

1 **Effect of CO₂ phase states and flow rate on salt precipitation in shale caprocks**
2 **– a microfluidic study**

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10
11 **Abstract**

12 Fracture networks inside the caprock for CO₂ storage reservoirs may serve as leakage pathways.
13 Fluid flow through fractured caprocks and bypass conduits, however, can be restrained or
14 diminished by mineral precipitations. This study investigates precipitation of salt crystals in an
15 artificial fracture network as a function of pressure-temperature conditions and CO₂ phase states.
16 The impact of CO₂ flow rate on salt precipitation was also studied. The primary research
17 objective was to examine whether salt precipitation can block potential CO₂ leakage pathways.
18 In this study, we developed a novel microfluidic high-pressure high-temperature vessel to house
19 geomaterial micromodels. A fracture network was laser-scribed on the organic-rich shales of the
20 Draupne Formation, the primary caprock for the Smeaheia CO₂ storage in Norway. Experimental
21 observations demonstrated that CO₂ phase states influence the magnitude, distribution and
22 precipitation patterns of salt accumulations. The CO₂ phase states also affect the relationship
23 between injection rate and extent of precipitated salts due to differences in solubility of water in
24 CO₂ and density of different CO₂ phases. Injection of gaseous CO₂ resulted in higher salt
25 precipitation compared to liquid and supercritical CO₂. It is shown that micrometer-sized halite
26 crystals have the potential to partially or entirely clog fracture apertures.

27

28 **Introduction**

29 Changes in Earth's climate since the onset of the industrial revolution have raised global concern
30 about the increasing level of greenhouse gases, particularly carbon dioxide (CO₂).¹ Carbon
31 capture and storage (CCS) in geological formations is considered a promising technology to
32 mitigate climate change caused by atmospheric anthropogenic CO₂.²⁻⁴ To evaluate a site for
33 geological CO₂ storage, storage capacity, injectivity, and containment efficiency should be
34 investigated thoroughly.⁵⁻⁷ Integrity and sealing capacity of caprocks is a critical parameter in
35 selecting a candidate.⁸⁻¹⁰ A potential leakage can render the project futile,¹¹ cause surface
36 movements and induced seismicity,¹² impact local ecosystems,¹³ contaminate groundwater,¹⁴⁻¹⁶
37 mobilize elements¹⁷ due to acidification and in the worst case may cause severe health issues.^{18,}
38 ¹⁹ The risk of leakage through caprocks might, however, be reduced through mineral
39 precipitation.²⁰⁻²² Several numerical investigations have proposed occurrence of salt precipitation
40 and clogging of leakage pathways in the caprocks during CO₂ injection.²³⁻²⁷

41 Underground injection of large volumes of supercritical CO₂ (scCO₂) that is
42 undersaturated with respect to water causes evaporation of formation water. As evaporation
43 continues, the concentration of dissolved salts in brine pore fluids increases. When the salt
44 concentration reaches the solubility limit, it will precipitate out of the aqueous phase, and salt
45 crystals will form in the porous or fractured media. Salt precipitation during CO₂ injection into
46 the geological formations can influence properties of both reservoir and top seal sequences.²⁸
47 Several field observations,²⁹⁻³³ experimental investigations,^{27, 34-37} and numerical studies³⁸⁻⁴² have
48 reported the occurrence of salt precipitates, mostly halite, during injection and storage. Despite
49 the rather comprehensive research, there are some inconsistencies between the reported results,
50 and lack of systematic investigations in some areas.⁴³ For instance, no published research

51 provides a systematic study on the effect of CO₂ phase states and thermodynamic conditions on
52 salt precipitation. Moreover, present inconsistencies regarding the extent and significance of salt
53 precipitates, and their influence on the CO₂ phase percolation pathways should be investigated.
54 While some authors^{27, 44, 45} suggest that salt crystals precipitate only in the brine phase, and thus,
55 have an insignificant impact on the flow pathways, several other literatures^{34, 46, 47} have shown
56 that great amount of salt can also precipitate in the CO₂ phase. The latter studies contradict the
57 former clogging model and propose that in the evaporation-precipitation process of salt
58 formation we may expect considerable changes in the static and dynamic properties of the
59 porous media.

60 Since the 1950's,⁴⁸ laboratory microfluidic experiments have been used to observe fluid
61 flow and solute transport within the porous media. The microfluidic experiments have proven to
62 be an effective tool to provide insights into flow and transport phenomena on micro- and macro-
63 scales.^{49, 50} While the vast majority of microfluidic investigations make use of synthetic and
64 engineered materials such as glass, silicon, and plastic, several recent research made use of real
65 rocks.⁵⁰⁻⁵³ Moreover, most of the micromodels cannot withstand elevated pressures and
66 temperatures that are representative of the realistic field conditions.

