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Impact of hydro-chemical conditions on structural and hydro-mechanical properties of chalk samples during dissolution experiments

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1 Highlights

- 2 • Permeability increase related to chalk dissolution is due to preferential
3 flowpaths
- 4 • The reactivity of homogeneous systems is determined by the hydro-
5 chemical conditions
- 6 • Initial large-scale structural heterogeneities reduce the reactivity of the
7 systems
- 8 • Pre-existing large-scale heterogeneities control the location of newly
9 created paths
- 10 • Initial micro-scale heterogeneities result in highly heterogeneous general
11 structures

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12 Abstract

13 The importance of karst reservoirs for water resources, and their complex-
14 ity in terms of structural properties and hydraulic responses, require a better
15 understanding of the formation and location of conduits in these systems, in
16 particular for chalk reservoirs. For this purpose, we conduct laboratory ex-
17 periments of acid solutions injection in chalk core samples using a homemade
18 experimental device. Three different flow rates and two acid concentrations
19 are applied on six samples at atmospheric conditions with Peclet numbers
20 ranging from 0.1 to 1.7 and Damköhler numbers from 10^{-6} to 10^{-3} . Hy-
21 draulic and chemical measurements are carried out during the experiments,
22 while petrophysical characterization is conducted on the samples before and
23 after the reactive percolation experiments. The analysis of these data shows
24 an increase in permeability of the rock samples due to calcite dissolution,
25 which is associated with the creation of preferential conduits. We also ob-
26 serve that the initial structural properties control the dissolution regime with
27 the following main conclusions. For homogeneous systems, the overall disso-
28 lution rate and percolation time are directly linked to the considered flow rate
29 and injected acid concentration. For heterogeneous systems, (i) pre-existing
30 large-scale structural heterogeneities control the location of newly created
31 paths while reducing the value of the dissolution rate, and (ii) micro-scale
32 heterogeneities result in highly heterogeneous general structures, which are
33 responsible for channels formation while applying low Damköhler numbers.

34 **Keywords**

35 Chalk, Reactive transport, Dissolution regime, Micro-tomography, Karst,
36 Wormholes

37 **1. Introduction**

38 Carbonate rocks are widely studied because of their important presence
39 on the Earth’s surface and their use for human activities, including geother-
40 mal energy and resources extration (Rege and Fogler, 1989; Chilingarian
41 et al., 1992; Noiriel et al., 2005; Moore and Wade, 2013). These forma-
42 tions, which present scale-dependent complex properties (Choquette and
43 Pray, 1970; Lucia, 1983; Lønøy, 2006), are characterized by a strong re-
44 activity. This is illustrated by the dissolution of carbonate rocks, which is
45 the result of thermodynamical disequilibrium between fluid and rock (Ford
46 and Williams, 2007) and leads to the formation of karsts.

47 Numerous laboratory experiments and numerical simulations have been
48 conducted on various carbonate rocks and under variable conditions in order
49 to understand how the dissolution process occurs in such systems. Golfier
50 et al. (2002) linked the initial conditions of dissolution and the resulting
51 dissolution patterns (from uniform dissolution to the formation of compact
52 wormholes) with the use of the adimensional Péclet (Pe) and Damköhler (Da)
53 numbers (Lasaga, 1984; de Marsily, 1986; Daccord et al., 1993). This is in
54 the line with numerous laboratory and theoretical experiments that demon-
55 strate the determinant impact of the fluid rate and structural properties on
56 the developed dissolution regimes (Fredd and Fogler, 1998; Singurindy and
57 Berkowitz, 2003; Noiriel et al., 2004; Luquot and Gouze, 2009; Smith et al.,

2013; Vialle et al., 2014; Menke et al., 2015; Lebedev et al., 2017). Nevertheless, the Damköhler number is difficult to calculate as demonstrated by the large number of techniques that have been considered for this purpose (Lasaga, 1984; Knapp, 1989; Luquot and Gouze, 2009; Garcia-Rios et al., 2015; Menke et al., 2015; Noiriél and Daval, 2017), mostly because of the complexity of determining the reaction rate K [s^{-1}]. As a result, linking the dissolution rate and regime, as well as the reaction localization, to the Pe and Da numbers is still challenging.

The structure is also known to be an important parameter in carbonate rock dissolution. Pore size distribution can be heterogeneous in carbonate rocks and affect the flow path through the rock. These heterogeneities in the pore structure lead to different dissolution mechanisms that occur inside the rock sample (Hoefner and Fogler, 1988; Noiriél et al., 2005; Vialle et al., 2013). For example, in fractured rock samples, the dissolution usually occurs along the main heterogeneities favouring a transport-controlled mechanism (Elkhoury et al., 2013; Garcia-Rios et al., 2017). In order to study how and where the dissolution occurs, as well as the resulting changes on the rock sample properties, various laboratory dissolution experiments were conducted on carbonate rocks at room and reservoir conditions on limestone rocks (Fredd and Fogler, 1998; Noiriél et al., 2004, 2005; Luquot and Gouze, 2009; Noiriél et al., 2009; Gharbi et al., 2013; Mangane et al., 2013; Vialle et al., 2013; Luquot et al., 2014a; Molins et al., 2014; Vialle et al., 2014; Steefel et al., 2015; Menke et al., 2017; Lebedev et al., 2017) and dolomite at reservoir conditions (Smith et al., 2013; Tutolo et al., 2014; Luhmann et al., 2014). Although most of these studies try to express the dissolution features with,

83 again, the Pe and Da numbers, they finally defined new dissolution features
84 linked to the rock heterogeneities (Noiriel et al., 2009; Luquot et al., 2014a;
85 Menke et al., 2017).

86 Most of the previous studies have been performed in (almost) homoge-
87 neous limestone rocks that are not representative of natural complex rocks
88 such as chalk. The latter is characterized by highly heterogeneous struc-
89 tures composed of variable-size shells and a high proportion of very small
90 pores (Fabricius, 2007). This special structure makes the determination of
91 a characteristic length difficult, inducing complications in the adimensional
92 numbers definition. It also results in unstable structures that are difficult
93 to reproduce experimentally and thus not well studied. A recent study has
94 investigated the different dissolution patterns occurring inside chalk by in-
95 jecting CO₂ at elevated pressure using in situ X-ray imaging (Yang et al.,
96 2018). They demonstrate the high sensibility of chalk to reactive fluid com-
97 pared to coupled geochemical and geomechanical processes, and show that
98 the microstructure is highly affected by material compaction, fracturing and
99 grain relocation. Nevertheless, they did not perform these experiments under
100 different dissolution regimes and the hydraulic properties are not monitored.

101 The present work attempts to give some answers on how conduits in chalk
102 form and what are the properties responsible for it. To this end, acid injec-
103 tions are conducted on six core samples of chalk at atmospheric conditions.
104 Three different flow rates and two acid concentrations are applied to the
105 samples with a homemade experimental device. The chemical and hydrody-
106 namic properties are recorded during the experiments, and the samples are
107 characterized with laboratory and images methods before and after experi-

108 ments. Evolution of all these properties coupled with the initial conditions,
109 is analyzed in order to observe in which proportion they are responsible for
110 the changes induced by the acid flowing through the rock.

111 **2. Materials and Methods**

112 *2.1. Rock properties and characterization*

113 We study six chalk samples, named N02, N03, N04, N05, N08 and N09,
114 that were cored in a unique flint chalk block from the lower Senonian located
115 in north-western France. The length of the cores is 20-30 mm and their
116 initial diameter of 18 mm results in 25 mm when surrounded with epoxy
117 resin and PVC pipe. Although most of the samples present pores in stick
118 shape without preferential orientation and with pre-existing fractures, some
119 discrepancies are observed between the samples (Figure 1).

