



Dynamics of water injection in an oil-wet reservoir rock at subsurface conditions: Invasion patterns and pore-filling events

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We use fast synchrotron x-ray microtomography to investigate the pore-scale dynamics of water injection in an oil-wet carbonate reservoir rock at subsurface conditions. We measure, *in situ*, the geometric contact angles to confirm the oil-wet nature of the rock and define the displacement contact angles using an energy-balance-based approach. We observe that the displacement of oil by water is a drainagelike process, where water advances as a connected front displacing oil in the center of the pores, confining the oil to wetting layers. The displacement is an invasion percolation process, where throats, the restrictions between pores, fill in order of size, with the largest available throats filled first. In our heterogeneous carbonate rock, the displacement is predominantly size controlled; wettability has a smaller effect, due to the wide range of pore and throat sizes, as well as largely oil-wet surfaces. Wettability only has an impact early in the displacement, where the less oil-wet pores fill by water first. We observe drainage associated pore-filling dynamics including Haines jumps and snap-off events. Haines jumps occur on single- and/or multiple-pore levels accompanied by the rearrangement of water in the pore space to allow the rapid filling. Snap-off events are observed both locally and distally and the capillary pressure of the trapped water ganglia is shown to reach a new capillary equilibrium state. We measure the curvature of the oil-water interface. We find that the total curvature, the sum of the curvatures in orthogonal directions, is negative, giving a negative capillary pressure, consistent with oil-wet conditions, where displacement occurs as the water pressure exceeds that of the oil. However, the product of the principal curvatures, the Gaussian curvature, is generally negative, meaning that water bulges into oil in one direction, while oil bulges into water in the other. A negative Gaussian curvature provides a topological quantification of the good connectivity of the phases throughout the displacement.

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I. INTRODUCTION

Multiphase flow in porous structures occurs in many natural and industrial systems such as blood flow [1], the movement of food and water within the intestinal tract of the human body [2], transport in porous membranes [3], carbon dioxide storage in geological aquifers [4,5], and oil recovery from reservoir rocks [6,7]. To understand the dynamics of fluid flow in porous materials, we need to study the processes that control its movement, which occur at the pore scale [8]. At the pore scale, the physics underlying the flow is mainly governed by capillary forces that control the fluid-fluid displacement, which depends on the porous medium geometry and wettability.

According to the wettability of the invading and displaced fluids, the displacement processes are termed drainage or imbibition. This definition applies for strictly hydrophilic or hydrophobic systems. However, many natural and manufactured porous media have a wettability that can be altered through contact with surface-active components of the fluids [9]. The resultant wettability controls a variety of processes from oil

recovery to gas exchange in leaves and the performance of fuel cells and batteries [8–13]. Hence, it is of great importance to study and quantify the dynamic nature of invasion patterns and the associated pore-scale events in porous media with an altered wettability. This is the main objective of our study; we now proceed with a discussion of the dynamics of multiphase flow in porous media.

When a porous medium is conceptualized, its void space is typically represented as a network composed of wide regions, the pores, that are connected together by narrower regions, the throats [8]. This network representation is sufficient to accurately characterize and track the filling sequence during displacement. When a nonwetting phase displaces the wetting phase, the process is called drainage: Here the nonwetting phase advances as a connected front through the pore space, displacing the wetting phase in the pore centers and confining it to wetting layers in the corners of the pore space.

Drainage can be described as an invasion percolation process [14], where the nonwetting phase progresses from pore to pore through the widest available throats. Filling is only possible if the nearest-neighbor pore or throat is already filled. An available throat is a throat adjacent to a pore already filled with the invading phase [14,15]. The capillary pressure for displacement P_c is defined through the Young-Laplace equation, for throats with a cylindrical cross section of radius

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74 r , by

$$P_c = \frac{2\sigma \cos \theta}{r}, \quad (1)$$

75 where σ is the interfacial tension between the fluids and θ is
76 their contact angle.

77 In this work, the displacement process we will investi-
78 gate is water injection in an oil-filled system with altered
79 wettability. In such systems, the contact angle is conven-
80 tionally measured through the denser phase, water, while
81 the capillary pressure is the pressure difference between oil
82 and water ($P_c = P_o - P_w$). During water injection, the water
83 pressure increases with time and invasion proceeds in order
84 of decreasing capillary pressure; the events with the largest
85 capillary pressure occur first. We will define a drainagelike
86 process for water injection as one represented by a contact
87 angle greater than 90° , where $\cos \theta$ is negative, and hence
88 the capillary pressure is also negative; the medium is water
89 repellent and water has to have a higher pressure than oil to
90 advance through the pore space. For a medium of constant
91 wettability (contact angle), filling the largest available throats
92 corresponds to a capillary-controlled displacement where the
93 invading fluid progresses through the porous medium at the
94 highest allowable capillary pressure (or lowest absolute value,
95 since the capillary pressure is negative).

96 As the nonwetting phase (water) passes from a narrow
97 throat into a wider pore, there is a sudden change in the local
98 capillary pressure which results in rapid filling of the invaded
99 pore and possibly further filling of multiple pores and throats
100 downstream of the invaded pore if they can also be invaded
101 at the prevailing water pressure. This fast filling is known as
102 a Haines jump [16]. To enable the displacement in multiple
103 pores during a Haines jump, the nonwetting phase retracts
104 from some throats, which we term Roof snap-off [8,17,18].
105 At the pore scale, the retraction of the nonwetting phase is
106 not a drainage process, but instead is an imbibition event,
107 where now the wetting phase displaces the nonwetting phase.
108 Snap-off can occur either in a pore that has just been invaded
109 by the nonwetting phase, local snap-off, or in another region
110 some distance way, distal snap-off [19].

111 Imbibition, where the contact angles are less than 90°
112 and the capillary pressure is positive, is considered a more
113 complex pore-scale process and its dynamics is often domi-
114 nated by snap-off [20]. Snap-off occurs when the layers of
115 the wetting phase start to swell in a throat, and if the wetting
116 layers touch and coalesce, the throat spontaneously fills with
117 the wetting phase, leading to a disconnection and trapping
118 of the nonwetting phase in the centers of the adjacent pore
119 [20–23]. The trapping of the nonwetting phase by snap-off
120 is favorable for CO_2 storage applications, where maximum
121 trapping of CO_2 (nonwetting phase) is desired, whereas it is
122 detrimental for oil recovery applications.

123 The early work of Lenormand *et al.* [21] provided infor-
124 mation on the dynamics of pore filling during drainage in
125 two-dimensional micromodels. The same behavior was also
126 observed by Datta *et al.* [24] in three dimensions, where
127 drainage was investigated in a pack of sintered glass beads
128 using confocal microscopy. However, it was not until recently
129 that advances in x-ray microtomography have allowed for
130 direct imaging of the rock pore space and the fluids within

131 it [25–28]. Many laboratory-based x-ray microtomography
132 studies have provided detailed descriptions of ganglia or dis-
133 connected nonwetting phase clusters at the end of imbibition
134 and drainage processes [29–32]. However, these studies only
135 report end point results at static conditions and hence do not
136 capture the displacement or pore-filling sequence which occur
137 on a much shorter timescale than that required for a single
138 scan (which can take several minutes or hours).

139 To increase the temporal resolution of imaging, fast syn-
140 chrotron x-ray microtomography can be used, which captures
141 the pore-scale displacement dynamics on a timescale of sec-
142 onds to around 1 min [18,19,22,23,33–35]. Berg *et al.* [18]
143 quantified the number of pores invaded by the nonwetting
144 phase (n -decane) during a Haines jump in a water-wet Berea
145 sandstone. Andrew *et al.* [19] further investigated interface
146 retraction and snap-off during CO_2 injection, drainage, in a
147 water-wet Ketton limestone. Moreover, Rucker *et al.* [23]
148 characterized the impact of the pore-scale viscous effects
149 on snap-off and coalescence events during imbibition in a
150 sandstone rock. However, to date, all the reported dynamic
151 studies were conducted in water-wet media. The displacement
152 dynamics have not been investigated for water invasion in
153 altered-wettability porous media.

154 In this study, we use synchrotron x-ray microtomography
155 to visualize the pore-scale dynamics during water injection
156 in a reservoir rock with altered wettability. A previous study
157 investigated the dynamics of water injection into a quarry
158 limestone (Ketton) which had been in contact with crude
159 oil [36]. The experimental conditions, mineralogy (mainly
160 calcite), fluids, and wettability alteration protocol of the study
161 conducted in Ketton are almost identical to our study in a
162 reservoir rock. As we show later, although the geometric
163 contact angles measured *in situ* are similar in the two cases,
164 the macroscopic manifestation in terms of displacement se-
165 quence, energy balance, and capillary pressure are different,
166 emphasizing the importance of the interaction of pore ge-
167 ometry and wettability on displacement. In the Ketton rock,
168 the behavior revealed mixed-wet conditions, defined by the
169 simultaneous filling of both small and large pores during water
170 injection, indicating that the displacement was controlled by
171 both pore geometry and wettability (local contact angles);
172 water invasion was not a drainagelike process [36]. How-
173 ever, reservoir rocks are likely to undergo a more significant
174 wettability alteration when in contact with crude oil [37,38],
175 rendering the surfaces largely oil wet (water repellent or
176 hydrophobic). Moreover, the reservoir sample has a wider
177 distribution of pore sizes than in a quarry Ketton sample.

