The Effect of Mixed Wettability on Pore-Scale Flow Regimes Based on a Flooding Experiment in Ketton Limestone

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Geophysical Research Letters

RESEARCH LETTER
10.1029/2018GL081784

Key Points:
- Ganglion dynamics in mixed-wet systems is observed
- Oil-filling events are more frequent and of larger size in mixed-wet systems and depend on the aging state/wettability of the rock surface
- This behavior may impact the overall relative permeability and must be considered in pore-scale flow simulations

Supporting Information:
- Supporting Information S1

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Citation:
Rücker, M., Bartels, W.-B., Singh, K., Brussee, N., Coorn, A., van der Linde, H., et al. (2019). The effect of mixed wettability on pore-scale flow regimes based on a flooding experiment in Ketton limestone. *Geophysical Research Letters*, *46*, 3225–3234. https://doi.org/10.1029/2018GL081784

Received 20 DEC 2018
Accepted 28 FEB 2019
Accepted article online 6 MAR 2019
Published online 18 MAR 2019

The Effect of Mixed Wettability on Pore-Scale Flow Regimes Based on a Flooding Experiment in Ketton Limestone

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Abstract Darcy-scale multiphase flow in geological formations is significantly influenced by the wettability of the fluid-solid system. So far it has not been understood how wettability impacts the pore-scale flow regimes within rocks, which were in most cases regarded as an alteration from the base case of strongly water-wet conditions by adjustment of contact angles. In this study, we directly image the pore-scale flow regime in a carbonate altered to a mixed-wet condition by aging with crude oil to represent the natural configuration in an oil reservoir with fast synchrotron-based X-ray computed tomography. We find that the pore-scale flow regime is dominated by ganglion dynamics in which the pore space is intermittently filled with oil and brine. The frequency and size of these fluctuations are greater than in water-wet rock such that their impact on the overall flow and relative permeability cannot be neglected in modeling approaches.

Plain Language Summary In geological systems, in particular in oil reservoirs, the wetting condition of rock, the preference of a fluid to be in contact with a surface in the presence of another fluid, has a significant impact on multiphase flow. Often a simplified picture based on static, wettability-dependent fluid configurations is used as a basis for modeling where the fluids are assumed to flow through the porous rock within definite connected pathways. Our research, which is based on a time series of 3-D images obtained during multiphase flow showing the pore-scale fluid configurations of the brine and oil, demonstrates that this picture is too simplistic. In reality the flow paths change. In systems in which one phase is strongly wetting those changes are fast, small, and rare. However, oil reservoirs are mostly mixed-wet as surface active components contained in crude oil alter the rock surface. In such mixed-wet situations, we observe that the movement is slower (minutes instead of seconds), is more frequent, and involves larger fluid volumes. This indicates a different flow regime that cannot be estimated from an extrapolation from strongly wetting rock. This has consequences for the way how multiphase flow in mixed-wet rock is described in models.

1. Introduction

Wettability, the preference of a surface to be in contact with one fluid in the presence of another immiscible fluid, is known to be a key property that controls multiphase flow in porous media. It therefore plays a role in various geological applications such as CO_2 sequestration (Chaudhary et al., 2013; Farokhpoor et al., 2013), and oil recovery (Abdallah et al., 2007; Agbalaka et al., 2008; Anderson, 1987b; Jadhunandan & Morrow, 1995). In oil reservoirs, crude oil or other organic material has been in contact with the mineral surfaces inside the pore space. As a consequence, a wettability alteration occurs from water-wet to mixed-wet or oil-wet conditions, depending on crude oil, brine, and rock specifics (Bartels et al., 2019) with spatially varying local contact angles greater than 90° (Anderson, 1986) depending on mineralogy and surface texture (Rücker, 2018; Schmatz et al., 2015). The wettability impacts both the capillary pressure-saturation relationship and relative permeability, which are used, for instance, in field-scale reservoir models to assess reservoir performance and hydrocarbon recovery strategies. The water relative permeability typically increases, and the oil relative permeability decreases for more oil-wet rock (Anderson, 1987b), which has a significant impact on the fraction of produced water in oil recovery.

