



Deposited via The University of Leeds.

White Rose Research Online URL for this paper:

<https://eprints.whiterose.ac.uk/id/eprint/183433/>

Version: Accepted Version

Article:

Wang, Q, Shen, J, Glover, PWJ et al. (2022) Oil production enhancement, asphaltene precipitation and permeability damage during CO₂-SAG flooding of multi-layer sandstone reservoirs. *Journal of Petroleum Science and Engineering*, 212. 110241. ISSN: 0920-4105

<https://doi.org/10.1016/j.petrol.2022.110241>

© 2022, Elsevier. This manuscript version is made available under the CC-BY-NC-ND 4.0 license <http://creativecommons.org/licenses/by-nc-nd/4.0/>.

Reuse

This article is distributed under the terms of the Creative Commons Attribution-NonCommercial-NoDerivs (CC BY-NC-ND) licence. This licence only allows you to download this work and share it with others as long as you credit the authors, but you can't change the article in any way or use it commercially. More information and the full terms of the licence here: <https://creativecommons.org/licenses/>

Takedown

If you consider content in White Rose Research Online to be in breach of UK law, please notify us by emailing eprints@whiterose.ac.uk including the URL of the record and the reason for the withdrawal request.

Oil production enhancement, asphaltene precipitation and permeability damage during CO₂-SAG flooding of multi-layer sandstone reservoirs

Qian Wang^{1*}, Jian Shen¹, Paul W.J. Glover², Piroska Lorinczi², Wei Zhao³

¹School of Resources and Geosciences, China University of Mining and Technology, Xuzhou, 221116, China

²School of Earth and Environment, University of Leeds, Leeds, LS2 9JT, UK

³China Petroleum Technology and Development Corporation, Beijing, 100028, China

Abstract: The process of CO₂-SAG flooding involves conventional miscible CO₂ flooding until breakthrough (BT), followed by a period of CO₂ soaking or shut-in, and then a continuation of the miscible CO₂ flooding. The SAG process provides different improvement in the oil recovery for different positions of each layer in multilayer reservoirs, and has different effects on the distribution of pore throat blocking and adsorption of asphaltene to mineral surfaces. In this paper, both miscible CO₂-SAG and conventional CO₂ flooding experiments have been carried out at reservoir conditions and on multi-layer systems composed of parallel connection of long cores. After CO₂-SAG flooding oil recovery factors (RF) of the low, medium and high permeability cores were 7.7%, 8.3%, and 7.6% higher compared to the RFs after CO₂ flooding. The respective fractional oil production (FOP) of each long core were 10.6%, 27.7%, and 61.6% after CO₂-SAG flooding, with less difference between each long core than CO₂ flooding. After CO₂ flooding, the permeability of the high permeability core at the injection end dropped by 24.5-25.8%, which is 5.5-14.3% higher than the value at the outlet. The permeability decrease due to CO₂-SAG flooding was 0.7-9.7% higher than that due to CO₂ flooding, and the distribution of permeability decline is more homogeneous. The contribution of the total permeability decrease attributable to asphaltene particle blockage due to CO₂ flooding was 84.7-62.7%, 5.2-10.1% higher than that due to CO₂-SAG flooding, gradually decreasing along the flow direction. Complex two phase flow of oil and gas is more likely to cause pore throat blockage instead of causing the adsorption of asphaltene precipitation.

30

31 **Keywords:** CO₂-SAG flooding, multilayer reservoirs, asphaltene precipitation, blockage and
32 absorption, permeability decline.

33

34 **Introduction**

35 The injection of CO₂ into reservoirs is a proven effective enhanced oil recovery (EOR)
36 method^[1-3]. Oil viscosity and interfacial tension reduction, volume swelling, light-hydrocarbon
37 extraction during CO₂ flooding are all important effects which contribute to the EOR process<sup>[4-
38 5]</sup>. Continuous miscible CO₂ flooding is a practical and efficient displacement technology^[6].
39 Regrettably, conventional CO₂ injection suffers from flow instability and viscous fingering,
40 and consequently, early CO₂ breakthrough^[7]. Especially, most oil reservoirs are composed of a
41 series of relatively layers with variable permeabilities. In these reservoirs, CO₂ breakthrough
42 occurs first from layers of high permeability. The gas pathway is established through these high
43 permeability layers, which results in a large volume of crude oil in lower permeability layers
44 being by-passed and, consequently, unproduced^[8-9].

45

46 The CO₂-soaking-alternating-gas flooding process (CO₂-SAG) is a combination of
47 conventional continuous miscible CO₂ flooding with a CO₂ soaking stage from the CO₂ huff-
48 and-puff process^[10]. In the first stage CO₂ is continuously injected into the reservoir in the same
49 way as in the conventional miscible CO₂ process. The CO₂-SAG process differs from
50 conventional CO₂ flooding by being stopped at breakthrough. The second stage of the CO₂-
51 SAG process is a soaking period, in which both the injector and producer are shut in. During
52 this period the injected CO₂ diffuses into the residual oil and water in the reservoir, accessing
53 those fluids with which the gas was not in contact during the dynamic first stage of the process.
54 The oil becomes larger in volume and significantly more mobile, allowing it to leave some of
55 the smaller and more inaccessible pores and occupy instead the CO₂ saturated high permeability

56 channels opened up by the initial flooding in Stage 1 to CO₂ BT^[11]. The third stage is another
57 simple miscible CO₂ flood to displace and recover the residual oil that was freed in Stage 2^[12].

58

59 The CO₂-SAG process results in better dissolution of CO₂ in crude oil than either the CO₂ huff-
60 and-puff process, which depends only on the diffusion of molecular CO₂, or conventional CO₂
61 flooding, where CO₂ only dissolves in the crude oil in direct dynamical contact with the flood
62 front. The improved interaction between CO₂ and crude oil that occurs during the soaking
63 process substantially promotes the miscibility of oil and CO₂, and increases the CO₂
64 displacement efficiency during secondary CO₂ flooding, with higher CO₂ utilization efficiency
65 and lower injection cost^[13].

66 No matter what kind of CO₂ flooding method is adopted, the CO₂ dissolution or light
67 component stripping of crude oil perturbs crude oil thermodynamically, which promotes the
68 precipitation and flocculation of asphaltenes^[14-15]. A proportion of these particles of asphaltene
69 become adsorbed onto mineral surfaces within the rock matrix altering the wettability and
70 hence capillary properties and permeability of the rock. The remaining asphaltene agglomerates
71 remain suspended in the fluid and are transported by the pore fluids until they become trapped
72 in pores and pre throats leading to blockages. These blockages can result in extremely
73 significant drops of permeability^[16-17].

74

75 Moreover, heterogeneity has a markedly important influence on the final efficacy of the CO₂-
76 SAG process^[20]. In multilayer reservoirs the enhancement depends on the quality of the
77 reservoir rock in a given layer and its position along the core as well as the proximity of other
78 layers with different flow characteristics. Reservoir heterogeneity between layers with different
79 permeability also affects the distribution and amount of reservoir damage after flooding^[18-20].

80 In addition, the adsorption and blockage of asphaltene precipitation cause different damage to
81 the permeability at different locations within the reservoir, with different adsorption and
82 blockage mechanisms^[21].

83

84 In order to formulate more targeted and effective measures in heterogeneous layered reservoir,
85 as well as to prevent or reduce the damage to rock permeability caused by asphaltene
86 precipitation, distinguishing the damage to permeability from blockage and adsorption is
87 required. As a result, the quantification of the influence of the CO₂-SAG process on oil recovery
88 must also be balanced by any deleterious effect on permeability.

89
90 There is a relatively small number of core-flooding experiments which have focused on the
91 technical potential of CO₂-SAG flooding. Nevertheless, they permit a number of key issues to
92 be targeted for further study, such as CO₂ injection flow rate and pressure, the parameters which
93 control the optimal CO₂ soaking period, the effect of water pre-flooding, cores with different
94 permeability were subjected to CO₂-SAG flooding experiments under different conditions^[12,22].
95 We have carried out SAG flooding experiments on cores with similar permeability but different
96 pore throat structures and single heterogeneous long cores, and studied the effects of pore
97 structure and linear heterogeneity on the micro and macro crude oil production improvement
98 of CO₂-SAG flooding and the distribution of permeability damage^[10,13]. Furthermore, there has
99 been no previous study of the combined improvement in hydrocarbon recovery and progress of
100 permeability damage in heterogeneous reservoirs consisting of multiple layers of rocks with
101 different pore microstructures after both types of flooding. In particular, there is a lack of
102 research on the distribution of asphaltene precipitation in the blocked and adsorbed state.

103
104 In this paper, CO₂-SAG and conventional CO₂ flooding have been carried out at reservoir
105 conditions on two assemblages of three long cores with different permeability ,which are
106 arranged in parallel in separate core holders and representing three parallel layers in a reservoir.
107 The porosity and permeability between the analogue cores in the two assemblages are almost
108 the same. The results presented in this paper cover the comparison of the efficiency of
109 miscible CO₂-SAG flooding with simple miscible CO₂ flooding, focusing on (i) fluid
110 displacement, (ii) oil production enhancement and its distribution, (iii) the distribution of
111 permeability damage due to the blockage and adsorption of asphaltene precipitation. The

112 progress and extent of each effect has been compared across each of the three different pore
113 microstructures (layers). The results furnish information allowing the advantages,
114 disadvantages, benefits and risks of different CO₂ flooding methodologies to be judged in
115 heterogeneous layered reservoir, especially with regard to reservoir damage and the saturation
116 of residual oil.

117

118 **Methodology**

119 **Materials**

120 A crude oil sample taken from the Jilin oilfield in the northeast of China and analyzed to obtain
121 its composition(table 1). The compositional results were used to synthesize a live oil, which
122 was subsequently used in all of the experiments. The proportion of *n*-C₅-insoluble asphaltene
123 in the Jilin oil sample was 3.18 wt% ^[10]. The minimum miscible pressure of the CO₂-crude oil
124 system was measured by slim-tube apparatus and discovered to be 20.6±0.4 MPa at
125 90±0.1°C^[10]. The relationship between asphaltene precipitation and the crude oil CO₂
126 concentration has also been measured previously^[10], asphaltenes begin to precipitate from crude
127 oil at a dissolved CO₂ concentration of 29.5mol%, and completely precipitate at 60 mol%. as
128 well as being predicted using the Flory-Huggins model^[15]. We note that the measured and
129 predicted values differ by <5%. The CO₂ solubility in the Jilin crude oil is 68.3 mol% and the
130 oil viscosity decreases from 2.11 mPa·s (0 mol% CO₂) to 0.62 mPa·s (68.3 mol% CO₂) at 23
131 MPa and 90°C ^[10].

132

133 This study used two types of brine. The first was prepared to the compositional recipe given in
 134 Table 2^[10]. The second was prepared from the same compositional recipe but with the addition
 135 of Mn²⁺, which was added to remove the signal arising from water when making nuclear
 136 magnetic resonance (NMR) measurements in order to obtain the oil distribution in the core^[23].

137

138 **Table 1.** Basic physical properties of live oil together with its compositional analysis (n-C5
 139 insoluble asphaltene content =3.18 wt%).

Property		Value			
Density (g/cm ³)		0.731±0.002 (90°C)			
Viscosity (mPa·s)		2.11±0.04 (90°C)			
Solution gas-oil ratio (m ³ /m ³)		44.7			
Bubble point pressure (MPa)		6.95			
Composition					
Carbon number	wt%	Carbon number	wt%	Carbon number	wt%
CO ₂	0.053	C9	4.640	C21	2.16
N2	0.422	C10	4.531	C22	2.304
C1	1.741	C11	3.947	C23	2.104
C2	1.126	C12	3.615	C24	2.088
C3	0.998	C13	3.261	C25	1.948
<i>i</i> C4	0.178	C14	2.908	C26	1.872
<i>n</i> C4	0.525	C15	2.633	C27	1.896
<i>i</i> C5	0.942	C16	3.615	C28	1.766
<i>n</i> C5	0.353	C17	3.567	C29	1.882
C6	1.365	C18	3.222	C30+	26.363
C7	2.52	C19	2.484	Total	100
C8	4.409	C20	2.563		

140

141

Table 2. Physicochemical properties of the reservoir brine.

Item	Value
Density (g/cm ³)	1.005
Viscosity at 25°C (mPa·s)	1.02
pH	7.04
K ⁺ (mg/L)	1473
Na ⁺ (mg/L)	3546
Ca ²⁺ (mg/L)	116

Mg ²⁺ (mg/L)	33
Cl ⁻ (mg/L)	5261
SO ₄ ²⁻ (mg/L)	1288
HCO ₃ ⁻ (mg/L)	1559
TDS (mg/L)	13276

142 TDS = Total dissolved solids.

143

144 The artificial long cores used in the tests are composed of epoxy resin and quartz sand with
 145 different grain size distributions, which were cold isostatically pressed^[24] (Figure 1). The
 146 petrophysical characteristics of these core samples are shown in Table 3. The long cores are
 147 approximately homogeneous (the difference between the porosity or permeability at any
 148 position in the sample is within $\pm 2.7\%$ and $\pm 3.3\%$ of the mean porosity or permeability value
 149 for the core, respectively). Three cores with different permeabilities and porosities were used
 150 in a triad to represent three reservoir layers with different permeabilities. Consequently, though
 151 the results discussed in this paper refer to three different cores, they represent analogue layers
 152 in a reservoir.

