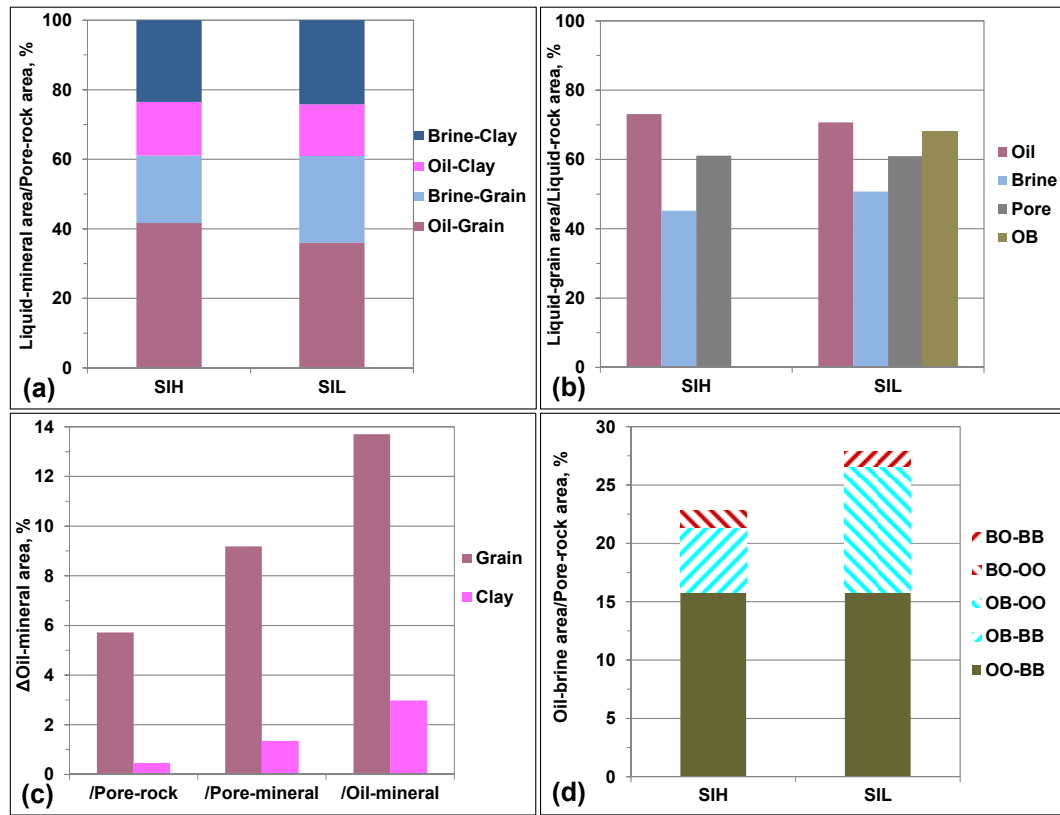


Figure 2.23 (a) Interfacial contact area of each (resolved) liquid (oil or brine) with grain or clay, relative to total pore-rock area, (b) Interfacial contact area of each liquid with grain, relative to liquid-rock area, (c) salinity-induced change in interfacial contact area of oil with grain or clay, normalized in three ways, and (d) oil-brine interfacial area, relative to total pore-rock area, for mini-plug 7_C. Here rock refers to grain plus clay, while mineral refers to grain or clay.

2.3.2.6 Oil/Brine Interfacial Mean Curvature

Calculation of the local mean curvature of the oil-brine interface provides further insight into wettability changes from SIH to SIL. From the Young-Laplace equation, capillary pressure is directly proportional to mean curvature, which in turn is dictated by the pore geometry and the contact angle. A subset of $1000 \times 887 \times 1800 \text{ voxel}^3$ was selected in the middle of the mini-plug 7_C tomograms, within which the area-weighted mean curvature of the resolved, segmented oil-brine interface was obtained using a Monge geometrical algorithm (49). The overall averaged results from the segmented macro-oil in SIH and SIL are listed in Table 2.5, for calculation without or with an additional pre-processing step prior to curvature calculation. In particular, to reduce the effect of occasional “outlier” oil voxels at interfaces, an erosion-dilation algorithm (50) was ran on the oil phase, as illustrated in Figure 2.24. By convention, mean curvature is defined as positive or negative if the oil-brine interface curves towards or away from the oil, respectively. The overall average without pre-processing suggests that low salinity

shifts the mean curvature to favour curving away from the oil. However, erosion-dilation switches the sign of the average mean curvature and eradicates the change from SIH to SIL, suggesting that the influence of stray oil voxels and their removal from the interface overpowers the trend from the small fraction of interface which is displaced in SIL.

Table 2.5 Average mean curvature, H , and total area of the resolved, segmented oil-brine interfaces of mini-plug 7_C after SIH and SIL.

	$H \text{ (}\mu\text{m}^{-1}\text{)}$		Area (mm^2)	
Interface	No pre-processing	Erosion-dilation	No pre-processing	Erosion-dilation
Oil/SIH	0.032	-0.010	121	128
Oil/SIL	0.023	-0.011	154	158

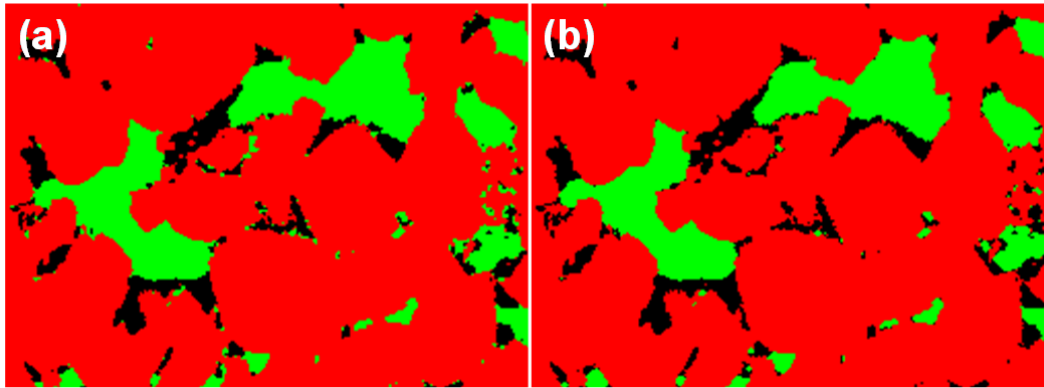


Figure 2.24 Subarea (1.3 mm x 1.0 mm) of segmented tomogram slice of mini-plug 7_C, (a) without additional processing of the oil phase, and (b) after its erosion-dilation. Red, green and black are grain, oil and brine, respectively.

Table 2.6 Average mean curvature, H , and total area of the four pore-occupancy categories segmented between SIH and SIL in mini-plug 7_C.

		$H \text{ (}\mu\text{m}^{-1}\text{)}$	Area (mm^2)
State	Interface category	Erosion-dilation	Erosion-dilation
SIH	OB-BB	-0.035	30.3
SIL	OB-OO	0.046	52.8
SIH	BO-OO	0.021	2.4
SIL	BO-BB	-0.199	3.2

To increase the sensitivity of the estimation of curvature change from SIH to SIL, the calculation was instead limited to the small fraction of oil-brine interfaces that moved between these two states, i.e. to the interfaces of OB and BO. The average mean curvature and area of each of these four categories of moving interfaces, calculated after erosion-dilation of the oil phase, are listed in Table 2.6. Interfaces OB-BB are those in SIH which moved due to brine advance to form an OB-OO interface in the SIL state. The mean curvature of these switches from negative in SIH to positive in SIL in Table 2.6. This local increase in oil-brine meniscus curvature implies a decrease in the water-advancing contact angle, and thus a shift toward more water-wet. Interfaces BO-OO are those in SIH which moved due to oil re-advance (secondary water-receding) to form a BO-BB interface in the SIL state. The mean curvature of these switches from positive in SIH to negative in SIL in Table 2.6. This local decrease implies an increase in secondary water-receding angle. However, owing to the very small volume of BO relative to OB, as reflected in their corresponding areas in Table 2.6, the contribution of water-advancing interfaces to the system is much higher than the slight counter-effect from water-receding interfaces.

To visualize oil blob movement from SIH to SIL, two representative examples of iso-surfaces were generated and are given in Figure 2.25. The first in Figure 2.25(a) shows oil in SIH which fills a pore body and covers most of its walls, and which is connected through one throat at left. During SIL, the blob detaches from the walls and retracts by local advance of low salinity brine. The shrinkage of the oil ganglion end is associated with increase in mean curvature of this OB interface in SIL, in line with the trend in Table 2.6. The second example in Figure 2.25(b) shows two snap-off events in which a large oil ganglion that is internally connected via two throats in SIH breaks into smaller, more disconnected oil blobs after SIL. The snap-off appears to be driven by detachment of oil from the pore body walls and subsequent thickening of these films of low salinity brine to destabilize the oil configuration in the throats. Again the more rounded OB interfaces enclosing oil in SIL lead to an increase in mean curvature, due to the rock grains becoming more water-wet.

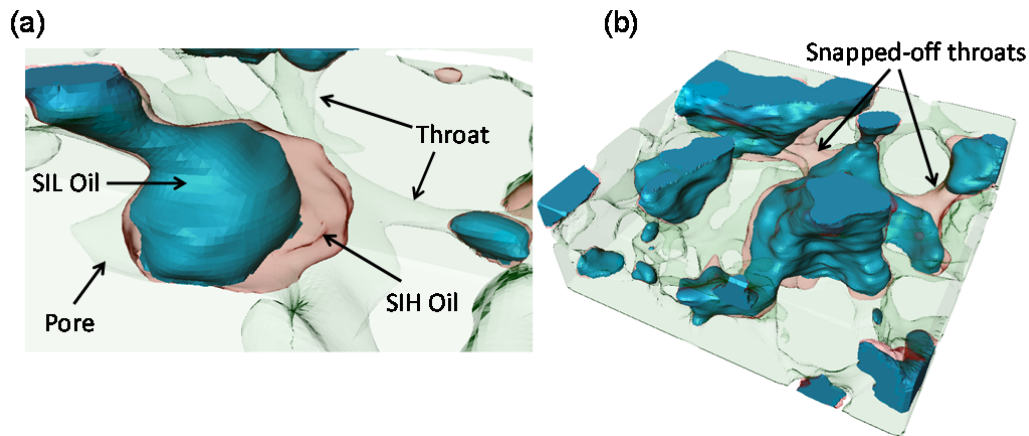


Figure 2.25 Iso-surfaces of oil blobs after SIH (brown) and SIL (green), showing (a) close-up of an oil ganglion detaching and receding in a single pore ($0.26 \times 0.16 \times 0.10$ mm), and (b) changes in oil distribution and connectivity, featuring snap-off events, over a larger sub-volume ($0.50 \times 0.46 \times 0.16$ mm).

2.4 Conclusion

Micro CT 3D imaging and analysis is a robust tool for studying multiphase fluid distributions within porous materials. A previous study of the low salinity effect in water flooding of Berea sandstone plugs, which showed fairly weak and variable responses, was mimicked here using mini-plugs subjected to immersion in sequences of these same high and low salinity brines for micro-CT imaging and analysis of recovery of the same crude oil by spontaneous imbibition. The imaged experiments also showed a fairly weak and variable low-salinity effect. Fines movement during SIH and SIL was occasionally seen, and sometimes appeared to stem from loosely-bound coring debris. This demonstrated that pore-scale mobilization of clay minerals by the oil-brine interface, at sufficiently low level as to not cause throat blocking and formation damage, can occur and contribute to the low salinity effect. However, most oil displacement did not appear (at tomogram resolution) to coincide with such fines movement. A mini-plug with additional recovery of 3.0% OOIP by low salinity in tertiary mode was selected for further image analysis. A methodology was developed to take advantage of acquisition and registration of a sequence of imaged states of this mini-plug to quantitatively segment oil and brine in resolved and sub-resolution pores. All metrics pointed to a slight shift towards a more water-wet state, mainly driven by oil in larger pores being preferentially detached from grain surfaces rather than from internal or external surfaces of pore-filling clay aggregates (primarily kaolinite). The results could imply that oil release from clay minerals is not the main mechanism of the

low salinity effect; conversely though, it could be argued that the small effect seen here for Berea sandstone was due to the absence of this primary cause.

3 Spontaneous Imbibition in Reservoir Sandstones

3.1 Introduction

Crude oil composition dictates oil viscosity and influences oil-brine interfacial tension and wettability alteration of rock, all of which have a direct and fairly well understood impact on water flood oil recovery via the mobility ratio, capillary number and contact angle. Enhanced oil recovery by low salinity brine injection acts via in situ changes in crude oil/brine/rock interactions (4,12). Accordingly, the links between oil composition and the low salinity effect are more subtle and less well understood. Some researchers have pointed to the importance of the relation between the oil's asphaltene/resin ratio and the content of water-in-oil dispersion in low salinity brine (51). Others have studied the effect of oil composition on low salinity water flooding of core plugs (52-59) and some of them proposed that the oil's acids migrate to the interface and cause recovery by weakening the oil film (60-62).

Non-destructive 3D imaging techniques such as micro-CT scanning can provide further pore-scale insight into the effect of oil composition and properties on low salinity flooding. In this chapter, micro-CT imaging and analysis were utilized to study mini-plugs of a clay-rich reservoir sandstone after spontaneous imbibition of high and low salinity brine. Sister mini-plugs of 5 mm diameter were restored using two crude oils, primarily distinguished by their high and low acid numbers. Each mini-plug was micro-CT imaged and analyzed in its states after spontaneous imbibition of seawater in secondary mode followed by low salinity brine (500 ppm NaCl) in tertiary mode. The segmented tomograms showed that all mini-plugs possessed very high residual oil saturation after immersion in seawater, implying a substantially oil-wet state. Subsequent immersion in the low salinity brine resulted in a significant tertiary recovery of 5.1 %PV for the high acid number oil, but much smaller for the low acid number oil. The tomograms were further analyzed to quantify the pore-scale changes in oil saturation, connectivity, interfacial areas and mean curvature giving rise to these differing responses.

3.2 Materials and Methods

3.2.1 Materials

All mini-plugs in the study were taken from the same piece of friable, clay-rich, North Sea reservoir sandstone. Its mineral composition from XRD as received from the supplying company is listed in Table 3.1. The crude oils used were two samples from neighboring fields, with similarly low density, viscosity and asphaltene content, but primarily distinguished by their total acid numbers (TAN) of 3 and <0.1 mg KOH/g oil. Both oils were pre-conditioned over formation water at 91°C for three days prior to use. The composition of the formation brine (FW), high (HS) and low (LS) salinity brines and their corresponding contrast brines (containing 0.4 M NaI) are listed in Table 3.2.

Table 3.1 Mineral composition of the reservoir sandstone from XRD.

Mineral	%
Quartz	33.0
Alkali Feldspar	16.1
Plagioclase	7.0
Muscovite/Illite	9.8
Mixed layer clays	0.2
Kaolinite	27.4
Chlorite	0.4
Calcite	0.0
Dolomite/Ankerite	0.6
Siderite	4.8
Pyrite	0.6

Table 3.2 Composition of brines used in the experiments.

Salt	FW (g/l)	HS (g/l)	HS contrast (g/l)	LS (g/l)	LS contrast (g/l)
NaCl	58.44	23.73	0.35	0.50	
CaCl ₂ .2H ₂ O	5.88	1.50	1.50		
MgCl ₂ .6H ₂ O	2.03	10.70	10.70		
KCl	1.49	0.76	0.76		
Na ₂ SO ₄		3.98	3.98		
NaHCO ₃		0.67	0.67		
SrCl ₂ .6H ₂ O	0.53	0.02	0.02		
BaCl ₂ .2H ₂ O	0.98				
NaI			59.96		59.96
TDS(g/l)	69.35	41.36	77.94	0.50	59.96
pH	6.10	8.10	7.60	6.40	6.30

The received rock piece was cleaned of its bulk oil, brine and surface-bound asphaltenes using toluene, methanol and azeotropic chloroform/methanol, and then dried. Owing to its fragility, intact mini-plugs could not be cored from it without support. To this end, the rock was partially infiltrated with molten paraffin wax at 75°C under ambient pressure and then cooled to 22 °C. Coring of three sister mini-plugs of 5 mm diameter and 16 mm length (referred to as A, B and C) was subsequently performed using a drill press with water as lubricant. The wax was removed from each by soaking (at 75 °C) and flow through (at 22 °C) of approximately 50 ml of heptane. All subsequent experiments were performed on naked mini-plugs with all faces open, in contrast to mini-plug mounting in a flow cell for water flooding which will be discussed in next chapter.

3.2.2 Experimental Methods

Figure 3.1 shows one of the mini-plugs, non-destructively imaged in 3D using micro-CT, which is the subject of this current chapter, and subsequently sectioned for imaging in 2D using BSEM and SEM-EDS, which will be the subject of Chapter 5. Between its micro-CT imaging in the dry state and its re-cleaning and sectioning for microscopy, each mini-plug underwent restoration for micro-CT imaging of its state after spontaneous imbibition of HS brine and in turn LS brine, following an experimental procedure that combined elements of that used in Chapter 2.

The protocol for restoration and imbibition applied to each 5 mm diameter mini-plug of the reservoir sandstone was largely similar to that used on the naked mini-plugs of Berea in Chapter 2, but now using the brines of Table 3.2, the two oils and the appropriate temperature conditions. In brief, each mini-plug was saturated with formation brine FW, by vacuum infiltration followed by isostatic pressurization up to 55 MPa for 24 h to dissolve and diffuse out any remaining air. Primary drainage to irreducible saturation S_{wi} was then performed by centrifugation in the high TAN oil for mini-plug A and the low TAN oil for mini-plugs B and C, in all cases at a spin speed of 3750 rpm ($P_c \sim 14$ psi) maintained for 1 h.

Each mini-plug was then aged in a sealed glass vessel in an oven at 91 °C for 11 days. The vessels used for mini-plug A and B were glass vials filled with their respective crude oil (pre-equilibrated with FW at this aging temperature) and sealed with epoxy, as

used in Chapter 2. The aging vessel for mini-plug C was of a different design as shown in Figure 3.2, comprising a test tube with ground glass stopper, containing bulk FW below the (low TAN) oil and mini-plug. The presence of bulk FW reduced the risk in the original design that water from the crude oil escapes through the vial seal during aging, which would lead to progressive dehydration of the connate brine in the mini-plug to re-hydrate the oil. Given the very small pore volume, and low S_{wi} , of the mini-plug, a slight reduction in water concentration within the comparatively large volume of the surrounding oil could lead to significant decrease in S_{wi} by drying during aging at this relatively high temperature.

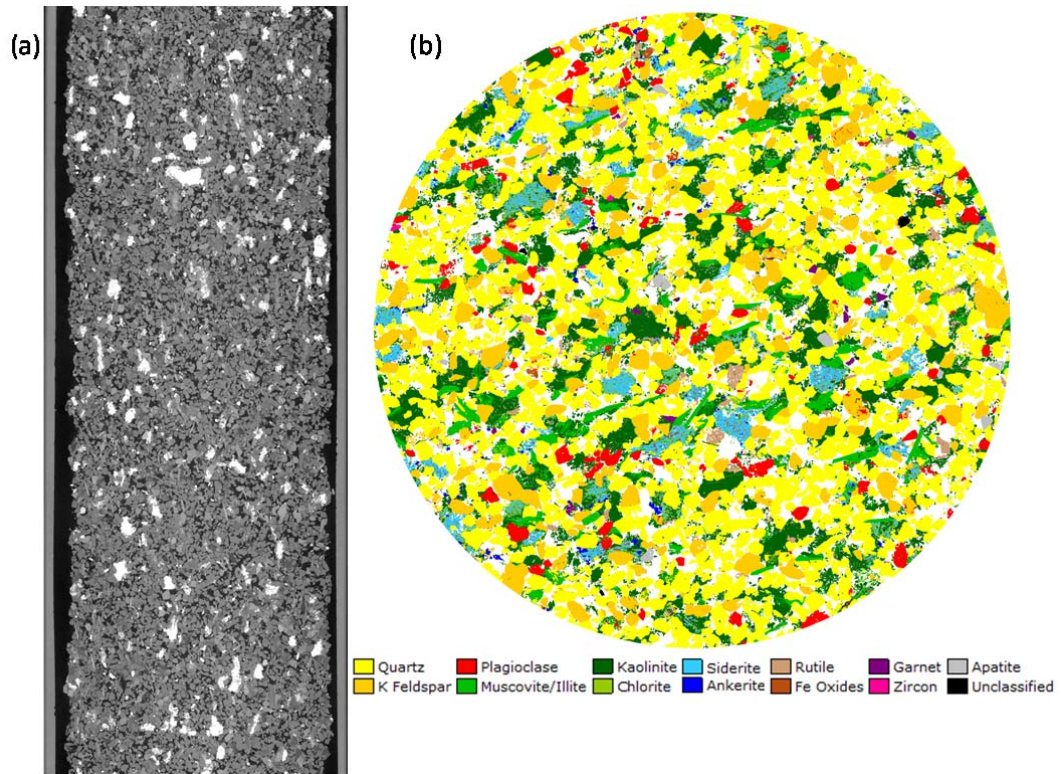


Figure 3.1 (a) Central longitudinal slice of the dry-state tomogram of the 5 mm diameter mini-plug A of reservoir sandstone in its aluminum-tube holder, with field of view of $5.6 \text{ mm} \times 14.2 \text{ mm}$ at $2.3 \text{ } \mu\text{m}$ voxel size, and (b) mineral map from QEMSCAN of a cross-section of the same mini-plug, masked to 4.2 mm diameter with $1.8 \text{ } \mu\text{m}$ pixel size.

After aging, each mini-plug was immersed in pre-heated HS brine, which was then maintained at $91 \text{ } ^\circ\text{C}$ for 7 days. This SIH spontaneous imbibition step was followed by cooling to room temperature ($22 \text{ } ^\circ\text{C}$) and transfer of the mini-plug into HS contrast brine (Table 3.2) for 3 days of diffusional exchange of Cl^- for the dopant ion I^- . The

mini-plug was re-scanned in this contrasted SIH state, mounted in its aluminum holder filled with this same brine. After scanning, the mini-plug was re-immersed in HS brine at room temperature for 2-3 days to re-exchange I^- for Cl^- , and then re-heated to 91 °C and immersed in the pre-heated LS brine, which was subsequently maintained at this temperature for 7 days. The SIL spontaneous imbibition step was then followed by exchange for the LS contrast brine and re-scanning in this contrasted SIL state by replicating the above-mentioned procedure.

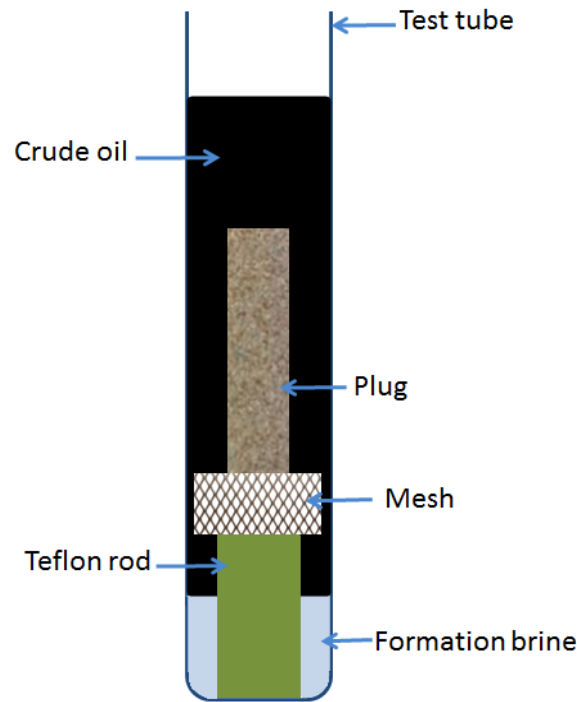


Figure 3.2 Diagram of aging vessel design used for mini-plug C.

Each mini-plug was then cleaned using decalin and methanol to remove bulk oil and brine, and re-scanned in this dry state after these procedures. It was then re-saturated with the HS contrast brine for its final scan in this saturated state. Mini-plug C broke during the centrifugation in decalin used to displace the oil, owing to the fragility of these small friable sandstone samples. Mini-plugs A and B were then soaked in methanol to remove the HS contrast brine, prior to drying and sectioning as described in Chapter 5. All of the scans were performed using HeliScan (FEI) micro-CT in order to

continuously image the majority of the mini-plug height, acquired at a voxel size of around 2.3 μm .

3.2.3 Image Processing and Analysis

The procedure used for processing and analysis of the series of tomograms (in the states: dry, SIH, SIL, dry post-flooding, and brine saturated) was similar to that in Chapter 2. Briefly, this consisted of 1) cylindrical masking, 2) spatial registration to the dry (post-flooding) tomogram, 3) two-phase segmentation of resolved (macro-)oil in the SIH and SIL states, 4) three-phase segmentation of macro-pores, macro-grains and microporous regions (referred to as clay aggregates) in the dry (post-flooding) state, 5) microporosity quantification within the clay aggregate phase using the difference tomogram of brine-saturated minus dry (post-flooding) states, and 6) micro-oil and micro-brine segmentation within the clay aggregate phase using the difference tomogram of brine-saturated minus SIH or SIL states.

Movement of macro-oil and -brine from high to low salinity was analyzed in the same manner as in Section 2.3.2.1, by using the difference tomogram of SIH minus SIL states to segment the four categories of occupancy of voxels within resolved pores, namely BB (brine-filled in SIH and SIL), OO (oil-filled in SIH and SIL), OB (oil-filled in SIH but brine-filled in SIL), and BO (brine-filled in SIH but oil-filled in SIL). Changes in micro-oil and -brine occupancy of voxels within clay aggregates were not analyzed since these could not be reliably assigned within the uncertainties in their segmentation.

3.3 Results and Discussion

3.3.1 Segmentation Procedure

Steps 2-5 listed in the section above are illustrated for mini-plug A in Figure 3.3, which displays the same subarea from a slice of the registered tomograms of SIH, dry (post-flooding), and brine-saturated minus dry (post-flooding), and their resulting segmentations of the above-mentioned phases. As a brine-saturated tomogram could not be obtained for the broken mini-plug C, steps 5-6 were omitted for this sample. Figure 3.4 and its zoom-in in Figure 3.5 show a cross-sectional slice of the tomograms of mini-plug C registered in its states after SIH and SIL, and their corresponding four-phase segmentations into resolved oil, brine and grain, plus clay aggregate. They also show

the further segmentation of resolved liquid that moves between these two states (OB and BO phases), obtained from their difference tomogram.

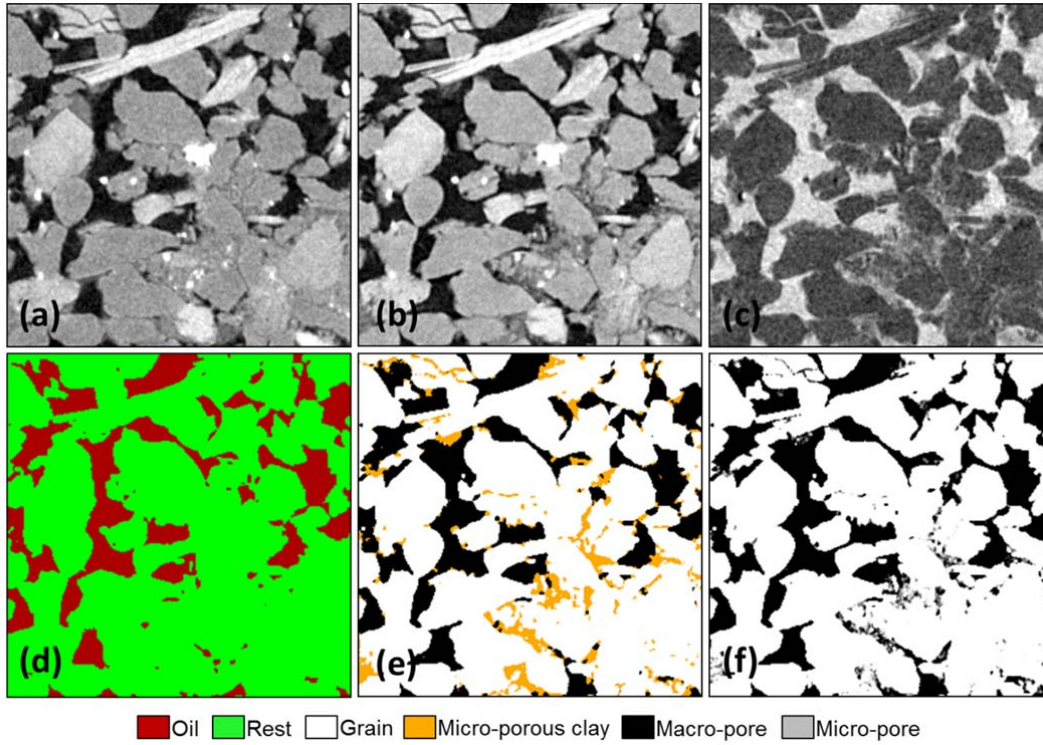


Figure 3.3 Subarea ($0.64 \text{ mm} \times 0.64 \text{ mm}$) of a slice from the tomograms of mini-plug A, registered between the states: (a) SIH, (b) dry (post-flooding), and (c) difference of brine-saturated minus dry (post-flooding), and after segmentation of (d) macro-oil in SIH from (a); (e) macro-pore, macro-grain and clay phase from (b); (f) microporosity quantification within clay from (c).

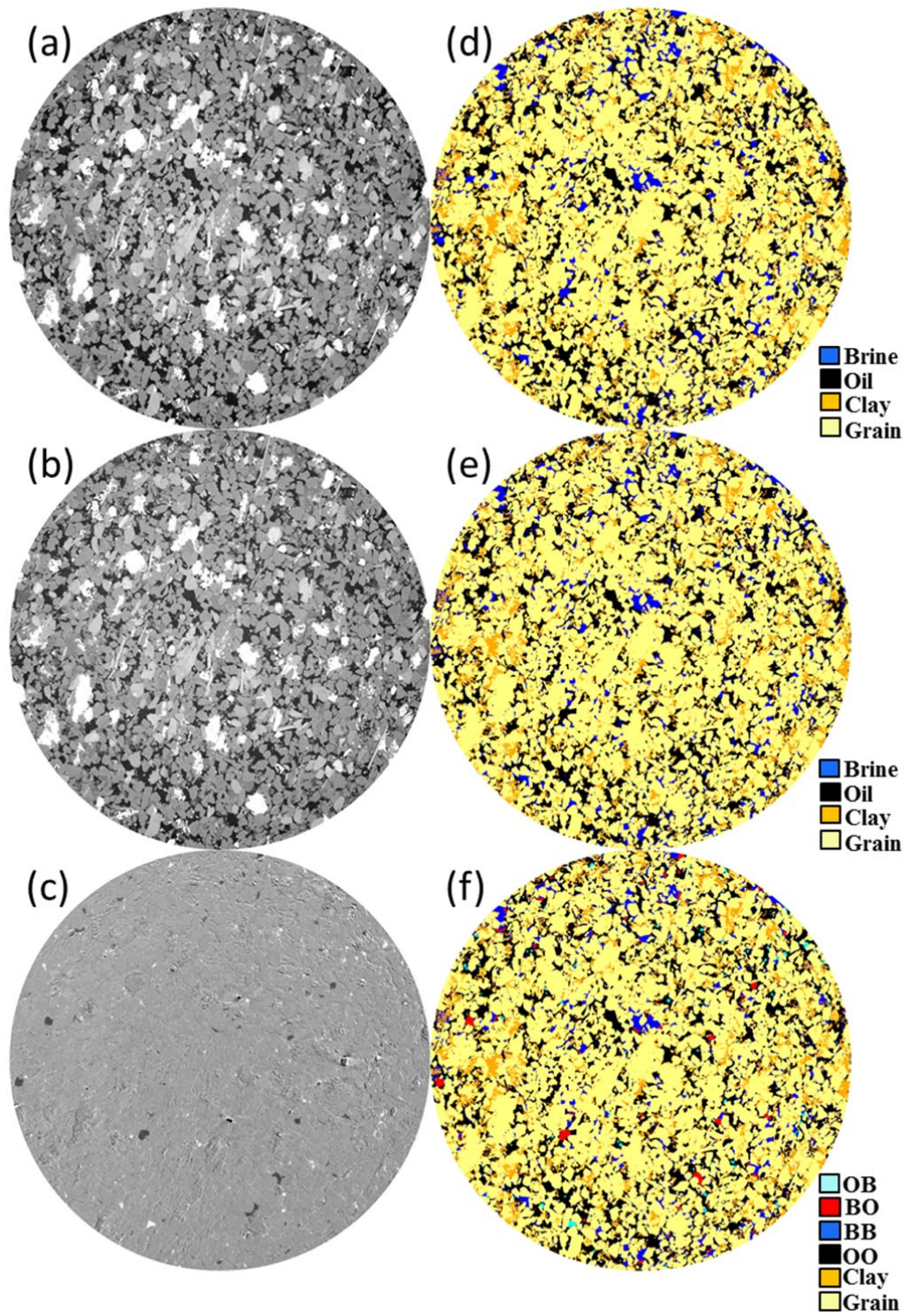


Figure 3.4 Tomogram cross-sectional slice of 5 mm diameter mini-plug C, masked to 4.2 mm $\times$ 4.2 mm, registered between the states (a) SIH and (b) SIL, also showing (c) their difference, (d) segmentation of SIH and (e) SIL into macro-oil, macro-brine, grain and clay , and (f) after further segmentation of the macro-liquids into their four occupancy classes

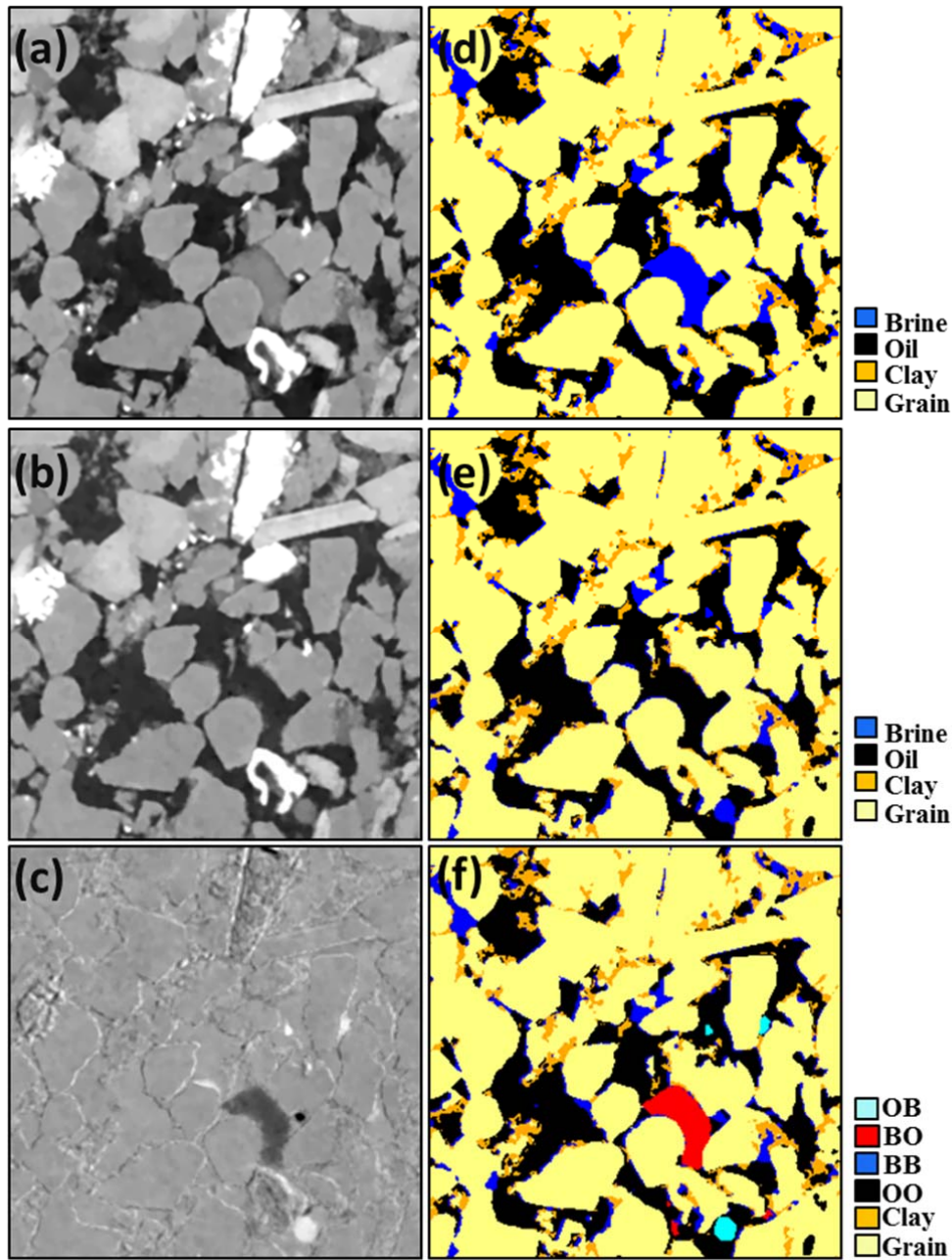


Figure 3.5 Subarea ($0.63 \text{ mm} \times 0.63 \text{ mm}$) from the corresponding tomogram cross-sectional slice in Figure 3.4(a)-(f).

3.3.2 Observations from the Flooded-State Tomograms

Figures 3.6-3.8 display central longitudinal slices of the sequence of registered tomograms in the dry, SIH and SIL states for mini-plug A (with high TAN oil) and B and C (both with low TAN oil). Recall that from XRD in Table 3.1, the rock comprises (by weight) 33% quartz, 16% feldspar, 7% plagioclase, 27% kaolinite, 10% muscovite/illite and 5% siderite. The darkest phase in the dry-state images (a) in Figures

3.6-3.8 is macro-pore, while the next brighter phase (dark gray) corresponds to pore-filling clays, mainly kaolinite, and the microporosity within them. Quartz and plagioclase grains are brighter, since they do not possess internal porosity; however, these two mineral classes are almost indistinguishable from their X-ray attenuation grayscale. Feldspar (potassium) grains are in turn somewhat brighter, and display some weathering, while muscovite/illite flakes and aggregates are brighter still, while the brightest grains are siderite.

Features that brighten from the dry to SIH state in images (b) contain contrast brine. These primarily occur as micro-brine (e.g. in the top right corner of Figure 3.7(b)), which most likely occupied these microporous regions throughout the restoration process. Some examples of macro-brine exist (e.g. blue arrows), most commonly in resolved pore throats, and are suggestive of brine advance during SIH from tighter locations originally occupied by connate brine. Based on visual inspection, brine-filled clay aggregates (e.g. purple circles) are generally less porous and tighter than their oil-filled counterparts (e.g. olive circles). Further brightening from the SIH to SIL state in images (c) corresponds to tertiary recovery (OB, e.g. cyan arrows), and is usually manifested as further advance of pore-throat menisci from SIH into pore bodies in SIL. No discernable changes in saturation within microporous regions occur in SIL, so the subsequent quantitative analysis focuses on macro-pores. The vast majority of macro-pore occupancy corresponds to OO (e.g. black arrows), i.e. pores which remain oil-filled throughout SIH and SIL.