Even though wettability is an important factor, it is rarely directly assessed. Instead, capillary pressure and relative permeability are determined in Darcy-scale core flood experiments. However, core flood experiments are time consuming and costly. Several computational approaches have been developed to predict relative permeability and capillary pressure (Armstrong et al., 2016; Blunt et al., 2002; Joekar-Niasar et al., 2008; Koroteev et al., 2014; Landry et al., 2014). To assess whether the modeled flow regimes and the predicted saturation functions are realistic, the underlying pore-scale processes need to be understood. So far most modeling approaches have been developed and/or validated under water-wet conditions (Armstrong et al., 2016; Blunt et al., 2002; Koroteev et al., 2014) assuming model systems (Landry et al., 2014; Masalmeh, 2002; Rabbani et al., 2017; Valvatne & Blunt, 2004), while for many subsurface applications mixed-wet scenarios with real crude oil are more relevant (Abdallah et al., 2007). One of the fundamental questions that our work addresses is whether pore-scale flow regimes under mixed-wet and water-wet conditions are different, by investigating the flow behavior of crude oil in rock that has undergone wettability alteration in a similar way as in the reservoir.

1.1. Pore-Scale Processes in Water-Wet Systems

Strongly water-wet systems are characterized by the aqueous phase coating the solid surface, that is, pore walls, while the oleic phase is nonwetting and therefore occupies mainly the center of pores (Anderson, 1987a). This has consequences for the mobility of water and oil phases: The oil phase has a high mobility as long as it is connected to the bulk. However, oil clusters may be trapped by capillary forces (Anderson, 1987a). In contrast, viscous effects may mobilize the oil and lead to less trapping. The balance between viscous and capillary forces is defined as the capillary number $N_c = u\eta/\sigma$, with liquid velocity u, viscosity η, and interfacial tension σ. Avraam and Payatakes (1995) studied the dependence of flow regimes on the capillary number N_c in 2-D micromodels and observed two flow regimes, connected pathway flow (where the two phases flow solely through the parts of the pores the respective phases percolate) and ganglion dynamics. Under a ganglion dynamics flow regime, clusters or ganglia of the nonwetting phase move through the entire pore space by breakup and reconnection.

Although these observations in 2-D micromodels can provide some insight into flow mechanisms, it can also be misleading. In many cases, micromodels are chemically homogeneous and have a significantly simplified structure and smooth surfaces, which means they do not represent the full complexity of natural systems (e.g., mixed wettability, surface texture; Blunt, 1997; Lenormand & Zarcone, 1984; Mohanty et al., 1987). In addition, percolation thresholds are different in 3-D compared to 2-D.

X-ray microcomputed tomography (μCT) does provide 3-D insight into the configuration of wetting and nonwetting phase fluids in the pore space at a resolution that even allows the assessment of local wetting conditions via the measurement of in situ contact angle (Andrew et al., 2014). With a temporal resolution of only several seconds, which may be obtained, for example, at synchrotron beamlines, the flow behavior of both model and natural systems can be studied (Armstrong et al., 2016; Berg et al., 2013; Bultreys et al., 2015; Dobson et al., 2016; Reynolds et al., 2017; Schlüter et al., 2016; Singh, Menke, et al., 2017).

From such experiments, we know that during two-phase flow in water-wet systems different types of filling events may occur. Examples of water-filling events are snap-off (Lenormand et al., 1983) and piston-like displacement (Dixit, McDougall, et al., 1998; Lenormand et al., 1983). Oil-filling events occur when the pore space initially filled with water is replaced by oil: Under strongly water-wet systems so-called Haines jumps, in which multiple pores are filled rapidly, are observed during drainage (Berg et al., 2013; Haines, 1930; Morrow, 1970). These events lead to significant rearrangement of the phases in the pore space (Andrew et al., 2015; Berg et al., 2013). During imbibition, smaller fluid rearrangements are observed due to oscillations of the fluid-fluid interface caused by pressure waves, as known from micromodel experiments (Moebius & Or, 2012). These oscillations may lead to reconnection of previously trapped clusters (Rücker et al., 2015) and therefore are considered as ganglion dynamics behavior.

The overall flow regime in water-wet situations is a combination of ganglion dynamics and connected pathway flow. However, most of the fluid flow occurs through connected pathways over most of the saturation range (Armstrong et al., 2016), and while ganglion dynamics has a large impact on the local fluid configurations (Berg et al., 2016) it has no or only a very limited flux contribution (Armstrong et al., 2016).

1.2. Mixed- and Oil-Wet Systems at the Pore Scale

Crude oil natural rock systems, though, are often mixed-wet, which means the wettability varies across the pore space with local contact angle values both above and below 90° (Salathiel, 1973). This variation of wettability can be due to mineral heterogeneities and after the exposure of a rough solid surface to oil phases rich in surface active components.

