Static Fatigue of Saline rocks under Different CO₂ phase Conditions

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Abstract

Static fatigue tests were conducted on core samples saturated with different phase CO₂ to evaluate the fatigue rate and bulk modulus under constant but stepped stress increment. There was re-appearance of primary fatigue at higher stress in all the samples. In the brine saturated sample, for a 4 MPa deviatoric stress increase, there was about 89% increase in primary fatigue rate with up to 16% more strain, up to 88% reduction in fatigue rate when fatigue goes from primary to secondary fatigue and a reduction in primary fatigue duration by 39% with a bulk modulus of 1.050 GPa. Also, the secondary fatigue rate in stress conditions that had the initial primary fatigue portion was up to 16% higher than the secondary fatigue rate for stress conditions that do not have a primary fatigue portion. Saturating the rock with different phase CO₂-brine caused a significant change in the fatigue behaviour and bulk modulus depending on the phase of the CO₂. While the effect of CO₂ phase on bulk modulus is most pronounced in the supercritical CO₂ phase (decrease of 22 %), change in fatigue rate is most pronounced on gaseous CO₂ phase (an increase of up to 45 %) especially when it is combined with brine (an increase of up to 93 %). The results of this study provide new insights into the deformation and response of rock's bulk moduli to different states of CO₂-brine that could exist in a CO₂ storage site and will be useful for the future site selection and maintenance of the geological storage projects.

Keywords: Primary fatigue; Intragranular pores; Bulk modulus; CO₂ Phasebrine; Stress corrosion.

1. Introduction

With successes in In-Salah, Sleipner, Snohit, and Otway CO₂ storage projects amongst others, underground storage of CO₂ has been demonstrated to be possible (Vilarrasa, Makhnenko, &

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Rutqvist, 2019). Concerns are now on the effect of the stored CO₂ on the reservoir rock given the need to ensure the long term integrity of the storage reservoir. Injection and storage of CO₂ in rocks change the properties of the rock through CO₂-brine-rock interaction. For instance, the strength of materials is dependent on the state of the material and the strength of silicate materials is dependent on fluid content (Charles, 1958a, 1958b; Colback & Wiid, 1965) and temperature (Charles, 1959; Le Roux, 1965) amongst other factors.

Geomechanical properties of reservoir rocks are affected when CO₂ is stored in them (Rutqvist, 2012). Injection and storage of CO₂ in reservoir rocks increases the volume of pore fluid and leads to a commensurate increase in pore pressure (Al-Zaidi, Fan, & Edlmann, 2018). This increase in pore pressure changes the effective stresses on the rock (Rutqvist, 2012; Zhang, 2017). The effective stress depends on the change in pore pressure while the confining stress remains constant. The magnitude of change in pore pressure depends on the volume of pore fluid. In geosequestration, the volume of CO₂ in the pore reduces with time following dissolution and mineralization, therefore the effective stress on the rock increases as the volume of CO₂ in the pore and the pore pressure reduces and each new effective stress regime triggers geomechanical changes in the rock's framework. Generally, this influence can be grouped into three mechanisms: thermal cooling, chemical degradation and stress change. From the literature review, all of these mechanisms have received attention; (Grgic, 2011; Hangx, Bakker, Bertier, Nover, & Busch, 2015; Hangx et al., 2013; Heap, 2009; Le Guen et al., 2007; Liteanu, Niemeijer, Spiers, Peach, & De Bresser, 2012; Oikawa, Takehara, & Tosha, 2008; Renard, Gundersen, Hellmann, Collombet, & Le Guen, 2005) and they showed that the effect of CO₂ on creep rate of reservoir rocks varies up to 50-75 times depending on the pore fluid, mineralogy and effective pressure. It has been explained that the mechanism for the change varies from intergranular pressure solution/pressure solution creep, matrix solubility, micro-cracking to stress corrosion cracking. Strong to a weak reduction in geomechanical

properties of rocks due to CO₂ storage has been reported by (Bemer & Lombard, 2010; Grombacher, Vanorio, & Ebert, 2012; Lamy-Chappuis, Angus, Fisher, & Yardley, 2016; Lei & Xue, 2009; S. Li et al., 2020; Makhnenko, Vilarrasa, Mylnikov, & Laloui, 2017; Mikhaltsevitch, Lebedev, & Gurevich, 2014; Muñoz-Ibáñez, Falcon-Suarez, Marín-Moreno, Delgado-Martín, & Mackin, 2020; Vanorio, Nur, & Ebert, 2011). Studies from (Han et al., 2020; Hangx et al., 2013; Marbler, Erickson, Schmidt, Lempp, & Pöllmann, 2013; Rinehart, Dewers, Broome, & Eichhubl, 2016) reported unclear changes in geomechanics due to CO₂ saturation of rocks. The variation in influence is seen to be due to differences in mineralogy.

Most researches on the effect of stored CO₂ on reservoir rocks have considered CO₂ in a supercritical state (Delle & Sarout, 2016; Fuchs et al., 2019; Liu, Suzuki, & Ito, 2020; Pimienta et al., 2017); this is because most CO₂ storage sites inject CO₂ at supercritical state. However, the behaviour of CO₂ is controlled by temperature and pressure conditions. Therefore, the stored CO₂ will not remain in the supercritical state throughout the storage history. Quite intuitively, because of the dynamic nature of the reservoir's physical conditions (Saraji, Piri, & Goual, 2014), there will be an evolution in the phase of the stored CO₂ as it migrates down and across the reservoir with time (Bachu, 2000). Studies have indicated that CO₂ injected and stored in the subsurface exist in different phases alongside brine over time (Bachu, 2000; Holloway, Vincent, & Kirk, 2006; Plug & Bruining, 2007)

There is a need to understand the effect of the different phases of CO₂ that could potentially exist in a CO₂ storage reservoir on the deformation and geomechanical properties of the reservoir rocks. In the light of the finding by Al-Zaidi et al. (2018) that the change in pore pressure (and thus effective stress) due to CO₂ injection depends also on the phase of the CO₂. It is necessary to understand how the change in pressure/stress from different phases of CO₂ that could be present in a CO₂ storage reservoir affects the deformation and geomechanical properties of the reservoir. This will enable a better understanding and prediction of the

behaviour of the reservoir and provide better information with which to constrain CO₂ storage modelling studies.

In this research, experimental fatigue tests (similar to creep test but under very short time) were performed on captain sandstone core samples to study how different CO₂ phase with brine under storage reservoir conditions affect the geomechanical properties of rocks. The combination of the brine and the different phases of CO₂ means that we have rock samples in five different CO₂-br states viz: dry sample, br saturated sample, gCO₂-br saturated sample, scCO₂-br saturated sample, and gCO₂ saturated sample. These various states represent the different CO₂-br states that a target CO₂ storage reservoir could be in nature and are replicated experimentally. A sample contained only brine, another sample contained gCO₂. One sample was tested as dry. Note that the prevailing temperature and pressure condition in the Ekofisk CO₂ storage field (CO₂stored website) from where the samples were recovered (Figure 1) is such that some amount of CO₂ is expected to exist in both gaseous and supercritical phases with the brine.