153



154

155

Figure 1. Schematic diagram of an artificial homogeneous long core.

156

157

Table 3. Fundamental characteristics of the core samples used in this work.

Flooding method	Core number	Length (cm)	Diameter (cm)	Permeability (mD)	Porosity (%)
	H ₁	50.2	2.52	25.7	14.4
CO ₂ flooding	H ₂	50.4	2.52	51.8	16.7
	H ₃	50.1	2.52	75.7	19.2

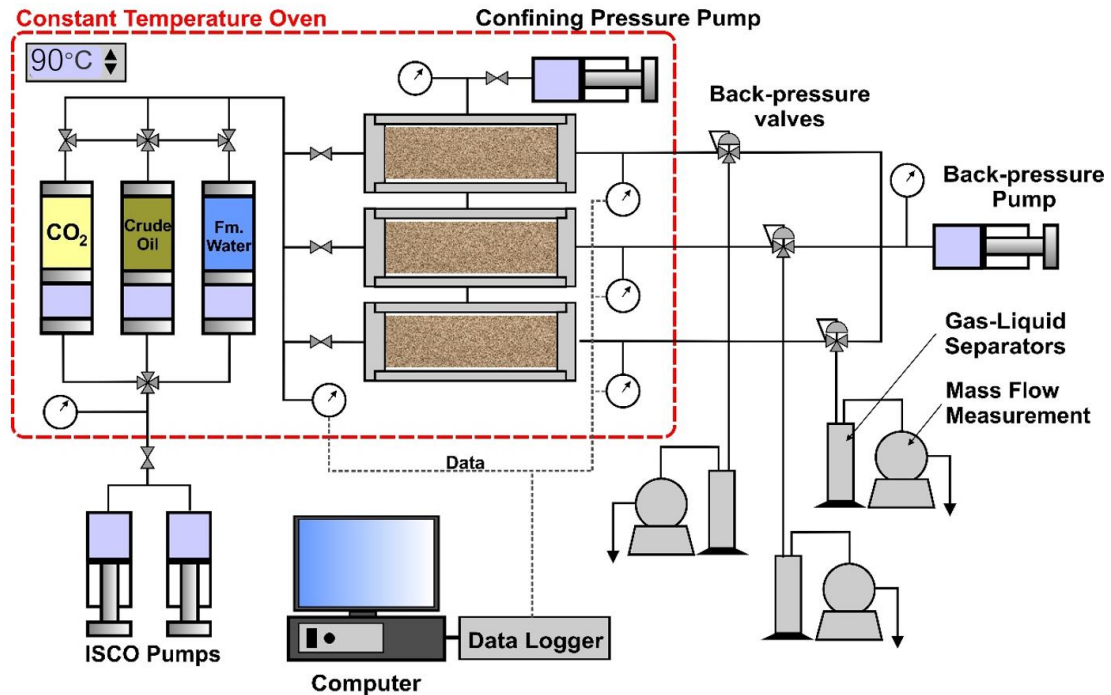
CO ₂ -SAG flooding	J ₁	50.3	2.52	26.3	14.1
	J ₂	50.1	2.53	50.1	17.1
	J ₃	49.8	2.52	76.2	18.8

158

159 **Core-flooding tests**

160 The flow diagram of core flooding apparatus used in this study is shown in Figure 2. In this
161 arrangement, three core holders (Hongda, China, $L=75$ cm, $T_{\max}=130^{\circ}\text{C}$, $P_{\max}=80$ MPa) are
162 positioned horizontally and connected in parallel in order to simulate a multilayer reservoir.
163 Process fluids (CO₂, live oil, and brine with MnCl₂ (Mn²⁺, 15g/L)) were delivered
164 independently to the cores (Figure 2) using three separate high-pressure cylinders (Hongda,
165 China; $T_{\max}=130^{\circ}\text{C}$; $P_{\max}=80$ MPa). The temperature of all core holders and tanks was ensured
166 by placing them in an oven (Hongda, China; $T_{\max}=120.0\pm 0.1^{\circ}\text{C}$). Displacement of CO₂, crude
167 oil, and brine into the multilayer core system was implemented using a dual ISCO syringe
168 pump. A second pump was used to apply a constant confining pressure. A third pump was used
169 together with three back pressure valves to ensure that the backpressure was controlled and
170 constant. A set of gas-liquid separators and mass flow meters was used to measure the fluids
171 produced from each core. All data, including pressure and flow data were collected and logged
172 using a computer.

173



174

175

Figure 2. Schematic diagram of flooding experiments.

176

177 Conventional miscible CO₂ core flooding tests were carried out on cores H₁, H₂ and H₃ in the
 178 following two steps.

- 179 (1) The oven and the core-flooding flow rig it contains was raised to 90°C and kept at this
 180 temperature for 24 hours to ensure a constant starting temperature in all parts of the
 181 apparatus inside the oven and all process fluids. Cores H₁, H₂ and H₃ were cleaned and
 182 dried, and then placed in their core holders. Each core was subjected to separate evacuation
 183 for 24 hours. Brine with MnCl₂ was injected into each core, separately. A maximum of 30
 184 HCPV of crude oil was then pumped into each core separately in order to attain the connate
 185 water saturations (S_{wc}) and initial oil saturations (S_{oi}) in each core. Subsequently, all core
 186 holders were left undisturbed for 24 hours in order to obtain equilibrium at reservoir
 187 conditions (90°C, 23MPa).
- 188 (2) A constant flow of CO₂ was injected at a rate of 18 cm³/h (This injection rate is based on
 189 the oilfield injection rate and the previous experiments^[10]. This rate will not lead to a rapid
 190 breakthrough of CO₂ BT, but a higher oil RF.) into all three cores at the same time from

191 the same inlet and at the same input pressure. The produced fluids from each core were
192 collected and measured individually but at the same output pressure (23 MPa) using the
193 back pressure pump and back pressure valves on each output line. The flow of CO₂ was
194 stopped when there was no further oil production from the multilayer system. Steps (1)
195 and (2) represent the core-flooding experiment using the conventional miscible CO₂
196 flooding process.

197
198 The miscible CO₂-SAG core flooding tests were carried out on cores J₁, J₂, J₃ using the
199 following four steps.

200 (3) Step (1) was repeated, but using cores J₁, J₂, J₃.

201 (4) Step (2) was conducted on the cores J₁, J₂, J₃, but stopping the core-flood as soon as CO₂
202 breakthrough (BT) occurred. This CO₂ injection will be called the primary injection.

203 (5) All three core holders were isolated during the CO₂ soaking stage by closing all input and
204 output valves. The length of time for this shut is a critical parameter which is discussed
205 later in the paper.

206 (6) The input and output valves were reopened, and CO₂ injection was recommenced into all
207 three cores at a constant flow rate of at 18 cm³/h as in Step (4). This secondary CO₂ flood
208 was continued until no further crude oil was produced.

209 The fluid volumes, injection pressures and production pressures and were monitored and
210 recorded continuously during the entire flooding process. The asphaltene content of all
211 produced oil was also measured.

212

213 Post-flooding tests

214 All the long cores were divided into 10 core plugs with the same length after flooding, the
215 resulting short cores were subjected to NMR testing (Mini-MR, Niumag, China) to obtain the
216 residual oil distribution by transverse relaxation time (T₂) spectrum analysis.

217

218 Asphaltene is soluble in aromatic hydrocarbons but not in alkanes. Other components of crude
219 oil are soluble in alkanes. Consequently, *n*-heptane can be used to clean cores of their non-
220 asphaltene oleic components^[25]. In this work, the short cores were cleaned with *n*-heptane using
221 the Soxhlet method (Soxhlet Extractor SXT-02, Shanghai Pingxuan Scientific Instrument CO.,
222 Ltd., China) which removed all oleic fluids remaining in the cores after flooding, but leaving
223 the asphaltene precipitation blocking pore throats and adsorbed to pore walls. Methanol was
224 used to remove any aqueous fluids remaining after the floods. Subsequently, all of the short
225 cores were dried. Their gas permeability was then measured. This permeability was the
226 permeability that had been affected by asphaltene precipitation both blocking pore throats and
227 due to adsorption to mineral surfaces.

228

229 It should be noted that due to the non-polar nature of cyclohexane on asphaltene dissolution,
230 cyclohexane reversal flooding can remove the asphaltene blocking pore throats. By contrast,
231 reverse flooding using toluene can remove any asphaltene adsorbed on mineral surfaces.
232 Cyclohexane reverse flooding was performed (flow rate =30 cm³/h until a stable differential
233 pressure was sustained) to measure any formation damage that had accrued from the
234 mechanical blocking of pores and pore throats^[15]. It was found that this process removed
235 asphaltene due to mechanical blockage of pore throats in all cores. The cores were then cleaned,
236 allowing the decline in permeability decline associated with asphaltene pore throat blockage to
237 be quantified.

238

239 Subsequently, the cores were subjected to reverse flooding with toluene^[16], in order to remove
240 adsorbed asphaltenes that could not be removed with cyclohexane. The cores were then cleaned
241 again, and the permeability was remeasured in order to obtain the permeability decline due to
242 the adsorption of asphaltenes directly to mineral surfaces.

243

244 **Results and Discussion**

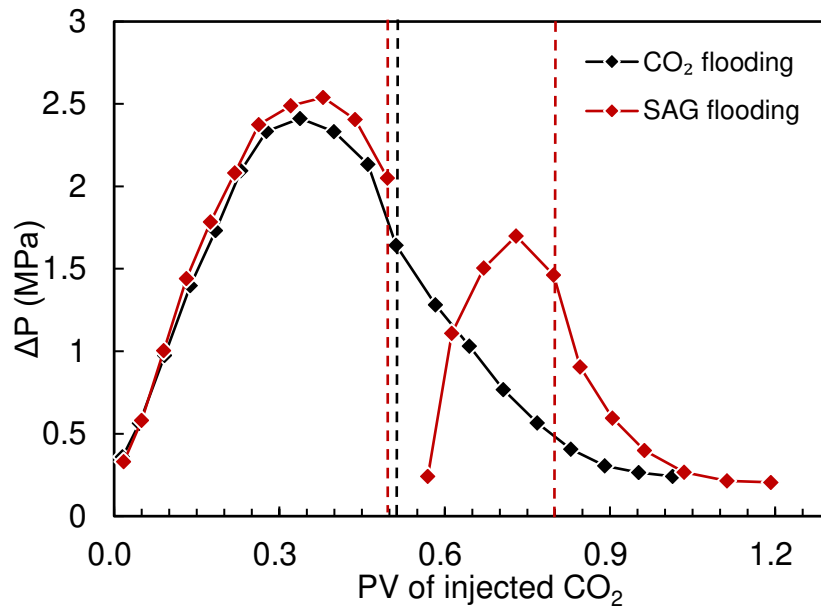
245 Differential pressures (ΔP)

246 Figure 3 shows that the dynamic trend of the ΔP values during CO_2 and SAG flooding are very
247 similar during the continuous CO_2 injection before CO_2 BT. The similar behavior is attributed
248 to the matched physical properties of the two groups of cores composing the three-layer system
249 (see Table 3), and suggests that their similar petrophysical properties result in similar
250 distributions of fluids at the start of the experiment and progressively during initial CO_2
251 flooding.

252

253 In the SAG flooding process, the CO_2 soaking stage was started after the CO_2 BT (occurring at
254 0.4961 PV), and then the secondary CO_2 flooding was performed (until 1.192 PV). During the
255 CO_2 soaking stage, the crude oil that had not previously interacted sufficiently with CO_2 had
256 the opportunity to adsorb CO_2 . As a consequence, the volume of this crude oil expanded and
257 its viscosity decreased, leading to the redistribution of fluids within the pores. The saturation
258 of the oil in the pores that had composed the well-connected and larger pore size gas channels
259 formed by the initial CO_2 flooding increased. Consequently, the displacement resistance of
260 SAG secondary flooding was greater than that during CO_2 flooding at same injected CO_2
261 volume, and less than that before CO_2 BT. The secondary CO_2 BT occurred more quickly due
262 to the higher gas saturation and lower oil viscosity in the rock at the beginning of the secondary
263 flooding. It is worth noting that the CO_2 BT only occurs in the high permeability layers during
264 CO_2 flooding and SAG flooding. There is no obvious CO_2 BT in the medium and low
265 permeability layers, and the displacement front of CO_2 flooding does not advance to the outlet
266 end.

267



268

269 **Figure 3.** Measured differential pressure (ΔP) during CO₂ flooding and SAG flooding.
 270 Vertical dashed lines show CO₂ BT for each flood.