120 Petrophysical non-destructive measurements that are carried out on the
121 cored samples are described in Leger and Luquot (2021) under the rock
122 named Normandie (label N). It includes rock conductivity monitoring, struc-
123 tural properties computation (formation factor F , cementation index m and
124 electrical tortuosity τ_e), pore size characterization with centrifugation, X-ray
125 tomography calculations resulting in the porosity of the macro phase, per-
126 meability, hydraulic tortuosity τ_h , relative pores size $\frac{S}{V}$, proportion of the
127 percolating phase PV and the pore size distribution represented as chord
128 length probability distribution. In addition to this data, 3D images obtained
129 from X-ray tomography calculations are used to extract the pore network of
130 the samples and their corresponding permeability (see details in Electronic
131 Supplement).

Figure 1: 2D vertical slices from 3D X-ray micro-tomography (XRMT) images of the initial structure of the six studied samples. N05 is the most homogeneous sample while N08 and N09 present a pre-existing filled channel and some pre-existing micro-cracks, respectively.

132 2.2. Experimental protocol and output

133 An acidic fluid composed of acetic acid CH_3COOH and sodium acetate
134 CH_3COONa , which are diluted in water previously equilibrated with chalk,
135 is injected through the core samples at atmospheric pressure and tempera-
136 ture using a homemade experimental device (Figure 2). The airtight sample
137 holder allows an injection distributed over the sample surface. The pH and
138 conductivity of the injected solution, as well as the difference in pressure
139 between the sample inlet and outlet, are continuously monitored, while pH,
140 conductivity and cation concentrations of the outlet fluid are measured with

141 regular sampling of 5 mL using the ICP (Ion Concentration Polarization)
 142 method for ion concentration. The protocol that is applied to each sample
 143 is described in details in Appendix A.1.

Figure 2: Experimental homemade percolation device composed of a beaker with JUMO sensors, a peristaltic pump (Gilson, MiniPuls3), an absolute pressure (Gems) and a differential pressure (Keller) sensor, Swagelok connectors, and a continuous acquisition system Labjack.

144 Five different experimental conditions are considered with two acidic con-
 145 centrations (C_0^1 and C_0^2) and three flow rates (Pe_1 , Pe_2 and Pe_3) defined by
 146 the Peclet number $Pe = \frac{ul}{d}$, with u the average flow velocity injected in each
 147 sample [m/s], l the characteristic length of the pores [m] and d the molecular
 148 diffusion in calcite [m^2/s] set to $5 \times 10^{-9} \text{ m}^2/\text{s}$. C_0^1 and C_0^2 are set to 10^{-3}
 149 and 10^{-2} mol/L of acid concentration, respectively, and the ranges of Pe_1 ,
 150 Pe_2 and Pe_3 are $[0.01, 0.2]$, $[0.05, 1.5]$ and $[0.1, 3.25]$, respectively. The latter
 151 values come from the pore size distributions provided in Leger and Luquot
 152 (2021) that are used here to define the characteristic length l , as done in pre-
 153 vious studies (Vialle et al., 2014; Menke et al., 2016). Table 1 summarizes the
 154 experimental conditions that are applied to the samples with N03 and N08
 155 being reproduction experiments. For each experiment, the evolution of the
 156 sample porosity $\phi(t)$ along time is deduced from the measured concentration
 157 of Ca ions with the methodology described in Appendix A.2.

Pe	C_0^1	C_0^2
Pe_1	N04	N09
Pe_2	N02	N03 & N08
Pe_3		N05

Table 1: Experimental conditions of the experiments. Pe_1 , Pe_2 and Pe_3 are associated with the flow rates 2.9, 25.2 and 63 mL/h, respectively.

After dissolution, the sample is submitted to the same characterization methods as before the experiments (Section 2.1) in order to evaluate the impact of the percolation experiment on the rock properties. This includes pore size characterization by centrifugation in the direction of the pressure difference and in the opposite one, which allows to characterize the possible anisotropy.

3. Results

3.1. Hydro-chemical results from percolation experiments

Figure 3 displays the evolution over time of the outlet pH values, fluid conductivities (σ_f) and calcium concentration [Ca] recorded during the percolation experiments. We observe that all these values are higher than the inlet ones, indicating that the main chemical reaction occurring during the experiments is calcite dissolution. We also observe that the shapes of these curves are similar, with a plateau at the beginning of the experiment that is followed by a decrease. At low inlet acid concentration C_0^1 , the decrease in pH, σ_f and [Ca] occurs 12 times later for N04 than for N02, with a flow rate 9 times lower. At high inlet acid concentration C_0^2 , we also observe some discrepancies, in particular for N03 and N08, which are submitted to the same experimental conditions, the decrease in the considered measurements occurring 4 times later for N03. Additionally, while the flow rate applied to

178 N05 is higher than N08, the experimental parameters decrease slower in the
 179 former case than in the latter. All these results show that the differences in
 180 time for a same acid concentration are not linear.

Figure 3: Evolution of the pH at the outlet of the experiments (pH_{out} , first row), the differences in fluid conductivity (σ_f , second row) and calcite concentration ($[\text{Ca}]$, third row) between the outlet and inlet of the percolating experiments with inlet acid concentration C_0^1 (first column, empty dots) and C_0^2 (second column, filled dots), and Peclet numbers Pe_1 (diamonds), Pe_2 (squares) and Pe_3 (circles).

181 Although the shapes of the curves are similar, the pH, σ_f and [Ca] values
182 observed on the plateau of each experiment are different and depend on the
183 inlet acid concentration. The outlet pH is one unit higher for C_0^1 than C_0^2 ,
184 while the outlet σ_f and [Ca] are lower when the inlet acid concentration is
185 lower. We observe that the outlet [Ca] is almost 10 times higher for the
186 experiments performed with C_0^2 than C_0^1 , where C_0^2 is 10 times higher than
187 C_0^1 .

188 Figure 4 shows the evolution of permeability over time that is calculated
189 from the monitored differential pressure with the permeability equation pro-
190 vided in Electronic Supplement. When pH, σ_f and [Ca] decrease, we observe
191 an increase in permeability. In some cases, a punctual decrease in permeabil-
192 ity is observed during the experiments, which is probably due to particles
193 dragging and local pores clogging in the sample, as observed in other studies
194 (Noiriel et al., 2005; Luquot et al., 2014a; Garing et al., 2015). Two per-
195 meability trends are shown: (i) an almost constant low permeability until it
196 suddenly increases and reaches the maximum value that is measurable by the
197 sensors for N09 and N04; (ii) an abrupt increase in permeability followed by
198 a moderate increase for the other samples. More specifically, N02 and N08
199 do not show a permeability increase as large as the other samples since their
200 final relative permeability k^* is lower than 100, whereas it reaches almost
201 1000 for the other samples.

Figure 4: Evolution of the normalized rock permeability k^* [-] during the percolating experiments, where k^* is defined as the permeability of the sample along the experiment normalized by its initial permeability. The dot represents the final value of permeability. Graphics are displayed according to experimental conditions: two inlet acid concentrations in columns (C_0^1 and C_0^2) and three Peclet numbers in rows (Pe_1 , Pe_2 and Pe_3).

3.2. Petrophysical and hydraulic results from laboratory measurements

3.2.1. Effective parameters

Table 2 shows the petrophysical and hydraulic properties obtained from laboratory measurements before and after the percolation experiments. We observe (i) no significant changes for the porosity, (ii) sharp increases for the permeability and the P and S waves velocities and (iii) decreases for the structural properties (i.e., formation factor F_L , cementation index m_L and

209 tortuosity τ_e).