67 In this study, we have developed a novel microfluidic high-pressure high-temperature
68 (HPHT) vessel to house geomaterial (natural rock or mineral chips) micromodel specimens.
69 Fracture patterns were laser-scribed on the organic-rich shales of the Draupne Formation, the
70 primary caprock for the Smeaheia CO₂ storage site (Northern Lights) in Norway. The primary
71 research objective was to examine the extent of salt precipitation in fracture networks of our
72 shale micromodel under different thermodynamic conditions and for various CO₂ phase states.
73 We have investigated whether precipitation of salt crystals can partially or entirely block

74 potential CO₂ leakage pathways in caprocks. Moreover, the impact of CO₂ injection flow rate on
75 salt accumulations was studied.

76

77 **Conceptual framework**

78 In a full-scale geological CO₂ sequestration, millions of tons must be stored underground. The
79 injection of dry or undersaturated scCO₂ with respect to water leads to dry-out of formation
80 water and changes in the physical and chemical properties of the evaporation zone.⁵⁴⁻⁵⁶ Figure 1
81 presents a schematic of a potential fracture healing mechanism and caprock sealing process due
82 to salt precipitation. The water solubility in CO₂ (H₂O mol %) in Figure 1 is calculated based on
83 the statistical associating fluid theory (SAFT).⁵⁶ SAFT is a semiempirical equation of state that
84 can model thermodynamic properties and accurately handle multicomponent phase equilibria at
85 low and high pressures for fluid mixtures.⁵⁷ The injected scCO₂ that is undersaturated with
86 respect to water becomes saturated after percolating through a substantial volume of brine-
87 saturated reservoir rock while the CO₂ plume migrates upward to reach the reservoir-caprock
88 interface. A rapid pressure and temperature drop during CO₂ leakage may, however, cause
89 adiabatic expansion and further cooling of leaking CO₂, and subsequently an increase in water
90 solubility in CO₂ within the salt zone (Fig. 1). Because derivative of water solubility with respect
91 to time will be positive within the proposed salt zone, the leaking CO₂ becomes undersaturated,
92 and therefore, can progressively evaporate more brine as it migrates through fractures in the
93 caprock.⁵⁶ Consequently, an evaporation front may form and a reduction in aperture and
94 permeability of leaking channels is expected due to precipitation of salt crystals.

95

96 **Materials and Methods**

97 **Description of experimental system**

98 A custom-designed stainless steel pressure vessel with an inspection window at the top was
99 constructed to house geomaterial micromodels (natural rock or mineral chips). Figure 2a depicts
100 a schematic of the top view and cross-section of the microfluidic pressure vessel. The
101 experimental pressure vessel consists of a bottom pedestal and a top cap. The bottom pedestal
102 provides hydraulic connection to the fluid inlet and outlet and holds the specimen. The top cap
103 carries the monitoring window and seals the pressure vessel. In addition to the top cap, an O-ring
104 outside perimeter of the sample holder keeps the injectant inside the pressurized chamber of the
105 cell (Fig. 2a). For further details refer to the Supporting Information. The microfluidic vessel was
106 tested for elevated pressure and temperature conditions before the experiments. It showed a safe
107 working pressure and temperature conditions up to 20 MPa and 80°C, respectively.

108 Figure 2b presents a schematic of the experimental setup. The microfluidic pressure
109 vessel was placed and coupled with an AFS 200 core flooding system (Core Laboratories). The
110 core flooding system is equipped with a forced convection benchtop oven (Despatch LBB
111 series), which combines horizontal and vertical airflow, and provides temperature uniformity
112 within the air bath. The fluid injection system comprises one dual-cylinder syringe pump
113 (Teledyne Isco, 100DM), which controls brine and CO₂ flow rates. A back pressure regulator
114 and a single-cylinder syringe pump (Teledyne Isco, 500D) control the fluid pressure inside the
115 system. Two pressure transducers monitor fluid pressure at the inlet and outlet of the pressure
116 vessel. Finally, three gas mass flow controllers (three different working ranges) detect CO₂ flow
117 after the back pressure regulator. High-pressure steel tubing, fittings, and valves were used for
118 plumbing inside the experimental system.