178 In this paper, we examine, *in situ*, (i) wettability and dis-
179 placement contact angles, (ii) invasion patterns (pore-filling
180 order), (iii) Haines jumps, (iv) snap-off events, (v) fluid
181 saturations, (vi) specific interfacial areas, and (vii) oil-water
182 capillary pressure. We validate the hypothesis that in a highly
183 heterogeneous porous medium with a significant wettability
184 alteration from an original water-wet state, the pore space
185 becomes largely water repellent and that water invasion is
186 a drainage-type invasion percolation process. This work is
187 important since non-water-wet surfaces are ubiquitous in na-
188 ture, e.g., in deep oil reservoirs, rice leaves, butterfly wings,
189 and human skin, as well as the fact that many surfaces are
190 designed to be fully or partially water repellent to improve

TABLE I. Thermophysical properties of the oil and water phases at the experimental conditions (8 MPa and 60 °C). The interfacial tension between oil and water was measured at 8 MPa and 60 °C using the pendant drop method. Data are from NIST [45], engineering toolbox [46], and Jianhua *et al.* [47].

Fluid	Composition (wt. %)	ρ (kg m ⁻³)	μ (mPa s)	σ (mN m ⁻¹)
water	80% deionized + 20% potassium iodide	1145.0	0.547	$\sigma_{ow} = 52.1$
oil	85% <i>n</i> -decane + 15% 1-iododecane	715.2	1.088	

191 their performance, e.g., textiles, medical and cosmetic devices
192 including surgical masks, fuel cells, and catalysts [8–13,39–
193 42]. Moreover, these time-dependent data are vital for the
194 validation of pore-scale models of multiphase flow.

195 II. MATERIALS AND METHODS

196 In this section, we provide details regarding the rock
197 and fluid properties, the methodology followed to establish
198 the reservoir wettability, flow apparatus, image acquisition,
199 and processing. The sample was initially prepared in-house
200 before transporting it to the synchrotron facility for imaging
201 the flooding experiment. All imaging was conducted at the
202 Diamond imaging beamline I13-2 (Diamond Light Source,
203 Harwell campus, Didcot, UK).

204 A. Rock and fluid properties

205 The experiment was conducted on a 3.85-mm-diam, 13.8-
206 mm-long cylindrical sample of a carbonate rock, extracted
207 from a large producing hydrocarbon reservoir in the Mid-
208 dle East. The mineralogical composition of the rock con-
209 sisted mainly of calcite (96.5% ± 1.9%), with small amounts
210 of dolomite (1.5% ± 0.3%), kaolinite (1.1% ± 0.2%), and
211 quartz (0.8% ± 0.4%) [43]. The reservoir rock is very hetero-
212 geneous with a wide distribution of pore sizes varying from
213 3.5 to 120 μm; see Fig. S1 for the pore-size distribution [44].
214 The measured helium porosity of the sample was 26%, with
215 the macro- and microporosities accounting for 16% and 10%,
216 respectively. In the context of our work, the macroporosity is
217 defined as that which can be directly resolved in the image
218 at the given resolution; the microporosity is the unresolvable
219 pore space in the image. The pore volume (PV) of the sample
220 corresponding to the total helium porosity was 0.0416 ml.

221 The experimental fluids used to represent the water and
222 oil phases were doped deionized water (20% wt. potassium
223 iodide) and doped *n*-decane (15% wt. 1-iododecane), respec-
224 tively. Doping provided a distinct x-ray attenuation between
225 the oil and water phases in the pore-scale images. The ther-
226 mophysical properties of the two fluids are listed in Table I.

227 B. Wettability alteration

228 The surface wettability of the rock sample was altered to
229 conditions representative of those in the subsurface, prior to
230 conducting the experiment [37,48]. To alter the wettability, the
231 rock was placed in contact with crude oil at conditions of high
232 temperature and pressure, which allows for the adsorption of
233 organic surface-active materials, from the crude oil, onto the
234 rock surfaces, rendering them oil wet [43]. To achieve this, we
235 performed the following steps. (i) First, the rock was cleaned
236 using methanol and left to dry in an oven for 24 h. (ii) The

rock pore space was then fully saturated with formation brine 237
(water containing the same salt composition as the aqueous 238
phase in the reservoir from which the rock was extracted) at 239
high temperature (80 °C) and high pressure (10 MPa). (iii) 240
Forty pore volumes of crude oil, from the same reservoir 241
in the Middle East, were initially injected from the bottom 242
of the sample with an increasing flow rate, from 0.001 to 243
0.1 ml/min. The flow direction was then reversed and crude 244
oil was injected from the top with the same flow rates and total 245
volume. (iv) After this, five pore volumes of fresh crude oil 246
were injected into the sample daily for a week at 0.05 ml/min. 247
(v) The sample was then maintained at the initially established 248
high pressure and temperature (80 °C and 10 MPa) conditions 249
for another three weeks. (vi) Finally, the sample was removed 250
and placed in a sealed crude oil bath at 80 °C before it was 251
transported to the synchrotron light source facility. Refer to 252
Table S1 in [44] for the crude oil properties. 253

254 C. Flow experiment and synchrotron imaging

255 The experimental apparatus used to conduct the flow ex-
256 periment in the synchrotron light source facility is shown in
257 Fig. 1. The sample was removed from the crude oil bath and
258 fitted in a cylindrical Viton sleeve. The top and bottom sides
259 of the Viton sleeve were then attached to metal endpieces which
260 were connected to the outlet and inlet flow lines, respectively.
261 This configuration was assembled inside a Hassler-type flow
262 cell made of carbon fiber that is x-ray transparent. The flow
263 cell was then placed in front of the synchrotron beamline to
264 start the experiment.

265 The flow experiment was initiated by flushing 20 pore vol-
266 umes of the oil phase (doped *n*-decane) through the sample at
267 a flow rate of 0.1 ml/min to replace the crude oil used to alter
268 the wettability. This step is essential to avoid the formation of
269 emulsions during the experiment [49]. The system was then
270 pressurized to the experimental conditions (8 MPa) and the
271 confining pressure to 10 MPa. The temperature in the system
272 was then raised to the experimental temperature (60 °C) using
273 an Omega flexible heater. At this point, a single high-quality
274 scan of the oil-saturated rock was acquired (hereafter called
275 the reference oil scan). While oil initially occupied almost
276 99% of the macropore space before water injection (measured
277 on the reference oil scan), water was initially present in the
278 microporosity and in the corners of the pore space.

279 The dynamic experiment was then started by injecting
280 water into the oil saturated rock at a very low flow rate,
281 0.15 μl/min, achieving a capillary number ($Ca = \mu q / \sigma$,
282 where σ is the oil-water interfacial tension, μ is the viscosity
283 of water, and q is the Darcy velocity of water) of $2.09 \times$
284 10^{-9} , which resulted in capillary-dominated flow conditions.
285 Furthermore, the low flow rate enabled the flow dynamics

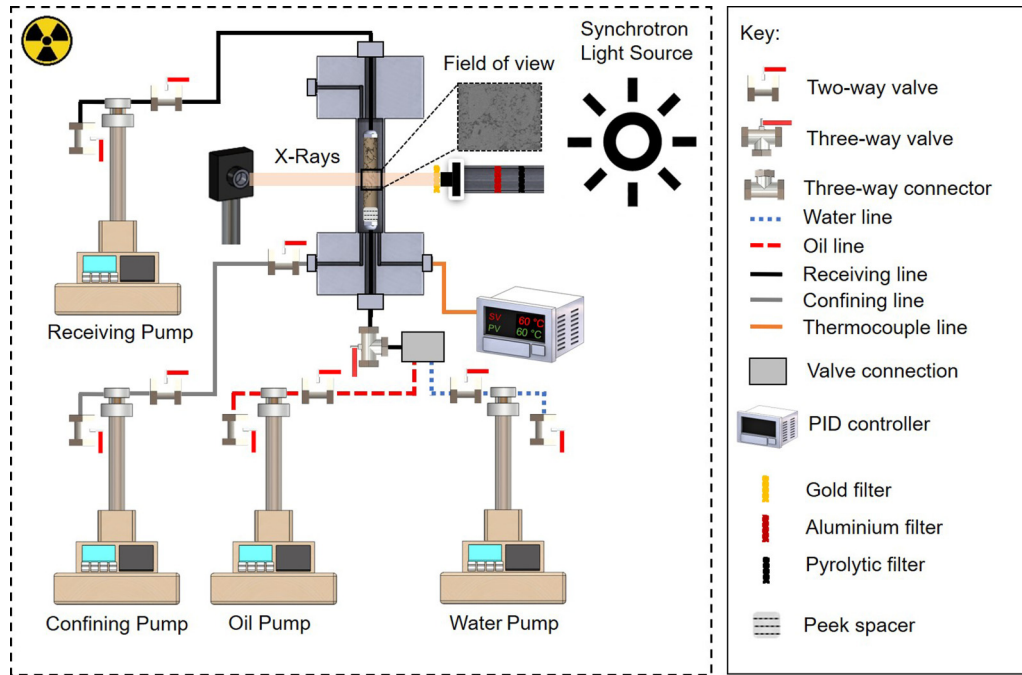


FIG. 1. High-pressure, high-temperature flow apparatus used to conduct the water injection experiment. The apparatus consisted of four syringe pumps, a carbon fiber flow cell, flexible heating jacket connected to a PID controller, a PCO edge camera, and a synchrotron light source.

