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Permeability evolution in sandstone due to injection of CO_2-saturated brine or supercritical CO_2 at reservoir conditions

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Abstract

We measured the change in permeability of two selected sandstones (Berea, Fonteinebleau) due to injection of CO_2-saturated ("live") brine, unsaturated ("dead") brine or supercritical (sc) CO_2 at reservoir conditions. We found that the permeability did not significantly change in a clean sandstone consisting of pure quartz (Fonteinemebleau) due to live or dead brine injection, although permeability changed due to $scCO_2$ injection by ~23%. The permeability in the Berea sandstone, however, changed due to live or dead brine injection, by up to 35%; this permeability reduction in Berea sandstone was likely caused by fines release and subsequent pore throat plugging as the damage was more significant at higher injection rates. We expect that this phenomenon – i.e. rock permeability reduction due to CO_2 injection into the formation – can have a significant and detrimental influence on CO_2 injectivity, which would be reduced accordingly.

Keywords: permeability reduction, sandstone, CO_2-saturated brine, live brine, supercritical CO_2, injectivity decrease

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1. Introduction

Injection of CO_2 deep into the subsurface is a recognized method to reduce anthropogenic greenhouse gas emissions [1]. During this process, CO_2 sweeps the target formation and is eventually immobilized by structural [2,3], residual [4-6], dissolution [7,8] or mineral [9.10] trapping mechanisms. The injected CO_2 is partially miscible with the resident brine (up to 0.01mol% of water can be dissolved in CO_2 at 323K and 20MPa, [11]; and up to 2.6mol% of CO_2 can dissolve in brine, [12]) and reacts with the water to form an acidic environment [8]:

$$CO_2(sc) + 3\ H_2O \leftrightarrow CO_2(aq) + 3\ H_2O \qquad (a)$$

$$H_2O + CO_2(aq) \leftrightarrow H_2CO_3 \qquad (b)$$

$$H_2CO_3 \leftrightarrow HCO_3^- + H^+ \qquad (c)$$

$$HCO_3^- \leftrightarrow CO_3^{2-} + H^+ \qquad (d)$$

Scheme 1: Formation and dissociation of carbonic acid.

When inspecting scheme 1 several conclusions can be reached:

a) as the partial CO_2 pressure is high at reservoir conditions, reaction (a) is shifted to the right, which causes
b) increased formation of carbonic acid (reaction (b)) according to Le Chatelier's principle, which again
c) significantly increases proton concentration (reaction (c)), thus significantly lowering the pH value.

Schaeff and McGrail [13] and Sigfusson et al. [14] report that the acidity created can reach significant levels (pH values 3-4 were measured at reservoir conditions for CO_2-saturated ("live") brine); and it is well established that such acidic environments can severely impact on the permeability and pore morphology of limestones: the acid "eats" into the carbonate forming large holes, so-called "wormholes" (e.g. [15-17]), which dramatically increase the permeability of the rock. This is a very significant effect, which, however, Gilfillan et al. [18] claim is a buffered reaction at reservoir scale (pH values increase to ~5.5).

Canal et al. [19] reported a similar effect in a Spanish sandstone, where live brine led to a four-fold increase of permeability. The sandstone Canal et al. [19] investigated contained 92.1vol% quartz, 5.0vol% kaolinite, 0.3vol% Mg-calcite, 0.5vol% K-feldspar, 0.1vol% muscovite, 0.9vol% goethite, 0.03vol% apatite and 0.1vol% rutile; based on chemical analysis of the effluents they concluded that mainly the Mg-calcite dissolved and was transported out of the plug. Indeed, sandstone typically contains considerable quantities of components (cements, clays) other than quartz (e.g. [20-23]), and these impurities usually have a substantially higher reactivity in an acidic environment than quartz [22,24]. Dissolution of such components is thus expected to increase permeability. However, sandstone is frequently considered to be pure quartz, and it is thus usually assumed that the permeability of sandstone reservoirs does not change due to CO_2 injection (e.g. [5,25,26]).

