Effect of CO$_2$ phase states and flow rate on salt precipitation in shale caprocks
– a microfluidic study

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Abstract

Fracture networks inside the caprock for CO$_2$ storage reservoirs may serve as leakage pathways. Fluid flow through fractured caprocks and bypass conduits, however, can be restrained or diminished by mineral precipitations. This study investigates precipitation of salt crystals in an artificial fracture network as a function of pressure-temperature conditions and CO$_2$ phase states. The impact of CO$_2$ flow rate on salt precipitation was also studied. The primary research objective was to examine whether salt precipitation can block potential CO$_2$ leakage pathways. In this study, we developed a novel microfluidic high-pressure high-temperature vessel to house geomaterial micromodels. A fracture network was laser-scribed on the organic-rich shales of the Draupne Formation, the primary caprock for the Smeaheia CO$_2$ storage in Norway. Experimental observations demonstrated that CO$_2$ phase states influence the magnitude, distribution and precipitation patterns of salt accumulations. The CO$_2$ phase states also affect the relationship between injection rate and extent of precipitated salts due to differences in solubility of water in CO$_2$ and density of different CO$_2$ phases. Injection of gaseous CO$_2$ resulted in higher salt precipitation compared to liquid and supercritical CO$_2$. It is shown that micrometer-sized halite crystals have the potential to partially or entirely clog fracture apertures.
Introduction

Changes in Earth’s climate since the onset of the industrial revolution have raised global concern about the increasing level of greenhouse gases, particularly carbon dioxide (CO$_2$).$^1$ Carbon capture and storage (CCS) in geological formations is considered a promising technology to mitigate climate change caused by atmospheric anthropogenic CO$_2$.$^{2,4}$ To evaluate a site for geological CO$_2$ storage, storage capacity, injectivity, and containment efficiency should be investigated thoroughly.$^{5-7}$ Integrity and sealing capacity of caprocks is a critical parameter in selecting a candidate.$^{8-10}$ A potential leakage can render the project futile,$^{11}$ cause surface movements and induced seismicity,$^{12}$ impact local ecosystems,$^{13}$ contaminate groundwater,$^{14-16}$ mobilize elements$^{17}$ due to acidification and in the worst case may cause severe health issues.$^{18,19}$ The risk of leakage through caprocks might, however, be reduced through mineral precipitation.$^{20-22}$ Several numerical investigations have proposed occurrence of salt precipitation and clogging of leakage pathways in the caprocks during CO$_2$ injection.$^{23-27}$

Underground injection of large volumes of supercritical CO$_2$ (scCO$_2$) that is undersaturated with respect to water causes evaporation of formation water. As evaporation continues, the concentration of dissolved salts in brine pore fluids increases. When the salt concentration reaches the solubility limit, it will precipitate out of the aqueous phase, and salt crystals will form in the porous or fractured media. Salt precipitation during CO$_2$ injection into the geological formations can influence properties of both reservoir and top seal sequences.$^{28}$ Several field observations,$^{29-33}$ experimental investigations,$^{27,34-37}$ and numerical studies$^{38-42}$ have reported the occurrence of salt precipitates, mostly halite, during injection and storage. Despite the rather comprehensive research, there are some inconsistencies between the reported results, and lack of systematic investigations in some areas.$^{43}$ For instance, no published research
provides a systematic study on the effect of CO$_2$ phase states and thermodynamic conditions on salt precipitation. Moreover, present inconsistencies regarding the extent and significance of salt precipitates, and their influence on the CO$_2$ phase percolation pathways should be investigated. While some authors\textsuperscript{27, 44, 45} suggest that salt crystals precipitate only in the brine phase, and thus, have an insignificant impact on the flow pathways, several other literatures\textsuperscript{34, 46, 47} have shown that great amount of salt can also precipitate in the CO$_2$ phase. The latter studies contradict the former clogging model and propose that in the evaporation-precipitation process of salt formation we may expect considerable changes in the static and dynamic properties of the porous media.