286 to be captured with a temporal resolution of 70 s. During
 287 water injection, the center of the sample was continuously
 288 scanned (hereafter called dynamic water injection scans).
 289 No, or minimal, displacement dynamics were observed after
 290 92.1 min of water injection, and hence the experiment was
 291 terminated.

292 The fast time-resolved synchrotron imaging was performed
 293 using a high photon flux pink beam with a peak photon energy
 294 of 15 keV. The x rays were filtered by placing a 1.3-mm
 295 pyrolytic carbon filter, a 3.2-mm aluminum filter, and a 10- μ m
 296 gold filter in the beamline. Only the center of the sample was
 297 imaged during the experiment, giving a $4.5 \times 4.5 \times 3.8$ mm³
 298 field of view with a PV of 0.02 ml as shown in Fig. 1. The
 299 imaged field of view covered the whole cross-sectional area
 300 of the sample. Imaging started when water was detected in
 301 the peek spacer. The size of the images was $1280 \times 1280 \times$
 302 1080 voxels, with a voxel size of 3.5 μ m. The high-quality
 303 oil scan was acquired with a total of 2000 projections and
 304 0.15-s exposure time. During water injection a total of 76
 305 tomograms were acquired over a period of 92.1 min, with 700
 306 projections and 0.065-s exposure time. The lower number of
 307 projections and exposure time allowed for the dynamic images
 308 to be acquired with a high temporal resolution (a complete
 309 tomogram was acquired every 70 s).

310 **D. Image processing**

311 The tomograms were then reconstructed to build three-
 312 dimensional (3D) pore-scale images of the rock and fluids
 313 within it. Figure 2 shows the same two-dimensional slice of
 314 the 3D pore-scale images taken after oil injection [Fig. 2(a)]
 315 and at the end of water injection [Fig. 2(b)]. All images were
 316 segmented using the machine-learning-based trainable Weka

317 segmentation method [50,51]. No filtering was applied to the
 318 images prior to segmentation as it can have an adverse effect
 319 on the quality of Weka segmentation [43]. Two approaches
 320 were adopted to segment the reference oil scan and the water
 321 injection scans. In the case of the high-quality oil scan, the
 322 classifier was trained by manually selecting voxels that belong
 323 to the oil and rock phases, which was then applied to segment
 324 the whole image [see Fig. 2(d)].

325 The segmentation of the dynamic water injection scans
 326 was performed in four steps. (i) First, all the 76 time-series
 327 raw water injection images were registered to the raw oil
 328 reference scan. (ii) Each water injection scan containing three
 329 phases (water, oil, and rock) was then subtracted from the oil
 330 reference scan, which contains mainly two phases (oil and
 331 rock), creating a subtracted image where the water phase can
 332 be clearly distinguished [see Fig. 2(c)]. (iii) Water was then
 333 segmented using Weka by training the classifier to identify
 334 the voxels that belong to the water phase [see Fig. 2(f)].
 335 (iv) The segmented water phase was then masked on the
 336 segmented oil reference scan resulting in the final segmented
 337 water injection image [see Fig. 2(e)]. A cylindrical mask was
 338 then applied on the segmented images to remove the unwanted
 339 regions, e.g., the Viton sleeve. The fast random algorithm was
 340 employed during all Weka segmentations alongside the mean
 341 and variance texture filters.

342 **E. Wettability characterization methods**

343 The segmented 3D pore-scale images can be used to char-
 344 acterize the wettability of the rock surface directly *in situ*.
 345 Wettability can be inferred from the measured spatial distribu-
 346 tion of contact angles between the fluids within the pore space,
 347 also known as the geometric contact angle θ_g [52–56]. While

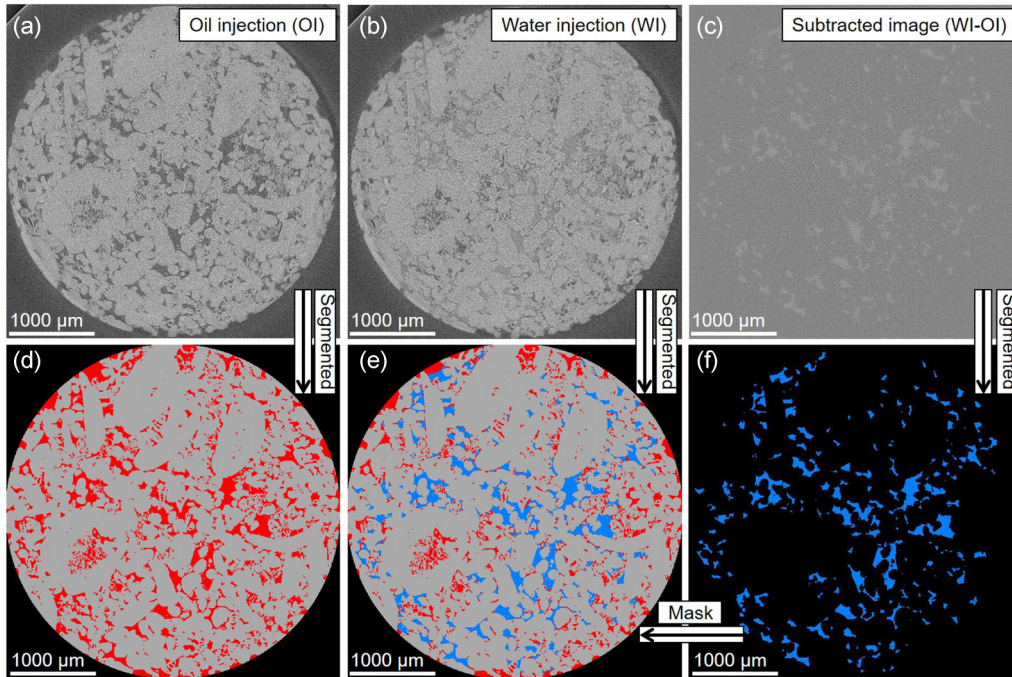


FIG. 2. Image segmentation workflow. The raw reference oil scan, 3.5 μm voxel size, in (a) was segmented directly using weka segmentation [see (d)]. To segment the water injection scan, 3.5 μm voxel size, in (b), it was first subtracted from the reference oil scan, in (a), to clearly distinguish the water phase, as shown in light gray in (c). The water phase in (c) was then segmented using weka, as shown in (f), and then masked on the segmented oil scan in (d) to give the final segmentation of the water injection scan [see (e)]. The mean and variance texture filters were used during weka segmentation.

348 the geometric contact angle provides useful information on
 349 wettability on a pore-by-pore basis, its value is measured at
 350 rest and hence it does not necessarily represent the actual
 351 value encountered during displacement because of contact
 352 angle hysteresis [57]. Moreover, it has been shown that the
 353 use of spatially distributed geometric contact angle values
 354 were insufficient to reproduce the water flooding behavior in
 355 altered-wettability media [58].

356 Therefore, we also use an alternative approach to define
 357 the contact angle associated with the fluid displacement in
 358 our system, known as the thermodynamic contact angle θ_t .
 359 Here θ_t is computed from an energy balance and considers the
 360 changes in saturation and interfacial areas from two consecu-
 361 tive water injection images (time steps) [59]

$$\cos \theta_t = \frac{\kappa \phi \Delta S_w + \Delta a_{wo}}{\Delta a_{ws}}, \quad (2)$$

362 where ΔS_w , Δa_{wo} , and Δa_{ws} are the differences, between
 363 two time steps, in water saturation, and specific interfacial
 364 areas between water and oil, and water and solid measured
 365 on the macroporosity. In addition, κ is the total curvature of
 366 the oil-water interface, discussed below, and ϕ is the imaged-
 367 based macroporosity. In our dynamic water injection images,
 368 we compute the thermodynamic contact angle between all
 369 the time steps and compare its value to the distribution of
 370 geometric contact angle.

F. Pore-filling analysis method

371 To quantitatively assess the order of pore filling during
 372 water injection, we developed an in-house algorithm that
 373

374 detects the size of the filled elements as the water front
 375 progresses through the pore space. For each time step i ,
 376 the algorithm identifies the pores occupied by the advancing
 377 water front and measures the size of the throats connected
 378 to it, also known as available throats for invasion, using the
 379 maximal ball network extraction code [60,61]. A throat is
 380 considered available whenever two pores connected to it are
 381 occupied by different phases (oil and water). Subsequently,
 382 the algorithm records the inscribed radius of the available
 383 throats, in i , that become invaded by water in the next time
 384 step $i + 1$. An available throat is considered invaded when
 385 both pores connected to it are filled with water and its center
 386 is also occupied by water. Finally, the algorithm generates a
 387 plot showing the size of the invaded available throats at time
 388 step $i + 1$ against the size of the available throats at time
 389 i to illustrate the order of filling during water injection. This
 390 approach is different from a conventional occupancy analysis
 391 that depicts the size of the invaded pores or throats at each time
 392 step against the size of all the pores or throats in the rock. Here
 393 we only consider the throats available for invasion, which are
 394 adjacent to the advancing water front.