On a molecular scale, wettability alteration is caused by the interaction of surface-active (polar) crude oil components with the mineral surfaces (Buckley et al., 1998). Variation in surface charges, associated with the mineral composition, cause variation of the local wettability. Surface-active components of the crude oil may also interact with the aqueous phase and are known to form emulsions (Freedman et al., 2000; Hannisdal et al., 2007; Kokal, 2002; Mandal & Bera, 2015; McLean & Kilpatrick, 1997; Opedal et al., 2009; Paso et al., 2009; Rezaei & Firoozabadi, 2014). How such emulsions impact flow behavior is not yet fully understood.

At the pore and pore network scale, wettability may also depend on the saturation history of the rock (Salathiel, 1973). If a pore was never occupied by oil, wettability might not be altered. Furthermore, surface roughness, facilitating the formation of thin water films, may prevent the oil from getting in touch with the surface (Herminghaus, 2000). For this reason, the wettability may vary on length scales from a fraction of a pore up to a few pores (AlRatrout et al., 2018).

So far 3-D studies on mixed-wet and oil-wet systems have focused on wettability characterization through observing fluid distributions and contact angle measurements before and after waterflooding (Alhammadi et al., 2017; Al-Raoush, 2009; Celauro et al., 2014; Geistlinger & Mohammadian, 2015; Iglauer et al., 2012; Murison et al., 2014; Singh et al., 2016).

However, all these studies miss the effect of wettability on flow dynamics (Bultreys et al., 2018; Singh, Scholl, et al., 2017; Zhao et al., 2016), that is, the connection between wetting behavior and pore-scale flow regimes. Our current understanding is often derived from the better understood strongly water-wetting scenario extrapolated to mixed-wet situations by only changing contact angles. It is not clear if this extrapolation is valid or whether pore-scale flow regimes and associated length and time scales experience a qualitative change. This is expected based on observations by Zou et al. (2018) who found indirect evidence for increased ganglion dynamics in mixed-wet systems but did not observe this directly. In this paper we assess the significance of ganglion dynamics in a mixed-wet system by acquiring times series of 3-D pore-scale fluid configurations from fast pore-scale imaging.

2. Materials and Methods

We use fast X-ray μCT imaging to investigate the flow regime during waterflooding in a rock aged in crude oil. These results are compared with strongly water-wet data from previous studies (Singh, Menke, et al., 2017).

2.1. Sample Selection and Preparation

Samples of Ketton carbonate (Muir-Wood, 1952) with a porosity of $\varphi = 24\%$ and permeability of $K = 3$D and a size of 5-mm diameter and 20-mm length were used for the μCT study. The samples were first cleaned with isopropanol then saturated with high salinity brine and desaturated with crude oil by flooding at the rate of 500 μl/min. The mobility ratio defined by $M_{w/o} = \mu_o/\mu_w$ was for the chosen system $M_{w/o} = 5.47$. The samples were aged for 1 week at an elevated temperature (70 °C) and pressure (3 MPa). The high-salinity brine contained 200 g/L potassium iodide (KI, ionic strength 0.6 mol/L), which functions as an X-ray contrast agent. The properties of the reservoir dead crude are shown in the supporting information (Tables S1 and S2).

2.2. Waterflood Experiments Using Fast μCT

The flooding experiments were performed at the TOMCAT beamline of the Swiss Light Source at the Paul Scherrer Institute, which is a fast synchrotron-based X-ray μCT facility. The samples were mounted on top of a flow cell described in (Armstrong et al., 2014) containing two remotely controlled piston pumps. The sample was flooded with a flowrate of 30 μl/min which corresponds to capillary dominated flow at $N_c = 2.3 \times 10^{-6}$. The images were captured 2 mm above the inlet with 7 s per full 3-D image with a voxel size of 3 μm (Bartels et al., 2017).

2.3. Image Processing

The images were reconstructed using the Paganin method (Marone & Stampanoni, 2012; Paganin et al., 2002), corrected for beam-hardening effects, and filtered with a nonlocal means filter (Buades et al., 2005; Buades et al., 2008; AVIZO 9.0, Thermo Fisher).