While the above observations generally apply to mini-plugs A-C in Figures 3.6-3.8, some differences exist between these three samples. Tertiary oil recovery (OB) is less frequent in mini-plug B than A. Mini-plug C contains most brine after SIH, with some large pore bodies being substantially occupied by macro-brine in this state. This could indicate that the different aging protocol used for this sample (in Figure 3.2) led to a somewhat less oil-wet state than for B. Instances of OB due to further advance of brine from SIH to SIL are quite frequent in mini-plug C, but are counterbalanced by the reverse effect of withdrawal of brine in pore bodies from SIH to SIL (BO, e.g. red arrows), which was only very rarely seen in A and B. Thus the OO category of macro-pore occupancy is least dominant in C.

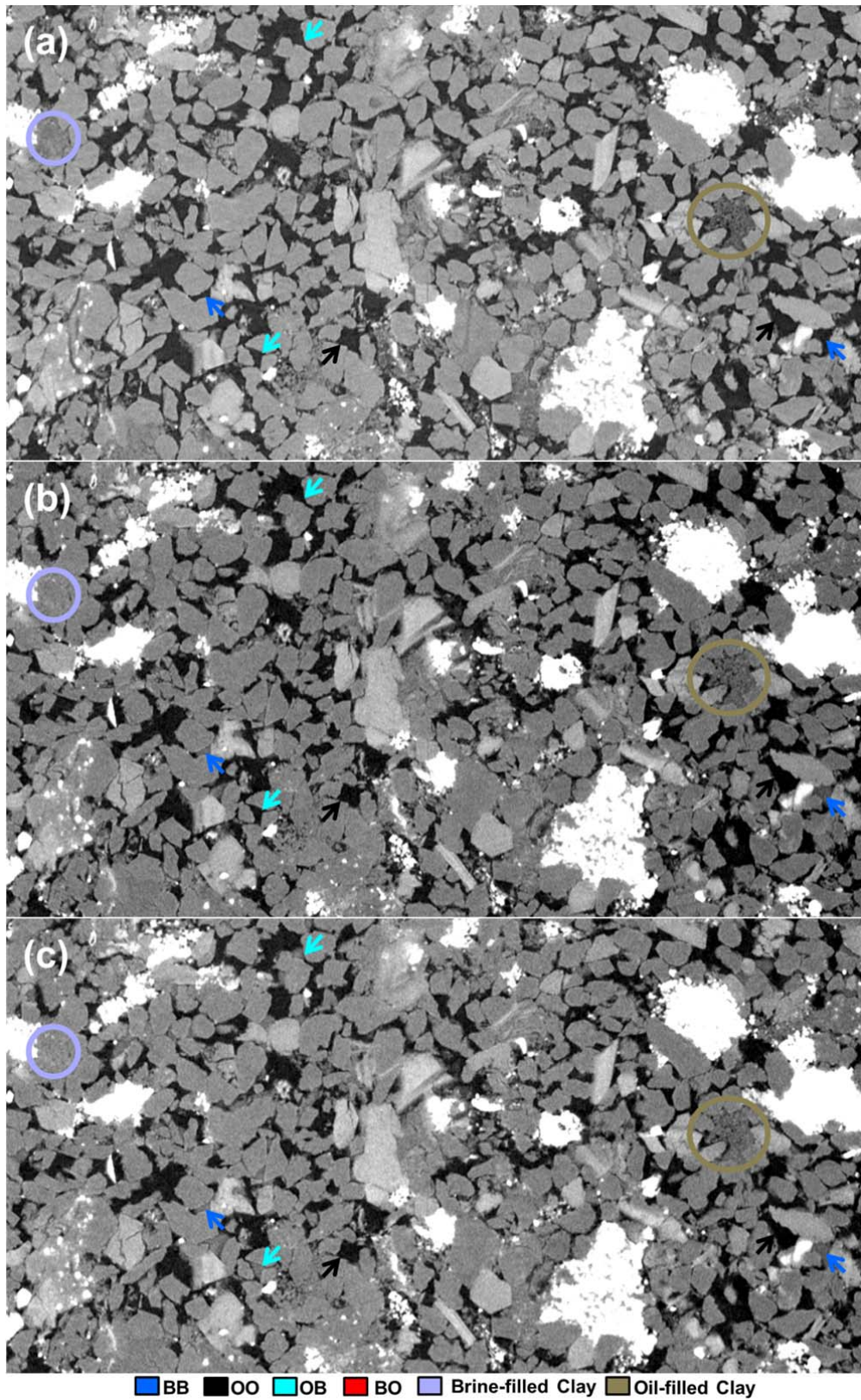


Figure 3.6 Subarea (1.6 mm $\times$ 3.0 mm) of a longitudinal slice from the tomograms of the 5 mm diameter mini-plug A, registered between the (a) dry state, and after (b) SIH and (c) SIL, with examples of the segmented oil and brine phases.

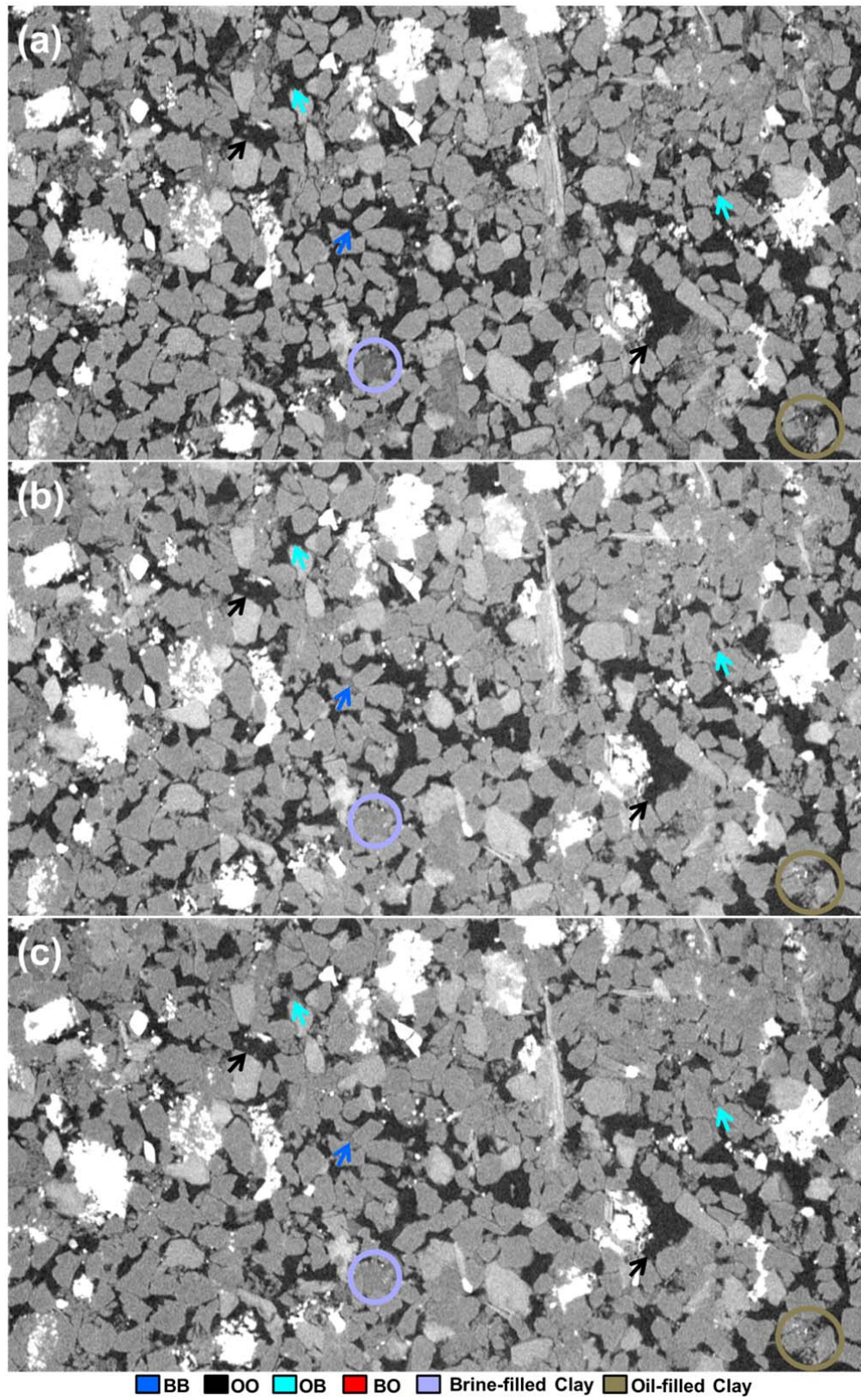


Figure 3.7 Subarea ($1.6 \text{ mm} \times 3.0 \text{ mm}$) of a longitudinal slice from the tomograms of the 5 mm diameter mini-plug B, registered between the (a) dry state, and after (b) SIH and (c) SIL, with examples of the segmented oil and brine phases.

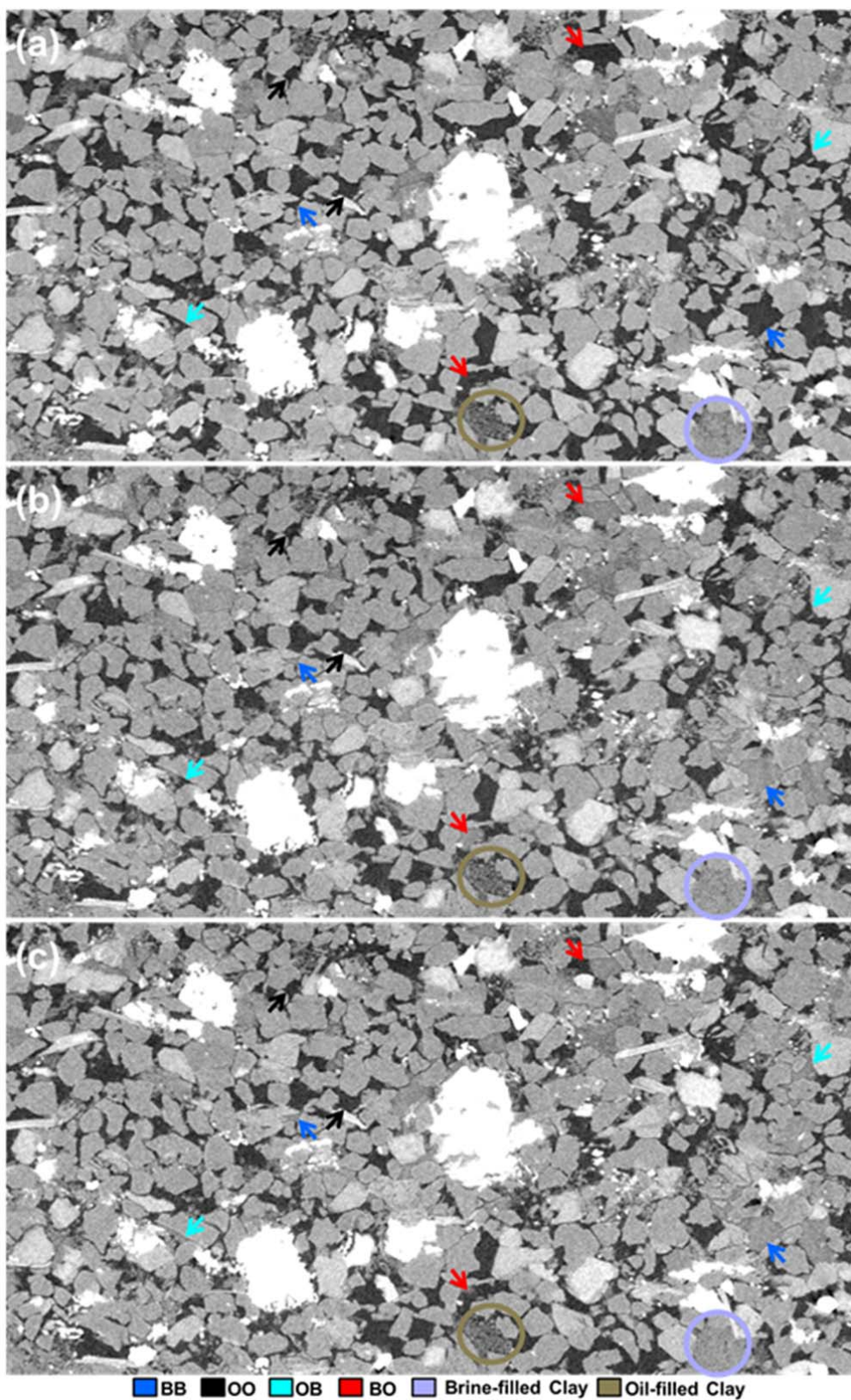


Figure 3.8 Subarea (1.6 mm $\times$ 3.0 mm) of a longitudinal slice from the tomograms of the 5 mm diameter mini-plug C, registered between the (a) dry state, and after (b) SIH and (c) SIL, with examples of the segmented oil and brine phases.

3.3.3 Segmentation Results

The results of the above-mentioned segmentation procedure for mini-plugs A-C are presented below, starting with the overall volume fractions in this sub-section and continuing with the measures of spatial distribution of the oil and its interfacial areas and mean curvature in the following sub-sections. Table 3.3 lists the volume averages of each segmented phase, beginning from the bulk volume fractions of grain (resolved solid mineral), clay aggregate (including their solid and microporous fractions) and resolved (macro-) pore. Microporosity within the clay was quantified from the difference tomogram of brine-saturated minus dry state; it is not provided for mini-plug C since it broke prior to the final workflow step of brine saturation. According to Table 3.3, calculated macro-porosity of all samples is consistently about 20% and the total porosity of mini-plugs A and B is about 24%.

Oil saturations in Table 3.3 are given as percentages of pore volume (PV), not of the fraction of it originally occupied by oil (OOIP), since the initial brine saturation S_{wi} after aging was not measured. All three mini-plugs possess high S_{or} after SIH compared to the corresponding results after HS water flooding in Chapter 4, owing to the limited scope for spontaneous imbibition into this substantially oil-wet state. For mini-plug A, its high value of S_{or} after SIH is significantly reduced by 5.1 p.u. after subsequent SIL, with all of this reduction corresponding to OB without any counteracting BO. Oil saturation in mini-plug B after SIH is even higher than for A, and is suggestive of virtually no secondary recovery during SIH. This could be interpreted as being caused by establishment of a more strongly oil-wet state in B due to the stronger attraction and adhesion of this low TAN oil to the predominantly acidic sites on the silicate minerals. Subsequent exposure to the LS brine resulted in much less tertiary recovery from B than from A.

To enable a fairer comparison of the role of oil acid number in the low salinity effect for this reservoir sandstone, the experiment for mini-plug B was repeated for its sister C using this same low TAN oil, but with the modification to the aging set-up shown in Figure 3.2, designed to instill a less oil-wet state. This indeed resulted in a lower value of residual oil saturation after SIH than in B, which in fact considerably undershot that in A after SIH. In spite of this, the low salinity effect was again much weaker in C than for the high TAN oil in A. Some oil movement took place from SIH to SIL in C, but the net incremental recovery was close to zero due to the cancelling contributions from OB

and BO. Thus irrespective of whether the initial wettability state was more or less oil-wet for the low TAN oil, the low salinity effect was stronger for the high TAN oil.

Table 3.3 Volume fractions of phases segmented from the entire masked volume of the series of registered tomograms of the 5 mm diameter mini-plugs A-C of reservoir sandstone. Porosity is given as percentage of total bulk volume (BV) and liquid saturations as percentages of total pore volume (PV).

Segmented Phase	A	B	C
Grain (%BV)	70.2	68.3	68.1
Micro-porous Clay (%BV)	10.1	12.6	11.9
Macro-Porosity (%BV)	19.7	19.2	19.9
Micro-Porosity (%BV)	4.6	4.5	-
Total Porosity (%BV)	24.3	23.7	-
So SIH (%PV)	78.4	89.0	71.5
So SIL (%PV)	73.3	87.7	71.4
So change (%PV)	5.1	1.3	0.1
OO (%PV)	73.5	87.1	68.9
BB (%PV)	21.4	11.0	25.9
OB (%PV)	5.1	1.9	2.6
BO (%PV)	0	0	2.6

3.3.4 Profiles of Residual Oil

The longitudinal profiles of resolved porosity and residual oil volume fraction, averaged over each cross-sectional slice, are plotted for each mini-plug in Figure 3.9. The profile is given over the entire imaged height of mini-plug A, but only over a sub-section of B and C in which the registration was most exact. In all cases the porosity profile is fairly uniform, owing to rock homogeneity, and residual oil after SIH and SIL is also quite uniformly distributed over these millimeter-centimeter scales. The corresponding profile of BO is to all intents zero throughout for mini-plugs A and B, while oil displacement OB increases somewhat in the upper half of A, over which the residual after SIH dips slightly (and SIL dips slightly more), possibly due to gravity. In mini-plug C, the curves of OB and BO almost coincide, and thus the internal oil

rearrangement from SIH to SIL occurs on small scales and averages out over larger scales.

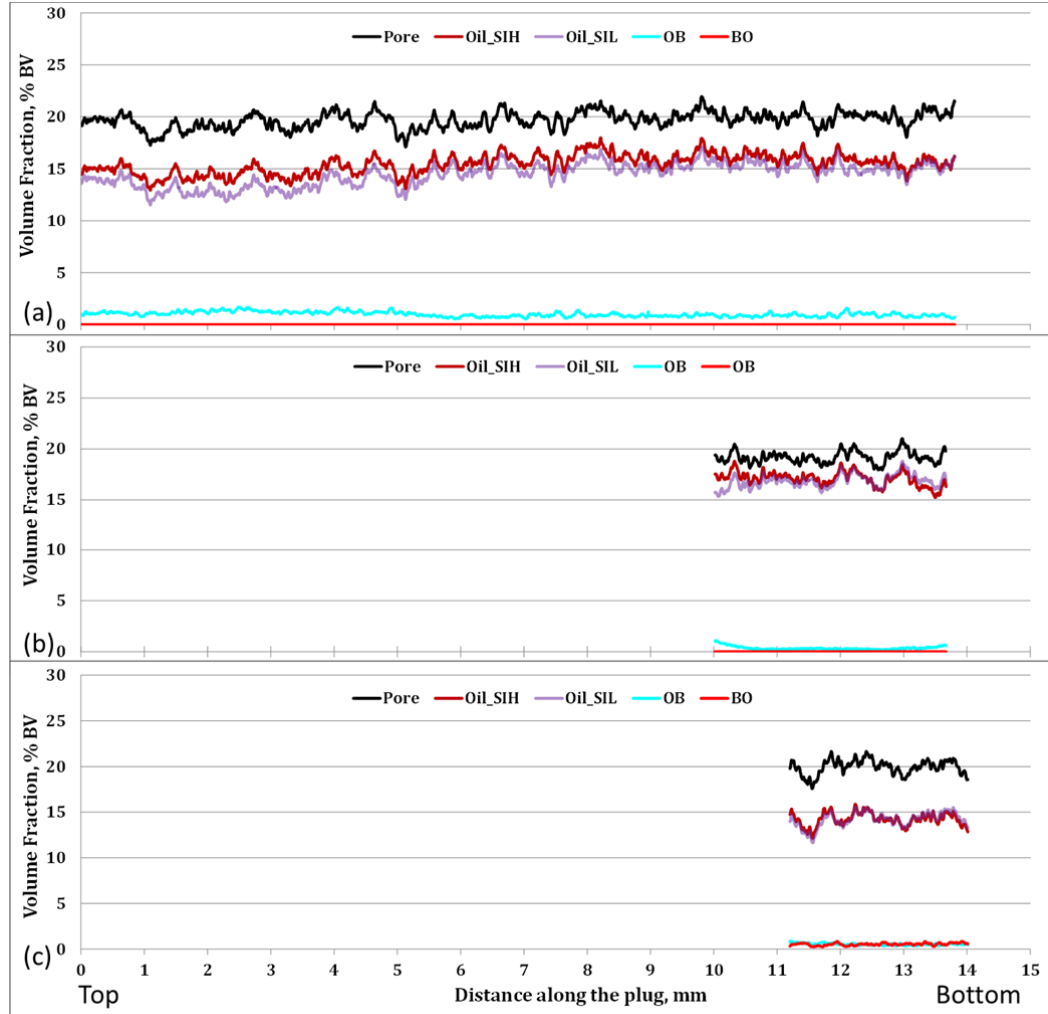


Figure 3.9 Longitudinal profiles of bulk volume fraction of macro-porosity, macro-oil after SIH and SIL, and OB and BO along the three mini-plugs (a) A, (b) B, and (c) C of the reservoir sandstone.

3.3.5 Pore-scale Distribution and Connectivity of Residual Oil

The resolved pore phase segmented from the dry-state tomogram of the mini-plug was partitioned into its constituent labeled pore bodies using a watershed algorithm (36), as shown in Figure 3.10. The resolved residual oil phase segmented from the registered tomograms of the SIH and SIL states was overlain onto this partition to calculate the

residual macro-oil saturation in each pore body, shown in the scatter plots of Figure 3.11.

In mini-plug A after SIH in Figure 3.11(a), the smallest pores are mainly filled with brine, while somewhat larger pores $\sim 10^{-5} \text{ mm}^3$ ($\sim 25 \text{ }\mu\text{m}$ equivalent sphere diameter, ESD) contain more oil than brine, evidencing the oil-wet state. Beyond this size, the distribution bifurcates into a major branch of oil-dominated pores (averaging around 85% saturation in the largest pores) and a minor branch down to much lower oil saturation, with substantial scatter in between. The most significant change after SIL is that this minor branch strengthens and the scatter increases, resulting in a downward shift in the average oil saturation to around 75% in pores above $\sim 10^{-3} \text{ mm}^3$ ($\sim 120 \text{ }\mu\text{m}$ ESD). This is due to the above-mentioned brine advance from small pores in SIH further into larger pore bodies in SIL.

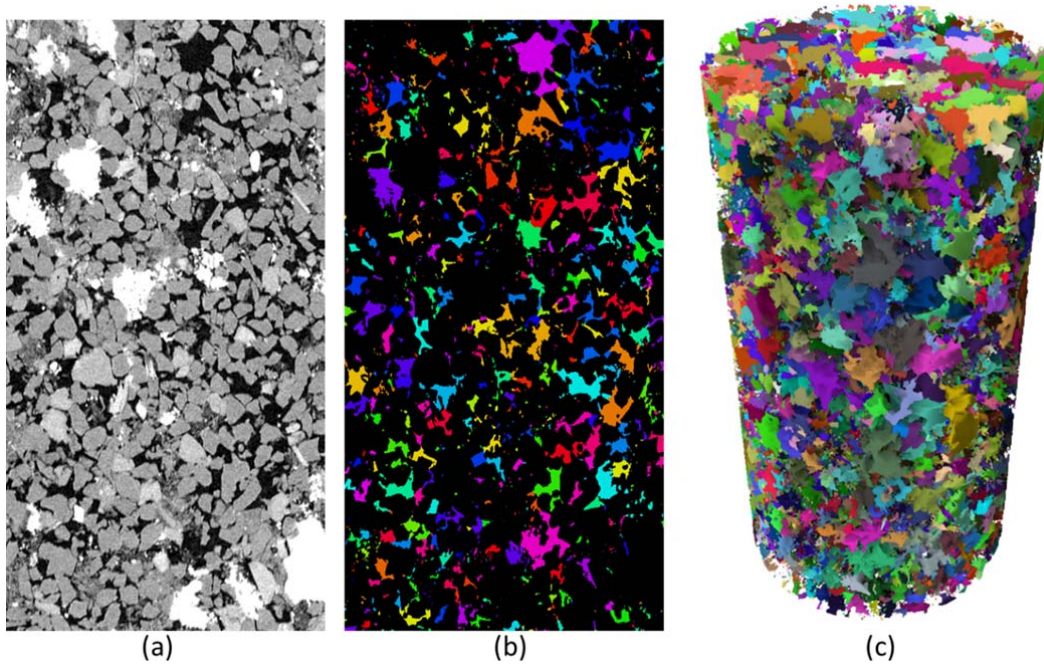


Figure 3.10 (a) Subarea ($1.6 \text{ mm} \times 3.0 \text{ mm}$) of a longitudinal slice of the dry-state tomogram of mini-plug B, (b) the corresponding pore partitioning in this slice, and (c) a 3D visualization of the partitioning of this same section. Each color represents one single pore body

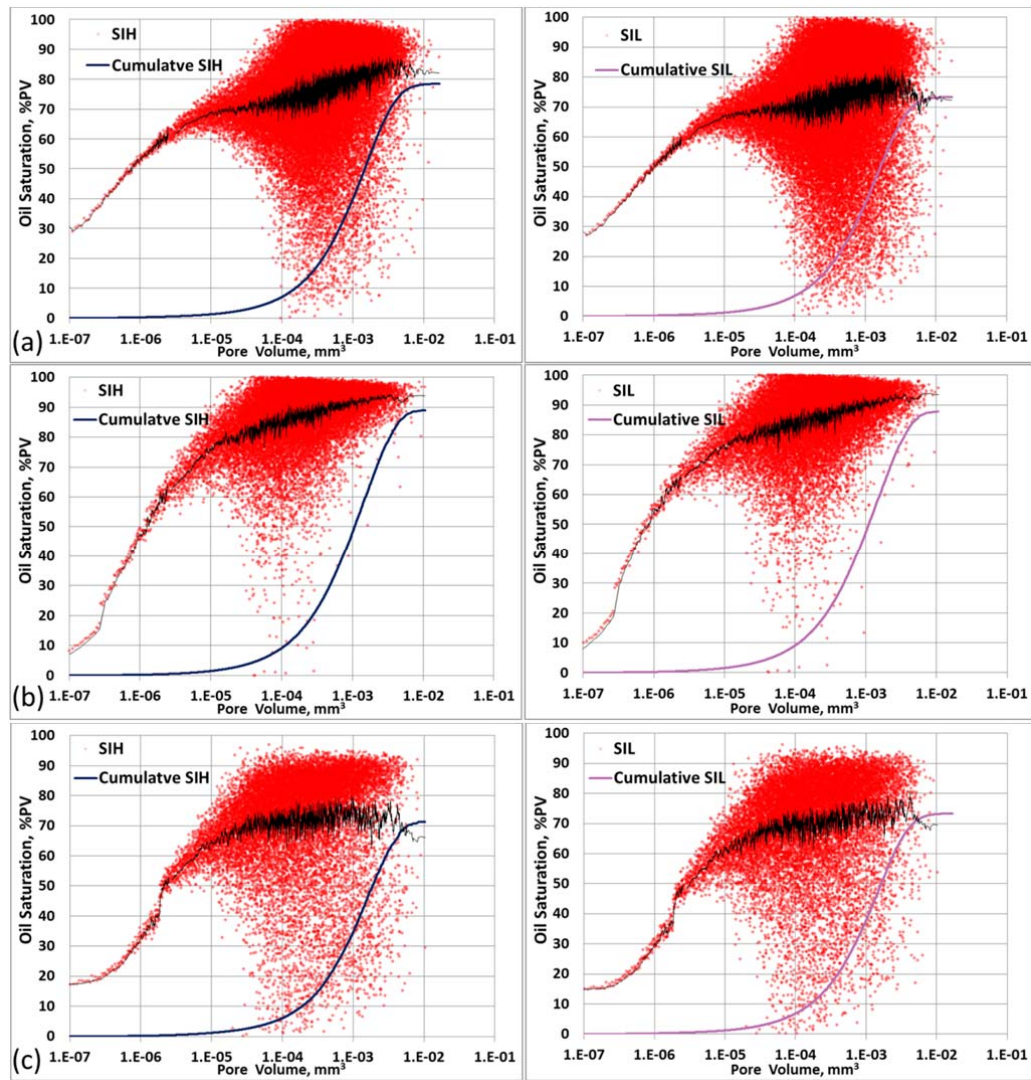


Figure 3.11 Scatter plot of residual oil saturation in each resolved pore body versus its individual volume (red points), also showing moving average (black line) and volume-weighted cumulative distribution (dark or light purple curve) after SIH (at left) followed by SIL (at right) for the three mini-plugs (a) A, (b) B, and (c) C.

For mini-plug B after SIH in Figure 3.11(b), the transition from brine-filled smaller pores to oil-filled larger ones is steeper than for A, suggesting a more oil-wet state, and the bifurcation at $\sim 10^{-5} \text{ mm}^3$ pore volume is very one-sided, with most larger pores having very high oil saturation (completely oil-filled to all intents). The only slight change caused by SIL is a small drop in oil saturation in pores $\sim 10^{-4} \text{ mm}^3$ ($\sim 60 \mu\text{m}$ ESD), as brine advances somewhat from tight pores into corners of these intermediate-sized pores. For mini-plug C after SIH in Figure 3.11(c), more brine is present in small pores (less oil-wet state) and oil saturation is also significantly lower in the largest pores, averaging just over 70%, and with great scatter. After SIL, the distribution

changes slightly due to displacement of oil from intermediate-sized pores and its re-accumulation in larger pores, in line with the tomograms shown in Figure 3.8 and the segmentation results of Table 3.3.

The corresponding results from oil connectivity analysis are shown in Figure 3.12, where the cumulative volume of residual oil after SIH and SIL is graphed versus the number of adjoining pores that each oil ganglion spans and occupies more than 50% of (47, 48). As the residual oil saturation and connectivity in these three mini-plugs are much greater than those in Chapter 2, oil volume is plotted here on a logarithmic scale. As expected, mini-plug A has the least connected oil after SIH, and connectivity decreases slightly further after SIL. Mini-plug B has the most connected oil after SIH, and exhibits virtually no change after SIL. Mini-plug C is intermediate to these two, and its curves after SIH and SIL coincide since the OB and BO interchange has little effect on connectivity. However, this form of analysis is not well suited to these states, in which even the most disconnected state (mini-plug A after SIL) has around 95% of its oil volume present in one giant cluster spanning the entire imaged volume.

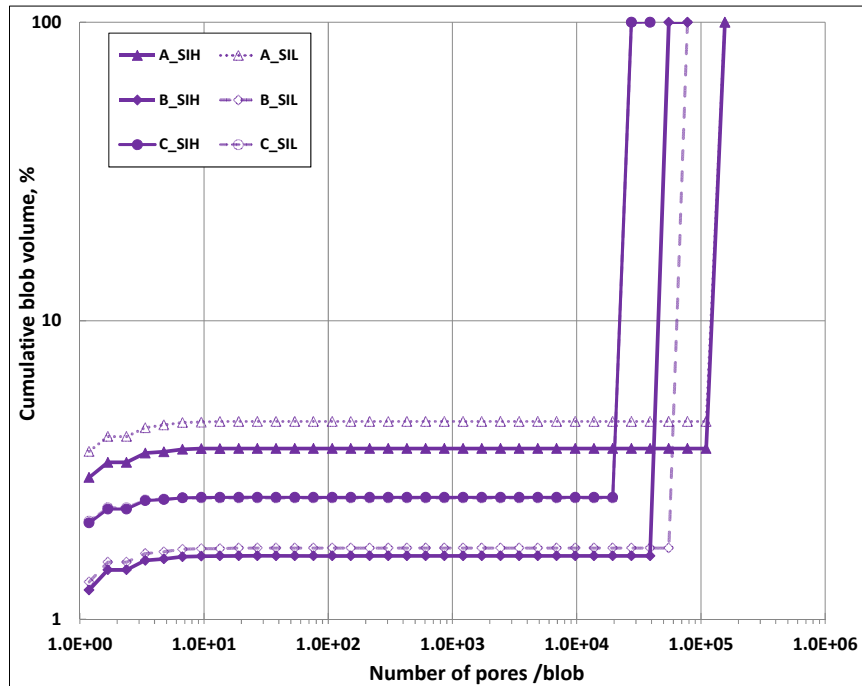


Figure 3.12 Cumulative distribution of residual oil volume after SIH and SIL for the three mini-plugs A-C, as a function of the number of connected pores spanned by each separate ganglion.

3.3.6 Interfacial Area of Residual Oil

To further understand residual oil changes from SIH to SIL, the contact area of macro-oil and -brine with the external surfaces of the two segmented rock phases of grains and clay aggregates were calculated for the three mini-plugs. The overall averaged percentage breakdown of total rock area into these four constituent combinations after SIH and SIL is shown in Figure 3.13. Grains provide around four times as much surface area as clay aggregates over the tomogram volume (at its given resolution). Oil contacts the majority share of both of these rock phases after SIH and SIL. For mini-plug A with greatest tertiary recovery, oil's share of grain area reduces somewhat relative to brine, while oil contact area with clay remains unchanged from SIH to SIL. For mini-plug B with least oil movement from SIH to SIL, oil contact area to grain and to clay are almost invariant. For mini-plug C with more oil movement but least overall tertiary recovery, oil slightly reduces its contact area to both grain and clay from SIH to SIL.

The left graphs of Figure 3.14 plot the percentage reduction from SIH to SIL in macro-oil area contacting grain or clay (from Figure 3.13), relative to the total interfacial area of i) grain plus clay, or ii) only grain or clay, or iii) only the fraction of grain or clay originally contacting oil in the SIH state. These progressively more sensitive measures of salinity-induced area change show that oil in mini-plug A (Figure 3.14(a)) preferentially detaches from grains; its contact area with external surfaces of clay aggregates is calculated to increase slightly from SIH to SIL, which presumably stems from slight inconsistencies in clay segmentation in these two states. This preference for detachment from grain over clay was also seen in Berea sandstone in Figure 2.23(c). The corresponding results for mini-plug B in the left graph of Figure 3.14(b) show no change in oil area contacting grain, and a slight increase in its area contacting clay, which becomes increasingly amplified when counted relative to the small area of clay and of clay contacting oil in SIH. This negative trend is again thought to arise from slightly inconsistent segmentation of clay between SIH and SIL. For mini-plug C in the left graph of Figure 3.14(c), more oil is removed from grain surfaces than from clays, but when normalized to account for the much smaller area of clay and of clay contacting oil, detachment is strongly skewed to prefer clay. The results suggest that significant oil recovery by low salinity, such as for spontaneous imbibition into mini-plug A of the reservoir sandstone and Berea sandstone (in Chapter 2), mainly occurs by removal of oil from grains, while oil re-arrangement in the absence of overall recovery,

such as for mini-plug C is instead driven by preferential detachment from clay aggregates.

The right graphs of Figure 3.14 plot the oil-brine interfacial area normalized by total pore-rock area and its breakdown into contributions from the four occupancy classes. As expected for these systems with high residual oil, its interfacial area to brine increases from SIH to SIL but remains small (usually less than 10%) relative to pore wall area. For mini-plug A in Figure 3.14(a), its oil-brine area after SIH is dominated by the fraction (OO-BB) that will remain unmoved after SIL, relative to the smaller fraction (OB-BB) that will move. Oil-brine area roughly doubles from SIH to SIL, as the fraction (OB-OO) of interface created by this oil removal (OB) becomes around the same overall size as the unmoved fraction. Mini-plug B in Figure 3.14(b) exhibits a similar change, but much slighter, owing to the smaller overall recovery. The results for mini-plug C in Figure 3.14(c) now also include the non-negligible contribution from oil re-entering brine-occupied pores (BO). Its unmoved oil-brine interfacial fraction (OO-BB) is much lower, and the fraction that will move from SIH is dominated by the part (BO-OO) associated with oil re-entry. However, oil-brine interface lost from SIH (BO-OO) and created in SIL (BO-BB) by this oil re-entry are of similar sizes, while the fraction lost from SIH (OB-BB) and created in SIL (OB-OO) by oil removal grows substantially and is chiefly responsible for the overall increase in oil-brine area in SIL.

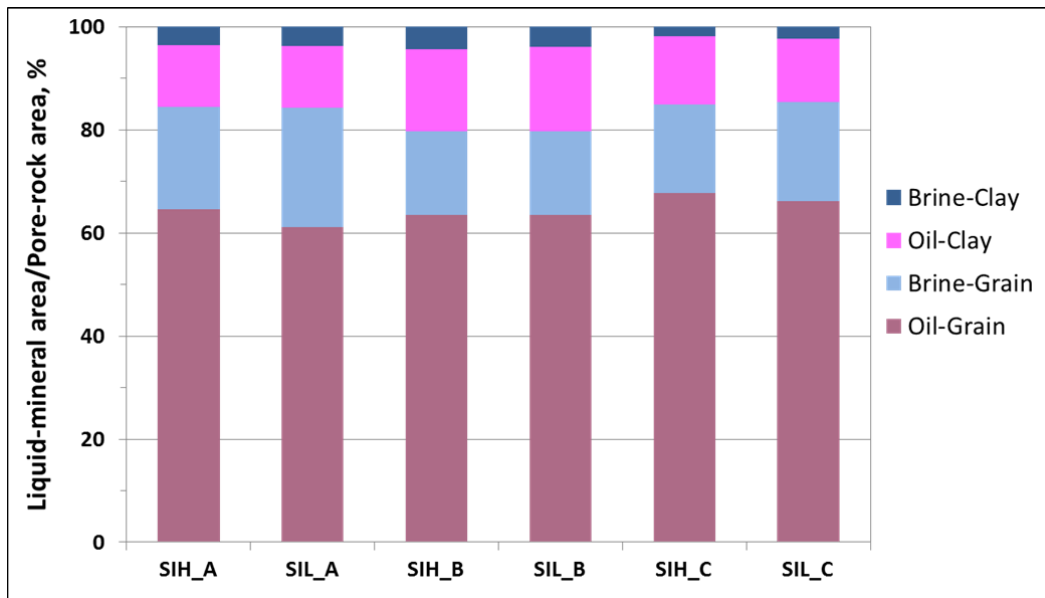


Figure 3.13 Interfacial area of liquid (oil and brine) contacting grain and clay aggregate, relative to total pore-rock area, for the three mini-plugs A-C after SIH and SIL.