395 If the rock has become uniformly oil wet (water repellent),
 396 we expect water injection to be a drainage process. If displace-
 397 ment proceeds by invasion percolation then we expect at every
 398 time step the largest available throats to be filled [14].

G. Minkowski functionals

399 In addition to characterizing the *in situ* wettability and
 400 order of pore filling, the segmented pore-scale images can be
 401 used to compute the four Minkowski functionals, which are
 402

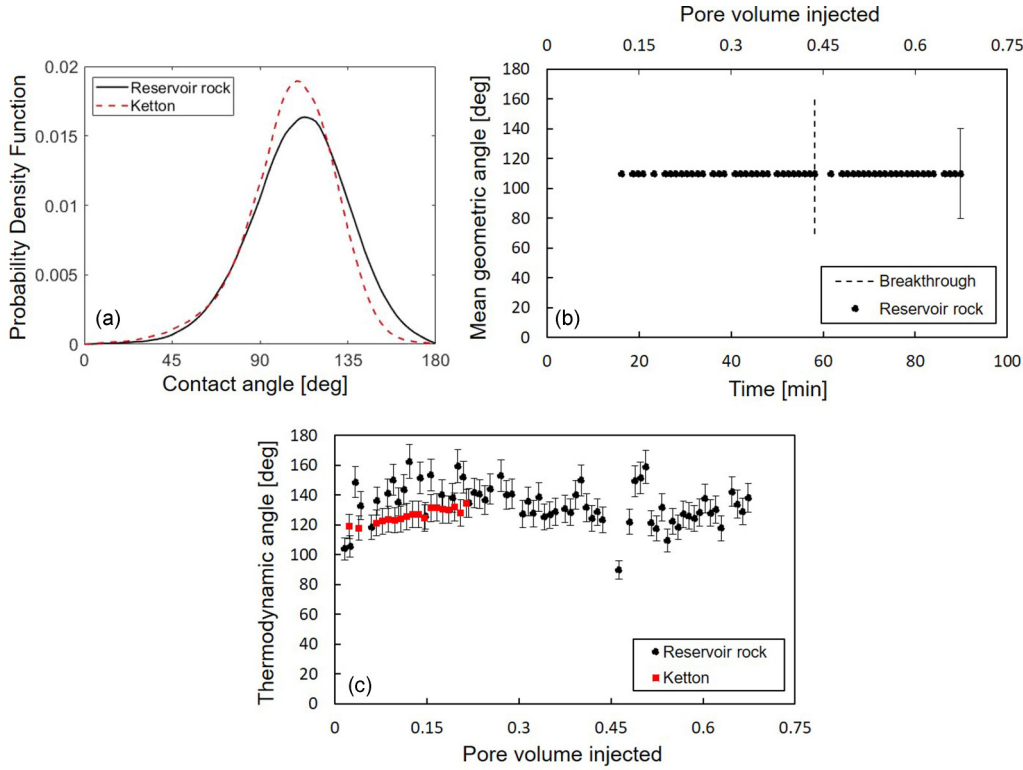


FIG. 3. (a) Normalized histograms of the measured *in situ* contact angles between oil and water in the reservoir sample (black) and in the Ketton limestone sample (red) at the end of water flooding. (b) Mean of the calculated geometric contact angle distributions in the reservoir sample plotted as a function of time and pore volume injected. (c) Calculated average value of the thermodynamic contact angle, using Eq. (2), with pore volumes injected in the reservoir sample (black) and in the Ketton sample (red). Error bars in (b) show the standard deviation, while in (c) it indicates the uncertainty in the measurements. The geometric and thermodynamic contact angles measured on Ketton are from Scanziani *et al.* [36].

403 morphological measures that provide a complete geometrical
 404 characterization of the fluids within the pore space [62–64].
 405 The zeroth-order Minkowski functional M_0 is the volume. In
 406 two-phase flow, this can be defined as the volume of each
 407 phase, which we obtained to calculate the saturation of the
 408 oil and water phases

$$S = \frac{v}{\phi V}, \quad (3)$$

409 where S is the fluid phase saturation defined here only in the
 410 macroporosity, v is the volume of the fluid phase in the pore
 411 space, ϕ is the macroporosity, and V is the image size (total
 412 volume).

413 Interfacial area is the first-order Minkowski functional M_1 ,
 414 from which we can define the specific interfacial area a
 415 between the fluids and the fluids and the solid (a has units
 416 of 1/length) [65]:

$$a = \frac{M_1}{V}. \quad (4)$$

417 We computed the specific interfacial area between water
 418 and oil (a_{wo}), oil and solid (a_{os}), and water and solid (a_{ws})
 419 from the segmented images.

420 The second-order Minkowski functional M_2 is the total
 421 curvature (the sum of the two principal curvatures) of the
 422 interface between two phases κ . Here κ can be related to the
 423 capillary pressure P_c through the interfacial tension σ using

the Young-Laplace equation [66]

$$P_c = \sigma \kappa. \quad (5)$$

424
 425 We estimated the capillary pressure between oil and water
 426 by measuring the curvature of their interface on the pore-scale
 427 images using a method previously described in the literature
 428 [66–71]. The 3D oil-water interface was extracted from the
 429 image and then smoothed with a kernel size of 5 in the
 430 direction of the aqueous phase (water). The average curvature
 431 was measured on the smoothed surface and multiplied by the
 432 interfacial tension (Table I) to obtain the capillary pressure
 433 from Eq. (5).

434 The third, and last, Minkowski functional M_3 is the surface
 435 integral of the Gaussian curvature, or the product of the two
 436 principal curvatures κ_1 and κ_2 [64]. The Gaussian curvature
 437 of the fluid-fluid interface can be used as a measure of the
 438 connectedness of the fluid phases in the pore space.

III. RESULTS AND DISCUSSION

439
 440 In this section, we analyze the segmented images to investi-
 441 gate the pore-scale dynamics during water injection in the
 442 reservoir rock. First, in Sec. III A, we compute the geometric
 443 and thermodynamic contact angles for each time step to
 444 characterize the wettability of the rock; we suggest that the
 445 thermodynamic angles provide a better quantification of the
 446 wettability during displacement. In Sec. III B, we examine

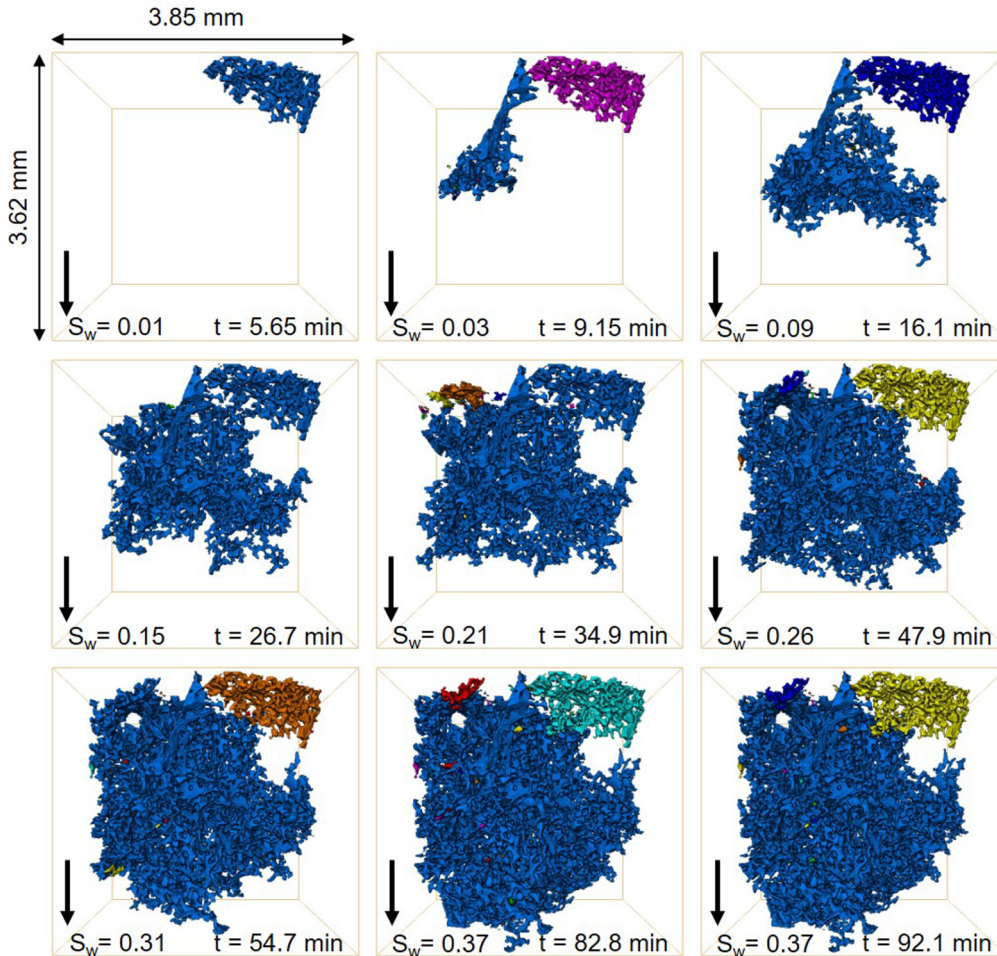


FIG. 4. Three-dimensional maps of the water phase connectivity during water injection shown at different time steps. During invasion, water advanced as a connected front displacing oil in the pore space. This displacement was accompanied by apparent drainage dynamic events, including Haines jumps ($t = 9.15$ min) and Roof snap-off ($t = 16.1, 47.9, 54.7, 82.8,$ and 92.1 min). The black arrow points towards the direction of flow.