Initial	Samples	ϕ_L	k_L	F_L	m_L	τ_e	Vp	Vs	
	N02	27.9	3.70	54.1	3.13	3.89	2.40	1.31	
	N03	38.0	11.19	8.3	2.19	1.78	2.36	1.18	
	N04	25.6	1.06	50.0	2.87	3.58	3.27	1.78	
	N05	37.8	9.07	7.8	2.12	1.72	2.35	1.25	
	N08	27.7	8.14	26.6	2.63	2.77	2.33	1.30	
	N09	27.2	0.71	24.2	2.45	2.57	2.97	1.64	
Final	Samples	ϕ_L	ϕ_{ch}	k_L	F_L	m_L	τ_e	Vp	Vs
	N02	27.9	28.1	220	17.3	2.23	2.20	3.77	1.77
	N03	35.7	38.3	2500	5.2	1.60	1.36	2.76	1.65
	N04	25.8	25.9	300	15.6	2.03	2.01	3.94	2.15
	N05	36.5	38.2	8000	5.2	1.63	1.38	2.80	1.85
	N08	29.7	28.8	230	11.7	2.03	2.03	3.74	2.01
	N09	27.2	27.4	300	15.0	2.08	2.08	3.89	1.83

Table 2: Petrophysical properties from laboratory measurements of samples at initial and final states, i.e., before and after the percolation experiments with porosity ϕ_L [%], permeability k_L [mD], formation factor F_L [-], cementation index m_L [-], electrical tortuosity τ_e [-], P and S wave velocities Vp and Vs [km/s]. The index L stands for Laboratory measurements and ϕ_{ch} is the final porosity calculated from Equation (A.2) with [Ca] measurements

210 In addition to these behaviors, two groups emerge from the results pre-
211 sented in Table 2. (i) N03 and N05 (gray rows in Table 2) have the highest
212 porosity and permeability, and the lowest electrical factors, at both initial
213 and final states. (ii) The other samples (N02, N04, N08 and N09) show
214 an opposite behavior with N02 displaying the highest electrical factors. In
215 terms of permeability, N05 is the sample displaying the highest increase with
216 k_L after experiment almost 1000 times higher than before the experiment,
217 while N02 and N08 permeability only increases around 60 and 30 times, re-
218 spectively. Concerning F_L and τ_e , N02 and N04 display the highest decrease
219 compared to N08 and N09. P waves velocities of N02 and N08 increase the

most compared to N04 and N09, which have the highest Vp before and after experiments. Nevertheless, after experiment, N02, N04, N08 and N09 reach similar values. In an opposite way, N03 and N05 keep small values of Vp with the lowest increase.

3.2.2. Pore diameter distribution

Figure 5 shows the pore diameters distributions that are obtained by centrifugation with very different distributions depending on the drainage direction. When samples are drained in the same direction as the injected flow during experiments, the water stuck into the samples is discharged by the same sample face than during experiments. The results suggest that there are more small pores and less large pores after the dissolution experiment (Figure 5b) than before (Figure 5a). On the contrary, when samples are drained in opposite flow direction, the inlet of samples during experiments is situated at the outlet of the centrifuge. The associated distribution (Figure 5c) is different from that obtained in the main direction, and more similar to the initial one. This difference indicates an anisotropy in the pore size distribution inside the core samples because the water drainage seems easier in the opposite direction of the flow applied during the experiments. This suggests that larger pores are present at the sample inlet. Moreover, after dissolution, a larger amount of small pores present at the sample outlet can prevent the water drainage in this direction, as observed by Luquot et al. (2014b) and Garing et al. (2015). This suggests local particles clogging with a decrease of the throat diameter and an increase of the suction pressure that is needed to drain.

Figure 5c being the most representative of the pore diameters distribu-

Figure 5: Pore diameters distribution for each sample from centrifugation.

245 tions, we use these results for comparing the pore diameter distributions
 246 before (Figure 5a) and after (Figure 5c) percolation. We observe that the
 247 quantity of micropores (pores smaller than $10 \mu\text{m}$) increases and that of large
 248 pores tends to decrease after percolation. In addition, some groups emerge
 249 from these data: (i) N03 and N05 display the largest amount of micropores

250 before and after experiment with a moderate increase of 10% and a larger
 251 increase for diameters between 0.5 and 3.5 μm ; (ii) N02 and N09 present
 252 the smallest increase in micropores proportion that is around 6%; (iii) N04
 253 and N08 largely increase their quantity of micropores with increases of 16%
 254 and 13%, respectively. The samples from the group described earlier (Sec-
 255 tion 3.2.1, samples N02, N04, N08 and N09) do not show the same evolution.
 256 N02 has a similar trend before and after percolation, while N09 displays sig-
 257 nificant increases and decreases in every diameter class. In N04 sample, the
 258 proportion of pores with diameters under 1.5 μm largely increases, while in
 259 N08 the proportion of the smallest pores, under 0.5 μm , increases.

260 *3.3. Results from tomographic images and pore network extraction*

261 *3.3.1. Effective parameters*

262 Table 3 shows the petrophysical and hydrodynamic properties obtained
 263 from the 3D X-ray microtomography images, before and after experiments.
 264 We observe that the porosity and permeability increase with the percolation
 265 experiments, the formation factor F_{XR} and the ratio of pore surface over
 266 pore volume $\frac{S}{V}$ decrease, while no significant changes are observed for the
 267 cementation index m_{XR} , tortuosity τ_h and percolating volume PV .

268 Samples show some disparities in petrophysical data with, again, some
 269 groups emerging. N03 and N05 present the highest increase in permeability,
 270 becoming the most permeable samples after experiments, whereas N08 and
 271 N09 display the lowest increase. The $\frac{S}{V}$ ratio also increases much more for
 272 N03 and N05 than for N08 and N09, which remain almost constant. It
 273 should be also noticed that, after experiments, all the samples have similar
 274 $\frac{S}{V}$ ratios around 100 mm^{-1} , excepted for N08 with 85 mm^{-1} . Concerning

Initial	Samples	ϕ_{XR}	k_{XR}	k_P	F_{XR}	m_{XR}	τ_h	$\frac{S}{V}$	PV
	N02	7.6	36.5	4.29	40.3	1.44	1.76	107.9	92.1
	N03	8.3	12.6	0.21	36.2	1.44	1.74	113.0	84.7
	N04	8.6	569	94.0	15.8	1.13	1.16	80.5	96.0
	N05	7.9	25.5	2.14	34.1	1.39	1.64	111.4	86.1
	N08	9.7	505	367.4	28.8	1.44	1.67	87.6	95.9
	N09	9.1	65.2	21.1	31.3	1.43	1.68	103.0	94.9
Final	Samples	ϕ_{XR}	k_{XR}	k_P	F_{XR}	m_{XR}	τ_h	$\frac{S}{V}$	PV
	N02	8.6	1466	585.6	33.1	1.43	1.68	100.7	93.1
	N03	8.9	8059	1983	24.7	1.33	1.48	103.5	86.4
	N04	10.0	2674	1064	25.1	1.40	1.58	97.1	94.6
	N05	8.8	11304	3781	26.6	1.35	1.53	100.9	89.1
	N08	10.4	1497	1056	25.5	1.43	1.63	85.0	95.7
	N09	10.0	1291	756.7	27.3	1.44	1.65	98.9	94.8

Table 3: Petrophysical properties from imaging calculations of samples at initial and final states, i.e., before and after the percolation experiments with porosity ϕ_{XR} [%], permeability k_{XR} and k_P [mD], formation factor F_{XR} [-], cementation index m_{XR} [-], tortuosity τ_h [-], ratio of pore surface over pore volume $\frac{S}{V}$ [mm⁻¹] and proportion of percolating volume PV [%]. XR and P stand for 3D X-ray images and PNM (Pore Network Model) calculations, respectively.

the electrical properties, we can note that N03, and to a lesser extent N05, present the strongest decrease in m_{XR} and τ_h . Before as after experiments, N02 is always the sample with the highest values of F_{XR} and τ_h .