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

In this study, we have developed a novel microfluidic high-pressure high-temperature (HPHT) vessel to house geomaterial (natural rock or mineral chips) micromodel specimens. Fracture patterns were laser-scribed on the organic-rich shales of the Draupne Formation, the primary caprock for the Smeaheia CO$_2$ storage site (Northern Lights) in Norway. The primary research objective was to examine the extent of salt precipitation in fracture networks of our shale micromodel under different thermodynamic conditions and for various CO$_2$ phase states. We have investigated whether precipitation of salt crystals can partially or entirely block
potential CO$_2$ leakage pathways in caprocks. Moreover, the impact of CO$_2$ injection flow rate on salt accumulations was studied.

**Conceptual framework**

In a full-scale geological CO$_2$ sequestration, millions of tons must be stored underground. The injection of dry or undersaturated scCO$_2$ with respect to water leads to dry-out of formation water and changes in the physical and chemical properties of the evaporation zone.$^{54-56}$ Figure 1 presents a schematic of a potential fracture healing mechanism and caprock sealing process due to salt precipitation. The water solubility in CO$_2$ (H$_2$O mol %) in Figure 1 is calculated based on the statistical associating fluid theory (SAFT).$^{56}$ SAFT is a semiempirical equation of state that can model thermodynamic properties and accurately handle multicomponent phase equilibria at low and high pressures for fluid mixtures.$^{57}$ The injected scCO$_2$ that is undersaturated with respect to water becomes saturated after percolating through a substantial volume of brine-saturated reservoir rock while the CO$_2$ plume migrates upward to reach the reservoir-caprock interface. A rapid pressure and temperature drop during CO$_2$ leakage may, however, cause adiabatic expansion and further cooling of leaking CO$_2$, and subsequently an increase in water solubility in CO$_2$ within the salt zone (Fig. 1). Because derivative of water solubility with respect to time will be positive within the proposed salt zone, the leaking CO$_2$ becomes undersaturated, and therefore, can progressively evaporate more brine as it migrates through fractures in the caprock.$^{56}$ Consequently, an evaporation front may form and a reduction in aperture and permeability of leaking channels is expected due to precipitation of salt crystals.

**Materials and Methods**

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

Figure 2b presents a schematic of the experimental setup. The microfluidic pressure vessel was placed and coupled with an AFS 200 core flooding system (Core Laboratories). The core flooding system is equipped with a forced convection benchtop oven (Despatch LBB series), which combines horizontal and vertical airflow, and provides temperature uniformity within the air bath. The fluid injection system comprises one dual-cylinder syringe pump (Teledyne Isco, 100DM), which controls brine and CO$_2$ flow rates. A back pressure regulator and a single-cylinder syringe pump (Teledyne Isco, 500D) control the fluid pressure inside the system. Two pressure transducers monitor fluid pressure at the inlet and outlet of the pressure vessel. Finally, three gas mass flow controllers (three different working ranges) detect CO$_2$ flow after the back pressure regulator. High-pressure steel tubing, fittings, and valves were used for plumbing inside the experimental system.

A Nikon SMZ stereo microscope (visible light) assisted in visualizing and digitally recording the microfluidic specimen within the pressure vessel (Fig. 2b). The imaging was performed at bright field condition through the vessel’s glass window. The Nikon SMZ is a Greenough-type stereo microscope that uses two separate optical paths and an angular offset to...
generate a three-dimensional image. The microscope’s trinocular head was equipped with a
digital camera, which provided a stream of high-resolution live images at 30 frames per second
through the ScopeView 3.0 software package. To analyze surface coverage of precipitated salt
crystals, the obtained experimental images were extracted from the recorded videos (1-hour
intervals) and processed following the published workflows.\textsuperscript{50, 58-60} The details are presented in
the Supporting Information.

Preparation of specimens

For the microfluidic HPHT experiments, we have developed a technique for fabrication of
specimens that can make use of a variety of natural and synthetic materials. In this study, we
used the Upper Jurassic organic-rich shales of the Draupne Formation. The shale samples were
acquired from well 16/8-3S in the Ling depression in the Norwegian North Sea. The Draupne
Formation comprises marine black shale, which is a rich source rock in the North Sea, and a seal
for the Middle Jurassic sandstone reservoirs in the area.\textsuperscript{61} More importantly, it is the primary
caprock for the Smeaheia\textsuperscript{62-64} CO\textsubscript{2} storage site (Northern Lights), the proposed full-scale CCS
project in Norway. The Draupne shale sample has a total porosity and matrix permeability in a
range of 20-30\% and nano- to pico-Darcy.\textsuperscript{65, 66} The MIP measurements showed a median pore
diameter of 27.5 nm and a critical pore throat diameter of 9 nm.\textsuperscript{65, 66} The BET-derived specific
surface area was 11 m\textsuperscript{2}/g.\textsuperscript{66} Given the pore space characteristics, matrix flow of injected CO\textsubscript{2}
requires extremely high capillary entry pressure and this was therefore considered unlikely for
the performed experiments. The use of shale core samples ensured that experimental substrate
represents realistic caprock properties.\textsuperscript{50, 67} In particular, it shows similar wettability and surface
free energy that influence nucleation and precipitation of salt crystals.

