Can a Fractured Caprock Selfheal?

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Abstract

The ability of geologic seals to prevent leakage of fluids injected into the deep subsurface is critical for mitigating risks associated with greenhouse-gas sequestration and natural-gas production. Fractures caused by tectonic or injection-induced stresses create potential leakage pathways that may be further enhanced by mineral dissolution. We present results from reactive-flow experiments in fractured caprock (dolomitic anhydrite), where additional dissolution occurs in the rock matrix adjacent to the fracture surfaces. Preferential dissolution of anhydrite left a compacted layer of dolomite in the fractures. At lower flow rate, rock-fluid reactions proceeded to near equilibrium within the fracture with preferential flow paths persisting over the 6-month duration of the experiment and a negligible change in permeability. At higher flow rate, permeability decreased by a dramatic two orders of magnitude. This laboratory-scale observation of self-healing argues against the likelihood of runaway permeability growth in fractured porous caprock composed of minerals with different solubilities and reaction kinetics. However, scaling arguments suggest that at larger length scales this self-healing pro-

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cess may be offset by the formation of dissolution channels. Our results have relevance beyond the greenhouse-gas sequestration problem. Chemical disequilibrium at waste injection sites and in hydrothermal reservoirs will lead to reactive flows that may also significantly alter formation permeability.

Keywords: *Reactive flow, Caprock integrity, Mineral dissolution, Mechanical deformation, Permeability alteration, Dolomitic anhydrite.*

1. Introduction

Injection of fluids into deep saline aquifers or depleted oil and gas reservoirs is a promising strategy for CO₂ sequestration [Hitchon et al., 1999; Bachu, 2000; Metz et al., 2005; Kumar et al., 2005] and waste fluids disposal [Tsang et al., 2008]. However, fluid injection increases pore pressure in the targeted geologic formation, creating vertical pressure gradients that can drive flow towards the surface. Successful long-term isolation of injected fluids requires geologic seals, or caprocks, with large vertical extent or very low permeability and ideally both. Lab-scale measurements of caprock permeability provide a means for predicting leakage rates through intact caprock. But, preexisting fractures in the caprock layer or fractures induced by the injection process can provide flow paths that are orders-of-magnitude more conductive than the intact rock.

Fracture permeability is influenced by the roughness of the fracture surfaces [e.g., Brown, 1987], the degree of mismatch (or shear displacement) between the surfaces [e.g., Wang et al., 1988; Mallikamas and Rajaram, 2005], the stress applied to the fracture [e.g., Cook, 1992; Durham and Bonner,

19 1994], and the gouge created during fracturing events [e.g., Faoro et al.,
20 2009; Elkhoury et al., 2011]. Predicting the potential for fractures to provide
21 leakage pathways is further complicated by the possibility for fracture perme-
22 ability to change with time due to injection-induced perturbations in stress
23 and fluid chemistry. Stress perturbations lead to mechanical deformation
24 and fracture propagation that can increase or decrease formation permeabil-
25 ity [Bandis et al., 1983; Liu, 2005; Elkhoury et al., 2006, 2011; Candela et al.,
26 2011; Renard et al., 2012; Mason et al., 2013]. Chemical disequilibrium be-
27 tween fluids and resident minerals leads to dissolution or precipitation that
28 further alter fracture porosity and permeability [Lowell et al., 1993; Durham
29 et al., 2001; Berkowitz, 2002; Chaudhuri et al., 2008; Wigand et al., 2009;
30 Smith et al., 2013; Mason et al., 2013; Noiriél et al., 2013; Elkhoury et al.,
31 2013].

32
33 The relative magnitudes of the timescales associated with advection through
34 a fracture (τ_a) and reactions at mineral surfaces (τ_r) determines the nature
35 of fracture permeability evolution (Figure S1). When thermodynamics fa-
36 vor mineral dissolution and the residence time is long relative to reaction
37 time scales (i.e., $\tau_a/\tau_r \gg 1$), dissolution-induced aperture growth occurs
38 predominantly along preferential flow paths. The resulting reaction-front in-
39 stabilities create the potential for runaway permeability increases [Durham
40 et al., 2001; Detwiler et al., 2003; Elkhoury et al., 2013]. Conversely, at
41 higher flow rates ($\tau_a/\tau_r \ll 1$) dissolution occurs more uniformly throughout
42 the fracture [Elkhoury et al., 2013] and may even be fastest in the smallest
43 aperture regions [Detwiler et al., 2003]. Furthermore, computational sim-

44 ulations of reactive alteration show that, because residence times within a
45 fracture depend upon the fluid velocity and fracture length, at higher flow
46 rates reaction instabilities can still occur, but at length scales larger than
47 typical laboratory experiments [Szymczak and Ladd, 2011; Elkhoury et al.,
48 2013].