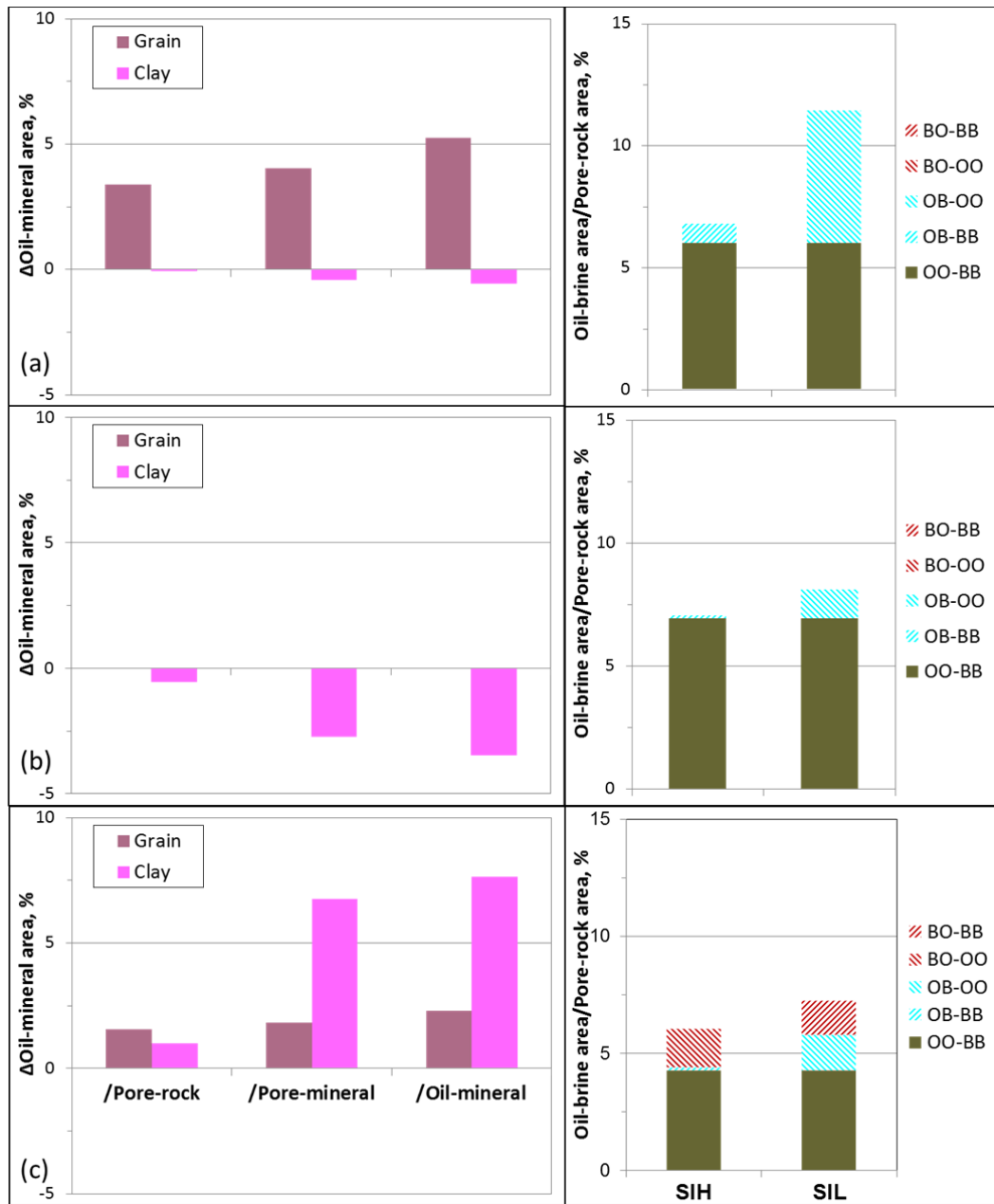


Figure 3.14 (Left) Salinity-induced change in interfacial contact area of macro-oil with grain or clay, normalized in three ways, where rock refers to grain plus clay and mineral refers to grain or clay, for mini-plugs (a) A, (b) B, and (c) C. (Right) Corresponding results for oil-brine interfacial area, relative to total pore-rock area.

3.3.7 Oil/Brine Interfacial Mean Curvature

To evaluate the shape of the oil-brine interface and to further investigate any shift in wettability from SIH to SIL, oil-brine interfacial mean curvature, H , was calculated using a Monge geometrical algorithm (49). Two approaches were employed; the first

used the segmented tomograms of the SIH and SIL states without any additional pre-processing, while the second removed the portion of the oil-brine interface lying within 15% of the range of distances to the grain surface prior to curvature calculation. This clipping (Figure 3.15) served to exclude the transition zone from oil to grain which often has a high uncertainty in segmentation due to partial volume effects or phase contrast. The resulting average values and standard deviations are listed in Table 3.4, again with the convention that positive or negative mean curvature corresponds to an interface curving towards or away from oil, respectively. The average value of mean curvature was obtained by fitting to its histogram peak rather than averaging over outputted values from all interfacial patches, in order to exclude the influence of extreme values at both ends. The averages in Table 3.4 from the two methods show somewhat similar trends from SIH to SIL; the method with clipping yields more reliable outcomes, based on its lower standard deviation. For this method, the average mean curvature increases from SIH to SIL for mini-plug A, very slightly increases for B and decreases for C, consistent with a weakening shift toward water wet, which is in line with the observed weakening oil recovery by low salinity from A to B to C.

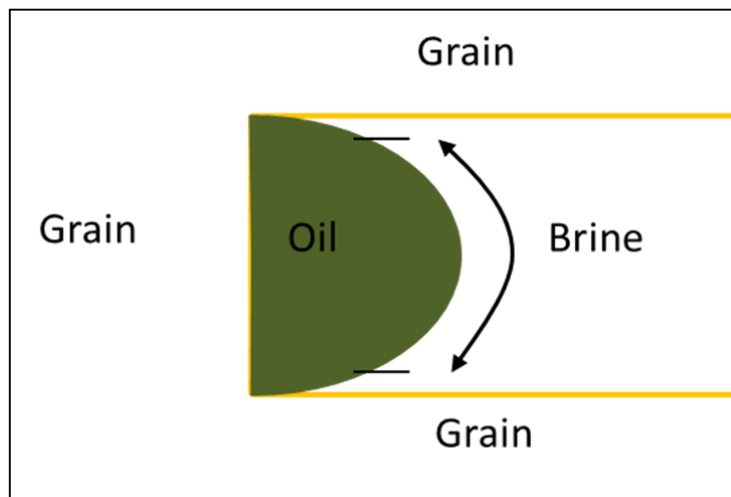


Figure 3.15 Schematic of central portion of oil-brine interface used in mean curvature calculation.

Table 3.4 Average mean curvature, H , of the resolved, segmented oil-brine interfaces, along with the equivalent capillary pressure (P_c), standard deviation (Std dev.) and standard error (Std error), within the three mini-plugs A-C after SIH and SIL, calculated either without pre-processing or with 15% clipping near grain surfaces.

Plug	State	No pre-processing					15% Clipping				
		H (voxel^{-1})	H^{-1} (μm)	P_c (mbar)	Std dev.	Std error	H (voxel^{-1})	H^{-1} (μm)	P_c (mbar)	Std dev.	Std error
A	SIH	-0.006	-386	-1.35	0.176	5.0e-6	-0.032	-73	-7.12	0.152	2.9e-6
	SIL	-0.001	-2320	-0.22	0.182	4.0 e-6	-0.029	-80	-6.5	0.158	2.9e-6
B	SIH	-0.002	-1118	-0.47	0.177	1.0 e-5	-0.028	-79	-6.58	0.149	2.9e-5
	SIL	-0.005	-447	-1.16	0.174	1.0 e-5	-0.027	-83	-6.27	0.149	2.8e-5
C	SIH	-0.025	-90	-5.78	0.182	7.7 e-6	-0.071	-32	-16.25	0.167	1.4e-5
	SIL	-0.036	-62	-8.39	0.182	6.7 e-6	-0.089	-25	-20.8	0.170	1.3e-5

As was also the case in Chapter 2, greater insight into recovery mechanisms from SIH to SIL can be obtained by restricting the analysis to the minority of oil-brine interfaces which moved between these two states. Table 3.5 gives the results thus derived from separate calculation of mean curvature on each of these four categories of moved interface, or only two for mini-plugs A and B in which instances of oil re-entering brine-occupied pores (BO) were virtually non-existent. The two methods of mean curvature calculation yield similar trends, namely that interfaces associated with oil removal decrease in curvature from SIH to SIL in all three mini-plugs. In other words, their initial configuration in SIH prior to recovery (OB-BB) is less strongly curved towards water than their final configuration in SIL after recovery (OB-OO). In particular, the average mean curvature of OB-BB menisci ($-0.021 \text{ voxel}^{-1}$ in Table 3.5) after SIH in mini-plug A is significantly higher than the overall SIH average (-0.032 in Table 3.4), which enables low salinity brine to displace oil from these less oil-wet locations. Oil removal in SIL proceeds until the average mean curvature of the corresponding new menisci (OB-OO; -0.030 in Table 3.5) equilibrates with the overall SIL average (-0.029 in Table 3.4). The same is true for mini-plug B, in which the average mean curvature of the before-state OB-BB menisci (0.000 voxel^{-1}) lies well above the SIH value (-0.028), while the corresponding average of the after-state OB-OO menisci (-0.031) lies close to the SIL value (-0.027). Tertiary recovery from B is thus limited by the closeness of the average mean curvature values in SIH and SIL states, as

mentioned above, and also by the relatively small OB-BB area of higher mean curvature over which oil displacement occurs.

The behavior of mini-plug C is distinctly different from A and B; average mean curvature after SIH is much lower and becomes even lower after SIL in Table 3.4. This is thought to be due to spontaneous formation of stable droplets of water in oil (with strong negative curvature towards water) in SIH and increasingly so in SIL, as can be seen in Figure 3.4. The creation and swelling of these droplets displaces oil, resulting in reduction in S_o (which is lowest in the SIH state for mini-plug C) or re-entry of oil into brine-occupied pores (which is most common in the SIL state for C). As shown in Table 3.5, these re-entering BO-BB menisci have higher curvature as the contact angle in this secondary receding mode is lower than for primary advance.

It is not known why these droplets were manifested in mini-plug C but not in B, which also contained this same low TAN crude oil. However, the overall weight of observations points to the high TAN oil in mini-plug A creating a less strongly oil-wet state after aging, making the oil more amenable to release from rock surfaces (especially grains) via wettability shift to more water-wet in the low salinity brine. On the other hand, the low TAN oil in B and C remains more strongly bonded to rock surfaces. In this bonded state, connate water is more likely to be disconnected, in which case its hydration via osmosis during immersion of the mini-plug in brines of lower salinity than the formation water can lead to creation of water droplets. It is also possible that such water droplets are more stable in the low TAN oil. However, this mode of oil displacement by internal water droplet formation is less efficient than meniscus advance via wettability shift as for mini-plug A in the high TAN oil.

Table 3.5 Average mean curvature, H , of the resolved, segmented oil-brine interfaces of each of the four categories having moved from SIH to SIL, along with the standard deviation (Std dev.) and standard error (Std error), within the three mini-plugs A-C, calculated either without pre-processing or with 15% clipping near grain surfaces.

Plug	State	Interface category	No pre-processing				15% Clipping			
			H (vxl^{-1})	H^{-1} (μm)	Std dev.	Std error	H (vxl^{-1})	H^{-1} (μm)	Std dev.	Std error
A	SIH	OB-BB	-0.002	-1160	0.129	4.1e-6	-0.021	-111	0.111	5.0e-6
	SIL	OB-OO	-0.021	-111	0.175	4.3e-6	-0.030	-77	0.171	3.6e-6
B	SIH	OB-BB	0.016	140	0.166	2.4e-4	0.000	∞	0.153	3.1e-4
	SIL	OB-OO	-0.028	-80	0.167	3.1e-5	-0.031	-72	0.163	4.5e-5
C	SIH	OB-BB	-0.042	-54	0.122	6.0e-5	-0.061	-37	0.113	7.4e-5
	SIL	OB-OO	-0.050	-45	0.170	1.5e-5	-0.077	-29	0.175	2.4e-5
	SIH	BO-OO	-0.024	-94	0.183	1.9e-5	-0.049	-46	0.177	2.2e-5
	SIL	BO-BB	0.025	90	0.188	1.9e-5	-0.006	-376	0.162	2.3e-5

3.3.8 3D Visualizations

To visualize in 3D the changes from SIH to SIL, sub-volumes of the segmented tomograms containing instances of oil movement were rendered using Avizo (FEI) software and shown in Figures 3.16 and 3.17. Two examples of oil displacement during SIL within mini-plug A are shown in Figure 3.16 (a-b). The first example shows oil ganglia breaking into smaller blobs during SIL, primarily due to advancing brine causing release of oil from grain surfaces and snap-off in pore throats between grains, while oil remains attached to the outer surfaces of clay aggregates. The second example from mini-plug A (Figure 3.16(b)) shows further instances of oil retraction and break-up by advance of low salinity brine in small pores and throats, again suggestive of shift to a more water-wet state. It also shows displacement of oil from one larger pore body, which appears to be a rare instance of water droplet creation in mini-plug A. Figure 3.16(c) shows instances of oil detachment from grain surfaces in mini-plug B, which are far less common than in A. Figure 3.16(d) shows an example from mini-plug C of the plentiful instances of coexistence of OB and BO. Residual oil in a large pore body after SIH is displaced (OB) by creation and growth of a water droplet during SIL (at left), which forces oil to re-invade brine-occupied pores (BO, at right).

To spatially visualize oil connectivity after SIH and SIL, iso-surfaces of cylindrical sub-volumes in the center of the three mini-plug tomograms were generated and shown in Figure 3.17. Oil is strongly connected throughout the pore bodies in all three mini-plugs after SIH. Oil ganglia disconnection after SIL can be seen in the bottom part of mini-plug A (black arrows), while the other two mini-plugs did not show any significant changes, which is consistent with the connectivity graphs in Figure 3.12.

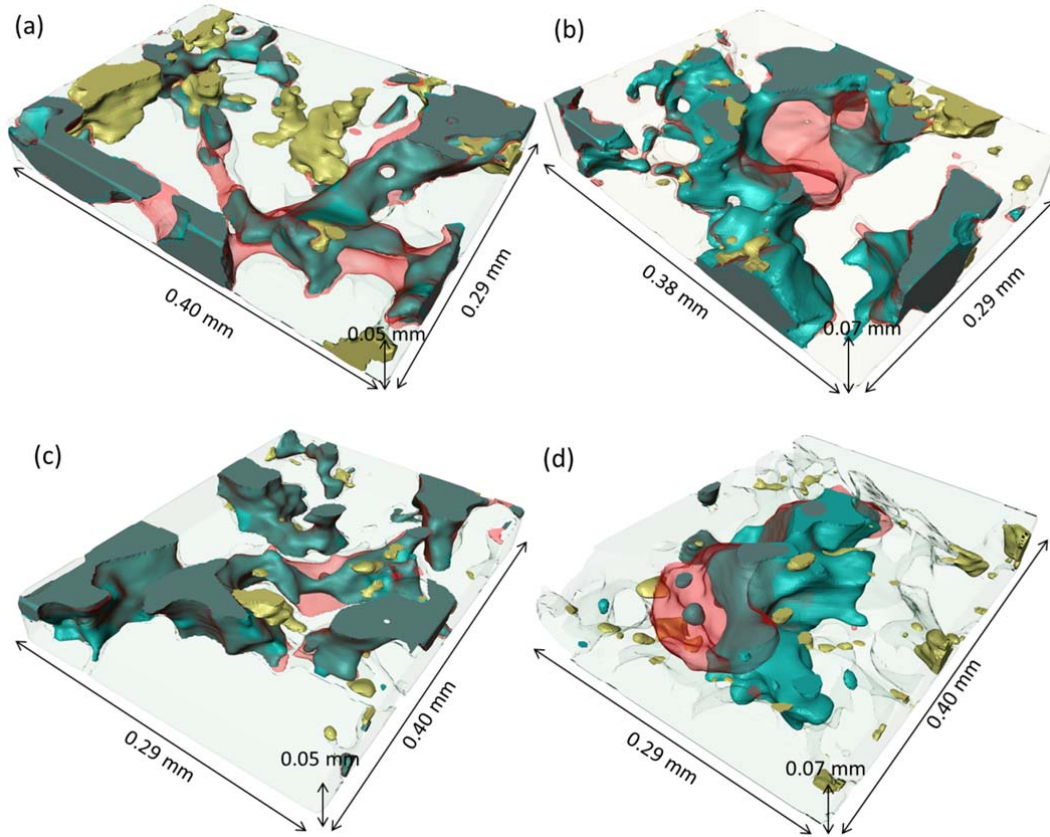


Figure 3.16 3D visualizations of SIH and SIL states in sub-volumes of mini-plugs (a–b) A, (c) B and (d) C. Residual oil after SIH and SIL is red and green, respectively, clays are yellow and grains are transparent.

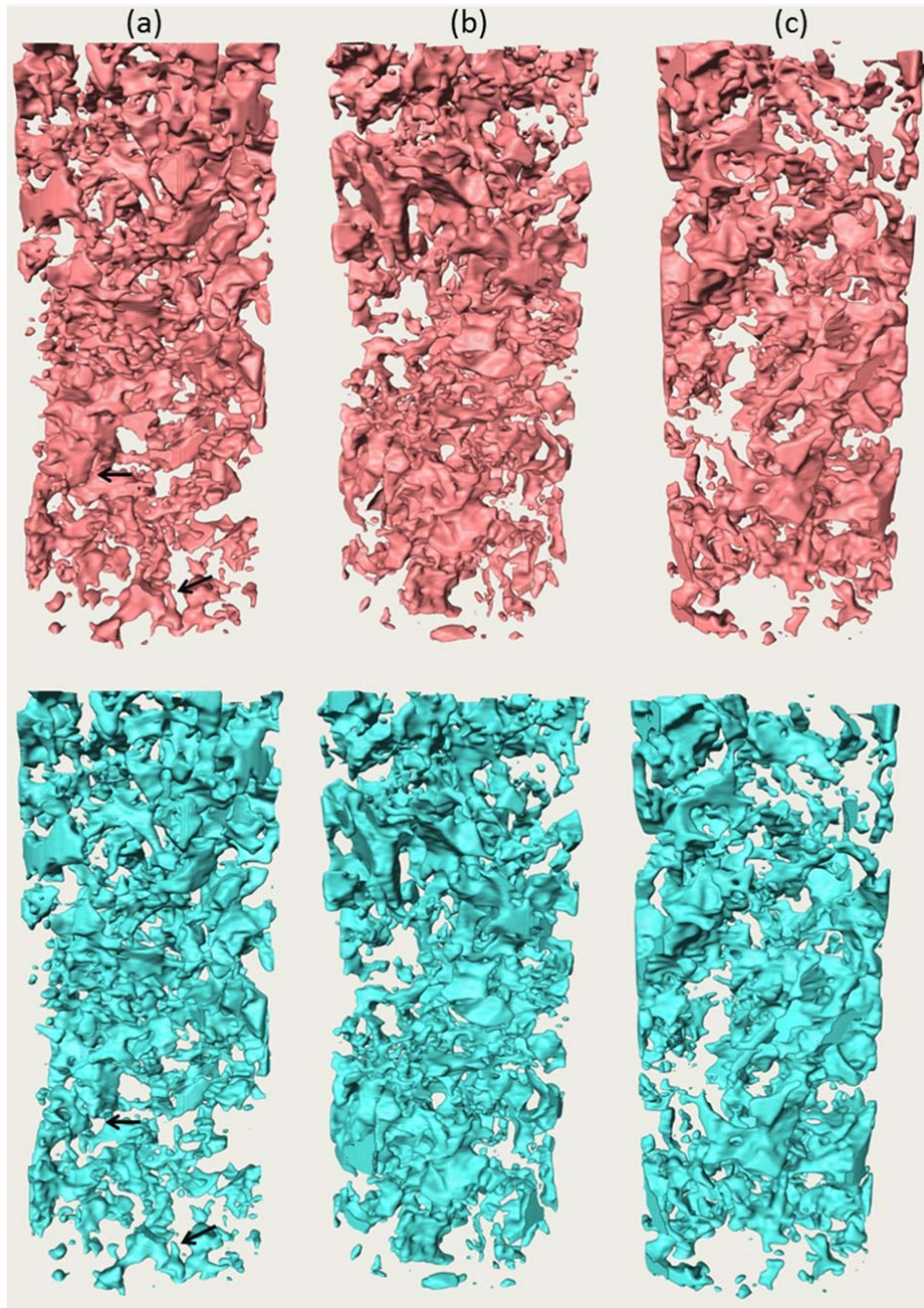


Figure 3.17 3D visualizations of cylindrical sub-regions ($1.01 \text{ mm} \times 0.45 \text{ mm}$) showing oil connectivity after SIH (top) and SIL (bottom) in mini-plugs (a) A, (b) B and (c) C. black arrows show disconnection in oil ganglia of sample A.

3.4 Conclusion

Spontaneous imbibition of high and low salinity brine into a clay-rich reservoir sandstone was studied by micro-CT imaging and analysis. Two crude oils of similar

viscosity, density and asphaltene content but with differing total acid number (TAN) were used in conjunction with three sister mini-plugs A, B and C. Mini-plug A with high TAN exhibited the greatest tertiary recovery (5.1% reduction in oil saturation) by spontaneous imbibition of low salinity brine. The additional recovery was mainly the result of brine advance from pre-existing menisci in throats and small pores to snap-off oil in throats and enter larger pore bodies. The high TAN oil was more amenable to release from grain surfaces than clay aggregates in the low salinity brine. The salinity-induced wettability shift was sufficient to displace oil from locations that were already more water-wet in the state after spontaneous imbibition of high salinity brine, but was insufficient to cause oil movement from more oil-wet locations. The low TAN oil exhibited much less tertiary recovery, irrespective of whether oil saturation after high salinity exposure was higher (mini-plug B) or lower (C) than that of A. This low TAN oil appeared to induce a more strongly oil-wet state after aging, which largely precluded recovery by brine meniscus advance, but which instead favored oil displacement by the alternative mechanism of water droplet creation and growth in larger oil-filled pores. This droplet formation, thought to be caused by osmosis, appeared to be a much less effective means of recovering additional oil than meniscus advance by wettability change.

4 Water Flooding of Reservoir Sandstones

4.1 Introduction

Secondary oil recovery from reservoirs is usually performed by water flooding using a readily available high-salinity brine, such as sea water. Researchers in the 1990's found that reduction of the injected brine salinity could improve oil recovery from reservoir sandstones in core plug water floods. Since then a large number of studies have been conducted to investigate the mechanism(s) underlying this low salinity effect. However, understanding still remains incomplete, and so prediction of EOR response by low salinity water flooding (LSW) is very uncertain (1-2).

Many groups have studied the low salinity effect and proposed various causes. In early work, the presence of clay, especially kaolinite, was recognized as a necessary condition for low salinity response in sandstones. Fines migration was proposed as a carrier for oil droplets (4) and also as a means to increase sweep efficiency (63). However, the low salinity effect was seen later in kaolinite-free sandstones (5,6), and also in the absence of observable fines movement; such movement is generally detrimental as it is likely to plug pore throats and consequently decrease permeability and injectivity of the rock system (30). The wettability state of a reservoir rock is one of the main controllers of multi-phase fluid flow and also plays a central role in LSW, as a shift in wettability toward a more water-wet state has been documented in many studies (27-32). Some researchers have addressed LSW mechanisms at the inter-molecular scale in terms of the crude oil/brine/rock repulsive and attractive electrostatic interactions that could give rise to this wettability shift. The electrostatics-driven mechanisms proposed include increase in brine pH (which has been frequently observed during LSW) (7), multicomponent-ion exchange (8), and double layer expansion (9). An osmotic stress mechanism was also put forward, in which the salinity gradient across two disconnected sides of an oil droplet can provide the driving force for oil displacement by water-swelling of the higher salinity (e.g. connate) side (14).

3D pore-scale visualization and image analysis of core flooding can give valuable insight and information regarding residual oil distribution, microscopic sweep efficiency, and oil-brine meniscus contact angles. To complement the results of the previous chapter, the same clay-rich reservoir sandstone as used there was further tested here for its high and low salinity brine flooding response. For this purpose, the mini-plug

was mounted in a simple holder, and was first restored to a realistic mixed-wet state by primary drainage and aging, after which recovery by injection of high salinity brine followed by low salinity water was performed. At the end of each of these two injection steps, and subsequent exchange of flood brine for contrast brine, the mini-plug was micro-CT scanned. Further high resolution 3D tomograms of the mini-plug were acquired in its dry state and after saturation with contrast brine. This sequence of tomograms were spatially registered, processed and analyzed for qualitative and quantitative studies of the amount and distribution of residual oil and its changes. A very strong capillary end effect limited the study, necessitating that different regions along or across the mini-plug were studied separately. Pore-scale statistics of oil occupancy and blob connectivity confirmed the presence of a small shift toward more water wetting during LSW. Image analysis of the interfacial areas between fluids, grains and clays provided direct evidence of oil detachment from clays during LSW.

4.2 Materials and Methods

4.2.1 Materials

The rock samples in this study were taken from the same plug of homogeneous, friable, North Sea reservoir sandstone, rich in kaolinite and muscovite, as used in Chapter 3. The crude oil used is the same as the low acid-number oil in Chapter 3, with a density of 0.8486 g cm^{-3} , viscosity of 11.6 mPa.s at $20 \text{ }^{\circ}\text{C}$, asphaltene content of $1.3\text{wt}\%$, and acid and base numbers of <0.1 and 0.91 mg KOH/g , respectively. Prior to the experiments, the oil was pre-conditioned above water in a sealed vessel at $94 \text{ }^{\circ}\text{C}$ for about two weeks, after which its water content was $0.22 \text{ wt}\%$, measured by Karl Fischer titration. The formation brine (FW), high salinity brine (HS, namely synthetic seawater) and low salinity brine (LS, namely 500 ppm NaCl) and their corresponding contrast brines (containing 0.4 M NaI) were of the same compositions as in Chapter 3, although their measured pH values varied slightly, as listed in Table 4.1.

The same procedure as described in Section 3.2.1 was used for cleaning the plug and subsequently coring the long mini-plugs with 5 mm or 8 mm diameter. Each wax-supported mini-plug was then encased in a holder/flow cell, comprising an aluminum tube with the annular gap between mini-plug and tube inner wall filled and sealed with Torr Seal or Epofix epoxy. The ends were cut to expose raw rock faces, so that the

length of the 5 mm or 8 mm diameter mini-plug segment was 18 mm and 25-38 mm, respectively. Threaded, stainless steel end-caps were then similarly glued to both cut ends to provide connections to the syringe pump and the micro-CT post (Figure 4.1). The wax was removed by soaking (at 75 °C) and flow through (at 22 °C) of approximately 50 ml of heptane, followed by water-vapor plasma cleaning to remove any thin wax remnants and restore a water-wet state.

Table 4.1 Composition of brines used in the experiments.

Salt	FW (g/l)	HS (g/l)	HS contrast (g/l)	LS (g/l)	LS contrast (g/l)
NaCl	58.44	23.73	0.35	0.5	
CaCl ₂ ·2H ₂ O	5.88	1.50	1.50		
MgCl ₂ ·6H ₂ O	2.03	10.70	10.70		
KCl	1.49	0.76	0.76		
Na ₂ SO ₄		3.98	3.98		
NaHCO ₃		0.67	0.67		
SrCl ₂ ·6H ₂ O	0.53	0.02	0.02		
BaCl ₂ ·2H ₂ O	0.98				
NaI			59.96		59.96
pH	6.6	7.7	7.8	6.4	7.4

4.2.2 Experimental Methods

Each mini-plug in its holder mounted on the post in Figure 4.1(c) was scanned using HeliScan micro-CT in its clean-and-dry state. If we assume that the detector size is 2500×2500 and the size of Aluminum tube is 0.5 mm then we would lose 0.4 um/voxel resolution in each scanning. It was then de-mounted from the post and evacuated for 45 min, prior to vacuum infiltration of the formation brine FW for 5 hours, followed by isostatic pressurization under this same brine to 20 MPa over 16 h. As the crude oil was of low viscosity, primary drainage on the syringe pump (at 22 °C) was performed by first injecting a more viscous mineral oil (Blandol with density of 0.84 g/cm³ at 20 °C and viscosity of 16 mm²/s at 40 °C), passing through 3.0 ml at a flow rate of 5 ml/h in each direction to create a uniformly low brine-saturation profile along the mini-plug. This was followed by the intermediate step of injection of decalin (3.0 ml at 5 ml/h in one direction) to mix with and displace the mineral oil (which would otherwise have led to precipitation of asphaltenes from the crude oil). Finally, the crude oil was injected (2.0 ml at 2 ml/h in the same direction) to completely replace the decalin. Owing to the

very small pore volume (of around 0.08 ml for the 5 mm diameter mini-plugs) and the comparatively large dead volume in the end caps, it was generally not possible to accurately measure the drained brine saturation.

After drainage, the mini-plug assembly was aged in the crude oil in a sealed glass vessel at 94 °C for 14 days. The water flooding sequence (with all injections performed at 82° C using brines pre-heated to this temperature) was subsequently started by injection of 0.68 ml of high salinity (HS) brine at a flow rate of 0.35 ml/h. Again due to the tiny volumes involved, monitoring and measurement of oil production was not feasible. The high salinity flooding step was followed by injection of HS contrast brine (0.42 ml at 0.175 ml/h), to thus exchange the NaCl in the HS brine for NaI (Table 4.1), in order to heighten oil/brine X-ray contrast. The flow rate of this injection was half that of HS injection (and the volume was less) to minimize any extraneous oil production during this contrast exchange step. The mini-plug assembly was then disconnected from the syringe pump and mounted using the threaded post (with bleed hole) on the micro-CT sample stage for helical scanning in this HS flooded (and contrasted) state.

After scanning, the post was unscrewed and the mini-plug assembly was reconnected to the syringe pump for injection of 0.42 ml of HS brine at 0.175 ml/h to exchange out the HS contrast brine. This was followed by injection of low salinity (LS) brine (0.68 ml at 0.35 ml/h, the same as for HS) and then LS contrast brine (0.42 ml at 0.175 ml/h, the same as for HS contrast) to re-introduce the 0.4 M NaI required for imaging. The mini-plug assembly was then remounted using its post and micro-CT scanned in this LS flooded (and contrasted) state. Afterwards, the mini-plug in its holder was cleaned by flow through of decalin and connate brine, followed by methanol, and then vacuum dried and remounted on its post for micro-CT scanning of this dry state post-flooding. The final step was saturation, using HS contrast brine, of the mini-plug in its holder, using the same procedure as for the initial formation brine saturation, followed once more by mounting and scanning.

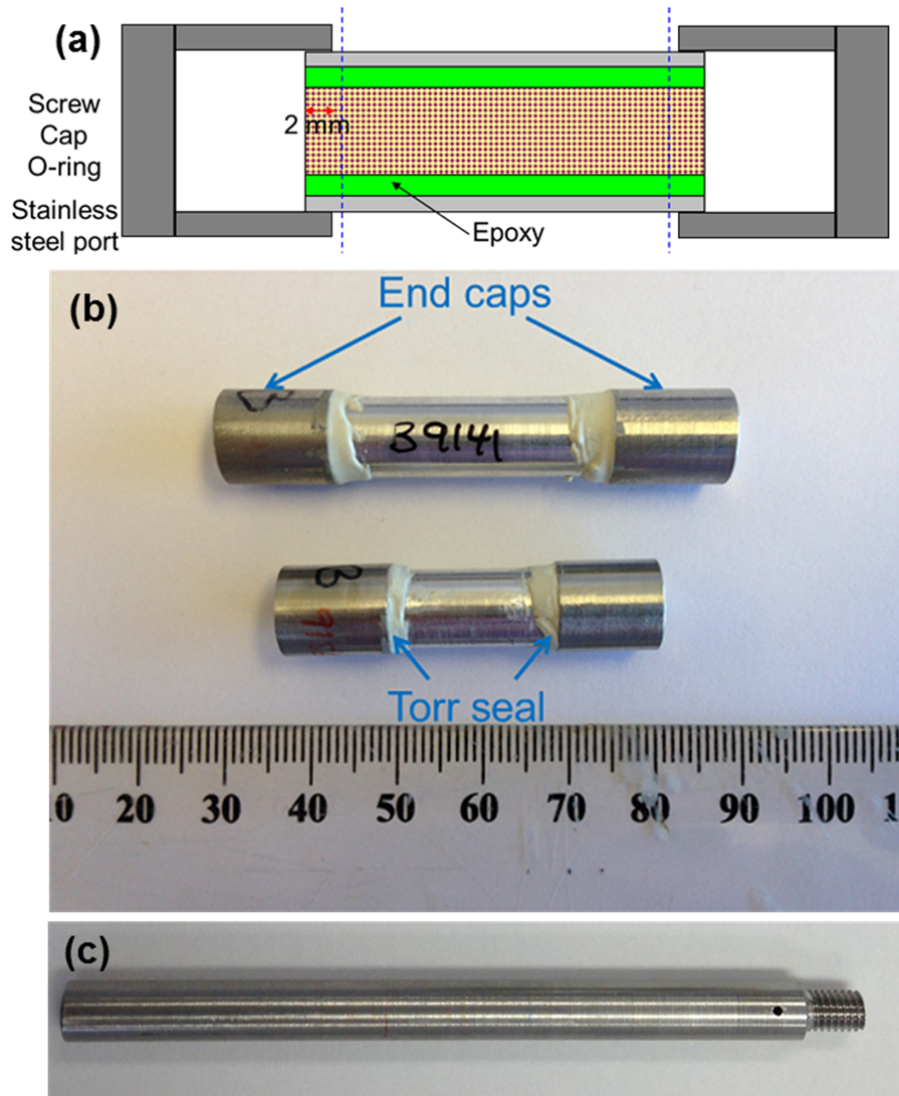


Figure 4.1 Mini-plug holder/flow cell (a) schematic, (b) photograph of the 8 mm diameter mini-plug holder, and (c) mounting post for micro-CT imaging.

4.2.3 Image Processing and Analysis

The study commenced with testing of mini-plugs of 5 and 8 mm diameter to determine the best choice of size in terms of the compromise between field of view and resolution. Each was micro-CT scanned (in its holder) at the ANU micro-CT facility (36), using a helical trajectory. The tomograms were collected in the sequence of states outlined in Section 4.2.2, at tomogram voxel size of $3.5\ \mu\text{m}$ and $5.3\ \mu\text{m}$, respectively. In particular, each such scan was acquired over 22 h using X-ray source settings of 80 kV and 110 μA . For the 5 mm diameter mini-plug, this yielded a tomogram of $1760 \times 1760 \times 3960$ voxel³ covering the middle section of 14 mm height across the full diameter. Figure 4.2

shows a comparison of tomogram slice subarea crops from these two mini-plugs in their dry state and at residual oil after HS flooding. Further, Figure 4.3 shows a central longitudinal slice of an 8 mm and 5 mm diameter mini-plug (in its holder) in its dry state.

In Figure 4.2(c), resolved pores (dark), grains (bright), and clays (intermediate gray) are clearly distinguished in the dry state. In Figure 4.2(d), the oil-filled region at left is clearly distinguished from the contrast-brine-filled region at right in this HS flooded state, and the curved meniscus separating them is readily resolved. However, in the analogs of these for the 8 mm diameter mini-plug in Figure 4.2(a-b), the features are much less clearly resolved and would be challenging to segment, even with the aid of tomogram registration and differencing. For this reason, only the results for the 5 mm diameter mini-plugs are presented and analyzed in the following sub-sections.

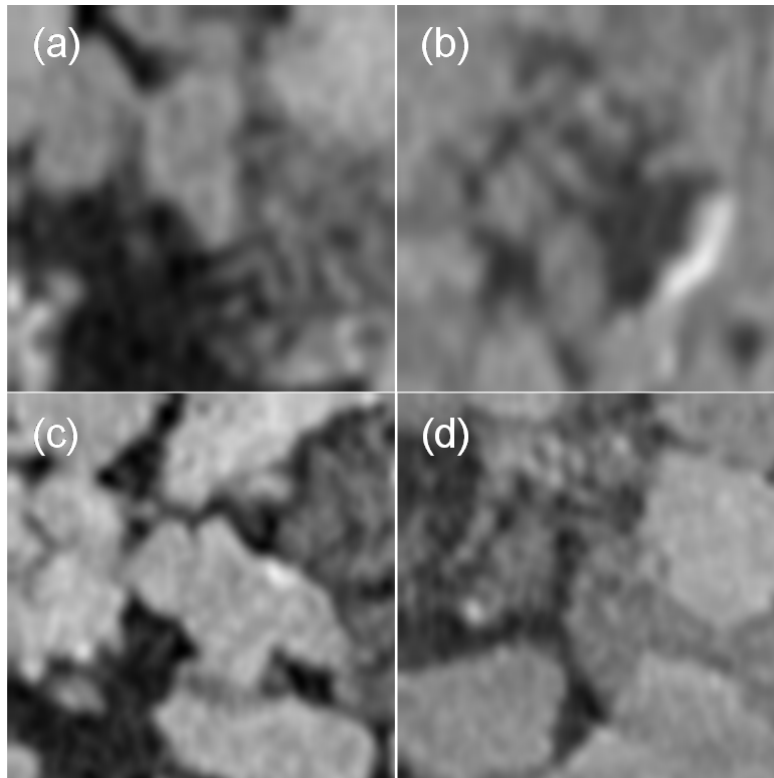


Figure 4.2 Comparison of different, non-registered subareas ($0.2 \text{ mm} \times 0.2 \text{ mm}$) from a tomogram slice of an 8 mm diameter mini-plug in its (a) dry state and (b) after HS flooding, and for a 5 mm diameter mini-plug in its (c) dry state and (d) after HS flooding.

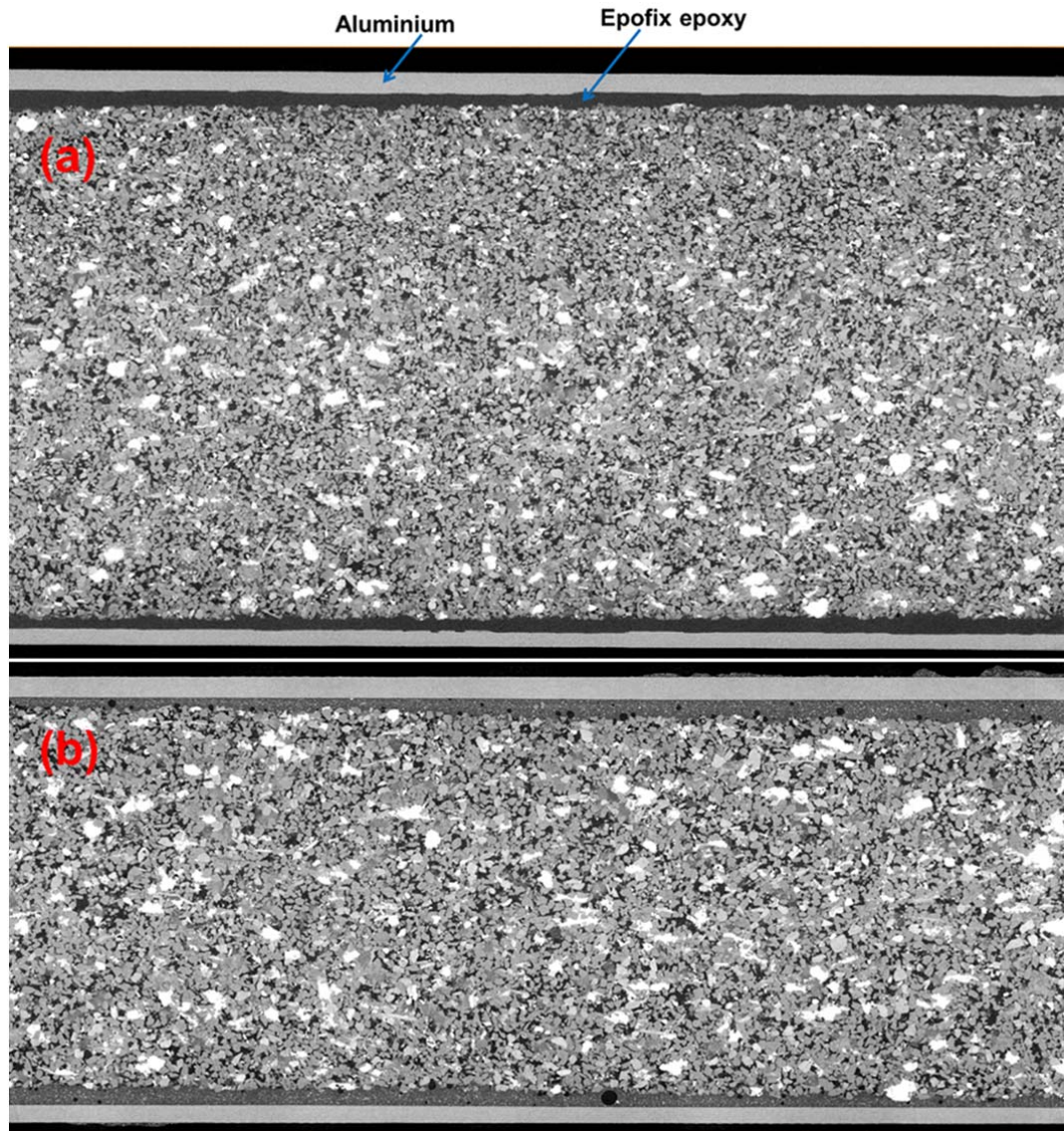


Figure 4.3 Central longitudinal slice (rotated sideways) of dry-state tomograms of the reservoir sandstone for an (a) 8 mm diameter mini-plug at 5.3 μm voxel size, and (b) 5 mm diameter mini-plug at 3.5 μm voxel size.

