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Novel adsorption mechanisms identified for polymer retention in carbonate rocks

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ABSTRACT

Hypothesis: High molecular weight polymers are widely used in oilfield applications, such as in chemical enhanced oil recovery (cEOR) technique for hydrocarbon recovery. However, during flow in a porous rock, polymer retention is usually a major challenge, as it may result in the decrease of polymer concentration or lead to plugging of pores with significant permeability reduction and injectivity loss. Hence, an understanding of the retention mechanisms will have a profound effect in optimizing the process of polymer flooding, in particular, for carbonate rocks, which hold more than half of the world's oil reserves. Therefore, in this study, the retention of hydrolysed polyacrylamide (HPAM) polymer, a commonly used chemical for EOR, is investigated during flow in Estaillades carbonate rock.

Experiments: A novel approach of investigating HPAM retention in Estaillades carbonate rock was carried out using Atomic force microscopy (AFM). Since Estaillades carbonate rock is ~98% calcite, HPAM retention was first characterised on a cleaved flat calcite mineral surface after immersing in HPAM solution. Afterwards, HPAM was flooded in Estaillades carbonate to observe the effect of flow dynamics on the retention mechanisms.

Findings: We find that the dominant mechanism for retention of HPAM on calcite after fluid immersion is polymer adsorption, which we believe is driven by the electrostatic interaction between the calcite surface and the solution. The thickness of the adsorbed layer on calcite is beyond 3 nm suggesting it is not adsorbed only flat on the surface. Different types of adsorbed layers were formed representing trains, and the more extended loops or tails with the largest polymer layer thickness about 35 nm, representing the longer loops or tails. Layers of this thickness will begin to impair the permeability of the rock. However, in Estaillades, thicker adsorbed layers are observed in different regions of the rock surface ranging between 50 and 350 nm. We suggest that this is due to either mechanical entrapment and/or polymer entanglement during flow in Estaillades carbonate rock, which will cause the major permeability impairment in porous rocks.

1. Introduction

High molecular weight polymers are of great importance in a variety of industrial applications, such as waste water treatment and in oil field applications, where polymer retention in a porous rock is of significant importance, in the context of chemical enhanced oil recovery [1,2]. Polymer solutions are used in enhanced oil recovery processes, because the remaining oil saturation is reduced, making the displacement of oil more effective and improving the sweep efficiency [3–7]. High molecular weight polyelectrolyte polymers of hydrolysed polyacrylamide (HPAM), in the million Dalton range are preferred, because low concentrations of such polymers will cause a significant increase in polymer solution viscosity, such that, the mobility of the polymer solution is lowered relative to the oil, thereby improving sweep efficiency. Since HPAM is a polyelectrolyte, at the molecular level, their structure changes due to the nature of the ionic strength, such that they may behave as a random walk of chains at high electrolyte concentrations and/or low charge density, whilst at low electrolyte concentrations the molecule is much more
expanded due to strong repulsion of same charges and ultimately adopts a rigid rod like conformation [8-10].

Furthermore, at the macro-scale these polymers show both shear-thinning and “shear thickening” rheology in porous media [6,7]. However, in bulk flow, they have a favourable shear thinning behaviour, which at high flow rates near the well bore and during injection will cause the viscosity to be low, meaning that the injection pressure remains low i.e., below the fracture pressure of the rock. Furthermore, there are technical challenges associated with the use of high molecular weight polymers like HPAM, for e.g., adsorption (or more generally retention), which reduces the permeability of the rock and the polymer concentration available for an effective sweep, because the polymer solution viscosity is reduced. Previous studies on polymer retention [11,12], were carried out mostly in sandstone rocks and successfully implemented both in the laboratory and commercially [5,13,14].

For carbonate rocks, the laboratory studies conducted have shown some success especially with oil-wet reservoir cores and in the use of modified polymer solutions [15-19]. In a pilot test carried out by Levitt et al. [20] in carbonate reservoirs, lower oil recovery, due to reduced oil bank formation caused by reservoir heterogeneity, is perhaps, the reason. No commercial full field level polymer flood, in a carbonate rock, has been successful at the time of writing. Therefore, an understanding of the root cause of polymer retention is required, in carbonate rocks, for an efficient flooding process, since more than half of the world's oil reserves are in carbonate rocks [21].