The experiments aims to evaluate the fatigue behaviour, fatigue rate, fatigue phase duration, static moduli (bulk modulus), and compressibility due to pressure/stress from the different CO₂-brine states. The results of this study will provide deep insights into the response of rock's bulk moduli and fatigue behaviour that can be possible from the different CO₂ phases that could exist in the Ekofisk CO₂ storage site alongside the brine. By extension, given that CO₂ injected in a supercritical state into dedicated CO₂ storage projects like Sleipner, Snohvit, Quest and In-Salah would have undergone phase transition, the effect of the large quantities of already stored CO₂ on the bulk modulus and fatigue behaviour of these storage reservoirs will be better understood and predicted in terms of the evolving CO₂ phase. The understanding of the mechanism of fatigue in porous rock will also be advanced.

Figure 1: Location map showing well 13/24a-6 (triangulated) where core samples were collected (adapted from Williams et al. (2016))

2. Materials and experimental setup

Captain sandstone core samples recovered from well 13/24a-6 from a depth of 1638.5-1640.3m (Figure 1) were used for the saturation and fatigue experiments. The diameters and lengths of each sample are shown in Table 1. The porosity shown for each sample was determined by weighing the samples in dry and water-wet states, measuring the grain volume and pore volume by submerging the samples in distilled water, and determining the bulk volume from measuring the dimensions of the samples. This was repeated four times for each sample. Therefore, the porosity shown in Table 1 is the average porosities calculated from the weight difference between the dry and wet core samples. To determine the average grain size, thin section slides were prepared from the samples, and imaged with a Hitachi SU8230 high-performance cold

field emission SEM, the SEM images were processed and analysed for grain size using Image J software.

Table 1: Measured properties of core samples.

Sample ID	Diameter (mm)	Length (mm)	Porosity (%)
dry	38.06	35.68	26
br	37.89	34.51	27
gCO2-br	38.21	35.24	26
scCO2-br	38.05	36.08	27
gCO2	38.08	36.26	27

A good similarity in the petrophysical and mineralogical properties of captain sandstone has mineralogical characterization of captain sandstone by previous workers such as Hangx et al. (2013) and Rice-Birchall (2018) showed similarity with quartz and feldspar being the major minerals alongside some amount of clay and calcite. Hangx et al. (2013) measured an average grain size of $\sim 200 \mu\text{m}$ while Rice-Birchall (2018) reported an average grain size of $\sim 250 \mu\text{m}$. Porosity and permeability measured by Hangx et al. (2013) ranged from 26.4 to 29.2% and 6.5×10^{-13} to $21.0 \times 10^{-13} \text{ m}^2$ ($6.6\text{E}+15$ to $2.1\text{E}+16 \text{ mD}$) respectively.

The samples used in this study (Figure 2) can be described as weak, structureless, stained whitish, sub-rounded, fairly sorted quartz arenites with an average grain size of $\sim 223 \mu\text{m}$. The mineralogical characterization and permeability measurement by Hangx et al. (2013) will be adopted for this study.

Figure 2: Photograph of the core sample

2.1 Experimental setup

The schematic of the experimental setup is shown in figure 3. It consists of a vacuum pump (Vacuubrang GMBH, model MZ 2D NT) for removing trapped gases to ensure complete saturation of brine in the samples, two pressure vessels (Parr instruments, IL, USA) with pressure range of 0-70 bar and 0-200 bar and upper temperature limit of 350 °C for holding the sample, brine and CO₂ in desired pressure conditions, an oven to maintain the temperature condition for the sample, brine and CO₂, a 250KN triaxial machine (MAND testing machines Ltd.) for the static fatigue test, a 3-70 MPa confining pressure pump (ELE) using silicon oil to supply confining pressure, a temperature regulator (custom built in University of Leeds with N2006P PID temperature controller and a K-type thermocouple with a precision of 0.2% and a resolution of $\pm 1^\circ\text{C}$) to keep the temperature of the sample and sample holder at 35°C during fatigue testing, pressure transducer (gems sensors and controls, range 0-100 MPa and precision of 0.25%) to measure and log the real-time pressure impacted on the sample and a microlink 751 multifunction data acquisition and control (set at 15 bits per channel, with each channel limited to ± 10 Vdc and a resolution of 0.8 mV over the ± 10 V range with a precision of $\pm 0.05\%$) to record the displacement data from the LVDT's and displayed on a PC using windmill software.

Fig 3: The experimental setup (1. Vacuum pump for saturating the sample with brine, 2. CO₂ gas cylinder, 3. Pressure vessel with control valve and brine saturated sample being flooded with CO₂, 4. Pressure vessel with control valve and CO₂-flooded-brine saturated sample in the oven, 5. Triaxial machine and compressor, 6. Temperature regulator, 7. A pressure transducer, 8. Displacement transducer, 9. Desktop computer)

2.2 CO₂ saturation and static fatigue test procedure

The different CO₂ phases and brine combinations that could be in the target CO₂ storage reservoir namely; dry, br saturated, gCO₂-br saturated, scCO₂-br saturated, and gCO₂ saturated were replicated experimentally. The following steps were followed to saturate the sample and conduct the test:

1. The samples were de-saline off its original salt content by immersion in de-ionized water for 402.5 hours and finally flushed with 100 pore volume de-ionized water at 3MPa pressure
2. 60600ppm NaCl solution was prepared to serve as brine (br). This is the concentration of brine in the captain sandstone formation where the samples were recovered according to CO₂ stored.
3. Samples to be used for br, gCO₂-br, and scCO₂-br saturated states were saturated in brine under vacuum for 7 days to allow enough time for complete saturation of the samples. Sample to be used in dry and gCO₂ saturated condition were not saturated in brine.
4. Samples for CO₂-brine saturated states (gCO₂-br and scCO₂-br) were put into the pressure vessels. Brine was poured into the vessel until the sample was completely immersed. The pressure vessel was then connected to the CO₂ cylinder and CO₂ was pumped into the vessel at 27°C, 50 bars, and 36°C, 100 bars respectively. The sample for gCO₂ state was connected to the CO₂ cylinder and CO₂ was pumped into it at 27°C, 50 bars. Samples for dry and Br states were not flooded with CO₂.

- 187 5. Samples for CO₂-brine saturated states (gCO₂-br and scCO₂-br) and sample for gCO₂
188 state were transferred to the oven. The P-T condition was held constant for 7 days. The
189 sample for br state was left in brine for a further 7 days.
- 190 6. Fatigue test was then carried out on each sample. Samples were inserted into the
191 sample holder compartment of the triaxial machine that had been lined with an elastic
192 Vuitton sleeve and a steel platen was placed on it to fill up the gap. Two lateral variable
193 differential transducers (LVDT's) were clamped via flexible metal cantilever to the
194 middle of the sample to measure lateral displacement. Axial displacement was
195 measured by two inbuilt and magnetically attached displacement transducers touching
196 the top and bottom of the sample. Both lateral and axial displacement transducers were
197 connected to the micro link 751 multifunction data acquisition and control for recording
198 and display. Pressure transducers connected to the PC delivers command controlled
199 load/stress to the sample.
- 200 7. Before each fatigue test, the sample and the sample holder compartment of the triaxial
201 machine were heated to a temperature of 35°C. This was then left for about 30 minutes
202 to ensure that the temperature stabilized across the sample. This is the prevailing
203 temperature at depth from which the samples were recovered. The confining and axial
204 stresses were then increased hydrostatically up till 16 MPa. This is the prevailing
205 pressure at depth from which the samples were recovered.
- 206 8. With steps 7 above, the sample has been brought to the reservoir stress and temperature
207 condition. Axial stress was then increased from 16 MPa to 16.75, 17.5, 19.0, and 22.0
208 MPa, and fatigue was observed for each increase in axial stress. With confining stress
209 held constant at 16MPa, the increase in axial stress corresponds to 0, 0.5,1.0, 2.0, and
210 4.0 MPa deviatoric stresses respectively.