The mini-plug tomogram sequences were processed and analyzed using the Mango software suite (42-44), starting with spatial registration of the images of the HS flooded, LS flooded and brine-saturated states to the corresponding dry-state image. Each tomogram was cylindrically masked to exclude the surrounding air, aluminum plug holder, epoxy sheath and damaged rock near the mini-plug periphery. Segmentation of the phases of interest was then performed as outlined in the following sub-section.

4.3 Results and Discussion

4.3.1 Segmentation Procedure

Three-phase segmentation was applied to separate the dry-state tomogram of the mini-plug into resolved pore (termed macro-pore), resolved grain, and sub-resolution features (referred to here as the clay phase). The difference between the brine-saturated and dry-state tomograms was then used to quantify the sub-resolution microporosity at each voxel within the clay phase. The total porosity is thus the sum of the macro-pores from the dry-state segmentation and microporosity from the difference. In the HS and LS flooded-state tomograms, pore space was segmented into the four phases of macro-oil and macro-brine (i.e. oil and brine in resolved pores) and micro-oil and micro-brine (i.e. oil and brine in microporosity within the clay phase), in a similar manner as in Chapter 2. In particular, macro-oil was directly segmented as the darkest phase in the flooded-state tomograms, from which macro-brine was obtained as the difference between segmented macro-pore and macro-oil. Figure 4.4 shows a registered cross-sectional slice of the tomogram of a 5 mm diameter mini-plug of the reservoir sandstone in its dry and flooded states and after the above-mentioned segmentations.

Micro-oil and micro-brine after flooding were segmented using the difference tomogram of the brine-saturated state minus the (HS or LS) flooded state, according to the protocol in Chapter 2. Specifically, voxels within the clay phase that are darker or lighter than a chosen threshold in this difference tomogram were identified as micro-brine or micro-oil, respectively, as input to segmentation by a converging active contours algorithm. Figure 4.5 displays another registered cross-sectional slice of the tomogram of this 5 mm diameter mini-plug in its two flooded states and after their full segmentations, now including micro-oil and micro-brine. The corresponding zoomed-in images of a subarea from this same slice are shown in Figure 4.6 to reveal the finer details. Also, the x-ray intensity difference between oil-filled and brine-filled clay aggregates which have been used to segment the micro-oil and micro-brine is shown in Figure 4.6(e). Owing to the relatively low concentration of NaI in the contrast brine (maintained at this low level to minimize perturbation of the flooded states during the subsequent exchange step), the intensities of these two sub-phases within the clay phase were somewhat difficult to distinguish above the noise level.

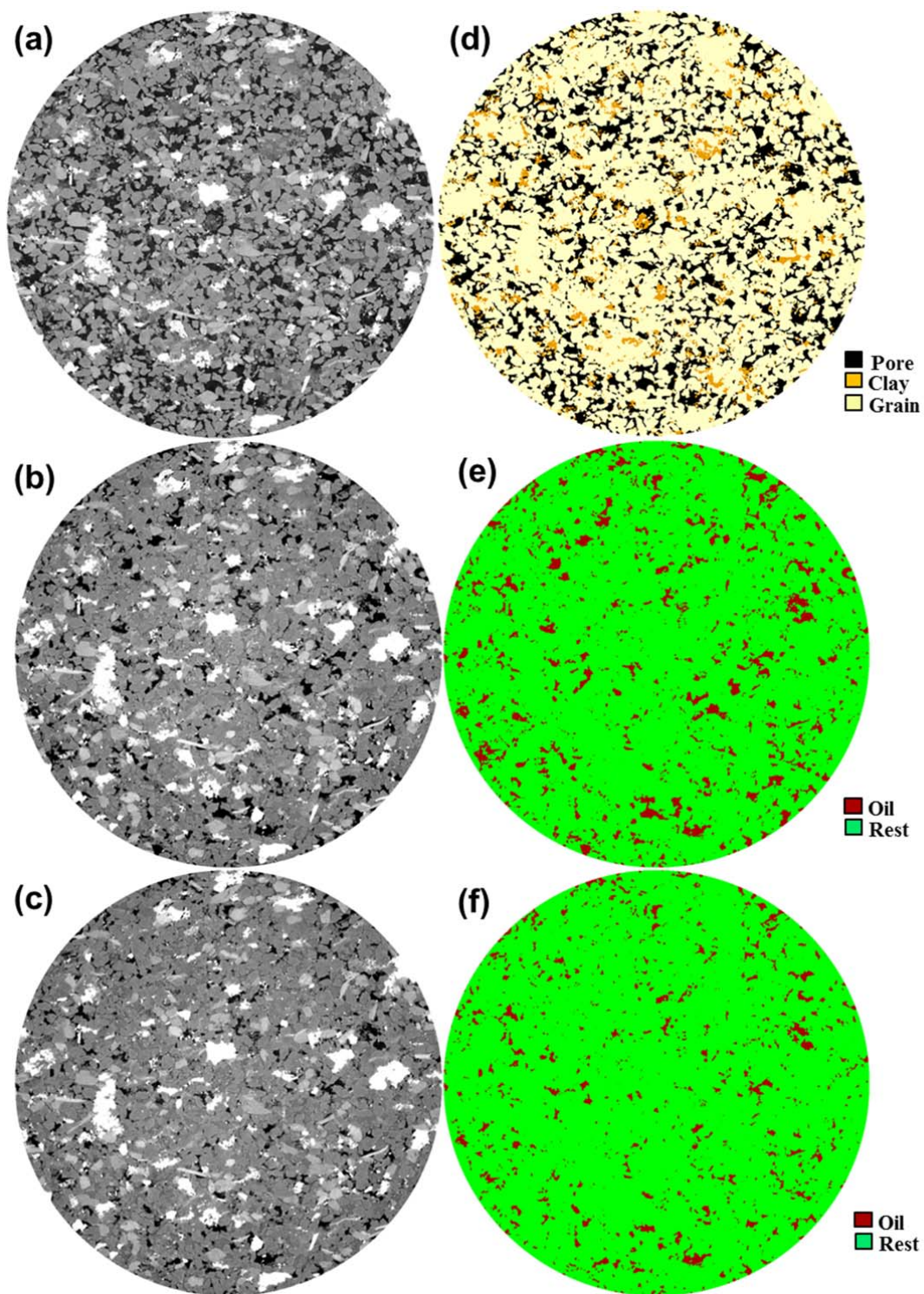


Figure 4.4 Tomogram cross-sectional slice of 5 mm diameter mini-plug of reservoir sandstone, masked to 4.0 mm $\times$ 4.0 mm, registered between the states: (a) dry, (b) HS flooded and (c) LS flooded, and after segmentation of (d) macro-pore, clay and macro-grain from the dry state, and macro-oil remaining after (e) HS flooding and (f) LS flooding.

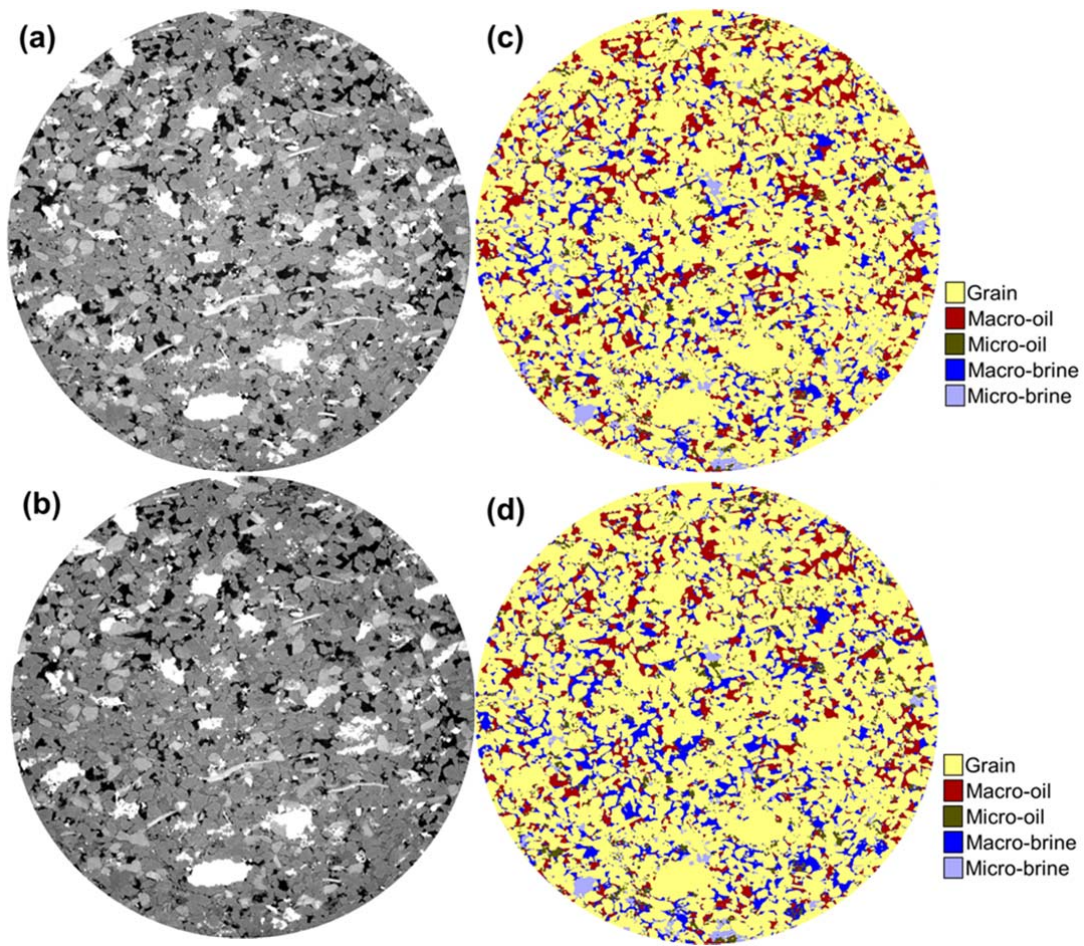


Figure 4.5 Tomogram cross-sectional slice of 5 mm diameter mini-plug of reservoir sandstone, masked to $4.0 \text{ mm} \times 4.0 \text{ mm}$, registered between the states: (a) HS flooded and (b) LS flooded, and after segmentation into grain, macro- and micro-fluids (oil and brine) for (c) HS flooded and (d) LS flooded.

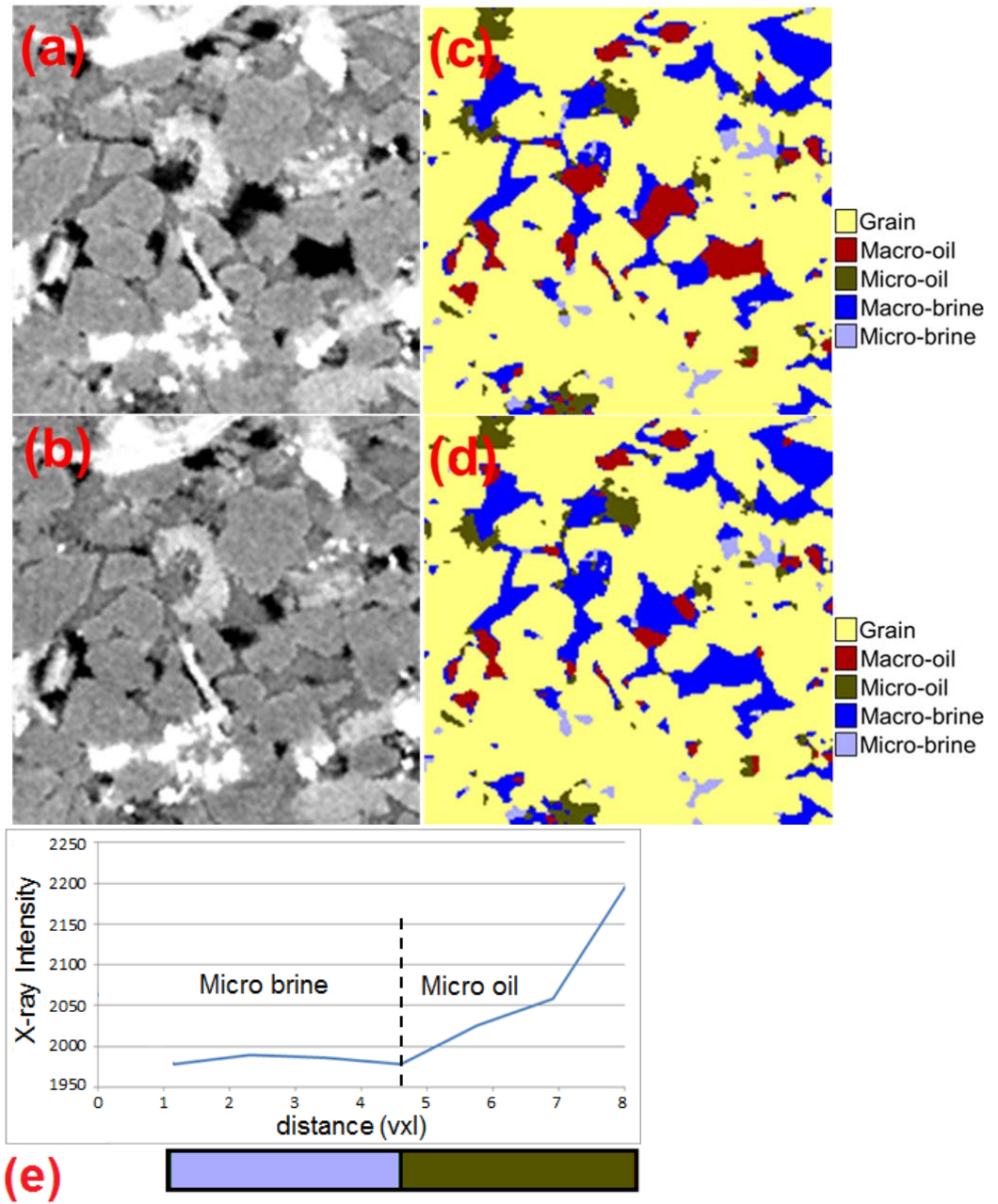


Figure 4.6 Subarea ($0.62 \text{ mm} \times 0.62 \text{ mm}$) of the tomogram cross-sectional slice in Figure 4.5 in the two flooded states and after their segmentations in (a)-(d) shown there, (e) X-ray intensity difference between micro-oil and micro-brine.

The following subsections present further observations and analysis of the tomograms of a 5 mm diameter mini-plug of the reservoir sandstone, and in particular of the distribution of residual oil over the mini-plug after HS and LS flooding. Characteristic sub-regions of the mini-plug are identified via the residual oil profiles, within each of which the segmented volume fractions are then presented, followed by further pore-

scale analysis of oil saturation, connectivity and interfacial areas, and their salinity-induced changes.

4.3.2 Observations from the Flooded-State Tomograms

Figure 4.7(a) displays a central longitudinal slice of the tomogram of a 5 mm diameter mini-plug of the reservoir sandstone in its dry state. Within the dry-state image, the identification of pore and mineral features based on their X-ray attenuation grayscales was provided in Chapter 3.3.2. Figure 4.7(b) shows this same registered slice of the mini-plug after saturation with the HS contrast brine. Macro-pores and pore-filling kaolinite aggregates are thus brightened to a level just below that of quartz and plagioclase (owing to the 0.4 M NaI dopant concentration of the contrast brine in Table 4.1). As mentioned above and in Chapter 2, the tomogram difference of the brine-saturated minus dry states is used to subtract off the contributions from all solid minerals in order to quantify the microporosity within the clay aggregates.

Figure 4.8(a-b) show this same registered slice of the mini-plug after HS and LS flooding, respectively. The darkest phase in these states is residual macro-oil, while the remainder of resolved pore space is filled with contrast brine, as in the brine-saturated state. Clay aggregates occupied by oil and brine are of similar local grayscale to that in their dry and brine-saturated states, respectively. Recovery by HS flooding was close to complete in the inlet half at bottom in Figure 4.8(a), where residual oil generally comprises disconnected small blobs contacting grains. However, recovery was poor in the outlet half at top in Figure 4.8(a), where oil remains as pore-filling and pore-connecting. This is presumably a capillary end effect, expected for slow water flooding (capillary number of 7×10^{-8}) of a mixed-wet or intermediate-wet state (2). The effect is extended further upstream by the mini-plug's small diameter and close proximity of its epoxy-sheathed (i.e. oil-wet) walls, despite its large length/diameter ratio of almost 4. The LS flood in Figure 4.8(b) had little overall influence on the already low oil saturation in the well-swept inlet half, but displaced the oil bank at the middle of the mini-plug to partially drive the end effect closer to the outlet, where recovery remained poor.

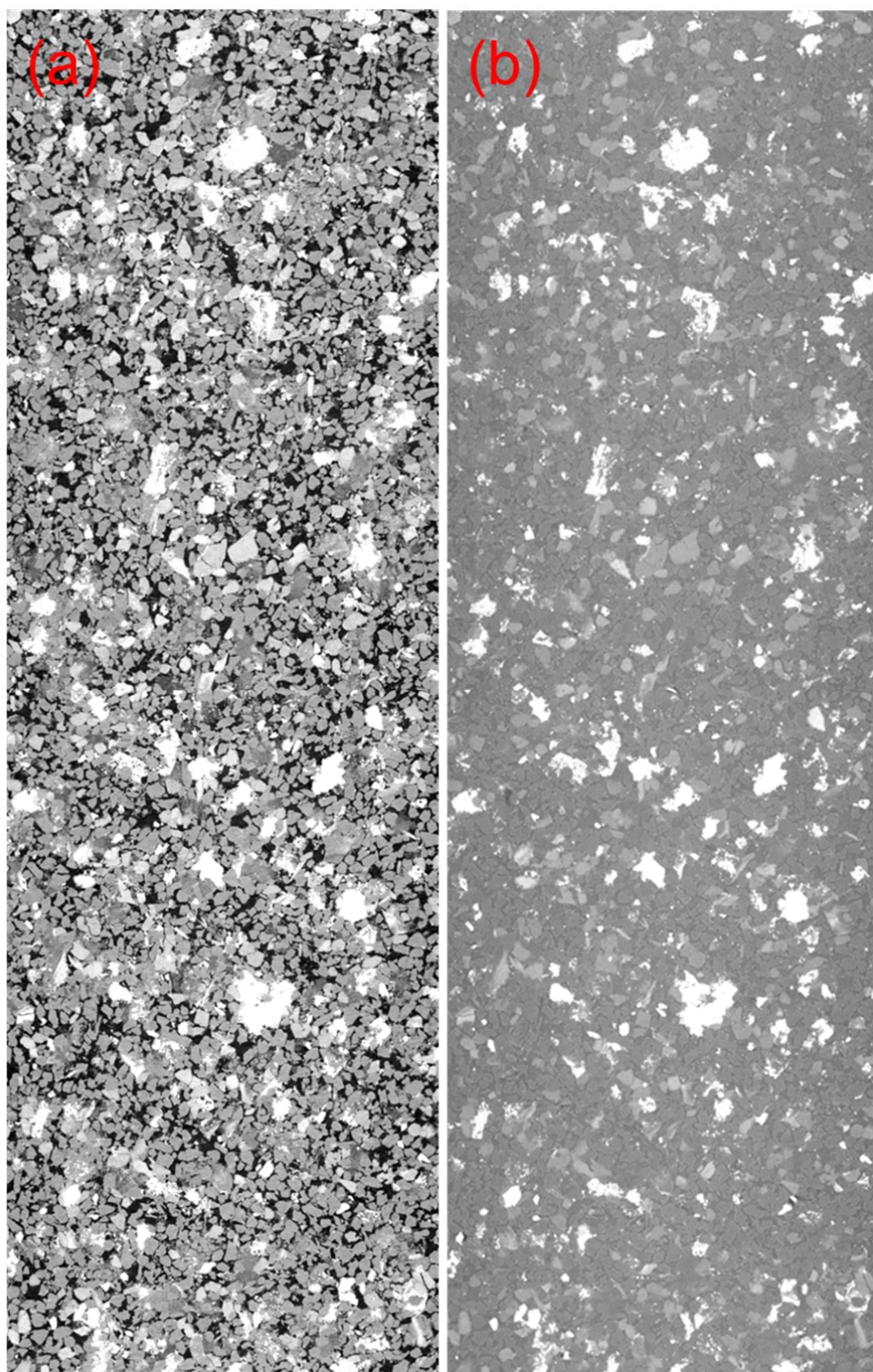


Figure 4.7 Tomogram longitudinal central slice of 5 mm diameter mini-plug of reservoir sandstone, masked to 12.5 mm $\times$ 4.0 mm, registered between the (a) dry state and (b) brine-saturated state.

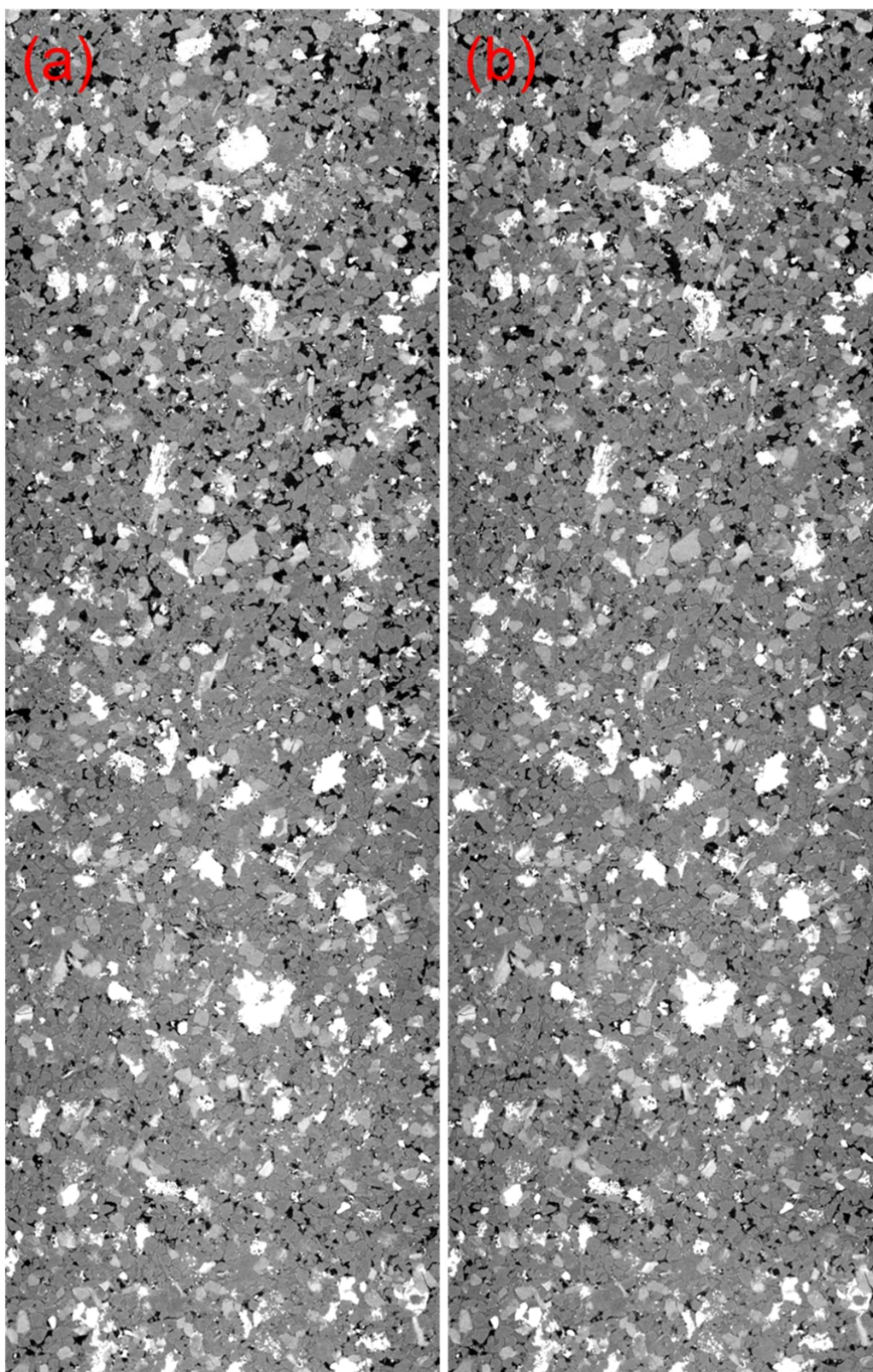


Figure 4.8 Tomogram longitudinal central slice (same as in Figure 4.7) of 5 mm diameter mini-plug of reservoir sandstone, masked to $12.5 \text{ mm} \times 4.0 \text{ mm}$, registered between the (a) HS and (b) LS flooded states. Bottom and top of the tomogram are nearest the inlet and outlet, respectively.

Since inlet and middle regions of mini-plug show extremes of response to HS and LS flooding, these two sub-regions were analyzed separately so as not to mix these effects, as described in Section 4.3.3. Figures 4.9 and 4.10 show a zoom-in of a subarea of the same central longitudinal slice as in Figures 4.7-4.8 from within the inlet and middle sub-regions, respectively, in the dry state and after HS and LS flooding (rotated so that the flood direction is right to left). Figures 4.11 and 4.12 provide an even greater zoom-in of a subarea within the inlet and middle sub-regions, respectively, from other longitudinal slices of these registered tomograms, to illustrate the segmented sub-categories of oil and brine. The same definitions and color scheme of occupancy of resolved pores as in Chapter 2 are used. Dark blue arrows (BB) indicate pores that remain brine-filled after both HS and LS floods, and similarly for the black arrows (OO) pointing to immobile oil. The cyan arrows (OB) show pores in which oil after HS flooding is replaced by brine after LS flooding, while red arrows (BO) indicate the reverse, i.e. where brine in pores after HS flooding is displaced by re-invading oil after LS flooding. In addition, purple and olive arrows point to brine- and oil-occupied microporosity within clay aggregates.

Many small macro-pores and micro-pores are brine filled. As no imaging of the aged state was performed, it is not known whether this brine was present there throughout restoration (likely the case within micro-pores) or entered during HS flooding. However, compared to the outcrop Berea samples in Chapter 2, the reservoir sandstone exhibits more residual oil in small pores and throats between grains, and also some within clay aggregates, especially within coarser microporosity bordering oil-occupied macro-pores. In line with this, residual oil in larger pores is much less prevalent and appears to have larger contact angles than in the Berea, and to be more intimately associated with pore walls, also leaving oil remnants there after displacement from the pore body. The reservoir sandstone is thus less water-wet than the Berea samples.

The zoom-in within the inlet sub-region in Figure 4.11 shows that while residual oil saturation is already low there after HS flooding, and changes little during LS flooding, significant pore-scale redistribution of oil occurs between these two steps. Local instances of brine displacing oil (OB) and of oil displacing brine (BO) are both frequent, implying that the residual after HS retains some connectivity through films and tight corner menisci. While salinity-induced changes in occupancy of micro-pores within clay aggregates are difficult to distinguish, it can be concluded that no substantial internal transformation appears to take place there during LS flooding.

The zoom-in within the middle sub-region in Figure 4.12 shows much greater oil displacement on LS flooding, which is more suggestive of secondary rather than tertiary recovery. The displacement is almost purely OB, without much counteracting BO, and mainly seems to take place via connected oil pathways without snap-off, and with oil remaining in corners and throats after LS flooding. This again points to a much less water-wet state than for Berea. The movement of the oil bank through this middle sub-region may have been caused by the extra pore volumes of injected LS brine (irrespective of its salinity) or by reduction in capillary end effect due to the slight lowering of oil-brine interfacial tension at low salinity (2).

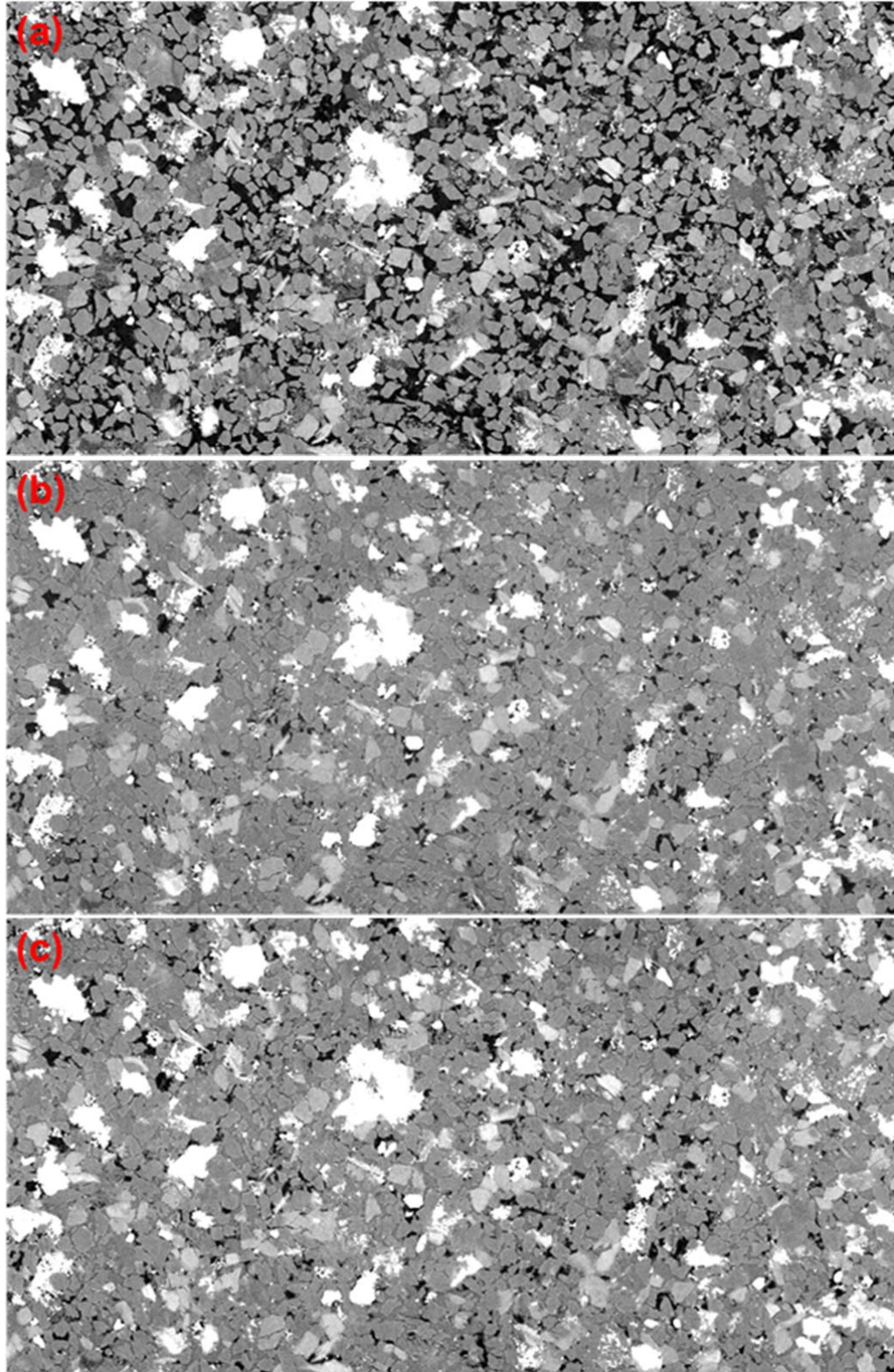


Figure 4.9 Subarea ($3.0 \text{ mm} \times 5.8 \text{ mm}$) of the tomogram longitudinal slice in Figures 4.7-4.8 (rotated 90° counter-clockwise), showing the inlet sub-region of the 5 mm diameter mini-plug of reservoir sandstone, registered between the (a) dry state, and after (b) HS and (c) LS flooding.

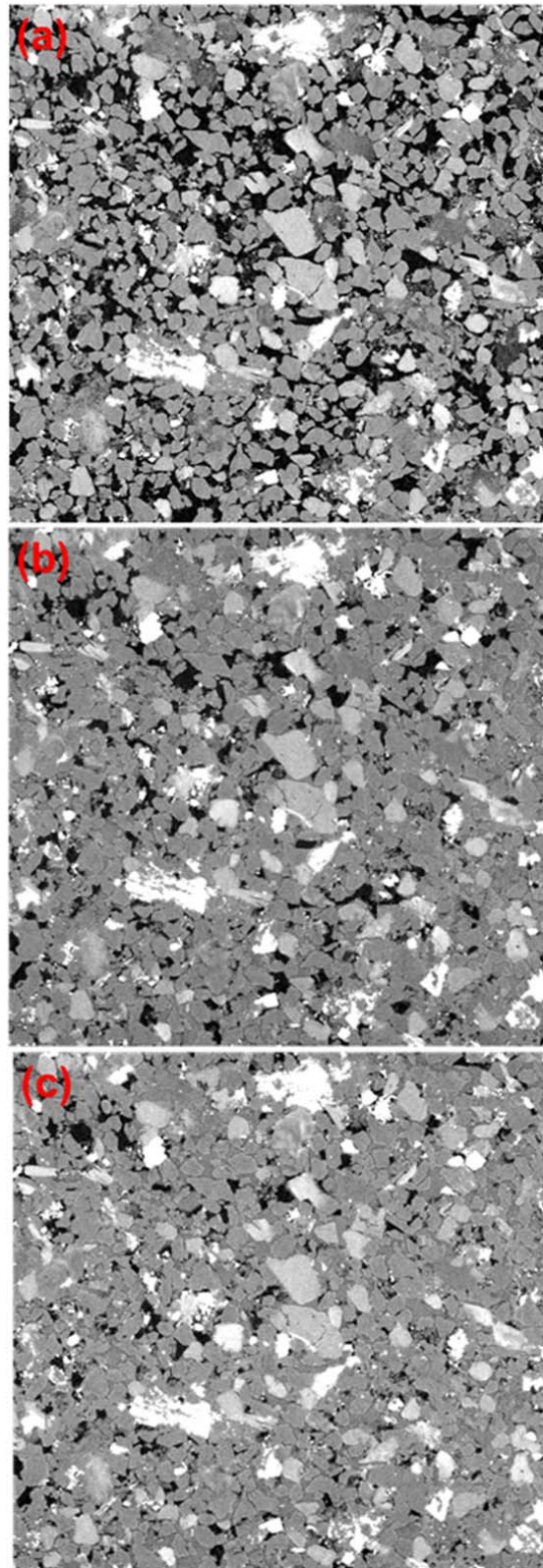


Figure 4.10 Subarea ($3.0 \text{ mm} \times 3.1 \text{ mm}$) of the tomogram longitudinal slice in Figures 4.7-4.8 (rotated 90o counter-clockwise), showing the middle sub-region of the 5 mm diameter mini-plug of reservoir sandstone, registered between the (a) dry state, and after (b) HS and (c) LS flooding.

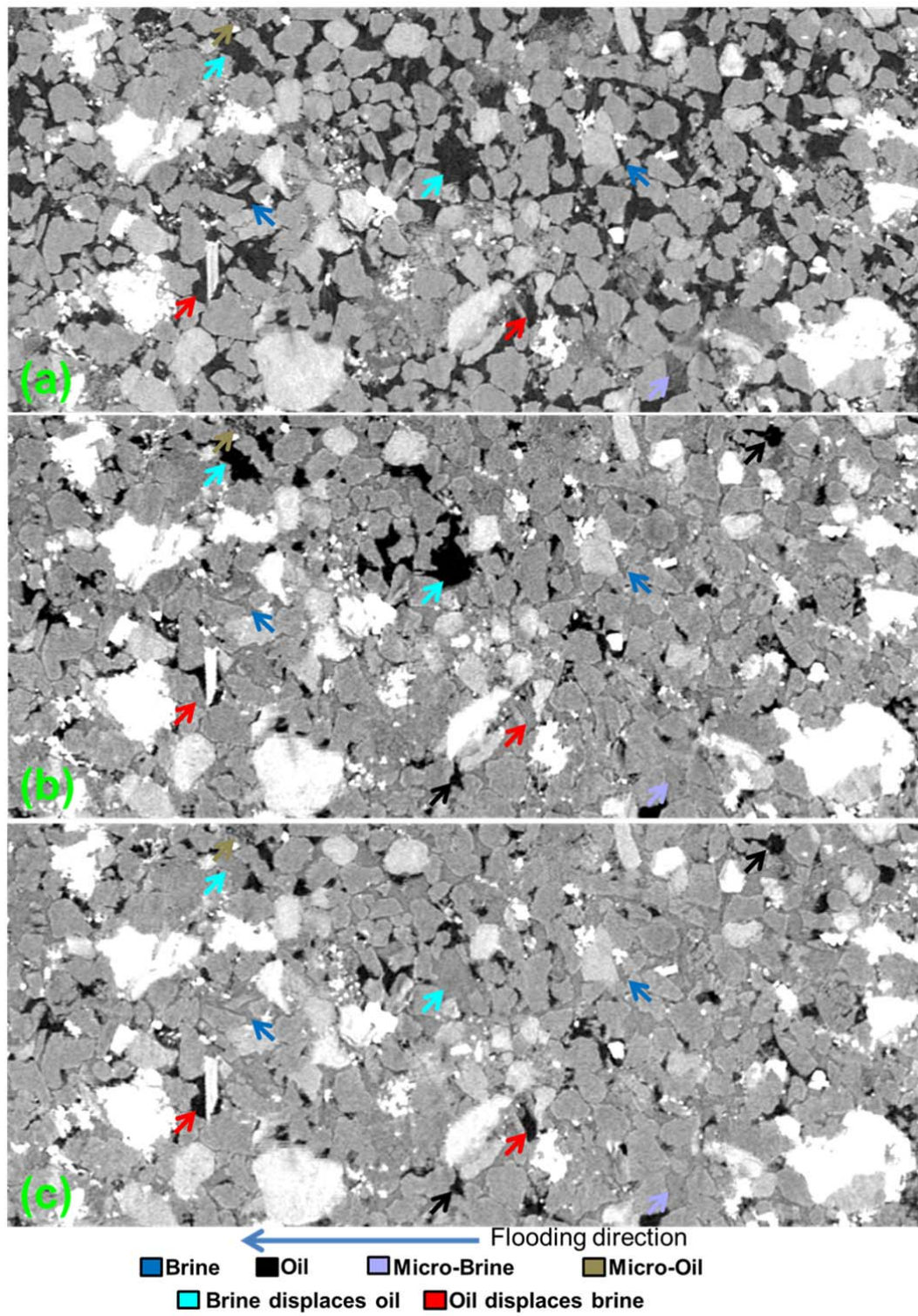


Figure 4.11 Subarea ($1.4 \text{ mm} \times 3.2 \text{ mm}$), within the inlet sub-region, of a tomogram longitudinal slice (rotated sideways) of the 5 mm diameter mini-plug of reservoir sandstone, registered between the (a) dry state, and after (b) HS and (c) LS flooding.