A phenomenon related to this, which received less attention, but which can also have a dramatic impact on reservoir permeability, is the decrease in permeability due to the injection of supercritical (sc) CO_2 and associated live brine flow. This effect has been observed by a number of researchers [27,28] who report permeability decreases up to 60% and hypothesize that it is caused by either mineral precipitation or fines migration.

From a carbon geo-storage project perspective this is a highly significant effect, because - as Wiese et al. [29] pointed out - aquifer permeability has a dominant effect on injectivities. Permeability and permeability changes thus need to be carefully assessed prior to CO_2 injection to avoid project failure.

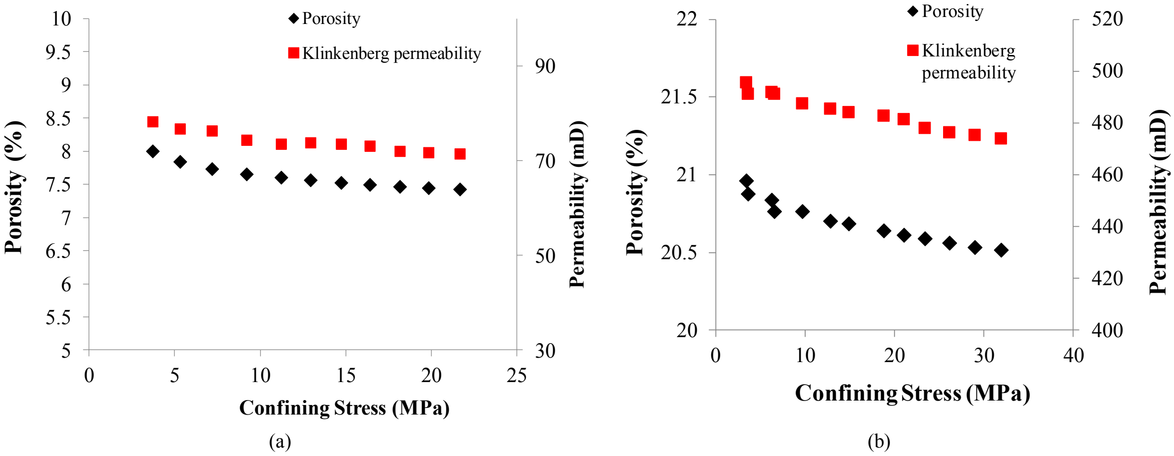
In this work we flooded sandstone plugs with live brine and $scCO_2$ and measured the permeability evolution with time; we demonstrate that the permeability reduction can be significant and is caused by fines migration, and not by mineral precipitation.

2. Experimental Methodology

A Berea and a Fonteinebleau sandstone plug were selected for the experiments, their petrophysical and chemical properties are listed in Table 1. Porosity and nitrogen permeability were measured as a function of confining stress with an AP-608 Coretest instrument; Figure 1 shows that porosity and permeability only slightly depended on effective stress. The compositions of the plugs were measured via XRD with a Bruker-AXS D8 Advance Diffractometer on fragments obtained from the same blocks just adjacent to the drill holes.

Table 1: Petrophysical and chemical properties of the sandstone plugs used in the experiments (porosity and permeability values reported were measured at 10.69MPa effective stress).

sample	porosity [%]	Klinkenberg permeability [mD]	composition	length [mm]	diameter [mm]
Berea	20.6	490	95wt% quartz, 4wt% alumina, 0.1wt% ferric oxide, 0.55wt% ferrous oxide, 0.25wt% magnesium oxide, 0.1wt% calcium oxide	80.7	38.7
Fonteinebleau	7.9	78.8	100wt% quartz	84.1	38.2



(a) (b)

Fig. 1. Porosity and Klinkenberg permeability of (a) Fonteinebleau, (b) Berea sandstone as a function of effective stress.