3.3.2. Resulting main flow paths

Micro-tomography images acquisition and pore network extraction allow to see the main flow paths in each sample after the dissolution experiments, as displayed in Figure 6. For all the core samples, we can observe that preferential flow paths are clearly visible across the entire cores. These main channels were not initially present in the samples, except for sample N08 (Figure 1), and were formed during the percolation experiment and dissolution process. The shape of the main flow path is similar for N02, N04 and

286 N09, and is characterized by a relatively straight conduit along sticky pores
 287 with few ramifications. N03 and N05 have more ramifications and several
 288 inlet points. N05 presents two conduits with only one percolating the entire
 289 sample. As mentioned before, N08 is a special case because its percolation
 290 follows a pre-existing whole.

Figure 6: Main path conduits of each sample depending on the experimental conditions: two inlet acid concentrations C_0^1 and C_0^2 in columns and three Peclet numbers Pe_1 , Pe_2 and Pe_3 in rows. For each sample, image from tomography acquisition is displayed on the left and image from PNM on the right. The arrow indicates the injected flow direction. The color scales represent the throat diameters in μm extracted from PNM calculations. The scale in the bottom right applies to all samples.

291 3.3.3. Pore size distribution and orientation

292 Equivalent pore size distribution is extracted from the 3-D images mea-
293 suring the chord length probability distribution and is displayed in Figure 7.
294 One of the main advantages of this measure is to statistically get information
295 concerning the pore orientation. We observe here that the pore size increases
296 with the experiments, the proportion of small pores (below $24\ \mu\text{m}$) decreas-
297 ing and the proportion of large pores (over $100\ \mu\text{m}$) increasing. N03 and
298 N05 have changed the most, dividing by two their quantity of small pores
299 and doubling their quantity of large pores. Samples also present an evolu-
300 tion in pore shape. Initially, N02 and N05 display spherical pores with no
301 preferential orientation. With the dissolution, the pore size of N02 increases
302 uniformly in the three space directions and remains spherical, whereas the
303 dissolution enlarges the pores of N05 along the flow direction (Z). Before
304 experiments, N03, N08 and N09 mostly present large pores transverse to the
305 flow direction (XY). After dissolution, large pores of N03 and N09 become
306 longer along the flow direction (Z), while they keep their initial shape in N08.
307 The dissolution does not seem to affect the pore shape of N08, as it follows
308 the initial conduit. N04 has another behaviour with large pores initially ex-
309 tended in Z direction, which are spherical after the experiment due to the
310 dissolution that enlarges its pores into the transverse flow direction.

Figure 7: Chord lengths distribution for each sample before (dotted lines) and after (solid lines) percolation. Lines with light colors are for average lengths along X and Y axes, while lines with dark colors are for chord lengths along Z axis.

4. Discussion

From the petrophysical results presented in Section 3 and obtained before and after the dissolution experiments, we can divide all the samples into two main groups: *Group1* with samples N03 and N05, and *Group2* with N02, N04, N08 and N09. In this section, we discuss how these two groups are impacted by the dissolution process and reversely how their specific properties control the reaction localization and rate.

318 4.1. Impact of dissolution on the measured properties

319 From the results presented in Section 3, the percolation experiments are
 320 responsible for a slight increase in the (chemical) porosity ($\phi_{ch} > \phi_L(\text{initial})$),
 321 and the macroscopic one evaluated by X-ray microtomography images (ϕ_{XR})
 322 for all the core samples. This is also shown in Figure 8 where the increases
 323 in ϕ_{ch} range from 0.08 to 0.35 %. Even if the increase in porosity seems
 324 weak, usual correlated parameters are strongly affected. Velocities of P and
 325 S waves increase for all the samples (Table 2). This is due to the creation of
 326 preferential paths inside the rock (Figure 6) through which the P and S waves
 327 propagate easily after dissolution. Consistently with their high porosity and
 328 their amount of ramifications, samples in *Group1* still have the smallest V_p
 329 after dissolution (Mavko et al., 2009).

Figure 8: Evolution of rock porosity (ϕ_{ch}) evaluated from Ca ions concentrations analyzed in the outlet fluid during percolating experiments and using Equation (A.2). $\Delta\phi$ is defined as the porosity measured at time t minus the initial porosity $\Delta\phi = \phi(t) - \phi_i$.

330 Usually, the acid passing inside carbonate rocks dissolves the matrix and
 331 enlarges the pores (Tutolo et al., 2020). However, after dissolution, the cen-
 332 trifugation results indicate that the quantity of macropores decreases while

333 the quantity of micropores increases (Figure 5). This unexpected pore di-
 334 ameters change is due to the particularities in the experimental protocol
 335 and in the range of investigation of pore diameters. Indeed, one can expect
 336 that the amount of macropores increases during acid fluid percolation (as
 337 observed in the XRMT images and in Tutolo et al. (2020)) and especially
 338 at the sample inlet, where the acid solution first interacts with the rock.
 339 Nevertheless, with the centrifugation method, the amount of large pores is
 340 under-estimated because the large pores located at the sample inlet are emp-
 341 tied before the first saturated sample weight measurement and consequently
 342 their volume is not taken into account. This under-evaluation can explain
 343 the low final laboratory porosity value ϕ_L compared to the one obtained by
 344 mass balance calculation ϕ_{ch} , as the first one is calculated from the saturated
 345 sample weight. Concerning the small pores, the range of investigation of the
 346 centrifuge is too small to quantify the amount of pores with diameters under
 347 $0.5 \mu\text{m}$. However, the large increase in the smallest measured range indicates
 348 that this pore section (smaller than $0.5 \mu\text{m}$) increases after the dissolution
 349 process as observed by Tutolo et al. (2020), who demonstrated that pores
 350 with diameters from 600 nm to $5 \mu\text{m}$ enlarge preferentially with dissolu-
 351 tion process. Even though, the proportion of micropores inside the samples
 352 is correlated with their effective porosity. Samples from *Group1* have the
 353 highest porosity and proportion of micropores with 88% after dissolution,
 354 consistently with Eberli et al. (2003)'s observations.

355 This phenomenon does not appear in the pore size distribution from chord
 356 length calculations (Figure 7). In this case, as expected, the dissolution
 357 experiments result in decreasing the amount of small pores and increasing

the amount of large pores. In *Group1*, the evolution of pore size distribution is the most significant with an important decrease in the amount of micropores. This implies an important decrease in the ratio $\frac{S}{V}$ (Table 3), where the lowest value of $\frac{S}{V}$ is observed before and after experiments for N08, because of its very low amount of small pores that is observed with all the calculation methods that we used.

We have seen that the dissolution process strongly affects the pore size diameter distribution, as well as others petrophysical parameters. These changes have consequences on other critical properties such as the rock permeability. We already know that small quantity of small pores is usually linked with high permeability (Weger et al., 2009), but some parameters interfere with this correlation. Before rock dissolution, N08 has one of the highest permeability (Tables 2 and 3) correlated with the lowest proportion of small pores (Figures 5 and 7). However, after dissolution, samples from *Group1* (N03 and N05) become the most permeable while displaying the highest proportion of small pores. This high proportion of small pores does not prevent a low tortuosity in these samples, usually associated with high permeability. However, it implies a relatively low percolating volume PV , around 87% for *Group1* compared to 95% for *Group2*. Low tortuosity is also usually directly linked to high connectivity. Before rock dissolution, when preferential conduit does not exist yet, a lot of large pores along the main flow direction are responsible for high tortuosity and low connectivity (Leger and Luquot, 2021). However, dissolution creates preferential paths along the main flow direction, enlarging the pores into this direction and connecting some isolated pores. Therefore, after rock dissolution, a large amount of

large pores parallel to the main flow direction becomes an indicator of high permeability, low tortuosity and high connectivity.