The images were segmented by combining threshold and watershed segmentation in a custom script described in the supporting information Text S1 and further processed using commercial image analysis software (AVIZO 9.0). The wettability of the system was assessed visually and by contact angle measurements following the workflow described in Andrew et al. (2014) based on the final image of the flooding sequence. Only menisci between oil and brine, which appeared within the volume initially occupied by oil, were considered. The 100 individual measurements were taken through the denser (brine) phase. Binarized images were used to determine and quantify event types by overlaying consecutive images as in Rücker et al. (2015).

2.4. Imbibition in a Water-Wet Sample

The results of the mixed-wet crude oil-brine-rock system were compared with a water-wet reference data set on the same rock (Ketton) published in Singh, Menke, et al. (2017). This reference data set represents a flooding experiment conducted at the synchrotron beamline I13-2 of the Diamond Light Source (UK). The Ketton rock sample had a diameter of 3.8 mm and a length of 10 mm. A 23-wt% KI solution was used as the aqueous phase and *n*-decane as the oleic phase. The mobility ratio was $M_{w/o} = 0.94$.This rock-fluid-fluid system showed strongly water-wet behavior. During the waterflood the brine phase was injected into the decane-saturated sample with a flow rate of 44.75 nl/min which corresponds to $N_c = 1.08 \times 10^{-9}$ for 4.6 hr. Following Lenormand et al. (1988) the mobility ratio and capillary number indicate that both experiments discussed in this work belong to the same flow domain and are therefore comparable. The images with a voxel size of 3.28 μm and a time resolution of 38 s have been reconstructed, filtered, and segmented following the workflow described in Singh et al. (2018). As for the mixed-wet sample the resulting images were used for event determination and quantification. Due to the low flow rate applied, only every 20th image was considered.

3. Results and Discussion

X-ray μCT allows one to observe the fluid configuration and distribution at the pore scale directly and to assess wettability of the system and its impact on flow behavior.

3.1. Analysis of Grayscale Images

An image obtained during the flooding experiment of the aged rock with fast X-ray μCT and the corresponding histogram of grayscale values are shown in Figure 1. Besides rock (gray), oil (black), and brine (white), we also observe an additional phase in the pore space with a grayscale value between that of the two fluids.

A thorough analysis discussed in Bartels et al. (2017) led to the conclusion that a water-in-oil-emulsion is responsible for this partial volume effect (supporting information Text S2). Emulsions in crude oil brine systems form in the presence of surface-active components (Kokal, 2002; McLean & Kilpatrick, 1997; Rezaei & Firoozabadi, 2014). Those components are also known to alter wettability (Buckley et al., 1998).

3.2. Wettability of the Aged Rock

The wettability can be assessed visually by inspection of the last scan of the flow sequence shown in Figure 2. Contrary to water-wet systems, some oil remains on the surface of the grains or within small pores and throats as shown in Figure 2b. Such oil-patches were also observed in oil-wet systems (Iglauer et al., 2012) and in mixed-wet 2-D micromodels (Jung et al., 2016) and indicate the existence of oil-wet surfaces.

The system shows a large-scale mixed wettability, in which crude oil mainly occupies larger pores (Dixit, Buckley, et al., 1998; Djurhuus et al., 2006). Such systems form as a result of primary drainage in which the oil invades into a water-wet rock and accumulates within the large pore bodies. Mineral surfaces in direct contact with crude oil will then experience aging. During this process those pores containing crude oil will turn more oil-wet. Hence, the sample remains water-wet in pores and throats without oil. During the waterflood the oil will stick to the surface in the large pores. Therefore, the fluid distribution after primary drainage remains preserved and is reflected by the initial fluid distribution at lower oil saturation (Figure S1).

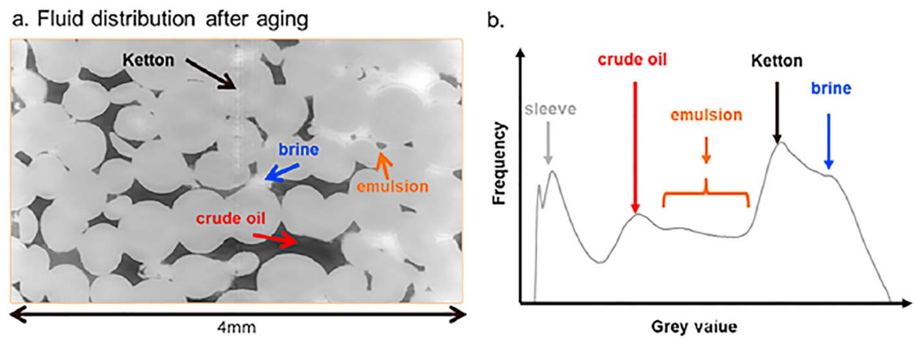

Figure 1. (a) In the grayscale images obtained at the beginning of the flooding experiment we see the rock (gray spheres), crude oil (black), and brine (bright phase). Furthermore, a third phase with an intermediate gray value appears in the pore space. (b) The corresponding grayscale value histogram illustrates that the intermediated phase is between the gray value of oil and rock, which indicates that the phase is an emulsion.