In general, the propagation of polymer solution in porous media is controlled by retention and inaccessible pore volume (IPV). The mechanism of polymer retention conceptually can comprise of polymer adsorption, mechanical entrapment and hydrodynamic retention [22] [see Fig. 1a]. In polymer adsorption, high molecular weight polymers attach to different polar points on the rock surface adopting the trains, loops and tails configuration [23,24] as shown in Fig. 1b. This process of adsorption is essentially irreversible, because certain parts of the polymer chain may detach, whilst other parts reattach onto the rock surface, it being very unlikely that all attached points of the polymer chain will detach from the rock surface at the same time [25]. Also, adsorption can be induced by surface charge, where unlike charges between the fluid and the rock mineral surface drives adsorption because of electrostatic interaction. For instance, sandstones are predominantly quartz, which are negatively charged. Therefore, retention with HPAM is minimised due to similar charges except in the event of clay swelling, due to screening of the surface charge by positively charged counter-ions present in the electrolyte occurring more nearest to the pore walls compared to the bulk [26-28]. Carbonate rocks are positively charged [29,30] therefore, retention increases due to difference in charge between the rock and polymer solution. However, there have been instances where carbonates and calcite minerals were found to be negatively charged depending on the pH and salinity conditions [27,31].

In the process of mechanical entrapment, large sized polymer molecules become trapped in the porous media, while hydrodynamic retention is when the polymer solution is hydrodynamically trapped in the pore space due to changes in flow rate. Some other phenomena which relate to entrapment of polymer solutions are filtration; where the polymer solution becomes filtered at the porous media entrance, trapping in dead-end pores and polymer chain bridging; where polymer chains form bridges and become trapped within the pore space above a critical pressure.
shear rate, especially in low permeability rocks [32]. Consequently, some retention mechanisms are reversible such as hydrodynamic retention due to changes in flow rate while others may not be, like adsorption [33,34].

There have been significant advancements in the description of polymer adsorption e.g., in the recent work of Ferreira & Moreno [5], in sandstone rocks, polymer adsorption was modelled by both type I and type IV adsorption isotherms depending on the overlapping concentration of the polymer and the modes of adsorption and re-adsorption. The fundamental question; however, is how the adsorption of a molecule monolayer lying on a flat substrate, assuming a thickness of a few nanometres, can possibly cause significant permeability reduction in pores of a few micrometers and larger. Perhaps the assumptions of molecules lying flat on the surface of minerals and monolayer adsorption, in general, are not applicable for the situation in the porous media application.

Numerous studies have investigated experimentally the cause of polymer adsorption on flat surfaces, using the surface forces apparatus, atomic force microscopy and ellipsometry [1,35-38]. Investigations of polymer solution flowing in capillaries by Grattoni et al. [39] showed that dynamic polymer retention (i.e. during flow) is significantly greater than static retention and termed the mechanism of retention in capillaries as adsorption entanglement, which implies that in the context of polymer flooding the porous media is more than an assembly of flat surfaces, but is rather an assembly of capillaries. Zitha et al. [40] suggests that polymer retention is primarily due to adsorption and bridging, by elongated polymer chains during flow. Polyacrylamide retention on silicate surfaces by Bessaies et al. [27], and some simulation work by Dang et al. [41] point to the nature of the polymer and the mineral surface as major faces by Bessaies et al. [27], and some simulation work by Dang et al. [41] point to the nature of the polymer and the mineral surface as major factors towards retention. This further implies the importance of the solution quality and surface heterogeneity, which in this case will notably impact the retention of polymer solution in porous media.

Significant impact on adsorption can also arise from the fact that mineral surfaces of carbonate rocks are often rough. Hence, investigations on rough surfaces by Chauveteau [32] using glass bead packs, showed that the mechanism of polymer retention was a consequence of flow-induced adsorption, where hydrodynamic forces normal to the pore walls become large, such that, it induces adsorption of polymer chains into region of previously adsorbed polymer layers. Most of these investigations focus on elastic rocks, such as sandstones. For this class of rock, the application in the field shows that in many cases, the adsorption/retention related problems can be controlled [42,43]. However, for carbonate applications, this is not the case as adsorption/retention is significantly larger, which in many field trials have led to the loss of injectivity [20,21] suggesting a much more significant and potential conceptual difference of the retention mechanism.

Therefore, the focus of this work is a detailed study on the mechanism of polymer retention on smooth and rough surfaces. This work studies the root cause of polymer retention in Estaillasses carbonate rock, using the latest state-of-the-art atomic force microscopy (AFM). The AFM, which is traditionally a topographical imaging technique capable of measuring surface features ranging from the micrometer to atomic scale. The images were obtained mechanically using a sharp tip, which raster-scans the surface of the sample. The tip is mounted on a cantilever and moved along the scanning grid, using piezoelectric transducers. The position of the tip is thereby monitored with a laser. In this study, we scanned the samples in quantitative imaging (QI)-mode with a PPP-NCHAuD probe obtained from NANOSENSORS™ (tip radius: < 10 nm, tip height: 10–15 μm, nominal force constant: 42 N/m), using a Nanowizard 4 AFM from JPK instruments (now Bruker). In the QI-mode, the tip is moved vertically towards and from the sample at each individual pixel, and then advances to the next pixel. This allows the full force profile at that point to be obtained, whilst approaching and retracting from the surface, and therewith to obtain additional information about the surface properties, such as the stiffness of the sample [45]. The stiffness (Young modulus – YM) of the probed surface, was estimated by fitting the Hertz model to the force profiles obtained at each point, the tip shape was considered parabolic, with a radius of 10 nm [46–51]. The Poisson ration was assumed to be 0.5. In addition to the automated fit, which considers the full force profile provided by JPK data processing software (JPK instruments), we conducted a manual fit by adjusting the fitting range for selected force-distance curves to probe the initial stiffness of the polymer layer.