To prepare specimens, we cut the shale samples in less than 2.5 cm diameter sizes and
dried at 40\°C for three days. The specimens were fabricated using the cold mounting procedure.
In the cold mounting procedure, the dried samples were placed inside a cylindrical plastic mold with 2.5 cm and 1.5 cm diameter and height, respectively, where the epoxy resin was added to the mold to fill it completely (Fig. S1, Supporting Information). The friable or porous samples can be vacuumed before adding the epoxy, or the sample can be impregnated with epoxy under vacuum if it is necessary. The mold was then left overnight to harden. Subsequently, a series of automatic grinding and polishing steps were followed to provide a flat, unscratched surface for laser scribing of designed fracture patterns. For more details refer to the Supporting Information. The cold mounting procedure does not change properties of the shale material. The injected fluids (bine and CO\textsubscript{2} phases) were partly in contact with epoxy at the inlet and outlet. However, no interaction between the epoxy and injectant is expected, and the epoxy plays a role as a non-reactive material within the system.

**Laser scribing of fracture patterns**

To scribe the designed fracture pattern on the shale specimens, we used a Rofin scribing laser at the microsystems and nanotechnology laboratory (MiNaLab) at the University of Oslo (UiO). The fracture network was scribed using a 532 nm laser at 25A, 15000 Hz and 200 mm/s. The scribing was performed twice with an interval time of 5 minutes between each execution to keep the sample heating to a minimum. Moreover, a high scanning speed, high power, and low frequency were selected to maximize ablation, minimize heating of the sample, and limit the heat affected zone. The laser-scribed fracture network is 19 mm long and 14 mm wide pattern. Subsequently, the ablated debris and heat affected material were cleaned to reach the undisturbed matrix of the shale specimen inside the fracture network. To remove the ablated debris, we used micro-scratcher blades under an optical microscope. The scratching procedure and micro-scale cleaning did not change the geometry of scribed patterns, but only widened and deepened the
fracture branches (Figs. S2-3, Supporting Information). Surface profilometry was then performed to capture geometry and dimensions of the eventual fracture planes before the experiment.

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

**Experimental procedure**

An aqueous solution of 3.4 M (200 g/l) sodium chloride prepared by adding NaCl (ACS regent grade, EMSURE®) to deionized water (Milli-Q water) was used to saturate the shale micromodel before the experiments. The salinity of brine was selected to represent undersaturated high-salinity formation water. A comprehensive list of experimental and numerical studies with such range of salinity or even higher is summarized in Miri and Hellevang. A bottle provided CO$_2$ (grade 5.2, scientific carbon dioxide, Praxair Norge AS) for injection into the fracture network. The experiments were conducted at nine pressure-temperature conditions, combining temperatures of 22, 40 and 60°C, with three pressures (1, 5 and 8 MPa). As a result, the flow of CO$_2$ was investigated for gaseous, supercritical and liquid CO$_2$ states (Table 1, Supporting Information). The experiments were performed at a flow rate of 20 cm$^3$ CO$_2$/min. In addition, to investigate the impact of CO$_2$ injection flow rate on the distribution and extent of salt precipitation, we injected gaseous (1 MPa) and supercritical CO$_2$ (8 MPa) with three different flow rates (5, 10 and 20 cm$^3$ CO$_2$/min) at 60°C. Three flow rates were selected to provide a comparative measure and also to examine whether salt precipitation can be avoided. The
estimated linear average velocity of CO$_2$ 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 depending on thermodynamic condition and injection rate until the matrix of shale micromodel became completely dry. For the tests with elevated temperatures (40 and 60°C), we left the mounted microfluidic pressure vessel at least for 4 hours within the forced convection oven before starting the experiment. It ensured an equilibrated temperature within the experimental setup. The back pressure regulator controlled the pressure levels, and the fluid injection was performed in a constant flow rate mode.