49

50 Under reservoir conditions, both pore pressure and fluid chemistry perturba-
51 tions are likely. Laboratory-scale experiments aimed at quantifying fracture
52 permeability evolution due to coupled deformation and dissolution demon-
53 strate a confounding range of behaviors: increased permeability [Elkhoury
54 et al., 2013], decreased permeability [Ellis et al., 2013] and nonmonotonic
55 changes in permeability [Polak et al., 2004]. Due to either experimental
56 constraints or expediency these studies often involve conditions that differ
57 from those encountered in the reservoir. For example it is difficult to ac-
58 curately measure small differential pressures in experiments carried out at
59 pore pressures of $O(10^7 \text{ Pa})$, so differential pressures are often $O(10^5 \text{ Pa})$ or
60 larger, resulting in pressure gradients of 10s or even 100s of MPa/m (head
61 gradients of 10^3 to 10^4). However, it is difficult to imagine the field condi-
62 tions under which such large pressure gradients would be sustained. This
63 results in experiments where $\tau_a/\tau_r \ll 1$ and dissolution occurs relatively uni-
64 formly throughout the fracture (regardless of aperture variability) and may
65 be fastest in small aperture regions. The resulting increasing stresses at
66 eroding contacts leads to pressure solution [Yasuhara et al., 2004] or brittle
67 failure [Detwiler, 2008] and subsequent permeability loss.

68

69 The choice of fluid chemistry also influences the evolution of fracture dis-
 70 solution. When studying the influence of CO₂ injection, a natural choice
 71 for injected fluid is a brine in equilibrium with host minerals equilibrated
 72 with CO₂ at reservoir pressure, which leads to influent fluids with pH $\lesssim$ 4
 73 [Elkhoury et al., 2013; Smith et al., 2013]. However, fluids leaking through a
 74 fractured caprock are likely to exhibit a wide range of compositions. Monitor-
 75 ing of reservoir fluids over 10 years of intermittent water and CO₂ injection at
 76 the Weyburn site show $5 < \text{pH} < 6$ [Burrowes and Gilboy, 2001]. This is due
 77 to a combination of buffering due to dissolution of CaCO₃ in the reservoir,
 78 mixing of injected water with CO₂-equilibrated brine, and propagation of in-
 79 creased pressures far beyond CO₂ plumes. This suggests that fluids expected
 80 to leak through a caprock will likely exhibit a wide range of compositions
 81 with near-equilibrium with CO₂ at reservoir pressure a low-pH end member.
 82 Using such low-pH fluids in laboratory experiments increases reaction rates
 83 with carbonates and decreases τ_r , thus shortening the required duration of
 84 experiments. However, it also has implications on permeability evolution
 85 as it will increase the value of τ_a/τ_r , leading to the formation of dissolution
 86 channels and increased permeability observed in some experiments [Elkhoury
 87 et al., 2013].

88

89 Despite the simplifications inherent in laboratory-scale studies, such experi-
 90 ments provide invaluable insights into the competing processes that lead to
 91 permeability alteration. However, the relevant simplifications must be placed
 92 in the proper context; for example, there is mounting evidence that, though
 93 initial fracture aperture variability plays an important role in establishing

94 the initial fracture permeability, it plays a second-order role in controlling
95 the evolution of the fracture aperture relative to the transport and reaction
96 timescales [Szymczak and Ladd, 2011; Elkhoury et al., 2013].

97

98 In this study, we performed reactive flow experiments in fractured cores from
99 a dolomitic anhydrite ($\text{CaMg}(\text{CaO}_3)_2$, CaSO_4) caprock. We explored the rel-
100 ative importance of advective and reactive timescales during flow of a reactive
101 fluid (water) in a mineral assemblage commonly found in caprocks overlying
102 oil and gas reservoirs. We present results from two experiments in frac-
103 tured cores with flow rates (and τ_a) differing by two orders of magnitude to
104 determine the potential for caprock self-healing under this range of param-
105 eters. We chose the duration of both experiments so that an equal amount
106 of mass dissolved from each sample, which required the low-flow-rate exper-
107 iment to run for 6 months. Unlike previous experiments with very reactive
108 fluids in carbonate cores, our experiments exhibited measurable dissolution
109 within the porous matrix adjacent to the fracture suggesting that the dif-
110 fusion timescale in the porous matrix is faster than the reaction time scale.
111 In both experiments, dissolution weakened the porous matrix adjacent to
112 the fracture, which led to a two-order-of-magnitude permeability decrease at
113 high flow rate and negligible permeability change at low flow rate.