The image processing, including the application of line levelling and a median filter, was conducted with the standard JPKSPM data processing software. The 3D visualization was obtained using MATLAB (R2018b).

### 2. Material and methods

In this section, characterisation of polymer retention on calcite mineral surface is discussed following the experimental set-up carried out for the investigation of polymer retention in a heterogeneous porous media.

#### 2.1. Polymer preparation

Hydrolysed polyacrylamide was obtained from SNF Floerger with a molecular weight range of 11–13 MDa (FP3330) and 18–20 MDa (FP3630) as shown in Table 1. Two solutions were prepared in the presence of brine purchased from Sigma Aldrich, the first (HPAM-Na) in the presence of 0.5% NaCl was prepared for characterising polymer retention on a bare calcite surface and (HPAM-Ca) in the presence of 0.5% CaCl₂ was used to investigate polymer retention in Estaillasses carbonate rock. We use CaCl₂ brine to achieve a target zero-shear rate viscosity between 0.01 and 0.05 Pas. During the preparation of polymer solution, ITW (15% Isopropanol, 7.5% thiourea and 77.5% water) a protective package to minimise polymer degradation was added at 20%, such that the final concentration of isopropanol is 20% of the polymer concentration. Afterwards, polymer powder was introduced, and mixed using a stirrer rod for 10 minutes following a magnetic stirrer for 48 hours to ensure individual polymer molecules had enough time to dissolve [44].

#### 2.2. Atomic force microscopy

Atomic force microscopy (AFM) is a topographical imaging technique capable of measuring surface features ranging from the micrometer to atomic scale. The images were obtained mechanically using a sharp tip, which raster-scans the surface of the sample. The tip is mounted on a cantilever and moved along the scanning grid, using piezoelectric transducers. The position of the tip is thereby monitored with a laser. In this study, we scanned the samples in quantitative imaging (QI)-mode with a PPP-NCHAuD probe obtained from NANOSENSORS™ (tip radius: < 10 nm, tip height: 10–15 μm, nominal force constant: 42 N/m), using a Nanowizard 4 AFM from JPK instruments (now Bruker). In the QI-mode, the tip is moved vertically towards and from the sample at each individual pixel, and then advances to the next pixel. This allows the full force profile at that point to be obtained, whilst approaching and retracting from the surface, and therewith to obtain additional information about the surface properties, such as the stiffness of the sample [45]. The stiffness (Young modulus – YM) of the probed surface, was estimated by fitting the Hertz model to the force profiles obtained at each point, the tip shape was considered parabolic, with a radius of 10 nm [46–51]. The Poisson ratio was assumed to be 0.5. In addition to the automated fit, which considers the full force profile provided by JPK data processing software (JPK instruments), we conducted a manual fit by adjusting the fitting range for selected force-distance curves to probe the initial stiffness of the polymer layer.

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<table>
<thead>
<tr>
<th>Description of polymer solutions.</th>
<th>Solution</th>
<th>Polymer Conc. (ppm)</th>
<th>Salt Conc. (wt.%)</th>
<th>Salt Conc. (mM)</th>
<th>Ionic strength (mM)</th>
<th>Polymer Mw (Da)</th>
<th>Polymer % (Pas)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HPAM-Na</td>
<td>2000</td>
<td>0.5</td>
<td>NaCl</td>
<td>86</td>
<td>18–20</td>
<td>0.6</td>
<td></td>
</tr>
<tr>
<td>HPAM-Ca</td>
<td>5000</td>
<td>0.5</td>
<td>CaCl₂</td>
<td>90</td>
<td>11–13</td>
<td>0.02</td>
<td></td>
</tr>
</tbody>
</table>
2.3. Polymer retention characterisation with calcite

2.3.1. Calcite crystal

Optical quality colourless, rhombohedral crystals of Iceland Spar calcite were purchased from Manchester Minerals, United Kingdom. The sample used for AFM experiment was obtained from the parent crystal by cleaving twice with a clean, sharp bladed tool to ensure that an original surface was exposed. The cleaved sample of ~ 7 mm length and a thickness of ~ 2 mm, was relatively smooth, and thus suited to nanoscale investigations of the solid-liquid interface. Cleavage was performed in air just prior to the measurements, and immediately placed within a stainless-steel fluid cell, with the inlet and outlet sealed with silicone tubing. The polymer solution was slowly injected through the silicone tubing using a syringe, until the calcite crystal was fully immersed. An additional reference sample was prepared using the same methodology, for a cleaved calcite immersed in 0.5% NaCl solution, without the polymer solution. For imaging the calcite sample with AFM, we chose a scan area of 10 μm x 10 μm with 256 x 256 sampling points using a set point of 30 nN and a z-length of 0.2 μm.