4.2. Relationship between rock structure and dissolution process

Even if the samples groups laid before dissolution mostly remain after it, some inconsistencies are highlighted in the evolution of N08 parameters. In this section, we discuss the role of the initial rock structure on the dissolution patterns and the evolution of petrophysical parameters. We will focus on samples N03 and N08, which have been submitted to similar experimental conditions (Table 1), while they present different initial structures (Figure 1). N03's initial structure is relatively homogeneous while N08 has a pre-existing heterogeneity corresponding to an altered zone with large porosity. Even though, the initial petrophysical properties of N08 are mostly similar to that of the other samples of *Group2* (Tables 2 and 3), except the initial permeabilities calculated from images, k_{XR} and k_P , which are much higher. This is due to the non-visibility of structures smaller than $12\ \mu\text{m}$, implying that the calculation considers that there are no small grains obstructing the altered zone and the fluid easily circulates through it. This initial low quantity of small pores (Figures 5 and 7) is responsible for the low ratio $\frac{S}{V}$ compared to other samples.

Even if both samples are dissolved with the same experimental conditions, the dissolution gives different results for N03 and N08. Before discussing these differences, we examine the similarities of chemical parameters. In both experiments, the output pH reaches the same values, as well as the final fluid conductivity and Ca concentration (Figure 3). Nevertheless, the curve breaks in pH, σ_f , [Ca] (Figure 3), permeability (Figure 4) and poros-

ity (Figure 8) occur at different times for N03 and N08. As we already know, during the percolation experiments, main flow paths are created (Figure 6). Several previous studies (Daccord, 1987; Fredd and Fogler, 1998; Golfier et al., 2002; Brosse et al., 2005; Szymczak and Ladd, 2009; Luquot and Gouze, 2009; Vialle et al., 2014; Guarracino et al., 2014; Menke et al., 2016) demonstrated that the formation of these preferential paths ends with a channel breakthrough at the sample outlet, inducing some changes in flow location inside the sample. The time at which the channel breaks through at the sample outlet is usually defined as the percolation time t_p . Here, the conduit in N08 sample percolates 4 times faster than in N03. However, the dissolution rate, defined as $R = [\text{Ca}] \times Q$, is similar for both experiments and around 5×10^{-8} mol/s. This value of R is consistent with studies performed in similar conditions on others limestone rocks, where R is the same in Noiriel et al. (2009) and is about 2×10^{-8} mol/s in Luquot et al. (2014a) and 8×10^{-7} mol/s in Vialle et al. (2014). This implies that the quantity of dissolved calcite needed to percolate in N08 sample is 4 times smaller than in N03 sample.

The porosity and permeability of N08 increase much less than that of N03 (Figures 8 and 4). Also, N08 keeps very similar values for electrical parameters in images calculations (F_{XR} , m_{XR} and τ_h in Table 3), whereas the pore shape and the pore size distribution remain very similar before and after the experiment (Figures 5 and 7). The main rock structure of the sample N08 does not seem to be really affected by the dissolution process at least at macroscopic scale. This can be explained by the fact that the acid preferentially dissolves the small grains, which present a potentially higher reactive

433 surface area, not visible in tomography images. Moreover, the pre-existing
 434 channel inside N08 makes the creation of a fully connected path through
 435 this sample relatively easy. It only consists in enlarging the initial path by
 436 dissolving these small grains and connecting the rest of the sample between
 437 the inlet and outlet. Therefore, a short experimental duration is enough to
 438 create a percolating path inside this specific sample. The laboratory tortu-
 439 osity (Table 2) is thus more affected (decreased) than the one measured from
 440 XRMT images (Table 3).

441 To conclude, the structure plays an important role in chalk dissolution in
 442 the case of important heterogeneities, leading to fast percolation, low increase
 443 in porosity and permeability, and weak changes in pore shapes and pore size
 444 distribution, as it has already been observed in fractured samples (Elkhoury
 445 et al., 2013; Garcia-Rios et al., 2017).

446 *4.3. Impact of the experimental conditions on porosity and permeability changes*

447 Since the pre-existing structural heterogeneity in N08 is responsible for
 448 remarkable differences in petrophysical parameters evolution and chemical
 449 experimental behavior, it will not be discussed in the following part where
 450 *Group2* now indicates samples N02, N04 and N09. Focusing on the impact
 451 of the experimental conditions on the dissolution and its consequences, we
 452 observe that the percolation time t_p defined in Section 4.2 is different for
 453 each sample (Figures 3, 4 and 8), which are subjected to different experi-
 454 mental conditions (Table 1). The conduit in N04 percolates the latest due
 455 to the combination of the lowest flow rate and the lowest inlet acid con-
 456 centration applied; N02 and N09 conduits percolate at similar faster times
 457 around 7.5 hours; and N03 and N05 conduits are created the fastest in

1.9 and 1.2 hours, respectively. In order to understand these differences, Figure 9 displays the relative calcite concentration $[Ca]^*$, the changes in porosity $\Delta\phi$ and the relative permeability k^* according to the quantity of acid injected in the sample over the experiment M_0 (in mol).

Figure 9: Evolution of chemical and hydrodynamic fluid parameters during percolating experiments depending on the acid quantity injected over time M_0 (mol). (a) $[Ca]^*$ is the calcite concentration changes between the outlet and inlet normalized by the injected acid concentration, (b) $\Delta\phi$ is the porosity evaluated from Ca concentration changes between the outlet and inlet, (c) k^* is the permeability changes normalized by the initial permeability.

These results lead to the following conclusions: (i) the creation of a percolating conduit in *Group2* (N02, N04 and N09) needs a lower quantity of injected acid than *Group1* (N03 and N05); (ii) the dissolution behavior depends on the inlet acid concentration; (iii) the quantity of injected acid M_0

466 until the conduit percolation is not linear with the flow rate applied. More
 467 precisely, for C_0^1 , the conduit percolation of N02 occurs for a lower M_0 than
 468 the N04 one, while a higher flow rate is applied to N02 sample. On the
 469 contrary, for C_0^2 , the lower the flow rate is, the lower M_0 is when conduits
 470 percolate. Additionally, Figure 9b displays lower slopes in porosity changes
 471 $\Delta\phi$ for *Group1* than *Group2*, which can be explained by the multiple ram-
 472 ifications along samples N03 and N05 being most likely created before the
 473 breakthrough (Figure 6). This dissolution shape, closed to homogeneous dis-
 474 solution, is known to promote more continuous porosity and permeability
 475 increases instead of a strong break slope at the percolation time (Luquot
 476 and Gouze, 2009). Concerning N04 and N09 from *Group2* that display the
 477 highest slopes, they are associated with low flow rates that induce transport
 478 regimes dominated by diffusion ($Pe_1 \ll 1$). This transport type results in
 479 an important front dissolution from the sample inlet (Golfier et al., 2002),
 480 implying a slow and progressive conduit creation in a tubular way with fi-
 481 nal reactive surfaces much smaller than before percolation and large paths
 482 already created at time t_p . This induces a sudden high increase in perme-
 483 ability, as it can be observed in Figure 9c. We also observe that N04 has a
 484 slope twice higher than N09 in $\Delta\phi$, as well as a twice higher value of calcite
 485 concentration $[Ca]^*$. This difference is mostly due to the acid concentration
 486 injected since a lower C_0 injected in N04 with similar flow rates implies that
 487 the acid consumption is less important and results in reactions more localized
 488 with smaller surfaces. For comparison, N02 and *Group1* (N03 and N05) are
 489 dissolved with higher flow rates associated with higher Peclet numbers (Pe_2
 490 and Pe_3) and a more advective acid transport inside the samples. This is

491 responsible for the permeability changes k^* patterns, where the permeability
 492 still increases after the conduit percolation. In this case, the reaction surface
 493 inside these samples being larger (more ramifications), the reaction takes
 494 place at more locations than in samples with conduits more tubular (Noiriel
 495 et al., 2009), increasing the quantity of rock dissolved.