447 the pore-filling events by qualitatively and quantitatively as- 467
 448 ssuming (1) the invasion patterns, (2) Haines jumps, and (3) 448
 449 snap-off events. We demonstrate that the water advance is an 449
 450 invasion percolation process. Finally, in Sec. III C, for each 450
 451 water injection time step, we quantify the Minkowski functionals 451
 452 describing (1) fluid saturations, (2) specific interfacial 452
 453 areas between the fluids and the fluids and rock, (3) oil-water 453
 454 capillary pressure, and (4) Gaussian curvatures. 454

455 A. Geometric and thermodynamic contact angles

456 The distribution of *in situ* geometric contact angles θ_g 456
 457 between oil and water was measured in a subvolume of 457
 458 size $1.75 \times 1.75 \times 1.75$ mm³, located in the center of the 458
 459 field of view, during water injection using the automated 459
 460 method developed by AlRatrouf *et al.* [53]. Figure 3 shows 460
 461 the distribution of the geometric oil-water contact angles in 461
 462 our reservoir rock compared to that measured on Ketton 462
 463 limestone by Scanziani *et al.* [36]. The mean of the geometric 463
 464 contact angle distribution in the reservoir rock is 110° with 464
 465 a standard deviation of $\pm 20^\circ$. This indicates that the rock 465
 466 surfaces are predominately oil-wet such that the rock tends 466

467 to be in contact with oil; water, the nonwetting phase, resides 467
 468 in the centers of the pores surrounded by oil-wetting layers 468
 469 (see Figs. 4 and 5). Given the oil-wet nature of the rock, we 469
 470 expect the displacement of oil by water to be drainagelike. 470
 471 Moreover, the wide range of pore sizes in the heterogeneous 471
 472 reservoir sample (Fig. S1 in [44]) suggests that ~~the control on~~ 472
 473 displacement is more likely to be controlled by radius than 473
 474 contact angle, which is discussed further in Sec. III B 1. The 474
 475 average geometric contact angle distribution in the reservoir 475
 476 rock is similar to that obtained on a Ketton limestone sample, 476
 477 $109^\circ \pm 19^\circ$, where the same wettability-alteration protocol 477
 478 was employed [36] [Fig. 3(a)]. However, as we will show later, 478
 479 the displacement behavior is very different. Furthermore, we 479
 480 observe that the mean geometric contact angle remains constant 480
 481 throughout the water flooding experiment in the reservoir 481
 482 rock [see Fig. 3(b)]. 482

483 Nevertheless, as mentioned earlier, the geometric contact 483
 484 angle is measured on a fixed oil-water interface. Many of the 484
 485 contacts between oil, water, and the solid are pinned and have 485
 486 a hinging contact angle between the low water-wet value when 486
 487 oil first entered the rock and a higher value needed for water 487
 488 to advance across an altered-wettability surface. Hence, the 488

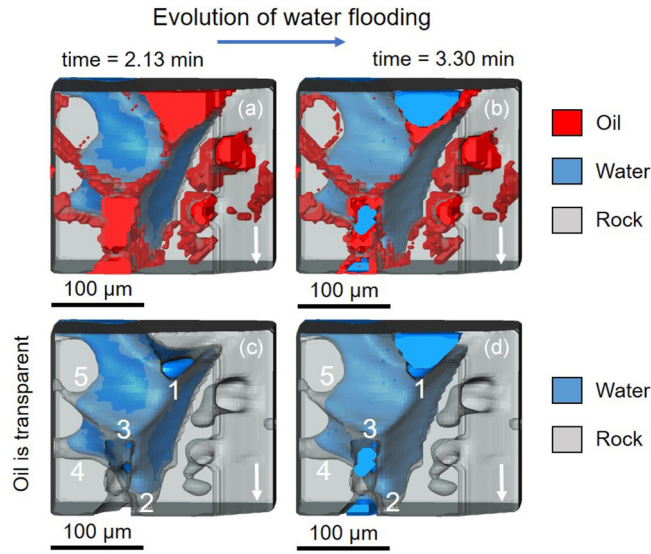


FIG. 5. Three-dimensional pore-scale images of a single pore ($210 \times 123 \times 175 \mu\text{m}^3$) showing the invasion pattern of water. (a) At time = 2.13 min, there are five throats connected to the pore that are available for subsequent water invasion. These throats are labeled from 1 to 5 in decreasing order of size in (c), where oil was rendered transparent to make it possible to visualize the throats. (b) and (d) At time = 3.30 min, the largest throats 1–3 get invaded by water, which indicates that water injection in an oil-wet medium is an invasion percolation process. The white arrow points towards the direction of flow, while the blue arrow refers to the evolution of water invasion.

geometric values do not necessarily represent the oil-water contact angles encountered during displacement, with a tendency to underestimate the values [57,59]. We therefore used Eq. (2) to calculate a thermodynamically consistent contact angle θ_t for each time step. The calculated thermodynamic contact angles are shown in Fig. 3(c): this represents the average oil-water contact angle for displacement consistent with the change in surface energy estimated from the images. Figure 3(c) indicates that the thermodynamic contact angle in the reservoir rock has a stable trend during water injection, with an average value of approximately $135^\circ \pm 10^\circ$. A lower θ_t was observed early on in the displacement, $103^\circ \pm 10^\circ$ and $105^\circ \pm 10^\circ$, indicating that, initially, water preferentially fills the less oil-wet pores, followed by the filling of increasingly oil-wet regions of the pore space. In the previous study on Ketton, the thermodynamic angle increased from 110° to 130° , shown in red in Fig. 3(c), throughout the displacement; however, it was still lower than the thermodynamic angle for the reservoir rock [36]. Hence, we observe that the thermodynamic angle provides a better discrimination between the two cases than the geometric angle which displayed a similar distribution. Although the difference in wettability captured by the thermodynamic angle is relatively modest, combined with a more heterogeneous pore-size distribution, it leads to a distinct displacement behavior, as presented next.

Furthermore, a recent modeling study has shown that to match experiments of water flooding in rocks with altered wettability, it is insufficient to use the geometric contact angle; instead, a larger contact angle should be used to account for contact angle hysteresis in the more oil-wet regions [58]. This

implies that the thermodynamic contact angle better captures the displacement in a model.

B. Pore-filling events

The pore-scale dynamics of water flooding were imaged for a total of 92.1 min, after which there was no significant change in the oil and water configurations in the pore space. Water breakthrough in the imaged field of view, 3.62 mm in length, occurred after 58.2 min, which corresponds to an injection of 0.45 PV of water. Figure 4 and movie S1 in [44] show images of the advancing water phase acquired at different time steps; each color represents a different water cluster.

We observe that water advances as a connected front displacing the oil phase in the pore space, which indicates that water injection in our oil-wet reservoir rock is a drainage process. Layer flow was inferred during displacement as oil, the wetting phase, was observed in the corners and roughness of the pore space (see Fig. S2 and movie S2 in [44]) as well as in the pore centers. Furthermore, water invasion was accompanied by drainage dynamics associated with interface advancing and retraction, e.g., Haines jumps and Roof snap-off (see Fig. 4); this further confirms that drainage was the displacement process in the experiment. Drainage and its associated dynamics were previously imaged in water-wet systems [18,34] but not in oil-wet media. Figure 4 shows that drainage dynamics continued even after breakthrough as water displaced more oil out of the pore space. This contrasts with the experiment on Ketton limestone, where no displacement was observed after breakthrough [36].

1. Invasion percolation

The time-series segmented images were analyzed to characterize the pore-filling order during water injection. First, we qualitatively assess the order of filling in a single pore occupied by oil and water (see Fig. 5). Figure 5(a) illustrates that water resides in the centers of the pore space confining oil to wetting layers and small corners, which is a common characteristic of predominantly oil-wet media [48]. At time equal to 2.13 min [Fig. 5(a)] there are five available throats for water to pass through to progress to the next pores. These available throats are labeled from 1 to 5 in a decreasing order of size in Fig. 5(c), where the oil phase was rendered transparent to make it possible to visualize the available throats. At time equal to 3.30 min [Figs. 5(b) and 5(d)], we observe that water invaded the centers of the largest available throats (1–3) to pass through, as they required the lowest absolute capillary entry pressures [Eq. (1)]. We presume that as water pressure increases during water injection, water first had sufficient pressure to invade the largest throat (1) and then progressively filled the smaller throats (2 and 3). However, this happens on a much shorter timescale than that required for a single scan, and hence was not captured in the experiment. Overall, the throats were filled in order of size, with the largest filled first, which indicates that water injection in this rock is an invasion percolation process.