2.3.2. Polymer characterisation on calcite

AFM topography image of HPAM-Na adsorbed onto the calcite surface is shown in Fig. 2. The imaged area 10 μm by 10 μm is composed of three readily visible regions: a thin polymer layer (between 3 and 10 nm thick) looking like freckles that is pervasive over the whole sample, with patches of medium thickness (25 nm), and areas that are much considerably thicker (35 nm) than the surrounding surface [52–55].

The force-distance curves are measured between the probe and the polymer layer on the calcite surface. As the probe is extended towards the surface of the polymer, no interaction occurs, until the probe touches the surface of the polymer layer at a certain distance, represented by the point of elevation in the approach curve. The interactions measured at these observed regions of low, medium, and high adsorbed polymer layer thickness are displayed, together with a control measurement of bare calcite surface in brine, illustrated in Fig. 2(c-f). Contrary to the measurements of the bare calcite surface in brine, that reveal no detectable interaction on approach Fig. 2c (AFM images of bare calcite can be seen in the work by Ricci et al. [56]), force curves obtained in the polymer solution, show consistent repulsive interactions, with the repulsive force increasing in magnitude with decreasing tip-sample separation and becoming longer ranged as adsorbed layer thickness is increased.

For regions with lowest adsorbed polymer layer thickness, a repulsive force is evident beginning from a tip-sample separation of 10 nm, before contact was made with the calcite surface. Force measurements conducted on regions of median height, a repulsive force at about 25 nm from the calcite surface, exponentially increasing before contact was made with the calcite surface. This is indicative of the adsorbed tail polymer structure being compressed. Likewise, at the highest adsorbed structure of long dangling polymer tails, the repulsive force rises even more steeply at 35 nm, where the tip pushes through to the calcite surface. In the supplementary information, we further confirm a polymer layer thickness of up to 40 nm in Fig. S1, by studying the force-distance curves at a different location, which represent the high polymer region.

Hysteresis is also present in all three adsorbed layer structures measured, as the retract curves do not follow the approach curves, as has been observed before for the interaction between polymer layers [36,39, 57,58]. This symbolises that, the polymer solution may have been pushed onto the rock surface and so does not relax quickly from the compression, as the tip disengages the calcite surface.

The interaction between polar groups on the polymer chain and polar sites of the calcite surface, would support the adsorption of flat-lying continuous chains of small loops and train structures, with thickness ~

![Fig. 2. HPAM-Na retention on calcite with 10 μm x 10 μm x - y axis. (a) height image indicating regions of high, medium, and low polymer retention (b) Young Modulus. The red regions are polymer layers having lower Young modulus compared to the yellow region (calcite surface) with higher Young modulus values. Force curves obtained from the AFM with Young Modulus fit for (c) calcite in brine (0.5% NaCl). Force-distance curves representing HPAM-Na retention on calcite for (d) low polymer region, representative of a monolayer adsorption of trains (e) medium polymer region, representing polymer tails, attached to previously adsorbed monolayer and (f) high polymer region, representing extended polymer tails and/or microgels, attached to previously adsorbed polymer layer. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)](image-url)
10 nm, constituting the thinnest adsorbed layer of polymer solution on the calcite surface. We believe polymer retention was predominant on the entire calcite surface, because of the affinity between the charged COO⁻ groups on the polymer chain and cations present on the calcite surface [56,59–61] as well as the hydrogen bonds between HPAM and the calcite surface as discussed by Wang et al. [55]. Areas of median thickness ranging between 10 and 25 nm, correspond to polymer chain tails, closely situated with areas where the adsorbed layer was thickest, ranging from 25 to 40 nm, denoting longer polymer chain tails and/or entangled chains, that are perpendicular to the calcite surface.

The force curves were fitted with the Hertz model to obtain the Young Modulus values, in other to have a more understanding of the stiffness. The automatic fits were obtained from the JPK software and the manual fits were carried out to ensure proper fitting by the software. The continuously low Young Modulus values obtained at all locations of the polymer treated sample is shown in Fig. 2b and Table 2, ranging in the order of 10⁷–10⁹ Pa for the automated fit and continuously in the range of 10⁸ Pa when fitted manually, compared to the non-treated sample with a continuous Young modulus in the range of 10¹⁰ Pa. This indicates a continuous surface coverage of calcite by HPAM and agrees with the AFM topography image, showing extensive microgel-like structures on the sites where highest amount of polymer layer thickness was observed.