114 2. Experimental Description

115 To minimize mineralogical heterogeneity between samples, we took both
116 samples from a single 15-cm-long, 9-cm-diameter core from the evaporite
117 that forms the first layer of caprock overlying the Weyburn-Midale reservoir

118 in Saskatchewan, Canada [Wilson and Monea, 2004]. We drilled 3.8-cm-
119 diameter sub-cores centered on tensile fractures within the larger core to
120 minimize the impact of damage caused during fracturing. Sample lengths
121 were 6.3 cm (EV1) and 4.9 cm (EV2) and the initial rock masses were 213 g
122 and 163 g for EV1 and EV2, respectively (See Table 1 for complete details of
123 the two experiments).

124

125 Although fractures provide preferential flow paths, the permeability of well-
126 mated fractures subjected to a confining stress typical of reservoir conditions
127 have permeabilities that are similar to intact cores [e.g., Durham and Bonner,
128 1994]. For the case of the dolomitic anhydrite cap rock used in our exper-
129 iments, the intact permeability is on the order of 10^{-19} m^2 [Smith et al.,
130 2013]. Thus, effective leakage pathways will require some shear displacement
131 of the fracture surfaces to create the potential for sustained flow at pressure
132 gradients consistent with those expected in the field. We increased the per-
133 meability in our well-mated tensile fractures by shear offsetting the fracture
134 surfaces prior to mating by 0.051 and 0.038 cm for EV1 and EV2, respec-
135 tively. We placed shims between the endcaps and rock sample (Figure S2) to
136 maintain these displacements when applying confining stress to the samples.
137 These fractures differ from shear fractures induced under significant normal
138 stress due to the absence of gouge; however, they provide the ability to care-
139 fully characterize the surface and fracture geometry prior to flow-through
140 experiments.

141

142 Under reservoir conditions, in regions not directly overlying the CO_2 plume,

dissolution will be relatively slow due to high ionic concentrations of typical reservoir fluids. To accelerate the dissolution and facilitate lab-scale experiments at reasonable timescales (months), we used de-ionized water as the reactive fluid. Furthermore, speciation calculations using PHREEQC [Parkhurst and Appelo, 1999], show that flowing water instead of CO₂-equilibrated brine increases the solubility of anhydrite, and only significantly influences the solubility of dolomite relative to anhydrite at very high pCO₂ (low pH) (see Appendix A for details).

To begin the experiments, we jacketed the fractured cores and secured them in a flow-through reactor and applied a 7 MPa confining stress (Figures S2 and S3). A high-pressure ISCO syringe pump controlled the confining pressure, while two additional ISCO syringe pumps, connected in parallel, continuously pushed de-aired de-ionized water at a temperature of 21°C through the fractured sample at a constant flow rate ($Q_{EV1} = 0.01$ ml/min and $Q_{EV2} = 0.6$ ml/min) with pressure controlled at the outlet (Figures S2 and S3 and Elkhoury et al. [2013] for additional details of the experimental apparatus).

Prior to each flow-through experiment, we characterized the fracture surfaces and reconstructed the aperture fields (Figure 1) using a high-resolution optical profilometer [Ameli et al., 2013; Elkhoury et al., 2013]. During experiments, we periodically analyzed effluent, using an ion chromatograph (Metrohm 850 Professional IC), for Mg²⁺, Ca²⁺ and SO₄²⁻ concentrations, c , which provided direct estimates of the evolving dissolution rates, $R(t) =$

168 $Q \times c(t)$. After the flow-through experiments, we characterized each sample
 169 differently. For EV1 we performed low-resolution x-ray computed tomog-
 170 raphy (CT) scans and then impregnated the sample, under vacuum, with
 171 red-colored epoxy and sliced it in sections perpendicular to the fracture. We
 172 used optical photographs of the slices to measure aperture profiles after the
 173 flow-through experiment. For EV2, we separated the two halves of the frac-
 174 tured core, with some difficulty, dried the core, and brushed off dolomite
 175 from the two halves of the sample. Then, we re-scanned the fracture surfaces
 176 with the optical profilometer [Ameli et al., 2013] and obtained the thickness
 177 of the evaporite layer that was altered by dissolution during the experiment.

178
 179 Due to the large difference in flow rates between the two experiments, we
 180 ran EV1 for 180 days and EV2 for 7 days to ensure a similar amount of total
 181 dissolution from both cores ($\sim 2.5\%$ of the initial total mass). To compare
 182 results from the two experiments, we normalized time, t , by $T = \frac{M_o}{R(t \sim 0)}$
 183 where M_o is the initial total mass of the sample. The cumulative mass dis-
 184 solved at time t is then $M(t) = \int_0^t R(\zeta) d\zeta$ and T is the time at which the
 185 entire rock mass would dissolve at the initial dissolution rate.