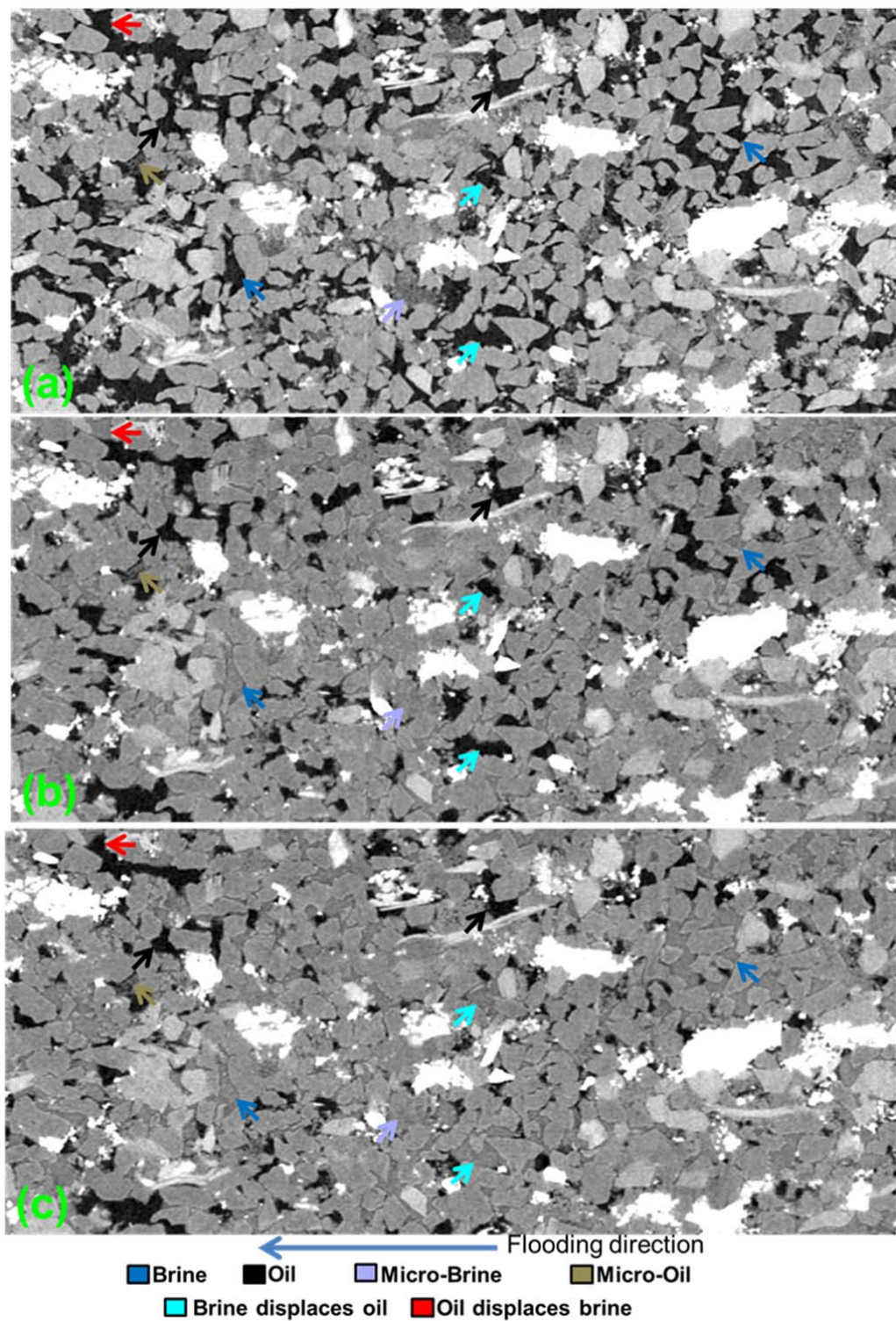


Figure 4.12 Subarea ($1.4 \text{ mm} \times 3.1 \text{ mm}$), within the middle sub-region, of a tomogram longitudinal slice (rotated sideways) of the 5 mm diameter mini-plug of reservoir sandstone, registered between the (a) dry state, and after (b) HS and (c) LS flooding.

4.3.3 Profiles of Residual Oil

The longitudinal profiles of resolved, segmented oil phase volume fraction within the 5 mm mini-plug of reservoir sandstone after HS and LS floods are plotted in Figure 4.13(a), along with that of the segmented macro-porosity. These slice averages were calculated within a cylindrical mask, referred to as the S mask, of radius 2.0 mm, to exclude the outer annulus of 0.5 mm thickness closest to the mini-plug periphery, containing damaged rock, intruding epoxy and a high saturation of oil associated with it. The corresponding radial profiles are given in Figure 4.13(b), averaged along the entire imaged height of the mini-plug.

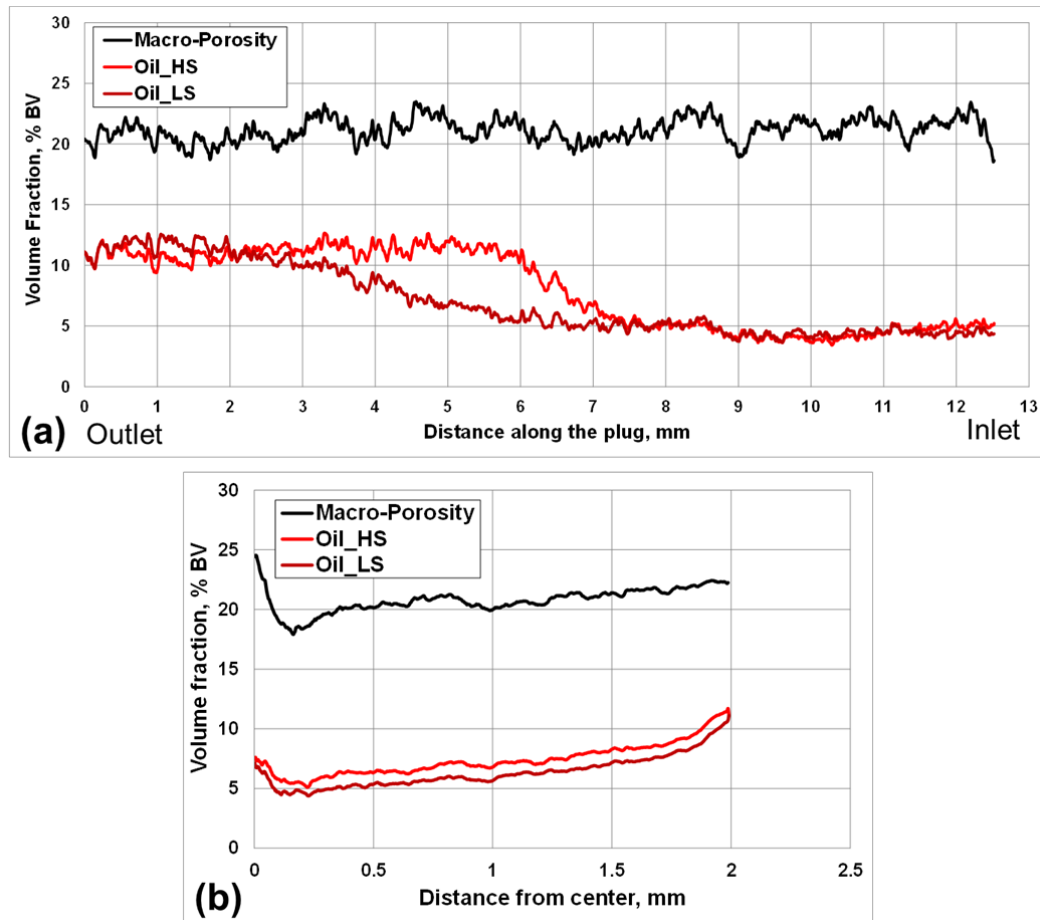


Figure 4.13 (a) Longitudinal and (b) radial profiles of bulk volume fraction of macro-porosity and macro-oil after HS and LS flooding for the 5 mm diameter mini-plug of the reservoir sandstone.

The longitudinal profiles of residual oil after HS and LS flooding are similarly low and flat towards the inlet end of the mini-plug, and both rise over the middle section to a similarly high plateau towards the outlet end, with the LS profile rising less steeply due to its displacement of the oil bank left by HS flooding. The macro-porosity profile is uniform along the whole imaged length, as expected from the homogeneity seen in Figure 4.7, further evidencing that the rise in the middle section is due to a capillary end effect or incomplete flooding. The radial profiles in Figure 4.13(b) show that the resolved oil volume fraction after both HS and LS increases relatively gently, and with roughly the same slope as that for macro-porosity, up to about 1.5 mm radial distance from the mini-plug axis. Beyond this, the oil volume fractions rise more sharply, due either to the affinity of oil for the epoxy sheath or to poor sweep near the periphery. To exclude this experimental artifact, a tighter cylindrical mask, referred to as the P mask, of radius 1.5 mm is applied to most of the subsequent analysis. Figure 4.14 compares the unmasked, S masked and P masked cross-section of the mini-plug tomogram after HS flooding.

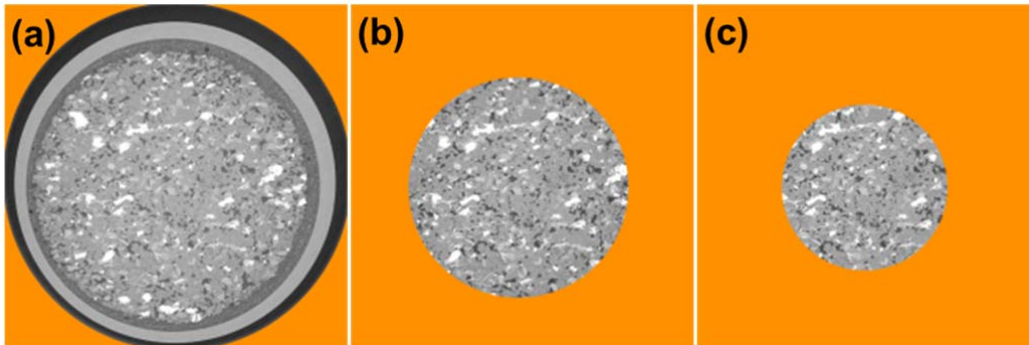


Figure 4.14 Tomogram cross-sectional slice of 5 mm diameter mini-plug of reservoir sandstone in its holder/flow cell after HS flooding, showing the views (a) unmasked, (b) after S masking beyond 4.0 mm diameter, and (c) after P masking beyond 3.0 mm diameter.

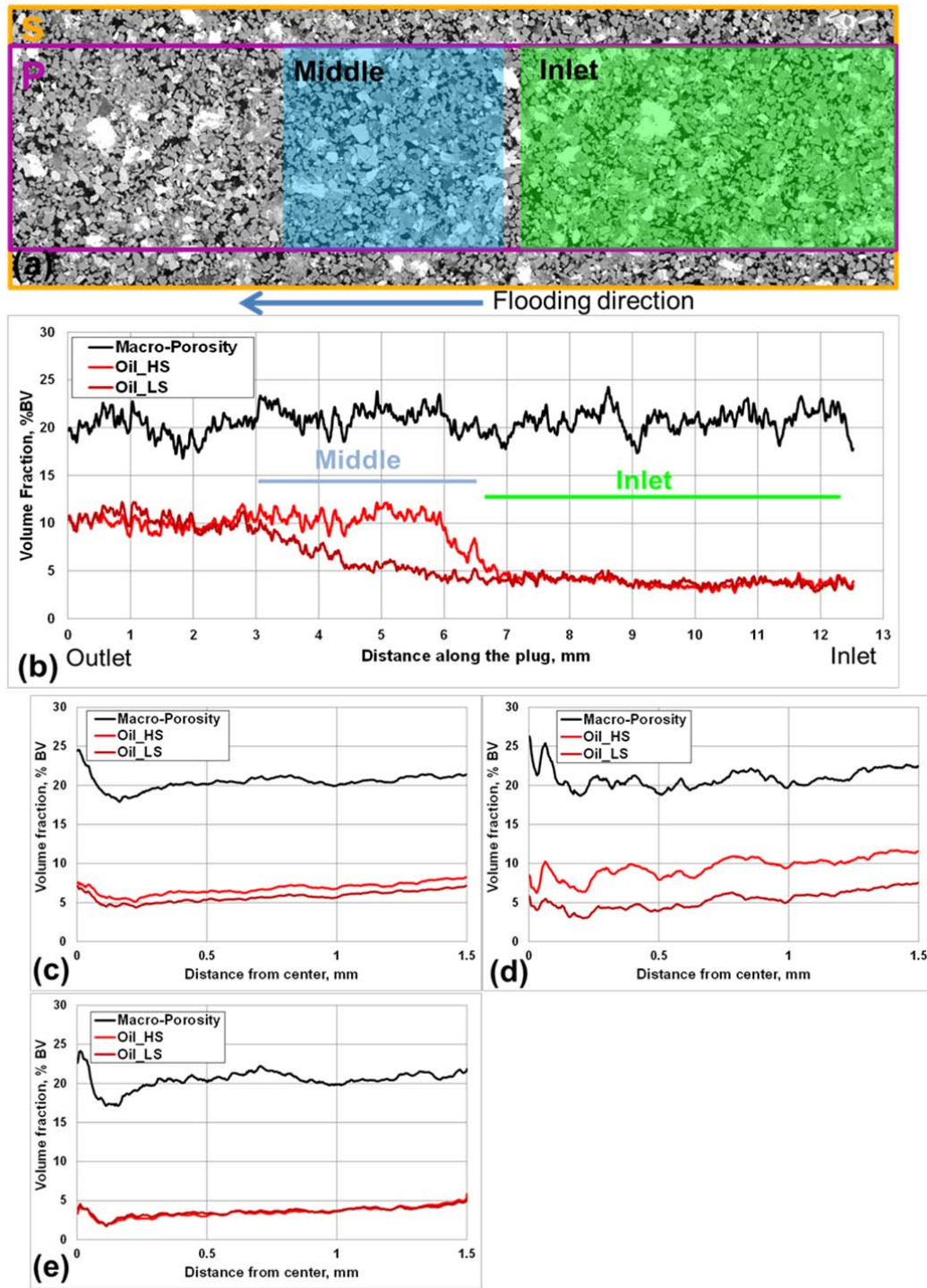


Figure 4.15 (a) Tomogram longitudinal central slice of 5 mm diameter mini-plug of reservoir sandstone, showing the S and P masks at 2.0 and 1.5 mm radius and the longitudinal sections defining the inlet and middle sub-regions, (b) longitudinal profiles of macro-oil and macro-porosity volume fractions within the P mask, and (c-e) radial profiles within the P mask, averaged over the (c) entire length, (d) middle sub- region and (e) inlet sub-region.

Based on the profiles in Figure 4.13, the four sub-regions of the mini-plug for separate analysis of residual oil in the following sub-sections were defined as follows, and as shown in Figure 4.15:

- S mask: radius of 2.0 mm and full imaged length of 12.5 mm
- P mask: radius of 1.5 mm and full imaged length of 12.5 mm
- Middle: radius of 1.5 mm and mid-section length of 3.1 mm
- Inlet: radius of 1.5 mm and inlet-section length of 5.9 mm.

Figure 4.15(b) shows the result of re-calculation of the longitudinal profiles in Figure 4.13(a) within the P mask, while Figure 4.15(c) shows the radial profile in Figure 4.13(b) (averaged over the entire length) now truncated at the P mask limit of 1.5 mm. Figure 4.15(d-e) show this same profile but re-calculated by averaging over only the middle or inlet section, respectively.

4.3.4 Segmentation

The results of the segmentation procedures outlined in Section 4.3.1 and applied to these 4 sub-regions defined in Section 4.3.3 are listed in Table 4.2. The total porosity within all analyzed sub-regions is around 24%, the majority of which comes from resolved pores and is similar to that in Table 3.3 for the sister mini-plugs of 5 mm diameter used in the spontaneous imbibition experiments. However, the macro- and micro-porosity in Table 4.2 are slightly higher and lower, respectively, by around 1 p.u. than in Table 3.3.

The majority of total oil saturation is also contributed by macro-pores. In terms of the change in macro-oil saturation from HS to LS floods, the incremental tertiary recovery (in %PV, not %OOIP, since the initial oil saturation - while presumably high - is not known) is 4.4% within the S mask, and 4.5% within the P mask (i.e. exclusion of the extraneous oil near the mini-plug periphery does not greatly affect the incremental average), but is 0% within the inlet sub-region, and 17.8% within the middle sub-region. This emphasizes that the capillary end effect can have a strong and misleading influence on LSW response.

Table 4.2 Volume fractions of phases (rows) segmented within the 4 regions (columns) of the registered tomograms of the 5 mm diameter mini-plug of reservoir sandstone. Porosity is given as percentage of total bulk volume (BV) and liquid saturations as percentages total pore volume (PV).

Segmented Phase	S mask	P mask	Inlet	Middle
Macro-Porosity (%BV)	21.2	20.7	20.7	21.1
Micro-Porosity (%BV)	3.2	3.4	3.3	3.2
Total Porosity (%BV)	24.4	24.1	24.0	24.3
S _o (Macro-oil) HS (%PV)	33.2	29.7	16.1	42.1
S _o (Macro-oil) LS (%PV)	28.8	25.2	16.1	24.3
S _o (Micro-Oil) HS (%PV)	1.7	1.9	1.3	2.3
S _o (Micro-Oil) LS (%PV)	2.0	2.3	1.6	2.4
S _o (Total) HS (%PV)	34.9	31.6	17.4	44.4
S _o (Total) LS (%PV)	30.8	27.5	17.7	26.7

Table 4.3 lists the segmented volume fractions from the sub-resolution features (referred to as the clay phase) which gave rise to the micro-oil saturations in Table 4.2. The total bulk volume fraction of clay phase coming from the three-phase segmentation of the dry-state tomogram of the 5 mm diameter mini-plug of the reservoir sandstone is around 7%. This is much less than the clay weight fraction provided by XRD in Table 3.1. The main reason for this discrepancy, as revealed by scanning electron microscopy in Chapter 5, is that much of the clay (especially kaolinite) occurs as very tight, low porosity, lithic fragments which possess very similar X-ray attenuation to quartz and plagioclase and were thus segmented into the grain phase. The clay phase from segmentation should thus more correctly be regarded as representing only the relatively high-porosity kaolinite booklet aggregates filling inter-granular space.

The difference tomogram of the brine-saturated state minus the flooded state was used to sub-divide this clay phase into its oil-filled and brine-filled fractions, listed in columns 2 and 3 of Table 4.3. The segmentation of microporosity greyscale within the clay phase, obtained from the difference tomogram of the brine-saturated state minus the dry state, gave the averages within the oil-filled and brine-filled fractions listed in columns 4 and 5 of Table 4.3. This microporosity average is substantially higher for oil, in line with the above observation that oil in pore-filling kaolinite tends to reside in the looser and coarser (often outer) parts of aggregates. Application of this microporosity

weighting to the oil-filled clay fraction gave the micro-oil saturation estimates in Table 4.2. The small contribution from micro-oil to total saturation actually increases slightly from HS to LS floods within all analyzed regions in Table 4.2. This is not thought to be real, but instead likely exposes limitations to segmentation accuracy within this small fraction of sub-resolution porosity, stemming from noise and artifacts (e.g. from beam hardening local to high density siderite) as mentioned above.

Table 4.3 Microporosity segmentation of oil-filled and brine-filled clays for all regions of the 5 mm diameter mini-plug of reservoir sandstone.

	Total Clay (%BV)	Oil-filled clays (%BV)	Brine-filled clays (%BV)	Oil-filled clays Micro-Porosity (%)	Brine-filled clays Micro-Porosity (%)
S mask HS	6.9	3.2	3.7	53.3	40.8
S mask LS	6.9	4.0	2.9	51.2	40.2
P mask HS	6.6	3.4	3.2	56.1	45.1
P mask LS	6.6	4.2	2.4	54.3	44.4
Inlet HS	6.4	2.3	4.1	57.8	46.5
Inlet LS	6.4	2.8	3.6	56.6	45.7
Middle HS	6.2	4.1	2.1	55.0	43.4
Middle LS	6.2	4.5	1.7	54.3	42.3

4.3.5 Pore-scale Distribution and Connectivity of Residual Oil

For quantification of pore-scale saturation and connectivity of resolved residual oil, the resolved pore space segmented from the dry-state tomogram was partitioned into its individual constituent pore bodies using a watershed algorithm (36). The segmented macro-oil after HS and LS flooding was then superposed onto this pore partition for generation of statistics per pore body. The scatter plots of residual oil saturation versus individual pore volume within the inlet and middle sub-regions are shown in Figure 4.16(a-d). The very smallest pores are brine-filled, and oil saturation rises with body size up to around 10^{-4} mm^3 , corresponding to the above-mentioned smallish pores (barely contributing to overall residual volume) that contain adhering oil remnants. Beyond this size, the scatter plot in the inlet sub-region bifurcates, as intermediate-sized pores which remain substantially oil-filled coexist with well-swept pores in which oil remains only as films or in corners. The latter, which were mainly absent in the Berea

spontaneous imbibition states of Chapter 2, dominate as pore size increases, and thus the average dips. From HS to LS floods, the change in the inlet sub-region in Figure 4.16(e) is roughly equally distributed between positive (OB) and negative (BO). Brine displacement of oil occurs preferentially in small-intermediate pores, but some of this oil re-enters larger, brine-occupied pores. The latter events are less frequent but weigh more volumetrically, since they result in greater saturation change in large pores.

In the middle sub-region (which exhibits greater scatter due to the more limited statistics), the bifurcation in saturation at pore sizes around 10^{-4} mm^3 is more evenly balanced after HS flooding, and so the average is roughly maintained by equal populations of larger pores with low and high oil occupation. The oil change plot in Figure 4.16(f) confirms that LS flooding greatly reduces oil saturation in these larger pores, and also in intermediate-sized pores due to the above-mentioned connections between them. Instances of BO are almost completely absent.

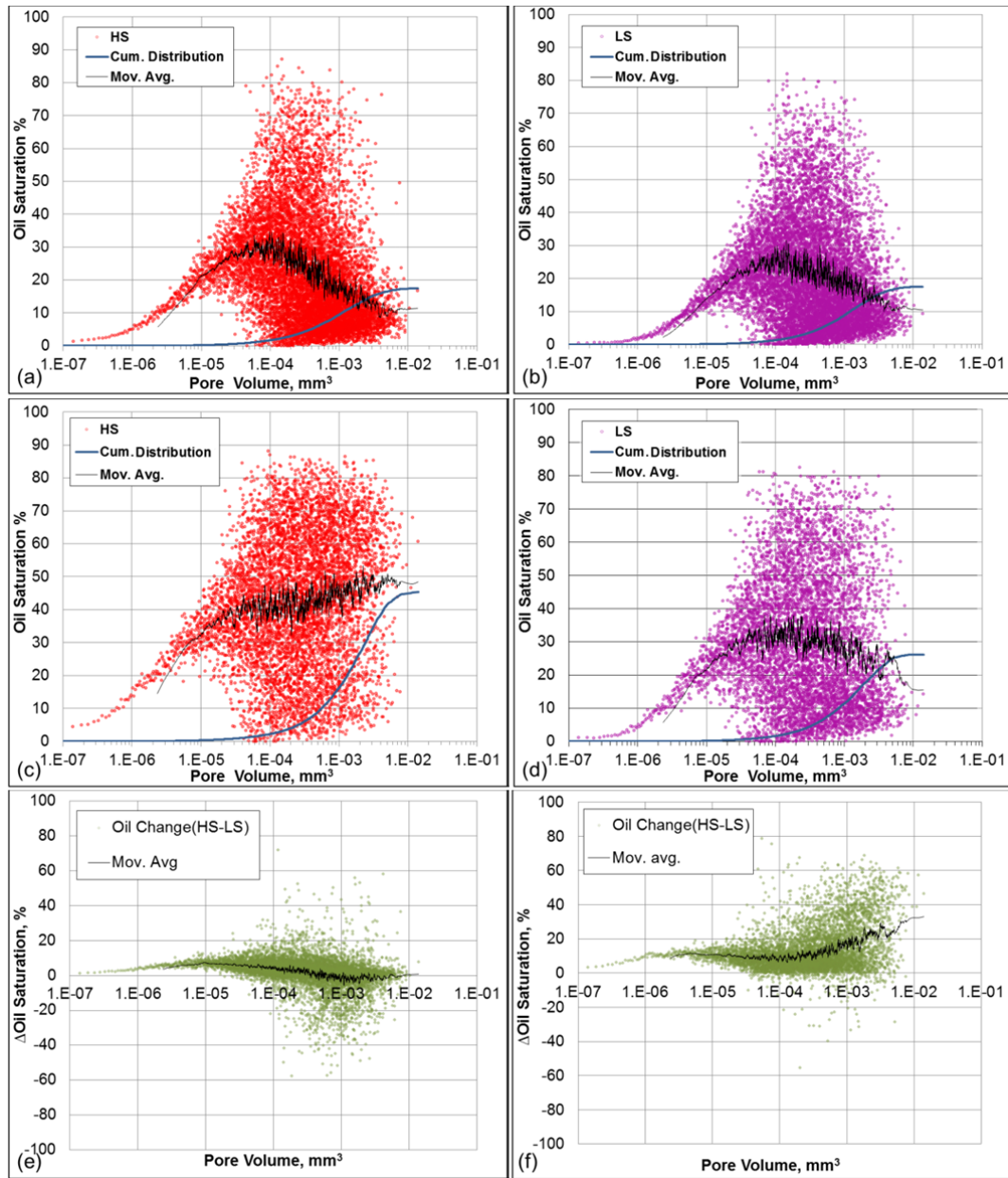


Figure 4.16 (a-d) Scatter plot of residual oil saturation in each resolved pore body versus its individual volume in the 5 mm diameter mini-plug of reservoir sandstone, also showing moving average (black line) and volume-weighted cumulative distribution (blue curve), within the (a-b) inlet and (c-d) middle sub-regions after HS and LS flooding. (e-f) Corresponding plot of change in residual oil saturation (HS minus LS) within (e) inlet and (f) middle sub-regions.

Figure 4.17 gives the cumulative distribution of oil volume after HS and LS flooding, now sorted by the size of each separate oil ganglion, in terms of the number of adjoining pores it spans and occupies more than 50% of. Within the S mask volume after HS flooding, Figure 4.17(a) shows a substantial fraction of singlets (i.e. oil blobs only spanning one pore), mainly contributed by the inlet sub-region, while most of the

rest of the oil volume (almost 70%) comprises one giant cluster. As expected, connectivity is decreased by exclusion by the P mask of the periphery, where oil saturation and connection via the epoxy walls is greater, and also by LS flooding. The separation of inlet and middle sub-regions in Figure 4.17(b) clarifies the trends. In the middle sub-region after HS flooding, more than 80% of residual oil volume is connected as one spanning cluster, which is broken down to occupy less than 30% after sweep of this oil bank by the LS flood. Ganglia sizes are very small in the inlet sub-region after HS flooding, with 70% of oil occurring there as singlets. Connectivity decreases further after LS flooding, partly due to the loss of oil from smaller pores, which more readily span and fulfil the 50% occupancy criterion. Although the inlet sub-region exhibits no overall oil recovery from LS flooding, this redistribution of oil from small to larger pores is consistent with a shift toward more water-wet.

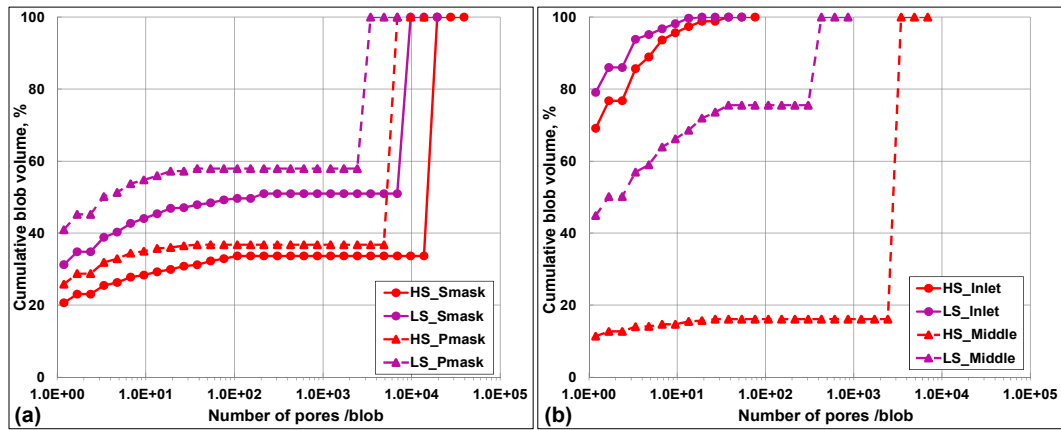


Figure 4.17 Cumulative distribution of residual oil volume in the 5 mm diameter mini-plug of reservoir sandstone after HS and LS flooding within (a) S mask and P mask, and (b) inlet and middle sub-regions, as a function of the number of connected pores spanned by each separate ganglion.

4.3.6 Interfacial Area of Residual Oil

Quantification of the contact area of residual oil with external surfaces of grains and clay aggregates and with brine can provide greater insight into recovery mechanism of HS and LS floods in each sub-region. Various statistical measures of interfacial areas and their changes are presented in Figures 4.18-4.20, using a surface density algorithm to smooth the voxelated areas. As was also the case in Chapters 2 and 3, this analysis is restricted to the resolved, segmented phases, since areas within the sub-resolution

features are unknown. Figure 4.18 displays the interfacial area of oil and brine contacting grain or clay, normalized to total pore-rock area (i.e. the sum of these four combinations), and with oil-brine area of this free interface added on top. Of the total pore-rock area, 80% comes from grains and 20% from external clay surfaces, in line with the previous results from Figure 3.13. The oil versus brine share of contact with grain or clay within each region qualitatively reflects the macro-oil saturation there, decreasing from middle to S mask to P mask to inlet after HS flooding (in the same order as in Table 4.2). Similarly, the oil contact with grain or clay reduces from HS to LS flooding, presumably for this same reason. However, this area decrease in the inlet sub-region occurs without any overall volume decrease there, which is consistent with the above-mentioned movement of oil from smaller to larger pores with proportionally less area. Oil-brine interfacial area generally decreases slightly from HS to LS.

Figure 4.19(a) re-plots the oil area contributions after normalization by oil volume within each of the 4 sub-regions; the schematic in Figure 4.19(b) aids in clarifying these changes with salinity. Within the middle sub-region, the ratio of oil contact area with grain or clay to oil volume remains constant from HS to LS flooding, while normalized oil-brine area increases. Oil is non-selectively removed from rock surface in proportion to its volume, accordingly decreasing its connectivity and increasing its brine interfacial area/volume, without any associated wettability change. Within the inlet sub-region, the above-mentioned decrease in oil-rock contact area from HS to LS flooding is (relatively speaking) more pronounced for clay than grain, while oil-brine area remains unchanged. As shown in Figure 4.19(b), this implies that release of oil from rock surfaces, due to a shift towards water-wet, and its coalescence with other oil, occur in a balanced way so that oil-brine area remains unchanged. The results within the P mask in Figure 4.19(a) are, as expected, an average of those for the middle and inlet sub-regions, which serves to show that separate analysis of these sub-regions is necessary to correctly interpret the low salinity effect.

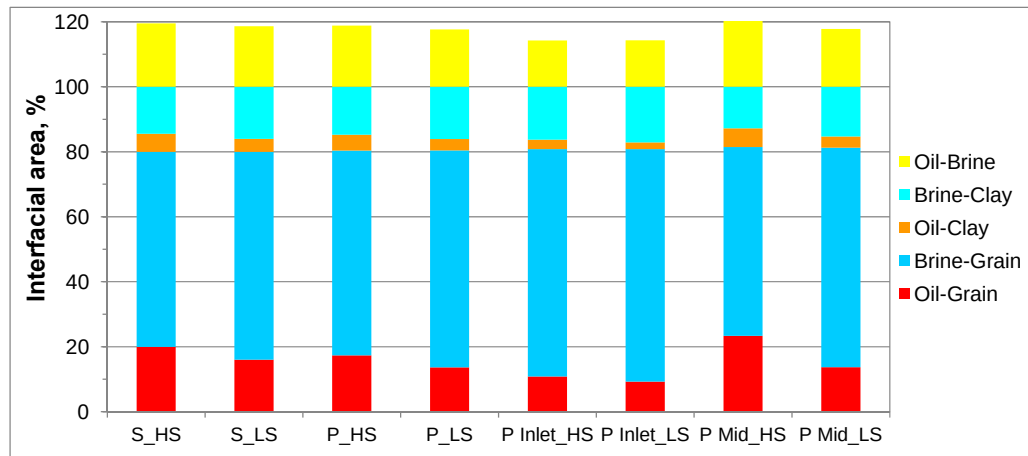


Figure 4.18 Interfacial area, normalized to total pore-rock area, of each segmented liquid macro-interface within the 4 regions of the 5 mm diameter mini-plug of reservoir sandstone.

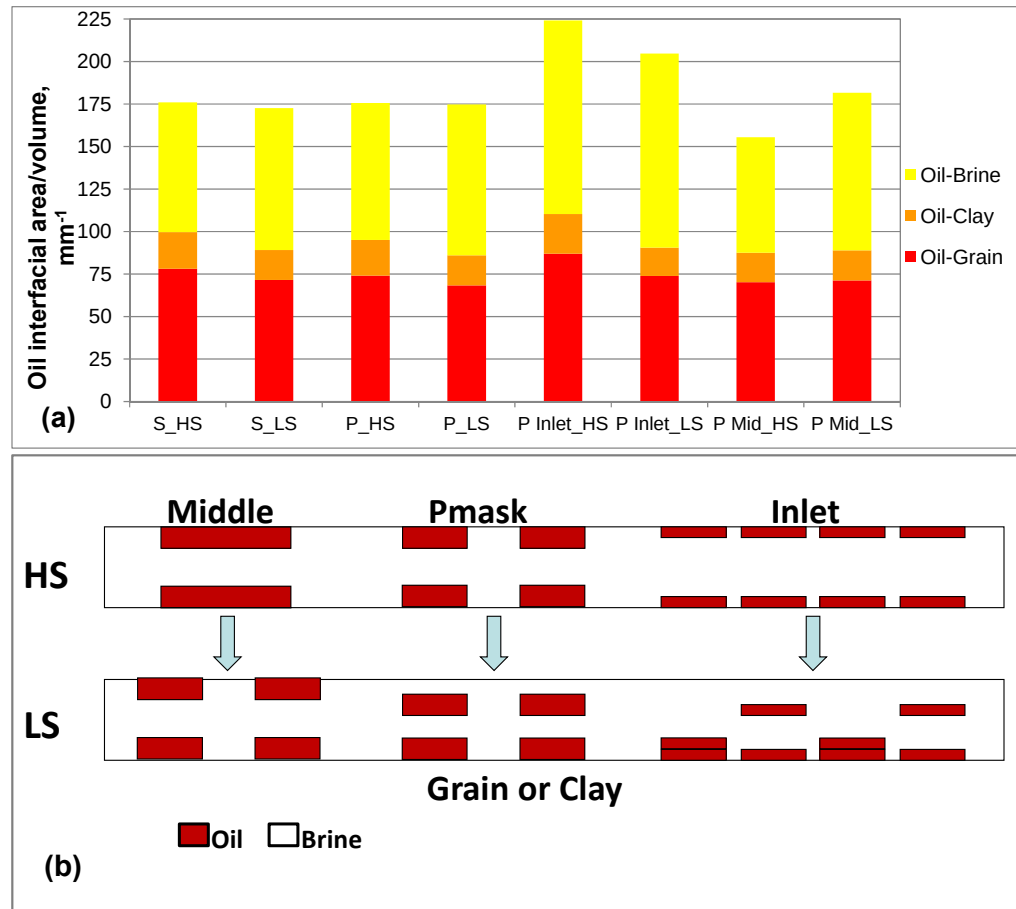


Figure 4.19 (a) Macro-oil interfacial area to grain, clay and brine, normalized by total macro-oil volume, within the 4 regions of the 5 mm diameter mini-plug of reservoir sandstone, and (b) schematic of oil movement consistent with these interfacial statistics.