119 A Nikon SMZ stereo microscope (visible light) assisted in visualizing and digitally
120 recording the microfluidic specimen within the pressure vessel (Fig. 2b). The imaging was
121 performed at bright field condition through the vessel's glass window. The Nikon SMZ is a
122 Greenough-type stereo microscope that uses two separate optical paths and an angular offset to

123 generate a three-dimensional image. The microscope's trinocular head was equipped with a
124 digital camera, which provided a stream of high-resolution live images at 30 frames per second
125 through the ScopeView 3.0 software package. To analyze surface coverage of precipitated salt
126 crystals, the obtained experimental images were extracted from the recorded videos (1-hour
127 intervals) and processed following the published workflows.^{50, 58-60} The details are presented in
128 the Supporting Information.

129

130 **Preparation of specimens**

131 For the microfluidic HPHT experiments, we have developed a technique for fabrication of
132 specimens that can make use of a variety of natural and synthetic materials. In this study, we
133 used the Upper Jurassic organic-rich shales of the Draupne Formation. The shale samples were
134 acquired from well 16/8-3S in the Ling depression in the Norwegian North Sea. The Draupne
135 Formation comprises marine black shale, which is a rich source rock in the North Sea, and a seal
136 for the Middle Jurassic sandstone reservoirs in the area.⁶¹ More importantly, it is the primary
137 caprock for the Smeaheia⁶²⁻⁶⁴ CO₂ storage site (Northern Lights), the proposed full-scale CCS
138 project in Norway. The Draupne shale sample has a total porosity and matrix permeability in a
139 range of 20-30% and nano- to pico-Darcy.^{65, 66} The MIP measurements showed a median pore
140 diameter of 27.5 nm and a critical pore throat diameter of 9 nm.^{65, 66} The BET-derived specific
141 surface area was 11 m²/g.⁶⁶ Given the pore space characteristics, matrix flow of injected CO₂
142 requires extremely high capillary entry pressure and this was therefore considered unlikely for
143 the performed experiments. The use of shale core samples ensured that experimental substrate
144 represents realistic caprock properties.^{50, 67} In particular, it shows similar wettability and surface
145 free energy that influence nucleation and precipitation of salt crystals.

146 To prepare specimens, we cut the shale samples in less than 2.5 cm diameter sizes and
147 dried at 40°C for three days. The specimens were fabricated using the cold mounting procedure.

148 In the cold mounting procedure, the dried samples were placed inside a cylindrical plastic mold
149 with 2.5 cm and 1.5 cm diameter and height, respectively, where the epoxy resin was added to
150 the mold to fill it completely (Fig. S1, Supporting Information). The friable or porous samples
151 can be vacuumed before adding the epoxy, or the sample can be impregnated with epoxy under
152 vacuum if it is necessary. The mold was then left overnight to harden. Subsequently, a series of
153 automatic grinding and polishing steps were followed to provide a flat, unscratched surface for
154 laser scribing of designed fracture patterns. For more details refer to the Supporting Information.
155 The cold mounting procedure does not change properties of the shale material. The injected
156 fluids (brine and CO₂ phases) were partly in contact with epoxy at the inlet and outlet. However,
157 no interaction between the epoxy and injectant is expected, and the epoxy plays a role as a non-
158 reactive material within the system.

159

160 **Laser scribing of fracture patterns**

161 To scribe the designed fracture pattern on the shale specimens, we used a Rofin scribing laser at
162 the microsystems and nanotechnology laboratory (MiNaLab) at the University of Oslo (UiO).
163 The fracture network was scribed using a 532 nm laser at 25A, 15000 Hz and 200 mm/s. The
164 scribing was performed twice with an interval time of 5 minutes between each execution to keep
165 the sample heating to a minimum. Moreover, a high scanning speed, high power, and low
166 frequency were selected to maximize ablation, minimize heating of the sample, and limit the heat
167 affected zone. The laser-scribed fracture network is 19 mm long and 14 mm wide pattern.
168 Subsequently, the ablated debris and heat affected material were cleaned to reach the undisturbed
169 matrix of the shale specimen inside the fracture network. To remove the ablated debris, we used
170 micro-scratcher blades under an optical microscope. The scratching procedure and micro-scale
171 cleaning did not change the geometry of scribed patterns, but only widened and deepened the

172 fracture branches (Figs. S2-3, Supporting Information). Surface profilometry was then performed
173 to capture geometry and dimensions of the eventual fracture planes before the experiment.

174 Scanning electron microscopy (SEM) and backscatter electron imaging (BEI) with
175 energy-dispersive x-ray spectroscopy (EDS) were used to investigate changes in microstructure,
176 elemental composition, and surface properties of specimens after the laser scribing. A Hitachi
177 SU5000 FE-SEM (Schottky FEG) at the Department of Geosciences (UiO) provided the SEM
178 analyses. The EDS was performed by the Dual Bruker XFlash and HR EBSD systems that are
179 integrated into the Hitachi SU5000 machine.