187 **3. Results**

188 Initial fracture aperture fields calculated for both samples allow a direct
 189 assessment of the relative similarity of the initial conditions for both exper-
 190 iments (Figure 1). Both fractures exhibit similar small-scale roughness and
 191 isolated regions of large fracture aperture caused by pieces of rock that were

192 damaged during fracturing. The median fracture apertures in the absence
193 of a confining stress are approximately 65 and 135 μm for EV1 and EV2,
194 respectively. Because the small-scale aperture variability is similar for both
195 fractures, we expect that the characteristics of the contact regions between
196 the fracture surfaces are qualitatively similar for the two experiments when
197 the 7 MPa confining stress was applied during flow-through experiments.
198 The difference in fracture aperture between the two samples is consistent
199 with the initial measured permeabilities of $2.0 \times 10^{-15} \text{m}^2$ and $5.6 \times 10^{-14} \text{m}^2$ for
200 EV1 and EV2, respectively.

201
202 We observed a striking difference in the evolution of permeability between ex-
203 periments EV1 and EV2 (Figure 2). For low flow rate (EV1), there was a neg-
204 ligible change in pressure differential over the 6-month duration of the exper-
205 iment indicating near-constant permeability. In contrast, for high flow rate
206 (EV2), the pressure differential across the fracture increased from $\sim 5 \text{kPa}$
207 to $\sim 700 \text{kPa}$ indicating more than two-order-of-magnitude decrease in per-
208 meability, κ , from 5.6×10^{-14} to $6.1 \times 10^{-16} \text{m}^2$ (Figure 2). It is especially
209 noteworthy that the fracture with the larger initial aperture (EV2) exhibited
210 the significant permeability reduction. To better understand this significant
211 difference in permeability evolution, we analyzed the changes in the spatial
212 distribution of mass within the two fractures.

213
214 At higher flow rate (EV2), dissolution of the anhydrite fracture surfaces left a
215 porous layer of dolomite within the fracture aperture (Figure 3). Because the
216 remaining layer of dolomite was more porous and weaker than the unaltered

217 dolomitic anhydrite fracture surface, the confining stress caused compaction
 218 of the dolomite layer. This resulted in a decreased sample diameter (perpen-
 219 dicular to the fracture). The magnitude of the diameter decrease was largest
 220 at the inlet end of the core and similar in magnitude to the initial mean
 221 aperture (Figure 4). We hypothesize that the decrease in permeability was
 222 due to compaction of the residual uncemented dolomite within the fracture.
 223 To test this hypothesis, we optically measured the dolomite grain sizes (3
 224 - 12 μm) and applied the Kozeny-Carman relation to estimate permeability
 225 of the compacted dolomite (7.5×10^{-17} - 1.2×10^{-15} m^2). The estimated range
 226 of κ encompasses the measured value of 6.1×10^{-16} m^2 (see Appendix B for
 227 details).

228
 229 At lower flow rate (EV1), dissolution of anhydrite also left a dolomite layer
 230 leading to a reduction in core diameter (perpendicular to the fracture) of
 231 approximately twice the initial mean aperture (Figure 4). Yet, unlike EV2,
 232 dissolution of anhydrite produced persistent conductive pathways through
 233 the dolomite layer (Figure 5 and 6). The initial fracture aperture exhibited
 234 small-scale aperture variability with isolated regions of aperture larger than
 235 $\sim 700 \mu\text{m}$ (Figure 6a). A low-resolution x-ray CT scan of the core (Figure
 236 5) provided a coarse measure of the aperture distribution at the end of the
 237 6-month experiment (Figure 6b). Though the resolution of this scan was too
 238 coarse (200 μm voxels) to resolve some regions of the aperture field. Figure
 239 6c shows that we can use the x-ray CT scan to differentiate between regions
 240 of contact (blue), regions occupied by a mix of residual dolomite (green) and
 241 open aperture (red). The number and size of regions with aperture $> 200 \mu\text{m}$

242 increased by the end of the experiment and a broad channel in the center of
243 the core contained a mix of residual dolomite and open aperture (Figures 7
244 and 8).