271

272 Pressure decay during the CO₂-soaking process

273 Figure 4 shows that the core fluid pressure declines rapidly as soon as the CO₂-soaking process
 274 begins, becoming progressively slower. The pressure-time curve can be approximated by a
 275 power-law, fits of which are also shown in the figure. This behavior arises from (i) dissolution
 276 of gas in the oil near the gas-oil interface, and (ii) gas diffusion deeper into the oil. Both of
 277 these processes depend on the partial pressure of gas already in the oil. As a result, dissolution
 278 becomes progressively less efficient until a steady-state is reached^[26-27].

279

280 In our case, the cores were soaked in brine and cleaned before the laboratory experiments were
 281 carried out. This process makes the cores water-wet, with water preferentially coating the
 282 surfaces of rock grains and completely filling the smallest pores. By contrast, crude oil and CO₂
 283 are non-wetting phases. Such non-wetting phases occupy the center of large and medium-sized
 284 pores and pore throats as far from the mineral surfaces as possible. The injected CO₂ prefers to
 285 be in contact with the crude oil in the center of the large pores and throats. Under these
 286 conditions, we expect that the initial swift pressure drop occurs as the result of efficient

287 dissolution of gas in oil with which it is in direct contact. Once the partial pressure of CO₂
288 within this oil approaches saturation, further decay will be controlled by gas diffusion within
289 the oil^[28-29]. However, gas diffusion through oil in small pores and between pores with small
290 pore throats will be slowed down by the greater tortuosity of the oil pathways through which
291 the gas must diffuse. The process of gas diffusion is therefore relatively slow^[30-31]. As a
292 consequence, there exists an optimal soaking time (T_c) at which the dissolution of CO₂ in oil is
293 maximized, allowing the oil to swell and develop greater mobility, while avoiding slow
294 pressure decay stage. This T_c is exhibited as an inflexion in the pressure decay.

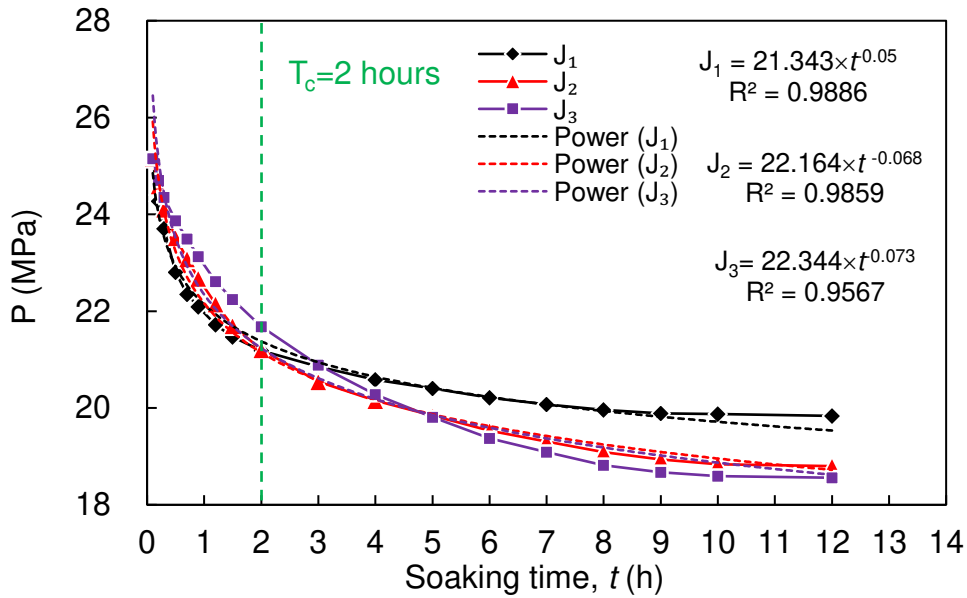
295

296 The determination of the T_c value can improve the efficiency of SAG flooding in oilfield
297 development. Usually, a pressure decay rate threshold value is established, and the soaking
298 stage is stopped when the decay rate is lower than this value. For example, in the results of this
299 experiment, when the pressure decay rate in the core J₃ is lower than 1 MPa/h (the pressure
300 decay of J₃ is the slowest among the three cores), $T_c=2$ h. When threshold value is applied in
301 oilfield development, the threshold value should be determined according to the specific
302 characteristics of the reservoir and the characteristics of pressure attenuation.

303

304 The greater the permeability, the greater the pressure decay rate. This is due to there being less
305 residual oil in the high permeability core at the beginning of the soaking stage, as well as to the
306 fact that the higher the CO₂ saturation, the larger the contact area between CO₂ and the fluid in
307 the core, and the better connectivity between the pores, the faster the diffusion of CO₂ in the
308 fluid in high-permeability core. By contrast, the lower the core permeability, the poorer the
309 connectivity between the pores, the lower the pressure decay rate, and the lower the final
310 equilibrium pressure, the greater the T_c value. Such a scenario is an indicator that lower
311 permeability cores require longer soaking times in order for the process to be effective.

312



313

314 **Figure 4.** Measured CO₂ pressure in the core plugs with respect to soaking time t , with best-
 315 fit power laws.

316

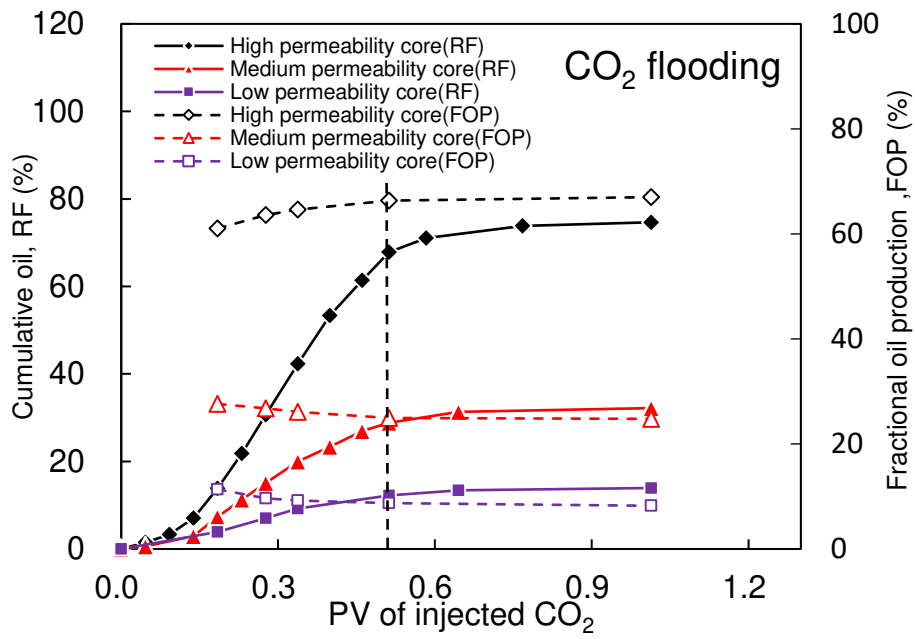
317 Oil recovery and produced fluids

318 Figure 5 and Table 4 show that the dynamic production of crude oil during the two flooding
 319 processes had similar characteristics up until CO₂ BT. The high-permeability layer had the
 320 highest oil RF as well as the fastest increase in RF. The fractional oil production (FOP) of high
 321 permeability layer is the largest, and gradually increases, while the FOP of medium and low
 322 permeability layers decreases gradually. This is because the high permeability layer presents
 323 the smallest capillary resistance, the resistance of CO₂ flooding is small, and as the
 324 displacement front advances faster in the high permeability layer, this displacement resistance
 325 becomes smaller^[32]. The difference in displacement resistance between layers with smaller
 326 permeabilities is greater. A larger proportion of injected CO₂ enters the high-permeability layer.

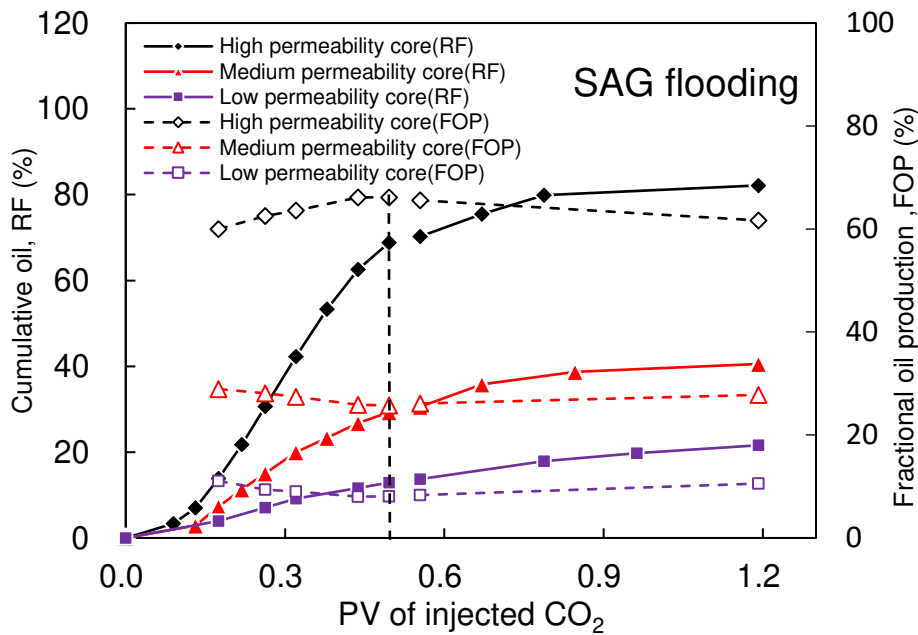
327

328 It is worth noting that there is a large difference between the ratio of the FOP of each layer
 329 (67:25:8) and the ratio of the initial permeability (75:52:26), which means that a relatively small
 330 difference in initial permeability would result in a huge difference in the FOP. In other words,
 331 the influence of the initial permeability difference on the oil production effect is magnified

332 upon CO₂ injection. The oil RF of the high, medium and low cores increased little (by 6.8%,
 333 3.4%, and 1.7%, respectively) after CO₂ BT during CO₂ flooding, even after a large volume of
 334 CO₂ is continuously injected (Table 4). The oil production after CO₂ BT mainly comes from
 335 high permeability layers. The oil production at this time depends mainly on the extraction of
 336 CO₂ on oil, and the utilization efficiency of CO₂ is very poor^[33].
 337



338



339

340 **Figure 5.** The cumulative oil RF and FOP of each long core. The vertical dashed line shows
 341 the CO₂ BT at the end of the preliminary flood.

342

343 **Table 4.** Oil RF and FOP of each long core.

Flooding method	Timing	Oil RF %			Oil FOP %		
		High	Medium	Low	High	Medium	Low
Simple CO ₂	At CO ₂ BT	67.8	28.8	12.2	66.4	24.9	8.7
	At flooding end	74.6	32.2	13.9	67	24.8	8.2
	$\Delta RF_1 \backslash \Delta FOP_1$	6.8	3.4	1.7	0.6	-0.1	-0.5
SAG	At CO ₂ BT	68.9	29.4	12.9	66.2	25.7	8.1
	At flooding end	82.2	40.5	21.6	61.6	27.7	10.6
	$\Delta RF_1 \backslash \Delta FOP_1$	13.3	11.1	8.7	-4.6	2	2.5
SAG-Simple CO ₂	$\Delta RF \backslash \Delta FOP$	7.6	8.3	7.7	-5.4	2.9	2.4

344 ΔRF_1 = Oil RF at flooding end - Oil RF at CO₂ BT

345 ΔFOP_1 = Oil FOP at flooding end - Oil FOP at CO₂ BT

346 ΔRF = Oil RF at flooding end (SAG) - Oil RF at flooding end (Simple CO₂)

347 ΔFOP = Oil FOP at flooding end (SAG) - Oil FOP at flooding end (Simple CO₂)

348

349 During the secondary flooding process after the soaking stage in SAG flooding, the cumulative
 350 recovery of each layer continued to increase, and the increased RF was 13.3%, 11.1%, and
 351 8.7%, respectively (Table 4). Compared with CO₂ flooding, the medium and low permeability
 352 cores attained relatively higher improvements in oil production, while the FOP of these layers
 353 also increased after CO₂ BT. This is due to the soaking stage alleviating the problem of
 354 inadequate contact between CO₂ and crude oil in the low and medium permeability layers. We
 355 observe, particularly, that the high permeability layer has the best oil production improvement
 356 after the soaking stage, while the FOP is reduced, indicating strongly that SAG not only
 357 improves effectively the RF of the overall multi-layer system, but can also improve effectively
 358 the oil production in low and medium permeability layers, reducing the difference in oil
 359 production in each layer caused by the difference in initial permeability.