9. Axial and lateral displacements (Δl and Δd) from both transducers, confining pressure, and axial load/stresses were recorded per second during the entire fatigue and displayed on the screen through the windmill software. These were processed to yield the axial(ϵ_a) and lateral(ϵ_L) strain, volumetric strain(ϵ_{vol}), fatigue rates(f_r), and fatigue duration(f_t) as well as bulk modulus and compressibility.

3. Results and discussion

The samples were saturated in the different phase CO₂-brine for 7 days, because in a prior experiment where CO₂ was flooded into a brine saturated sample immersed in excess brine, it was observed that for the first five days of CO₂ flooding, and there was a gradual drop in CO₂ pressure until the sixth day when the CO₂ pressure stabilized. This indicates that the CO₂ was actively dissolving into the excess and pore brine and forming an acidic solution for the first five days until the sixth day when all the brine became saturated with CO₂. Note that the acidification of the brine started from the first day with a daily increase in the concentration of the acidic brine until the brine is completely acidified (saturated). Therefore, the effect of the resulting acidic pore fluid on the properties of the rock can be said to have started gradually from the first day and increased as the concentration of the brine increased. From literature, Olabode and Radonjic (2013) had reported a substantial change in pH of effluent from shale flooded in CO₂-brine in just 3 days and that change in pH of the effluent was higher in the earlier days. Pimienta et al. (2017) studied CO₂ injection and effect of residence time on dissolution and rock integrity and found that the pore brine acidifies just after 2 hours of exposure to leading to calcite dissolution and a significant increase in the brine's concentration in calcium cations and commensurate change in rocks' physical properties such as porosity, permeability.

Since this research seeks to evaluate the effect of change in effective stress due to increase in pore fluid (acidic brine) formed by dissolution of different phases of CO₂ into brine on the fatigue behaviour and geomechanical properties of the rocks, It was decided that excess of 5 days would be good enough for the acidic brine to have affected the properties of the rocks.

To provide an understanding of the effect of CO₂ phase on the microscopic fatigue behaviour, fatigue rate, fatigue phase duration, bulk modulus, and compressibility; the time-dependent lateral and axial strain of all the rock samples under constant but stepped compressive stress were measured and analysed following the ideal rock creep model with three distinct phases; primary, secondary and tertiary phases (Heap, 2009). The end of each creep phase is marked by the point of inflection on the curve and are distinct in terms of the mechanism and rate of deformation. The axial strain (ϵ_a) and lateral strain (ϵ_L) of the rocks were taken as the averaged $\Delta L/L$ from the top and bottom displacement and averaged $\Delta d/d$ displacements respectively. Volumetric strain (ϵ_{vol}) was taken as ($\epsilon_{vol} = \epsilon_a + 2\epsilon_L$). Fatigue rate (f_r) was taken as (ϵ_{vol}/t) for each fatigue phase observed and fatigue duration (f_t) was taken as the time for fatigue to change from one phase of fatigue to another. This study assumes that all the samples are identical. The gap in the core holder was filled with steel platen during fatigue testing and a correction was applied to the axial displacement using equation 1 (Ergo Tech manual).

$$\text{Platen correction (0 – 50kN)} = \frac{-270.66 + \sqrt{270.66^2 + 11364 \times \text{Load}}}{5682} \quad (1)$$

where load is in kN.

This study is the first in a series. Since tertiary phase fatigue represents macro-deformation and we aim to study only the microscopic fatigue, the choice of duration of the static fatigue test and the deviatoric stress applied was therefore informed by the need to avoid tertiary phase fatigue at this stage while also ensuring that the deviatoric stress applied is comparable to that which can be induced by CO₂ injection and storage. Secondly, given the large porosity of the rock, we aimed to bring the samples to a consolidated (constant microstrain rate) and an

equilibrated pore pressure condition before proceeding with the strength testing. Hence the duration of the static fatigue test was chosen to achieve just these and not more.

Deviatoric stress is the stress differential between axial stresses (σ_1) and confining stress (σ_3) due to increasing axial loading. In this study, the deviatoric stress represents the change in effective stress due to the CO₂ phase-brine state. Deviatoric stress in the range of 0-4 MPa was chosen to represent scenarios where pore pressure is equalized with confining pressure (i.e. effective stress of 0) up till when pore pressure drops by 4 MPa (effective stress of 4MPa) following CO₂ dissolution and mineralization. The conservative range was chosen because the change in stress due to injection of CO₂ into brine saturated reservoir is expected to be low as explained by Rutqvist (2012) and suggested by differential pressure results obtained by Al-Zaidi et al. (2018).

In this study, deviatoric stress (σ_{ev}) is taken as:

$$\sigma_{dev} = \sigma_1 - \sigma_m \quad (\text{where } \sigma_m = (\sigma_1 + 2\sigma_3)/3)$$

$$\sigma_{dev} = \frac{2}{3} (\sigma_1 - \sigma_3) \quad (2)$$

The bulk modulus (K) and compressibility (β) were measured only from the hydrostatic loading portion (where $\sigma_1 = \sigma_3$). Bulk modulus is given as equation 3 and compressibility is taken as the inverse of the bulk modulus.

$$K = \frac{\Delta\sigma_1}{\Delta\epsilon_{vol}} \quad (\text{where } \Delta\epsilon_{vol} = \Delta\epsilon_a + 2\Delta\epsilon_L) \quad (3)$$

3.1 Fatigue behaviour

Figures 4 and 5 show the fatigue behaviour of the brine saturated sample under constant but stepped deviatoric stress conditions, which represents the fatigue behaviour of the natural reservoir. Any deviation seen in the other samples is therefore due to the phase of CO₂ with which it was saturated. The fatigue behaviour of the other samples is presented as supplemental

material (section A-H). The primary and secondary creep phases for all the samples were similar. The tertiary fatigue phase was not used for this study because it represents macroscopic deformation. it is seen that only fatigue curves for the hydrostatic and 4 MPa deviatoric stress levels showed the primary fatigue phase albeit very short-lived. The brevity of the primary fatigue in the hydrostatic curve maybe because the samples were recovered from depth and have been pre-stressed resulting in reduced diagenetic porosity and micro-cracks which are usually impacted during primary fatigue. With time, the fatigue progressed from the primary phase to the secondary phase where plastic grain dilation/contraction is normally dominant.