245
246 To further explore the details of the flow channels, Figure 7 shows before
247 and after cross-sections of the fracture along the profile shown in Figure 6.
248 Figure 7a shows a cross section of the profile from the initial reconstructed
249 aperture field. If the dissolution were uniform throughout the fracture, a re-
250 duction in sample diameter would correspond to decreased aperture. Figure
251 7b shows the same aperture profile from figure 7a shortened by the change in
252 core diameter. Optical photographs of sample sections perpendicular to the
253 fracture, after impregnating the sample with epoxy, show a markedly larger
254 aperture (Figures 7c, 7d). We point out four main observations in figure 7d:
255 i) fracture healing (e.g. locations 1 and 2), ii) increase and persistence in
256 aperture (e.g. location 3), iii) a dolomite layer bounded by diffusive fronts
257 into the matrix (e.g. locations 4 and 5), and iv) presence of additional voids
258 within the dolomite layer surrounding the fracture that are additional po-
259 tential flow paths (e.g. location 6).

260
261 In addition to dissolution from the fracture walls, we highlight the propaga-
262 tion rate of the diffusive-reactive front into the matrix. The diffusion length
263 scale $W_d = \sqrt{D_M t_f}$, where t_f is the duration of the experiment and D_M the
264 matrix diffusion coefficient, controls the thickness of the layer. D_M , is related
265 to molecular diffusion, D_m , by $D_M = D_m \phi^n$ where ϕ is porosity and n the
266 cementation factor. For Anhydrite $\phi^n \sim 10^{-3}$, hence $D_M = 10^{-12} \text{ m}^2/\text{s}$. For

267 EV1 ($t_f = 180$ days) $W_1 \sim 4000 \mu\text{m}$ is consistent with observed length scales
268 in optical imaging of sample slices (Figure 7) and x-ray CT-scans (Figure
269 5). For EV2 ($t_f = 7$ days), $W_2 \sim 800 \mu\text{m}$ is consistent with optical imaging
270 of the sample (Figure 3) and scanning of fracture surfaces before and after
271 dolomite removal.

272

273 Figure 8a shows a photograph of a slice with conductive carbon tape on the
274 side so the sample could be examined under an SEM with reduced charge
275 accumulation without sputtering. Figure 8b is a high-resolution x-ray image
276 perpendicular to flow (compared to figure 5) of the slice in figure 8a where we
277 can clearly see the persistence of the fracture and the highlighted dolomite
278 region surrounding the fracture (darker gray level). Unfortunately we gained
279 access to the high-resolution x-ray system only after slicing the core (Figure
280 5) and we were only able to obtain the high resolution x-ray CT scan of one
281 slice. An example of an EDS spectrum away from the fracture (blue square,
282 figure 8c) shows a clear signal of the dolomitic anhydrite (presence of both Mg
283 and S peaks) while spectra around the fracture (red circle, Figure 8d) show
284 a clear absence of anhydrite (lack of the S peak). EDS spectra of the powder
285 brushed off the fractured sample after pulling the two halves of the core apart
286 (Figure S4) confirmed that the fracture infilling was predominantly dolomite.

287

288 Figure 9 plots the concentrations of Ca^{2+} and SO_4^{2-} against dimensionless
289 time. Though we also measured Mg^{2+} concentrations, they were persistently
290 more than two orders of magnitude smaller than Ca^{2+} concentrations and
291 thus not shown in Figure 9. The effluent concentrations are normalized by the

292 equilibrium concentration, which we measured by dissolving a finely ground
 293 piece of the core cut from the end of one of the samples in deionized water for
 294 approximately 2 weeks. The effluent from EV1 was near saturation during
 295 the entire 6-month experiments, with a slight decrease in concentrations at
 296 later time. We suspect this decreased concentration was due to the forma-
 297 tion of the dissolution channel observed in Figures 6 and 7. EV2 exhibited
 298 effluent concentrations that were significantly below the equilibrium concen-
 299 tration over the duration of the experiment with an increase that coincided
 300 with the significant decrease in permeability.

301

302 The cumulative mass transfer (Figure 10), derived from measurements of
 303 effluent concentration with time, $c(t)$, reflects the strong difference in per-
 304 meability evolution for the two experiments (Figure 2). As expected, at
 305 early times, for both experiments, the cumulative mass dissolved, $M(t)/M_o$,
 306 has a slope of 1 as a function of t/T , because the concentration of Ca^{2+}
 307 ions remains relatively constant during the initial phase of each experiment
 308 suggesting the dissolution rate is constant. At later times, the dissolution
 309 rate at low flow rate decreased by 20%. This is consistent with the devel-
 310 opment of dissolution channels, which causes flow to bypass large regions of
 311 the fracture reducing effective reactive surface area. On the other hand, for
 312 high flow rate, dissolution was more uniform throughout the fracture and
 313 the larger ΔP caused more flow through the adjacent intact rock matrix
 314 (and more contact with dissolving anhydrite) resulting in an 80% increase
 315 in dissolution rate. Dissolution of anhydrite and the residual dolomite layer
 316 surrounding the fractures are prevalent in both experiments (Figure S5a). In

the case of low flow rate (EV1) the fracture aperture persisted. Additionally, the dolomite layer surrounding the fracture included localized voids which may provide additional flow paths (Figure S5b). In the case of high flow rate (EV2), the dolomite layer was uniform leading to fracture closure (Figure S5c).