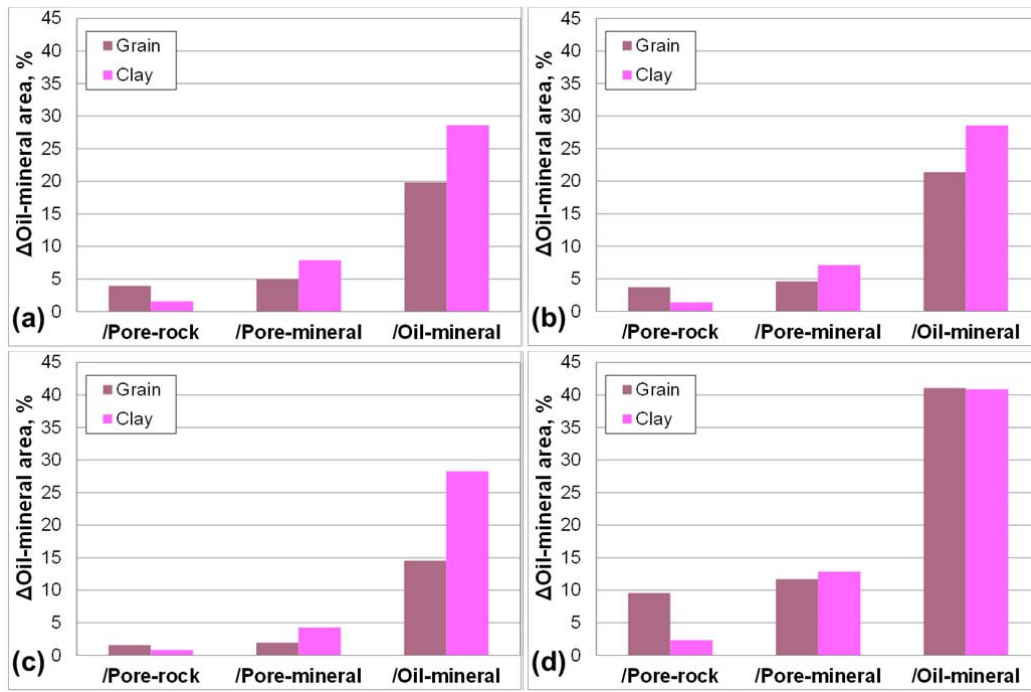


Figure 4.20 Salinity-induced change in interfacial contact area of macro-oil with grain or clay, normalized in three ways, where rock refers to grain plus clay and mineral refers to grain or clay, within the (a) S mask, (b) P mask, (c) inlet and (d) middle sub-regions, of the 5 mm diameter mini-plug of reservoir sandstone.

Figure 4.20 plots the percentage reduction from HS to LS flooding in macro-oil area contacting grain or clay, relative to the total interfacial area of i) grain plus clay, or ii) only grain or clay, or iii) the fraction of grain or clay originally contacting oil after HS flooding. Normalized in this first way, the low salinity-induced detachment of oil occurs more frequently from grain than clay, since total grain area is 4 times greater than clay area (from Figure 4.18). Normalization in the second way, counting oil release from grain relative to grain area only, and similarly for clay, allows for a fairer assessment. By this measure, low salinity displays a preference for release from clay over grain. Normalization in the third way, counting oil release from grain relative to grain area originally contacting oil in HS only, and similarly for clay, provides the fairest assessment, since the fraction of these surfaces that were not originally in contact with oil are excluded from consideration.

By this third measure (i.e. rightmost pair of bars in Figure 4.20), oil release from grain and clay during LS flooding within the middle sub-region are equally preferred in Figure 4.20(d). This is consistent with the above-mentioned finding that the sweep of the oil bank there is not a true low salinity effect and does not involve in situ wettability

change. Further, by this third measure, oil release from clay during LS flooding is strongly preferred over grain within the inlet sub-region in Figure 4.20(c), as was also apparent from Figure 4.19(a). Thus the low salinity-induced shift toward water-wet that drives the rearrangement of oil in this well-swept inlet region principally comes from clay aggregate surfaces. This preference for removal from clay was also seen for mini-plug C of Chapter 3, in which oil rearrangement also occurs without additional oil recovery during SIL. In short, the system has the potential for preferential oil detachment from clay in the LS flood, but this was not strongly manifested in the saturations, as the HS flood substantially disconnected the residual oil in the inlet half and left an end effect which dominated the outlet half. The corresponding results within S mask or P mask in Figure 4.20(a-b) are averages over these two extreme sub-regions, from which the trends are less clear.

To further illustrate the oil re-distribution and recovery within the inlet and middle sub-regions, Figure 4.21 shows 3D visualizations of residual oil after HS and LS floods. The 3D isosurfaces in Figures 4.21(a-b) from the inlet sub-region show the further disconnection of oil in small pores and its partial reconnection (coalescence) in larger pores. The dramatic oil recovery and disconnection within the middle sub-region is apparent from Figures 4.21(c-d); while the HS flooded residuals in the two sub-regions are strikingly different, their LS residual counterparts are much more similar.

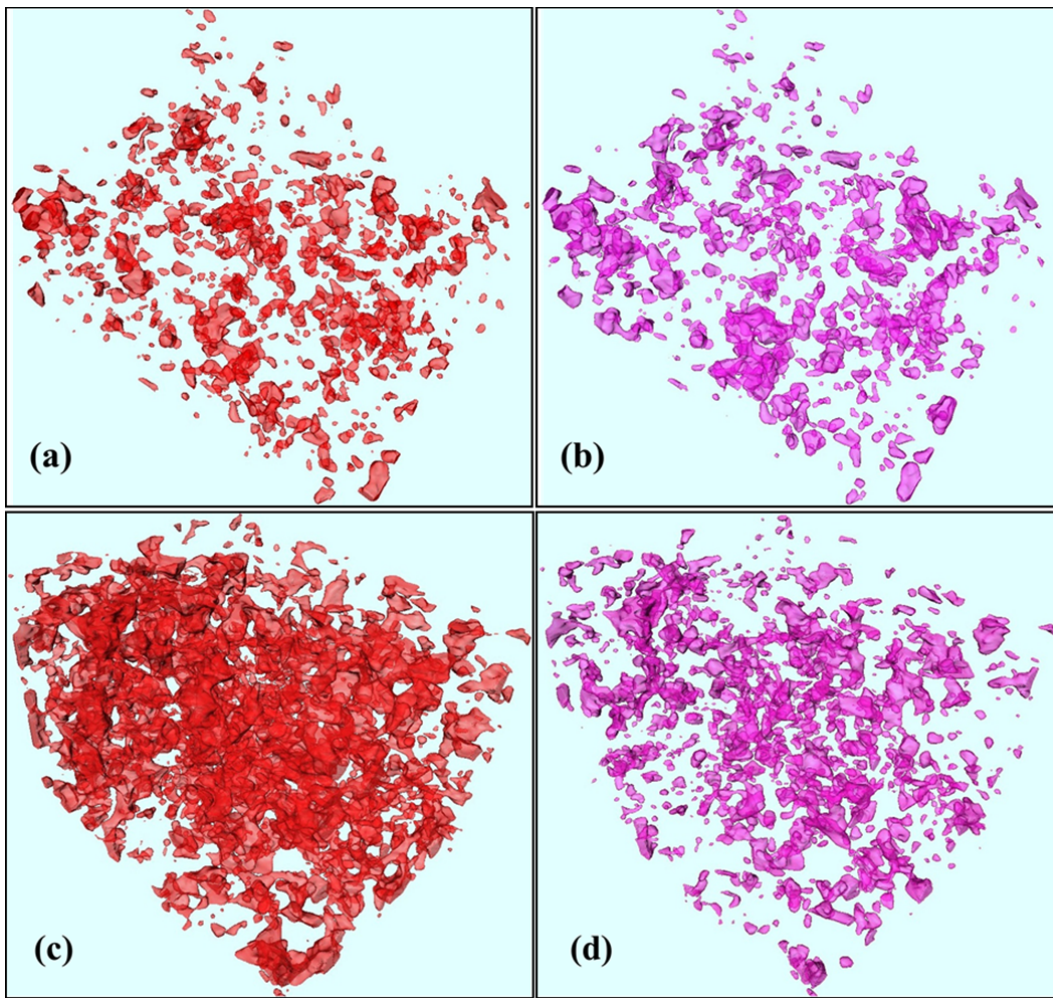


Figure 4.21 3D visualizations of residual oil for a sub-volume ($1.4 \times 1.1 \times 1.0 \text{ mm}^3$) of the 5 mm diameter mini-plug of reservoir sandstone, within the inlet sub-region after (a) HS and (b) LS floods, and the middle sub-region region after (a) HS and (b) LS floods.

4.4 Conclusion

Reservoir sandstone core plug restoration and water flooding experiments were miniaturized to mini-plugs to facilitate pore-scale investigation of the low salinity effect by micro-CT. A substantial capillary end effect was typically present after high salinity flooding, with relatively high residual oil saturation extending from the outlet to midway along the mini-plug. The strong end effect expected for slow injection into a mixed-wet rock was reinforced by the mini-plug's small diameter and epoxy-sheathed (i.e. oil-wet) walls. Low salinity flooding lessened the end effect by reducing the sharpness of the oil bank near the mini-plug middle. Although a strong capillary end effect limited the scope for analysis, different regions were defined and analyzed individually. In the middle section of the mini-plug, oil saturation typically reduced

from 42 to 24% after low salinity flooding, with the interfacial area of oil release being proportionally equal between grains and clay aggregates. This artificial low-salinity effect was presumably mainly due to the slight reduction in oil-brine interfacial tension. The other half of the mini-plug, from the inlet to its middle, was well swept by the high salinity flood to leave small oil blobs clinging to rock. Tertiary low-salinity flooding had little effect on the average oil saturation there (typically remaining at 16%). However, pore-scale analysis revealed a tendency for oil to move from smaller to larger pores and to become somewhat more disconnected. Most significantly, oil preferentially detached from clay aggregates rather than grains in the inlet half. Instances of fines mobilization by low salinity flooding were rarely seen at the tomogram resolution.

5 Microscopy Study of Low Salinity Water Flooding

5.1 Introduction

Mineralogy has always been recognized as an important factor in determining whether and to what extent the low salinity effect is operative in a given sandstone (62). Clay minerals – especially but not exclusively kaolinite – were identified as a necessary component (4,5,6,65-67). Plagioclase has been postulated as a grain mineral of possible relevance to low salinity EOR, as it can alter brine pH depending upon salt concentrations (68). Dissolution of cement minerals has also been discussed as a contributing factor (13,69,70). Although there are few works that studied the bulk mineralogy and its relation to the low salinity brine (71), no comprehensive study has been performed to directly compare local mineralogy to local oil release by low salinity brine. The 3D tomographic analysis in the preceding Chapters 2-4 correlated oil release to the two mineral classes of grains and pore-filling clay aggregates segmented from the tomograms. However as noted there, segmentation based on X-ray attenuation grayscale is a primitive tool for distinguishing different minerals and their spatial distribution, compared to SEM with energy-dispersive X-ray spectroscopy (EDS), which is the standard tool for mineral mapping, albeit in 2D.

This chapter complements the non-destructive micro-CT 3D imaging and analysis of the reservoir sandstone samples in Chapters 3-4 by performing SEM-EDS 2D mineral mapping on polished embedded sections of these same mini-plugs after cleaning. These 2D maps were registered (22,39) into their corresponding virtual cross-section through the tomograms of each mini-plug. In this way, the salinity-induced release of oil could be directly and quantitatively compared to the mineral originally contacting it at each location in the plane. Further, other pieces of these cleaned samples were imaged by Field Emission SEM (FESEM) to qualitatively discern the presence or absence of asphaltene films on grain or clay surfaces which dictate the pore-scale wettability.

5.2 Materials and Methods

The 5 mm diameter mini-plugs A, B and C from the spontaneous imbibition study of Chapter 3 and the sister mini-plug from the water flooding study of Chapter 4, all of which were taken from the same North Sea reservoir sandstone plug, were re-cleaned

from their final micro-CT-imaged state of saturation with contrast brine. This cleaning to remove the salts and water was performed by methanol immersion and exchange at room temperature for one week. Methanol immersion will only remove the salts and water and it will not affect the asphaltene signature on grain surfaces. The main challenge of our cleaning method was centrifuging the samples in solvents since this rock was very friable. Therefore we decided to leave the samples for longer time in the methanol and changing the methanol three or four times.

Each mini-plug was then cut crosswise into two pieces using a Struers saw with rotating diamond blade and a water-based cooling liquid. The smaller piece was used for very high resolution FESEM imaging of mineral surfaces near the raw cut or broken surface. Preparation of each rock piece for this mode of imaging was simply performed by mounting it on an aluminum stub using double-sided carbon tape, as shown in Figure 5.1. No conductive coat was applied to the sample, since even thin coats of e.g. carbon or platinum can obscure the asphaltene deposit to be imaged. The high resolution imaging was carried out using a Zeiss Ultra Plus FESEM microscope operated at low accelerating voltage (1 kV) and small aperture at small working distance (around 2 mm), to maximize resolution and minimize beam charging and damage of the organic deposits of interest.

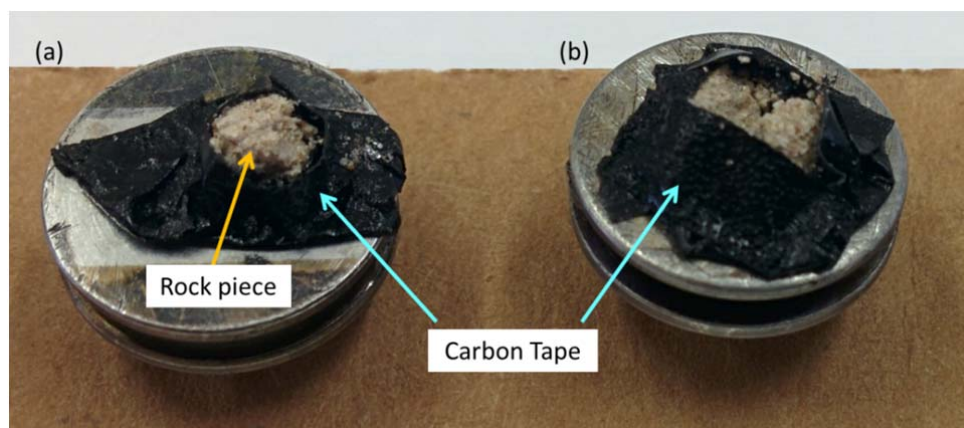


Figure 5.1 Pieces of reservoir sandstone mini-plugs a) A and b) B, each mounted on a SEM stub using carbon tape.

The larger of the two cut pieces of each mini-plug was used for SEM-EDS mineral mapping, which requires a flat, smooth surface for quantitative analysis. For this purpose, each mini-plug piece was embedded in Epofix epoxy, prepared by pre-mixing

resin and hardener in the mass ratio of 25 to 3. The cleaned, dried mini-plug piece was placed in a mold in a vacuum vessel and evacuated for 30 minutes, prior to vacuum infiltration by the epoxy mix for 1 hour. This was followed by positive pressurization at 250 kPa for one day to allow further penetration of resin into smaller pores and dissolution of trapped air bubbles. The embedded mini-plug piece was removed from its mold and cut crosswise, after which the cut surface was polished using a Struers Tegramin polishing machine. For cases in which some pores remained incompletely filled with resin, the impregnation and polishing procedure was repeated. The polished surface was quickly cleaned by ethanol and water, directly followed by drying with nitrogen. The polished surface of the mini-plug embedded in its epoxy button was carbon coated to minimize beam charging and thermal damage during its SEM imaging (see Figure 5.2).

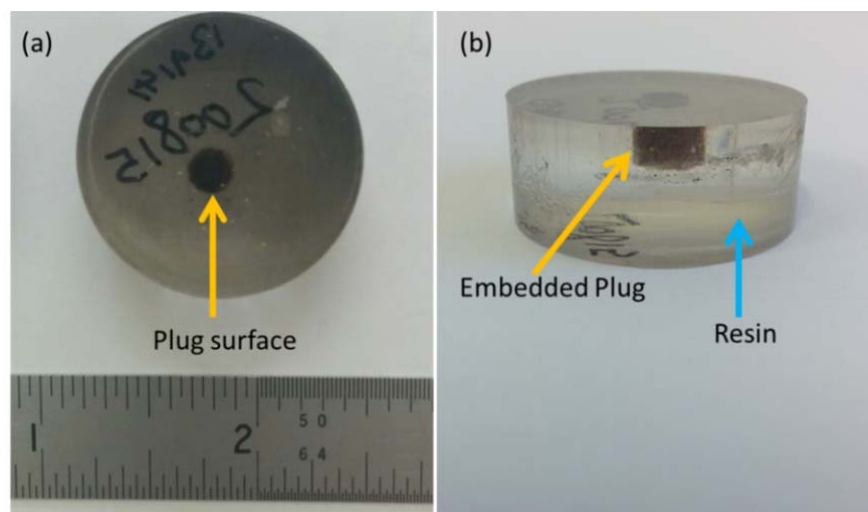


Figure 5.2 Polished embedded section of mini-plug B in (a) top view and (b) side view.

5.3 Results and Discussion

5.3.1 SEM-EDS Mineral Mapping and Registration into Tomograms

Each coated, polished embedded mini-plug button was then mounted in a carousel sample holder which was loaded into the chamber of a Quanta 650 FEG (FEI) microscope. The full cross-section of the 5 mm diameter mini-plug was first imaged with back-scattered electrons (BSEM) at beam accelerating voltage of 8 kV and working distance of 10 mm, using MAPS (FEI) software to automate the acquisition of a grid of overlapping tile images with 500 nm pixels, and the stitching of these tiles into

one continuous mosaic image of the entire surface. The mini-plug section was then analyzed using QEMSCAN (FEI) for automated SEM-EDS acquisition and mineral identification. The scanning was performed at beam accelerating voltage of 15 kV and working distance of 13 mm using QEMSCAN iMeasure software to acquire and stitch a SEM-EDS mosaic image of the full cross-section of the mini-plug at around 2 μm pixel size. Further refinement and quality assessment of the mineral classification was subsequently performed using QEMSCAN iExplorer software.

The 2D BSEM image was then registered using Mango software into its corresponding virtual cross-section through the sequence of registered tomograms of the mini-plug (from Chapters 3-4). This then allowed the 2D SEM-EDS mineral map, after its in-plane alignment with the BSEM image, to be registered into this same matching cross-section of the mini-plug. Table 5.1 summarizes the modal mineralogy obtained from all sections taken through all mini-plugs. Figure 5.3 shows for mini-plug A the BSEM image and SEM-EDS mineral map of its section 2, along with the corresponding registered slice of its tomogram in the dry state and after spontaneous imbibition of high (SIH) and low (SIL) salinity brine. Table 5.1 verifies the homogeneity of the mini-plugs, across the set of which the variations in mineralogy are only slight. Note though that there is a discrepancy between mineralogy from SEM-EDS and from XRD (performed on nearby material) in Table 3.1. In particular, XRD predicts less quartz and correspondingly more kaolinite and muscovite/illite.

Table 5.1 Modal mineralogy of each cross-section taken from the 5 mm diameter mini-plugs of reservoir sandstone analyzed by QEMSCAN.

Mini-plug	A_slice1	A_slice2	A_slice3	B	C	Waterflood slice1	Waterflood slice2	Waterflood slice3	Waterflood slice4
Mineral	Area%	Area%	Area%	Area%	Area%	Area%	Area%	Area%	Area%
Quartz	50.2	50.1	49.8	52.2	50.7	55.1	48.8	49.7	51.6
K Feldspar	13.7	13.7	13.9	13.9	13.3	14.7	15.2	13.1	14.6
Plagioclase	4.6	3.8	4.5	3.7	4.1	4.5	4.8	3.7	3.9
Muscovite/Illite	5.2	5.7	5.2	4.5	5.1	4.7	4.6	5.1	4.4
Biotite	0.0	0.0	0.0	0.1	0.1	0.1	0.0	0.1	0.0
Kaolinite	15.1	16.5	15.6	16.1	19.3	12.9	16.0	17.8	15.3
Chlorite	2.2	1.8	2.1	1.6	1.0	0.8	1.7	1.7	1.3
Siderite	5.4	4.4	5.1	4.1	3.0	3.8	4.6	5.4	5.3
Ankerite	0.6	0.5	0.7	0.6	0.5	0.7	0.6	0.6	0.4
Garnet	0.1	0.2	0.3	0.3	0.2	0.3	0.2	0.2	0.3
Zircon	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.0	0.1
Rutile	1.2	1.6	1.5	1.4	1.6	1.2	1.8	1.3	1.4
Fe Oxides Spinel	0.8	0.6	0.7	0.5	0.3	0.4	0.4	0.5	0.4
Pyrite	0.1	0.0	0.1	0.4	0.0	0.1	0.4	0.1	0.0
Apatite	0.4	0.4	0.1	0.3	0.2	0.2	0.1	0.1	0.2
Unclassified	0.4	0.6	0.4	0.5	0.4	0.5	0.9	0.9	0.9
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0

Half of the mineral content by area (volume) is quartz. The rest of the silicate grains are Na-plagioclase, which has almost exactly the same brightness (grayscale values) as quartz in micro-CT and in BSEM owing to their similar X-ray attenuation and electron density, and more commonly K-feldspar, the grains of which are brighter and slightly weathered. Most of the muscovite/illite (of similar brightness to K-feldspar in micro-CT and BSEM) is generally in the form of muscovite flakes oriented parallel to bedding; illite does not seem to occur separately as grain linings. By far the most common clay is kaolinite, which occurs both as internally porous aggregates (darkest in micro-CT and BSEM) of booklets filling inter-granular space, and as lower porosity aggregates and grain-sized particles, sometimes interlayered or mixed or juxtaposed with muscovite. The former were correctly identified as clay (microporous) phase in the tomogram segmentations of Chapters 3-4, while the latter generally were incorrectly classified as grain phase as they are largely indistinguishable in micro-CT from the true grain minerals quartz and plagioclase. Siderite aggregates (bright in micro-CT and BSEM) are very commonly occurring and are intermingled with chlorite (which seldom appears elsewhere), Na-plagioclase and ankerite.

The sequence of registered cross-sectional images such as for section 2 of mini-plug A – the sample in Chapter 3 which contained the oil with high acid number and exhibited the greatest tertiary recovery – in Figure 5.3 allow the oil distribution after SIH and SIL to be overlain onto the corresponding BSEM image, which serves as a five times higher resolution version of the dry-state tomogram, and most importantly on the SEM-EDS mineral map. In this way, locations of tertiary oil recovery, where pores brighten from the SIH to SIL tomograms due to replacement of oil (dark) by brine (intermediate gray) can be directly compared to the neighboring mineralogy. Three zoom-ins from cropped subareas within Figure 5.3 which exhibit tertiary recovery are shown in Figures 5.4-5.6. Cyan arrows point to oil removal from tomogram-resolved pores during SIL (category OB), while blue and maroon arrows indicate microporous kaolinite aggregates occupied by brine (brighter than in the dry-state tomogram) or oil (unchanged gray shade from the dry-state tomogram), respectively.

The first example in Figure 5.4 contains kaolinite as pore-fill and grains at left (with higher internal porosity, one of which is indicated by the blue arrow) and right (with lower porosity), which are brine-filled in SIH (and SIL) and presumably were so throughout the restoration process. Macro-pores between quartz grains neighboring both

of these locations contain brine in SIH, probably resulting from its spontaneous advance from these kaolinite aggregates. Further advance of brine over these quartz surfaces occurs during SIL (indicated at left with the cyan arrow). The second example in Figure 5.5 again features kaolinite which remains brine-filled throughout, including aggregates with low internal porosity (e.g. blue arrow) and one with higher porosity (maroon arrow) in which oil has fully penetrated the larger pores in this looser aggregate. After SIH, brine has advanced over quartz and K-feldspar grain surfaces to occupy the corners of macro-pores, near the bottom left and top right, which do not exhibit further advance during SIL. Brine also advances in SIH to occupy part of a larger macro-pore, bounded by quartz, K-feldspar and Na-plagioclase, where further advance over Na-plagioclase and quartz occurs during SIL (cyan arrow). In the third example in Figure 5.6, the fine pores within kaolinite aggregates, whether of high or low porosity, remain brine-filled throughout, although again with oil penetrating the larger pores within looser pore-filling aggregates (e.g. maroon arrow). After SIH, brine has advanced over K-feldspar and quartz in one large macro-pore body, and advances further in SIL (cyan arrow), despite the fact that the surfaces of the neighboring kaolinite remain lined with oil.

The overall impression from mini-plug A containing the high acid number oil is that brine advance in macro-pores during SIH occurs in more water-wet locations on the external surfaces of kaolinite aggregates and K-feldspar grains, which maintained during aging their connate brine filling tight interior pores or lining surface roughness. Brine advance from SIH to SIL only occurs from these pre-existing menisci, with a preference for the larger ones which are less strongly curved towards water as discussed in Chapter 3. This brine advance in tertiary mode appears to mainly occur over quartz grains, presumably partly since this is the most common grain mineral.

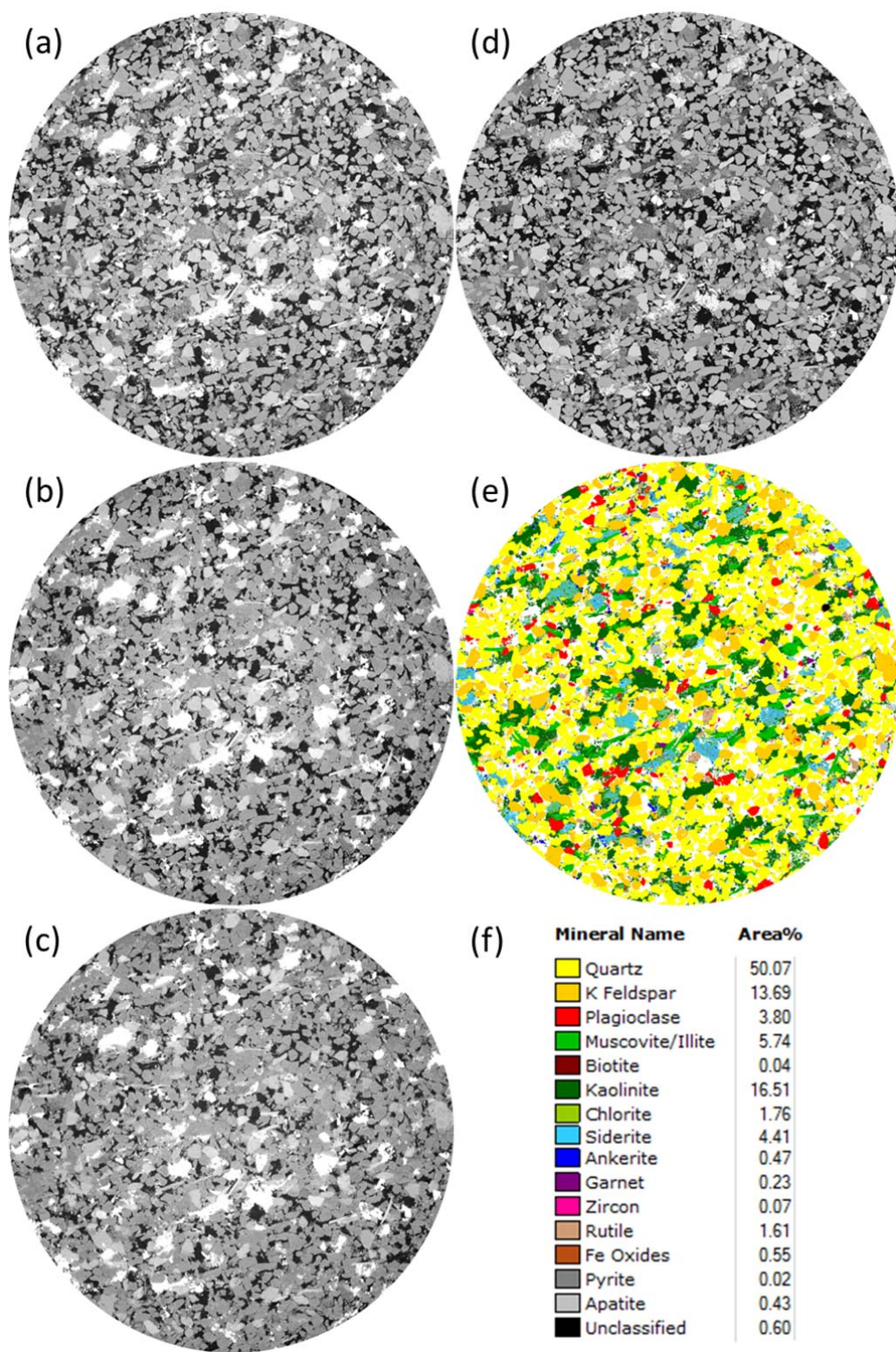


Figure 5.3 Cross-sectional slice of the registered tomograms of mini-plug A in its (a) dry state and after (b) SIH and (c) SIL, corresponding and aligned to the polished section 2 imaged by (d) BSEM and (e) SEM-EDS for mineral mapping, with color legend and modal mineralogy given in (f).

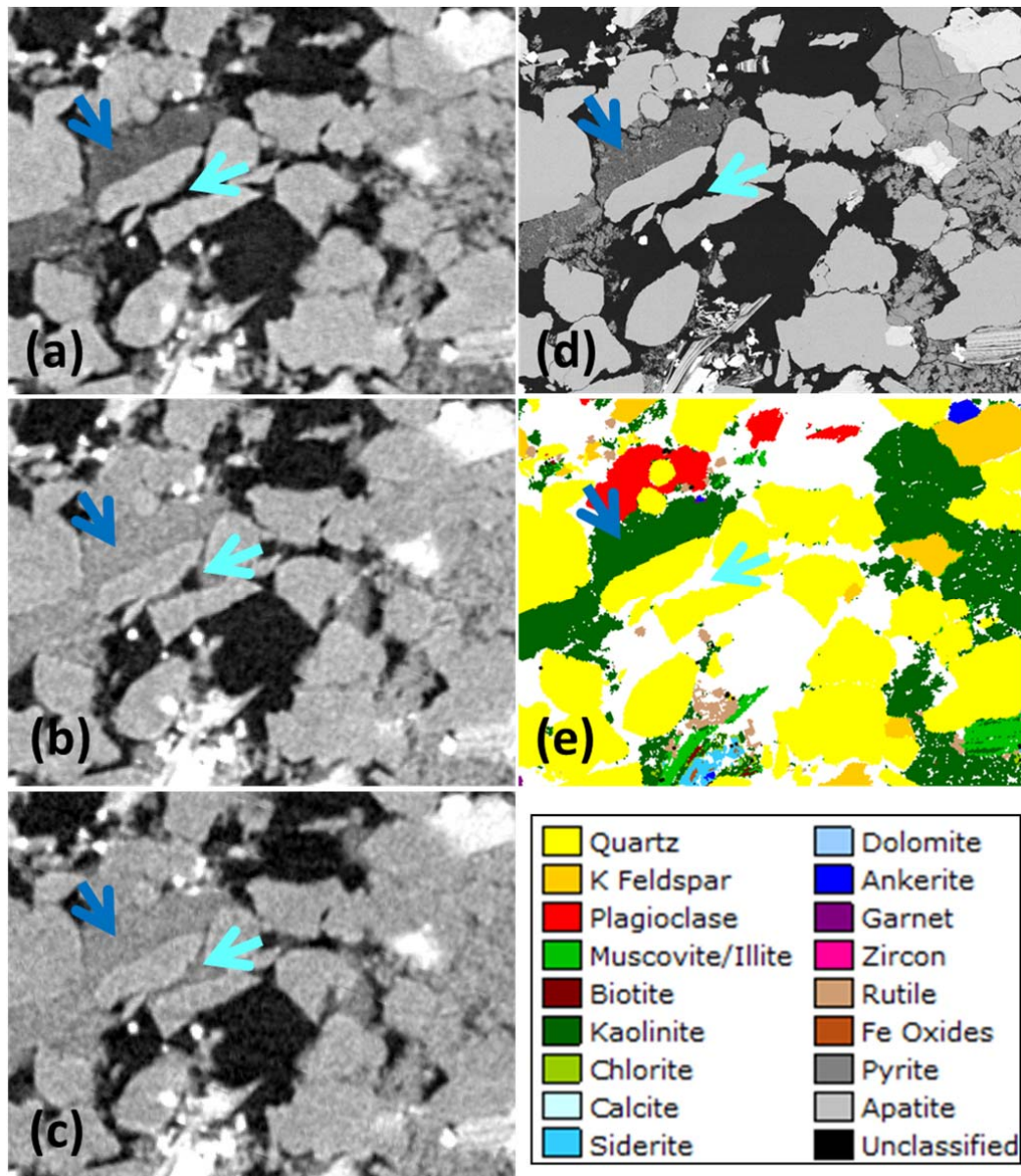


Figure 5.4 Subarea 1 (0.54 mm × 0.41 mm) of section 2 of mini-plug A from Figure 5.3, registered between the (a) dry tomogram, (b) SIH tomogram, (c) SIL tomogram, (d) BSEM image, and (e) SEM-EDS mineral map. Blue arrow is brine-filled clay and cyan arrow is OB region.

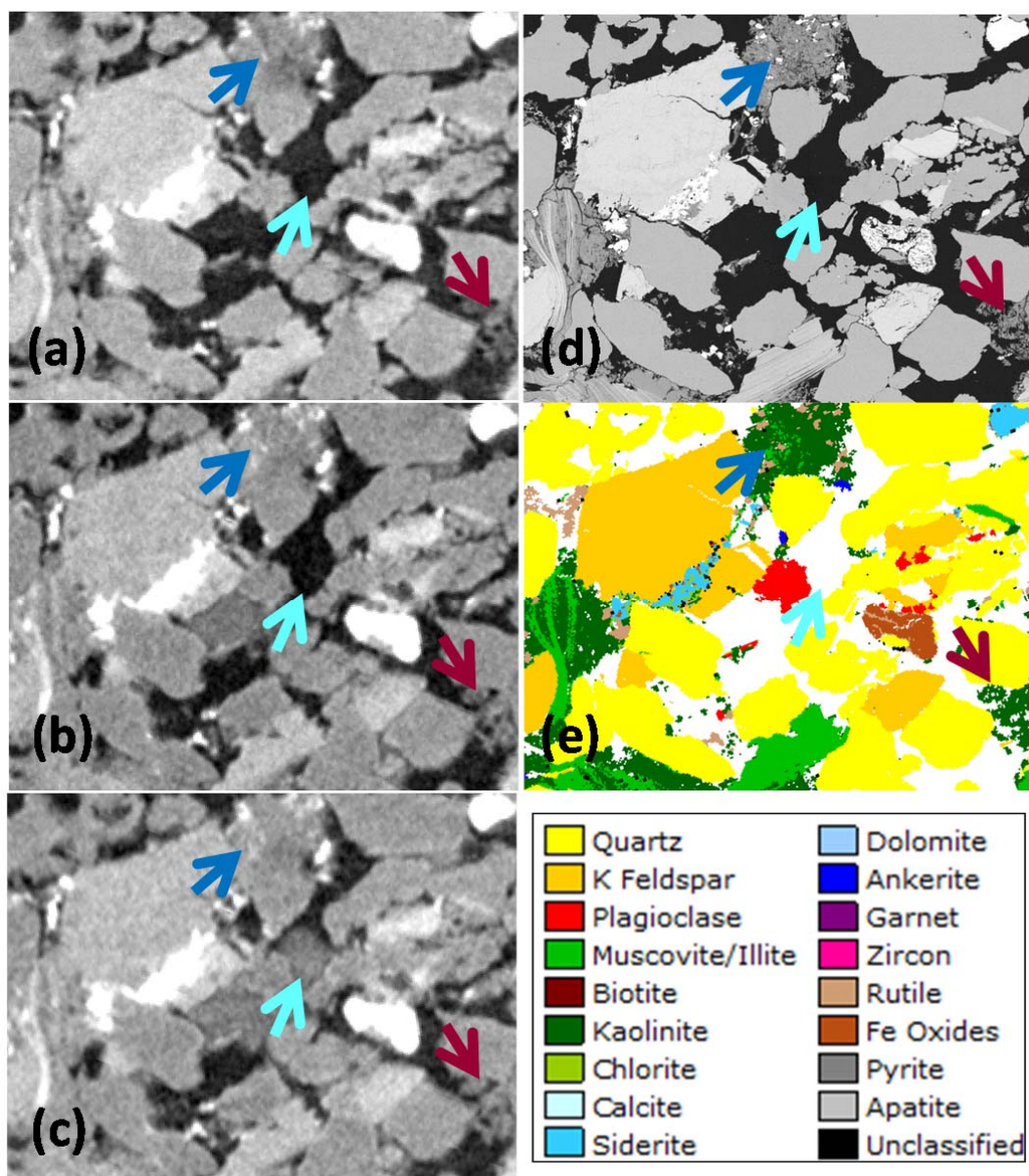


Figure 5.5 Subarea 2 (0.54 mm × 0.41 mm) of section 2 of mini-plug A from Figure 5.3, registered between the (a) dry tomogram, (b) SIH tomogram, (c) SIL tomogram, (d) BSEM image, and (e) SEM-EDS mineral map. Blue arrow is brine-filled clay, cyan arrow is OB region and maroon arrow is oil-bearing clay

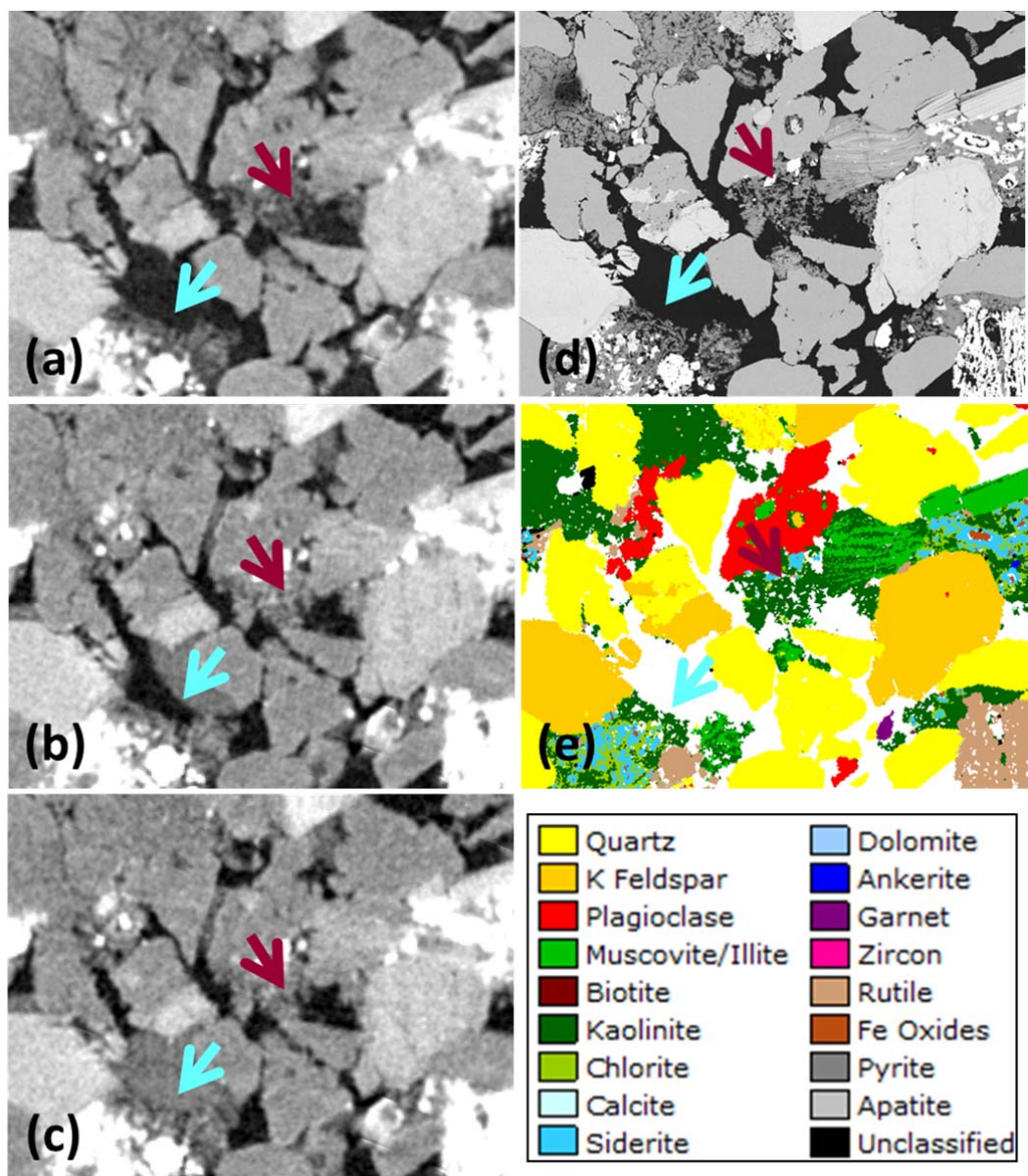


Figure 5.6 Subarea 3 (0.54 mm × 0.41 mm) of section 2 of mini-plug A from Figure 5.3, registered between the (a) dry tomogram, (b) SIH tomogram, (c) SIL tomogram, (d) BSEM image, and (e) SEM-EDS mineral map. Cyan arrow is OB region and maroon arrow is oil-bearing clay

Recall from Chapter 3 that mini-plug B contained the oil with low acid number and exhibited a much weaker low salinity effect on spontaneous imbibition compared to mini-plug A. A subarea from the 2D BSEM image and SEM-EDS mineral map of its polished section, and the corresponding subarea of the registered slice of its tomograms in the dry state and after SIH and SIL are shown in Figure 5.7. Several kaolinite-rich sub-regions are identified by SEM-EDS, mainly of low porosity at left (e.g. blue arrow), with a more porous fine aggregate at center, and looser aggregates of coarser booklets at right, all of which are brine-filled. After SIH, brine has advanced to occupy the pores associated with the agglomerate (at center) of muscovite, kaolinite and weathered Na-plagioclase and rutile grains, presumably by using their brine-filled fine pores and brine-lined surfaces as a precursor to imbibition. Further advance over quartz and Na-plagioclase grains into the largest pore body occurs during SIL (cyan arrow). Near the top right, a brine droplet formed on a cracked quartz grain after SIH allows subsequent advance during SIL to bridge the pore between this and the neighboring K-feldspar grain (cyan arrow). However, instances of these are relatively infrequent in mini-plug B for this low acid number oil.