Figure 4: Fatigue curve for br sample for different deviatoric stresses

Figure 5: Combined fatigue curves under different deviatoric stresses from 0 to 4MPa for br sample.

3.2 Fatigue rate

The fatigue rate of the primary fatigue phase increased by 342%, 89%, 117% and 77.5% in the 4 MPa stress level when compared to hydrostatic stress level for dry, br, scCO₂-br, and gCO₂ respectively. The primary fatigue rate for the gCO₂-br reduced by 40%. The increase in fatigue rate demonstrates the effect of increased stress on fatigue rate (Fjar, Holt, Raaen, Risnes, & Horsrud, 2008; Ngwenya, Main, Elphick, Crawford, & Smart, 2001) however, the increase in fatigue rate was varied due to the phase CO₂ with which each sample was flooded with (Li et al., 2018) while the reduction in the fatigue rate for gCO₂-br may be the effect of the accelerated fatigue rate at higher stress due to pore stress corrosion of the gCO₂-br.

The secondary fatigue rates for the dry sample are 14.2, 11.8, 12.1, 12.7, 14.6 microstrain per second for hydrostatic, 0.5, 1, 2, and 4 MPa deviatoric stress levels respectively. The secondary fatigue rate for the other samples are shown in Table 2, the trend suggests that the secondary

fatigue rate and recorded strain increased with increasing stress level. But, the rate of increase is much lower than the primary fatigue at stress levels where both phases of fatigue apply with primary fatigue rate decreasing by 76 and 94.5% for dry, 80 and 88% for br, 88.6 and 74.5% for gCO₂-br, 80.3, 91.2% for scCO₂-br, and 86, 91.6% for gCO₂ for hydrostatic condition going into the secondary fatigue on the hydrostatic and 4 MPa stress levels respectively. The secondary fatigue rates compared to each other were seen to be higher for stress levels that had the primary fatigue phase i.e the hydrostatic and 4MPa stress levels respectively. For example, 14.2μS/s and 14.6 μS/s for dry, 15.3 μS/s and 17 μS/s for br, 16.7 μS/s and 22.4 μS/s for gCO₂-br, 19.5 μS/s and 19.0 μS/s for ScCO₂-br and 15.0 μS/s and 16.3 μS/s for gCO₂). This may be because the closure of pores and micro-cracks by primary fatiguing creates volume space for more grain dilation/contraction for the immediate secondary fatigue. The secondary fatigue rate was almost equal for the other stress levels.

Table 2: Table of measured fatigue rate and Bulk modulus for all samples.

S ID	σ_{dev}	Primary f_f (microstrain/sec)	Primary f_t (sec)	Secondary f_f (microstrain/sec)	Secondary f_t (sec)	K (GPa)	β (GPa ⁻¹)
dry	0	59.7	333	14.2	1377	1.2164	0.8221
	0.5		--	11.8	1786		
	1		--	12.1	1786		
	2		--	12.7	1760		
	4	264.0	88	14.6	1646		
br	0	75.8	294	15.3	1500	1.050	0.9524
	0.5		--	12.8	1847		
	1		--	13.1	1842		
	2		--	14.2	1757		
	4	143.6	180	17.0	1552		
gCO ₂ -br	0	146.4	181	16.7	1629	0.9184	1.0888
	0.5		--	14.6	1894		
	1		--	15.6	1817		
	2		--	17.3	1703		
	4	87.8	356	22.4	1441		
	0	98.9	284	19.5	1474	0.8236	1.2142
	0.5		--	16.3	1798		

scCO ₂ -br	1		--	16.5	1802		
	2		--	17.1	1787		
	4	214.7	148	19.0	1709		
	0	109.7	203	15.0	1535	0.9195	1.0875
	0.5		--	13.4	1784		
gCO ₂	1		--	13.2	1855		
	2		--	14.6	1753		
	4	194.7	137	16.3	1675		

Results from our primary fatigue rate (Table 2) show that fatigue rate depends on deviatoric stress (K. Peng, Zhou, Zou, & Yan, 2019) and agrees with results from conventional creep experiments in which a 10% change in differential stress resulted in more than two orders of magnitude change in creep strain rate (Heap, 2009). The secondary fatigue rates were seen to be much lower than the primary fatigue rate and smaller for all the stress levels of all the samples. This is expected, because secondary fatigue requires more stress (Goodman, 1989), given that the mechanism at this stage is boundary re-alignment and grain contraction/dilation. The secondary fatigue rate for the gCO₂-br sample was most varied under the different stress conditions. This can be attributed to the continuous and slow nature of the effect of gCO₂-br on the rock grains such that at a slightly different stress level, a slightly different plastic response is produced. This variation in rate is not noticed in the gCO₂ sample because brine is needed to create this effect. It was observed that the secondary fatigue phase preceded by primary fatigue showed higher secondary fatigue rates. This is because primary fatigue creates more volume for secondary fatigue to propagate. This effect is accentuated in the gCO₂-br sample more than any other samples for the higher stress levels.

3.3 Fatigue phase duration, total strain, and bulk modulus

The primary fatigue phase in the hydrostatic stress level lasted for 19.5% and 3.8% of the fatigue duration for that stress level and of the entire fatigue duration respectively for the dry sample, 16.4% and 3.3% for br, 10% and 2% for gCO₂-br, 16.2% and 3.2% for scCO₂-br and 11.7% and 2.3% for gCO₂. For the 4 MPa stress level, the primary fatigue phase lasted for only 5% of the fatigue duration for that stress level and 1% of the entire fatigue duration for dry,

10% and 2% for br, 19% and 3.9% for gCO₂-br, 8.2% and 1.6% for scCO₂-br and 8% and 1.5% for gCO₂. This reduced fatigue duration is the effect of increased stress on fatigue duration and is seen to be varied due to the effect of the saturating state of CO₂ and brine. Primary fatigue duration under hydrostatic stress condition was longest in the dry sample (3.8% of its total fatigue duration) suggesting that the duration of fatigue of the other samples have been affected by the stresses due to the respective CO₂ phases as seen by the higher primary fatigue rates of all the other samples. Comparing the primary fatigue duration at hydrostatic stress level for br and other CO₂ bearing samples showed a reduction with gCO₂-br having the highest reduction. Kranz (1980) reported that increasing stress by a few kbar on a granite sample decreased the time-to-failure by an order of magnitude. Baud and Meredith (1997) reported a substantial effect of increased stress on creep duration and rate as they observed that a 10% decrease in stress increased failure duration from 30 minutes to about 24 hours. The primary fatigue duration for the higher stress condition was longest for the gCO₂-br (3.9%) indicating that the weakening effect of the gCO₂-br is mild. So, the impact of the weakening can be seen more at a higher stress level in the form of longer fatigue duration and higher fatigue rate.