4. Discussion

Our experimental results showed a striking difference in behavior. We attribute this difference to the change in flow rate between the two experiments. Decreasing the flow rate increases the residence time of the fluid within the fracture, τ_a , without significantly changing the timescale of the dissolution reaction, τ_r . This dependence of dissolution on the Damköhler number ($Da = \tau_r/\tau_a$) has been observed in previous experimental studies where uniform dissolution is observed for large Da and channeled dissolution for small Da [Durham et al., 2001; Elkhoury et al., 2013]. Furthermore, at large Da the uniform dissolution can preferentially erode contacting asperities leading to the potential for decreased permeability [Detwiler, 2008]. However, these previous experimental studies showed permeability decreases that were relatively small compared to those observed in EV2. The substantial permeability decrease observed in EV2 resulted from relatively uniform dissolution throughout the fracture with concurrent dissolution of anhydrite within the porous matrix immediately adjacent to the fracture. For the dissolution reaction to propagate into the fracture matrix, the timescale associated with the dissolution reaction in the pores, τ_r , must be longer than

341 the timescale of diffusive transport through a pore. This allows dissolved
342 Ca^{2+} and SO_4^{2-} ions to diffuse from the pore space faster than these ions are
343 produced by the dissolution reaction. Thus, a region of undersaturated fluid
344 propagates into the porous matrix over time.

345
346 The dissolution process is further complicated in a polyminerallic rock such
347 as the dolomitic anhydrite used in our experiments. Solubility differences for
348 the different minerals can result in alteration of the structure of the porous
349 matrix. In this case, dissolution of the more soluble anhydrite left residual
350 uncemented dolomite grains filling the void space of the fracture. This has
351 implication for the strength of the fracture because contact regions consist-
352 ing of intact dolomitic anhydrite are transformed to uncemented dolomite
353 grains. In our constant-confining-stress experiments, this resulted in normal
354 deformation of the fracture, but it is also likely that the dissolution pro-
355 cess significantly reduced the shear strength of the fracture. This weakening
356 and compaction process differs fundamentally from compaction caused by
357 pressure solution observed in saturated granular anhydrite subjected to high
358 stresses [Pluymakers et al., 2014]. Such chemically-induced compaction oc-
359 curs when the pore fluid is near equilibrium with anhydrite; diffusion of ions
360 from contact regions leads to halos of supersaturation and mineral precip-
361 itation which gradually fills (heals) the pore space. However, advection of
362 undersaturated fluid from an underlying carbonate reservoir will compete
363 with this process, because it will enhance dissolution (of both gouge and
364 fracture surfaces) and inhibit precipitation.

365

366 Any study consisting of a limited number of experiments must consider the
 367 potential impact of sample variability on the results. In our case, both sam-
 368 ples were subcores from the same 15-cm length of core such that variability
 369 in sample mineralogy is representative of the small-scale heterogeneity within
 370 this formation. Furthermore, both fractures were tensile fractures subjected
 371 to a carefully controlled shear displacement such that small-scale aperture
 372 variability was similar despite a difference in mean apertures. A previous
 373 study in two fractures with very different initial apertures (a saw cut, bead-
 374 blasted core and a naturally fractured core) demonstrated that changing
 375 flow rate (or Da) had a much stronger influence on results than significant
 376 variations in initial aperture distributions [Elkhoury et al., 2013]. These ex-
 377 perimental observations support analytical and computational analysis of the
 378 role of aperture variability on the development of reaction-front instabilities
 379 [Szymczak and Ladd, 2012]. Though the mineralogy of the cores used in our
 380 previous study differs from those used here, we expect that the importance
 381 of Da on the dissolution process relative to variations between samples tran-
 382 scends fluid and mineralogic compositions used in experiments.

383
 384 In the context of CO₂ sequestration, the chemical composition of the fluids
 385 in the reservoir and the degree of reservoir over- or under-pressurization will
 386 clearly play a role in the evolution of the permeability of caprock fractures.
 387 We contend that leakage, or the development of dissolution-induced preferen-
 388 tial pathways is unlikely in the absence of fractures due to the extremely low
 389 intact permeability of most caprock formations. Smith et al. [2013] subjected
 390 intact cores from the same formation to flow of a CO₂-equilibrated brine

and observed the formation of wormholes due to preferential dissolution of dolomite within the core. However, their experiments required excessively large pressure gradients (700 Bar/m), and most likely unsustainable in the field, to induce flow through the low-permeability ($\sim 10^{-19}\text{m}^2$) cores.