180

181 **Experimental procedure**

182 An aqueous solution of 3.4 M (200 g/l) sodium chloride prepared by adding NaCl (ACS reagent
183 grade, EMSURE[®]) to deionized water (Milli-Q water) was used to saturate the shale micromodel
184 before the experiments. The salinity of brine was selected to represent undersaturated high-
185 salinity formation water.⁶⁸ A comprehensive list of experimental and numerical studies with such
186 range of salinity or even higher is summarized in Miri and Hellevang⁴³. A bottle provided CO₂
187 (grade 5.2, scientific carbon dioxide, Praxair Norge AS) for injection into the fracture network.
188 The experiments were conducted at nine pressure-temperature conditions, combining
189 temperatures of 22, 40 and 60°C, with three pressures (1, 5 and 8 MPa). As a result, the flow of
190 CO₂ was investigated for gaseous, supercritical and liquid CO₂ states (Table 1, Supporting
191 Information). The experiments were performed at a flow rate of 20 cm³ CO₂/min. In addition, to
192 investigate the impact of CO₂ injection flow rate on the distribution and extent of salt
193 precipitation, we injected gaseous (1 MPa) and supercritical CO₂ (8 MPa) with three different
194 flow rates (5, 10 and 20 cm³ CO₂/min) at 60°C. Three flow rates were selected to provide a
195 comparative measure and also to examine whether salt precipitation can be avoided. The

196 estimated linear average velocity of CO₂ inside the fracture branches is approximately 10⁻⁴ to 10⁻⁵ m/s, which can be expected in leakage pathways.⁶⁹ The experiments lasted for 12 to 30 hours
197 depending on thermodynamic condition and injection rate until the matrix of shale micromodel
198 became completely dry. For the tests with elevated temperatures (40 and 60°C), we left the
199 mounted microfluidic pressure vessel at least for 4 hours within the forced convection oven
200 before starting the experiment. It ensured an equilibrated temperature within the experimental
201 setup. The back pressure regulator controlled the pressure levels, and the fluid injection was
202 performed in a constant flow rate mode.
203

204

205 **Results and discussion**

206 **Configurations of precipitated salt crystals**

207 Three flow mechanisms influenced saturation of brine within the microfluidic specimen. First,
208 two-phase viscous displacement pushed the brine outside the fracture network. Subsequently,
209 various forms of saturation patches, such as pools, domes and brine films on fracture surfaces,
210 were formed due to capillary forces. Finally, an evaporation regime dried the residual brine
211 saturation inside the fracture network and matrix of the shale micromodel. For the detailed
212 description and graphical representation refer to the Supporting Information (Fig. S4). These
213 flow mechanisms were dominant at different time scales and lasted differently. The water
214 solubility in CO₂ phase (Fig. 1b) controlled the brine evaporation flux into the CO₂ stream and
215 determined duration of the drying regime.³⁴ At all nine pressure-temperature conditions, covering
216 the three CO₂ phase states, and for the three injection rates, we observed that salt crystals
217 precipitate in two distinct forms: (a) large and semi-large (100-300 μm) single cubic crystals of
218 halite in the aqueous phase; and (b) dense micrometer-sized (<20 μm) halite crystals on the
219 interface of rock and CO₂ stream. Figures 3 and 4 illustrate the growth of a single halite crystal in

220 a brine dome, and precipitation of micrometer-sized salt aggregates on the fracture surfaces,
221 respectively.