To normalise the effect of increased stress on the strain and allow for comparison between the hydrostatic and 4 MPa fatigue behaviour, $f_r \times f_t$ was used as the total strain in the primary phase. The $f_r \times f_t$ for the primary fatigue phases show that despite the reduced fatigue duration for the 4 MPa stress level, 16.9%, 16%, 18%, 13%, and 19.8% more microstrains were recorded for dry, br, gCO₂-br, scCO₂-br, and gCO₂ samples respectively. This observation indicates that of the volume of strain recorded under the hydrostatic stress condition, there was more volume of intragranular and intergranular pores and micro-cracks that could not be affected by the hydrostatic stress condition (X. Li, Qi, & Zhang, 2020). This suggests that primary fatiguing at lower stress levels may not close up all the genetic pores and micro-cracks as some smaller intragranular and inter-granular pores and micro-cracks are shielded by the rock's effective

strength. This makes sense given that the rocks are pre-stressed. That the difference between the volume of strain recorded in the primary fatigue phase at low and high-stress are highest for the gCO₂ (19.8%) and gCO₂-br (18%) shows that gaseous CO₂ may be corroding weak margins of the rock matrix at a mildly rate such that higher stress is required to cause significantly more volumetric strain. A similar view has been expressed by Le Guen et al. (2007). The difference between the volume of strain recorded at the primary phases of the low and high stress is lower for br than the dry rock and lowest for scCO₂-br and may indicate that the stress corrosion of these two states happened at a faster and stronger rate such that the grain materials were weakened enough to be deformable at lower stress condition. The volumetric microstrain which represents the highest change in volume recorded for all samples from the 0 to 4 MPa deviatoric stress cycle is presented in Table 3. There was some volumetric microstrain during the hydrostatic loading phase of the test but this was excluded. The result shows that the dry sample has the lowest volumetric change during the hydrostatic loading and throughout the test while the scCO₂-br sample showed the highest change in volumetric expansion during the hydrostatic loading and throughout the test.

Table 3: Volumetric microstrain recorded in each sample through the entire test

Sample	ϵ_{vol} at $\sigma_1 - \sigma_m = 0$ (μS)	ϵ_{vol} at $\sigma_1 - \sigma_m = 4$ MPa (μS)
dry	13115	16105
br	14433	17793
gCO ₂ -br	17205	21559
scCO ₂ -br	18313	21764
gCO ₂	14370	18315

Comparing the bulk modulus of the br and the CO₂-br samples show the accelerating role of CO₂ in weakening the rocks similar to what has been reported by (Bemer & Lombard, 2010; Grombacher et al., 2012; Mikhaltsevitch et al., 2014; Vanorio et al., 2011). The bulk modulus of the dry sample was 1.2164 GPa and the compressibility was 0.8221 GPa⁻¹. The bulk modulus and compressibility of the other samples are shown in table 2. This shows a general reduction in the bulk modulus (strength) of the rocks according to the sample state. In all the samples

tested, the primary fatigue phase under hydrostatic stress conditions was very brief. With an increase in stress, the fatigue progressed from the primary phase to the secondary phase where plastic grain dilation/contraction is normally dominant.

3.4. Comparison of fatigue behaviour, rate, and modulus between Br sample and phase CO₂ samples

Figures 6 and 7 show the percentage difference of the measured parameters between the br and the other CO₂ bearing samples. This is to show the effect the phase of CO₂ had on the other samples by showing the percentage difference between each sample and br assumed to represent the natural reservoir state.

Figure 6: Percentage difference in primary fatigue rates for 0, 4 MPa and average secondary fatigue rate between br and other samples showing the change in strain rate caused by the different phase of CO₂

Figure 7: Percentage difference in bulk modulus and compressibility between br and other samples showing the change in bulk modulus and compressibility caused by the different phase of CO₂

From Figure 6, it is seen that the primary fatigue rate is higher for all samples containing CO₂ compared to the br sample at both low stress and high stress. This suggests that stress corrosion due to pore fluid is interfering with the strain rate. Reduction of the stiffness of the rock is due to stress corrosion, inducing more strain at lower stress leaving less possibility of primary fatigue at higher stress, especially for the scCO₂-br sample while reduction of stiffness, inducing more strain due to stress corrosion at higher stress was seen in the gCO₂-br and gCO₂ samples. The average secondary fatigue rate of all samples, when compared to the dry, is seen to increase the most in the scCO₂-br sample. This means that this state of CO₂ has the strongest weakening effect on the grain fabric such that grain dilation and boundary re-alignment is most pronounced. This also explains why this sample state has the greatest change in bulk modulus and compressibility. Results of fatigue rate under various CO₂ conditions by Le Guen et al. (2007); Renard et al. (2005) and Liteanu et al. (2012) have reported 50-75 50 and 50 times increase in fatigue rates respectively. This research shows 93%, 30%, and 45% increase in primary strain rate at low stress for gCO₂-br, scCO₂-br, and gCO₂ samples respectively when compared to the primary strain rate of brine saturated sample.

Results of static modulus from this research agree with consistent strong reduction effect observed by Bemmer and Lombard (2010); Vanorio et al. (2011) and Delle and Sarout (2016) as we observed 13, 22 and 12% reduction in bulk modulus for gCO₂-br, scCO₂-br and gCO₂ samples respectively when compared to brine saturated sample. This also agrees with Le Guen et al. (2007) that supercritical CO₂ has the most effect on P-velocity among the other states of CO₂. Comparing the results from br and gCO₂ samples show that CO₂ affects the fatigue rate and bulk modulus of rock significantly without brine, while the presence of brine is seen to greatly accelerate this fatigue rate by up to 57 and 20% for low and high stress respectively, bulk modulus changed only by 10%. This means that the deformation rate and bulk modulus of the reservoir will be significantly affected by CO₂ storage. Stress corrosion due to pore fluid determines the extent of the effect on fatigue rate and modulus. Stress corrosion under supercritical CO₂ condition was seen to be stronger at lower stress levels thus affecting bulk modulus the most while stress corrosion due to gaseous CO₂ was seen to be at a mild rate at low stress. Peng et al. (2020) found that pressurized gases could penetrate micro-cracks and pores and affect failure rate. For the gCO₂-br sample, stress corrosion was higher at high-stress levels. All these CO₂-brine states interfered with the fatigue rates and modulus as seen in Table 1.

The result from this study shows that CO₂ affects the strain rate recorded at both low and higher stress conditions as it is seen that the fatigue rate of CO₂ flooded rocks is significantly different from what it was when the rock was brine saturated only. The effect is seen to be sensitive to the phaseCO₂-brine state. For instance, the difference in the recorded strain at high and low stress was higher for gCO₂ and gCO₂-br samples compared to the scCO₂-br samples. This shows that gCO₂ and gCO₂-br have a higher impact on the rock at higher effective stress compared to the scCO₂-br sample. This implies that if a reservoir is gCO₂-br dominated, there will be a greater reduction in the modulus of the rock at higher effective stress compared to a

scCO₂-br dominated reservoir. On the other hand, the scCO₂-br saturated sample when compared to the gCO₂-br samples shows that there was less difference between volumes of strain recorded at low stress and higher stress. It, therefore, implies that if a reservoir is dominated by scCO₂-br, the volumetric strain will proceed at a lowered difference in rate between the low and high stress (nearly the same strain throughout the storage history) when compared to the gCO₂-br dominated reservoir. It goes to say that the effect of change in effective stress on geomechanical properties of the reservoir will be most pronounced if the reservoir contains gCO₂-br compared to scCO₂-br. The average secondary fatigue rate was highest in the scCO₂-br saturated sample, this makes sense given that the rock's properties is immediately affected by the scCO₂-br. Therefore, the secondary phase of fatigue seems to be enhanced by the prior effect.

