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On the characterization of poroperm relationships and reactive surface areas during heterogeneous dissolution induced by CO₂ injection in limestone reservoir

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Abstract

Numerical programs for simulating flow and reactive transport in porous media are essential tools for predicting reservoir properties changes triggered by CO₂ underground injection. At reservoir scale, meshed models in which equations are solved assuming that constant macroscopic properties can be defined in each cells, are widely used. However, the parameterization of the dissolution - precipitation problem and of the feedback effects of these processes on the flow field is still challenging. The problem arises from the mismatch between the scales at which averaged parameters are defined in the meshed model and the scale at which chemical reactions occur and modify the pore network geometry. In this paper we investigate the links between the dissolution mechanisms that control the porosity changes and the related changes of the reactive surface area and of the permeability. First, the reactive surface area is computed from X-ray microtomography data obtained before and after a set of dissolution experiments of pure calcite rock samples using distinctly different brine - CO₂ mixtures characterizing homogeneous to heterogeneous dissolution regimes. The results are used to validate the power law empirical model relating the reactive surface area to porosity proposed by Luquot and Gouze (2009). Second, we investigate the spatial distribution of the effective hydraulic diameter and of the tortuosity, two structural parameters that control permeability, in order to explain the different porosity-permeability relationships observed for heterogeneous and homogeneous dissolution regimes. It is shown that the increase of permeability is due to the decrease of the tortuosity during homogeneous dissolution, whereas the permeability increase is due both to the decrease of the tortuos-

ity and the increase of hydraulic diameter during heterogeneous dissolution. For the intermediate dissolution regime, identified to be the optimal regime for increasing permeability with small changes in porosity, the increase of permeability results from a large increase in the mean effective hydraulic diameter of the sample.

Key words: reactive transport, carbon storage, permeability, X-ray microtomography

1. Introduction

Dissolution of a porous medium creates, under certain conditions, some highly conductive channels. Experimental and theoretical studies show that, for a given fluid composition undersaturated with respect to the rock-forming mineral(s), the dissolution pattern is determined by the injection rate. When the undersaturated fluid is injected at a very high rate, its low residence time produces uniform dissolution because the dissolution rate is controlled by the kinetic barriers, and the fluid remain undersaturated over long distances. Conversely, at intermediate to low flow rates, heterogeneous dissolution patterns (e.g.: wormhole-like structures) may develop due to the initial and growing heterogeneity of velocity field triggered by the variability (at all scales) of the reservoir hydrodynamic properties. Under certain conditions, channeling may develop even for “almost” homogeneous media. With the exception of some weathering processes occurring in the first few meters of the earth (e.g.: karst formation), natural processes in aquifers and reservoirs are usually characterized by low flow rates and by the mixing of fluids being very close to thermodynamical equilibrium with the rock-forming minerals. Consequently, heterogeneous dissolution features are poorly observed at depth. However, heterogeneous dissolution may be triggered by anthropogenic forcing, such as the injection at depth of exogene fluids using boreholes. So far, heterogeneous dissolution regimes have been investigated mainly for the stimulation of oil wells using acidification techniques for enhancing near-well permeability in carbonate reservoirs (Golfier, Zarcone, Bazin, Lenormand, Lasseux, and Quintard (2002); Kalia and Balakotaiah (2007); Cohen, Ding, Quintard, and Bazin (2008)). Indeed, the formation of localized conductive channels (wormholes) is recognized as the most efficient way to increase permeability while minimizing the consumption of acid. Similar processes are expected when massively injecting CO₂ in carbonate reservoirs. While

limestone oil/gas reservoirs are occasional, deep saline aquifers are often limestones (Bachu, Gunter, and Perkins (1994)). In these rocks, the injection of massive volumes of supercritical CO₂ (scCO₂) may induce rapid and sustainable dissolution of the carbonate minerals in contact with the CO₂-enriched pore water in the vicinity of the scCO₂ front. The position of this front, where large concentration gradient develops, will move according, for instance, to the injection rate, the porosity and the temperature-pressure-salinity dependent CO₂ solubility, until all the CO₂ is dissolved and the water-minerals equilibrium state is recovered. As a result, the reservoir will be locally exposed to distinctly different chemical forcings, inducing heterogeneous or homogeneous dissolution processes depending on the effective mass transfer rates and reactants renewal. These distinct dissolution regimes will cause specific modifications of the porosity (ϕ) and permeability (k), with furthermore potentially important alteration of the dispersivity (both mixing and spreading of the CO₂ and of the reaction products) and of the mechanical properties of the reservoir along the migration path of the CO₂-enriched pore water.