222 The single cubic crystals of halite mainly formed in brine domes very early in the
223 evaporation regime. The large halite crystals precipitated only after brine domes had established
224 and the domes could remain stable until the salt concentration in the trapped brine reached the
225 solubility limit. As temperature increased from ambient condition (about 22°C) to 40 and 60°C,
226 the brine domes occurred less often and as a result, single large cubic crystals precipitated
227 infrequently. The first salt precipitation event at 22°C was the large and semi-large halite
228 crystals. Moreover, the single salt crystals happened to form more frequently when CO₂ was
229 injected in the gaseous phase. Video 1 (Supporting Information) communicates precipitation
230 dynamics of a large halite crystal in the aqueous phase near the inlet. As Figure 3 and Video 1
231 show, a cubic salt crystal forms in the brine dome owing to locally increased solute
232 concentration and sufficient time before brine dome thinning or diminishing starts (Fig. 3b-c).
233 The movements and rotations of the cubic salt crystal inside the isolated brine dome suggest that
234 the halite crystal began to grow inside the aqueous phase without any attachments to the
235 surrounding fracture surfaces. While CO₂ stream was evaporating residual brine out of the
236 specimen, the salt crystal continued to grow in all three dimensions (Fig. 3d-g). However, as the
237 initial crystal that was immersed in brine became more prominent, it partly protruded into the
238 surrounding CO₂ stream (Fig. 3h). As documented by Miri et al.³⁴, because of the hydrophilic
239 nature of the salt crystals the protruding exteriors are covered with an aqueous film. The
240 surrounding CO₂ stream could quickly evaporate the brine film, and the layer became
241 supersaturated. It led to further formation of salt microcrystals and surface roughening of the
242 single cubic halite crystal, which in turn contributed to more precipitation (Fig. 3i-k). The growth
243 of the crystal came to an end when the brine dome vanished.

244 As evaporation continued and salt concentration in the remaining brine inside the fracture
245 network reached the solubility limit, precipitation of micrometer-sized halite crystals started
246 (Fig. 4a-b). Video 2 (Supporting Information) demonstrates how micrometer-sized salt crystals
247 precipitated on the rock-CO₂ interface. While the experimental time was moving forward and the
248 evaporation front progressed from the inlet toward the outlet, new spots in the fracture network
249 experienced supersaturation, and eventually salt accumulation (Fig. 4). As Figure 4 and Video 2
250 illustrate, micrometer-sized halite crystals on the fracture surfaces grew very fast, separate
251 patches became connected (Fig. 4c-d), and left behind massive salt bodies that could block
252 fracture branches (Fig. 4e-f). Experimental observations suggest that coverage of these localized
253 salt accumulations depends on the access to brine feeding sources, which could provide brine for
254 further growth. Residual brine patches inside the fractures, brine films on the fracture surfaces,
255 and potentially brine inside the microcracks of the shale can act as brine feeding sources.
256 Although several authors, for instance Ott et al.²⁷, proposed limited precipitation of salt crystals
257 due to available solute in the trapped brine, results of the present study indicated that the
258 localized salt accumulations are notably greater than the residual brine patches inside the fracture
259 network alone.

260 Despite massive precipitation patterns of the micrometer-sized salts, closer observation
261 revealed that these aggregates have a porous structure of densely precipitated crystals (Fig. S6,
262 Supporting Information). The tightly packed halite aggregates show a distribution of narrow pore
263 throats between the crystals. These salt precipitates produce a porous medium with potential
264 large capillarity.³⁴

265

266 **Location and distribution of precipitated salt crystals**

267 Experimental results also provided insight on where in the fracture network salt crystals
268 precipitate and how separate accumulations distribute and develop. It can be of great significance
269 for constructing clogging models for salt precipitation during CO₂ storage. While large single
270 cubic crystals showed limited occurrences and coverage, and consequently insignificant impact
271 on permeability, the growth of the micrometer-sized crystals could influence flow pathways
272 within the fracture network. As Figure 4 and S5 (Supporting Information) illustrate, the
273 micrometer-sized crystals mainly formed on the fracture walls and to a lesser extent at the
274 bottom surface of the fractures. While the evaporation was progressing, the supersaturated
275 clusters expanded, and localized salt accumulations precipitated. The salt bodies subsequently
276 grew bigger because of further precipitations adjacent to the initial salt aggregates in addition to
277 the evaporation of imbibed brine on the present halite crystals (Fig. S5). The recently
278 precipitated aggregates, in turn, provided further surface area for evaporation, nucleation, and
279 growth of the salt crystal. Until the brine feeding sources were available, the surface area for salt
280 precipitation progressively expanded and consequently, the localized salt accumulations grew
281 larger and larger. The subsequent salt crystals, hence, formed both on the fracture surfaces and
282 on the previously precipitated salt accumulations. Because of the additional surface area for
283 growth and availability of brine feeding sources, accumulations of micrometer-sized salt crystals
284 could partially or entirely plug the fracture branches (Fig. 4 and S5).

285 Another observation was regarding the relative growth of two separate and neighboring
286 salt bodies. As shown in Figure S5 (Supporting Information), the experimental observations
287 demonstrated that, whether the two adjacent and detached salt bodies were sitting on the same or
288 opposite fracture walls, they show an affinity for growth toward each other. It was noted that the
289 growth speed is relatively more toward the adjacent salt accumulation compared to free fracture
290 walls, which can be the result of a concentration gradient between the two salt bodies. When
291 enough brine was accessible, the two salt accumulations could become connected. As a result,

292 the rate of growth and density of salt accumulations increased notably. The intensity of reflected
293 light from the salt accumulations provided an indication of their density.

