Geophysical early warning of salt precipitation during geological carbon sequestration

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Sequestration of industrial carbon dioxide (CO2) in deep geological saline aquifers is needed to mitigate global greenhouse gas emissions; monitoring the mechanical integrity of reservoir formations is essential for effective and safe operations. Clogging of fluid transport pathways in rocks from CO2-induced salt precipitation reduces injectivity and potentially compromises the reservoir storage integrity through pore fluid pressure build-up. Here, we show that early warning of salt precipitation can be achieved through geophysical remote sensing. From elastic P- and S-wave velocity and electrical resistivity monitoring during controlled laboratory CO2 injection experiments into brine-saturated quartz-sandstone of high porosity (29%) and permeability (1660 mD), and X-ray CT imaging of pore-scale salt precipitation, we were able to observe, for the first time, how CO2-induced salt precipitation leads to detectable geophysical signatures. We inferred salt-induced rock changes from (i) strain changes, (ii) a permanent ~ 1.5% decrease in wave velocities, linking the geophysical signatures to salt volume fraction through geophysical models, and (iii) increases of porosity (by ~ 6%) and permeability (~ 7%). Despite over 10% salt saturation, no clogging effects were observed, which suggests salt precipitation could extend to large sub-surface regions without loss of CO2 injectivity into high porosity and permeability saline sandstone aquifers.

Deep siliciclastic saline aquifers are among the preferred options for geological CO2 sequestration (GCS), because of their low reactivity to CO2 and high storage capacities1. The storage efficiency is determined by the porosity (reservoir capacity), while the effectivity of the injection is controlled by the permeability (connectivity of the effective pore volume). Any changes in the storage capacity and/or injection efficiency during GCS activities may compromise the integrity of the reservoir2,3, and hence needs further study for long-term and safe sequestration of CO2.

The CO2 injected in a reservoir advances as a plume by displacing a fraction of the resident brine4,5. The injected CO2 partially dissolves in the parent brine while inducing evaporation of water. These two mechanisms, together with capillary pressure gradients towards the injection source, molecular diffusion of saline ions within the brine, CO2 gravity (buoyancy) and self-enhancing salt crystallization phenomena, can trigger complex salt precipitation patterns in porous media6. CO2-induced salt precipitation can lead to a significant decrease of up to 15% in porosity, and up to 85% in permeability7. Eventually, this phenomenon can dramatically impact the injection efficiency, as observed off-shore in the Tubåen Formation at the Snøhvit Field8.

Several studies have addressed the mechanisms and location of salt precipitates in saline aquifers during CO2 storage, and the negative consequences for the injectivity9–14. Numerical simulations predict significant salt-induced pressure build-up around the CO2 injection well, the preferential salt precipitation area15–17, even for high permeability rocks and low injection rates18,19. Experimental studies have confirmed CO2—induced salt precipitation in porous media from lab-on-chip experiments6,20 and core scale flow-through tests21–23. Experimental observations show that the precipitation process starts after a transition period post—CO2 injection, forming early pore scale crystals in the brine, followed by late polycrystalline aggregates at the CO2—brine interface7. The velocity and extent of the process depend on CO2 injection flow rate18, brine mobility14, pore network geometry19,
and the physical properties of both fluids defined by the temperature, pressure and composition, particularly brine salinity.

Simple engineering mitigation strategies can be applied in the reservoir to prevent the salt precipitation during CO2 injection activities in the field. For instance, fresh water-washing—a technique originally used in gas-producing wells to avoid salt clogging that has been proposed for GCS prior to CO2 injection. Early detection of salt precipitation is crucial for timely mitigation strategies and ultimately for preserving reservoir integrity. However, this requirement contrasts with the lack of experimental and modelling studies aimed at the identification of CO2-induced salt precipitation from field-scale monitoring datasets, especially geophysical remote sensing.

We conduct CO2 flow-through tests, using a high porosity–permeability non-reactive sandstone to isolate the CO2-induced salt precipitation phenomenon. Here we integrate elastic and electrical resistivity measurements, X-ray micro-CT imaging, and rock physics modelling, to assess the potential of combined seismic and electromagnetic surveys for early detection of CO2-induced salt precipitation.

Core flood experiments. This study involves two CO2 injection experiments (denoted as CSMe and NOCe) on a high porosity (~29%), high permeability (~1660 mD) synthetic quartz-rich sandstone, saturated with high salinity (XNaCl = 25% wt. NaCl) synthetic brine. The experiments were conducted using two experimental setups for high pressure multi-phase flow-through tests (CSMe and NOCe rigs, Fig. 1), under constant hydrostatic confining pressure (Pc = σ1 = σ2 = σ3 = 25 MPa), pore pressure (Pp = 5.5 MPa), and room temperature (~20 °C).