2.4. Core-flood investigation

2.4.1. Estaillades

Estaillades is a Cretaceous bioclastic limestone from the Estaillades quarry in south east France. The rock has a typical porosity φ = 30% and permeability of ∼ 100 mD [62]. It consists predominantly of calcite (97.9%) with minor quartz (2.1%) components [63]. Due to its bioclastic composition, the rock has a complex pore-structure illustrated by the micro-CT image, shown in Fig. 3a and b, containing heterogeneities across different length scales.

Estaillades has a dual-porosity system as shown by the mercury intrusion porosimetry (MIP) results shown in Fig. 3c. It is a rock commonly used for flow dynamics investigations during core flooding experiments [64,65].

2.4.2. Core-flood experiment

Two sets of core flooding experiments were carried out on Estaillades with core characteristics listed in Table 3 and set up detailed in Fig. 4. The first core flood experiment was a drilled core sample with a large size of length 10 cm and diameter 3.8 cm, investigating polymer rheology and the implications of permeability impairment. Due to the small sized samples required by the AFM, the second core flood experiment had core of length 2 cm and diameter 0.5 cm for sub-pore scale assessment of polymer retention with AFM.

2.4.2.1. Core-flood investigations to assess rheology. The core holder for the first flooding experiment [see Fig. 4a], which investigates rheology and permeability impairment, was fabricated with stainless steel. The Estaillades core was introduced into the core holder, sealing with a dual-epoxy adhesive araldite 2014, purchased from RS Components, Ltd UK, such that the core becomes coated with araldite resin. The pressure transducers used were purchased from Keller UK Ltd, with ratings of 100, 30, and 10 bar with an accuracy of 0.05% full scale. The set up was built to allow for five pressure measurement. Three measurements within the core, and two measurements upstream and downstream of the core. The epoxy glue was drilled through three openings on the core holder, in order to allow PT2, PT3 and PT4 direct pressure measurements on the core. Pump A was used for fluid injection, while Pump B acted as a pressure regulator.

As evident from the characterisation of polymer solution on calcite, where microgel-like structures were observed (Fig. 2a). The formulation of the polymer solution injected into Estaillades core was refined, such that, the solution viscosity was reduced to 0.02 Pa by using a lower molecular weight and introducing a divalent salt of CaCl₂. This was done because of the low permeability and heterogeneity of Estaillades and to achieve a target flooding viscosity that is between 10 and 50 times the viscosity of water [66,67]. The divalent cation was also introduced to allow for a more practical scenario of the salts present in an actual reservoir.

A filtration step was also introduced, such that the polymer solution was filtered using a 2 µm filter paper under a pressure of 5 bar in a filtration cell, to remove any microgels, and the filtration ratio was estimated to be about 1.01. The equation for filtration ratio was obtained from Thomas [68] and defined as the time for 100th ml minus the time for the 80th ml divided by the time for the 80th ml minus the time for the 60th ml and expressed in Eq. (1) as follows;

\[
FR = \frac{t_{60} - t_{80}}{t_{100} - t_{80}}
\]

Before injecting the polymer solution into the core [see Fig. 4a], CO₂ was injected for about 10 min to remove dirt and debris. We use CO₂ instead of inert gas because the pressure required for dissolving CO₂ during subsequent brine saturation to remove any gas phase is simply much less than for e.g., nitrogen or other inert gases. Afterwards, brine was injected into the core to flush out CO₂ [65,69]. The pressure drop was recorded during brine injection, and the permeability of the core was estimated based on the Darcy equation in Eq. (2) [4,70].

\[
k = \frac{u \cdot L}{\Delta P}
\]

where k is the permeability, u is the brine viscosity, L is the length of the core, u is the fluid velocity and ΔP is the pressure drop across the core. The residual resistance factor (RRF) is also estimated in Eq. (3) [68].

\[
RRF = \frac{k_{pre-polym}}{k_{post-polym}}
\]

where \(k_{pre-polym}\) is the permeability of the core before polymer injection and \(k_{post-polym}\) is the permeability of the core after polymer is injected.

Afterwards, polymer solution (HPAM-Ca) was injected at different flowrates ranging from 1 ml/min to 40 ml/min. The stabilised pressure drops between PT2 and PT4 were recorded. The core was flushed afterwards with brine to remove the polymer solution and the permeability determined.