After the porosity and permeability tests, each plug was wrapped in PTFE tape, Aluminum foil, and again PTFE tape. The specimen was then covered by a heat-shrinkable PTFE sleeve, which was cured with a heat gun, and finally placed in a rubber sleeve. For a flooding experiment, a plug was then housed in a high pressure elevated temperature core holder, which was initially vaccumed for more than 24 hours (to remove air), and then saturated with dead brine (5 wt% NaCl + 1 wt% KCl in deionized water). Subsequently the confining stress was increased to 10.69MPa, the rig heated to 323K (± 1K) and brine pore pressure was increased to 10MPa by a high precision syringe pump; these thermophysical conditions approximately correspond to a storage formation at 1000m depth. Finally dead brine was injected into the plug with a second high precision syringe pump at constant flow rates, which were stepwise increased (0.3, 1, 2, 3, 5, 10, 20, 50 mL/min); this flooding sequence was repeated with live brine; the live brine was prepared in a mixing reactor described earlier [30]. The pressure drop across the plug was continuously measured with high accuracy pressure sensors (Keller 33X, accuracy = ±1500Pa), and the associated dynamic permeability was calculated with Darcy's law. For the Fonteinebleau plug, three permeability tests with dead and live brine were performed, but between each test $scCO_2$ was injected, again at increasing flow rates up to capillary pressures of ~80kPa (the detailed procedure for this measurement is described elsewhere [31]).

3. Results and discussion

Figure 2 shows the pressure drop evolution with time measured for the Berea sample for the different flow rates used (left: dead brine; right: live brine). As expected a higher flow rate increased the pressure drop significantly; furthermore, it is clear that the pressure drop also continuously and significantly increased with time for constant flow rates. This effect was stronger for live brine injection, but it was also observed for dead brine. An increasing pressure gradient is equivalent to a decreasing brine permeability as illustrated in Figure 3.

The decrease in permeability Δk was related to the injection flow rate, a higher flow rate led to larger Δk, Table 2. This is an indication of fines transport, which should be more significant at higher flow rates as then the shear stresses which release the fines are higher [32]. Moreover, if one hypothesizes that reactive transport, the second possible plugging mechanism, see above, is responsible for the Δk, then it would be expected that the Damköhler number (= ratio of reaction timescale to convective mass flow timescale) is reduced at higher flow rates thus more plugging should happen at lower flow rates. This is therefore indirect evidence that the formation damage is caused mainly due to fines migration. In addition, the permeability continuously and smoothly dropped with progressing time and we expect a further drop with further extended injection time. This is consistent with Sayegh et al.'s [27] results; we note that Sayegh et al. [27] observed an increase in permeability at significantly longer time scales.

The overall permeability decrease for live brine lied between 10% (1 mL/min flow rate) to 35% (50mL/min flow rate), which is consistent with data reported by Sayegh et al. [27] and Mohamed et al. [28]. This drop in permeability is highly significant and implies that injectivities will be detrimentally affected during live brine migration through a storage formation having similar geochemical characteristics as Berea sandstone. We note that live brine is present in all reservoir volumes swept by $scCO_2$, including the advancing brine front which has been loaded with CO_2 [33] and deeper areas into which live brine sinks due to gravitational instabilities [34].

The picture for Fonteinebleau sandstone was quite different though: essentially brine permeability was only marginally affected by live or dead brine, Figures 4-6 and Table 2. We explain this difference with the different chemical composition of Fonteinebleau (Table 1), Fonteinebleau is pure quartz, and apparently does not easily release colloids or fines. However, injection of $scCO_2$ into the Fonteinebleau plug significantly decreased brine permeability (by ~23%) and a milky-coloured effluent was observed; cp. Figure 6: $scCO_2$ was injected after each test, the permeability was reduced substantially after the first CO_2 injection (change from test 1 to test 2), but not after the second CO_2 flood.