294

295 **Effect of CO₂ phase state (pressure and temperature conditions)**

296 The CO₂ phase state and thermodynamic conditions were observed to control physics of salt
297 precipitation. As is shown in Figure 5, the CO₂ phase states influenced magnitude, distribution
298 and precipitation pattern of localized salt accumulations. The percentage of salt surface coverage
299 throughout the experiment for different thermodynamic conditions is demonstrated in Figure 6a.
300 During injection of dense phases (liquid and scCO₂) more brine was flushed out of the fracture
301 network and lower residual saturation established because of the higher imposed viscous forces.
302 As a result, a lower amount of brine was available in the fracture network, and limited
303 accumulation of salt crystals was observed. As presented in Figure 5 and 6a, within the pressure-
304 temperature range of present study, the overall conclusion is that decrease in pressure results in a
305 decrease of total salt coverage. However, the relationship is not one-to-one, and some retrograde
306 trends were detected. Here, we discuss the experiments by P= pressure, T= temperature, and Q=
307 flow rate. All the experiments in Figure 5 are performed at Q= 20 cm³ CO₂/min. For instance,
308 coverage and distribution of salt aggregates in the P5T22 and P5T40 experiments were relatively
309 similar (Fig. 5b and 5e), but P5T60 test indicates higher and denser precipitates compared to
310 latter cases (Fig. 5h). While there is a clear difference between P1T40 and P1T60 salt bodies
311 (Fig. 5d and 5g), the P8T40 and P8T60 were very similar in distribution and coverage (Fig. 5f
312 and 5i). In descending order of eventual salt coverage, gaseous, liquid and supercritical CO₂
313 phases can be listed. At 20 cm³ CO₂/min flow rate (Fig. 6a), the average precipitation is 11%,
314 3% and 0.8% for gaseous, liquid and supercritical CO₂, respectively. Moreover, injection of
315 liquid CO₂ (P8T22) resulted in bigger micrometer-sized crystals compared to other phases (Fig.

316 5c). In Figure 6b, we plotted the maximum water flux into the CO₂ stream versus the total salt
317 coverage for each experiment. We have calculated the maximum water influx (H₂O mol %) by
318 multiplying the injected CO₂ volume by water solubility in CO₂ at the pressure-temperature
319 condition of a given experiment. As Figure 6b demonstrates, there is a relatively strong
320 correlation ($R^2 \approx 0.87$) between the maximum water influx and salt coverage. The higher the
321 maximum water flux, the higher the salt coverage. The results for the dense phases (liquid and
322 scCO₂) are located at the bottom left of the plot. Whereas the calculations for the tests with
323 gaseous CO₂ are extended to the top right, where higher water flux is calculated, and extensive
324 salt accumulations are observed (Fig. 6b). While water solubility in gaseous CO₂ (Fig. 1) can
325 explain the extent of precipitated salts in Figure 5, the observed results for PIT60 experiment
326 remain an unresolved question, and thus, the corresponding maximum water flux was not shown
327 in Figure 6b. The PIT60 experiment for clarification was performed twice. However, the
328 outcome and the salt accumulations were similar.

329 Several studies^{27, 38, 40} have attempted to introduce a critical velocity above which
330 massive salt accumulation can be avoided. As reviewed by Miri and Hellevang⁴³, previously
331 published research have not considered the impact of thermodynamics and CO₂ phase states on
332 the critical velocity. Present results suggest that the extent of micrometer-sized precipitates is
333 influenced by CO₂ phase states and pressure-temperature conditions. Even at high injection flow
334 rates (20 cm³ CO₂/min), precipitation of salt crystals was observed (up to 24% surface coverage
335 for PIT40 test) (Fig. 6a). The results also indicate that the CO₂ phase state affects the
336 relationship between injection rate and extent of salt accumulations (Fig. 7). Figure 7
337 demonstrates a stronger impact of the rate on salt coverage during injection of scCO₂ compared
338 to gaseous CO₂ as reducing the rate to 5 cm³ CO₂/min caused significant salt accumulation even
339 for the dense phase of scCO₂. The impact of flow rate was more significant for scCO₂ because of
340 the higher density and greater viscous pressure imposed during scCO₂ injection. We propose

341 further detailed research to explore the interdependence between the critical velocity, CO₂ phase
342 state, and thermodynamic conditions.