2.4.2.2. Core-flood investigations to assess retention with AFM. Prior to the AFM measurements, the second Estaillades carbonate sample was placed in a Viton sleeve and mounted into the flow cell, and a differential pressure transducer was connected across the sample as shown in Fig. 4b. A confining pressure of 2 MPa was applied to the sample within the flow cell. The sample was flushed with brine to remove air, keeping the back pressure at 4 MPa (with the confining pressure always kept at an additional 2 MPa over the pore pressure). Once the air was removed, the sample was returned to ambient pressure (and a confining pressure of 2 MPa).

The polymer was then injected to displace the brine. This was undertaken at a constant flow rate of 0.05 ml/min, until the pressure drop across the sample had plateaued (at which point the system was assumed

<table>
<thead>
<tr>
<th>Table 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Young Modulus with automatic and manual Hertz model fit of HPAM-Na retention on calcite, at no polymer (only 0.5% NaCl) low, medium, and high polymer.</td>
</tr>
<tr>
<td>----------------------------------</td>
</tr>
<tr>
<td>Hertz Model fit</td>
</tr>
<tr>
<td>Automatic</td>
</tr>
<tr>
<td>Manual</td>
</tr>
</tbody>
</table>
to be at equilibrium). Afterwards, the sample was retrieved from the flow cell, whilst constantly keeping it within the brine solution of 0.5% CaCl₂.

The Estaillades sample after polymer flooding was scanned by the AFM, along the radial surface of the pores adjacent to the cut edge of the Estaillades core [see Fig. 4c] [45,71,72] on a 10 μm × 10 μm area, with 128 × 128 sampling points, using a set point of 180 nN and z-length of 2 μm to accommodate for the sample roughness. A dry reference was obtained from a twin sample. The sample was scanned using the same settings as in the polymer flood experiment except a lower set point of 140 nN.

**Table 3**

<table>
<thead>
<tr>
<th>Core characteristics</th>
<th>Core flood 1 (Rheology and permeability investigation)</th>
<th>Core flood 2 (retention investigation with AFM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Estaillades Core flood 1</td>
<td>Length 10 cm</td>
<td>Diameter 3.8 cm</td>
</tr>
<tr>
<td></td>
<td>Porosity 32%</td>
<td>Permeability 128 mD</td>
</tr>
<tr>
<td></td>
<td>Pore volume 36.19</td>
<td></td>
</tr>
<tr>
<td>Estaillades Core flood 2</td>
<td>Length 2 cm</td>
<td>Diameter 0.5 cm</td>
</tr>
<tr>
<td></td>
<td>Porosity 30.4%</td>
<td>Permeability 175 mD</td>
</tr>
<tr>
<td></td>
<td>Pore volume 34.23</td>
<td></td>
</tr>
</tbody>
</table>

**Fig. 3.** μCT greyscale images of an Estaillades carbonate (a) 2D-slice and (b) 75% cut 3D-volume, consisting of different recrystallized fossils, the rock shows a complex pore-structure and a dual porosity as shown in the MIP-curve in (c). (adapted from Ref. [64]).

**Fig. 4.** Core flooding experimental setup for flooding polymer solution (HPAM-Ca), in order to (a) investigate rheology and changes to core permeability. The Estaillades core has a length of 10 cm and diameter of 3.8 cm (b) investigate mechanism of polymer retention with AFM. Core length is 2 cm and a diameter of 0.5 cm (c) Estaillades core sample showing the radial surface that was imaged with AFM [34].
3. Results

In this section, we present the results obtained from the measurements of polymer rheology and retention in Estaillades carbonate.

3.1. Rheology of HPAM

Results presented in Fig. 5 were obtained using the larger core sample, where HPAM-Ca was injected at different velocities. In Fig. 5a, the apparent viscosity is estimated using the well-known Darcy equation in Eq. (2) and the result of the apparent viscosity as a function of Darcy velocity are presented. As the shear rate increases, the in-situ rheology changes from shear thinning to shear thickening at a critical Darcy velocity of 3 ft/day corresponding to 0.01 mm/s. As the shear rate continues to increase, a second critical Darcy velocity of 10 ft/day (0.035 mm/s) is reached. This introduced a sudden reduction in polymer apparent viscosity, which we believe is related to either polymer retention, where some polymer solution is retained within the rock or polymer degradation, where some polymer chains are broken into smaller chains leading to a reduction in solution viscosity. The simulation work by Pierleoni et al. [73] showed that shearing of polyelectrolyte polymers can lead to the destruction of polymer chain blob thereby reducing chain length [8,73].

The permeability of the rock before and after polymer injection were compared to assess structural alteration of the rock by polymer flooding. The changes in permeability were determined at conditions when brine was injected before and after polymer injection. The results shown in Fig. 5b for pressure drop as a function of the Darcy velocity show a large difference in pressure drop. The residual resistance factor (RRF) was determined to be 2.8 suggesting that retention is still within the low range based on K.Sorbie [4]. However, we estimated a permeability reduction of ~ 55%.