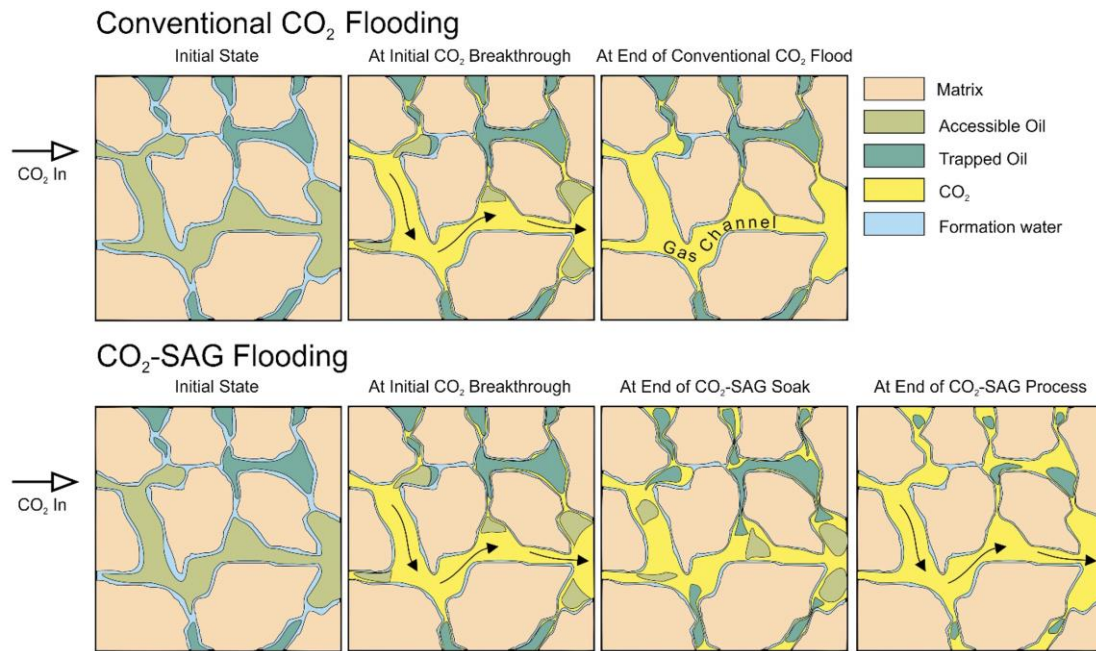
360

361 We found that the final oil RF of each layer of SAG flooding is 7.6%, 8.3%, and 7.7% higher
362 than that of CO₂ flooding, i.e., approximately the same improvement for all of the layers,
363 irrespective of their petrophysical properties (Table 4). Moreover, the difference in the FOP of
364 each long core is, relatively speaking, smaller, which indicates that in the multi-layer reservoirs
365 with different permeability CO₂-SAG flooding is generally more effective than miscible CO₂
366 flooding in displacing oil, helping to tap the oil production potential of medium and low
367 permeability layers.

368

369 Figure 6 shows the progression of the conventional CO₂ flooding process and the CO₂-SAG
370 flooding process. In both cases the initial state is shown on the left-hand side of the figure and
371 injected CO₂ flows from left to right. The figure does not include changes due to asphaltene
372 precipitation or pore blocking. The rock is assumed to be water-wet, and formation water is
373 shown in blue. Oil is shown in two shades of green, according to whether it is accessible or
374 trapped. For the purposes of this discussion ‘accessible oil’ is that which is mobile under normal
375 CO₂ flooding conditions. This implies that the fluid pressure differences during flooding are
376 greater than the capillary pressures retaining the oil in the pores, and further implies that
377 accessible oil is to be found in the larger pores, and these pores are also linked by larger pore
378 throats. By contrast, ‘trapped oil’ is that which occupies the smaller pores or pores only
379 accessed by small pore throats. These oil accumulations are subjected to capillary pressures
380 which are too high for them to be moved by the normal process of CO₂ flooding.

381



382

383 **Figure 6.** The progression of conventional CO₂ flooding and CO₂-SAG flooding processes

384

exemplified using a microstructural/microfluidic model.

385

386 In the case of conventional CO₂ flooding process, injected CO₂ is not the wetting fluid. It
 387 preferentially moves through pores with lower capillary pressures, either displacing oil or
 388 occupying space between the oil and undisplaced oil. Since CO₂ has a much lower density and
 389 viscosity than either oil or water, it is able to penetrate into small pores, even if it has little
 390 ability to displace the oil from them. Consequently, by the time the CO₂ has broken through
 391 (centre top panel of the Figure 6), there are three observations (i) CO₂ has displaced (and
 392 produced) a large proportion of the accessible oil in the large pores, (ii) the flooding pathway
 393 now predominantly contains gas, and this gas channel has a high permeability, which by-passes
 394 oil in the remainder of the rock, and (iii) a small amount of residual accessible oil exists, for
 395 which production depends on a marginal interplay between flooding pressures and the capillary
 396 pressure. If flooding progresses after breakthrough, these final accumulations of oil will be
 397 eventually produced (top left panel of the Figure 6).

398

399 In the case of CO₂-SAG flooding, the story up until CO₂ breakthrough is the same as described
 400 previously. During the soaking procedure, the remaining accessible and trapped oil undergo

401 two changes. First, the oil expands as CO₂ dissolves in the oil. The limited space in pores
402 implies that some of the oil moves in response the subsequently increased fluid pressures.
403 Second, solution of CO₂ in the oil also reduces the oil viscosity, making it more mobile. The
404 result of these two effects results in the remaining accessible oil and some of the trapped oil
405 extruding towards and into the high permeability gas channel. This situation is shown in the
406 bottom third panel from the left. The presence of the CO₂ around the oil has changed its
407 properties and brings the oil towards the high permeability channel. The promotion of oil RF
408 by the miscible effect requires a certain amount of time and space for the interaction of CO₂
409 and crude oil, the soaking stage provides longer time of interaction. The second CO₂ flood is
410 now capable of producing the more mobile extruded oil (bottom right-hand panel in the Figure
411 6).

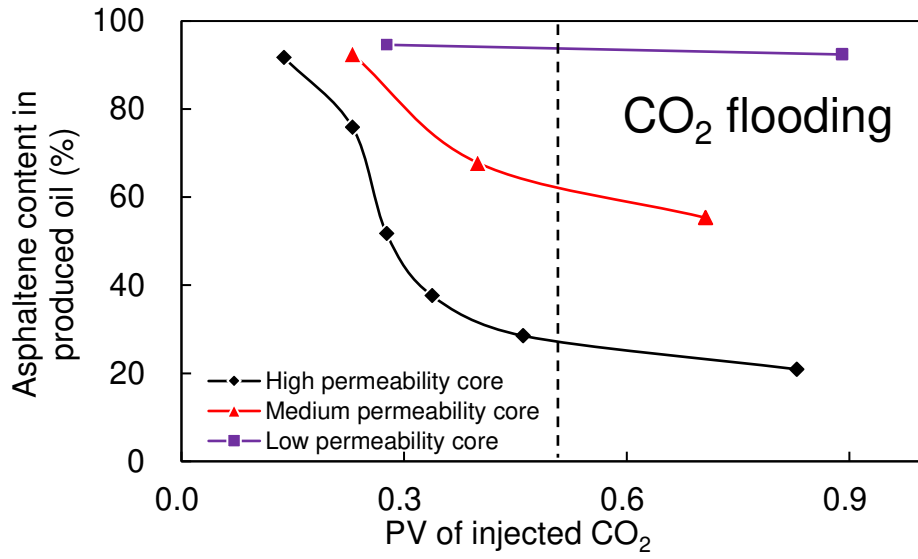
412

413 The asphaltene content of the produced crude oil decreases rapidly before CO₂ BT, as shown
414 in Figure 7, with the production of crude oil, while the asphaltene content in the produced oil
415 in the initial stage remained at 90%, and this part of the crude oil hardly came into contact with
416 the injected CO₂. There is an increase in the CO₂ dissolved in the crude oil as the displacement
417 front progresses, which leads to increased asphaltene precipitation in the core and less
418 asphaltene in the produced oil.

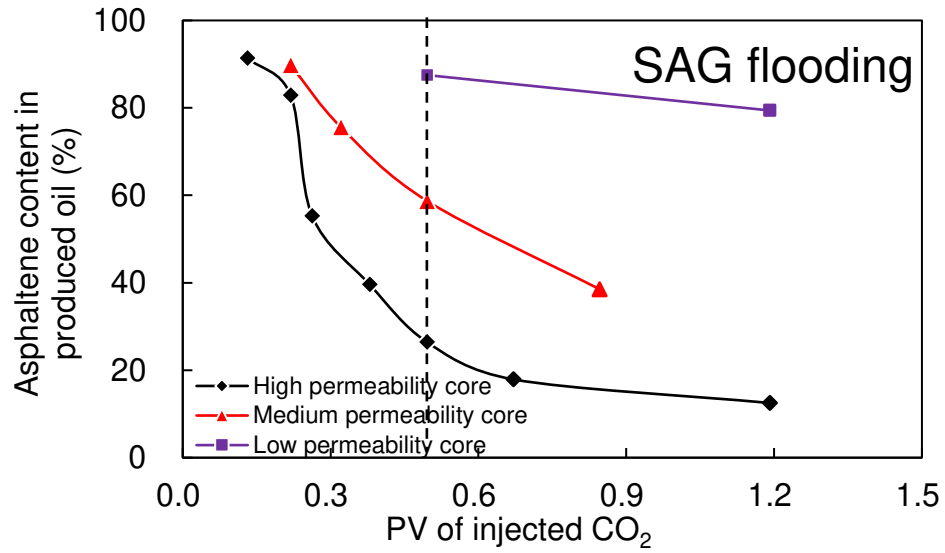
419

420 The asphaltene content of the produced oil after soaking was found to be smaller than that for
421 miscible CO₂ flooding at the same amount of injected CO₂. This may be ascribed to the larger
422 amounts of CO₂ dissolved in the residual oil as a result of the soaking process, resulting in
423 greater asphaltene precipitation, more asphaltene are deposited in the core during SAG
424 flooding.

425



426



427

428 **Figure 7.** Asphaltene content in produced oil and PV of injected CO₂ during flooding.

429

430 Oil RF distribution

431 The NMR spectrometry provides the T_2 relaxation time signal amplitude of the oil in each short
 432 core plug (long cores are cut equally) after the experiments^[34]. The oil RF of the cores at
 433 different locations was calculated according to the volume of produced oil, saturated oil, and
 434 the total intensity of the residual oil signal amplitude (Figure 8).

435

436 The oil RFs in the high permeability long core after conventional CO₂ flooding (Figure 8 upper
437 panel) decreases gently along the injection direction. However, the oil RFs towards the middle
438 ($L=22-27$ cm) of the medium permeability layer exhibits a large variation, and the oil RF
439 distribution along the injection direction is divided into two parts with gradual decrease, which
440 may be attributed to the displacement front staying in this part of the rock ($L=22-27$ cm) rather
441 than advancing to the outlet at the end of the displacement by the development of fingering
442 sufficient to ensure at least one gas channel breaks through. The same observation occurs at L
443 $=12-17$ cm in the low permeability long core, but this variation is smaller. For the medium and
444 low permeability cores there is little variation of the oil RF in the latter half of the core, implying
445 that the crude oil in the core with $L > 17$ cm is not driven directly by CO₂. Compared with the
446 medium permeability long core, the displacement front in the low permeability long core is
447 closer to the injection end.

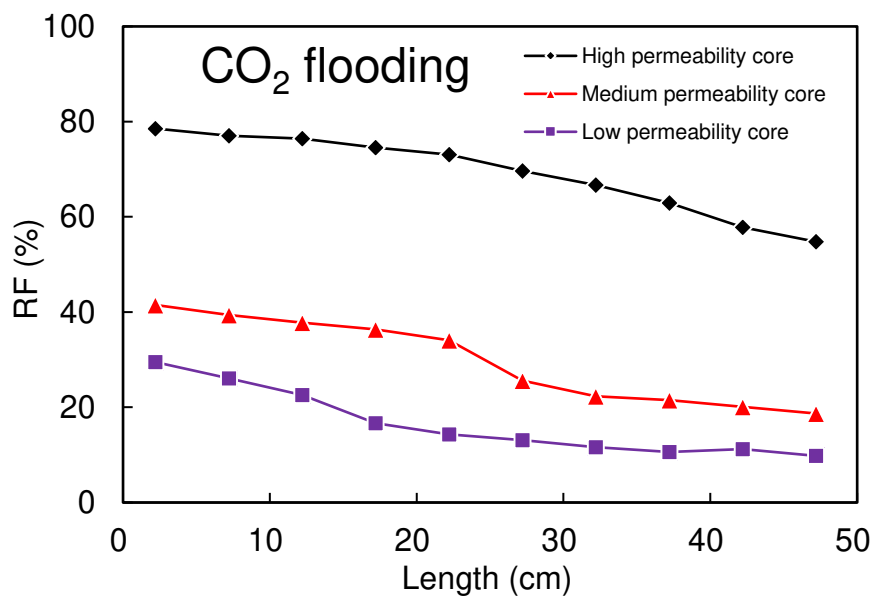
448

449 For CO₂-SAG flooding, the oil RFs in each long core is large than that after conventional CO₂
450 flooding (Figure 9 lower panel). The curve variation ($L =17-32$ cm) also appears in the high
451 permeability layer. However, the soaking stage causes this variation to become flat, but the
452 variation range becomes larger. There are two trends in the distribution of oil RF in high
453 permeability layer. The pattern of oil RF in the rocks towards the injection end is relatively
454 uniform, and varies little. The amount of oil RF near the outlet end shows an obvious gradual
455 downward trend along the injection direction, and shows that the soaking process improves the
456 efficiency of the residual oil at the injection end and middle being driven out during the
457 secondary displacement process.