Results and discussion

Configurations of precipitated salt crystals

Three flow mechanisms influenced saturation of brine within the microfluidic specimen. First, two-phase viscous displacement pushed the brine outside the fracture network. Subsequently, various forms of saturation patches, such as pools, domes and brine films on fracture surfaces, were formed due to capillary forces. Finally, an evaporation regime dried the residual brine saturation inside the fracture network and matrix of the shale micromodel. For the detailed description and graphical representation refer to the Supporting Information (Fig. S4). These flow mechanisms were dominant at different time scales and lasted differently. The water solubility in CO$_2$ phase (Fig. 1b) controlled the brine evaporation flux into the CO$_2$ stream and determined duration of the drying regime.$^{34}$ At all nine pressure-temperature conditions, covering the three CO$_2$ phase states, and for the three injection rates, we observed that salt crystals precipitate in two distinct forms: (a) large and semi-large (100-300 µm) single cubic crystals of halite in the aqueous phase; and (b) dense micrometer-sized (<20 µm) halite crystals on the interface of rock and CO$_2$ stream. Figures 3 and 4 illustrate the growth of a single halite crystal in
a brine dome, and precipitation of micrometer-sized salt aggregates on the fracture surfaces, respectively.

The single cubic crystals of halite mainly formed in brine domes very early in the evaporation regime. The large halite crystals precipitated only after brine domes had established and the domes could remain stable until the salt concentration in the trapped brine reached the solubility limit. As temperature increased from ambient condition (about 22°C) to 40 and 60°C, the brine domes occurred less often and as a result, single large cubic crystals precipitated infrequently. The first salt precipitation event at 22°C was the large and semi-large halite crystals. Moreover, the single salt crystals happened to form more frequently when CO\textsubscript{2} was injected in the gaseous phase. Video 1 (Supporting Information) communicates precipitation dynamics of a large halite crystal in the aqueous phase near the inlet. As Figure 3 and Video 1 show, a cubic salt crystal forms in the brine dome owing to locally increased solute concentration and sufficient time before brine dome thinning or diminishing starts (Fig. 3b-c). The movements and rotations of the cubic salt crystal inside the isolated brine dome suggest that the halite crystal began to grow inside the aqueous phase without any attachments to the surrounding fracture surfaces. While CO\textsubscript{2} stream was evaporating residual brine out of the specimen, the salt crystal continued to grow in all three dimensions (Fig. 3d-g). However, as the initial crystal that was immersed in brine became more prominent, it partly protruded into the surrounding CO\textsubscript{2} stream (Fig. 3h). As documented by Miri et al.\textsuperscript{34}, because of the hydrophilic nature of the salt crystals the protruding exteriors are covered with an aqueous film. The surrounding CO\textsubscript{2} stream could quickly evaporate the brine film, and the layer became supersaturated. It led to further formation of salt microcrystals and surface roughening of the single cubic halite crystal, which in turn contributed to more precipitation (Fig. 3i-k). The growth of the crystal came to an end when the brine dome vanished.
As evaporation continued and salt concentration in the remaining brine inside the fracture network reached the solubility limit, precipitation of micrometer-sized halite crystals started (Fig. 4a-b). Video 2 (Supporting Information) demonstrates how micrometer-sized salt crystals precipitated on the rock-CO$_2$ interface. While the experimental time was moving forward and the evaporation front progressed from the inlet toward the outlet, new spots in the fracture network experienced supersaturation, and eventually salt accumulation (Fig. 4). As Figure 4 and Video 2 illustrate, micrometer-sized halite crystals on the fracture surfaces grew very fast, separate patches became connected (Fig. 4c-d), and left behind massive salt bodies that could block fracture branches (Fig. 4e-f). Experimental observations suggest that coverage of these localized salt accumulations depends on the access to brine feeding sources, which could provide brine for further growth. Residual brine patches inside the fractures, brine films on the fracture surfaces, and potentially brine inside the microcracks of the shale can act as brine feeding sources. Although several authors, for instance Ott et al.,$^{27}$ proposed limited precipitation of salt crystals due to available solute in the trapped brine, results of the present study indicated that the localized salt accumulations are notably greater than the residual brine patches inside the fracture network alone.