5. Concluding Remarks

Our results highlight the influence of the transport and reactive times scales, τ_a and τ_r respectively, even during experiments where significant reactions within the rock matrix were expected ($\tau_d/\tau_r \ll 1$). For smaller values of τ_a/τ_r , our experiments point at fractured dolomitic anhydrite self healing due to a combination of anhydrite dissolution and compaction of the core caused by normal stresses. However, when using lab-scale experiments to infer expected field-scale behavior, it is critical to consider the scaling behavior of different mechanisms. We note that τ_a/τ_r increases with the fracture length, L , which suggests the potential for channel formation and increasing likelihood of persistent leakage pathways at the field-scale. Furthermore, the constant-flow boundary conditions used in our experiments, and many other experimental studies, led to relatively constant τ_a/τ_r over the duration of the experiment. In the field, constant pressure boundary conditions may be more appropriate. Under such conditions, decreasing permeability caused by healing mechanisms will lead to reduced flow and increased τ_a/τ_r , in turn increasing the potential for the formation of preferential channels. The concurrent compaction of dolomite surrounding the fracture introduces an additional time scale, which further influences the permeability evolution

415 of fractures. These scaling behaviors argue against the likelihood of frac-
416 tured caprocks healing by the combined influence of chemical reactions and
417 mechanical deformation because an increased τ_a/τ_r is favorable under reser-
418 voir conditions.

419
420 In addition to implications for permeability evolution relevant to greenhouse-
421 gas sequestration [Wilson and Monea, 2004; Metz et al., 2005; Haszeldine,
422 2009], our results showing significant alteration of the porous matrix adjacent
423 to fractures highlight a significant alteration of the rock strength [Wintsch
424 et al., 1995]. For the hydrostatic stress applied in our experiments, the dis-
425 solution process resulted in significant normal deformation of the fractures.
426 Such significant dissolution-induced deformation in the subsurface can redis-
427 tribute stresses, which may further alter fracture permeability.

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437 manuscript.

438

Figure 1: Initial aperture fields measured for samples EV1 and EV2 and the corresponding histograms. The colors represent values of $\log(\text{aperture})$, with aperture measured in μm . These aperture fields correspond to the fracture in the absence of an applied normal stress.

Figure 2: Pressure differential (ΔP) between inlet and outlet plotted against normalized time (t/τ) for samples EV1 and EV2 for flow rates of 0.01 ml/min and 0.6 ml/min respectively. The increase in ΔP for EV2 corresponds to a two order-of-magnitude decrease in permeability.

Figure 3: Photographs of the fracture in sample EV2 (a) before and (b) after the flow-through experiment, which highlight the formation of an off-white layer of dolomite filling the fracture. Separating the fracture surfaces revealed (c) an approximately 800- μm -thick layer of dolomite between the fracture surfaces.

Figure 4: Change in sample diameter perpendicular to the fracture. Sample length is measured from the outflow. EV1 decreased in diameter on average three times more than EV2. The slope of $\Delta d_{\perp}$ is twice steeper for EV2 ($78 \mu\text{m}/\text{cm}$) compared to EV1 ($37 \mu\text{m}/\text{cm}$).

Figure 5: x-ray CT-scan cross-section of sample EV1 (low flow rate) after the flow-through experiment. Arrow a) points at the consolidated and compacted dolomite layer surrounding the fracture. It is the same region highlighted in Figure 7 by arrows 4 and 5. Arrow b) points at a dissolved region into the bulk close to the inlet. Arrows c) and d) point at aperture locations larger than $200\text{ }\mu\text{m}$ (resolution of the x-ray CT-scan).

Figure 6: Fracture alteration of sample EV1 (low flow rate). a) initial aperture field obtained from mating the two fracture surfaces scanned with a white light profilometer; b) Fracture surface projected from a low-resolution 3D x-ray CT-scan of the sample after the flow-through experiment (the color scale was inferred from measured x-ray absorption coefficients); c) The discretization of panel b) into 3 regions, open aperture (red), mixed region (green) and contact (blue). The gray dashed line across the three panels identifies the location of the slice shown in figure 7.

Figure 7: Fracture aperture and profiles of sample EV1 near the outlet (Figure 6): a) Aperture reconstructed from measured fracture surfaces before flow-through [Ameli et al., 2013]; b) Same as a) with a uniform aperture reduction of $550\ \mu\text{m}$ (average sample diameter reduction perpendicular to the fracture); c) Measured aperture, after the flow-through experiment, obtained from slices of the fractured sample after impregnating with epoxy (d).