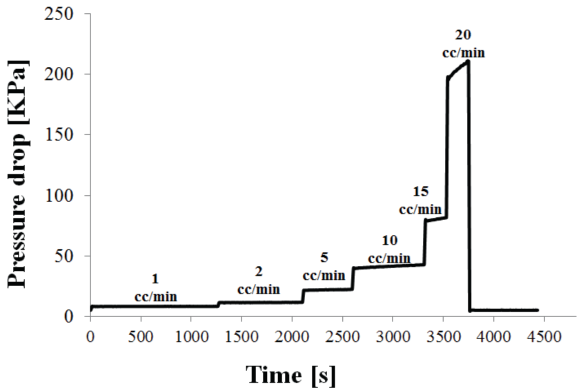


Fig. 2a. Change in pressure drop across the Berea sample as a function of dead brine injection time and injection rate.

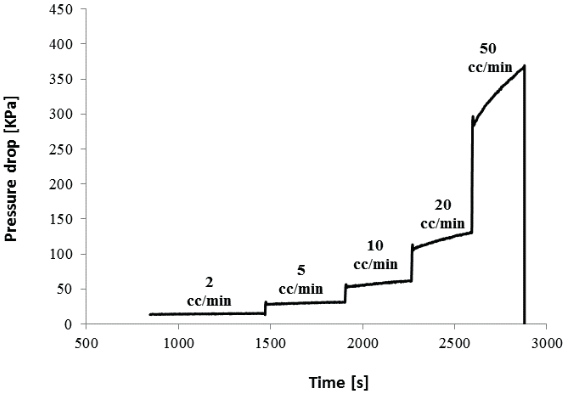


Fig. 2b. Change in pressure drop across the Berea sample as a function of live brine injection time and injection rate.

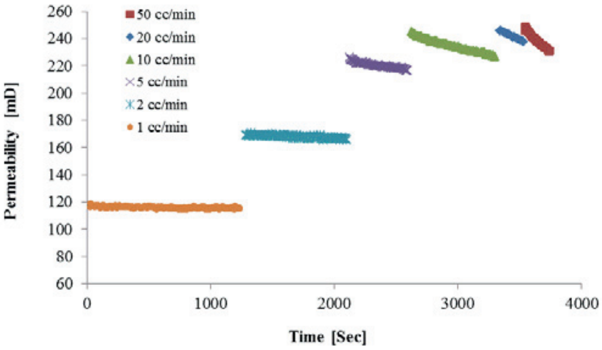


Fig. 3a. Change in permeability of the Berea sample as a function of dead brine injection time and injection rate.

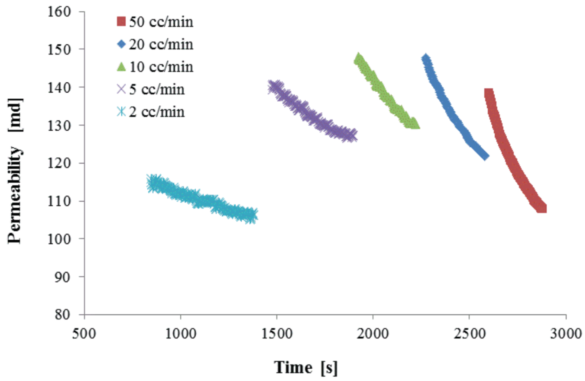


Fig. 3b. Change in permeability of the Berea sample as a function of live brine injection time and injection rate.

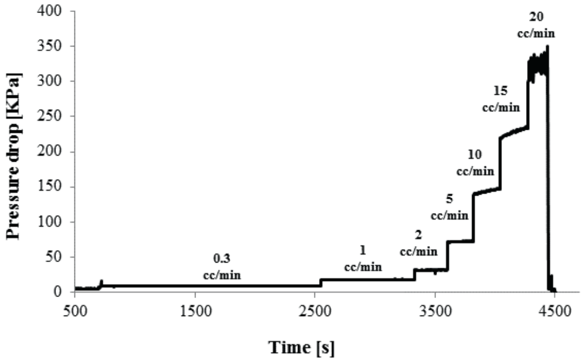


Fig. 4a. Fonteinebleau test 1: change in pressure drop across the sample as a function of dead brine injection time and injection rate.