CSMe aimed at analysing the distribution of CO2, brine, and CO2-induced precipitation of salt crystals in the rock using micro-X-ray computed tomography (XCT) scans. In the first step, 17 pore volumes (PV) of brine were injected through the rock at a flow rate of ~0.2 cm3 min⁻¹, followed by a XCT (lasting ~24 h). Next, CO2 gas

Figure 1. CSMe and NOCe experimental rigs.
(CO₂) was injected into the sample at ~0.2 cm³ min⁻¹ continuously for 24 h (~200 PV), followed by a second XCT scan (~24 h). From the XCT, we developed a four-phase segmentation analysis to obtain the CO₂, brine, quartz grain and salt volumetric fractions. Then, the sample was dried, cut and prepared into thin sections to compare with the original sample to assess the total salt content in the porous medium. Finally, the sample was subjected to X-ray diffraction (XRD) and scanning electron microscopy with energy dispersive spectroscopy (SEM–EDS) analysis to assess the precipitation of secondary minerals resulting from the CSMe test (see Supplementary Information). For the thin section analysis, we developed a three-phase (pore space, quartz grain and salt) segmentation analysis.

In the NOCe, we measured geophysical (ultrasonic compressional and shear, P and S, wave velocities and electrical resistivity) and hydro-mechanical (axial strains) properties, under three flooding conditions: (i) initial 25% NaCl brine flow-through the brine saturated sample (~10 PV); (ii) CO₂(g) injection flow displacing the brine from the saturated sample (drainage episode; ~75 PV); and (iii) 25% NaCl brine flow through the partially CO₂ saturated sample (imbibition episode; ~30 PV). During the test, we alternated between two flow (Q) regimes: active measuring periods when Q was above 0, and interludes (Q = 0) without data collection. The test was repeated twice, named hereafter as NOCe Test-1 and Test-2, respectively.

Results and discussion

Salt saturation estimate (CSMe). XCT image analysis (Fig. 2) shows that CO₂ and brine occupied 42% and 50% of the total pore volume, respectively, after CO₂ injection (i.e., second scan), yielding a salt saturation (SNaCl) of ~8% (Table 1). During the scanning the vessel was sealed, limiting the brine salinity to the dissolved ions within the pore water. Considering that the XCT scan lasted ~24 h, SNaCl likely increased during scanning and therefore 8% represents a lower bound of SNaCl in the CO₂-brine-rock system after two days of CO₂ exposure (i.e., one day of CO₂ injection and one for the scan).

Theoretically, using mass balance considerations, in our closed system, one single halite crystal of density ρH₂O = 2100 kg m⁻³ formed from the brine (ρNaCl = 1190 kg m⁻³ and salinity XNaCl = 25% wt) occupying the available pore space post-test (i.e., 1 – S CO₂) would fill 8.2% of the total pore volume (i.e., SNaCl/theoretical) (1 - S CO₂) X NaCl/ρ NaCl/ρ NaCl. However, thin section analysis (Fig. 3) reveals the subsequent drying process led to a final SNaCl/observed ~19% ±2% derived from 2D-thin section to 3D transformation29,30. This analysis indicates that the salt precipitates around the rock grains mainly as an agglomerate of halite microcrystals, as previously observed. This finding is corroborated by SEM–EDS analysis (Fig. 4) and XRD post-testing, which also shows NaCl crystals sometimes coexisting with nacolite (NaHCO₃) as subsidary (further information in Supplementary Information). For practical reasons, we adopt the physical properties of the major component observed (i.e., halite) for the whole salt fraction and estimate a salt-aggregate micro-porosity of ~56.7% ±2%, resulting from the ratio between theoretical and thin-section estimated SNaCl post-test (f NaCl/observed; f NaCl/observed) = 1 - S NaCl/theoretical/S NaCl/observed. This micro-porosity fraction is below the image resolution for both the XCT and thin section processing. Accounting for this micro-porosity, the SNaCl determined from XCT scan drops to 3.5%, indicating the salt precipitation was still in an early stage after two days exposed to CO₂.