Anticipating the modification of the reservoir properties during the injection period (on the scale of years) and the repository period (millennial scale) is a critical issue to design the injection operations and assess the storage performance and safety. However, modeling heterogeneous mass transfers in highly reactive systems is still challenging. Two fundamental difficulties concern i) the measurement and the implementation in the numerical models of the reactive surface area changes ($S_r(t)$) that controls the effective reaction rate, and ii) the parameterization of the constitutive relationship that models permeability changes ($k(t)$) at the Darcy's scale corresponding to the mathematical discretization of the transport equation (de Marsily (1986)). Both $S_r(t)$ and $k(t)$ are controlled by the porosity changes $\phi(t)$, and more specifically by the modifications of the pore network at scales smaller than Darcy's scale. This mismatch between the characteristic scales at which reactions occurs and the scale (Darcy's scale) at which flow and transport parameters are defined is a major concern for guaranteeing the predictiveness of the simulations.

Because of the lack of explicit information, usually modelers assume a constant value of the reactive surface area or use simple empirical models based on the ratio of surface-to-volume of spheres or other simple geometries (e.g. Xu, Apps, and Pruess (2003), Xu, Apps, Pruess, and Yamamoto (2007); Pruess, Xu, Apps, and Garcia (2003); White, Allis, Moore, Chid-

sey, Morgan, Gwynn, and Adams (2005); Zerai, Saylor, and Matisoff (2006); Noiriél, Luquot, Madé, Raimbault, Gouze, and Van Der Lee (2009)). For homogeneous dissolution of homogeneous media, the spherical grain proxy model may be valid, assuming that the reactive surface area is calibrated from laboratory measurements in reactors. However, the grain surface area are deduced usually from BET measurements (Brunauer, Emmett, and Teller (1938)) or simply from geometric or mineral mass considerations (e.g. Hodson, Lee, and Parsons (1997); Gautier, Oelkers, and Schott (2001)), inducing large uncertainties (Hodson (2006)). Conversely, heterogeneous dissolution concerns, by definition, only a fraction of the porous media and therefore the reactive surface area cannot be modeled as constant or ubiquitously controlled by the average grain diameter of the rock-forming minerals. In this case, the determination of the reactive surface area requires a specific attention and further experimental investigations. So far, direct measurement of the reactive surface area for heterogeneous dissolution is not possible. In contrast, changes in the reactive surface area during dissolution can be deduced from the analysis of dissolution experiments. In instance, Noiriél, Gouze, and Bernard (2004) used X-ray microtomography (XMT) image-matching techniques to determine the average reactive surface area at different elapsed time during flow-through-core dissolution experiments. Yet, this technique is a highly time consuming procedure and furthermore can be applied only to small sub-domains (i.e. size of few pores). Alternatively, Luquot and Gouze (2009), evaluated the reactive surface area changes during flow-through-core dissolution by the inversion of the time-resolved porosity data, using a fitted power model relating the reactive surface area to porosity at Darcy's scale.

As the different dissolution regimes depend on the flow rate, it is essential to account for the changes in permeability while dissolution progresses. According to the Kozeny-Carman equation (Kozeny (1927); Carman (1937)), Darcy's scale permeability is related to porosity, tortuosity and the pore diameter. All together, these parameters are used to indirectly characterize the head losses produced by the pore space. In practice, information retrieved from measurements on borehole cores is usually restricted to porosity and some 2D evaluations (using cross sections) of the pore size and of the geometrical tortuosity which can be very different from the hydraulic tortuosity (Ben Clennell (1997)). Furthermore, it is probable, that the effective tortuosity is different from the tortuosity of its projection in 2D. Often, it is assumed that the inverse of tortuosity scales as a power law of porosity for porosities ranging from 0.4 to 0.5 (Adler and Thovert (1998); Avellaneda and Torquato

(1991); Dias, Teixeira, Mota, and Yelshin (2006)). However, for lower values of porosity in carbonates, it is probable that porosity alone does not explain tortuosity and that the definition of pore size radius is useless.

Finally, in term of modeling issues, porosity change is the only available parameters (from computing mineral dissolution) at Darcy's scale, and, in practice, the objective is to relate permeability changes to porosity. Obviously, evaluating permeability $k(t)$ from porosity $\phi(t)$ is not a trivial problem, as permeability depends on the structure of the entire pore space of the rock at time t . However, theoretically, permeability can be related to porosity on condition that an adequate pore space model is applied which reflects both the rock type and the dissolution regime. Another practical condition is that the model used to relate k to ϕ contains only few lumping parameters that can be measured, or at least extrapolated, from experimental data. Moreover, in the case of heterogeneous dissolution the length scale and time scale characterizing the validity domain of the model must be determined.