This research shows that among the CO₂-brine states, the scCO₂-br has the greatest effect on the rocks material compared to the other CO₂-brine states, hence the greatest reduction in bulk modulus (greatest increase in compressibility) and highest volumetric strain seen in the scCO₂-br sample. It is thought that the higher impact of scCO₂-br over gCO₂-br on the modulus and deformation of rocks maybe because the density of scCO₂ is larger than gas and can itself behaves as a liquid resulting in more drag effect coupled with the ability of scCO₂ to dissolve organic materials easily (Chitanvis, Patterson, Spall, & Laintz, 1998).

In all the samples tested, there was re-appearance of primary fatigue in the 4MPa deviatoric stress levels after secondary fatiguing for the 0.5, 1, and 2MPa deviatoric stress levels. Scholz (1968) had disagreed with a previous assumption that each phase of fatigue occurs only once and explained that there is a possibility of re-occurrence of a phase of fatigue if the stress condition changes. In our experiment, the reappearance of primary fatigue in the 4MPa deviatoric suggests that some smaller diagenetic intragranular and/or inter-granular micro-cracks and pores are shielded from the impact of stress by the effective strength of the rock

until the stress is high enough to overcome the shielding work of the effective strength as illustrated in Figure 8. It is assumed that creep rate diminishes with time, if this were true and the limits of static fatigue were approached, the effect of fatigue would cease. However, this is not the case as fatigue is usually seen to progress until complete failure if stress is maintained. Scholz (1968) however posited that this assumption may not hold for long term fatigue as it never ceases and continues until complete failure. Our experiment finds that this assumption may not hold for rocks that have pores at multiscale even in the short term. We found that each phase of fatigue contributes an increment to total strain (X. Li, Qi, & Zhang, 2020) but this contribution is not constant and the fatigue rate are affected by CO₂ phases. Also, the strain produced by a given fatigue phase is different if the stresses are different. For instance, the primary fatigue phase in the dry sample produced 16.9% more strain under 4MPa deviatoric stress compared to hydrostatic stress conditions. Similarly, Scholz (1968) studied the size distribution of micro-fracturing events during constant strain rate experiments and found that the strain tends to become statistically greater with increasing stress.

Figure 8: Rock fatigue under different stresses. (1) Grain boundary, (2) Major Intergranular pore, (3) Intragranular pore (4) Intergranular pore (smaller and shielded), (5) micro-crack. (A) Original grain and pore structure (B) grain and pore structure during primary fatigue; Notice major intergranular pores are closed up due to primary fatigue (at hydrostatic stress in this research). (C) Grain and pore structure during secondary fatigue at 0.5, 1 and 2 MPa stresses in this research; notice there is dilation, contraction, and realignment of grain boundaries with the intragranular pores and micro-cracks unaffected. (D) Grain and pore structure after re-appearance of primary fatigue at 4 MPa. A and D show the primary fatigue scenario while B and C show secondary fatigue but note that the latter part of the A and D fatigue test had secondary fatigue as shown by all the fatigue curves.

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505   Figures 9a-j are micro-CT images of all the samples acquired before and after compression
506   respectively. They are seen to contain relatively smaller intragranular pores and cracks that are
507   noted to be responsible for the re-appearance of primary fatigue. After compression, it is seen
508   that the volume of the intragranular pores was reduced under high stress. We opine that the
509   volume of the intergranular pores and crack remained unaffected by the 0, 0.5, 1 and 2 MPa
510   deviatoric stress cycles as illustrated in figure 8 and that the reduction in its volume as seen in
511   Figures 9 (b, d, f, h, and j) is due to the imposition of 4 MPa deviatoric stress and corresponds
512   to the period of re-appearance of primary fatiguing.

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(a): Dry sample before compression

(b): Dry sample after compression

(c): br sample before compression

(d): br sample after compression

(e): gCO₂-br sample before compression

(f): gCO₂-br sample after compression

(g): scCO₂- br sample before compression

(h): scCO₂- br sample after compression

(i): CO₂ sample before compression

(j): CO₂ sample after compression

Figures 9a-j: Micro-CT images of samples used before and after compression. Notice that all the samples show a reduction in porosity and grain smoothening after compression but the magnitude of the reduction varies according to the state of the sample with gCO₂- br and scCO₂- br showing the highest reduction. The micro-CT images were taken at approximately the same locations in the core sample.

To provide a preliminary quantitative assessment of the change in porosity, 2D slices of CT images of each sample before and after compression was analysed using ImageJ and the results are presented below in Table 4. 3D image processing and assessment of the quantitative change in porosity is a subject of our future research. It is seen that the total pore area, percentage pore area, and average pore size of all the samples reduced after compression. The greatest reduction however was seen in the gCO₂-br sample.

Table 4: Porosity measured from a 2D CT image slice of the different sample states before and after compression

Sample ID	Total Pore area (mm ²)		Average pore area (mm ²)		Percentage pore area (%)	
	Before	After	Before	After	Before	After
dry	15.67	9.92	0.073	0.026	42.78	27.93
br	19.97	10.42	0.045	0.043	29.34	26.67
gCO ₂ -br	21.78	6.15	0.089	0.024	27.41	8.17
scCO ₂ -br	21.95	16.34	0.096	0.040	26.34	19.52
gCO ₂	23.41	21.05	0.077	0.054	31.03	27.87

3D-view videos of a sample before and after compression (videos A and B respectively) are provided as supplemental material to provide detailed information on the general reduction in pores due to primary fatigue as well as the reduction in intragranular pores due to the appearance of primary fatigue at high deviatoric stress. This clearly shows that the mechanism for primary fatigue is pore and crack closure and that the effective stress of rocks shields smaller intragranular pores from primary fatigue at low stress.

4. Conclusions

This research has evaluated the effect of different phases of CO₂ with brine on deformation rate and bulk modulus in sample reservoir rocks. The result of this work can be applied to predicting the effect the different possible existing phases of CO₂ in giant CO₂ storage fields such as Sleipner, In Salah, etc. will have on the deformation and bulk modulus of the reservoir rocks. Main conclusions are summarised as below:

- At low and high stresses, the strain rate for all the CO₂ bearing samples was higher compared to the brine saturated sample except for gCO₂-br where it was lower at high stress. The magnitude of the change in strain rate depends on the state of the sample with the gCO₂-br having the highest change/response (93% and 39 %) followed by gCO₂ (45% and 35 %) and then ScCO₂-br (35% and 50 %) for low and higher stress respectively. Increased strain rate for CO₂ flooded rocks is valid for lower stress conditions (in a stepped test) or initial fatigue stages (in a constant stress test).