Geophysical data analysis (NOCe). The NOCe CO₂(g) injection test lasted approximately five days (~115 h) and it was repeated twice, with an effective flow-through time of ~40 h that led to ~110 pore volumes (PV) throughput each (Fig. 5). Both tests show similar trends for all the measured properties except for the strains. Around 2% hysteresis effect of P- and S-wave velocities (Vp and Vs) suggests a change in the physical properties of the sample during the experiment. On the other hand, the transport properties of the sample remained undiminished (under the experimental conditions), as indicated by an almost constant pore pressure gradient (ΔPp) throughout the NOCe for each pore fluid (i.e., brine flow in E1brine and E5; CO₂ from E1CO₂ to E4) within the range of flow rates 0–2 cm³ min⁻¹.

The CO₂ arrival (episode E1- CO₂ after 9 PV of brine flow; Fig. 5), led to a resistivity increase of ~50%. Electrical resistivity tomography (ERT) images (Fig. 6) show preferential pathways localized peripherally by the inlet–outlet ports on the axial platens (diagonally opposite one other); the invariant differential pore pressure (ΔPp) throughout the NOCe for each pore fluid (i.e., brine flow in E1-brine and E5; CO₂ from E1-CO₂ to E4) within the range of flow rates 0–2 cm³ min⁻¹.

After the initial gas-pushing water piston fluid substitution effect30, each interlude leads to a redistribution of the two-phase fluids due to capillary effects that enhances salt precipitation31,32. During the interlude E1-E2, in the absence of effective pressure variations, the axial strain (εx) increased (more significantly during the first test; Fig. 5). Since our quartz-rich sandstone is barely reactive to CO₂, we interpret sample dilation as being caused by local salt-induced volumetric increase effects, previously observed in CO₂-brine tests in sandstones under hydrostatic confining conditions33 and in air-brine systems under uniaxial loading34. In this regard, it has been recently demonstrated35 that salt crystals may exert pressures against pore walls up to ten times higher than the confining pressure used here (up to 150 MPa at the 50 μm observation microscope). Sample dilation continued during episode E2 accompanied by a weak decrease in both Vp and Vs by ~2%, and a resistivity increase by ~25%, in agreement with previously reported data26,36,37. Overall, E1 and E2 have similar pore fluid distributions (Fig. 6), and small geophysical variations, which can be explained by minor mechanical-chemical changes in the outer part of the sample.

The most significant changes in the elastic properties of the rock sample occur after the second interlude (from E2 to E3; Fig. 5), with Vp and Vs increasing by ~3% and Vp ~0.5%, respectively, in both tests. These changes
contrast with the positive deformation of the sample (i.e., inflation) and the theoretical lowering of $V_p$ for an increasing $CO_2$ content\textsuperscript{5,36}. However, our results agree with the scarce data reported about changes of elastic wave properties associated with salt precipitation in high porosity sandstone\textsuperscript{8,38}. During E3 and E4, resistivity, strains,

**Figure 2.** Salt precipitation evidence from the sandstone used in the CSMe. Examples of XCT scans before and after $CO_2$ injection in 2D (a, b), and 3D (a 2.5 mm$^3$ volume portion) post-$CO_2$ injection (c 1–3), including segmentation (a.1, b.1, c.1–c.2).
and V_s progressively increase while V_p decreases with CO2 injection. Despite a few sharp variations seen for all the parameters during the interlude E3–E4, E3 and E4 show similar trends that agree with those previously observed during CO2-brine drainage tests in sandstone31,34,36,37,39. During the last episode (E5, forced imbibition), the original brine flows through the sample, partially saturated in CO2. All the measured parameters recover to their original values except axial strains in barely five PV (Figs. 5, 6), a rapid recovery previously observed in CO2-brine-quartz systems under imbibition31,35. Resistivity totally recovered its original values. VP and VS carry ~1% of negative hysteresis at the end of the first test, and up to 1.5% after the second, with a minimum decrease from the end of Test-1 to start of Test-2. After the NOCe Test-2, the sample showed an increase of the original porosity, by ~6%, and permeability, by 7%.

Saturation uncertainties. In a natural reservoir, a constant brine salinity scenario should be expected provided that salt clogging does not occur; in our test, the brine salinity progressively decreases as salt saturation increases. Since we calculate pore fluid saturations from the measured electrical resistivity and Archie’s laws31,35, we must first consider any changes in brine salinity caused by the CO2 drying process. The observed changes in bulk resistivity are mainly related to (i) a fluid substitution effect (i.e., high resistive CO2 displacing the original brine in the porous medium), and (ii) a progressive decrease of the original brine salinity with CO2 (i.e., ions-depleted residual brine due to salt precipitation). Each of these two factors reduces resistivity and affects the transformation of electrical resistivity into saturation differently.