Mini-plug C in Chapter 4 also contained the low acid number oil, but at much lower saturation after SIH, and with substantial oil movement but very little overall tertiary recovery, since local oil displacement (OB) during SIL was accompanied by an equal volume of oil re-entry into brine-filled pores (BO). Within the subarea shown in Figure 5.8, brine after SIH entered the pore bodies near the center of the field of view, and also displaced oil from the pores at the bottom right, leaving oil films and remnants on their bounding mineral surfaces. After SIL, further brine advance has occurred, removing oil from the large quartz grain indicated by the lower cyan arrow, and creating a brine bridge between a Na-plagioclase and K-feldspar grain (upper cyan arrow). A brine droplet has appeared in the middle of the pore body above this; nucleation and growth of such droplets was rare in mini-plugs A and B but much more common in C after SIH and increasingly so after SIL. The oil displaced by this meniscus advance and droplet growth then re-fills the pore at the bottom right (red arrow).

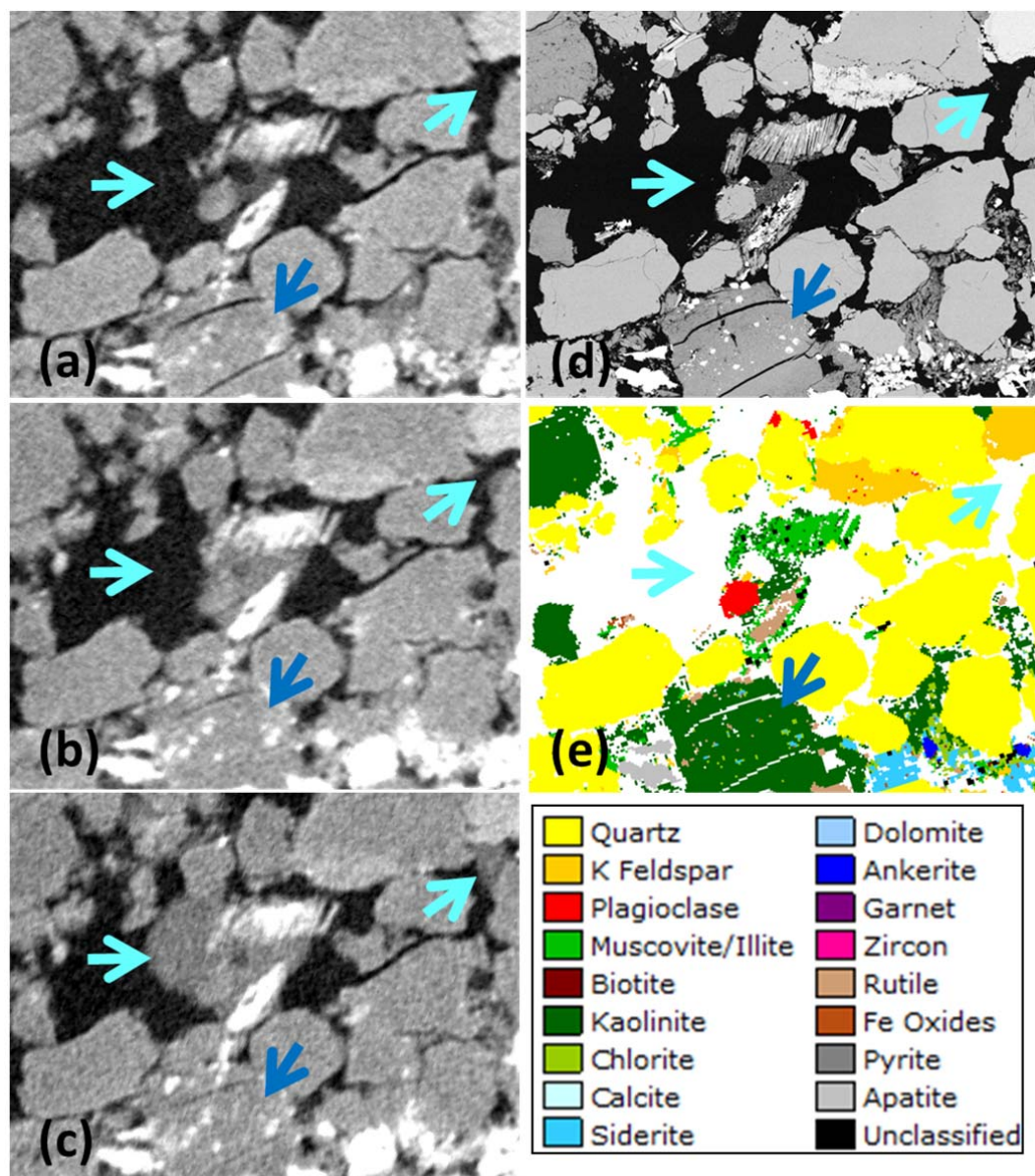


Figure 5.7 Subarea (0.54 mm × 0.41 mm) of section of mini-plug B, registered between the (a) dry tomogram, (b) SIH tomogram, (c) SIL tomogram, (d) BSEM image, and (e) SEM-EDS mineral map. Blue arrow is brine-filled clay and cyan arrow is OB region.

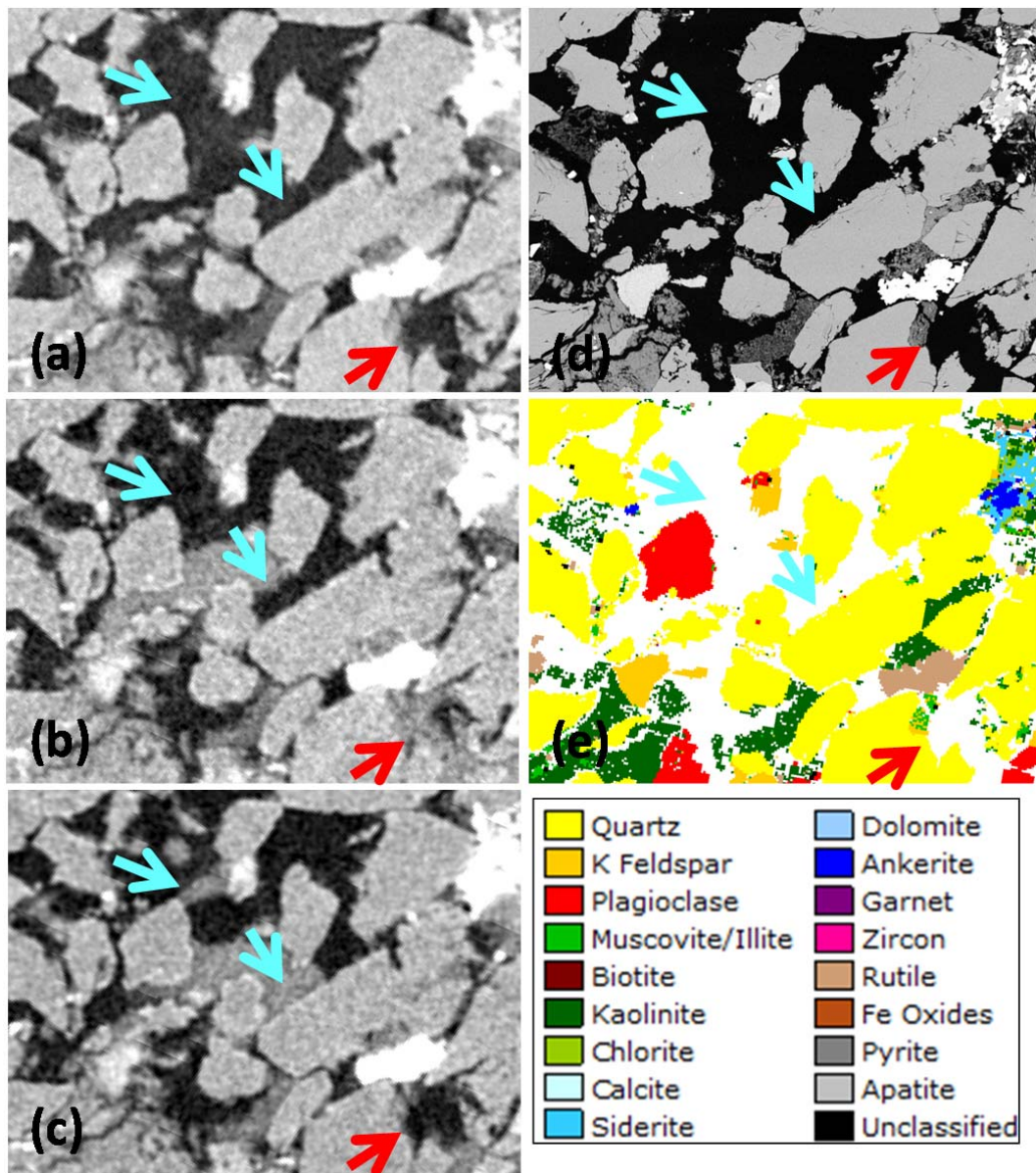


Figure 5.8 Subarea (0.54 mm × 0.41 mm) of section of mini-plug C, registered between the (a) dry tomogram, (b) SIH tomogram, (c) SIL tomogram, (d) BSEM image, and (e) SEM-EDS mineral map. Cyan arrow is OB region and red arrow is BO region.

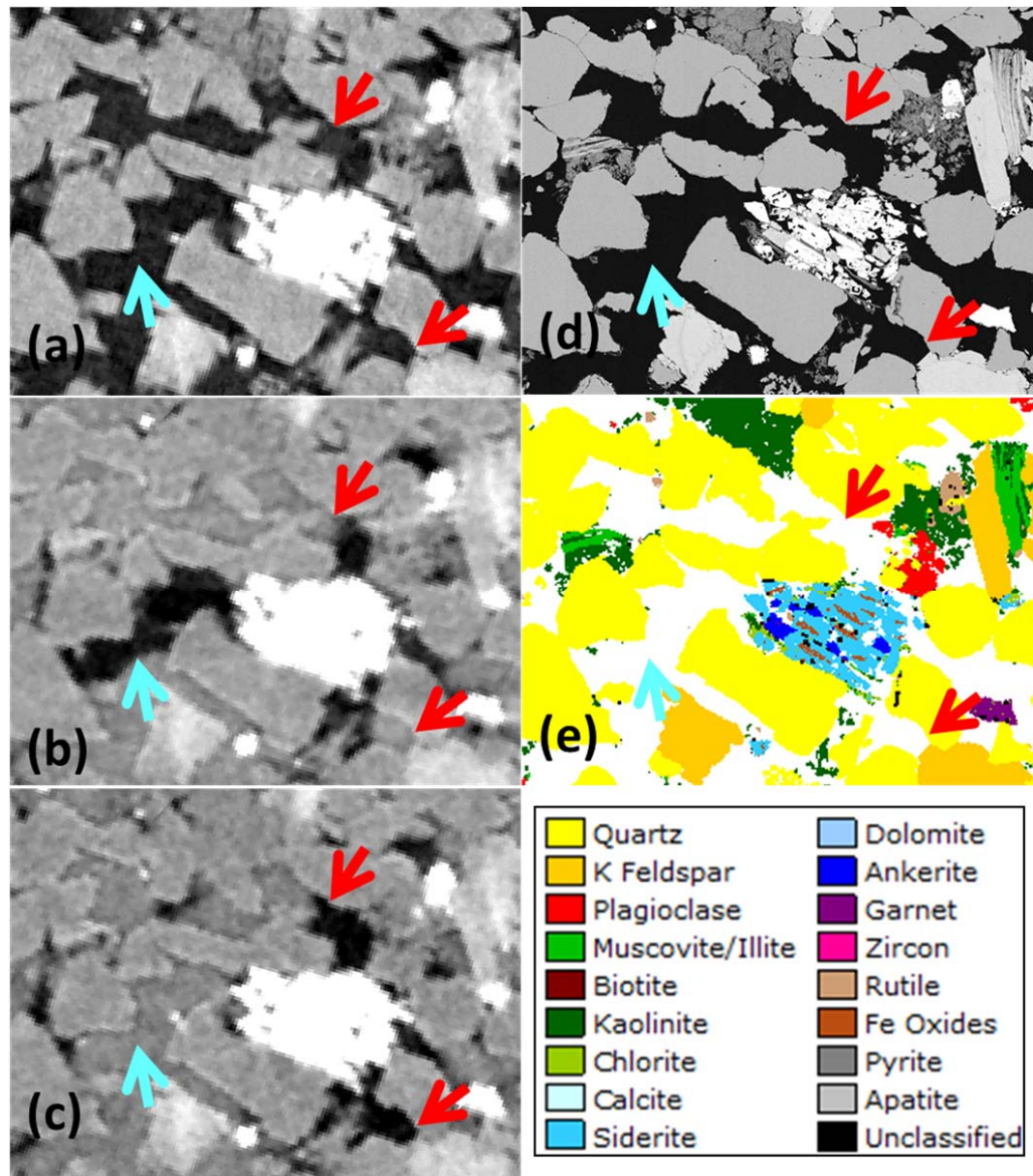


Figure 5.9 Subarea (0.54 mm × 0.41 mm) of section within the inlet sub-region of the mini-plug that underwent water flooding, registered between the (a) dry tomogram, (b) HS flooded tomogram, (c) LS flooded tomogram, (d) BSEM image, and (e) SEM-EDS mineral map. Cyan arrow is OB region and red arrow is BO region.

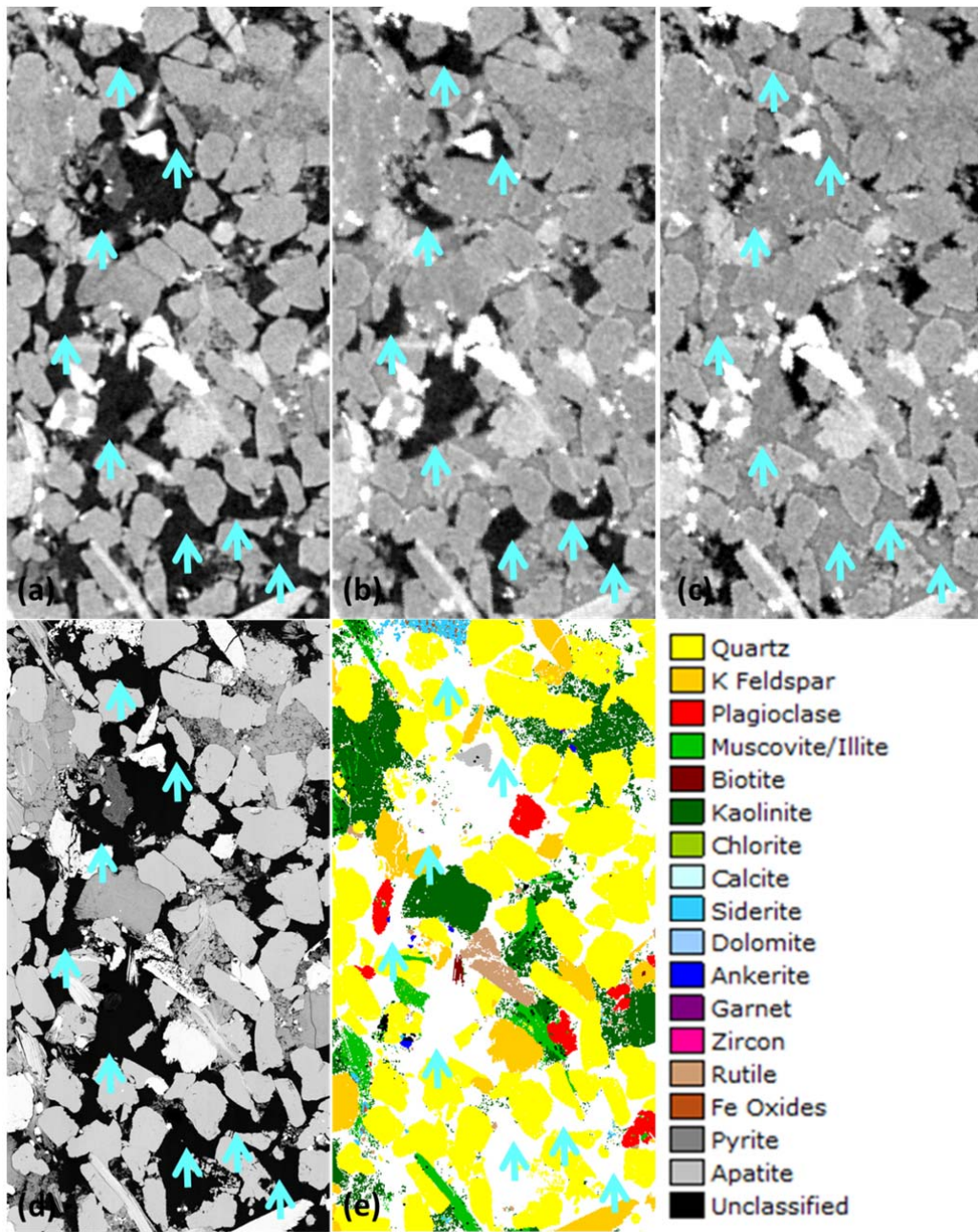


Figure 5.10 Subarea (1.34 mm $\times$ 0.70 mm) of section within the middle sub-region of the mini-plug that underwent water flooding, registered between the (a) dry tomogram, (b) HS flooded tomogram, (c) LS flooded tomogram, (d) BSEM image, and (e) SEM-EDS mineral map. Cyan arrow is OB region.

Figures 5.9 and 5.10 show a subarea from the inlet and middle sub-regions of the mini-plug of the reservoir sandstone that contained the low acid number oil and underwent water flooding with the high (HS) and in turn low (LS) salinity brine in Chapter 4. The inlet sub-region was well swept by the HS flood, and its residual there exhibited pore-

scale movement without any overall additional recovery in the LS flood. Oil saturation after HS flooding rose from small to large in the middle sub-region, due to a strong capillary effect in the outlet half; the LS flood shifted this oil bank further towards the outlet, resulting in substantial additional recovery from the middle sub-region by this false low salinity effect.

Figure 5.9 shows the distribution of the small residual oil in the inlet sub-region after HS flooding, which fills some intermediate-large pores while other pores contain only remnants as films and in corners. Comparison to the BSEM and SEM-EDS images shows that kaolinite aggregates are brine filled (throughout), and oil mainly contacts quartz grains and external surfaces of kaolinite aggregates, while K-feldspar grains appear cleaner. After LS flooding, oil filling larger pores is locally displaced, often almost completely emptying the pore (cyan arrow), with this removal mainly occurring from quartz grains. The displaced oil in turn displaces brine from neighboring pores to swell or advance the oil present there (red arrows); this local secondary drainage again appears to mainly occur over quartz grains. The preference for oil removal from clay surfaces by LS flooding, as inferred in Chapter 4, is thus partly due to this tendency for quartz grains to both lose and re-gain oil. The oil and brine occupancy of siderite-chlorite-ankerite-plagioclase aggregates generally cannot be analyzed from micro-CT as their high attenuation masks any changes in their pore occupancy. However, it is likely that the aggregate in Figure 5.9 contains oil, which acts as a conduit for this displaced oil (OB) to pass through and displace brine (BO) from its neighboring pore.

In the subarea of the middle sub-region in Figure 5.10, residual oil after HS flooding is plentiful and is associated with virtually all minerals present – quartz, kaolinite (outer surfaces), Na-plagioclase, muscovite, biotite, rutile, apatite, and to a lesser extent, K-feldspar. During LS flooding, oil is partially removed from most of these same minerals, although to a lesser extent from biotite, rutile and apatite (although these dense minerals are rare). Oil displacement appears to be more related to pore structure than mineralogy, with more removal occurring from larger open pores.

5.3.2 3D Mineral Mapping

As mentioned above, mineral identification from SEM-EDS is far more sensitive than from micro-CT, but is limited to 2D sections. One remaining challenge is to use the registration of the SEM-EDS mineral map with its corresponding slice of the rock tomogram to guide a more refined segmentation of minerals in 3D than the simple division into grain and clay phases in Chapters 2-4. An attempt at a more advanced segmentation was performed by multiple subdivision of the tomogram intensity histogram into appropriate grayscale sub-intervals, which served as seeds for further segmentation by a converging active contours algorithm. A typical result is illustrated in Figure 5.11, in which the dry-state tomogram of mini-plug A was segmented into seven mineral phases or classes. Quartz and Na-plagioclase comprise one class, as do K-feldspar and muscovite since these two also possess very similar X-ray attenuation. The segmentation of kaolinite is largely accurate within the microporous aggregates (since these are distinguishably darker in micro-CT), while the less porous, more granular (brighter) kaolinite is partly misidentified as quartz/Na-plagioclase, as is its mixtures with muscovite. The segmentation also correctly identifies siderite in some locations, although its fine-scale aggregation with chlorite, Na-plagioclase and ankerite is partly lost in the segmentation or is re-assigned to the above-mentioned lower-density (darker) classes or to a mixed class of higher density (brighter) minerals. This mixed class contains chlorite, ankerite, biotite, rutile, garnet and apatite. Pyrite and zircon are separately distinguished from these by virtue of their even higher density.

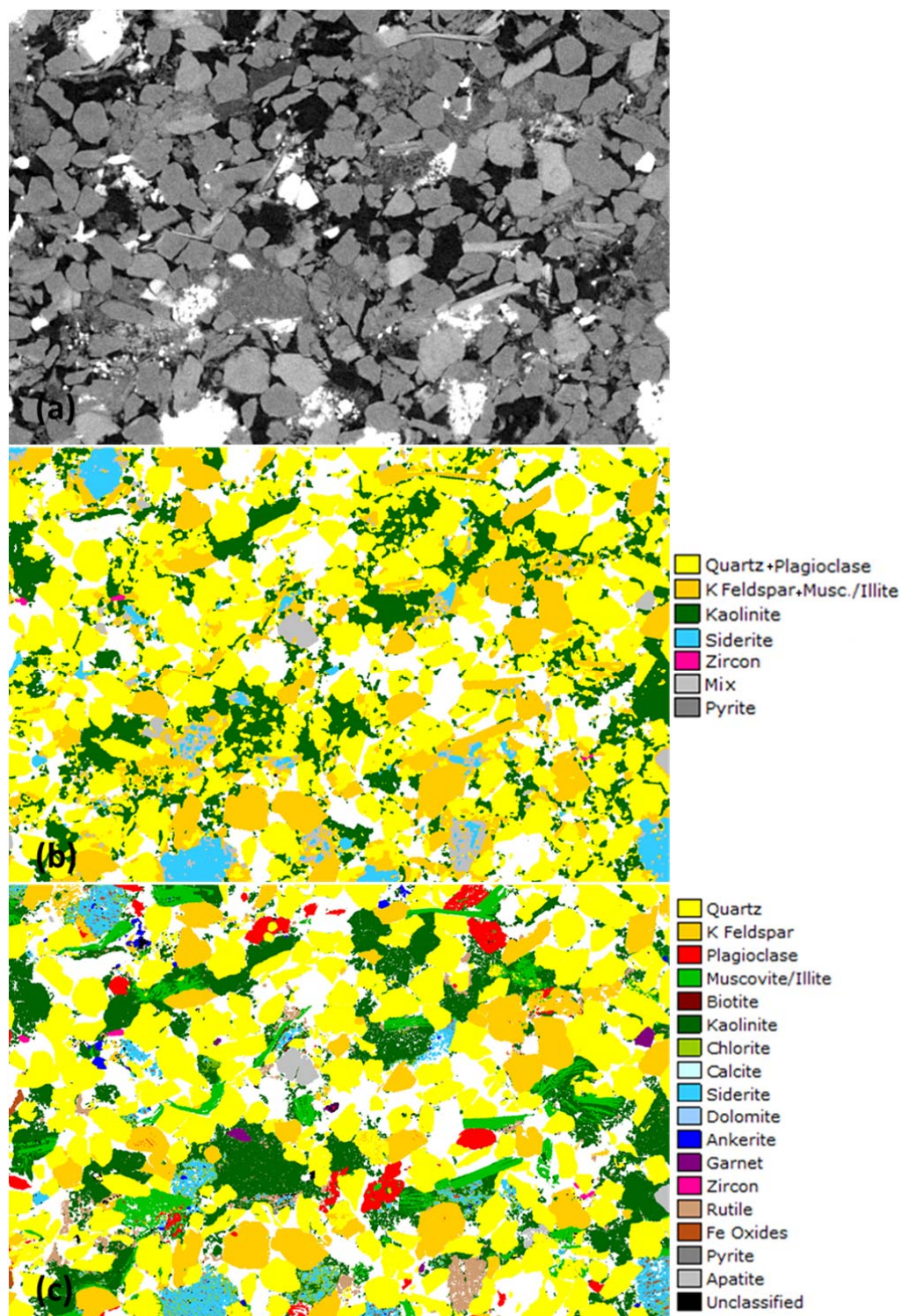


Figure 5.11 Subarea (1.90 mm × 1.25 mm) of section 2 of mini-plug A, showing the (a) dry-state tomogram and (b) its segmentation into seven mineral classes, guided by (c) the registered SEM-EDS mineral map.

5.3.3 2D Surface Area Analysis

The overlay of the registered oil distributions, from micro-CT imaging of the mini-plug after exposure to high and low salinity brines, onto the 2D SEM-EDS mineral maps of polished sections not only provides visualizations of oil release from minerals (as in Figures 5.3-5.10) but also allows calculation of oil area per mineral statistics. The quantification was performed by combining the voxel segmentation of the resolved oil phase in the SIH and SIL states (including their decomposition into sub-phases of pore occupancy) with the mineral assignment at each pixel from QEMSCAN. In their plane of registration, the occupancy of each voxel of resolved, segmented pore (oil or brine in SIH or SIL, and OB, BO, etc) at the boundary to rock phase was noted against the QEMSCAN mineral identification of the corresponding or nearest pixel. A smoothing algorithm was applied to the voxelated interface (i.e. the 1D bounding curve in this plane) to calculate the overall contact area (boundary length) of oil with each mineral over the polished section within the cylindrical mask.

The results for mini-plug A, B and C (from Figures 5.3-5.8 and Chapter 3), and the inlet and middle sub-regions of the water flooded mini-plug (from Figures 5.9-5.10 and Chapter 4) are presented in Figures 5.12-5.16, respectively. Graph (a) in each displays the relative surface area of each mineral, i.e. its interfacial area with resolved pore space as a percentage of the total over all minerals. Minerals that contribute less than 1% of total area - specifically biotite, garnet, zircon, Fe oxides, pyrite and apatite - have been omitted. The surface area (bounding curve length) of each mineral is strongly correlated to its volume (planar area) in Table 5.1, with the exception of kaolinite, which possesses much greater surface/volume at this resolution. As a result, kaolinite and quartz present roughly equal areas (each around 35% of the total), while all other minerals possess substantially less (the third most prevalent mineral, K-feldspar, contributes only 9%).

Graph (b) in Figures 5.12-5.16 plots the area of contact of each mineral with resolved oil in the high salinity state, as a percentage of the total oil contact area. Compared to the available pore area in (a), proportionally more oil contacts quartz (around 45% of the total) and less oil contacts kaolinite (around 25% of the total) in the SIH state of mini-plugs A, B and C at high oil saturation. This is consistent with the above observations that kaolinite is more frequently associated with brine, in the form of connate plus any imbibed brine advancing from it. K-feldspar surfaces again contribute around 9% to oil area after SIH in these three mini-plugs, and the other minerals all lie

below 5%. Of these, oil is slightly under-represented on the surfaces of muscovite and siderite, while it is slightly over-represented on Na-plagioclase. In the other mini-plug (of Chapter 4), after its high salinity water flooding to lower residual oil saturation (especially in the inlet sub-region), oil contact with quartz and kaolinite is more in line with their total available areas (Figures 5.15-5.16). In fact, oil is over-represented on kaolinite (40% of total oil area) in the inlet sub-region, implying that the oil that becomes associated with these clay aggregate surfaces has a stronger tendency to resist removal during HS flooding. On the other hand, oil is under-represented on siderite and K-feldspar in both sub-regions.

Graph (c) in Figures 5.12-5.16 plots the reduction in contact area of each mineral with oil from SIH to SIL, normalized in three ways in analogy to the area analyses of Chapters 2-4, namely relative to i) total interfacial area of all minerals with pore space (i.e. the normalization used in graph (a)), or ii) interfacial area of the mineral in question with pore space (i.e. the value for the mineral in graph (a)), or iii) interfacial area of the mineral in question contacting oil after SIH (i.e. the value for the mineral in graph (b)).

As mini-plug A with the high acid number oil responded most strongly to the low salinity brine, three polished sections were prepared from it and the results in Figure 5.12 are averages over these three. According to the first normalization in Figure 5.12(c) in the leftmost set of bars, oil releases from a total of 1.2% of total rock surface area from SIH to SIL. More than half of this low salinity-induced release is from quartz, as expected for this most predominant mineral, which has 4.5 times greater area of release compared to kaolinite (the second most prevalent mineral). After factoring out the area of each mineral, the distribution (in the middle set of bars in Figure 5.12(c)) is generally much more uniform, e.g. Na-plagioclase becomes almost on par with quartz, although kaolinite remains 4 times lower than quartz. The rightmost set of bars in Figure 5.12(c) provides the fairest assessment of the true tendency for oil release during SIL from each mineral, when taken relative to its oil contact after SIH. Since oil after SIH is over- and under-represented on quartz and kaolinite surfaces, respectively, this final normalization further reduces the count of relative oil release from quartz and increases that from kaolinite. However, kaolinite remains lowest of all minerals, with less than half the relative oil release of quartz, and the second most prevalent clay, muscovite, is second lowest. Both of these clays released less than 3% (area-wise) of their originally contacting oil. The low salinity effect from spontaneous imbibition in

mini-plug A thus does not appear to be directly related to preferential release from clays. In fact, release is most preferred from surfaces of siderite, followed by rutile and Na-plagioclase.

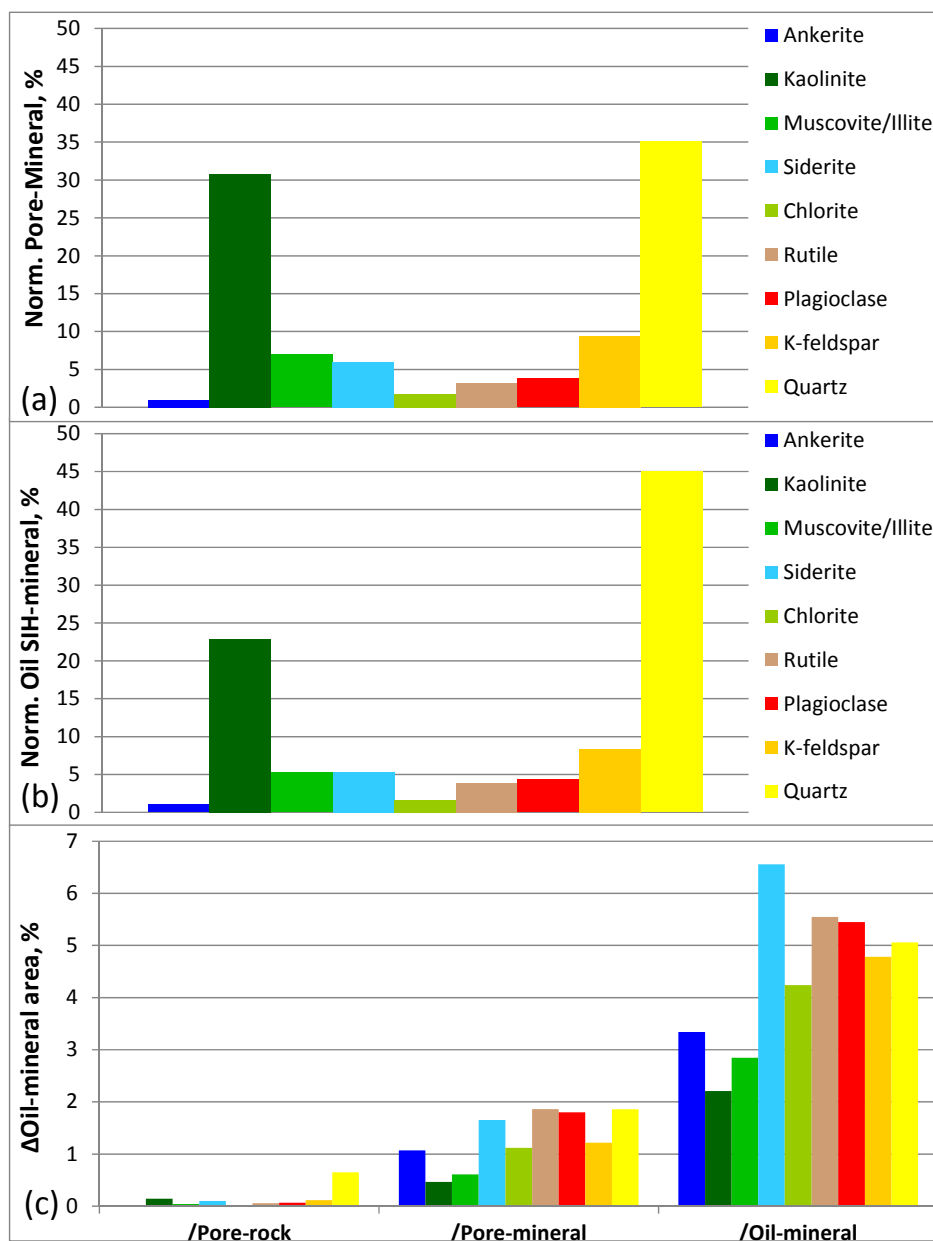


Figure 5.12 Statistics of pore and oil interfacial area with minerals for mini-plug A with the high acid number oil, from overlay of the tomographic oil distributions onto the 2D SEM-EDS mineral maps of sections. (a) Pore area of each mineral as percentage of total, (b) interfacial area of each mineral contacting oil after SIH as percentage of total, and (c) reduction in interfacial area of oil contacting mineral from SIH to SIL, normalized in three ways.

The corresponding normalizations of the reduction in contact area of each mineral with oil from SIH to SIL for mini-plug B with the low acid number oil are shown in Figure 5.13(c). As expected from the very weak tertiary recovery, the overall area of oil release is much smaller (more than 4 times less) than for mini-plug A in Figure 5.12(c). Moreover, all of the 9 main minerals in mini-plug A released at least 2% of their attached oil by low salinity brine, whereas all in mini-plug B showed less than 2% of oil removal from their external surfaces. However, the three normalized measures per mineral are each reasonably well correlated between A and B, so that the latter behaves roughly as a scaled-down version of the former. In particular, kaolinite and muscovite again show the least removal relative to their interfacial areas with pore space and with oil after SIH. It thus appears that the effect of the acid number of the oil on tertiary recovery in low salinity brine does not stem from specific and local unlocking of the intermolecular bonds between oil acid groups and particular mineral surface groups. Some small differences do exist though - K-feldspar is less reduced from A to B, and Na-plagioclase is more reduced, than most of the other minerals.

The corresponding results for mini-plug C with the low acid number oil in Figure 5.14(c) are markedly different, in line with the distinction in Chapter 3 that this sample exhibited a substantial volume fraction of oil re-invasion of brine-filled pores (BO) that almost exactly matched the oil displacement (OB) to yield almost no net recovery. The area analysis shows that overall oil contact area actually exhibits a net increase, of almost 1% of total pore area, from SIH to SIL. In particular, only the iron-containing minerals siderite and ankerite display a reduction in contact area. Kaolinite exhibits a relatively slight increase in contact area, while secondary spreading of oil is greatest over K-feldspar.