The aim of this paper is to investigate the phenomenological links between the dissolution regime, the reactive surface area and the porosity-permeability relationship on the basis of XMT measurements. The first objective is to compute reactive surface area from XMT data and compare them to the reactive surface area obtained by Luquot and Gouze (2009) in order to test the validity of the power model relating the reactive surface area to porosity. The second objective is to investigate the spatial distribution of the two structural parameters that control permeability at first order, namely the effective hydraulic diameter and the tortuosity, in order to explain the distinctly different porosity-permeability relationships observed by Luquot and Gouze (2009) for heterogeneous and homogeneous dissolution regimes and discuss their use for modeling application.

2. Characterisation of limestone dissolution during CO₂ injection

2.1. Rationales

When dissolved in the pore water (usually a brine), CO₂ decreases strongly its pH and produces highly reactive geochemical systems where distinctly different regimes of dissolution may occurs according to the spreading and the ongoing fate of the CO₂. As already noticed, localized (self-organized) dissolution was observed and reproduced at laboratory scale in the frame of the studies related to well acidification techniques (Fredd and Fogler (1998); Daccord, Lietard, and Lenormand (1993); Golfier et al. (2002); Cohen et al.

(2008)). The interactions between the transport of the low pH fluid (either directly injected from the well or produced by the dissolution of scCO₂ in the vicinity of the well), the chemical reactions, and the heterogeneities encountered at different scales, control the unstable behaviour of the mass transfers and the characteristics of the dissolution patterns. While the dissolution progresses, the pH and cation concentration increases and more homogeneously distributed dissolution is observed.

Darcy’s scale parameters are required for reservoir scale modeling purposes. While the definition of Darcy’s scale effective parameters is straightforward for homogeneous dissolution regimes (de Marsily (1986)), the scale effects and the initial meso-scale heterogeneity of the pore network make the prediction of wormhole-like dissolution much more difficult. Nevertheless, the studies referenced above emphasized the usefulness of the dimensionless Damköhler number $Da \equiv \bar{\vartheta}l/\bar{u}$ and the dimensionless Peclet number $Pe \equiv \bar{u}l/\bar{d}$ as complementary criteria for determining the occurrence of the different dissolution regimes (at Darcy’s scale) as a function of the average renewing of the reactant at the reaction surface by diffusion (\bar{d} is the average effective diffusion coefficient in m².s⁻¹) and advection (\bar{u} is the average water seepage velocity in m.s⁻¹) and of the average dissolution velocity $\bar{\vartheta}$ (in s⁻¹). In the following, over-lined parameters (e.g. \bar{u}) denote sample-scale-averaged values. For the macroscopically homogenous porous media studied here, it is assumed that these values characterise Darcy’s scale processes.

Low values of Da corresponds to the homogeneous dissolution of the rock controlled by surface-reaction kinetics, whereas the dissolution is controlled by the transport of the reactants and consequently heterogeneous dissolution patterns develop, for high values of Da . The carbonate dissolution velocity $\bar{\vartheta}$ is usually approximated by a linear function of the intrinsic kinetic rate coefficient \bar{r} (in m⁻².s⁻¹), the reactive surface area S_r and the dimensionless saturation coefficient ($\bar{\Omega} = \bar{\Pi}/K$) that quantifies the disequilibrium state of the water-mineral system with $\bar{\Pi}$ the ion activity product and K the equilibrium constant of the reaction under consideration (Lasaga (1998)):

$$\bar{\vartheta} = \bar{r}S_r (1 - \bar{\Omega}) . \tag{1}$$

The values of the intrinsic kinetic rate coefficient can be calculated from batch reactor measurements as a function of the temperature, the pH and the partial pressure of CO₂ (Alkattan, Oelkers, Dandurand, and Schott (1998); Pokrovsky, Golubev, and Schott (2005)). Whereas \bar{r} can be considered as a

known parameter and $\bar{\Omega}$ can be evaluated from water sample analysis, measuring S_r , which is expected to be highly variable depending on the dissolution regime, is challenging. To date, direct measurements are impossible and standard models based on simple reactive grain geometry are inappropriate to account for both the complex structure of most of the porous limestones and the localisation of the dissolution for high Da values. Note that the concept of the reactive surface area, as defined in equation 1, is different depending of the dissolution régime. In the case of heterogeneous dissolution, S_r is no more proportional to the fluid-rock interface area, but maps the heterogeneity of the velocity field. In this case, S_r can be considered as an macroscale effective coefficient encompassing both the pore interface structure and the flow heterogeneity.