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

Location and distribution of precipitated salt crystals
Experimental results also provided insight on where in the fracture network salt crystals precipitate and how separate accumulations distribute and develop. It can be of great significance for constructing clogging models for salt precipitation during CO\textsubscript{2} storage. While large single cubic crystals showed limited occurrences and coverage, and consequently insignificant impact on permeability, the growth of the micrometer-sized crystals could influence flow pathways within the fracture network. As Figure 4 and S5 (Supporting Information) illustrate, the micrometer-sized crystals mainly formed on the fracture walls and to a lesser extent at the bottom surface of the fractures. While the evaporation was progressing, the supersaturated clusters expanded, and localized salt accumulations precipitated. The salt bodies subsequently grew bigger because of further precipitations adjacent to the initial salt aggregates in addition to the evaporation of imbibed brine on the present halite crystals (Fig. S5). The recently precipitated aggregates, in turn, provided further surface area for evaporation, nucleation, and growth of the salt crystal. Until the brine feeding sources were available, the surface area for salt precipitation progressively expanded and consequently, the localized salt accumulations grew larger and larger. The subsequent salt crystals, hence, formed both on the fracture surfaces and on the previously precipitated salt accumulations. Because of the additional surface area for growth and availability of brine feeding sources, accumulations of micrometer-sized salt crystals could partially or entirely plug the fracture branches (Fig. 4 and S5).

Another observation was regarding the relative growth of two separate and neighboring salt bodies. As shown in Figure S5 (Supporting Information), the experimental observations demonstrated that, whether the two adjacent and detached salt bodies were sitting on the same or opposite fracture walls, they show an affinity for growth toward each other. It was noted that the growth speed is relatively more toward the adjacent salt accumulation compared to free fracture walls, which can be the result of a concentration gradient between the two salt bodies. When enough brine was accessible, the two salt accumulations could become connected. As a result,
the rate of growth and density of salt accumulations increased notably. The intensity of reflected light from the salt accumulations provided an indication of their density.

Effect of CO₂ phase state (pressure and temperature conditions)
The CO₂ phase state and thermodynamic conditions were observed to control physics of salt precipitation. As is shown in Figure 5, the CO₂ phase states influenced magnitude, distribution and precipitation pattern of localized salt accumulations. The percentage of salt surface coverage throughout the experiment for different thermodynamic conditions is demonstrated in Figure 6a. During injection of dense phases (liquid and scCO₂) more brine was flushed out of the fracture network and lower residual saturation established because of the higher imposed viscous forces. As a result, a lower amount of brine was available in the fracture network, and limited accumulation of salt crystals was observed. As presented in Figure 5 and 6a, within the pressure-temperature range of present study, the overall conclusion is that decrease in pressure results in a decrease of total salt coverage. However, the relationship is not one-to-one, and some retrograde trends were detected. Here, we discuss the experiments by P= pressure, T= temperature, and Q= flow rate. All the experiments in Figure 5 are performed at Q= 20 cm³ CO₂/min. For instance, coverage and distribution of salt aggregates in the P5T22 and P5T40 experiments were relatively similar (Fig. 5b and 5e), but P5T60 test indicates higher and denser precipitates compared to latter cases (Fig. 5h). While there is a clear difference between P1T40 and P1T60 salt bodies (Fig. 5d and 5g), the P8T40 and P8T60 were very similar in distribution and coverage (Fig. 5f and 5i). In descending order of eventual salt coverage, gaseous, liquid and supercritical CO₂ phases can be listed. At 20 cm³ CO₂/min flow rate (Fig. 6a), the average precipitation is 11%, 3% and 0.8% for gaseous, liquid and supercritical CO₂, respectively. Moreover, injection of liquid CO₂ (P8T22) resulted in bigger micrometer-sized crystals compared to other phases (Fig.
In Figure 6b, we plotted the maximum water flux into the CO\(_2\) stream versus the total salt coverage for each experiment. We have calculated the maximum water influx (H\(_2\)O mol %) by multiplying the injected CO\(_2\) volume by water solubility in CO\(_2\) at the pressure-temperature condition of a given experiment. As Figure 6b demonstrates, there is a relatively strong correlation (R\(^2\) \approx 0.87) between the maximum water influx and salt coverage. The higher the maximum water flux, the higher the salt coverage. The results for the dense phases (liquid and scCO\(_2\)) are located at the bottom left of the plot. Whereas the calculations for the tests with gaseous CO\(_2\) are extended to the top right, where higher water flux is calculated, and extensive salt accumulations are observed (Fig. 6b). While water solubility in gaseous CO\(_2\) (Fig. 1) can explain the extent of precipitated salts in Figure 5, the observed results for P1T60 experiment remain an unresolved question, and thus, the corresponding maximum water flux was not shown in Figure 6b. The P1T60 experiment for clarification was performed twice. However, the outcome and the salt accumulations were similar.