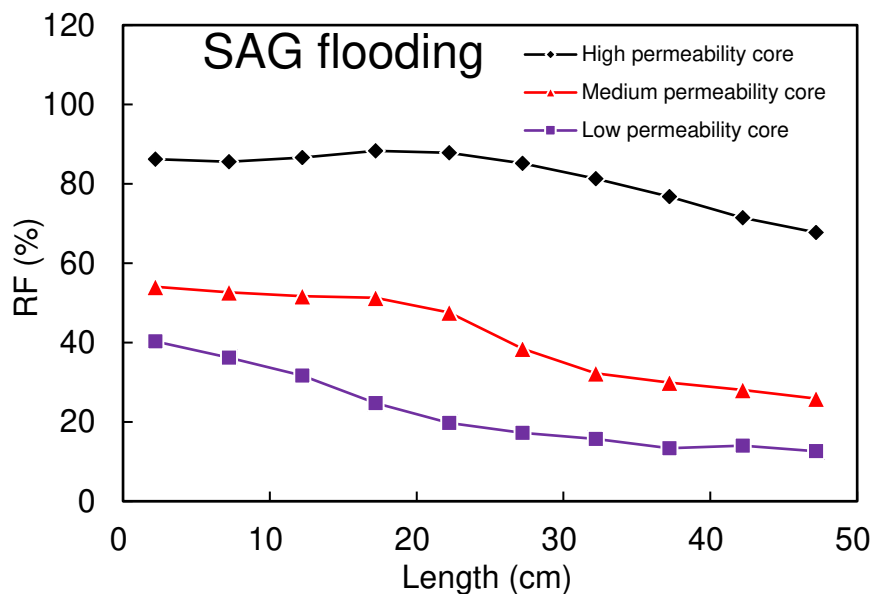
458

459 If the position of the displacement front in the same permeability core after CO₂ flooding is
460 compared to that after SAG flooding, we observe that the displacement front in the low and
461 medium permeability layers is not advanced significantly during secondary flooding as a result
462 of the soaking stage. The soaking does not significantly expand the CO₂ swept volume, but

463 only enhances the CO₂ displacement effect in the core pores that have been swept by CO₂ before
 464 CO₂ BT.
 465



466



467

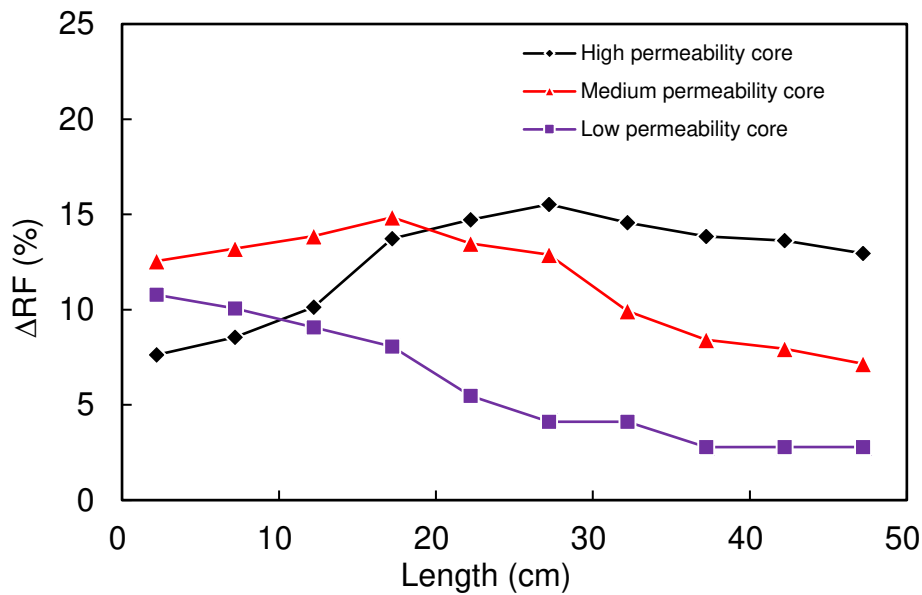
468 **Figure 8.** Oil recovery calculated according to the signal amplitude in T_2 spectrum by NMR
 469 tests along the cores.

470

471 The distribution of the difference between the final oil RF of the two floods is shown in Figure
 472 9. The parameter ΔRF ($\Delta RF(\%) = RF(SAG) - RF(CO_2)$) represents the degree of improved oil

473 production of SAG flooding compared to conventional CO₂ flooding. For the high permeability
 474 long core, the improvement in oil production along the injection direction gradually increases,
 475 reaches a maximum value in the middle ($L = 27$ cm), and then slightly decreases. The
 476 improvement in RF that occurs during the soaking stage is controlled by several factors, (i) the
 477 amount of residual oil at the start of the soaking phase, and (ii) the amount and distribution of
 478 CO₂ retained in the pores at the beginning of the soaking.

479



480

481 **Figure 9.** The difference in oil RF between the flooding processes as a function of length
 482 along the cores.

483

484 Proximally to the injection end, there is a larger saturation of retained CO₂, but production from
 485 this zone has been good (at least for the high permeability core), so there is only a small amount
 486 of residual oil. Consequently, there is less scope for the soaking process to be effective, which
 487 leads to values of $\Delta RF = 7.62\%$ for the high permeability core. However, more residual oil is
 488 present for the low and medium permeability cores, which results in a larger improvement in
 489 recovery factor ($\Delta RF = 12.55\%$, $\Delta RF = 10.78\%$, respectively); the medium permeability core
 490 performing better than the low permeability core because it allows access to more CO₂.

491

492 The amount of residual oil at the start of the soaking phase gradually increases along the
493 injection direction, but the amount of CO₂ retained at the beginning of soaking gradually
494 decreases. Consequently, the central portions of the high and medium permeability long cores
495 provide the best oil production enhancement and hence the greatest ΔRF (about 14.85% and
496 15.53%, respectively). The low permeability core does not exhibit this behaviour because its
497 low permeability reflects the fact that its pores are sufficiently small that even though a large
498 saturation of residual oil is retained after initial flooding, there is little invasion of CO₂ to enable
499 much of it to be produced after soaking.

500

501 The values of ΔRF fall again towards the output end of each long core, reflecting that although
502 the retained oil saturation is high, the CO₂ saturation is low. It is here that there is the greatest
503 difference between the three different permeability long cores, with the greatest improvement
504 occurring for the high permeability long core (ΔRF=12.96%).

505

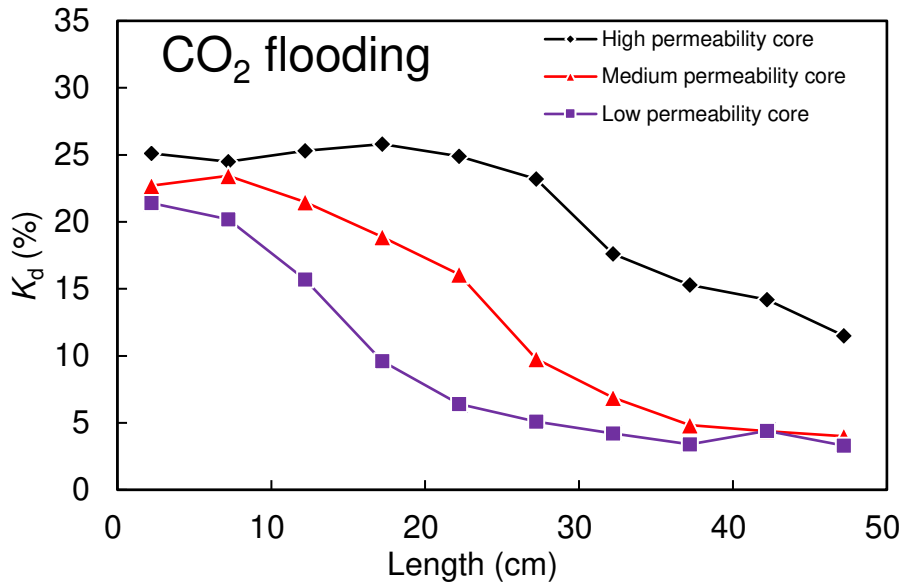
506 In summary, the soaking stage leads to an overall improvement in the recovery factor for cores
507 of all permeability and at all locations, but the best improvements were in the middle of the
508 medium and high permeability cores (around 15%) and proximally to the injection end of the
509 low and medium permeability cores (around 12%).

510

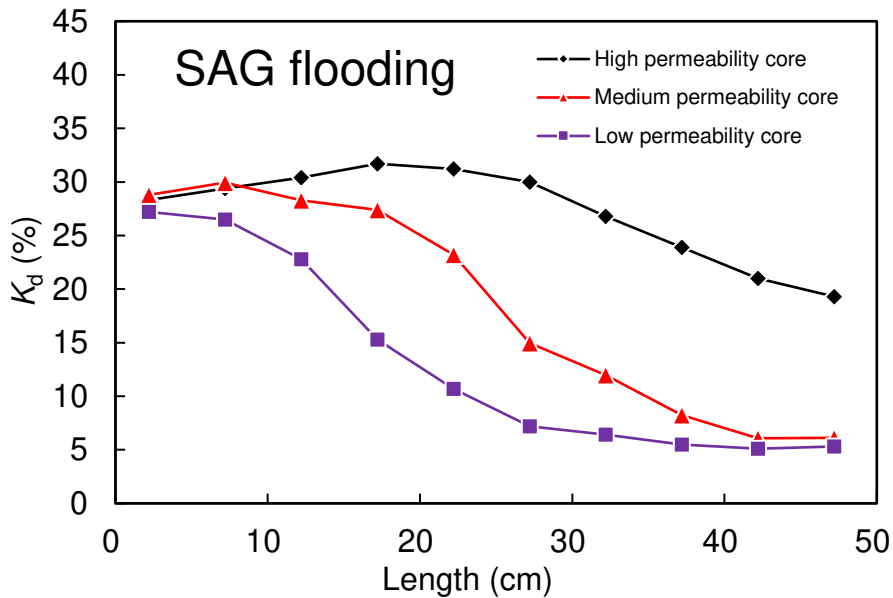
511 Permeability damage

512 We defined a permeability decline parameter as K_d after flooding ($K_d = 100 \times (K_b - K_a) / K_b$, which
513 is reported as a percentage, and where K_b is the pre-flooding permeability of the core and K_a is
514 permeability of the core after flooding, Figure 10).

515



516



517

518 **Figure 10.** The spatial distribution of the reduction in permeability along the cores due to
 519 precipitation of asphaltene.

520

521 It would be expected that permeability decline is associated with the precipitation of asphaltene
 522 which reduces the water wettability of the rock as well as blocking flow pathways . It has been
 523 hypothesized^[10] that the amount of permeability reduction is controlled by (i) the extent of the
 524 precipitation of asphaltene, (ii) the efficiency of asphaltene particle migration (initial
 525 permeability of the rock which depends on its pore microstructure), and (iii) the efficiency with

526 which such particles can block pore-throats. We also recognize that cores and reservoir
527 formations with higher oil recovery factors have, hosted the passage of more CO₂ during initial
528 flooding. It would therefore be expected that these rocks would be more likely to exhibit
529 increased asphaltene precipitation and hence a greater decline in permeability^[37-38].

530

531 After conventional CO₂ flooding, the permeability near the injection end ($L=0-27$ cm) of the
532 high permeability long core underwent a reduction of about 25%. Moving more distally from
533 the injection face, the degree of permeability reduction decreases until it is 11.5% at the output
534 face (Figure 10 top panel). This pattern of permeability damage is the result of the continuous
535 advancement of the CO₂ flooding front, the continuous solution of CO₂ in the crude oil, the
536 consequent formation, precipitation and migration of asphaltene particles, followed by the
537 adsorption of asphaltene onto grain surfaces and their blockage of pore throats.

538

539 The permeability decline of the medium and low permeability long core follows a similar
540 pattern, but undergoes a slightly smaller permeability reduction at the injection end (about 23%
541 for $L=0-7.5$ cm), but then steadily declines until the permeability reduction only about 4% at
542 the output face.

543

544 It is clear from Figure 10 that CO₂-SAG flooding causes greater damage to permeability than
545 conventional miscible CO₂ flooding for all positions along all three cores. The SAG flooding
546 process provides a similar pattern of permeability reduction for all locations in all three long
547 cores. This is because during the soaking process larger amounts of CO₂ are dissolved in the
548 residual oil, which leads to a concomitant increase in asphaltene precipitation, and which then
549 narrows and blocks pore throats more effectively^[35-36]. This view is supported by the decrease
550 in the amount of asphaltene in the produced oil compared to that in the initial oil (Figure 7).
551 Previously^[10] it has been noted that, the pattern of permeability decline along the cores was
552 smoother for CO₂-SAG flooding compared to CO₂ flooding, and this has been associated with
553 the soaking leading to a more homogeneous precipitation of asphaltene.