| CT-Run (CSMe) | Volume fractions (%) | Saturation |
|---------------|----------------------|------------|
|               | CO2 | Brine | Quartz | NaCl^ | S_{NaCl} | S_{CO2} | S_{brine} |
| Before CO2    | 0   | 29.7  | 69.6   | 0.7   |          |         |          |
| After CO2     | 12.7| 15.1  | 69.0   | 3.2   | 0.08     | 0.42    | 0.50     |

| Thin sections | Area fractions (%) |
|---------------|--------------------|
|               | Pores | Grains | NaCl^ | S_{NaCl} |
| Original sample | 27.5 ± 0.5 | 71.4 ± 0.5 | 2.1 ± 0.2 | 0.0 |
| Fully dried after CSMe | 22.5 ± 1.0 | 67.5 ± 1.0 | 10 ± 0.2 | ~0.19 |

Table 1. XCT scan and thin section processed results. *General volume fraction error of 1% and saturation uncertainty of ± 0.01. ^NaCl phase contains NaCl plus others isotropic minerals.

Figure 3. Salt precipitation evidence from thin sections of (a) the original sandstone used in the CSMe and (b) after full drying post-testing, including segmentation (a.1, b.1).
Pore fluids saturation in a CO₂-brine system can be calculated from electrical resistivity, combining the first, $\Phi^{-m} = \frac{R_{b,0}}{R_w}$, and second, $S_n = \frac{R_w}{R_{b,i}} \Phi^{-m}$, Archie's laws for fully and partially saturated porous media, respectively. In these expressions, $R_b$ is the bulk resistivity of the sample with subscripts 0 and i indicating full and partial saturation, $R_w$ is the resistivity of the pore fluid, $\Phi$ the porosity, $S_n$ the brine saturation, and $m$ and $n$ are the cementation and saturation exponents, empirically derived for each particular rock.

The dissolved CO₂ (less than 5% vol. at the experimental conditions), is invisible to our resistivity and ultrasonic detection tools, and therefore neglected in the saturation calculations based on Archie's expressions above. This simple transformation is valid for invariable porous framework systems, i.e., in the absence of dissolution/precipitation phenomena. However, the XCT scanning showed a minimum $S_{NaCl}$ (aggregate microcrystalline) of 8% for our experiments. CO₂-induced salt growth progressively changes the bulk electrical properties of the rock, by changing both the porosity and brine resistivity. Therefore, to calculate $S_n$, the combination of the first and second Archie's laws has to be modified to account for each state of the rock with respect to the original values (subscripts i and 0, respectively), as follows:

In Eq. (1), we consider constant cementation ($m$) and saturation ($n$) exponents, because the salt aggregates observed in our CSMe test are suspended at the CO₂-brine interface (Fig. 2). However, the cementation exponent is likely to increase in more advanced drying stages. Note that the change in water resistivity between stages is explicitly considered in Eq. (1), but the change in porosity due to salt precipitation is not. The micro-metre salt crystals are surrounded by highly conductive water films feeding the crystallization process.

At laboratory conditions (20 °C), if we consider a closed system where all the original brine contributed its ions to halite formation, the $R_w$ would have increased according to the expression $R_w = \left( \frac{4 \times 10^5}{S \times T} \right)^{0.88}$, with $S$ being the brine salinity (in ppm) and $T$ the temperature (in Fahrenheit). However, some backflow of brine towards the injection point, particularly during interludes, might have partially contributed to salinity recovery. We consider the transition between a backflow completely renewing the resident brine (i.e., constant salinity), to no backflow leading to a progressively NaCl-depleted brine (Fig. 7). In our test, the degree of brine saturation estimated from bulk resistivity data should lie between both cases.

Combining elastic and electrical properties. Salt can form either away from the mineral grains (non-cementing salt), or at grain contacts bridging mineral grains (cementing salt). Image analysis suggests a transition from non-cementing salt at early stages of salt formation (XCT images; Fig. 2) to cementing salt after fully drying (thin sections; Fig. 3). Early detection of this transition in the field using geophysical monitoring techniques is essential to initiate mitigation strategies in a timely manner, before both injectivity and ultimately the mechanical integrity of the reservoir are compromised (as suggested by the mechanical hysteresis observed in our data).

The bulk elastic properties of rocks are sensitive to the rock frame and pore fluid elastic properties, and to the distribution of fluids in the porous medium for multiple fluids (e.g., uniform/patchy). Hence, to infer such a transition in the salt distribution from our geophysical data, we can use the so called uncemented and cemented sand models, and introduce them into Biot-Stoll poroelastic formulation to calculate frequency-dependent P and S wave velocity and attenuation. This approach has been applied previously to understand and assess quantitatively the impact of marine methane hydrate on these properties. Due to the similarities in the distribution of hydrate and salt in the pores, we adopt these models using the physical properties (bulk and shear moduli, and density) of halite.