Several studies\(^{27, 38, 40}\) have attempted to introduce a critical velocity above which massive salt accumulation can be avoided. As reviewed by Miri and Hellevang \(^{43}\), previously published research have not considered the impact of thermodynamics and CO\(_2\) phase states on the critical velocity. Present results suggest that the extent of micrometer-sized precipitates is influenced by CO\(_2\) phase states and pressure-temperature conditions. Even at high injection flow rates (20 cm\(^3\) CO\(_2/\)min), precipitation of salt crystals was observed (up to 24% surface coverage for P1T40 test) (Fig. 6a). The results also indicate that the CO\(_2\) phase state affects the relationship between injection rate and extent of salt accumulations (Fig. 7). Figure 7 demonstrates a stronger impact of the rate on salt coverage during injection of scCO\(_2\) compared to gaseous CO\(_2\) as reducing the rate to 5 cm\(^3\) CO\(_2/\)min caused significant salt accumulation even for the dense phase of scCO\(_2\). The impact of flow rate was more significant for scCO\(_2\) because of the higher density and greater viscous pressure imposed during scCO\(_2\) injection. We propose
Effect of injection flow rate

As illustrated in Figure 7, the higher the injection flow rate, the lower the salt coverage. The precipitated salt crystals were significant at 5 cm$^3$ CO$_2$/min injection rate with 19% and 14% coverage for gaseous- and scCO$_2$, respectively (Fig. 7c and 7f). At 5 cm$^3$ CO$_2$/min injection rate, the salt accumulations notably affected CO$_2$ flow pathways inside the fracture network and blocked part of the fracture apertures in addition to major part of the inlet. Figure 6c presents coverage of the salt precipitates during the experiments. Decreasing injection flow rate caused evaporation regime to last for a more extended period. The experimental time as a consequence increased from approximately 12 hours to a maximum of 30 hours (Fig. 6c). However, once precipitation started, it progressed quickly for all three injection rates but lasted longer for lower rates (Fig. 6c). Reducing injection flow rate also caused the initial salt accumulations to precipitate closer to the inlet, and from there toward different branches of fracture network.

As Miri and Hellevang discussed, three drying regimes (diffusive, capillary and evaporative) affect the precipitation of salt crystals based on stabilized capillary and evaporative fluxes. When the injection flow rate was decreased, the drying mechanism transforms from pure evaporative to more capillary and diffusive. In other words, reduction of injection pressure gradient made it easier for the capillary pressure gradient to drive brine toward the inlet, support more evaporation and cause more salt precipitation. A high injection rate introduces a higher pressure gradient and suppresses the capillary backflow towards the inlet and evaporation front. The reduced capillary backflow, in turn, reduces the possibility of intensive salt accumulation. The observed results, thus, contradict the studies suggesting that an increase in
evaporation rate causes more salt precipitation than the increase in capillary backflow.\textsuperscript{41, 42}

Considering mechanisms that influence salt precipitation\textsuperscript{43}, massive accumulations form only when conditions for capillary backflow and salt capillary suction are favorable. The performed experiments in this study show that when capillary regimes overcome viscous forces, a considerable amount of salt crystals precipitated because of the access to brine feeding sources through a continuous water phase on fracture surfaces.\textsuperscript{34} Such brine feeding sources are residual patches, films, and even microcracks.