The effluent polymer solution after polymer injection in the core were characterised in a rheometer and compared with same polymer solution prior to injection in the core sample. The results in Fig. 5c showed a decrease in the zero-shear rate viscosity from 20 mPas to 4 mPas. These results of increased pressure drop and changes to the fluid viscosity suggests polymer retention, which changed the geometric structure of the rock and possibly degradation of the polymer chains. These results also show that, with low permeability rock cores, retention, and degradation of HPAM polymers is very probable and the mechanism of retention will be discussed in the subsequent sections.

3.2. Imaging HPAM retention on mineral surfaces in 3D porous rock (Estaillades)

Estaillades carbonate core was first imaged in air with AFM and the results are presented in Fig. 6. The height map in Fig. 6a shows the degree of rock roughness, with regions of hills and valleys. The yellow regions are representative of the rock peaks and the dark regions representative of the valleys. As the AFM tip is not able to pass through the narrow pores, it is likely that some of the valleys represent the inlets to the nanopores, reflected by the MIP curves in Fig. 3c. This assumption is supported by the similar diameter of about 600–700 nm in the valleys to the lower peak pore-diameter of the MIP results. Furthermore, the structural attributes of the rock need to be considered in interpreting the force-distance curves obtained, because the structures may redirect the tip on approach to the surface which causes slide artefacts or even prevent the contact of the tip with the underlying surface entirely.

The Young Modulus (YM) of the displayed structure is represented in Fig. 6b. The yellow regions, which are stiffer, represent higher YM values, where the peaks of the rock are situated, while dark regions represent the edges of the rock. However, the lower YM values, which represent the dark regions are a consequence of the sliding of the tip along the sharp edges before the very tip touches the rock surface.

In the presence of HPAM-Ca, after imaging with the AFM, the polymer solution adhered to the surface of the rock sitting at the peaks and edges of the rock, as can be seen in Fig. 6a of the height map. In the Young Modulus map of Fig. 7b, the region marked "x" in Fig. 7a representing the rock mineral surface in the height map, has a higher YM value compared to the region marked "z", in Fig. 7a where we believe adsorbed HPAM is present. The HPAM retained on the rock surface after polymer injection, is represented by the red areas in the YM map, which are the softer areas, compared to the YM values of the rock surface, which are much stiffer. The images in Fig. 7a suggest that the mechanism of retention is related to both adsorption and mechanical entrapment. However, this will be discussed in more detail in the discussion section.
The 3-dimensional height map in Figs. 6c and 7d is a clear depiction of the roughness of Estaillades rock surface. In Fig. 7d, the roughness of the rock is high with a high peak to valley ratio, but we observe less-stiff regions, due to HPAM retention on the rock represented in red, along the peak and edges of the rock confirming the observations in Fig. 7a and b.

The force-distance curves in Fig. 7c were obtained from Fig. 7a, in the region marked “x”, which were fitted with the Hertz model to obtain the Young Modulus values. Similar to the characterisation on the calcite mineral, the automatic fits were obtained from the JPK software and the manual fits were carried out to ensure proper fitting by the software. The YM values were significantly higher for Estaillades mineral surface than the adsorbed polymer layer in both automatic and manual fits, suggesting that the region marked “x”, due to a lesser stiffness, is definitely an adsorbed polymer layer than the region marked “x”, which is clearly the mineral surface. Also, close ranged YM values of ~ 25 MPa and 20 MPa were estimated in the highest adsorbed polymer layer on calcite surface and in the region marked “x” of the Estaillades surface as shown in Tables 2 and 4 respectively. To further confirm our results of...
the different regions of polymer retention, and regions of Estaillades mineral surface, force-distance profiles at different locations of Fig. 7a, were carried out, and the results are shown in Fig. S2 – S4 of the supplementary information.

4. Discussion

Calcite is positively charged at neutral pH [30], thus attractive electrostatic interactions between Ca$^{2+}$ on the calcite surface and negatively charged COO$^-$ groups in HPAM, will drive the adsorption of the polymer onto the mineral surface by electrostatic interaction. The formation of surface-polymer hydrogen bonds also makes a substantial contribution to the adsorbed layer structures. Indicated in Fig. 2, three different ranges of polymer layer thickness (low, medium and high), are spread over the entire surface of the calcite mineral. Regions of low polymer layer thickness between 3 and 10 nm have a continuous widespread adsorption on calcite, in the form of small loops and trains. This is due to the high percent hydroxyls; hence, increased amount of polyacryl acid group on the HPAM backbone; together with the high salinity of the brine. This reduces the hydrodynamic size, and increases the density of the polymer chain loops and trains close to the calcite surface, allowing for more surface coverage [5]. The medium polymer adsorption layer of 25 nm represent tails, while the high polymer adsorption layers of 35 nm are representative of either longer length tails, entangled HPAM molecules or weakly cross-linked HPAM microgels [74–77].