Figure 4. Scanning electron microscope (SEM) images showing salt crystals (NaCl) coating the original sample grains, in three zoom-in scales (from a to c), after full drying post-testing, corroborated by Energy Dispersive Spectroscopy (EDS) analysis (Supplementary Information).
Using these model predictions, we can explain the observed evolution of the CO$_2$-brine-salt-sandstone system from changes in the compressional and shear wave velocities with brine saturation, with both the NOCe Test-1 and Test-2 showing very similar results (Fig. 8). We assume that non-cementing salt only modifies the bulk modulus of the fluid. In contrast, cementing salt modifies both the shear and bulk moduli of the dry granular frame. Hence, $V_S$ can be significantly affected by cementing salt but not by non-cementing salt (only minor changes can occur due to changes in bulk density of the rock).

Figure 5. Results of two consecutive brine-CO$_2$ flow-through tests (Test-1, black solid line and solid dots; Test-2, grey solid line and open triangles) in synthetic sandstone during the NOCe. Up- and downstream differential pore pressure ($\Delta P_p$) and total outlet flow ($Q$), P- and S-wave velocities ($V_p$, $V_s$), bulk electrical resistivity ($R_b$), and axial strains ($\varepsilon_a$ in %) are plotted versus pore volume (PV) and experimental time for three flooding episodes (E): brine flow (E1$_{brine}$, below 9 PV), CO$_2$ replacing brine (E1$_{CO2}$ to E4; drainage), and brine replacing CO$_2$ (E5; imbibition). Geophysical properties and strains are presented normalized with respect to initial values of Test-1. Solid vertical lines indicate interludes between episodes (i.e., Q = 0).
For P-waves, the change in $V_p$ from $E_1_{\text{brine}}$ (brine flow) to $E_1_{\text{CO}_2}$ (CO$_2$ flow) can be explained by the presence of up to ~4% of solid non-cementing micro-crystalline NaCl into the pore space during Test-1 (~2% for Test-2), partially reabsorbed during the interlude $E_1$-$E_2$ (Fig. 8a). The most significant change in $V_p$ occurs from $E_2$ to $E_3$. During this interlude, the drying through evaporation is likely to be enhanced by capillary and diffusive mechanisms, leading to a higher crystallization rate$^{7,26}$. The model indicates a sharp $S_{\text{NaCl}}$ increase from $E_2$ ($S_{\text{NaCl}}$ ~ 1%) to $E_3$ ($S_{\text{NaCl}}$ ~ 13% in Test-1 and ~14% in Test-2). The brine remaining in the pore space is then NaCl-depleted and salt crystallization stabilizes, leading to a (CO$_2$—brine) fluid substitution stage with some salt reabsorption phenomena at the end of the episode $E_4$.

For S-waves, $V_s$ reflects an early rock weakening effect during the transition from brine to CO$_2$ injection ($V_s$ drops from $E_1_{\text{brine}}$ to $E_1_{\text{CO}_2}$), likely associated with poorly attached silica cement or grains, removed during early stages of the CO$_2$ flooding due to sudden changes in the bulk properties (i.e., early salt nucleation) of the pore fluid (Fig. 8b). This early weakening effect is observed in both NOCe tests, but more significantly in Test-1. To isolate the CO$_2$-induced salt precipitation effect after this early weakening, we project the modelling results to fit the data after $E_1_{\text{CO}_2}$ (grey bands and grey lines in Fig. 8b) by considering the final $V_s$ value of each test as $V_s$. From $E_1_{\text{CO}_2}$ to $E_3$, the $V_s$ data scatter (within the ultrasonic measurements error band) over the whole range of results for the non-cementing salt modelling (i.e., $S_{\text{NaCl}}$ from 0 to 14%). The clear increase in $V_s$ from $E_3$ to $E_4$

**Figure 6.** 2D electrical resistivity tomography acquired during the NOCe Test-1 (star points in Fig. 5). The images are vertical planes crossing the centre of the sample, containing the inlet (IL) and outlet (OL) pore fluid ports as marked by solid triangles.
can be explained by considering a transition (red arrows in Fig. 8) from only non-cementing salt in E3, to non-cementing salt with a small fraction (0.1%) of cementing salt in E4 (red curve in Fig. 8); grey solid curve for the projection in Fig. 8b). Finally, brine is injected into the sample, and rapidly replaces (and dissolves) the salt-rich CO2-brine mixture in the pore space.