343

344 **Effect of injection flow rate**

345 As illustrated in Figure 7, the higher the injection flow rate, the lower the salt coverage. The
346 precipitated salt crystals were significant at 5 cm³ CO₂/min injection rate with 19% and 14%
347 coverage for gaseous- and scCO₂, respectively (Fig. 7c and 7f). At 5 cm³ CO₂/min injection rate,
348 the salt accumulations notably affected CO₂ flow pathways inside the fracture network and
349 blocked part of the fracture apertures in addition to major part of the inlet. Figure 6c presents
350 coverage of the salt precipitates during the experiments. Decreasing injection flow rate caused
351 evaporation regime to last for a more extended period. The experimental time as a consequence
352 increased from approximately 12 hours to a maximum of 30 hours (Fig. 6c). However, once
353 precipitation started, it progressed quickly for all three injection rates but lasted longer for lower
354 rates (Fig. 6c). Reducing injection flow rate also caused the initial salt accumulations to
355 precipitate closer to the inlet, and from there toward different branches of fracture network.

356 As Miri and Hellevang⁴³ discussed, three drying regimes (diffusive, capillary and
357 evaporative) affect the precipitation of salt crystals based on stabilized capillary and evaporative
358 fluxes. When the injection flow rate was decreased, the drying mechanism transforms from pure
359 evaporative to more capillary and diffusive.⁴³ In other words, reduction of injection pressure
360 gradient made it easier for the capillary pressure gradient to drive brine toward the inlet, support
361 more evaporation and cause more salt precipitation. A high injection rate introduces a higher
362 pressure gradient and suppresses the capillary backflow towards the inlet and evaporation
363 front.^{38, 40, 70, 71} The reduced capillary backflow, in turn, reduces the possibility of intensive salt
364 accumulation. The observed results, thus, contradict the studies suggesting that an increase in

365 evaporation rate causes more salt precipitation than the increase in capillary backflow.^{41, 42}
366 Considering mechanisms that influence salt precipitation⁴³, massive accumulations form only
367 when conditions for capillary backflow and salt capillary suction are favorable. The performed
368 experiments in this study show that when capillary regimes overcome viscous forces, a
369 considerable amount of salt crystals precipitated because of the access to brine feeding sources
370 through a continuous water phase on fracture surfaces.³⁴ Such brine feeding sources are residual
371 patches, films, and even microcracks.

372 In the evaporation front, a major part of water mass exchange occurs when a constant
373 flow of CO₂ stream with low water vapor pressure passes through the micromodel. It brings
374 about a significant brine saturation gradient across the evaporation front and gives rise to a
375 capillary pressure gradient that pushes brine toward the evaporation front. Miri et al.³⁴ showed
376 that because of the large capillarity of localized salt accumulations, they could imbibe brine over
377 long distances. Imbibing brine out of the shale microcracks provides additional brine source for
378 feeding the evaporation front. As capillary-driven backflow of the aqueous phase and salt
379 capillary suction mechanisms continuously provide more brine, the brine will evaporate on the
380 available surface area, and the salt accumulations will grow bigger. The bigger the salt body, the
381 higher the imbibed brine, and the faster the growth rate. When viscous forces at higher injection
382 rates resist the capillary forces and disturb the continuous supply of brine, the salt accumulations
383 will not have the chance to grow substantially (Fig. 7a and 7d).

384

385 **Environmental implication for geological CO₂ storage**

386 Ensuring secure and safe subsurface CO₂ storage is among the critical considerations regarding
387 CCS projects. Pre-existing and induced fractures in the caprocks may serve as leakage pathways
388 within the CO₂ storage sites (Fig. 1).^{9, 72, 73} Fluid flow through fractured caprocks and bypass
389 conduits, however, can be restrained or diminished by precipitation of minerals.⁷⁴ Our

390 microfluidic experiments on the organic-rich shale of Draupne Formation demonstrated that
391 precipitation of significant amount of micrometer-sized salt crystals is expected at field-scale
392 flow rates (low CO₂ flow rates). At the interface of the reservoir and fractured caprock, leakage
393 and upward flow of injected CO₂ may reduce brine saturation in the fractures and causes a local
394 development of drying zones. While the drying zones progress, local salting-out spots form and
395 various feeding sources provide uninterrupted access to brine through capillary forces. As
396 shown, micrometer-sized salt crystals that precipitate on the interface of fracture walls and CO₂
397 stream have the potential to partly or entirely block fracture apertures and consequently leakage
398 pathways. The development of salt crystals toward the point where leakage begins, the affinity of
399 salt bodies to become connected, and extent of accumulations suggest that salt precipitation
400 during leakage of CO₂ can be considered as a fracture healing mechanism. Because of the
401 buoyant migration of CO₂ plume over time, we expect a low saturation of brine at the interface
402 of reservoir-caprock. It considerably reduces the risk of re-dissolution of precipitated salts inside
403 the leaking fractures with re-saturation of brine pore fluid.