In the evaporation front, a major part of water mass exchange occurs when a constant flow of CO\textsubscript{2} stream with low water vapor pressure passes through the micromodel. It brings about a significant brine saturation gradient across the evaporation front and gives rise to a capillary pressure gradient that pushes brine toward the evaporation front. Miri et al.\textsuperscript{34} showed that because of the large capillarity of localized salt accumulations, they could imbibe brine over long distances. Imbibing brine out of the shale microcracks provides additional brine source for feeding the evaporation front. As capillary-driven backflow of the aqueous phase and salt capillary suction mechanisms continuously provide more brine, the brine will evaporate on the available surface area, and the salt accumulations will grow bigger. The bigger the salt body, the higher the imbibed brine, and the faster the growth rate. When viscous forces at higher injection rates resist the capillary forces and disturb the continuous supply of brine, the salt accumulations will not have the chance to grow substantially (Fig. 7a and 7d).

\textbf{Environmental implication for geological CO\textsubscript{2} storage}

Ensuring secure and safe subsurface CO\textsubscript{2} storage is among the critical considerations regarding CCS projects. Pre-existing and induced fractures in the caprocks may serve as leakage pathways within the CO\textsubscript{2} storage sites (Fig. 1).\textsuperscript{9, 72, 73} Fluid flow through fractured caprocks and bypass conduits, however, can be restrained or diminished by precipitation of minerals.\textsuperscript{74} Our
microfluidic experiments on the organic-rich shale of Draupne Formation demonstrated that precipitation of significant amount of micrometer-sized salt crystals is expected at field-scale flow rates (low CO\textsubscript{2} flow rates). At the interface of the reservoir and fractured caprock, leakage and upward flow of injected CO\textsubscript{2} may reduce brine saturation in the fractures and causes a local development of drying zones. While the drying zones progress, local salting-out spots form and various feeding sources provide uninterrupted access to brine through capillary forces. As shown, micrometer-sized salt crystals that precipitate on the interface of fracture walls and CO\textsubscript{2} stream have the potential to partly or entirely block fracture apertures and consequently leakage pathways. The development of salt crystals toward the point where leakage begins, the affinity of salt bodies to become connected, and extent of accumulations suggest that salt precipitation during leakage of CO\textsubscript{2} can be considered as a fracture healing mechanism. Because of the buoyant migration of CO\textsubscript{2} plume over time, we expect a low saturation of brine at the interface of reservoir-caprock. It considerably reduces the risk of re-dissolution of precipitated salts inside the leaking fractures with re-saturation of brine pore fluid.

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63. GASSNOVA Feasibility study for full-scale CCS in Norway; Oslo, Norway, 2016; p 63.


Caption of Figures

**Figure 1.** A conceptual framework for potential clogging of leakage pathways in the caprocks due to salt precipitation. Within the pressure-temperature conditions of the salt zone, water solubility in CO\(_2\) increases as pressure decreases. A rapid leakage, thus, may result in salt precipitation in the caprock even for CO\(_2\) that is initially saturated with respect to water. The water solubility in CO\(_2\) is calculated using the statistical associating fluid theory (SAFT).\(^5\)\(^6\) The schematic of geological CO\(_2\) storage was modified from DNV.\(^7\)\(^5\) The numbers show the correspondence in pressure-temperature conditions with the modeled water solubility in CO\(_2\) during a potential upward leakage.

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

**Figure 3.** The dynamics of growth for a large single cubic crystal of halite in the aqueous phase (brine dome). It also demonstrates how the crystal grows when it partly protrudes into the surrounding CO\(_2\) stream. The subfigures are time-lapse images of an experiment at pressure = 5 MPa, temperature = 22°C, and flow rate = 20 cm\(^3\) CO\(_2\)/min.

**Figure 4.** The dynamics of salt precipitation for micrometer-sized crystals of halite that form on the interface of rock and CO\(_2\) stream. The boxed region shows the zoomed area in Figure 3. The subfigures are time-lapse images of an experiment at pressure = 1 MPa, temperature = 22°C, and flow rate = 20 cm\(^3\) CO\(_2\)/min. The white-outlined surfaces describe the fracture walls, and the blue-outlined areas inside the fractures are precipitated salt crystals.