For a precise quantification of the evolution of the three pore phases, we would need to account for the progressive ions depletion of the original brine, which could be significant, as shown in Fig. 7; this would require monitoring of pore water conductivity during the CO2 flooding, which is missing in this experiment. Instead, we have added one single horizontal error bar to reflect the uncertainty associated with the increasing pore water resistivity for each episode (E1–E5).

The transition from non-cementing to cementing salt (E4) occurs after a substantial SNaCl increase from E2 to E3 of (from ~2 to ~12% in Test-1 and up to ~14% in Test-2) well-defined by ~3% increase in VP (Fig. 8a). This rapid SNaCl increase occurs in the absence of CO2 flow (interlude E2–E3). By contrast, during flowing episodes, changes in rock properties are better explained by fluid substitution mechanisms as data points within each episode evolve towards higher CO2 saturations.

Figure 7. Bulk resistivity versus degree of brine saturation considering an initial brine salinity (S) of 25 × 10^4 ppm, a constant temperature of ~20 °C, and the ions-depleting effect associated with the precipitation of salt (SNaCl salinity) in a closed system.

Insights of salt distribution in geological reservoirs. From the constant response of our pore pressure sensors for different flow rate conditions all through the NOCe tests, we conclude that any clogging effects due to salt induced porosity reduction were insignificant. The distribution of gas-induced salt precipitation in a porous medium can be described through the Peclet (Pe = LV/D), and Damköhler (Da = Lkr / V for Pe > 1) numbers (reference length, L; effective flow velocity, V; diffusion coefficient of salt in water, D; kinetic rate constant, kr). Pe determines the importance of advective (Pe > 1) and diffusive (Pe < 1) transport, while Da describes to which extent the dissolution/precipitation processes are dominated by fluid velocity or mineral reactivity. For Pe > 1, salt precipitation would occur close to the injection zone, whereas Pe < 1 would lead to a homogeneous distribution; the crystallization process is controlled by diffusion when Da > 1. In our closed system, the calculation of Da is not straightforward, as it varies with the ions concentration decay in original brine with the increasing SNaCl. In the NOCe, the Pe changes from the order of 10^4 (advective regime) during flowing episodes (i.e., V > 0), to null during interludes (i.e., V = 0), and the system is completely controlled by the diffusion (i.e., Da tends to infinity). Since this change in Pe is expected to enhance the homogenization of salt precipitation, it explains the SCO2 and SNaCl backwards transition from E1CO2 to E2 during Test-1 (Fig. 8a).

Overall, upon detection of CO2-induced salt precipitation in a reservoir formation through seismic and electromagnetic geophysical surveys, reducing or stopping the CO2 injection is advisable for high porosity and permeability reservoirs and low brine salinity (e.g., Sleipner CCS field). However, stopping or reducing the CO2 injection (i.e., minimum Pe; maximum Da), might have undesirable effects for reservoirs with lower porosity and permeability and higher brine salinity. In these latter reservoirs, the higher capillarity of the rock could lead to self-enhancing salt growth phenomena, rather than salt reabsorption and homogenization, which would extend the salt precipitation to large sub-surface regions. In turn, this would reduce the effectiveness of common clogging mitigation techniques, such as fresh water flooding, mainly focused on the surroundings of the injection well.
Furthermore, salt would be prone to fill (micro-) pores and start cementing the rock, thus modifying rock mechanical properties. During the GCS post-injection stage, natural aquifer recharge might lead to re-dissolution of salt crystals, this time with permanent changes in rock mechanical properties, as suggested by the hysteresis shown by the axial strain (only ~5% recovery) during the NOCe, together with the VP and VS drop and the increase of the original porosity and permeability, during NOCe Test-1 and Test-2.

Conclusions
During a set of CO2 flow-through experiments using a synthetic sandstone of well-known petrophysical properties, we have found evidence of CO2-induced salt precipitation from X-ray micro-CT imaging and of detectable geophysical signatures (elastic waves and electrical resistivity) associated to this phenomenon. Our results show for the first time how elastic wave velocities, when combined with electrical resistivity measurements, can be used to detect early stage salt precipitation during CO2 injection into reservoir sandstones. Based on our experimental results, we conclude:

1. The precipitation of salt induced by CO2 injection into brine saturated sandstones significantly affects measurable geophysical properties of the original rock formation, i.e., compressional and shear wave velocity, and electrical resistivity. During early stage injection, salt precipitates away from grain contacts (non-cementing),
then starts to cement the rock grains after a certain threshold salt saturation is achieved (10% in our experiment).