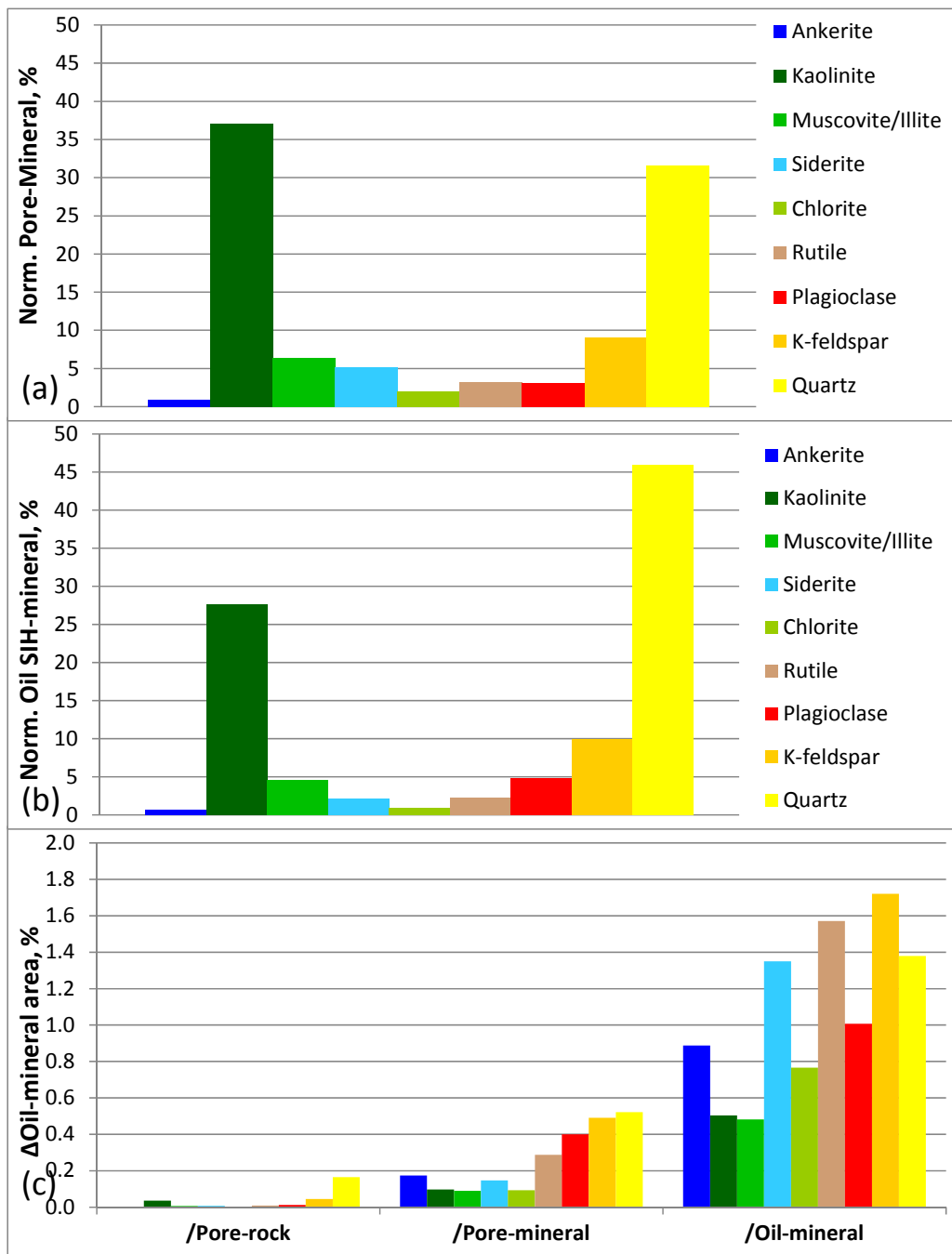


Figure 5.13 Statistics of pore and oil interfacial area with minerals for mini-plug B with the low acid number oil, from overlay of the tomographic oil distributions onto the 2D SEM-EDS mineral maps of sections. (a) Pore area of each mineral as percentage of total, (b) interfacial area of each mineral contacting oil after SIH as percentage of total, and (c) reduction in interfacial area of oil contacting mineral from SIH to SIL, normalized in three ways.

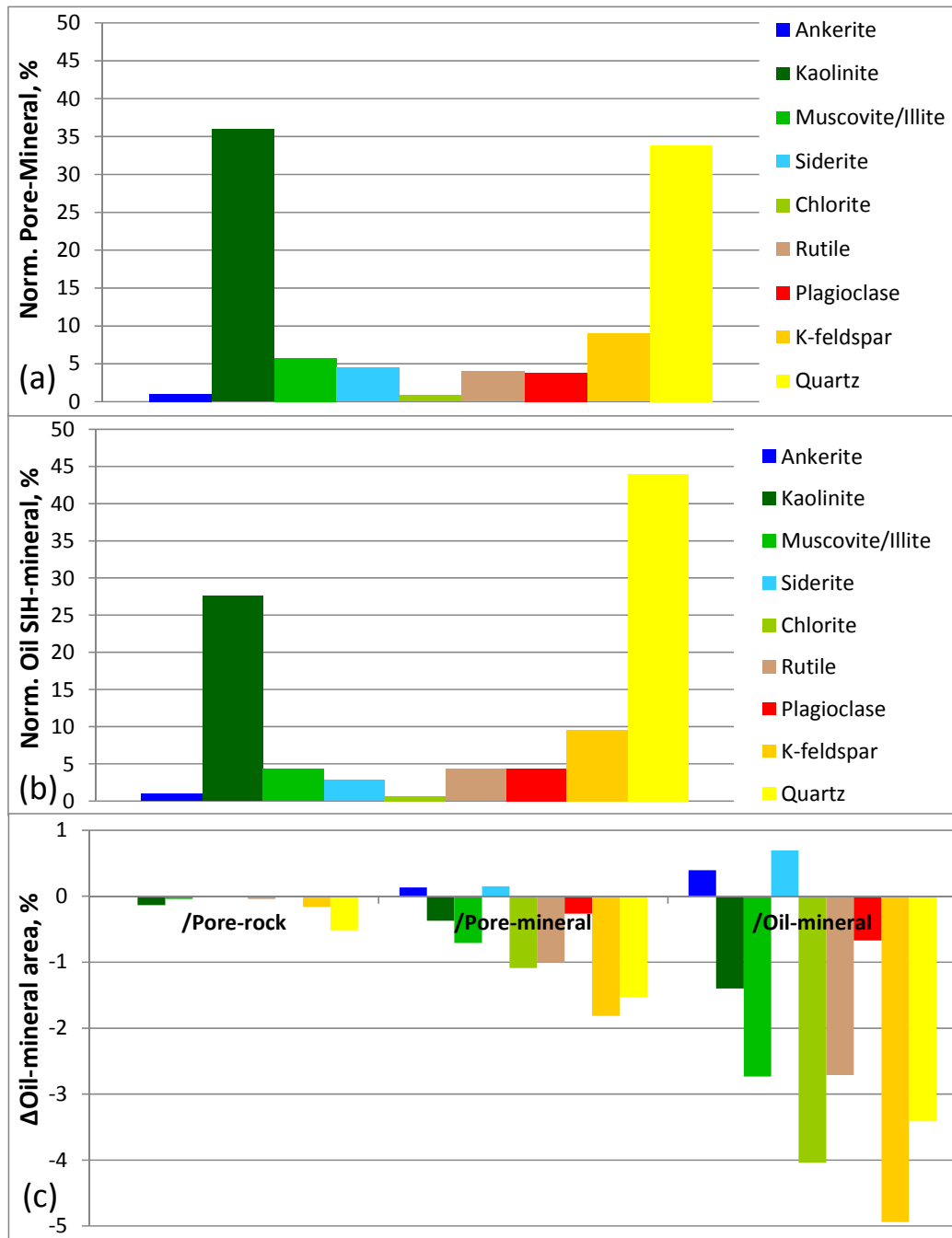


Figure 5.14 Statistics of pore and oil interfacial area with minerals for mini-plug C with the low acid number oil, from overlay of the tomographic oil distributions onto the 2D SEM-EDS mineral maps of sections. (a) Pore area of each mineral as percentage of total, (b) interfacial area of each mineral contacting oil after SIH as percentage of total, and (c) reduction in interfacial area of oil contacting mineral from SIH to SIL, normalized in three ways.

The results of oil release in tertiary mode for the other mini-plug with low acid number oil, now from HS to LS water flooding rather than spontaneous imbibition, are presented in Figures 5.15(c) and 5.16(c) within the inlet and middle sub-regions,

respectively. The inlet sub-region also exhibited substantial rearrangement of oil (OB and BO) with little net recovery, as for mini-plug C, and its contact areas in Figure 5.15(c) actually increase for all minerals after low salinity flooding. Relative to their pore or oil areas after HS flooding, this increase in oil contact area is now greatest for siderite and ankerite. However, it should be re-emphasized that pore and oil segmentation from the tomograms are most error prone in the vicinity of dense minerals such as siderite. In line with the results from mini-plug C, this low salinity-induced increase in oil contact area is much less (relative to area after high salinity) for kaolinite than for the most common grain minerals quartz and K-feldspar. This area increase from SEM-EDS is inconsistent with the decrease inferred from tomogram-extracted mineral areas in the analogous graphs in Figure 4.20(c) within the inlet sub-region (similarly for mini-plug C in Figure 3.14(c)). However the inference there that oil release was favored from kaolinite aggregates over grain minerals is not inconsistent with the result here that less re-spreading of oil occurs over kaolinite than over grain minerals.

The middle sub-region of this mini-plug was poorly swept after high salinity flooding, due to a strong capillary end effect, and showed substantial recovery on low salinity flooding, with virtually no re-entry of oil to displace brine (BO). Accordingly, the area changes in tertiary mode in Figure 5.16(c) are again all positive as for mini-plugs A and B. Again, relative release of oil from kaolinite and muscovite in low salinity is less than from quartz and K-feldspar, as was the case for all other samples, irrespective of the strength or lack of low salinity effect. However, the tertiary-mode release from kaolinite in this middle sub-region, where the low salinity effect is not operative, is almost five times less than from quartz and K-feldspar, compared to around two times less in mini-plug A (Figure 5.12(c)), in which the low salinity effect was substantial. Note that the results in Figure 5.16(c) are inconsistent with the corresponding findings from tomogram-derived mineral areas in Figure 4.20(d) within this middle sub-region, in which relative release from clay and grain surfaces was roughly equal. One likely contribution to this inconsistency is the limitation to accuracy of mineral segmentation from tomograms, as mentioned above, especially for cases such as this reservoir sandstone in which kaolinite-rich lithic fragments are incorrectly segmented as grain phase together with quartz, Na-plagioclase and K-feldspar. This issue is touched upon in the next sub-section.

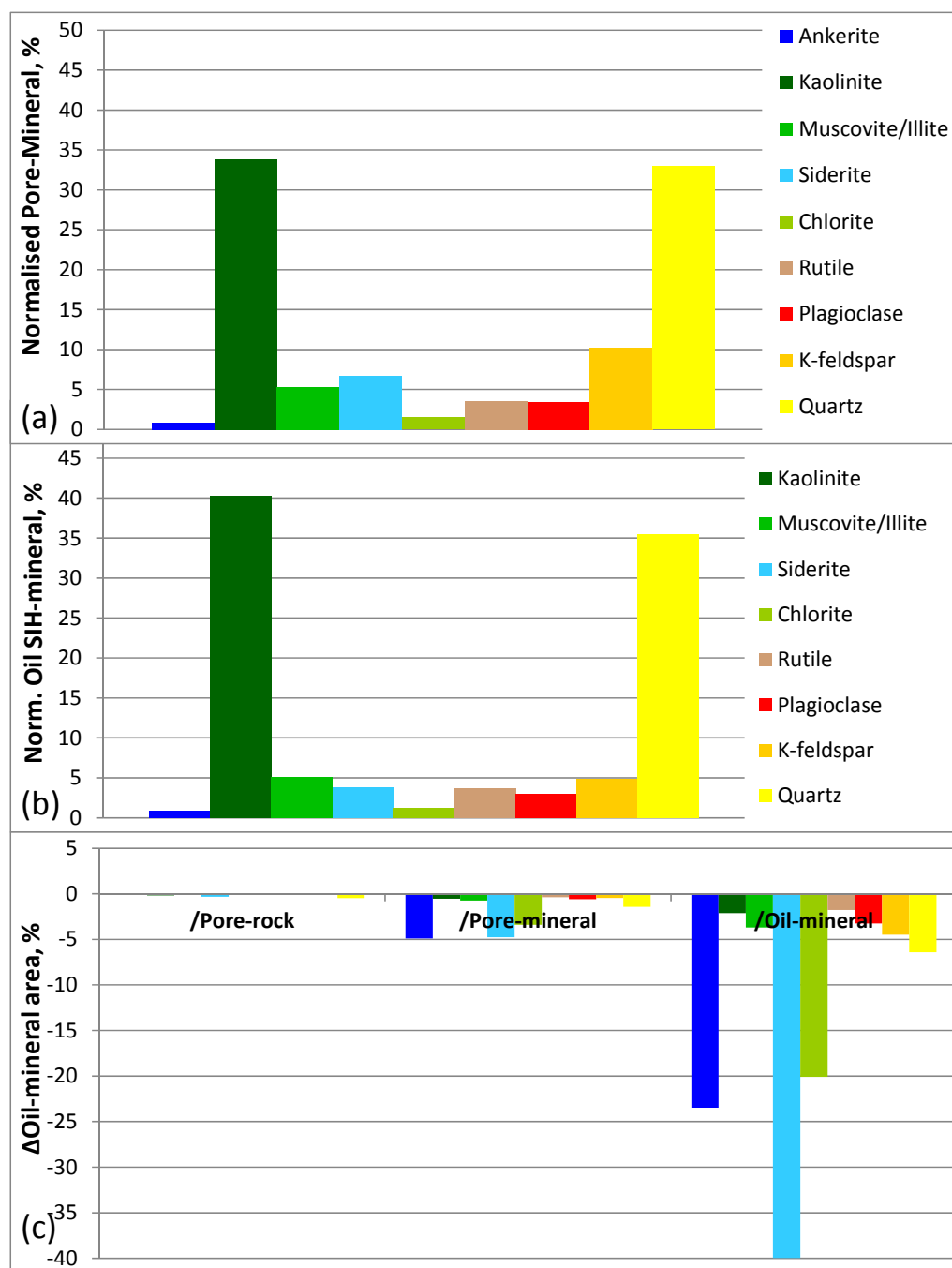


Figure 5.15 Statistics of pore and oil interfacial area with minerals for the inlet sub-region of the water flooded mini-plug containing the low acid number oil, from overlay of the tomographic oil distributions onto the 2D SEM-EDS mineral maps of sections. (a) Pore area of each mineral as percentage of total, (b) interfacial area of each mineral contacting oil after HS flooding as percentage of total, and (c) reduction in interfacial area of oil contacting mineral from HS to LS floods, normalized in three ways.

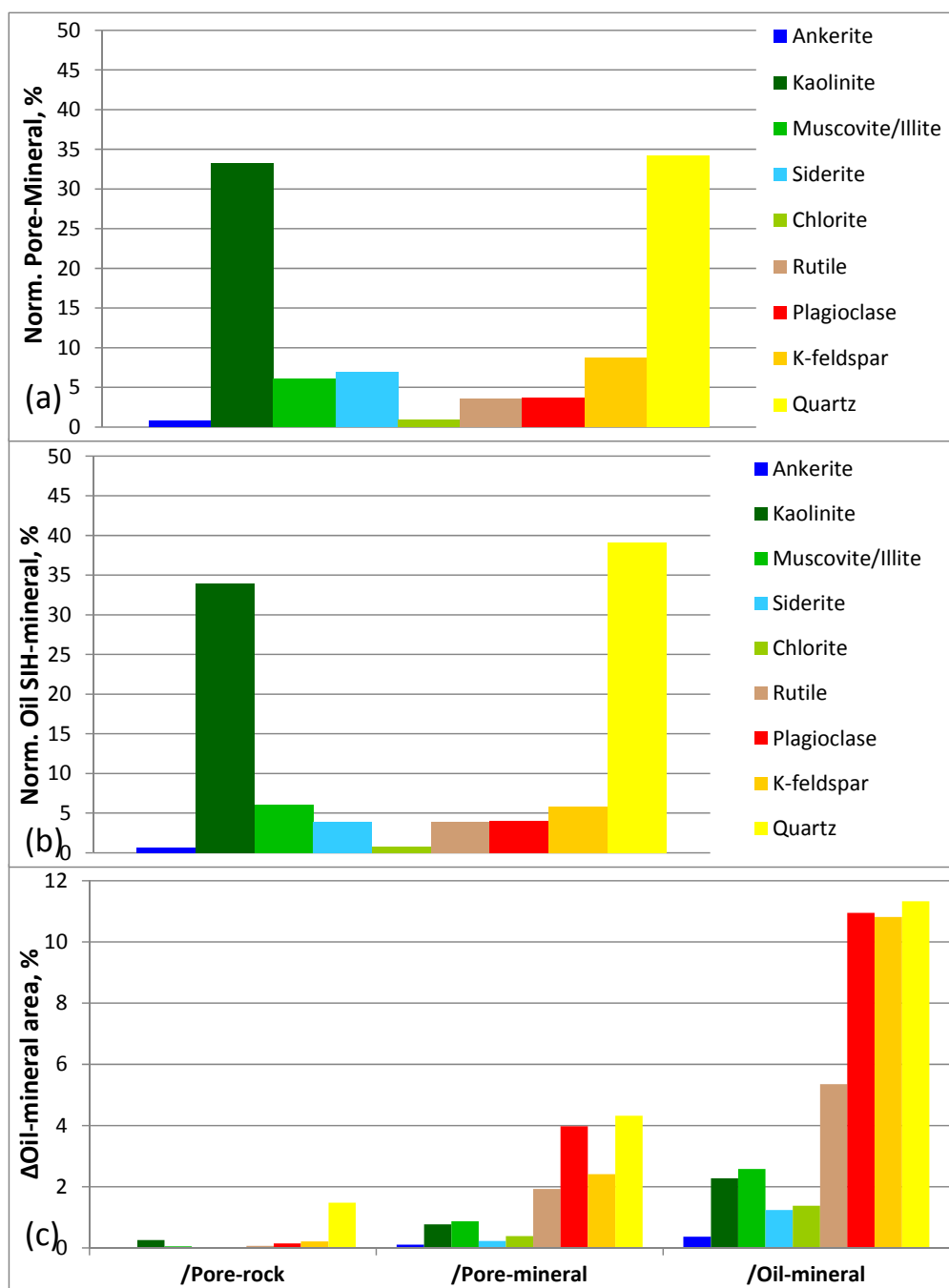


Figure 5.16 Statistics of pore and oil interfacial area with minerals for the middle sub-region of the water flooded mini-plug containing the low acid number oil, from overlay of the tomographic oil distributions onto the 2D SEM-EDS mineral maps of sections. (a) Pore area of each mineral as percentage of total, (b) interfacial area of each mineral contacting oil after HS flooding as percentage of total, and (c) reduction in interfacial area of oil contacting mineral from HS to LS floods, normalized in three ways.

5.3.4 3D Surface Area Analysis

Future work should aim to combine the approaches in Chapter 5 and Chapters 3-4, by using the SEM-EDS mineral mapping of polished sections to refine the primitive segmentation of minerals in the tomogram into the two phases, grain and clay. One preliminary attempt to segment multiple mineral phases based on correlations between SEM-EDS mineralogy and tomogram grayscale (X-ray attenuation) within the section and its registered tomogram slice was presented in Section 5.3.2 for mini-plug A. In particular, the tomogram was segmented into seven mineral phases, of which the main five were denoted:

- K: Kaolinite, together with spurious contributions from other low density minerals, mainly quartz;
- Q + P: Quartz and Na-plagioclase (indistinguishable), together with small spurious contributions from other low density minerals, mainly kaolinite;
- Kf + M/I: K-feldspar and muscovite/illite (almost indistinguishable), together with small spurious contributions from low density minerals (mainly quartz and kaolinite) and intermediate density minerals;
- S: Siderite, together with spurious contributions from other intermediate and high density minerals, mainly Fe oxides, rutile and chlorite;
- Mix: Mixture of intermediate and high density minerals, mainly siderite, apatite, chlorite, rutile and ankerite.

These five phases naturally contain overlaps and also group together some minerals of distinctly different characters and morphologies, e.g. K-feldspar and muscovite. The new mineral phases from Section 5.3.2 were then inputted into the tomographic analysis of the area of their interfaces to pore and to oil after SIH and SIL in analogy to that in Section 3.3.6, i.e. performed over the 3D volume of the registered tomograms of mini-plug A, rather than just the 2D planes of the polished sections. The analogues of Figure 5.12(b) and (c) from SEM-EDS and Figures 3.13 and 3.14(a) from primitive segmentation into grain and clay, are shown in Figure 5.17. The graph in Figure 5.17(a) of the area fraction of oil in SIH shows a distribution across these five main mineral phases that is fairly consistent with Figure 5.12(b). The contribution from kaolinite is now much greater than its underestimate of 17% from the clay phase in Figure 3.13; in fact it now exceeds the fraction from SEM-EDS in Figure 5.12(b) since some quartz is binned into this segmented kaolinite phase K as mentioned above.

The graph in Figure 5.17(b) of the area fraction of oil release from SIH to SIL is also reasonably in line with Figure 5.12(c). Irrespective of the normalization, oil release from kaolinite is consistently shown to be much less favored than from quartz (plus Na-plagioclase). Primitive segmentation in Figure 3.14(a) gave an even more extreme result, namely that oil actually increased its contact area over clay phase from SIH to SIL. It is possible that the overall slight positive release from kaolinite in Figures 5.12(c) and 5.17(b) is the sum of negative release (spreading) over the surface of pore-filling kaolinite aggregates (which were segmented as clay phase in Chapter 3) and positive release from the surface of kaolinite-rich lithic grains (which thus would behave more similarly to other grains). Note also that the mineral segmentation in Figure 5.17(b) correctly ranks the low salinity-induced oil release relative to the SIH state (rightmost set of bars) as increasing from K to Mix (mainly from ankerite, chlorite and rutile) to Kf + M/I to Q + P to S phases, as predicted from SEM-EDS sectional analysis.

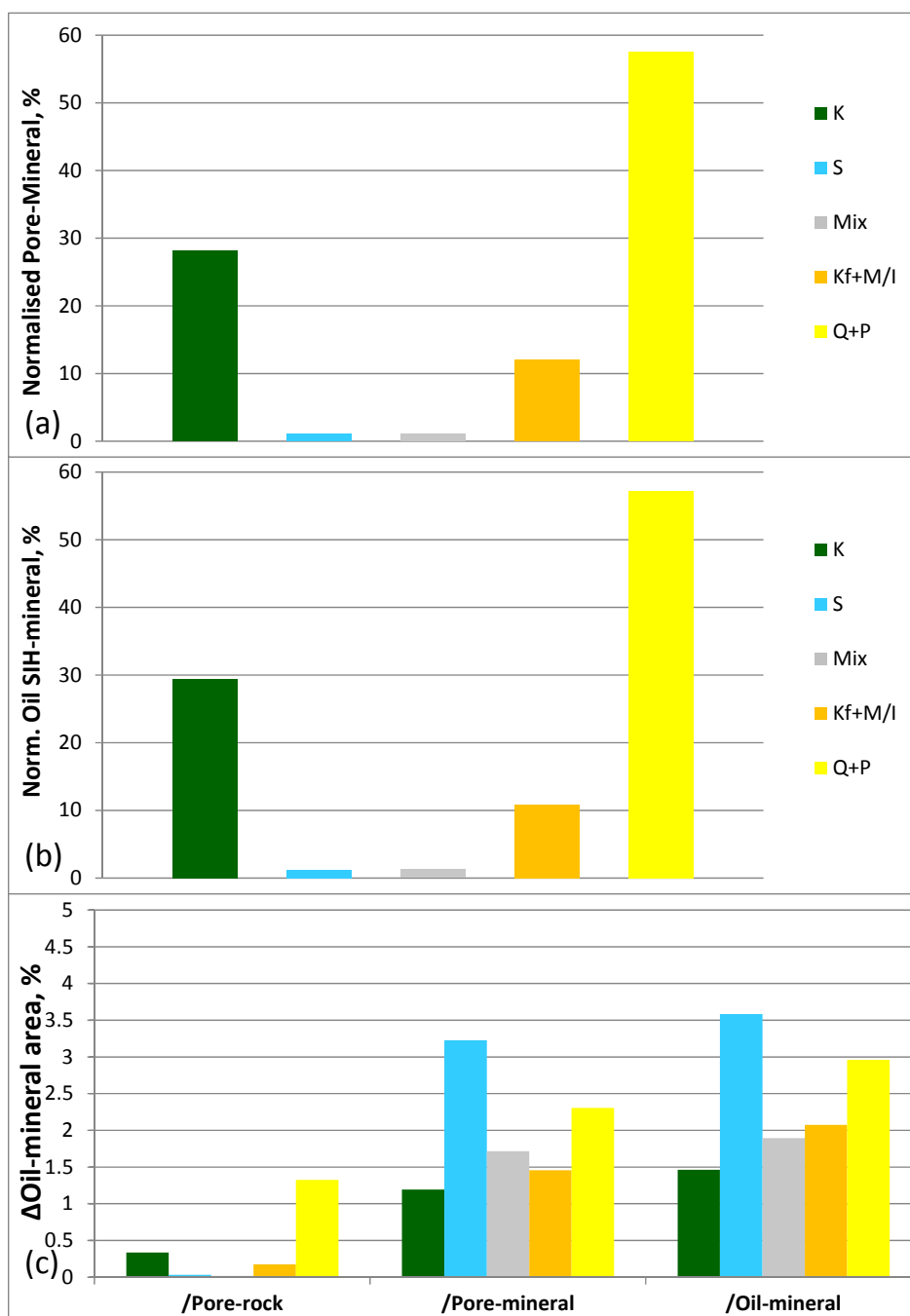


Figure 5.17 Statistics of oil interfacial area with mineral for mini-plug A with the high acid number oil, from SEM-EDS-guided tomogram segmentation of mineral phases: K (kaolinite), S (siderite), Mix (various intermediate-high density minerals), Kf + M/I (K-feldspar plus muscovite/illite), and Q + P (quartz plus Na-plagioclase). (a) Interfacial area of each mineral phase contacting oil after SIH as percentage of total, and (b) reduction in interfacial area of oil contacting mineral phase from SIH to SIL, normalized in three ways.

5.3.5 FESEM Imaging of Pore-Scale Wettability

The raw surface of the sister half of each mini-plug was imaged using FESEM up to very high resolution to discern the local presence or absence of asphaltene films on mineral surfaces, which dictate the pore-scale wettability and which remain bound to the surfaces after removal of the overlying bulk oil and brine. This mode of imaging involved focusing on native mineral surfaces, which were relatively unaffected by the cutting or fracturing, at increasing high magnification until the presence of asphaltene film could be distinguished by its characteristic nodular texture of aggregated primary nanoparticles. Unlike the BSEM and SEM-EDS mosaic imaging of the polished section, FESEM images were only acquired at isolated sites of interest over the surface, and were not registered into their corresponding location in the mini-plug tomogram. A selection of fairly representative high-resolution images of mini-plugs A and B are shown in Figures 5.18 and 5.19, respectively. Locally water-wet (clean) subareas and more oil-wet subareas bearing adsorbed/deposited asphaltenes are indicated by green and red dashed lines, respectively.

Figure 5.18(a) shows a detail of quartz or Na-plagioclase grains littered with some kaolinite platelets; parts of the grain surfaces at lower right and upper left bear a thin, patchy deposit of asphaltene, while the remainder appears clean, as do the quartz grains in (b). Image (c) is of a euhedral grain surface, the right half of which is covered by a very thin film of asphaltene which also decorates the kaolinite platelets, while the brighter region circled in green appears clean, as does the aggregate of kaolinite booklets in (d). The quartz or Na-plagioclase grains shown at higher magnification in (e) and (f) are also largely clean, aside from occasional crusty patches of asphaltene deposit circled in red. The overall impression from all acquired images is that mini-plug A is fairly clean, although the sporadic, thin asphaltene deposits apparently suffice to adhere and pin oil to limit its detachment or recovery by spontaneous imbibition in the SIH and SIL states.

For mini-plug B in Figure 5.19, around half of the facets of the quartz or Na-plagioclase grain in image (a) bear an uneven, crusty deposit (one part of which is circled in red). The more exposed surfaces of the K-feldspar grain in (b) appear to be coated in an asphaltene film, while the angular, ridged surfaces at the top are cleaner, presumably due to retention of brine. Image (c) and its higher magnification zoom-in within the blue rectangle in (d) show that many edges of kaolinite platelets in this booklet bear an

asphaltene film, while the basal planes appear cleaner, due to less chemical affinity for oil and/or stronger capillary forces holding brine in these crevices. While the majority of the grain surfaces in (e) and (f) are covered with asphaltene, clean spots in their midst are clearly apparent and are also present in (a). The more rounded examples of these clean spots presumably correspond to brine droplets which prevented asphaltene deposition during aging, while more polygonally-shaped spots were probably protected from oil exposure by lining kaolinite platelets, which were subsequently stripped from the grain during oil recovery.

The overall impression from the sets of FESEM images of these two samples is that a greater fraction of surfaces in mini-plug B are coated with asphaltene, which is generally also thicker than in A. These qualitative observations of greater oil-wetness of mini-plug B are in line with the lesser recovery and much weaker low salinity effect seen from micro-CT imaging and analysis in Chapter 3. It appears that the low acid number oil in B leads to a heavier deposition of asphaltene during aging, which precludes spontaneous imbibition during SIH and reduces the scope for wettability shift to more water wet by removal of the deposit during SIH. In comparison, the thinner, patchy deposit from the high acid number oil in mini-plug A is likely to be more conducive to recovery during SIL, at least from the locations where oil is most weakly anchored.

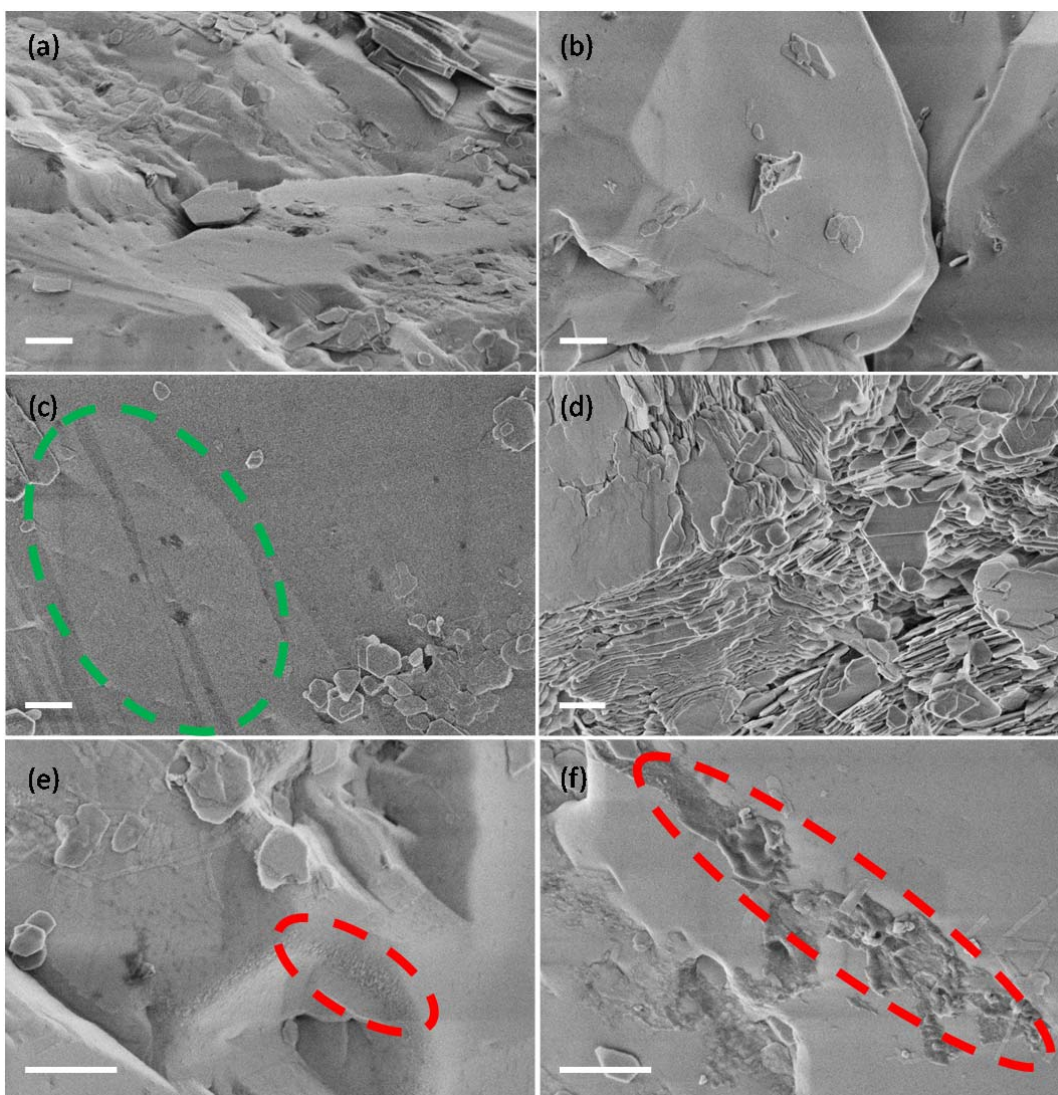


Figure 5.18 FESEM images of mineral surfaces of mini-plug A near a raw surface, with 500 nm scale bars.

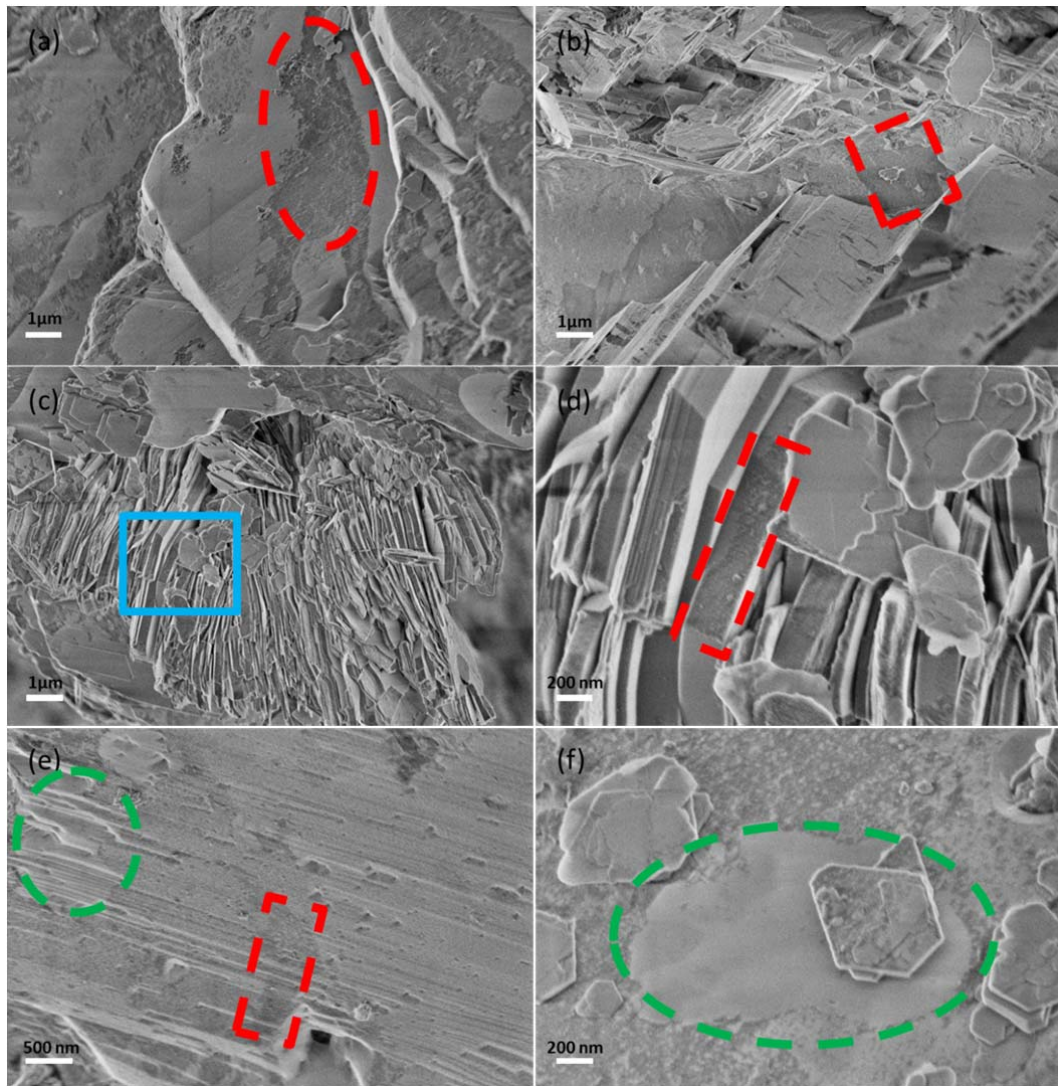


Figure 5.19 FESEM images of mineral surfaces of mini-plug B near a raw surface.

5.4 Conclusion

In this chapter, the same mini-plugs of the reservoir sandstone that underwent 3D tomographic imaging and analysis of spontaneous imbibition or water flooding experiments in Chapters 3 and 4 were further analyzed using microscopy techniques. SEM and SEM-EDS imaging and mineral mapping were performed on polished cross-sections of the mini-plugs, and these 2D images were registered into their corresponding virtual slice in the tomograms. In this way the tomographic distributions of residual oil after high and low salinity were overlain onto the mineral maps to quantify oil removal from the surfaces of each mineral. The mini-plugs from Chapter 3,

which gave little spontaneous imbibition of high salinity brine, showed less oil adhering to kaolinite than to quartz, relative to their available areas. Oil removal by spontaneous imbibition of low salinity brine was less favored from kaolinite (and from muscovite) than from silicate grains (quartz, K-feldspar and Na-plagioclase). Release from minerals was naturally much greater for the high acid number oil with a substantial low salinity effect than for the low acid number oil with little effect, however no particular mineral(s) contributed disproportionately to this difference, suggesting that the dependency of the effect on acid number is not markedly mineral-specific. In addition to SEM-EDS, ultra-high resolution images of raw cut sections of these same mini-plugs (after spontaneous imbibition of low salinity brine and cleaning) were acquired using FESEM to visualize down to nano-scales the polar components of oil remaining on mineral surfaces. Asphaltene films from the high acid number oil were less prevalent, thinner and more patchily distributed on the rock surfaces than for the low acid number oil. This suggested a stronger shift towards water-wet, in line with the tomographic evidence.

6 Summary

This thesis introduces several new tools to study the low salinity water flooding at the pore scale utilizing tomography and microscopy techniques. Chapter 2 develops a new technique in order to take advantage of series of registered 3D micro CT tomograms to discriminate various present phases of rock samples i.e. macro-oil and brine, micro-oil and brine, grain and clay aggregates. This technique is applicable to the most of micro CT studies of transport in porous media. This protocol was improved and used in Chapter 3 to investigate influence of oil composition (mainly acidic materials) in low salinity spontaneous imbibition of reservoir sandstones. Our finding shows that high TAN oil is more responsive than low TAN oil to the low salinity brine.

Chapter 4 addresses oil recovery by low salinity water flooding in series of core flood tests and concluded that oil configuration in pores after low salinity water flooding implies that rock becomes more water wet. Although strong capillary end effect dominated the mini-plug, analysis of region of interest was performed to remove the true low salinity effect from the artificial contribution to oil recovery.

Chapter 5 integrates the tomography and microscopy techniques to study oil recovery of previous experiments from external surfaces of local minerals. FESEM analysis of pore surfaces also provided further insight into the wettability of rock structures after low salinity water flooding.

Future Work

With recent advances in digital core analysis, the potential future research would be investigating the low salinity water flooding at reservoir temperature and pressure. This can assist to understand and investigate the low salinity effect in more realistic reservoir conditions. Further, the low salinity effect can be investigated on standard core samples with both region of interest (ROI) and whole core scanning to reduce the uncertainties and errors due to the size of mini-plugs and help researchers to scale up information from small mini-plugs to the standard core samples.

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