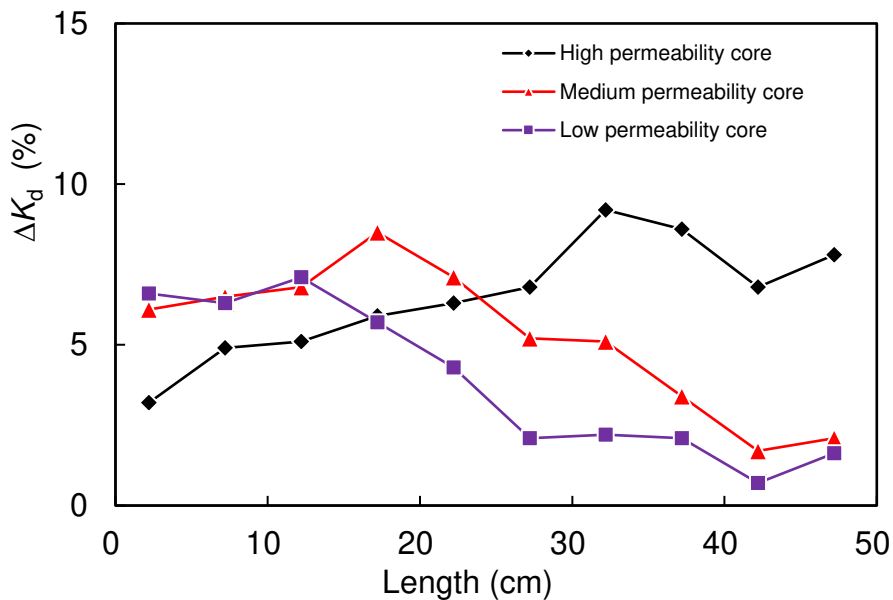
554

555 It is possible to quantify the percentage difference in K_d between the two flooding processes^[10]
556 using $\Delta K_d(\%) = K_d(\text{SAG}) - K_d(\text{CO}_2)$, which is shown in Figure 11.

557

558 The ΔK_d value in the high permeability layer increases in the direction of injection. The closer
559 to the outlet end, the more residual oil at CO_2 BT. Compared with CO_2 flooding, the additional
560 precipitation of asphaltene associated with the soaking stage of the CO_2 -SAG process is greater,
561 and the asphaltene precipitation during the secondary flooding process has a relatively large
562 impact on the core permeability at the outlet end.

563



564

565 **Figure 11.** The difference in permeability decline (ΔK_d) between the two flooding processes.

566

567 The distribution trend of ΔK_d in the low and medium permeability long cores decreases along
568 the injection direction, which is exactly the opposite of the trend of ΔK_d distribution in the high
569 permeability long core. This also suggests that interaction of CO_2 and oil during the soaking
570 stage occurs mainly in the pores swept and affected by injected CO_2 before CO_2 BT, that is, in
571 the core near the injection end in low and medium permeability long cores. The processes of

572 CO₂ soaking and secondary flooding increased the permeability decline of these cores, and did
573 not have a substantial influence on the reduction in the permeability of the cores near their
574 outlet end.

575

576 The ΔK_d of the cores proximal to the injection face in the medium and low permeability cores
577 is higher than the ΔK_d near the injection face of the high permeability long core. The significant
578 additional permeability decline near the injection face in the low permeability core is worthy
579 of attention, and corresponding measures should be taken at the corresponding injection well
580 during the SAG flooding process. It shows that CO₂ soaking and secondary flooding has a
581 substantial influence on the permeability decline of the injection end and middle in medium
582 permeability long core, while only affects ΔK_d at the injection end in low permeability. It also
583 shows that the CO₂ soaking and secondary flooding have a weak propulsion effect on the
584 displacement front, but it significantly increases the permeability decline of the cores that has
585 been swept by CO₂ at CO₂ BT. In short, the distribution characteristics of ΔK_d and ΔRF are
586 basically similar.

587

588 In this work we confirm the earlier observation^[10] that CO₂-SAG flooding produces greater
589 permeability damage and a higher oil recovery factor than simple miscible CO₂ flooding. As
590 before^[10], we have used a single parameter (K_{dp}) to take account of both oil recovery
591 improvement and permeability damage. Here, $K_{dp} = K_d/RF$ measures the amount of
592 permeability decrease, or damage, per unit increase recovery factor, and is shown for both
593 flooding processes in Figure 12.

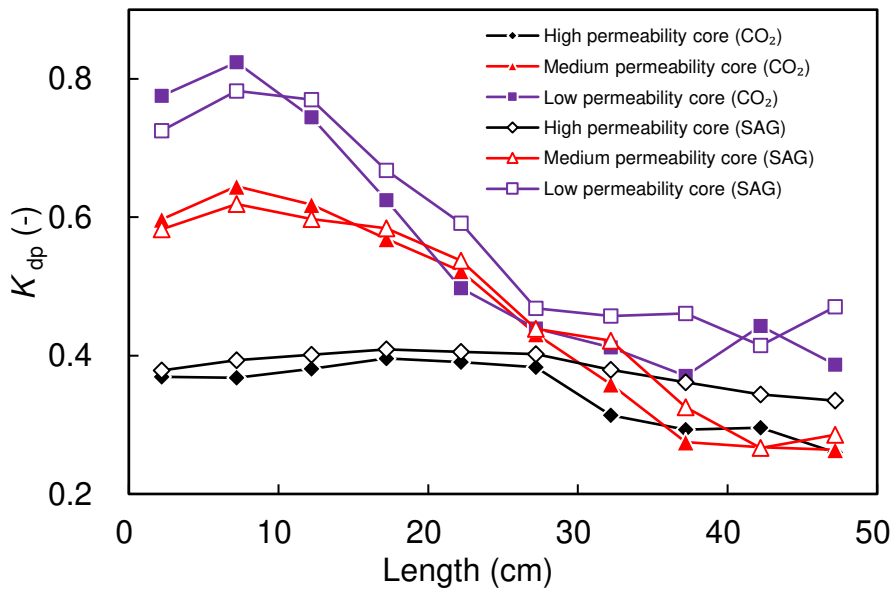
594

595 The K_{dp} value of the high permeability core is the smallest, and the K_{dp} value of the low
596 permeability long core is the largest. This indicates that the large permeability not only leads
597 to high oil recovery, but also weakens the decline in permeability resulting from precipitation
598 of asphaltene. It is clear that high initial permeabilities are relatively insensitive to permeability
599 decline caused by both adsorption of asphaltene precipitation and blockage of pore throats by

600 asphaltene particles. The value of K_{dp} in the high permeability core changes only slightly along
 601 the injection direction, while its value shows a marked decrease in the flow direction for the
 602 low and medium permeability cores.

603
 604 These observations arise because the gasflood front has advanced as far as the outlet face in the
 605 high permeability long core but has only advanced partially along the other two cores even
 606 though viscous fingering ensures that breakthrough has occurred. The value of K_{dp} falls rapidly
 607 in the vicinity of the flood front, which occurs at approximately 20 ± 7 cm and 27 ± 7 cm for the
 608 low and medium permeability cores, respectively. As a consequence, it may be said that
 609 although some oil is produced from the injection end of the low and medium permeability long
 610 core, damage to the core permeability is more significant than for the high permeability core.

611



612

613 **Figure 12.** The distribution of the K_{dp} value along cores after flooding. The K_{dp} parameter
 614 represents the percentage permeability decline per unit increase in recovery factor, and for
 615 which large values are worse than small values.

616

617 In the high permeability long core, the difference in K_{dp} after CO₂ flooding and SAG flooding
 618 only exists in the cores near the outlet end, which shows that although the CO₂ soaking and

619 secondary flooding at the outlet end have effectively improved the oil production effect, they
620 have caused relatively greater damage to permeability. Also, compared with CO₂ flooding, the
621 improvement in oil production of SAG flooding in the middle cores is less than the damage to
622 permeability.

623

624 Blockage and adsorption of asphaltene precipitation

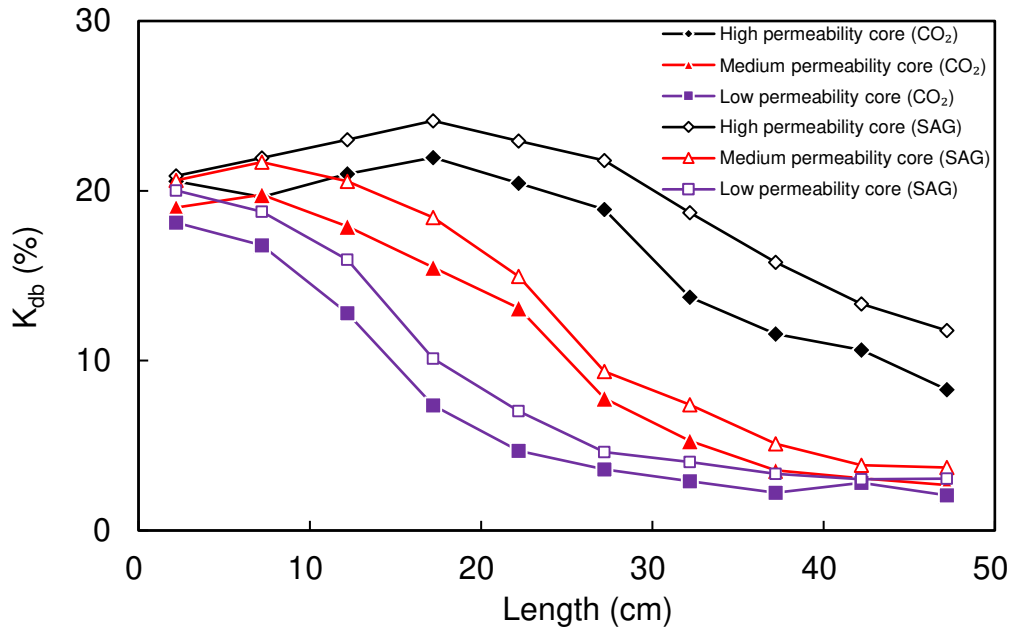
625 The permeability decline due to adsorption and blockage effects of asphaltene precipitation can
626 be separated in order to calculate the two kinds of decline percentage values through cleaning
627 and flooding after the flooding experiments using special solvent (the cleaning process and
628 calculation are shown in the “Post-flooding tests” section)^[39].

629

630 Figure 13 shows the decrease in permeability caused by asphaltene precipitation blockage of
631 pore throats after flooding ($K_{db}=100\times(K_{abc} - K_a)/ K_b$), where K_{abc} is the permeability after the
632 sample has only been cleaned of blockages. The parameter K_{da} is the decrease in permeability
633 caused by asphaltene precipitation adsorption ($K_{da}=100\times(K_{afc} - K_{abc})/ K_b$), where K_{afc} is the
634 permeability after the sample has been fully cleaned of blockages and adsorbed precipitation.

635 It will be noted that $K_d= K_{db}+K_{da}$. In addition, we define $R_b=100\times K_{db}/K_d$, which represents the
636 percentage of permeability decline caused by asphaltene particle blockage with respect to the
637 total permeability decline (Figure 14). Here, $R_a=100-R_b$ is the fractional decrease in
638 permeability caused by the adsorption of asphaltene with respect to the total permeability
639 decline.

640



641
 642 **Figure 13.** The distribution of the reduction in permeability due to asphaltene pore blocking
 643 along cores after flooding, quantified by K_{db} , where small values represent small effects from
 644 the pore blocking mechanism.

645

646 It is commonly considered^[40-41] that the degree of asphaltene precipitation required to block
 647 pore throats is related (i) to the overall extent of asphaltene precipitation, (iii) the asphaltene
 648 particle size distribution, and (iii) the asphaltene particle mobility, all of which are inter-
 649 dependent. The longer the migration distance of the fluid carrying asphaltene precipitation in
 650 the pore throats, the greater its velocity, the longer the flooding time, the smaller the size of the
 651 pore throats, and the more fluid that flows through the pore throat, the higher probability the
 652 pore throat will be blocked, the more serious the blockage will be^[42]. However, in the same
 653 core, the permeability decline caused by asphaltene precipitation adsorption is only related to
 654 the scale of asphaltene precipitation. Moreover, small particles have less ability to block pore
 655 throats, but are very mobile (Stokes law), while large particles block pores throats easily but
 656 are less mobile^[43].

657

658 Figure 13 shows that the fall of permeability caused by the asphaltene particle blockage in each
 659 layer at the injection end is similar. The high permeability core has low resistance to CO₂ flow

660 resulting in more CO₂ being injected, which in turn leads to the deposition of more asphaltenes.
661 Hence, it would be expected that the permeability decline caused by blockage should be greater
662 for this high permeability core than the other cores, which is not observed. It is possible that
663 the initial large permeability of the rock protects it from permeability damage even if there is a
664 greater deposition of asphaltene^[6]. By contrast, the lower permeability cores flow less CO₂ and
665 hence less asphaltene is deposited. However, the asphaltene has a greater potential to cause
666 permeability decline because the pathways for fluid flow are smaller and less well connected.
667 Hence, the similarity in K_{db} between all cores near the injection face is simply due to the
668 proportionality between initial permeability and the potential for damage which that
669 permeability provides through asphaltene precipitation.