Figure 8: (a) Optical photograph and (b) high-resolution x-ray CT scan of an EV1 slice after flow-through. Inset in (a) is a zoomed region surrounding the fracture close to the conductive carbon tape. (c) and (d) are EDS spectra of the regions away from the fracture (blue square) where we can clearly see the signal of the dolomitic anhydrite and regions surrounding the fracture (red circle). Both dolomite and anhydrite are present in (c) and only dolomite in (d).

Figure 9: Temporal evolution of Ca^{2+} and SO_4^{2-} concentrations for both low flow rate (EV1) and high flow rate experiments (EV2). The overlap of both concentrations indicates negligible dolomite dissolution. This concentration, $c(t)$ is used to obtain the cumulative mass dissolved shown in figure 10

Figure 10: Normalized cumulative dissolved mass ($M(t)/M_o$) as a function of normalized time (t/τ). $M(t)$ is obtained from measurements of ion concentrations $c(t)$, using ion chromatography (Figure 9). The rate of dissolved mass at early stage does not change (black dashed line slope 1). However, the rate increased for high flow rate (EV2, slope 1.8, green dotted line) while it slightly decreased for the smaller flow rate case (EV1, slope 0.8, dotted orange line).

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557 **Appendix A. Chemical Analysis**

558 Dissolution of a mixture of anhydrite and dolomite involves the following
559 primary reactions:

560 This suggests that when only anhydrite is dissolving, concentrations of Ca^{2+}
561 and SO_4^{2-} should be equal as observed in our experiments (Figure 9).

562

563 Results from speciation calculations using PHREEQC [Parkhurst and Ap-
564 pelo, 1999] at conditions representative of our experiments and the Weyburn
565 reservoir (Figure ??) show the range of potential equilibrium concentrations
566 for different ions. At small pCO_2 dolomite dissolution is negligible (Figure
567 S6a). However, under reservoir conditions, still the amount of dissolved an-
568 hydrite is larger than that of dolomite since $\text{SO}_4^{2-} > \text{Mg}^{2+}$ (Figure S6b).
569 The equilibrium concentrations are relatively insensitive to the presence of
570 other ions but responsive to the increased pressure [Parkhurst and Appelo,
571 1999]. Note that high values of pCO_2 under the experimental conditions
572 are meaningless since it would be impossible to have $\log(\text{pCO}_2) > 0$ un-
573 der these conditions. The corresponding pH curves are shown in Figure S7.
574 The speciation results highlight the relevance of our experimental results to
575 reservoir conditions as they show a clear range of realistic conditions un-
576 der which dolomite dissolution will be limited (Figure S6). Note, Hangx

et al. [2010] describe preliminary batch experiments in which they quantified CaCO_3 precipitation in anhydrite samples at elevated pCO_2 ; all of the calculations presented here yielded a positive saturation index for CaCO_3 which supports the potential for CaCO_3 precipitation. However, our calculations suggest the saturation index decreases with increasing pCO_2 due to increased carbonic acid in solution.

Appendix B. Estimating Permeability of EV2 using Kozeny-Carman

We use the Kozeny-Carman equation to estimate the permeability range of sample EV2 as an exercise that shows order of magnitude consistency between measured and estimated values of permeability. The Kozeny-Carman equation

$$Q = -d_e^2 \left[\frac{n^3}{(1-n)^2} \frac{W d}{180 \mu} \right] \nabla P$$

relates the flow rate Q and pressure gradient ∇P across the sample where d is the diameter of the core, W the thickness of the dolomite layer, μ the viscosity of the fluid, n the porosity and d_e the grain size [Bear, 1972]. Using values of $Q = Q_{EV2} = 0.6 \text{ ml/min}$, $W \sim 800 \mu\text{m}$ and $n = 0.3$, $\mu = 10^{-3} \text{ Pa s}$, and sample length $L = 4.9 \text{ cm}$. The range of grain sizes, d_e , was estimated qualitatively by optical means to be 3 - 12 μm . The grain sizes range yields pressure differences ΔP range of 365 - 5835 kPa. The measured pressure difference of 700 kPa is well within the estimated range (Figure 2). The high porosity is qualitatively consistent with the ease with which most of the dolomite could be brushed off the sample after separating and drying the two halves.

599 In order to express our results as a permeability range, we use Darcy's law to
600 relate the estimated pressure gradient range to permeability values. For EV2,
601 the estimated pressure range and the imposed flow rate, Q_{EV2} , produce the
602 reported range of permeability in the text; 7.5×10^{-17} - 1.2×10^{-15} m² which
603 encompasses the measured value of 6.1×10^{-16} m² (Figure 2).