In the Estaillades carbonate rock, the degree of HPAM retention increased due to rock roughness, which induced more retention by mechanical entrapment. In Fig. 7a, retention of HPAM occurred at different regions, with the region marked “x” having an apparent thickness of ~80 nm, as shown by the force-distance curves in Fig. 7c, albeit the difficulty in knowing the true height of polymer retention on rough mineral surfaces. Consequently, there are other regions, where the apparent thickness of the adsorbed polymer layer in Fig. 7a is larger, having thickness of up to ~350 nm [78]. We show the force-distance curves in Fig. S2 and Fig. S3 of the supplementary information. In these larger regions, we presume the effect of adsorption entanglement, as discussed in the work of Grattoni et al. [25], for polymer adsorption during flow in a capillary.

Furthermore, in places the polymer layer thickness was observed to be larger in Estaillades, ranging between ~50 nm and ~350 nm in Fig. 7a, compared to the thickness observed on calcite, ranging between ~3 nm and ~35 nm. Mechanical entrapment is likely to be the reason for increased retention because during flow, more polymer chains may get attached onto previously adsorbed polymer layer, increasing the thickness of the polymer layer. This is captured in Fig. 7a in the region marked “x”, which we believe represents one of the highest points on the rock surface closest to the Viton sleeve used during core flood injection, such that, some of the polymer chains would appear to become entangled by hooking onto the loops of previously adsorbed polymer chain layer, as the polymer solution flows through the rock. We also note that in some areas, polymer seems to be present in the valleys between calcite grains, see the regions indicated in Fig. 7a (labelled as microgel bridging), where in the YM image of Fig. 7b, softer regions are detected which are likely to be polymer solutions. Again, this may be due to the entanglement of polymers in solution adsorbed directly on the mineral surface and causing bridging. Therefore, these results suggest a situation where the underlying adsorption induces more retention by mechanical entrapment and has the capability of creating even larger sized adsorbed polymer layers or aggregates that may form microgels in-situ of the porous media. Consequently, this study shows that the thickness of an adsorbed polymer layer on a flat mineral surface, which is between 3 and 40 nm, in combination with more polymer retention caused by mechanical entrapment is much of a challenge for low permeability carbonate rocks, because an adsorbed polymer layer thickness of ~350 nm can fill the 0.69 μm pores (if filled on both sides of the pore) in Estaillades [Fig. 3c] and definitely lead to an impairment in the permeability.

5. Conclusion

Estaillades carbonate is known to possess a wide distribution of porethroat sizes, with nano and micro pores, and in this work, the dynamic retention of HPAM has been studied to understand the mechanism of polymer retention in the complex rock structure of Estaillades carbonate. The retention of HPAM, which was first characterised on a flat calcite surface, was found to be by adsorption, suggesting electrostatic interactions between negatively charged polymer chains and the positively charged calcite surface. The adsorption was arranged as trains, loops and tails with the tails representing entangled polymer chains, as an extra layer on the previously adsorbed layer on the flat calcite surface [74–77]. After flooding HPAM in Estaillades, a significant increase in the rock pressure-drop was a strong indication that the rock structure had been altered with the rock permeability decreasing by ~55%. The AFM study revealed some structural changes in the rock, where larger sized polymer aggregates of different layer thickness ranging between 50 and 350 nm were formed in-situ of the porous media due to mechanical entrapment as a result of the rock roughness [39].

Results show that the mechanism of polymer retention (adsorption by electrostatic interaction) on a flat calcite surface also takes place in the rock (because Estaillades contain 98% calcite mineral) with an additional effect of mechanical entrapment, which leads to the formation of thicker polymer layers within the rock pore space, which within narrow constraints of the rock, may have the potential to lead to pore blockage, or partial blockage, and hence, lead to the permeability impairment observed.

Therefore, this study provides a basis for the effective flooding of polymer solutions in low permeability porous media structures like carbonate reservoirs, where the actual cause of the permeability impairment is shown, to ensure that the consequence of polymer retention in reservoirs can be minimised.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jcis.2021.100026.

Table 4

<table>
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<th>Young Modulus with automatic and manual Hertz model fit for Estaillades mineral surface and adsorbed polymer layer (HPAM-Ca) on Estaillades.</th>
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<tr>
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<td>Hertz model fit</td>
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<tr>
<td>Automatic</td>
<td>731 MPa</td>
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<tr>
<td>Manual</td>
<td>1300 MPa</td>
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