670

671 In the high permeability long core, K_{db} gradually increases along the injection direction, and
672 then drops rapidly after reaching its maximum in the middle of the core ($L=17$ cm), and finally
673 the value at the outlet end is smaller than at the inlet end. One possible reason for this is that
674 the CO₂ injected at the injection end and the middle part interacts with the crude oil to a greater
675 extent, resulting in a large amount of asphaltene precipitation, which is continuously captured
676 and accumulated during the migration of the fluid, blocking or reducing pores and throats, and
677 which then accelerates the capture of asphaltene precipitation particles. Consequently, the
678 asphaltene precipitation trapped by the pore throats accumulates in a large amount in the middle
679 of the long cores. The amount of asphaltene precipitation along the injection direction becomes
680 progressively less, and the K_{db} value also becomes smaller. The value of K_{db} after the CO₂-
681 SAG process is higher than that after miscible CO₂ flooding. The CO₂ soaking produces more
682 asphaltene precipitation, and the secondary flooding increases the movement of the fluid
683 carrying the asphaltene precipitation, enhancing the filtration of the asphaltene precipitation in
684 the fluid by the pore throats. The value of K_{db} in the low and medium permeability long cores
685 decreases continuously along the injection direction, and the K_{db} value of the low permeability
686 layer decreases rapidly. this is also due to the position of the displacement front that determines
687 the distribution of K_{db} .

688

689 The K_{db} values at the middle of the three long cores are quite different, while the K_{db} values of
690 the middle and low permeability long cores at the outlet end are similar, but are different from
691 those values for the high permeability long core. The distribution of K_{db} at the middle and outlet
692 is similar to that of K_d . This is also due to the position of the CO_2 flooding front in the medium
693 and low permeability layers. It also shows that blockage is the dominant factor in determining
694 K_d in the middle of the long cores and at their outlets.

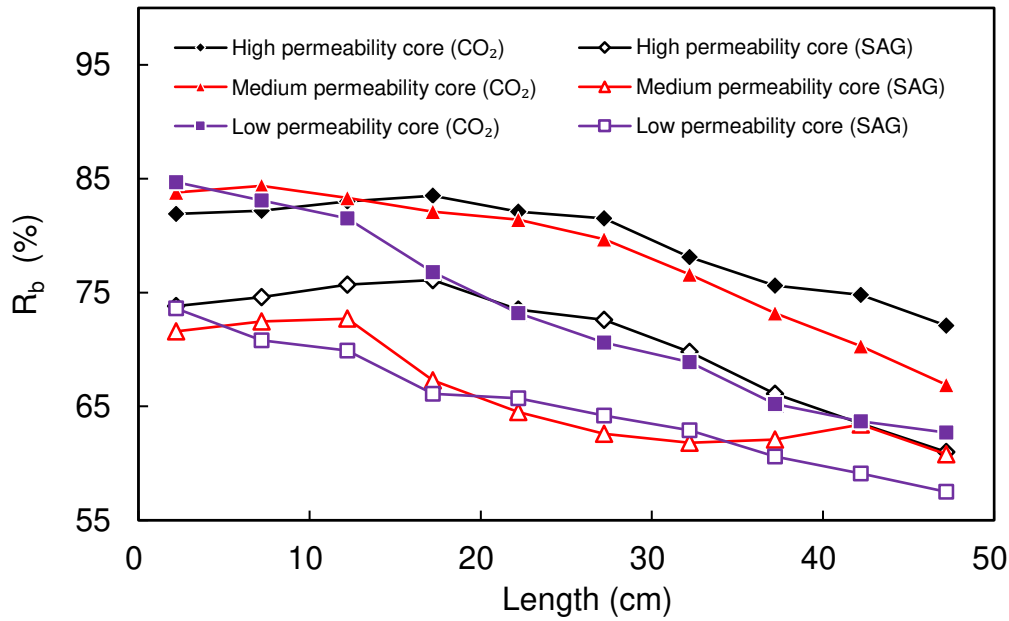
695

696 In addition, there is a certain difference in K_{db} at the inlet end of the low and medium
697 permeability layers after CO_2 -SAG and miscible CO_2 flooding, indicating that CO_2 soaking and
698 secondary flooding increase the degree of asphaltene precipitation to block pores. At the outlet
699 end, CO_2 soaking and secondary displacement have little effect on the degree of asphaltene
700 precipitation to block pore throats.

701

702 After CO_2 flooding, the R_b values at the injection end of the three long cores are similar, the
703 difference between them becoming larger along the core in the direction of flooding (Figure
704 14). The R_b of the core at $L=0-27$ cm in the high permeability long core remains almost
705 unchanged, and the R_b value of the cores decreases slowly at $L=27-50$ cm. However, R_b in the
706 low and medium permeability long cores gradually decreases along the injection direction.

707



708

709 **Figure 14.** The distribution along cores after flooding of the amount of permeability
 710 reduction attributed to pore throat blocking with respect to the total permeability reduction
 711 and expressed as a percentage, R_b .

712

713 Although CO₂ BT occurred in the high permeability layer, the flooding front advanced to the
 714 outlet end. However, compared with the cores at the injection end and the middle, the
 715 interaction between crude oil and CO₂ at the outlet end is not so strong, and the pores swept by
 716 CO₂ are also fewer. In the low and medium permeability long cores, the locations near the outlet
 717 end are not even swept by CO₂. It seems that the sweeping and flooding of CO₂ is the key factor
 718 for pore throat blockage by asphaltene precipitation. It is possible that the complex two phase
 719 flow of oil and gas is more likely to cause pore throat blockage instead of causing the adsorption
 720 of asphaltene. The two phase flow of gas and oil near the outlet end is less than at the injection
 721 end, hence the influence of asphaltene adsorption on the permeability damage gradually
 722 increases towards the outlet end of the core^[44].

723

724 The R_b value exhibited by the high permeability long core is the largest of all three. This is
725 because (i) the injected CO_2 flows predominantly through this core, (ii) the flow rate in this
726 core is largest, (iii) the two phase flow of oil and gas is more complex, and (iv) asphaltene
727 precipitation blockage in this core leads to a higher percentage of permeability decline. In
728 addition, the R_b value after SAG flooding is lower than that of CO_2 flooding. This is due to the
729 fact that no fluid migration occurs during the soaking stage, and the asphaltenes produced
730 during the soaking stage reduce the permeability in an adsorbed state.

731

732 After SAG flooding, the R_b values of the three layers at the injection end are relatively close,
733 and the R_b value of the high permeability layer is the largest. The distributions of R_b in the low
734 and medium permeability long cores are relatively close, and the difference between the high
735 and medium permeability long cores in the middle of long cores is larger. After CO_2 flooding
736 and SAG flooding, the R_b distribution trend of the medium permeability layer is quite different,
737 which indicates that the CO_2 soaking in the middle of the medium permeability long core has
738 a greater influence on the adhesion state of asphaltene particles, which leads to an increase in
739 the proportion of adsorbed asphaltene. It is worth noting that $K_{db}(\text{SAG}) > K_{db}(\text{CO}_2)$, however
740 $R_b(\text{SAG}) < R_b(\text{CO}_2)$

741

742 Regardless of the displacement method, the damage to rock permeability (>55%) caused by
743 asphaltene precipitation blockage in pore throats is higher than the damage caused by
744 asphaltene adsorption. This is because pore blockage damages the connectivity between the
745 pores and pore throats in a targeted manner. By contrast, asphaltene adsorption only reduces
746 the size of both pores and pore throats wherever the precipitation occurs. While rock
747 permeability will occur by such a mechanism most of the adsorption has no effect on overall
748 pore connectivity and that which happens to occur at the site of pore throats closes them only
749 slowly and often partially, thus retaining much of the previous connectivity^[45].

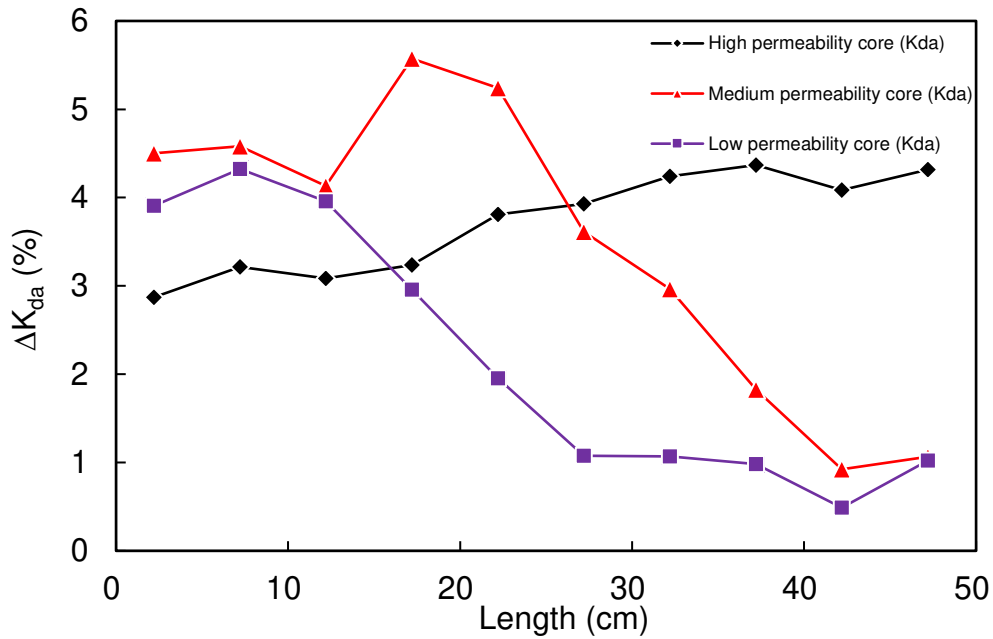
750

751 During the process of recovering the core permeability by cleaning the core of asphaltene
752 deposits and hence removing pore throat blockages and adsorbed asphaltene precipitation,
753 which occurred after flooding, it was observed that the asphaltene blocking pore throats was
754 easier to remove than the adsorbed asphaltene precipitation, the latter of which required a large
755 volume of solvents for long-term cycle cleaning. It is worth noting that the permeability values
756 of all core plunger were tested again after being thoroughly cleaned, the permeability of the
757 same long core at different positions fluctuates less than 3%, and the homogeneity of the long
758 cores is confirmed.

759

760 The values of ΔK_{da} ($\Delta K_{da} (\%) = K_{da}(SAG) - K_{da}(CO_2)$) are the difference in permeability (K_{da})
761 of the layers with the same permeability caused by asphaltene adsorption after the two types of
762 flooding process. The distributions of ΔK_{da} along each of the three long cores are shown in
763 Figure 15. The ΔK_{da} in the high permeability long core gradually increases along the injection
764 direction, which indicates that compared with CO_2 flooding, the closer to the outlet end, the
765 stronger the tendency of asphaltene precipitation absorption caused by CO_2 soaking. This is
766 due to there being more residual oil with higher asphaltene content in the cores near the outlet
767 end at the beginning of the CO_2 soaking process.

768



769

770 **Figure 15.** The distribution of the difference in the permeability damage caused by asphaltene
 771 adsorption, ΔK_{da} between the two flooding processes.

772

773 However, the distribution trends of ΔK_{da} in the low and medium permeability cores are just the
 774 opposite, showing a downward trend along the injection direction. This pattern is also partially
 775 the effect of the CO_2 flooding front stays in the cores after CO_2 BT in the high permeability
 776 long core, which causes CO_2 soaking to increase asphaltene precipitation adsorption at the
 777 injection end and also towards the middle of the medium and low permeability long core. This
 778 is also confirmed by the fact that the ΔK_{da} of the high-permeability layer at the injection end is
 779 much larger than that of the low and medium permeability long core.

780

781 **Conclusions**

782 Reservoir condition miscible CO_2 flooding and CO_2 -SAG flooding experiments have been
 783 carried out on 'multilayer' sandstone system. The distributions of differential pressure, residual
 784 oil, recovery factor and permeability damage by asphaltene precipitation blockage and
 785 adsorption were quantified. The main findings are summarized below.

786

787 The overall oil recovery factors after CO₂-SAG flooding for the high, medium and low
788 permeability long cores, are 7.6%, 8.3%, 7.7% higher than conventional CO₂ flooding. The
789 fractional oil production of the high, medium and low permeability long cores were 61.6%,
790 27.7%, 10.6% after CO₂-SAG flooding, the difference between each layer is less than for
791 conventional CO₂ flooding.

792

793 The displacement fronts in the low and medium permeability layers are not significantly
794 advanced due to the soaking stage, which does not significantly expand the sweeping volume,
795 and only enhances the CO₂ displacement effect in the pores that have been swept by CO₂ before
796 CO₂ BT.

797

798 After conventional CO₂ flooding, the permeability of the high permeability core near the
799 injection end has a relatively homogeneous drop distribution by 24.5-25.8%, which is 5.5-
800 14.3% higher than that of the core near the outlet end, and gradually decreases. The reduction
801 in permeability for CO₂-SAG flooding is larger than that for conventional CO₂ flooding.