In addition, surface roughness of a rock may lead to a small-scale mixed-wet pattern. During primary drainage only the peaks of the rock surface contact the crude oil and are altered to oil-wet, while the deep holes on the surface related to the microporosity of the rock remain water-wet (Alyafei & Blunt, 2016; Kovscek et al., 1993; Schmatz et al., 2017). The resolution of the recorded μCT images is not sufficient to observe such a pattern, but the contact angle distribution obtained in this system indicates its presence. When the volume of an oil cluster is larger than the oil-wet parts of the surface, the menisci of this cluster would rest at the edge of the oil-wet patch and hence form a water-wet contact angle (Israelachvili, 2011; Naidich et al., 1995). When the volume is smaller, the oil drop would spread along the patch and likely be below the image resolution and hence no contact angle is determinable.

The contact angles show a distribution between 20° and 90° (Figure 2c). Compared to the water-wet Ketton limestone with an inert model oil investigated in Scanziani et al. (2017) the mixed-wet Ketton sample aged

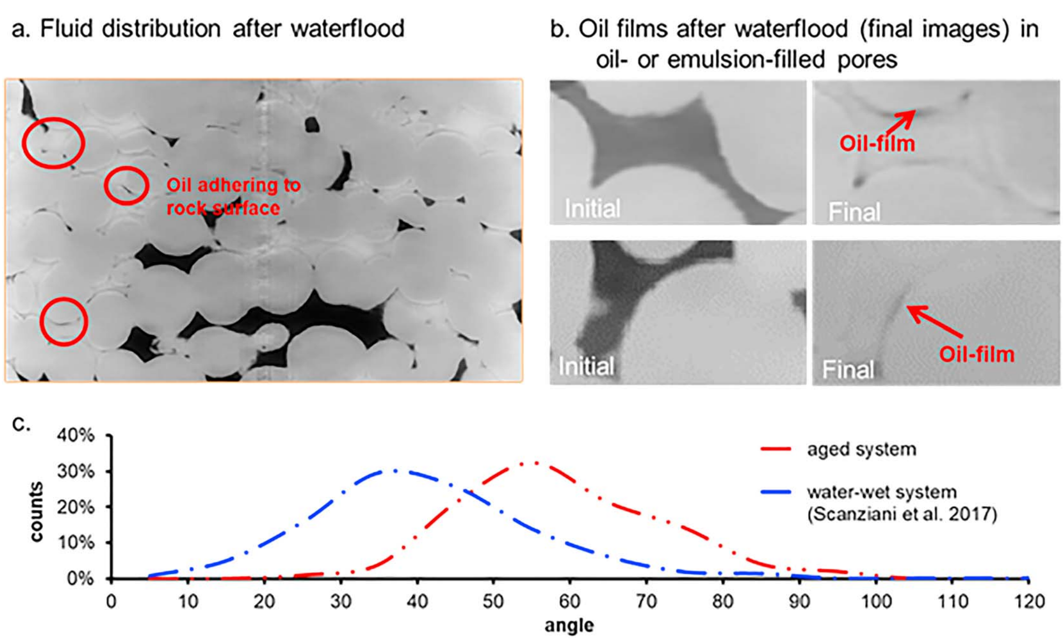

Figure 2. (a) After waterflooding we observe a reduction of the oil saturation. Some of the oil remains in the narrow regions of the pore space or adheres to the rock surface, which indicates a mixed wet system. (b) The oil adheres to the rock surfaces in pores initially occupied by emulsion or oil. (c) After the waterflood the aged system shows predominantly water-wet contact angles. Compared to a water-wet decane-brine system obtained from previous studies (Scanziani et al., 2017), a shift by 20° toward more oil-wet conditions could be detected.