Using the pore-filling analysis described in Sec. IIF, the filling sequence was quantified in all the pores adjacent to the advancing water front in the dynamic images during water

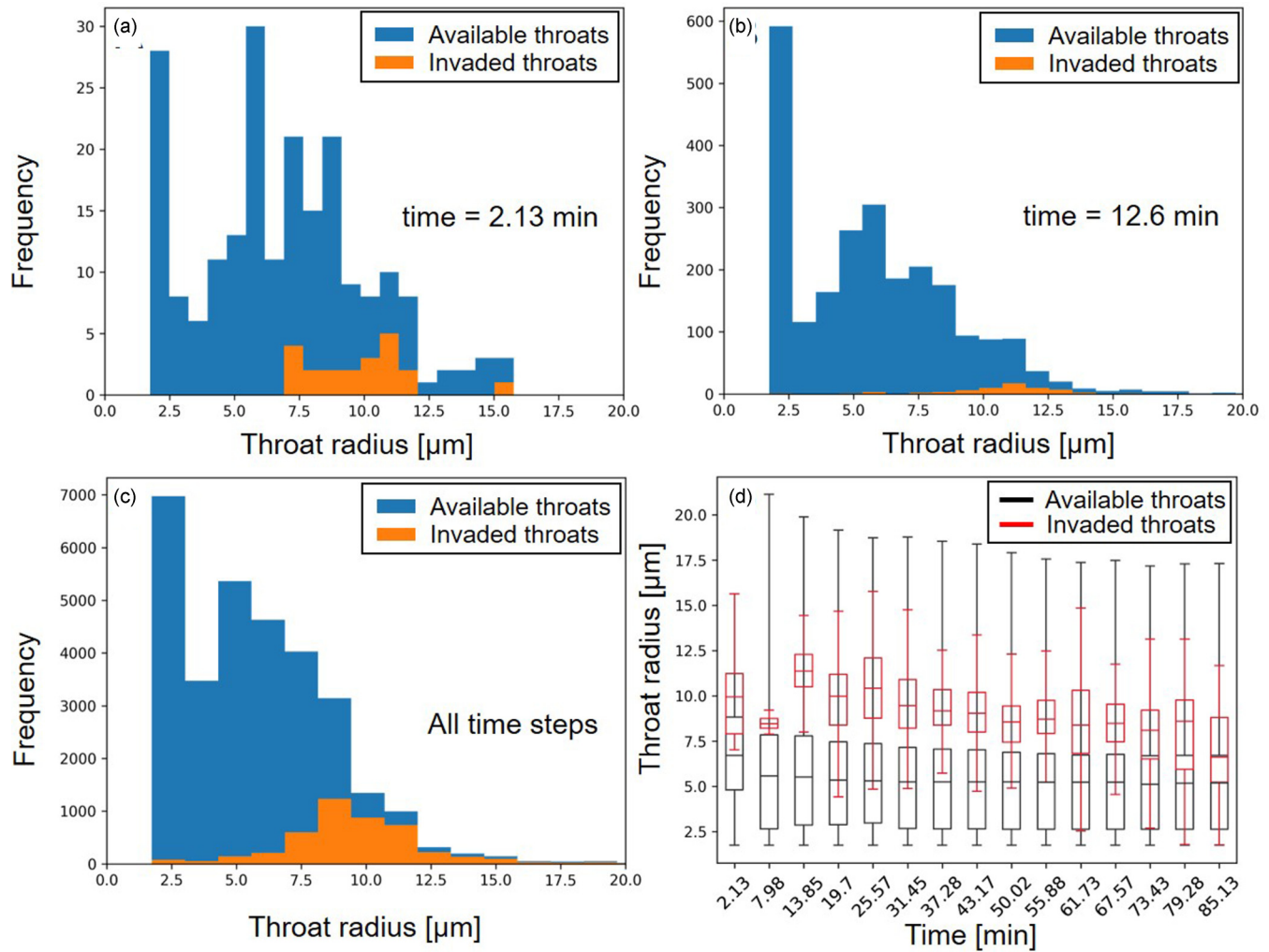


FIG. 6. Pore-filling analysis conducted by plotting the size of invaded throats against the size of all the available throats for water invasion. The sizes of throats filled are plotted at time (a) 2.13 min and (b) 12.6 min. (c) Accumulation of the pore-filling analysis results at all the time steps. (d) Box plot of the cumulative pore-filling results in (c) shown as a function of time.

576 injection. For each time step, the size of the invaded throats
 577 is plotted against all the available throats for invasion (see
 578 Fig. 6). Figures 6(a) and 6(b) show that the advancing water
 579 front invades the largest available throats at time steps of 2.13
 580 and 12.6 min, respectively, which again confirms that water
 581 injection in oil-wet media is an invasion percolation process.
 582 This behavior is further inferred from the cumulative result of
 583 all the 76 time steps shown in Fig. 6(c), indicating that water
 584 almost always invades the largest throats during displacement.

585 To show the significance of invasion percolation in our
 586 oil-wet rock, we generated a box plot for the invaded throats
 587 against the available throats for every five time steps [see
 588 Fig. 6(d)]. Figure 6(d) shows that the portion of the available
 589 throats invaded by water always lies within the largest 5% of
 590 the available throats for invasion. This indicates that the dis-
 591 placement in our heterogeneous oil-wet system is mainly size
 592 controlled, as filling larger throats requires a lower absolute
 593 value of the oil-water capillary pressure, and that wettability
 594 has a little effect. This is attributed to the wide pore size
 595 distribution of the rock sample selected (Fig. S1 in [44]). The
 596 impact of wettability on displacement is marked early on,
 597 where the less-oil-wet pores were filled by water first (see

Fig. 3). It is also unlikely that the later filling sequence is
 determined by a correlation between contact angle and throat
 radius, where the larger throats also have a smaller contact
 angle (favoring filling): Previous work on a similar reservoir
 rock has shown that there is weak tendency for larger pores
 and throats to be more oil-wet with large contact angles [9].

Wettability is expected to play a greater role in displace-
 ment in systems with a more uniform pore and throat size dis-
 tributions. More specifically, it has been previously observed
 in the Ketton limestone sample with similar wettability condi-
 tions but a narrower pore size distribution, where both geom-
 etry and wettability controlled the displacement sequence and
 pores of all size were filled during water injection [36].

2. Haines jumps

Haines jumps were observed on single- and multiple-pore
 levels during water injection. Figure 7 shows the rapid filling
 of multiple pores during a Haines jump and quantifies the
 specific interfacial area of water before and after its retraction
 from the narrower regions. First, we notice a slow increase
 in the water saturation between time steps 3.30 and 7.98 min

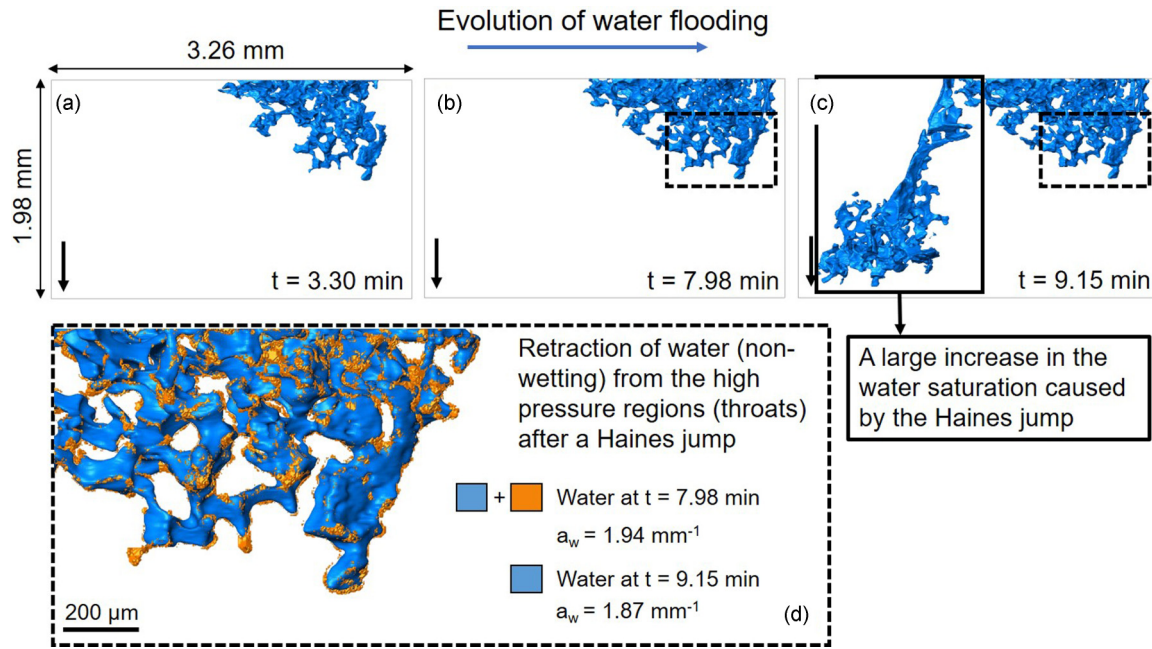


FIG. 7. Three-dimensional images of the water phase at different time steps illustrating the rapid filling of multiple pores during a Haines jump. (a) and (b) Slow increase in the water saturation, which was followed by a large increase in the water saturation caused by the Haines jump in (c). (d) The specific interfacial area of water is lower in the high-pressure region, marked by the dashed line, after the Haines jump due to water retraction. The black arrow points towards the direction of flow, while the blue arrow refers to the evolution of water invasion.