2. The precipitation of salt triggers detectable changes in compressional wave velocity (up to 3%) that can be differentiated from pore fluid substitution effects with the aid of electrical resistivity, based on the latter’s sensitivity to electrically insulating gas phases like CO₂. While compressional wave velocity is sensitive to both non-cementing and cementing salt precipitation, shear waves velocity is predominantly sensitive to the fraction of cementing salt.

3. During CO₂-induced salt precipitation, pore fluid salinity changes have to be considered to successfully estimate the evolution of CO₂, brine and salt saturations from electrical resistivity.

4. CO₂-induced salt precipitation may lead to dilation of the rock frame, even in high porosity and permeability sandstones that are barely reactive to CO₂. Hence, early detection of salt precipitation is crucial to preserve reservoir injectivity properties and mechanical integrity.

Materials and methods

Rock samples and pore fluid. We created a homogeneous synthetic sandstone of high (effective) porosity (φ = 0.29; He-pycnometry), and high absolute permeability kₐ₃ = 1660 mD (N₂-permeameter), to avoid salt-induced clogging during CO₂ injection. Following the manufacturing procedure described in Falcon-Suarez, et al., we used sorted, coarse grained (diameter > 500 μm) sand and low cement-to-grain ratio to ensure high porosity and permeability (with a final dry density \( \rho_d \approx 1826 \text{ kg/m}^3 \)) and to avoid clay conductivity and clogging effects. The composition of the sample was ~97% quartz, ~3% albite (X-ray diffraction, XRD, analysis with a Philips X’Pert pro XRD-Cu X-ray tube), which ensures the applicability of the original Archie’s laws without applying corrections related to the presence of clay minerals in the rock. From the original sample, we extracted two core plugs of (sample A) 2 cm length, 1.2 cm diameter, and (sample B) 2 cm length, 5 cm diameter, for the CSMe test and for the NOCe tests, respectively.

We used a 25% NaCl synthetic brine solution prepared with deionized water in both tests, keeping NaCl concentration slightly below the saturation point to promote rapid crystallization during CO₂-induced evaporation. To ensure the saturation condition, the samples were first oven-dried, then saturated with the experimental brine via imbibition under vacuum conditions, and finally flushed at 5 MPa with the experimental brine solution to enhance the dissolution of remaining air in the system. At the pore pressure used in this test, the salinity of the brine has negligible effect on the mutual solubility of CO₂ and brine.

CSMe setup and test configuration. The brine saturated sample A contained in an in-house developed Aluminium pressure vessel was pressure equilibrated for one night at the target \( P_c \) (25 MPa) and \( P_p \) (5 MPa) conditions, and left for one night for stress-strain equilibrium. Then, the test started with a brine flow episode at 0.2 cm³ min⁻¹, up to completing 17 PV of brine flow-through. Immediately after, the first XCT-scanning was carried out lasting ~ 24 h. Next, CO₂ was injected in the sample at variable flow rate (0.1—0.2 cm³ min⁻¹) con- tinuously during 24 h (Peclét’s number \( Pe\sim 60 \), reaching ~ 200 PV of collected pore fluid volume downstream. Immediately after, the second XCT-scanning was conducted.

The pressure vessel setup consisted of an aluminium tube sealed with commercial high-pressure fittings, and three flow-through lines for confining, and inlet and outlet pore pressure. The sample A was jacketed and plugged with in-house manufactured endcaps, allowing pore fluid flow-through while isolating the sample from the confining hydraulic oil. Pressure vessel connecting lines were flexible to ensure free twisting of the vessel within the XCT instrument during XCT image acquisition. We performed the measurements using a Xradia Micro XCT-400. Tomographic images were collected in increments of 0.1 degrees of rotation with a background reference image generated from 10 averaged individual scans preceding installation of the pressure vessel. The reference image was subtracted from the measurement images to give adjusted values for the sample and vessel without background effects. Optimal tomography angles were calculated using specialist software XM-Controller 8.1.7546 (XRadia Inc.; https://www.xeiss.com/microscopy/int/products/x-ray-microscopy ), and measurements were obtained with 0.5 × and 4 × lens yielding resolutions of approximately 25 and 3 microns, respectively. For this study, we only used the latter (high resolution image set). Tomographic images were generated following beam hardening and centre shift corrections to ensure optimal image quality in the reconstructed images, using Avizo software version 9.5.0 (https://www.wei.com/software/avizo-user-guide ). The XCT-images were segmented using a 3D weka semi-automated segmentation to characterize the four phases of interest: CO₂, brine, quartz and the rest, which included ore minerals and salt (Fig. 2). First, we selected a sub-sample (~1.5 mm³) and obtained the four phases; second, we extrapolated the results to the whole sample, following the procedure described in Callow, et al.