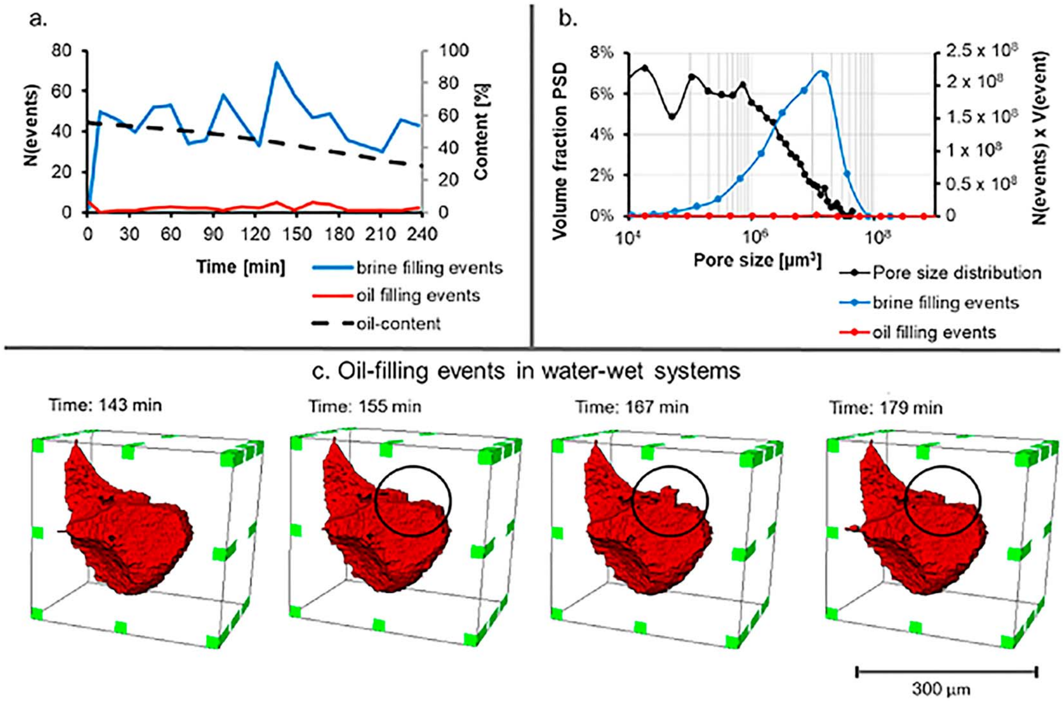

Figure 3. (a) Number of oil- and water-filling events as a function of time detected in the unsteady state waterflood experiment in a water-wet Ketton sample (supporting information Data S2). The event size distribution in comparison with the pore size distribution of the rock reveals that water-filling events cover up to multiple pore bodies, while no oil-filling event larger than 10^6 μm^3 was detected (b). In water-wet systems, oil-filling events represent fluctuations of the menisci of the oil phase (red) as shown in (c). In rare cases such fluctuation may lead to reconnection of previously disconnected clusters (Rücker et al., 2015). However, none of the fluctuations detected in this experiment showed such a behavior.

with crude oil peaks at higher contact angle indicating a more oil-wet state, though still on the water-wet side. In combination with the oil-film observed in the μCT images this finding underpins a mixed-wet small pattern.

The brine/crude/rock system analyzed in this study shows both a mixed-wet large and mixed-wet small pattern, which means that wettability varies between and within pores. While static conditions can be used to assess wettability of the systems, they do not show the impact of the mixed wettability patterns on flow. Dynamic imaging is required for this purpose.

3.2.1. Physics of Oil-Filling Events in Water-Wet Systems

Imbibition experiments on water-wet sandstone samples have revealed that connected pathway flow dominates the system. However, Rücker et al. (2015) also observed small coalescence events commonly associated with ganglion dynamics. These coalescence events cause an increase in connectivity of the oil phase but do not contribute significantly to the overall flux of the oil (Armstrong et al., 2016; Berg et al., 2016).