618 [Figs. 7(a) and 7(b), respectively]. However, as soon as the
 619 Haines jump occurs at time equal to 9.15 min, water rapidly
 620 fills multiple pores, resulting in a large increase in the water
 621 saturation [see Fig. 7(c)]. The movement of the advancing
 622 water interface during a Haines jump is very rapid and cannot

623 be captured with the temporal resolution of this experiment
 624 (70 s); micromodel studies have shown that the pores drain on
 625 a millisecond timescale [72].

626 Furthermore, we observe a rearrangement of the water
 627 phase in the pore space associated with the Haines jump,

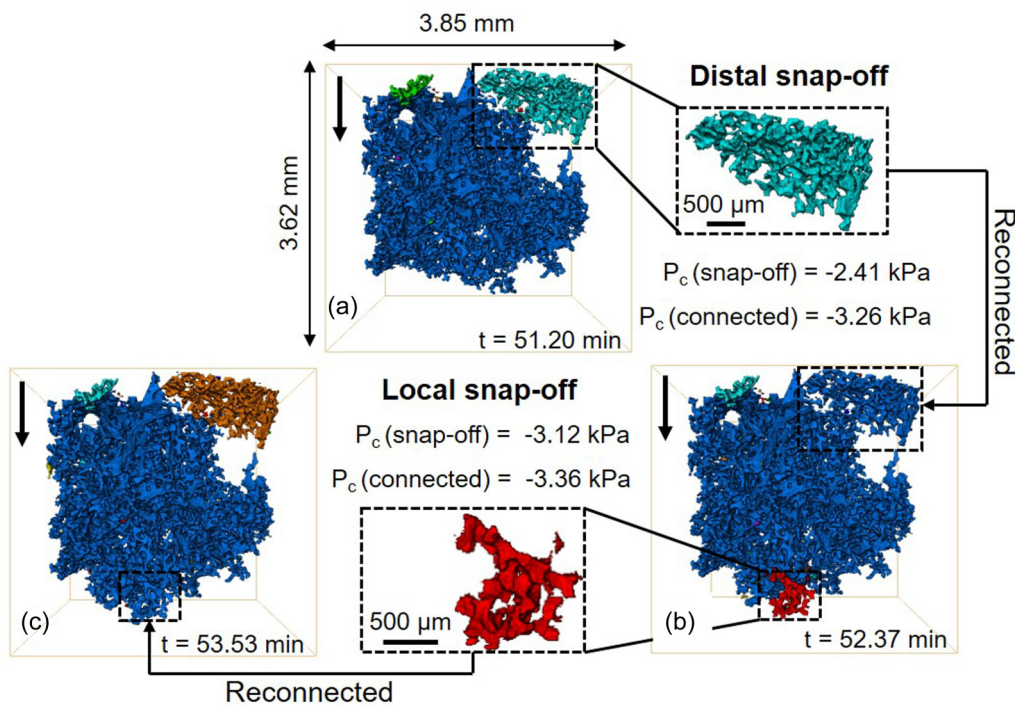


FIG. 8. Three-dimensional images illustrating the occurrence of local and distal snap-off during water injection. Only the water phase is shown; each color represents a disconnected water phase cluster. The black arrow points towards the direction of flow.

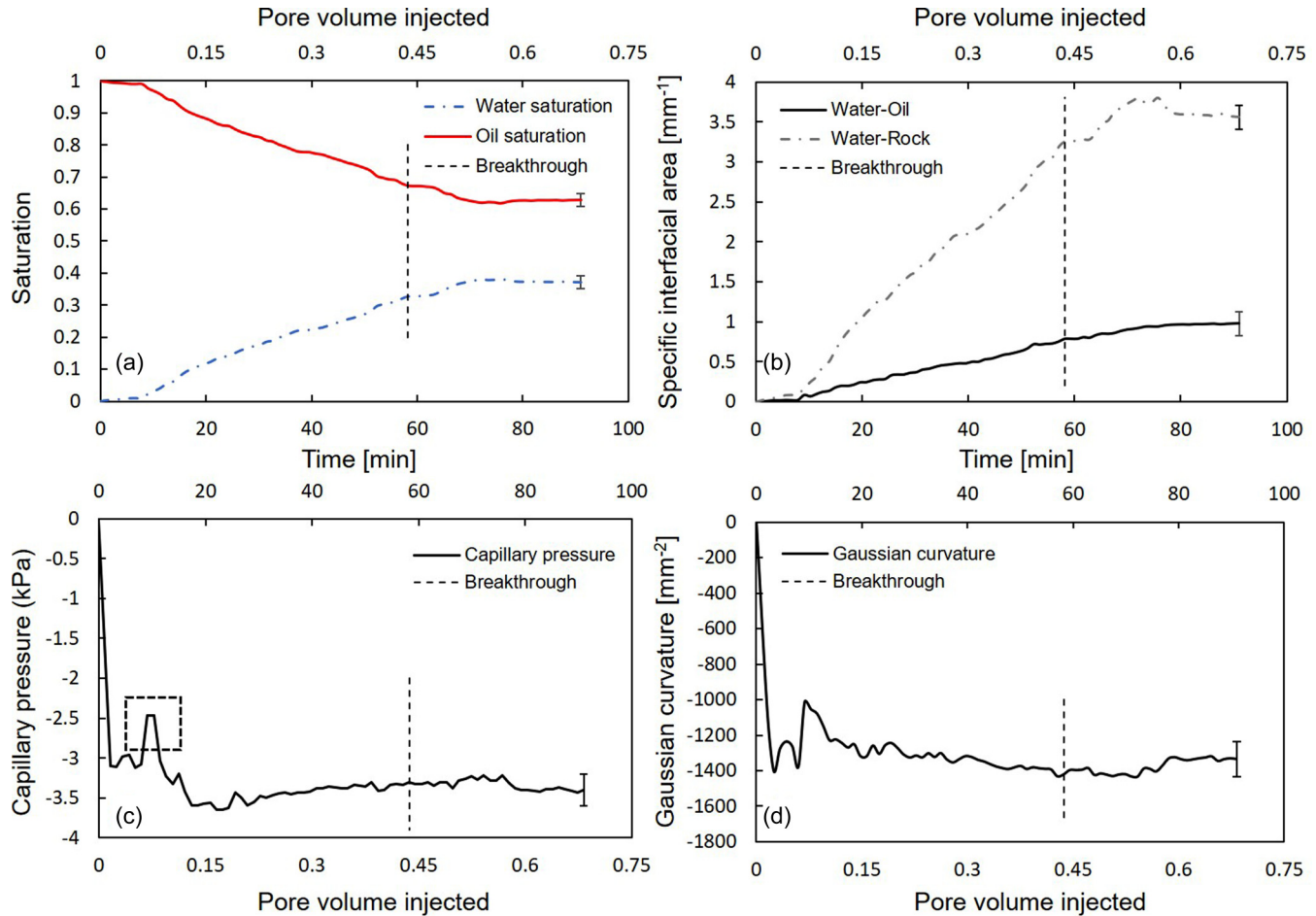


FIG. 9. Minkowski functionals. (a) Oil and water saturation profiles as a function of time and pore volume injected. (b) Change in specific interfacial areas of oil-water and water-rock interfaces with time and pore volume injected. (c) Oil-water capillary pressure plotted as a function of time and pore volume injected. (d) Change in Gaussian curvature of the oil-water interface with time and pore volume injected. The dashed line represents the time of water breakthrough in the imaged field of view. The dashed square in (c) shows a sudden change in the local capillary pressure which corresponds to the filling of multiple pores during a Haines jump, illustrated in Fig. 7. Error bars indicate the uncertainty in the measurements.

628 where water retracts from the high-pressure regions (throats)
 629 and flows towards regions of lower water pressure to supply
 630 the rapid filling. This is shown in Fig. 7(d), where water has
 631 a lower specific interfacial area of 1.89 mm^{-1} at time equal
 632 to 9.15 min after the Haines jump compared to 7.98 min,
 633 where water had a specific interfacial area of 1.94 mm^{-1} . We
 634 notice that water, shown in blue, has retracted from the throats,
 635 shown in orange, in the region marked with a dashed line. The
 636 effect of multiple-pore filling during Haines jumps is more
 637 marked early in the water flooding experiment, when most
 638 pores are occupied by oil only.

3. Local and distal snap-off

639 We observed the two types of snap-off, local and distal,
 640 during the water flooding experiment (see Fig. 8). Distal
 641 snap-off occurs due to the retraction of water, the nonwetting
 642 phase, from the narrower regions of the pore space during
 643 a Haines jump (Fig. 7), some distance away from the jump
 644 itself. The retraction of water is an imbibition process, which
 645 can result in snap-off and disconnection of the water phase as
 646

shown in Fig. 8(a). Next we measured the capillary pressure
 in the system using the method described in Sec. II G. The
 measurements show a lower absolute value of the local capil-
 lary pressure for the disconnected water ganglion (-2.41 kPa)
 compared to the connected water cluster (-3.26 kPa), which
 indicates that the trapped water ganglion reaches a new state
 of capillary equilibrium in the pore space. Furthermore, as
 water invasion proceeds, its local capillary pressure decreases
 (higher water pressure), allowing it to reaccess the throat
 where snap-off occurred, and hence it will reconnect with the
 stranded ganglion as shown in Fig. 8(b).