**Figure 5.** The influence of CO\(_2\) phase states and pressure-temperature conditions on the micrometer-sized salt accumulations. All the experiments were performed at a flow rate of 20 cm\(^3\) CO\(_2\)/min. The subfigures are recorded at the end of each experiment when the shale matrix became completely dry. The white-outlined surfaces describe the fracture walls, and the blue-outlined areas inside the fractures are precipitated salt crystals.

**Figure 6.** Analysis of salt surface coverage on the fracture network of shale specimen. (a) Effect of CO\(_2\) phase states and pressure-temperature conditions, where salt surface coverage is plotted against the experimental elapsed time. The experiments were performed at an injection rate of 20 cm\(^3\) CO\(_2\)/min. (b) Effect of CO\(_2\) phase states and pressure-temperature conditions, where maximum water flux during the test is plotted versus salt surface coverage; (c) Effect of CO\(_2\) flow rate, where salt surface coverage is plotted against the experimental elapsed time. The experiments were performed at a temperature of 60°C. The notations stand for P= pressure, T= temperature, Q= flow rate. A maximum 4% uncertainty for the salt precipitation data points can be considered.

**Figure 7.** The influence of CO\(_2\) injection flow rate on the micrometer-sized salt accumulations. It shows the results for (top) gaseous, 1 MPa, and (bottom) supercritical CO\(_2\), 8 MPa, at 60°C when CO\(_2\) was injected at three different flow rates (20, 10 and 5 cm\(^3\) CO\(_2\)/min).
The notations stand for P= pressure, T= temperature, Q= flow rate. The subfigures are recorded at the end of each experiment when the shale matrix became completely dry. The white-outlined surfaces describe the fracture walls, and the blue-outlined areas inside the fractures are precipitated salt crystals.
Supporting Information

Additional details including a description of shale sample fabrication, microfluidic specimen preparation and mounting it into the pressure vessel, experimental conditions, analysis of salt surface coverage, and flow mechanisms. Figures showing fabrication procedure of shale sample, SEM micrograph of fracture pattern, surface profilometry, effect of different flow mechanism, growth and distribution pattern of micrometer-sized salt crystals, and microstructure of micrometer-sized halite crystals. Videos communicating growth dynamics of a large single cubic crystal in the aqueous phase, and micrometer-sized crystals on the interface of rock and CO$_2$ stream.
dual-cylinder syringe pump
CO₂
hydraulic connection
H₂O
CO₂
Brine
H₂O
pressure transducer
gas mass flow controller
forced convection benchtop oven
accumulator
digital camera
Microfluidic pressure vessel
back pressure regulator
gas mass flow controller
low
medium
high
back pressure regulator
accumulator
H₂O
H₂O
Brine
CO₂
electrical connection
computer system
top cap
screw
protection layer
glass window
O-ring
sample holder
inlet-outlet
dual-cylinder syringe pump
bottom pedestal
pressure transducer
a. 0 min
b. 1 min
c. 105 min
d. 120 min
e. 200 min
f. 245 min
g. 310 min
h. 360 min
i. 365 min
j. 375 min
k. 395 min
l. 450 min

fracture walls
brine-saturated channels
shale matrix
inlet
brine dome
drying of shale matrix
thinning of brine dome
drying of brine dome
protruding into CO₂ stream
CO₂ stream
growth of salt crystal
tiny salt crystals covering a cubic crystal
surface roughening
Figure 3

- Inlet
- Outlet
- Fracture walls
- Shale matrix
- Micrometer-sized salt crystals
- Progress of evaporation front
- Capillary back-flow
- 4 mm scale

- Figure 3

- 330 min
- 390 min
- 425 min
- 465 min
- 525 min
- 720 min

- Growth and connection of salt accumulations

- Dried shale matrix

- Salt crystals
a. P1T22
b. P5T22
c. P8T22
d. P1T40
e. P5T40
f. P8T40
g. P1T60
h. P5T60
i. P8T60

fracture walls
dried shale matrix

salt crystals

Gas

Liquid

Gas

Sc

Gas

Sc
Gas

dried shale matrix

fracture walls

CO$_2$ stream

Outlet

Inlet

4 mm

Sc

Salt crystals

P1T60, Q20

P1T60, Q10

P1T60, Q5

P8T60, Q20

P8T60, Q10

P8T60, Q5