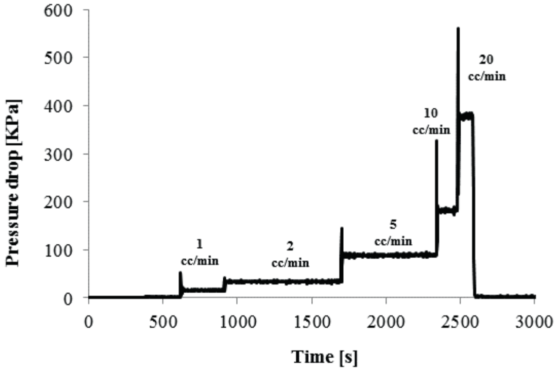


Fig. 4b. Fonteinebleau test 3: change in pressure drop across the sample as a function of dead brine injection time and injection rate.

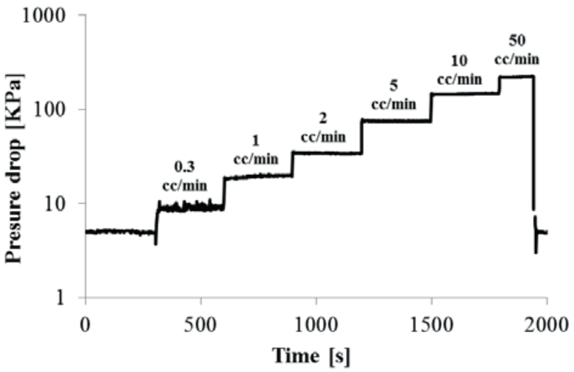


Fig. 5a. Fonteinebleau test 1: change in pressure drop across the sample as a function of live brine injection time and injection rate.

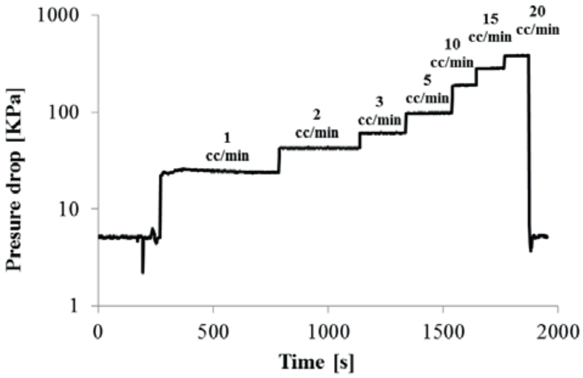


Fig. 5b. Fonteinebleau test 2: change in pressure drop across the sample as a function of live brine injection time and injection rate.

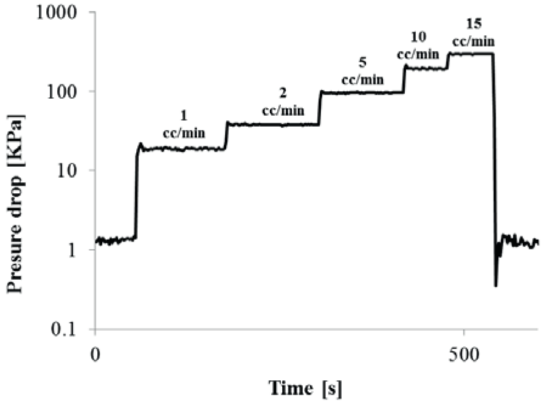


Fig.5c. Fonteinebleau test 3: change in pressure drop across the sample as a function of live brine injection time and injection rate.