After the test, the sample was left to dry under atmospheric conditions. Then, thin sections were obtained from both the original and the tested samples, to assess the total salt content in the porous medium. The images were analysed using Fiji-ImageJ software version 2.0.0-rc-68/1.52 g (https://fiji.sc) to measure the total salt in the sample. The blue-resin method used to make the thin sections allowed the segmentation of the obtained in plane-polarized light images into four domains: pores (blue), grains (light grey), cement (brownish), and salt (black regions: isotropic salt crystals and ore minerals). The processing consisted of a threshold filtering to define the pores (ϕ) and salt (S) fractional areas, and then transform it to grey scale to calculate the salt saturation as \( S_{NaCl} = S / (\phi + S) \).

NOCe setup and test configuration. The rig is configured around a triaxial cell core holder under accurate control (ISCO pumps) of confining and pore pressure. The rubber sleeve inside the vessel has 16 stainless steel electrodes connected to an electrical resistivity tomography data acquisition system. Using a tetra-polar
located directly up- and downstream of the sample. The injection of both the brine and CO₂ were carried out (NOCe tests) at the UK National Geoscience Data Centre (NGDC) repository (https://doi.org/10.5285/6c9d5aa-f1f2-49a9-868e-3d2d5947ad54).

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Elastic wave modelling: rock with salt in the pores. Our modelling of elastic wave parameters follows Ecker, et al.51 approach that considers two idealized models for solid phase precipitation in the pores (gas hydrate in their case and salt in this work). We combine the stiff uncemented and cemented sand models46,47 using MAT-LAB (R2017a) to calculate the frame properties of the dry rock, and applied Biot-Stoll48–50 to calculate P and S-wave velocity and attenuation over the whole brine saturation range at a frequency of 550 kHz. Fluid density, viscosity and compressibility at the experimental pressure, temperature and salinity conditions were calculated using the High Pressure International EOS for brine59 and data from the National Institute of Standards and Technology (https://webbook.nist.gov/chemistry/fluid/) for CO₂.

Data availability
Data presented in this study will be publically available: (1) the XCT data (CSMe tests) at the OSF (https://osf.io/) and the Colorado School of Mines website (https://crusher.mines.edu/publications/); and (2) the geophysical data (NOCe tests) at the UK National Geoscience Data Centre (NGDC) repository (https://doi.org/10.5285/6c9d05aa-f1f2-49a9-868e-3d2d5947ad54).

Received: 20 February 2020; Accepted: 26 August 2020
Published online: 05 October 2020

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Acknowledgements

We have received funding from the United Kingdom’s National Environment Research Council (grant NE/ R013535/1 GASRIP), the Research Council of Norway through RCN-CLIMIT (grant OASIS—280472) and the DHI/Fluids consortium at the Center for Rock Abuse at Colorado School of Mines (CSM) for laboratory micro-X-ray CT tests. We acknowledge support from Dr Mathias Pohl and Dr Mandy Schindler during the construction of the setup for the micro X-ray CT tests, from Dr Laurence North regarding the geophysical data, from Dr Sourav Sahoo regarding the sample preparation in the rock physics laboratory at the National Oceanography Centre, Southampton, Richard Pearce regarding the XRD and SEM-EDS analysis, and the British Ocean Sediment Core Research Facility (BOSCORF) for their expertise and facilities.

Author contributions

I.H.F. contribution roles include conceptualization, data curation, formal analysis, funding acquisition, investigation, methodology, project administration, resources, validation, visualization and writing—original draft; K.L. contribution roles include conceptualization, methodology, supervision, visualization and writing—review & editing; H.M.M. contribution roles include software, validation and writing—review & editing; B.C. contribution roles include conceptualization, methodology, supervision, visualization and writing—review & editing; A.B. contribution roles include data curation, formal analysis and writing—review & editing; M.P. contribution roles include funding acquisition, resources, supervision and writing—review & editing; A.B. contribution roles include funding acquisition, resources, supervision and writing—review & editing.

Competing interests

The authors declare no competing interests.

Additional information

Supplementary information is available for this paper at https://doi.org/10.1038/s41598-020-73091-3.

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