496 These results are completed with the good correlation that we observe
 497 between our data and the well-known power-law relating permeability and
 498 porosity $k = \phi^n$ (Kozeny, 1927; Carman, 1937) shown in Figure 10. Exponent
 499 n values found from the power law stand between 140 (N05) and 338 (N02),
 500 which are much higher than those found in the literature, with for instance
 501 $n = 3$ for granular packings in constant structure formation in Kozeny (1927)
 502 and Carman (1937), or $1 < n < 2.5$ for channels formation in limestone
 503 dissolution (Beckingham, 2017; Sabo and Beckham, 2021). Higher values
 504 are found in the literature when studying limestone dissolution with $5 <$
 505 $n < 11$ (Menke et al., 2015, 2016), $n = 5$ (Poonoosamy et al., 2020), $n = 13$
 506 (Noiriel et al., 2004), $4 < n < 24$ (Garing et al., 2015), $10 < n < 20$ (Bernabé
 507 et al., 2003) and $n = 75$ (Noiriel et al., 2005). This is mostly due to the
 508 important heterogeneities created during the reaction in limestone (Brace,
 509 1980; Lucia, 1995; Vialle et al., 2013; Menke et al., 2016) and the relationship
 510 between the permeability and the pores roughness (Noiriel et al., 2004) and
 511 connectivity (Gueguen and Dienes, 1989), the latter being not homogeneous
 512 inside a karstified sample (Vialle et al., 2013). Here, the values are higher
 513 than the values found in the literature, except for some fracture samples
 514 (Noiriel et al., 2005), which highlights the strong heterogeneities created in
 515 our rock samples. In addition, we can mentioned that the lowest n value is

516 obtained for sample N05 with the most ramified dissolution process, whereas
 517 the largest one is obtained for N08 characterized by a strong heterogeneity.
 518 Attempt to improve the porosity-permeability relationship with a critical
 519 porosity as done in Luquot and Gouze (2009) was not successful in this work
 520 and requires deeper analysis.

Figure 10: Permeability over porosity for all the samples. n is the power exponent from the Kozeny-Carman law $k = \phi^n$.

521 4.4. Linking the dissolution rate and percolation time with the Damköhler 522 number

523 Damköhler number definition

524 Considering that the experiments are conducted under diffusion-dominant
525 transport regimes ($Pe \leq 1$ except for N05) and focusing on Damköhler num-
526 ber expressions that do not require to define the reaction rate K , we use
527 expressions (1) and (2) developed by Knapp (1989) and Menke et al. (2015),
528 respectively,

$$Da = \frac{\alpha S_r r L^2}{C_{eq} d} \quad (1)$$

$$Da = \frac{\pi r l}{n_{Ca} d}. \quad (2)$$

529 In expression (1), α is the stoichiometric coefficient of element i in the
530 mineral ($\alpha=1$ for Ca in calcite $CaCO_3$); S_r is the reactive specific surface area
531 [m^{-1}] set to either the ratio $\frac{S}{V}$ that is provided in Table 3 or $\frac{S}{V_{Ca}}$ with V_{Ca} the
532 calcite volume in each sample; r is the kinetic rate for a flat and pure sam-
533 ple (calcite) with no transport limitation [$mol/m^2/s$]; L is the characteristic
534 length of the system set to the length of the pores l as for diffusion-dominant
535 regimes (Menke et al., 2015) and C_{eq} is the equilibrium concentration of
536 element i (Ca^{2+} , here) [mol/L]. The kinetic rates r are extrapolated from
537 values found in Pokrovsky et al. (2009). For a temperature of 25°C and
538 an equivalent CO_2 partial pressure of 2 and 7 atm, corresponding to the
539 C_0^1 and C_0^2 acid concentrations respectively, the equivalent kinetic rates are
540 3×10^{-5} $mol/m^2/s$ and 5×10^{-5} $mol/m^2/s$, respectively. Note also that the
541 parameter S_r , usually considered as a fitting parameter (Noiriel and Daval,
542 2017), is not well defined because (i) it is underestimated when using the
543 ratio $\frac{S}{V}$ obtained by imagery calculations that ignore small pores (smaller
544 than the pixel size) and (ii) it requires to determine the saturation index Ω
545 that is set to 0 here when using the ratio $\frac{S}{V_{Ca}}$ (Luquot and Gouze, 2009).

546 In expression (2), n_{Ca} is the number of moles of calcite per volume unit
 547 [mol/m³] defined as $n_{\text{Ca}} = \frac{\rho_{\text{calcite}}(1 - \phi)}{M_{\text{calcite}}}$ and equals to 1.7×10^4 mol/m³ for
 548 the most porous samples (*Group1*) and 2×10^4 mol/m³ for the least porous
 549 samples (*Group2*).

550 Figure 11 show the Damköhler numbers $Da_{\frac{S}{V}}$ and $Da_{\frac{S}{V_{\text{Ca}}}}$ obtained with
 551 expression (1) by setting S_r to $\frac{S}{V}$ and $\frac{S}{V_{\text{Ca}}}$, respectively, and Da_M obtained
 552 with expression (2). $Da_{\frac{S}{V}}$ presents the lowest values and $Da_{\frac{S}{V_{\text{Ca}}}}$ the highest
 553 because the values of $\frac{S}{V}$ are much smaller than that of $\frac{S}{V_{\text{Ca}}}$. Da_M values are
 554 similar to $Da_{\frac{S}{V_{\text{Ca}}}}$ with slightly lower values as well as less variability between
 555 the samples. $Da_{\frac{S}{V}}$ seems not to be the most representative calculation be-
 556 cause of the debatable choice of S_r as $\frac{S}{V}$ (Noiriel and Daval, 2017). However,
 557 it is difficult to determinate which is the correct one, each one having its own
 558 definition, approximation and hypothesis. In all the cases, Da numbers are
 559 lower than 1, meaning that the reaction rate is low compared to the transport
 560 rate standing for an uniform dissolution according to Golfier et al. (2002).
 561 However, Figure 6 displays conduits in each sample, meaning that the disso-
 562 lution is not uniform, as observed by Menke et al. (2016) who found similar
 563 results and conclude to a channelisation dissolution regime. To create this
 564 dissolution pattern, the flow rate is relatively high inside the sample, and the
 565 rock heterogeneities allow a preferential conduit to form where the reactant
 566 is focused. During our dissolution experiments, the flow and Pe number are
 567 much lower than in Menke et al. (2016) experiments and even in these con-
 568 ditions the initial structural rock properties seem to control the localization
 569 and shape of the reaction.

570 *Dissolution rate and percolation time analysis*

Figure 11: Damkohler numbers from three different calculations. $Da_{\frac{S}{V}}$ (red circles) and $Da_{\frac{S}{V_{Ca}}}$ (blue triangles) (Knapp, 1989) display results from Equation (1) with S_r either set to $\frac{S}{V}$ or $\frac{S}{V_{Ca}}$. Da_M (black squares) (Menke et al., 2015) presents results from Equation (2).

Figure 12 and Table 4 show the evolution of the dissolution rate R and percolation time t_p depending on the experimental conditions (Pe and Da numbers).

The increase in flow rate ($\frac{Q_{N03}}{Q_{N09}} = 9$ and $\frac{Q_{N05}}{Q_{N09}} = 22$) induces an increase in Pe numbers for samples N09, N03 and N05. The corresponding Da numbers are quite constant for those calculated with the Menke equation (Da_M) while $Da_{\frac{S}{V_{Ca}}}$ increases with Pe increase. The dissolution rate increases linearly with the Pe number (Figure 12 and Table 4) while the percolation time t_p (Figure 12) decreases with Pe increase and Da decrease (for $Da_{\frac{S}{V_{Ca}}}$). However, the total quantity of dissolved calcite until breakthrough ($[Ca]_d$) and the quantity of dissolved calcite per quantity of injected acid ($[Ca]^\#$) increase with the Pe increase (Table 4). These changes are higher between N09 and N03 compared to N03 and N05 because of the differences in flow rates injected into the samples. This is also related to the difference in conduits shape after experiments (Figure 6), N09 having a tubular conduit while N03

Figure 12: Samples with their values of dissolution rate R (on the top) and percolation time t_p (on the bottom) plotted depending on Pe and Da numbers. On the left, samples are displayed for Da calculated with Equation (1), while on the right, they are displayed for the calculations with Equation (2).