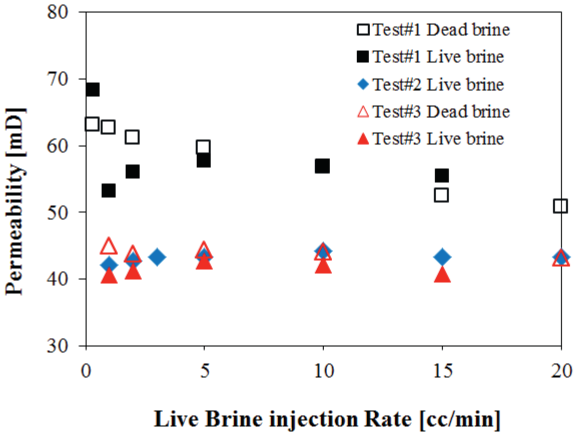


Fig. 6a. Changes in brine permeability of the Fonteinebleau sample as a function of live brine injection time and injection rate for the three tests conducted.

Table 2: Permeability changes in Berea and Fonteinebleau sandstone due to dead or live brine injection.

sample	Flow rate [mL/min]	Brine permeability before flooding [mD]	Brine permeability after flooding [mD]	Permeability change [%]
Berea - dead brine	1	116.5	116.0	0.5
	2	169.2	166.0	3.1
	5	226.3	216.8	9.5
	10	245.0	226.9	18.0
	20	245.6	237.7	7.9

	50	248.2	230.3	17.8
Berea - live brine	1	104.9	96.9	7.9
	2	138.9	122.3	16.5
	5	164.4	148.5	16.0
	10	169.3	150.9	18.4
	20	168.7	141.8	26.9
	50	161.1	125.6	35.5
Fonteinebleau – test 1 Dead brine	0.3	62.9	60.4	2.4
	1	62.1	61.6	0.5
	2	61.0	60.6	0.3
	5	56.4	56.0	0.4
	10	56.7	54.8	1.8
	15	52.7	48.1	4.6
	20	50.8	48.3	2.5
Fonteinebleau – test 1 live brine	0.3	68.3	62.6	5.7
	1	53.2	52.6	0.6
	2	56.5	56.3	0.2
	5	57.3	57.1	0.1
	10	57.0	56.8	0.1
	15	55.3	54.9	0.4
Fonteinebleau – test 3 dead brine	1	45.3	44.8	0.5
	2	44.1	42.9	1.1
	5	44.5	44.2	0.2
	10	44.6	44.4	0.1
	20	43.0	42.9	0.1
Fonteinebleau – test 3 live brine	1	40.5	40.1	0.4
	2	42.8	42.4	0.3
	5	42.6	42.5	0.1
	10	42.0	41.8	0.1
	15	41.0	40.8	0.1

Conclusions

We conclude that the permeability of sandstone storage rock can be significantly reduced by live brine or $scCO_2$ flow. The Berea sample was probably damaged by fines release, migration and pore throat plugging as higher permeability reductions were observed for higher flow rates (while mineral precipitation in a hypothesized reactive transport model should increase plugging with reduced flow rate). We measured a maximum drop in permeability of 35%; consistent with data reported by Sayegh et al. [27] (up to 60% drop reported), or Mohamed et al. [28] (up to 53% drop reported). We note, however, that after extended time (4-10 hours) Sayegh et al. (1990) measured an increase in permeability, but the permeability never reached again the original value and remained substantially reduced. It is thus likely that live brine movement through typical sandstone storage rock (which contains impurities such as cements and clays) damages the reservoir. We also note that dead brine, particularly at higher flow rates, can significantly reduce permeability. Furthermore we observed that live or dead brine injection did not significantly affect the permeability of a clean sandstone (Fonteinebleau); however, injection of $scCO_2$ substantially reduced the Fonteinebleau rock permeability (by ~ 23%). Considering that permeability is – apart from formation thickness - the dominant variable determining injectivities [29], these effects should be assessed in more detail and we recommend that these relationships should be evaluated for all storage rocks.

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