- The averaged secondary strain rates of all the samples increased compared to the brine saturated sample and the highest increase was in the ScCO₂-br (22 %) followed by gCO₂-br (20 %). The change due to gCO₂ is negligible.
- All the CO₂ containing samples showed reduced bulk modulus and increased compressibility compared to the brine saturated sample consistent with Espinoza et al. (2018). The highest change in bulk modulus and compressibility was seen in scCO₂-br (22 and 27 %) followed by both gCO₂-br and gCO₂ at (13 and 14 %) respectively.
- Comparing the results from Br and CO₂ saturated samples show that the state of the sample affects the fatigue rate and bulk modulus of dry rock significantly. We would expect an increase of up to 57% and 10% on the fatigue rate and bulk modulus respectively if the rocks were wet with brine only.
- The phase of CO₂ matters. While the effect of CO₂ on bulk modulus is most pronounced in the supercritical CO₂ phase (decrease of 22 %). The primary fatigue rate is most affected by the gaseous CO₂ phase (an increase of up to 45 %) especially when it is combined with brine (an increase of up to 93 %). The later impacted directly on the grain material while the former impacted on the effective stress.
- Primary fatigue was also seen to be capable of been shielded by the rock's effective stress if the stress condition is low or not applied for a long enough time most especially if the material has wide micro-pores and crack size range. This mechanism of fatigue explains why fatigue in the porous material is continuous under constant stress and why a plastically deforming rock may begin to fatigue when the stress is increased.
- The shielding effect is significantly affected by CO₂ depending on the phase of the CO₂ as well as the presence of other fluids. Stress corrosion due to pore fluid determines the extent of the effect on fatigue rate and modulus

- Further research is needed to know the effect of the phase of CO₂ on tertiary fatigue as well as the phase of CO₂ that affects dry reservoir the most.

Acknowledgment

This work was sponsored by the Petroleum Technology Development Fund (PTDF), Nigeria [PTDF/ED/PHD/ADP/1058/17]. We thank Dr. John Martin and Dr. Carlos Grattoni at the University of Leeds, UK for assistance in conducting the triaxial tests and useful discussions. We also thank the British Geological Society (BGS) for providing the core samples. The first author is grateful to Abubakar Tafawa Balewa University, Bauchi for study leave granted.

References

- Al-Zaidi, E., Fan, X., & Edlmann, K. (2018). The Effect of CO₂ Phase on Oil Displacement in a Sandstone Core Sample. *Fluids*, 3(1), 23.
- Bachu, S. (2000). Sequestration of CO₂ in geological media: criteria and approach for site selection in response to climate change. *Energy conversion and management*, 41(9), 953-970.
- Baud, P., & Meredith, P. (1997). Damage accumulation during triaxial creep of Darley Dale sandstone from pore volumetry and acoustic emission. *International Journal of Rock Mechanics and Mining Sciences*, 34(3-4), 24. e21-24. e10.
- Bemer, E., & Lombard, J. (2010). From injectivity to integrity studies of CO₂ geological storage-chemical alteration effects on carbonates petrophysical and geomechanical properties. *Oil & Gas Science and Technology–Revue de l’Institut Français du Pétrole*, 65(3), 445-459.
- Charles, R. (1958a). Static fatigue of glass. I. *Journal of Applied Physics*, 29(11), 1549-1553.
- Charles, R. (1958b). Static fatigue of glass. II. *Journal of Applied Physics*, 29(11), 1554-1560.
- Charles, R. (1959). *The strength of silicate glasses and some crystalline oxides*. Paper presented at the Proceedings of the international conference on atomic mechanisms of fracture.
- Chitanvis, S. M., Patterson, C. W., Spall, W. D., & Laintz, K. E. (1998). Dynamics of particle removal by supercritical carbon dioxide. In *Supercritical fluid cleaning* (pp. 70-86): Elsevier.
- Colback, P., & Wiid, B. (1965). The influence of moisture content on the compressive strength of rocks. *Geophysics*.
- Delle, C., & Sarout, J. (2016). Effects of water and supercritical CO₂ on the mechanical and elastic properties of Berea sandstone. *International Journal of Greenhouse Gas Control*, 55, 209-220.
- Espinoza, D. N., Jung, H., Major, J. R., Sun, Z., Ramos, M. J., Eichhubl, P., . . . Dewers, T. A. (2018). CO₂ charged brines changed rock strength and stiffness at Crystal Geyser, Utah: Implications for leaking subsurface CO₂ storage reservoirs. *International Journal of Greenhouse Gas Control*, 73, 16-28.
- Fjar, E., Holt, R. M., Raaen, A., Risnes, R., & Horsrud, P. (2008). *Petroleum related rock mechanics* (Vol. 53): Elsevier.
- Fuchs, S. J., Espinoza, D. N., Lopano, C. L., Akono, A.-T., Werth, C. J., ddd, . . . jjj. (2019). Geochemical and geomechanical alteration of siliciclastic reservoir rock by supercritical CO₂-saturated brine formed during geological carbon sequestration. *International Journal of Greenhouse Gas Control*, 88, 251-260.
- Goodman, R. E. (1989). *Introduction to rock mechanics* (Vol. 2): Wiley New York.