For better comparison with the results obtained from the waterflood in the mixed-wet Ketton limestone, additional analysis was performed on data provided by Singh, Menke, et al. (2017). The results obtained from this experiment are shown in Figure 3a, were the number of oil- and water-filling events as a function of time is plotted. A filling event represents a change in fluid phase occupancy of the pore-space. In a water-filling event the oleic phase is replaced by the aqueous phase and in an oil-filling event, the aqueous phase is replaced by the oleic phase. Only events larger than 10^4 μm^3 (corresponding to $7 \times 7 \times 7$ voxels) were considered as smaller events are likely to be related to fluctuations of the interface or noise. During the waterflood the number of water-filling events is significantly larger than the number of oil-filling events. In total only 43 oil-filling events were detected. The size of oil-filling events did not exceed 10^6 μm^3, while the water-filling events often fill multiple pores (Figure 3b). Figure 3c shows examples of the detected oil-filling events. Other than observed in Rücker et al. (2015), none of the oil-filling events caused reconnection of disconnected oil clusters. A reason for this may be the different rock structure (in the sandstone rock some throats are shorter than in a structure composed of more rounded grains, such as Ketton limestone). Rücker

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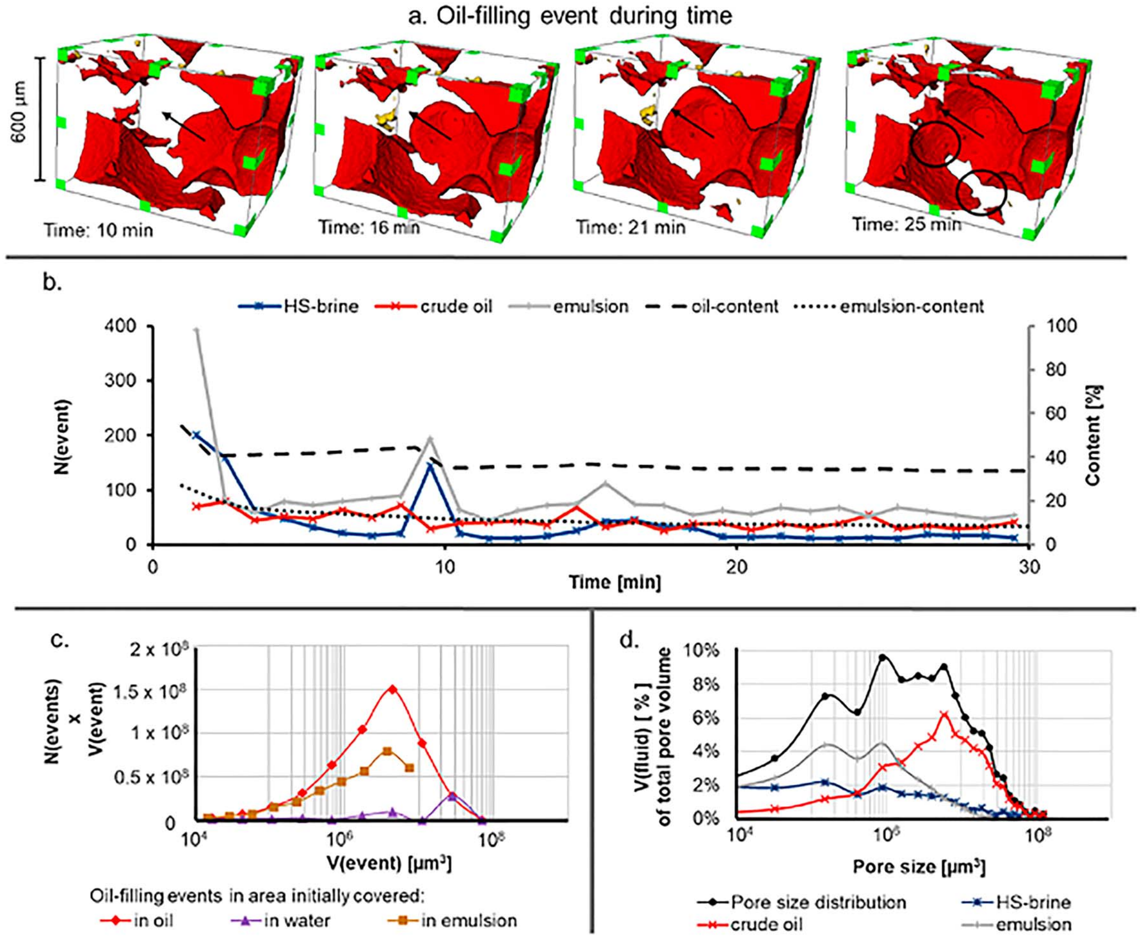

Figure 4. The oil-filling events observed in this study can cover full pore bodies. (a) The oil cluster (red) moves with time progressively until it connects with the surrounding oil phase. (b) The frequency of the three event types, water-filling, oil-filling, and emulsion-filling events, for each time step shows that the number of oil- and emulsion-filling events is similar to the number of water-filling events. (c) The volume associated with oil-filling events detected on surfaces initially covered with oil or emulsion compared to surfaces initially covered with water. (d) The initial fluid distribution compared to the pore size distribution (adapted from Bartels et al., 2017).

et al. (2015) provided supporting evidence that the reconnection events are a result of meniscus fluctuation. These fluctuations may fill short (relating to length, not width) throats. However, if these throats are too large, these fluctuations may not reach the neighboring clusters and hence do not reconnect the oil.