802

803 The percentage permeability drop caused by asphaltene precipitation blockage is 84.7-62.7%
804 of the total permeability drop after CO₂ flooding, which represents 5-10% greater decrease in
805 permeability than that caused by CO₂-SAG flooding.

806

807 **Acknowledgments**

808 Thanks are given to the China Scholarship Council for funding the opportunity of the lead
809 author to research at The University of Leeds, UK. This research is supported by National
810 Natural Science Foundation of China, “The formation mechanism of residual gas and liquid in
811 coal seam and the geological constraints for effective production” (41872171).

812

813 **References**

- 814 (1) Cao, M. and Gu, Y., 2013. Oil recovery mechanisms and asphaltene precipitation
815 phenomenon in immiscible and miscible CO₂ flooding processes. *Fuel*, 109, pp.157-166.
- 816 (2) Lei, H., Yang, S., Zu, L., Wang, Z. and Li, Y., 2016. Oil recovery performance and CO₂
817 storage potential of CO₂ water-alternating-gas injection after continuous CO₂ injection in a
818 multilayer formation. *Energy & Fuels*, 30(11), pp.8922-8931.
- 819 (3) You, J., Ampomah, W. and Sun, Q., 2020. Development and application of a machine
820 learning based multi-objective optimization workflow for CO₂-EOR projects. *Fuel*, 264,
821 p.116758.
- 822 (4) Wang, L., He, Y., Wang, Q., Liu, M. and Jin, X., 2020. Multiphase flow characteristics and
823 EOR mechanism of immiscible CO₂ water-alternating-gas injection after continuous CO₂
824 injection: A micro-scale visual investigation. *Fuel*, 282, p.118689.
- 825 (5) Qian, K., Yang, S., Dou, H., Wang, Q., Wang, L. and Huang, Y., 2018. Experimental
826 investigation on microscopic residual oil distribution during CO₂ Huff-and-Puff process in tight
827 oil reservoirs. *Energies*, 11(10), p. 2843.
- 828 (6) Wang, Q., Yang, S., Lorinczi, P., Glover, P.W. and Lei, H., 2019. Experimental
829 Investigation of Oil Recovery Performance and Permeability Damage in Multilayer Reservoirs
830 after CO₂ and Water–Alternating-CO₂ (CO₂–WAG) Flooding at Miscible Pressures. *Energy &*
831 *Fuels*, 34(1), 624-636.
- 832 (7) Han, J., Lee, M., Lee, W., Lee, Y. and Sung, W., 2016. Effect of gravity segregation on CO₂
833 sequestration and oil production during CO₂ flooding. *Applied energy*, 161, 85-91.
- 834 (8) Chen, X., Li, Y., Tang, X., Huang, Q., Sun, X., Luo, J., 2021. Effect of gravity segregation on
835 CO₂ flooding under various pressure conditions: Application to CO₂ sequestration and oil
836 production. *Energy*, 2021, 226, p.120294.
- 837 (9) Khan, M.Y. and Mandal, A., 2021. Improvement of Buckley-Leverett equation and its
838 solution for gas displacement with viscous fingering and gravity effects at constant pressure for
839 inclined stratified heterogeneous reservoir. *Fuel*, 285, p.119172.
- 840 (10) Wang, Q., Shen, J., Lorinczi, P., Glover, P., Yang, S. and Chen, H., 2021. Oil production
841 performance and reservoir damage distribution of miscible CO₂ soaking-alternating-gas (CO₂-
842 SAG) flooding in low permeability heterogeneous sandstone reservoirs. *Journal of Petroleum*
843 *Science and Engineering*, 204, p.108741.
- 844 (11) Zhang, J., Zhang, H.X., Ma, L.Y., Liu, Y. and Zhang, L., 2020. Performance evaluation
845 and mechanism with different CO₂ flooding modes in tight oil reservoir with fractures. *Journal*
846 *of Petroleum Science and Engineering*, p.106950.
- 847 (12) Li, Z. and Gu, Y., 2014. Soaking effect on miscible CO₂ flooding in a tight sandstone
848 formation. *Fuel*, 134, pp. 659-668.
- 849 (13) Wang, Q., Wang, L., Glover, P. and Lorinczi, P., 2020. Effect of pore-throat microstructure
850 on miscible CO₂ soaking-alternating-gas (CO₂-SAG) flooding of tight sandstone
851 reservoirs. *Energy & Fuels*, 34(8), pp.9450-9462
- 852 (14) Jafari, B., Ghotbi, C., Taghikhani, V. and Shahrabadi, A., 2012. Investigation on
853 asphaltene deposition mechanisms during CO₂ flooding processes in porous media: a novel
854 experimental study and a modified model based on multilayer theory for asphaltene
855 adsorption. *Energy & fuels*, 2012, 26(8), pp.5080-5091.

- 856 (15) Lei, H., Yang, S., Qian, K., Chen, Y., Li, Y. and Ma, Q., 2015. Experimental investigation
857 and application of the asphaltene precipitation envelope. *Energy & Fuels*, 29(11), 6920-6927.
- 858 (16) Cho, J., Kim, T.H., Chang, N. and Lee, K.S. Effects of asphaltene deposition-derived
859 formation damage on three-phase hysteretic models for prediction of coupled CO₂ enhanced
860 oil recovery and storage performance. *Journal of Petroleum Science and Engineering*, 2019,
861 172, 988-997.
- 862 (17) Wang, Q., Yang, S., Glover, P.W., Lorinczi, P., Qian, K. and Wang, L., 2020. Effect of
863 Pore-Throat Microstructures on Formation Damage during Miscible CO₂ Flooding of Tight
864 Sandstone Reservoirs. *Energy & Fuels*, 34(4), 4338-4352.
- 865 (18) Cui, G., Zhu, L., Zhou, Q., Ren, S. and Wang, J., 2021. Geochemical reactions and their
866 effect on CO₂ storage efficiency during the whole process of CO₂ EOR and subsequent
867 storage. *International Journal of Greenhouse Gas Control*, 108, p.103335.
- 868 (19) Hematfar, V., Maini, B. and Chen, Z.J., 2018. Experimental investigation of asphaltene
869 adsorption in porous media due to solvent injection and effects on relative
870 permeability. *International Journal of Multiphase Flow*, 99, pp.174-185.
- 871 (20) Shen, Z. and Sheng, J., 2017. Investigation of asphaltene deposition mechanisms during
872 CO₂ huff-n-puff injection in Eagle Ford shale. *Petroleum Science and Technology*, 35(20),
873 pp.1960-1966.(21) Li, Z., 2014. Optimum Timing for CO₂-EOR After Waterflooding and
874 Soaking Effect on Miscible CO₂ Flooding in a Tight Sandstone Formation (Doctoral
875 dissertation, Faculty of Graduate Studies and Research, University of Regina).
- 876 (22) Norouzi, H., Rostami, B., Khosravi, M., & Shokri Afra, M. J., 2019. Analysis of secondary
877 and tertiary high-pressure gas injection at different miscibility conditions: mechanistic
878 study. *SPE reservoir evaluation & engineering*, 22(01), 150-160.
- 879 (23) Mathur, A., Ali, S., Woodland, C., Hudson, K., Barnes, C., Von Gonten, W.D. and
880 Belanger, C., 2021, July. Using NMR and Steady State Permeability Measurements to Study
881 Drilling Fluid Invasion Into the Tight Mississippian Ratcliffe Carbonate and Its Impact on Oil
882 Production. *In SPE/AAPG/SEG Unconventional Resources Technology Conference. OnePetro*.
- 883 (24) Liu, G., Jiang, H., Li, J., Wang, M., Chen, F., Ding, S. and Lu, X., 2015. Evaluation of the
884 performance of polymer gels mixed with asphalt particle as a novel composite profile control
885 system. *Journal of Industrial and Engineering Chemistry*, 26, pp.309-314.
- 886 (25) Abedini, A., Farshid, T. On the CO₂ storage potential of cyclic CO₂ injection process for
887 enhanced oil recovery. *Fuel*, 2014, 124, 14-27.
- 888 (26) Abedini, A., Torabi, F. Oil recovery performance of immiscible and miscible CO₂ huff-
889 and-puff processes. *Energy & Fuels*, 2014, 28(2), 774-784.
- 890 (27) Li, S., Qiao, C., Li, Z. and Hui, Y., 2018. The effect of permeability on supercritical CO₂
891 diffusion coefficient and determination of diffusive tortuosity of porous media under reservoir
892 conditions. *Journal of CO₂ Utilization*, 28, pp.1-14.
- 893 (28) Jin F., Chen S., Wei B., Wang, D., Yang, W., Wang, Y., Lu, J., 2021. Visualization of CO₂
894 foam generation, propagation and sweep in a complex 2D heterogeneous fracture network. *Fuel*,
895 302: 121000.

- 896 (29) Cui, G., Wang, Y., Rui, Z., Chen, B., Ren, S. and Zhang, L., 2018. Assessing the combined
897 influence of fluid-rock interactions on reservoir properties and injectivity during CO₂ storage
898 in saline aquifers. *Energy*, 155, pp.281-296.
- 899 (30) Nowrouzi, I., Manshad, A.K. and Mohammadi, A.H., 2019. Effects of dissolved carbon
900 dioxide and ions in water on the dynamic interfacial tension of water and oil in the process of
901 carbonated smart water injection into oil reservoirs. *Fuel*, 243, pp.569-578.
- 902 (31) Yang, D., Gu, Y. and Tontiwachwuthikul, P., 2008. Wettability determination of the
903 reservoir brine-reservoir rock system with dissolution of CO₂ at high pressures and elevated
904 temperatures. *Energy & Fuels*, 22(1), pp.504-509.
- 905 (32) Al-Bayati, D., Saeedi, A., Myers, M., White, C. and Xie, Q., 2019. An Experimental
906 Investigation of Immiscible- CO₂ -Flooding Efficiency in Sandstone Reservoirs: Influence of
907 Permeability Heterogeneity. *SPE Reservoir Evaluation & Engineering*, 22(03), pp.990-997.
- 908 (33) Cui, M., Wang, R., Lv, C. and Tang, Y., 2017. Research on microscopic oil displacement
909 mechanism of CO₂ EOR in extra-high water cut reservoirs. *Journal of Petroleum Science and
910 Engineering*, 154, pp.315-321.
- 911 (34) Li, S., Wang, Q., Zhang, K. and Li, Z., 2020. Monitoring of CO₂ and CO₂ oil-based foam
912 flooding processes in fractured low-permeability cores using nuclear magnetic resonance
913 (NMR). *Fuel*, 263, p.116648.
- 914 (35) Fassihi, R., Turek, E., Honarpour, M. and Fyfe, R., 2020, August. Investigation of
915 Permeability Impairment Due to Asphaltene Precipitation During Gas Injection EOR in a Major
916 GoM Field. *In SPE Improved Oil Recovery Conference*. OnePetro.
- 917 (36) Zanganeh, P., Dashti, H. and Ayatollahi, S., 2018. Comparing the effects of CH₄, CO₂, and
918 N₂ injection on asphaltene precipitation and deposition at reservoir condition: A visual and
919 modeling study. *Fuel*, 217, pp.633-641.
- 920 (37) Abouie, A., Tagavifar, M. and Sepehrnoori, K., 2018, April. Wettability alteration and flow
921 coupling in gas flooding of asphaltenic reservoirs. *In SPE Improved Oil Recovery Conference*.
922 OnePetro.
- 923 (38) Glover, P.W.J. and Walker, E., 2008. Grain-size to effective pore-size transformation
924 derived from electrokinetic theory. *Geophysics*, 74(1), pp. E17-E29.
- 925 (39) Fakher, S. and Imqam, A., 2019. Asphaltene precipitation and deposition during CO₂
926 injection in nano shale pore structure and its impact on oil recovery. *Fuel*, 237, pp.1029-1039.
- 927 (40) Kord, S., Mohammadzadeh, O., Miri, R. and Soulgani, B.S., 2014. Further investigation
928 into the mechanisms of asphaltene deposition and permeability impairment in porous media
929 using a modified analytical model. *Fuel*, 117, pp.259-268.
- 930 (41) Sim, S.S.K., Okatsu, K., Takabayashi, K. and Fisher, D.B., 2005, October. Asphaltene-
931 induced formation damage: effect of asphaltene particle size and core permeability. *In SPE
932 Annual Technical Conference and Exhibition*. OnePetro.
- 933 (42) Minssieux, L., 1997, February. Core damage from crude asphaltene deposition.
934 *In International Symposium on Oilfield Chemistry*. OnePetro.
- 935 (43) Soulgani, B.S., Tohidi, B., Jamialahmadi, M. and Rashtchian, D., 2011. Modeling
936 formation damage due to asphaltene deposition in the porous media. *Energy & Fuels*, 25(2),
937 pp.753-761.

- 938 (44) Nasri, Z. and Dabir, B., 2014. Network modeling of asphaltene deposition during two-
939 phase flow in carbonate. *Journal of Petroleum Science and Engineering*, 116, pp.124-135.
- 940 (45) Davudov, D. and Moghanloo, R.G., 2019. A new model for permeability impairment due
941 to asphaltene deposition. *Fuel*, 235, pp.239-248.