- Grgic, D. (2011). Influence of CO₂ on the long-term chemomechanical behavior of an oolitic limestone. *Journal of Geophysical Research: Solid Earth*, 116(B7).
- Grombacher, D., Vanorio, T., & Ebert, Y. (2012). Time-lapse acoustic, transport, and NMR measurements to characterize microstructural changes of carbonate rocks during injection of CO₂-rich water. *Geophysics*, 77(3), WA169-WA179.
- Han, J., Han, S., Kang, D. H., Kim, Y., Lee, J., & Lee, Y. (2020). Application of digital rock physics using X-ray CT for study on alteration of macropore properties by CO₂ EOR in a carbonate oil reservoir. *Journal of Petroleum Science and Engineering*, 189, 107009.
- Hangx, S., Bakker, E., Bertier, P., Nover, G., & Busch, A. (2015). Chemical–mechanical coupling observed for depleted oil reservoirs subjected to long-term CO₂-exposure—A case study of the Werkendam natural CO₂ analogue field. *Earth and Planetary Science Letters*, 428, 230-242.
- Hangx, S., van der Linden, A., Marcelis, F., Bauer, A., Ill, kkkk, . . . iii. (2013). The effect of CO₂ on the mechanical properties of the Captain Sandstone: Geological storage of CO₂ at the Goldeneye field (UK). *International Journal of Greenhouse Gas Control*, 19, 609-619.
- Heap, M. J. (2009). *Creep: time-dependent brittle deformation in rocks*. UCL (University College London),
- Holloway, S., Vincent, C. J., & Kirk, K. (2006). Industrial carbon dioxide emissions and carbon dioxide storage potential in the UK.
- Kranz, R. L. (1980). The effects of confining pressure and stress difference on static fatigue of granite. *Journal of Geophysical Research: Solid Earth*, 85(B4), 1854-1866.
- Lamy-Chappuis, B., Angus, D., Fisher, Q. J., & Yardley, B. W. (2016). The effect of CO₂-enriched brine injection on the mechanical properties of calcite-bearing sandstone. *International Journal of Greenhouse Gas Control*, 52, 84-95.
- Le Guen, Y., Renard, F., Hellmann, R., Brosse, E., Collombet, M., Tisserand, D., & Gratier, J. P. (2007). Enhanced deformation of limestone and sandstone in the presence of high fluids. *Journal of Geophysical Research: Solid Earth*, 112(B5).
- Le Roux, H. (1965). The strength of fused quartz in water vapour. *Proceedings of the Royal Society of London. Series A. Mathematical and Physical Sciences*, 286(1406), 390-401.
- Lei, X., & Xue, Z. (2009). Ultrasonic velocity and attenuation during CO₂ injection into water-saturated porous sandstone: Measurements using difference seismic tomography. *Physics of the Earth and Planetary Interiors*, 176(3-4), 224-234.
- Li, Yang, D., Zhong, Z., Sheng, Y., Liu, X., ddd, . . . ddd. (2018). Experimental investigation on the micro damage evolution of chemical corroded limestone subjected to cyclic loads. *International Journal of Fatigue*, 113, 23-32.
- Li, S., Zhang, S., Zou, Y., Ma, X., Ding, Y., Li, N., . . . Kasperczyk, D. (2020). Pore structure alteration induced by CO₂–brine–rock interaction during CO₂ energetic fracturing in tight oil reservoirs. *Journal of Petroleum Science and Engineering*, 107147.
- Li, X., Qi, C., & Zhang, P. (2020). A micro-macro confined compressive fatigue creep failure model in brittle solids. *International Journal of Fatigue*, 130, 105278.
- Liteanu, E., Niemeijer, A., Spiers, C., Peach, C., & De Bresser, J. (2012). The effect of CO₂ on creep of wet calcite aggregates. *Journal of Geophysical Research: Solid Earth*, 117(B3).
- Liu, B., Suzuki, A., & Ito, T. (2020). Estimating the seepage effect of SC-CO₂ and water fracturing with a steady-state flow model considering capillary and viscous forces at the pore scale. *Journal of Petroleum Science and Engineering*, 184, 106483.
- Makhnenko, R. Y., Vilarrasa, V., Mylnikov, D., & Laloui, L. (2017). Hydromechanical aspects of CO₂ breakthrough into clay-rich caprock. *Energy procedia*, 114, 3219-3228.
- Marbler, H., Erickson, K. P., Schmidt, M., Lempp, C., & Pöllmann, H. (2013). Geomechanical and geochemical effects on sandstones caused by the reaction with supercritical CO₂: an experimental approach to in situ conditions in deep geological reservoirs. *Environmental earth sciences*, 69(6), 1981-1998.

- Mikhaltsevitch, V., Lebedev, M., & Gurevich, B. (2014). Measurements of the elastic and anelastic properties of sandstone flooded with supercritical CO₂. *Geophysical Prospecting*, 62(6), 1266-1277.
- Muñoz-Ibáñez, A., Falcon-Suarez, I. H., Marín-Moreno, H., Delgado-Martín, J., & Mackin, P. (2020). Transport properties of saline CO₂ storage reservoirs with unconnected fractures from brine-CO₂ flow-through tests. *Journal of Petroleum Science and Engineering*, 184, 106551.
- Ngwenya, B. T., Main, I. G., Elphick, S. C., Crawford, B. R., & Smart, B. G. (2001). A constitutive law for low-temperature creep of water-saturated sandstones. *Journal of Geophysical Research: Solid Earth*, 106(B10), 21811-21826.
- Oikawa, Y., Takehara, T., & Tosha, T. (2008). *Effect of CO₂ injection on mechanical properties of Berea Sandstone*. Paper presented at the The 42nd US Rock Mechanics Symposium (USRMS).
- Olabode, A., & Radonjic, M. (2013). Experimental investigations of caprock integrity in CO₂ sequestration. *Energy procedia*, 37, 5014-5025.
- Peng, Fan, J., Zhang, X., Chen, J., Li, Z., Jiang, D., & Liu, C. (2020). Computed tomography analysis on cyclic fatigue and damage properties of rock salt under gas pressure. *International Journal of Fatigue*, 134, 105523.
- Peng, K., Zhou, J., Zou, Q., & Yan, F. (2019). Deformation characteristics of sandstones during cyclic loading and unloading with varying lower limits of stress under different confining pressures. *International Journal of Fatigue*, 127, 82-100.
- Pimienta, L., Esteban, L., Sarout, J., Liu, K., Dautriat, J., Delle Piane, C., & Clennell, M. B. (2017). Supercritical CO₂ injection and residence time in fluid-saturated rocks: Evidence for calcite dissolution and effects on rock integrity. *International Journal of Greenhouse Gas Control*, 67, 31-48.
- Plug, W.-J., & Bruining, J. (2007). Capillary pressure for the sand-CO₂-water system under various pressure conditions. Application to CO₂ sequestration. *Advances in Water Resources*, 30(11), 2339-2353.
- Renard, F., Gundersen, E., Hellmann, R., Collombet, M., & Le Guen, Y. (2005). Numerical modeling of the effect of carbon dioxide sequestration on the rate of pressure solution creep in limestone: Preliminary results. *Oil & gas science and technology*, 60(2), 381-399.
- Rice-Birchall, E. (2018). Geomechanical and geochemical analysis of the Captain X Sandstone Member in relation to CO₂ sequestration.
- Rinehart, A. J., Dewers, T. A., Broome, S. T., & Eichhubl, P. (2016). Effects of CO₂ on mechanical variability and constitutive behavior of the Lower Tuscaloosa Formation, Cranfield Injection Site, USA. *International Journal of Greenhouse Gas Control*, 53, 305-318.
- Rutqvist, J. (2012). The geomechanics of CO₂ storage in deep sedimentary formations. *Geotechnical and Geological Engineering*, 30(3), 525-551.
- Saraji, S., Piri, M., & Goual, L. (2014). The effects of SO₂ contamination, brine salinity, pressure, and temperature on dynamic contact angles and interfacial tension of supercritical CO₂/brine/quartz systems. *International Journal of Greenhouse Gas Control*, 28, 147-155.
- Scholz, C. (1968). Mechanism of creep in brittle rock. *Journal of Geophysical Research*, 73(10), 3295-3302.
- Vanorio, T., Nur, A., & Ebert, Y. (2011). Rock physics analysis and time-lapse rock imaging of geochemical effects due to the injection of CO₂ into reservoir rocks. *Geophysics*, 76(5), O23-O33.
- Vilarrasa, V., Makhnenko, R. Y., & Rutqvist, J. (2019). Field and laboratory studies of geomechanical response to the injection of CO₂. In *Science of Carbon Storage in Deep Saline Formations* (pp. 159-178): Elsevier.
- Williams, J. D., Fellgett, M. W., Quinn, M. F., eee, eee, fff, . . . ddd. (2016). Carbon dioxide storage in the Captain Sandstone aquifer: determination of in situ stresses and fault-stability analysis. *Petroleum Geoscience*, 22(3), 211-222.

716 Zhang, C.-L. (2017). Examination of effective stress in clay rock. *Journal of Rock Mechanics and*
717 *Geotechnical Engineering*, 9(3), 479-489.

718