Local snap-off occurs in the newly filled pores by the
 invading water front as shown in Fig. 8(b). As water passes
 through a narrow throat into the adjoining pore, the local
 capillary pressure will suddenly change, allowing the oil-
 wetting layers in the throat to swell. If the capillary pressure
 reaches the threshold for snap-off, the throat will sponta-
 neously fill with oil, trapping water as a disconnected gan-
 gion in the center of the pore [73]. Again, the snapped-off
 ganglion attains a new position of equilibrium with a lower
 absolute value of capillary pressure (-3.12 kPa) compared to

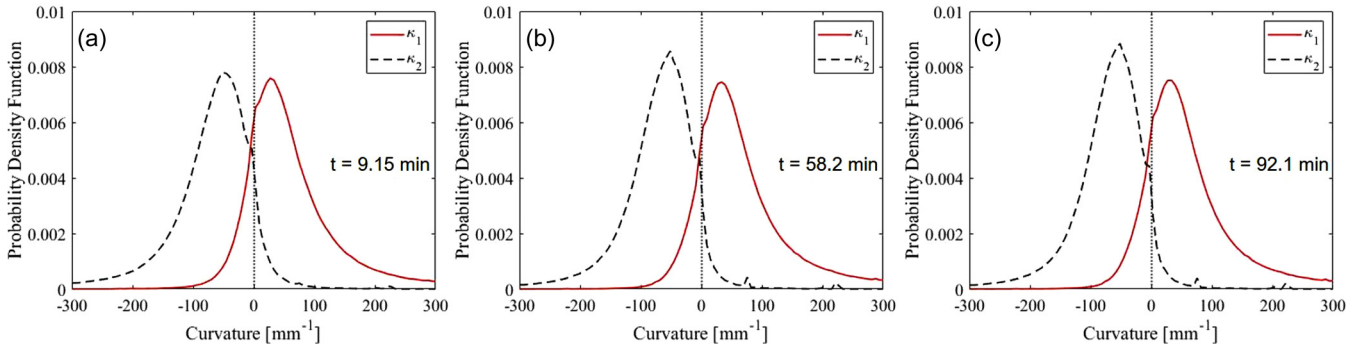


FIG. 10. Normalized histograms of the two principal curvatures κ_1 and κ_2 of the oil-water interface at three time steps: (a) $t = 9.15$ min, (b) $t = 58.2$ min, and (c) $t = 92.1$ min. Here κ_1 is defined to be the larger curvature.

668 the connected water phase (-3.36 kPa). As water progresses
 669 through the pore space, the trapped ganglion is reconnected
 670 [see Fig. 8(c)]. These snap-off events have been previously
 671 observed using fast synchrotron studies in water-wet media
 672 during oil invasion but not in oil-wet systems [18,19].

673 **C. Saturation, interfacial area, and capillary pressure**

674 The saturation of oil and water in the macropores was com-
 675 puted using Eq. (3) on the segmented water injection images
 676 [see Fig. 9(a)]. Figure 9(a) and movie S3 in [44] show that
 677 the water saturation linearly increased with time even after the
 678 observed breakthrough in the imaged field of view (58.2 min).
 679 A noticeable increase in the water saturation was recorded at
 680 9.15 min, corresponding to the rapid filling of multiple pores
 681 caused by the Haines jump event shown in Fig. 7. The water
 682 and oil saturations stabilize to $(38 \pm 2)\%$ and $(62 \pm 2)\%$,
 683 respectively, after 78.1 min, which corresponds to an injection
 684 of 0.58 PV of water; further injection of water does not
 685 displace oil out of the pore space. The low oil recovery factor
 686 seen is attributed to water invading the centers of the pores,
 687 leaving oil connected in thick wetting layers in the corners
 688 and crevices of the pore space. This behavior was observed in
 689 previous water flooding static experiments conducted on the
 690 same rock type [74].

691 The oil-water and water-rock interfaces were extracted
 692 and smoothed [75] to measure their specific interfacial areas
 693 [Eq. (4)]. Figure 9(b) shows that the water-rock and oil-
 694 water specific interfacial areas increase with time during water
 695 injection.

696 Furthermore, the interfacial curvature of the extracted oil-
 697 water interface was measured and substituted in Eq. (5) along-
 698 side the interfacial tension, 52.1 mN/m (Table I), to char-
 699 acterize the capillary pressure of the system [see Fig. 9(c)].
 700 A strongly negative capillary pressure, -3.5 kPa, indicates
 701 that the macropores are indeed oil wet such that on average
 702 water bulges into oil with a higher pressure. This capillary
 703 pressure is higher than the value of -2.4 kPa measured for
 704 a Ketton sample which, as previously discussed, displayed
 705 more mixed-wet behavior [36]. The dashed square in Fig. 9(c)
 706 at 9.15 min shows the sudden change in the local capillary
 707 pressure that caused the Haines jump in Fig. 7.

708 The Gaussian curvature of the oil-water interface was
 709 computed and plotted as a function of time and pore volumes
 710 of water injected in Fig. 9(d). While the sum of the curvatures

is negative, in most cases one curvature is negative and the
 other positive, giving a negative Gaussian curvature. This
 indicates that the phases are well connected in the pore space,
 implying that oil and water flow simultaneously, although oil
 flow is slow since it is confined to movement in wetting layers.
 Furthermore, we plotted, at three time steps (9.15, 58.2, and
 92.1 min), the two principal curvatures (κ_1 and κ_2 , where
 we define $\kappa_1 > \kappa_2$) (see Fig. 10). We observe that although
 the two curvatures have similar distributions, the negative
 curvature κ_2 is more shifted to the left, which results in the
 negative mean curvature, represented by the capillary pressure
 in Fig. 9(c) and the negative Gaussian curvature shown in
 Fig. 9(d). Forming negative and positive principal curvatures
 is a necessary condition for the oil and water phases to remain
 continuous in the pore space, implying a structure with many
 redundant loops [36].

727 **IV. CONCLUSIONS AND FUTURE WORK**

728 This work has provided pore-scale insights into the dy-
 729 namics of two-phase fluid flow during water injection in an
 730 oil-wet reservoir rock. We have used fast synchrotron x-ray
 731 microtomography to visualize the displacement of oil by
 732 water and investigate the pore-scale dynamics by examining
 733 (i) *in situ* wettability and displacement contact angles, (ii)
 734 pore-filling order, (iii) Haines jumps, (iv) snap-off events, (v)
 735 fluid saturations, (vi) specific interfacial areas, (vii) oil-water
 736 capillary pressure, and (viii) Gaussian curvature.

737 We observed that the displacement of oil by water is a
 738 drainagelike process. Measurements of local contact angle
 739 and the estimation of a value based on energy balance during
 740 the displacement confirmed that the medium was oil-wet
 741 (water repellent). Hence, the order of pore filling followed
 742 an invasion percolation pattern, where throats filled in order
 743 of size, with the largest filled first. This is akin to drainage
 744 processes in water-wet systems. Water, the nonwetting phase,
 745 advances as a connected front displacing oil in the centers of
 746 the pore space; oil is confined to movement in wetting layers.

747 We observed drainage-associated dynamics, e.g., Haines
 748 jumps and snap-off, before and after water breakthrough in the
 749 imaged rock section. Haines jumps were observed in single
 750 and multiple pores, alongside the rearrangement of the non-
 751 wetting phase, water, to supply this rapid filling; water retracts
 752 from the high-pressure regions (throats) and flows towards
 753 regions of low water pressure. Furthermore, the two types of

754 snap-off in drainage processes, local and distal snap-off, were
 755 observed. In both snap-off events, the trapped (disconnected)
 756 water ganglion reaches a new position of capillary equilibrium
 757 in the pore space; the water ganglion has a lower absolute
 758 capillary pressure than that of the connected water cluster.

759 The water saturation stabilized to $(38 \pm 2)\%$ after the
 760 injection of only 0.58 pore volumes of water; further injection
 761 of water did not produce more oil. This was ascribed to
 762 the existence of oil in thick connected wetting layers in the
 763 corners of the pore space, where the access of water is limited.
 764 The oil-wet nature of the surface results in a negative capillary
 765 pressure; the Gaussian curvature is also negative, which leads
 766 to well-connected oil and water phases in the pore space.

767 Overall, we have elucidated the invasion patterns and
 768 pore-filling events during water injection in a reservoir rock
 769 which manifests an oil-wet behavior. The same methods and
 770 analysis can be used to characterize signature of two-phase
 771 flow dynamics and help design carbon storage, subsurface

contaminant transport, fuel cells, batteries, and chemical reac-
 tors, for instance, as well as providing benchmark data for the
 validation and calibration of pore-scale models. Future work
 can investigate the impact of wettability on flow in different
 porous media such as soils, packed bed reactors, batteries, fuel
 cells, and microfluidic devices.

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