586 and N05 have ramified conduits.

587 For the considered injected acid concentration, a change of Pe conditions,
588 from Pe_1 to Pe_2 , induces an increase by one order of magnitude in the dis-
589 solution rate (Figure 12). On the contrary, the percolation time depends on
590 the acid concentration as its decrease is higher for a high acid concentration.
591 The dissolution rates for N02 and N09 are quite similar as well as the dis-
592 solution shape, characterized by tubular conduit (Figure 6). Consequently,
593 the Pe and Da diagram does not help us to predict the dissolution shape.
594 Nevertheless, these observations allow seeing that a 10 times increase in acid

Samples	Pe	Da_M	$Da_{\frac{s}{V_{Ca}}}$	R	t_p	$[Ca]_d$	$[Ca]^\#$
N02	0.76	$4.97e^{-5}$	$7.30e^{-4}$	$6.69e^{-9}$	7.77	$1.87e^{-4}$	0.96
N03	0.79	$9.64e^{-5}$	$8.52e^{-4}$	$5.17e^{-8}$	1.88	$3.49e^{-4}$	0.74
N04	0.11	$4.81e^{-5}$	$8.26e^{-5}$	$6.89e^{-10}$	93.92	$2.33e^{-4}$	0.96
N05	1.68	$5.73e^{-5}$	$1.33e^{-3}$	$1.31e^{-7}$	1.17	$5.48e^{-4}$	0.75
N08	0.79	$8.38e^{-5}$	$8.02e^{-4}$	$4.49e^{-8}$	0.45	$7.27e^{-5}$	0.49
N09	0.09	$8.21e^{-5}$	$9.33e^{-5}$	$5.86e^{-9}$	7.27	$1.53e^{-4}$	0.52

Table 4: Table of experimental properties of each sample. Pe is the average Pe calculated with lowest and largest l , Da_M is calculated from Equation (2), $Da_{\frac{s}{V_{Ca}}}$ is calculated from Equation (1), R is the dissolution rate [mol/s], t_p is the percolation time [h], $[Ca]_d$ is the total quantity of dissolved calcite until conduit percolation [mol] and $[Ca]^\#$ is the quantity of dissolved calcite per quantity of injected acid [mol/mol].

concentration and a 9 times increase in flow rate have similar consequences on the dissolution. Indeed, these changes lead to similar decreases in percolation times t_p and dissolved calcite rates $[Ca]_d$. N02 and N09 conduits both percolate around 7.5 hours with a $[Ca]_d$ around $1.7e^{-4}$ mol, and present similar conduits shape (Figure 6). N09 conduit percolates faster than the N02 one because of the pre-existing micro-cracks inside the sample, which make easier the conduit formation.

To sum up, in the case of Da calculated with Equation (1) ($Da_{\frac{s}{V_{Ca}}}$), for each injected acid concentration, higher the Pe is, higher the Da is. Therefore, more the transport is advective (Pe increases), more the reaction is dominant compared to the transport (Da increases). However, in the case of Da calculated with Equation (2) (Da_M), the increase in Pe is not associated with changes in Da. Also, as seen earlier, a low Da is logically linked with a low C_0 . For sample N05, the Da is relatively low due to the advective dominated transport. The dissolution rate R follows Pe and $Da_{\frac{s}{V_{Ca}}}$, since it is smaller when both numbers are smaller. However, it is also sharply

611 related to the acid concentration, which is much smaller when C_0 is smaller
612 for similar Pe and Da conditions.

613 5. Conclusions

614 In this study, we try to identify which parameter most controls the chalk
615 dissolution at pore scale and then the karstification. The flow rate and the
616 initial concentration of acid injected inside the rock seem to be important
617 factors regarding dissolution patterns. Dissolution rates of calcite and per-
618 colation time of formed conduits are directly linked to these two parameters.
619 However, the structure seems to also have a decisive impact on dissolution.
620 We previously see that chalk is defined by an important heterogeneous mi-
621 crostructure (Leger and Luquot, 2021), composed of a lot of small compo-
622 nents, leading to a high structural heterogeneity. This is responsible for
623 special patterns during dissolution. The local heterogeneities induce a very
624 large exponent in the porosity-permeability power law of Kozeny (1927) and
625 Carman (1937). The dissolution regime inside each sample is dependent on
626 the rock structure, as it has been shown in several previous studies. In sam-
627 ples with high initial porosity (N03 and N05), the surface reaction is larger
628 and the dissolution is more uniform than in samples with lower initial poros-
629 ity (N02, N04, N08 and N09). Also, rock heterogeneities are responsible for
630 channel formation inside the samples during the dissolution while calculated
631 Peclet and Damköhler numbers define an uniform dissolution, as previously
632 demonstrated in Menke et al. (2016). In this study, we could reproduce dis-
633 solution features similar to mini-karst as observed at larger scale in chalk
634 environments. We demonstrate that the localization of the chalk dissolution

⁶³⁵ is mainly linked to the specific small scale heterogeneities and not directly
⁶³⁶ predictable using dimensionless parameters such as Da and Pe numbers.

637 **Appendix A. Experimental procedure**

638 *Appendix A.1. Experimental protocol*

639 The following protocol is applied to each sample. The sample is placed
640 under vacuum condition during a minimum of 12 hours. Then, the sample is
641 saturated at low flow rate with water in equilibrium with the rock. Equilib-
642 rium water is then injected at increasing and decreasing flow rates in order
643 to clean the pore phase and remove free particles into the samples. When
644 pressure changes are linear with flow rate changes, the sample is considered
645 cleaned and flow rate is fixed at the wanted one. The initial permeability is
646 deduced at this starting stage from the pressure drop and the given flow rate
647 with the equation provided in Electronic Supplement. Then, the acid solu-
648 tion is injected through the core sample. Experiments are considered over
649 when pressure sensors are out of measurement capabilities. At this point,
650 water at equilibrium with rock is injected in order to calculate a final rock
651 permeability. The flow rate is increased slowly and step by step to avoid
652 to damage the sample. This protocol is applied to experiments that are
653 conducted with various acid concentrations and flow rate. The acid concen-
654 trations are all buffered to a pH of 4 and the flow rates are chosen such as
655 the experiments could be done over reasonable time to observe the effect of
656 acid injection while being low enough to limit grains separations.

657 *Appendix A.2. Experimental output*

658 For each experiment, the evolution of the sample porosity $\phi(t)$ along
659 time is deduced from the measured concentration of Ca ions with the fol-
660 lowing methodology. From the pressure measurements, the permeability k is
661 calculated using Darcy's law (equation provided in Electronic Supplement).