Even though no reconnection events were observed, these findings do confirm the movement of oil in water-wet systems. However, these oil-filling events are low in frequency and small in displaced volume. In water-wet rock water-filling events dominate the fluid distribution.

3.2.2. Physics of Oil-Filling Events in Mixed-Wet Systems

Compared with water-wet systems the oil-filling events observed in the mixed-wet case appear significantly different. Figure 4a shows such an event. An oil cluster (red) connected to the inlet starts to fill a pore body. With time (over 15 min) the oil cluster grows until it contacts with another oil cluster. In the mixed-wet case full pore bodies are involved in the displacement of water by oil, while in the water-wet case the reconnection of ganglia appears only in throats or restrictions in the pore space.

Not only does the event type differ in mixed-wet systems, but also the frequency and volume of oil-filling events (larger than 10^4 μm^3) are significantly higher. Figure 4b shows the number of water-, oil- and emulsion-filling events counted for each time step. In addition, Figure 4c shows the corresponding event size distribution of the oil phase on aged (initially oil- and emulsion-covered) surfaces and nonaged (initially water-covered) surfaces. The largest oil-filling events observed have the size of the largest pores indicated in the pore size distribution in Figure 4d.

Figure 4d also shows the fluid distribution after aging. As observed visually in Figure 2a oil fills most of the larger pores, while the water-phase and the emulsion occupy predominantly the smaller pores. Nevertheless, the volume of oil involved in larger-sized oil-filling events is significantly higher for pores initially covered with emulsion than with water, which hints to a dependency of these oil-filling events on the aging state of the rock surface.

These findings show the strong relationship between the event type and the wetting state of the surface. Oil-wet surfaces reduce the energy required for an oil clusters to move and leads to oil-filling events covering up to full pore bodies with a higher frequency compared to water-wet systems.

It is known from studies on water-wet systems that oil-filling events, even if they do not contribute directly to the overall flux, impact the relative permeability significantly due to their ability to change the connectivity (Rücker et al., 2015). Considering the high frequency and the large volumes involved in oil-filling events in mixed-wet systems, the flux contribution of ganglion dynamics to the overall flow cannot be neglected and could have an even larger impact on the overall flow regime in mixed-wet systems than known from water-wet systems.

4. Conclusions

The flow regime in a mixed-wet rock-crude oil-brine system showed significantly more ganglion dynamics than in water-wet rock. In the associated flow regime oil moves via oil-filling events and snaps off. Oil-wet surfaces reduce the energy required for oil clusters to move and enables larger and more frequent oil-filling events. Those differ significantly from oil-filling events in a water-wet system. As such, oil-filling events are known to affect the oil configuration in the rock and the connectivity of the oil phase. This behavior may impact the overall relative permeability and must be considered in pore-scale flow simulations. A simple extrapolation of the flow regime from water-wet conditions appears insufficient to capture the dynamics and connectivity of the oil phase.

Acknowledgments
We acknowledge the Paul Scherrer Institute, Villigen, Switzerland, for the provision of synchrotron radiation beamtime at Tomcat beamline of the SLS and would like to express thanks for assistance during the session. Furthermore, we would like to acknowledge Alex Schwing and Rob Neiteler for the design of the setup and instrumentation; Fons Marcelis for sample preparation; Christian Hinz, Arne Jacob, Christian Wagner, Steven Flesch, and Frieder Enzmann for support during the beamline; and Martin Fernø, Alessio Scanziani, and Axel Makurat for helpful discussions. We gratefully acknowledge Shell Global Solutions International B.V. for permission to publish this work. The water-wet Ketton data are available from Singh and Blunt (2018; https://doi.org/10.5285/3aa44060-d4fd-453f-9e5b-7d885ad5089f). The mixed-wet Ketton data are available from Rücker et al. (2019; http://www.digitalrocksportal.org/projects/202).

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