404

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611

612 Caption of Figures

613 **Figure 1.** A conceptual framework for potential clogging of leakage pathways in the
614 caprocks due to salt precipitation. Within the pressure-temperature conditions of the salt zone,
615 water solubility in CO₂ increases as pressure decreases. A rapid leakage, thus, may result in salt
616 precipitation in the caprock even for CO₂ that is initially saturated with respect to water. The
617 water solubility in CO₂ is calculated using the statistical associating fluid theory (SAFT).⁵⁶ The
618 schematic of geological CO₂ storage was modified from DNV.⁷⁵ The numbers show the
619 correspondence in pressure-temperature conditions with the modeled water solubility in CO₂
620 during a potential upward leakage.

621 **Figure 2.** (a) A schematic of the top view and cross-section of the designed microfluidic
622 pressure vessel; (b) A schematic representation of the laboratory set-up used in the HPHT salt
623 precipitation experiments.

624 **Figure 3.** The dynamics of growth for a large single cubic crystal of halite in the aqueous
625 phase (brine dome). It also demonstrates how the crystal grows when it partly protrudes into the
626 surrounding CO₂ stream. The subfigures are time-lapse images of an experiment at pressure = 5
627 MPa, temperature = 22°C, and flow rate = 20 cm³ CO₂/min.

628 **Figure 4.** The dynamics of salt precipitation for micrometer-sized crystals of halite that
629 form on the interface of rock and CO₂ stream. The boxed region shows the zoomed area in
630 Figure 3. The subfigures are time-lapse images of an experiment at pressure = 1 MPa,
631 temperature = 22°C, and flow rate = 20 cm³ CO₂/min. The white-outlined surfaces describe the
632 fracture walls, and the blue-outlined areas inside the fractures are precipitated salt crystals.

633 **Figure 5.** The influence of CO₂ phase states and pressure-temperature conditions on the
634 micrometer-sized salt accumulations. All the experiments were performed at a flow rate of 20
635 cm³ CO₂/min. The subfigures are recorded at the end of each experiment when the shale matrix
636 became completely dry. The white-outlined surfaces describe the fracture walls, and the blue-
637 outlined areas inside the fractures are precipitated salt crystals.

638 **Figure 6.** Analysis of salt surface coverage on the fracture network of shale specimen. (a)
639 Effect of CO₂ phase states and pressure-temperature conditions, where salt surface coverage is
640 plotted against the experimental elapsed time. The experiments were performed at an injection
641 rate of 20 cm³ CO₂/min. (b) Effect of CO₂ phase states and pressure-temperature conditions,
642 where maximum water flux during the test is plotted versus salt surface coverage; (c) Effect of
643 CO₂ flow rate, where salt surface coverage is plotted against the experimental elapsed time. The
644 experiments were performed at a temperature of 60°C. The notations stand for P= pressure, T=
645 temperature, Q= flow rate. A maximum 4% uncertainty for the salt precipitation data points can
646 be considered.

647 **Figure 7.** The influence of CO₂ injection flow rate on the micrometer-sized salt
648 accumulations. It shows the results for (top) gaseous, 1 MPa, and (bottom) supercritical CO₂, 8
649 MPa, at 60°C when CO₂ was injected at three different flow rates (20, 10 and 5 cm³ CO₂/min).

650 The notations stand for P= pressure, T= temperature, Q= flow rate. The subfigures are recorded
651 at the end of each experiment when the shale matrix became completely dry. The white-outlined
652 surfaces describe the fracture walls, and the blue-outlined areas inside the fractures are
653 precipitated salt crystals.

654 Supporting Information

655 Additional details including a description of shale sample fabrication, microfluidic specimen
656 preparation and mounting it into the pressure vessel, experimental conditions, analysis of salt
657 surface coverage, and flow mechanisms. Figures showing fabrication procedure of shale sample,
658 SEM micrograph of fracture pattern, surface profilometry, effect of different flow mechanism,
659 growth and distribution pattern of micrometer-sized salt crystals, and microstructure of
660 micrometer-sized halite crystals. Videos communicating growth dynamics of a large single cubic
661 crystal in the aqueous phase, and micrometer-sized crystals on the interface of rock and CO₂
662 stream.