662 Concentration of Ca ions are measured for each outlet sampled fluid that
 663 is collected at time t_i ($i = 1, \dots, N$) with N the number of samples. The
 664 porosity can be deduced from this concentration $[Ca]_{t_i}$ with the following
 665 steps. (i) The calcium carbonate mass $m_{CaCO_3 t_i}$ dissolved between times t_{i-1}
 666 and t_i is calculated from Equation (A.1), which is based on the equivalence
 667 between the quantity of Ca measured in the sampled fluid and the quantity
 668 of dissolved $CaCO_3$ from the rock, in mol, and expressed as

$$m_{CaCO_3 t_i} = \frac{([Ca]_{t_i} - [Ca]_{t_0})(t_i - t_{i-1})Q}{M_{Ca}} M_{CaCO_3} \quad (A.1)$$

669 with $[Ca]_{t_i}$ the calcium concentration at the sampling time t_i [g/m³], $[Ca]_{t_0}$
 670 the initial calcium concentration [g/m³], $t_i - t_{i-1}$ the time spent since the
 671 last sampling [s], Q the flow rate [m³/s], and M_{Ca} and M_{CaCO_3} the molecular
 672 masses of calcium and calcium carbonate, respectively [g/mol]. (ii) The vol-
 673 ume of dissolved calcium carbonate in the rock sample between each sampling
 674 step, $V_{CaCO_3 t_i}$, is obtained by dividing $m_{CaCO_3 t_i}$ by the density of calcium car-
 675 bonate that is set to 2.7×10^6 g/m³. (iii) The porosity ϕ_{t_i} is deduced from
 676 the following expression

$$\phi_{t_i} = \phi_{t_{i-1}} + \frac{V_{CaCO_3 t_i}}{V_{ech}} \quad (A.2)$$

677 with V_{ech} the sample volume [m³]. The initialization of the previous equation
 678 for $t = 0$ is made by using the initial laboratory porosity ϕ_L .

679 **Electronic Supplement: Procedure and algorithm for OpenPNM**
680 **software**

681 *Procedure for pore network extraction*

682 The 3D images obtained from X-ray tomography calculations are used
683 to extract the pore network of the samples with the open-source software
684 OpenPNM that is described below (Gostick et al., 2016). The permeability
685 k of the resulting extracted pore networks is calculated with Darcy’s law as

$$k = \frac{QL\mu}{A\Delta P},$$

686 where Q is the flow rate [m³/s], L the sample length [m], μ the dynamic
687 viscosity of water [Pa.s] set to 0.001 Pa.s, A the surface of fluid injection [m²]
688 and ΔP the differential pressure between the inlet and outlet of the sample
689 [Pa]. The flow rate resulting from a chosen gradient pressure that is applied
690 to the sample is determined by Stokes equation.

691 OpenPNM tool is working on Scipy Stack from Anaconda navigator,
692 which is a Python console. The method used here is the watershed segmen-
693 tation compiled with the SNOW algorithm, previously used and explained
694 by Gostick (2017). The extraction process needs segmented images in 8 bits
695 format with two distinct labels: 0 for pore voxels and 255 for rock voxels.
696 Our images from chalk samples being too large for OpenPNM, a binning
697 of 2 is applied on each image by dividing the number of voxels by 2 in the
698 three spatial directions. Additionally, we only consider the connected poros-
699 ity by removing the isolated pores. Once the segmented image is imported,
700 an Euclidian distance map of the void space and a Gaussian filter with the
701 parameter sigma set to 0.4 are applied. It results in an image with one peak

702 at each pore center, based on a maximum radius of 5 pixels. Then, some
 703 filters are implemented to clean false generated peaks and obtain a map of
 704 pore centers. The next step consists in applying the watershed segmentation
 705 to identify regions where pores are located. The SNOW algorithm is then
 706 used to extract the pore network from the image, generating the network
 707 composed of pores and throats. Then, a resolution label of 0.01 is applied to
 708 the network in order to identify which pores are located on sample surfaces.
 709 The network can be exported into different file formats for visualization and
 710 treatments. To operate permeability computation on the network, a clean-
 711 ing step is necessary, consisting in removing isolated pores. In our case, the
 712 image has been cleaned previously, so this step is not changing the network.

713 *Algorithm for pore network extraction and permeability computation*

```

    714     Algorithm used on segmented images with OpenPNM
    715     print('Read libraries')
    716     import os
    717     import imageio
    718     import scipy as sp
    719     import numpy as np
    720     import openpnm as op
    721     import porespy as ps
    722     import scipy.ndimage as spim
    723     import matplotlib.pyplot as plt
    724     from porespy.filters import find_peaks, trim_saddle_points, trim_nearby_peaks
    725     from porespy.tools import randomize_colors
    726     from skimage.segmentation import watershed
  
```

```

727     ps.visualization.set_mpl_style()
728     np.set_printoptions(precision=4)
729     np.random.seed(10)
730     print('Read image')
731     path = 'path to image folder'
732     file_format = '.tif'
733     file_name = 'filename'
734     file = file_name + file_format
735     fetch_file = os.path.join(path, file)
736     im = imageio.mimread(fetch_file, memtest='image_size')
737     im = np.array(im, dtype=bool)
738     print('Gaussian filter')
739     sigma = 0.4
740     dt = spim.distance_transform_edt(input=im)
741     dt = spim.gaussian_filter(input=dt, sigma=sigma)
742     print('Identify peaks')
743     peaks = find_peaks(dt=dt, r_max=5)
744     print('Initial number of peaks: ', spim.label(peaks)[1])
745     peaks = trim_saddle_points(peaks=peaks, dt=dt)
746     print('Peaks after trimming saddle points: ', spim.label(peaks)[1])
747     peaks = trim_nearby_peaks(peaks=peaks, dt=dt)
748     peaks, N = spim.label(peaks)
749     print('Peaks after trimming nearby peaks: ', N)
750     print('Regionalyze step')
751     regions = watershed(image=-dt, markers=peaks, mask=dt > 0)

```

```

752     regions = randomize_colors(regions)
753     print('Image regionalized visualisation')
754     fig, ax = plt.subplots()
755     ax.imshow((regions*im)[:, :, 100], cmap=plt.cm.nipy_spectral);
756     print('Network creation with SNOW algorithm')
757     net = ps.networks.regions_to_network(regions*im, voxel_size=voxel_size)
758     print('Update network')
759     pn = op.network.GenericNetwork()
760     pn.update(net)
761     prj = pn.project
762     print('Export VTP')
763     prj.export_data(filename='path_and_filename', filetype='vtk')
764     print('Export network')
765     ps.io.to_openpnm(pn, 'path_and_filename')
766     print('Resolution label')
767     resolution_label=0.01
768     op.topotools.label_faces(pn,resolution_label)
769     geo = op.geometry.GenericGeometry(network=pn, pores=pn.Ps, throats=pn.Ts)
770     print(pn)
771     print('Export VTP_reso')
772     prj.export_data(filename='path_and_filename', filetype='vtk')
773     print('Export CSV_reso')
774     prj.export_data(filename='path_and_filename', filetype='csv')
775     print('Check health')
776     h = pn.check_network_health()

```



```

777     op.topotools.trim(network=pn, pores=h['trim_pores'])
778     h = pn.check_network_health()
779     print(h)
780     print('Calculate porosity')
781     print(ps.metrics.porosity(im))
782     print('Assign water phase and physics')
783     # Assign phase
784     water = op.phases.Water(network=pn)
785     # Assign physics
786     phys_water = op.physics.Standard(network=pn, phase=water, geometry=geo)
787     print('Assign Algorithm and boundary conditions from left to
788 right')
789     # Assign Algorithm and boundary conditions
790     perm = op.algorithms.StokesFlow(network=pn)
791     perm.setup(phase=water)
792     perm.set_value_BC(pores=pn.pores('right'), values=0)
793     perm.set_value_BC(pores=pn.pores('left'), values=101325)
794     perm.run()
795     water.update(perm.results())
796     print('Calculate effective permeability from left to right')
797     # Calculate effective permeability
798     resolution = pixel.resolution
799     Q = perm.rate(pores=pn.pores('left'), mode='group')[0]
800     A = 3.14159265 * (((im.shape[1] * resolution) / 2)**2)
801     L = im.shape[0] * resolution

```

```

802     mu = water['pore.viscosity'].max()
803     delta_P = 101325 - 0
804     K = Q * L * mu / (A * delta_P)
805     print('The value of K from right to left is: K/0.98e-12*1000:.2f
806     mD')

```

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