Going back the definition of Pe and Da , it is important to stress that these parameters are defined according to a functional length l that, by definition, characterizes the distance for which it is pertinent to compare advection rate with diffusion rate and reaction rate with reactant renewal rate, respectively. This means that averaged value of the parameters must be definable over a characteristic distance l that is usually attached to the mean correlation length of the heterogeneities or to the sample size in case of homogeneous media. However, ϑ and \bar{u} are scale-dependent when heterogeneities develop due to transport-controlled dissolution. Note that it is also the case for the effective diffusion coefficient which depends on the medium average tortuosity $\bar{\tau}$ and porosity $\bar{\phi}$: $\bar{d} \propto \bar{\phi}d_0/\bar{\tau}$. These remarks emphasize that in practice the use of Da as a parameter in models is attached to a specific observation scale l and furthermore it involves determining a reference value (i.e. $Da = 1$). To fulfil these requirements, it is necessary to measure simultaneously l -averaged values of ϑ and u , or alternatively ϕ and k for a given set of flow rates, inlet fluid compositions and hydro-chemical properties of the reservoir.

2.2. The experiments

Laboratory flow-through experiments using reservoir core samples and conditions representative of in situ injection of CO_2 in saline aquifers are few. Recently Luquot and Gouze (2009) reported original results from a set of reactive flow experiments through limestone reservoir samples at 100 °C and 12 MPa total pressure (P). These experiments aimed at characterizing mass transfers occurring i) near the injection well, where the aquifer fluid is almost saturated with CO_2 (i.e. $P_{\text{CO}_2} \approx P$), and ii) at increasing distances from the injection well, where the fluid displays lower P_{CO_2} values and higher divalent

cation concentrations produced by rock dissolution along the fluid pathway. In the present paper, we will investigate the spatial and temporal distribution of the hydro-chemical properties within the samples first analysed by Luquot and Gouze (2009) in term of Darcy’s scale processes.

The experimental procedure consists in injecting CO₂-enriched brine through a sample core of 9 mm diameter (D) and 18 mm length (L). The reservoir rock used in Luquot and Gouze’s study is an oolitic limestone cored at depth 1635 m in the Middle Jurassic Mondeville formation of the Paris Basin. This formation is a potential target for CO₂ injection. The rock is essentially composed of mm-scale recrystallized ooliths, partially cemented with micritic calcite. The bulk rock composition is 99% calcite (0.7% quartz, 0.2% pyrite, and 0.1% kaolinite). X-Ray diffraction, SEM and cathodoluminescence provide information on the precise nature of the mineral phase. All observations indicate that both the micritic cement and the ooliths are composed of calcite of average formula Ca_{0.99}Mg_{0.01}CO₃. Consequently, because the Mg content of the calcite is negligible, the representative dissolution reaction is $\text{CaCO}_3 + \text{H}^+ \rightarrow \text{Ca}^{++} + \text{HCO}_3^-$, with the equilibrium constant $K(T = 100 \text{ }^\circ\text{C}) = a_{\text{Ca}}a_{\text{HCO}_3}/a_{\text{H}} = 0.168$, where a_i is the activity of species i (Lasaga (1998)).

Before being mixed with CO₂, the composition of the brine used in the experiment is that measured in the aquifer and is thermodynamically at-equilibrium with calcite (Coudrain-Ribstein and Gouze (1993)). The artificial brine composition is obtained by dissolving laboratory-grade CaCl₂, MgCl₂ and NaCl salts in deionised water. The inlet fluid composition is given in Table 1. The CO₂-enriched fluid is obtained by mixing the artificial brine pumped by a motorized dual piston pump system with liquid CO₂ stored in a second motorized piston pump. Mixing is performed at the targeted test pressure ($P = 12$ MPa), but at low temperature (5 °C). Then, the mixture is heated up to the desired temperature in a coil. The expected P_{CO_2} (i.e. $P_{\text{CO}_2} = 2.5, 6, \text{ and } 10$ MPa) is obtained by controlling the flow rate ratio of the water and the liquid CO₂. The fluid is monophasic as long as P_{CO_2} is lower than the lower value of the pressure in the circuit. Therefore, a back pressure controller, consisting of a computer-controlled serial dual valve system, is fitted at the outlet of the percolation circuit. The back pressure controller imposes a constant pressure drop whatever the flow rate, while maintaining the desired pressure in the circuit with fluctuations less than 5%. A detailed description of the experimental apparatus and procedures is given in Luquot and Gouze (2009). The sample surrounded

by a silicon jacket is fitted inside the percolation cell, where both axial and radial confining pressures are applied to the sample. It is essential to apply a controlled confining pressure to mimic the natural conditions and balance the fluid injection and void the deviatoric stresses that might irreversibly damage the sample. Outlet fluids are sampled recurrently for cation analysis using ICP-AES techniques. The flow rate is maintained constant at $Q = 1.9 \times 10^{-8} \text{ m}^3/\text{s}$ for all the experiments.

The experiment protocol is as follows. First, the sample is scanned by XMT using the ID19 beam line of the European Synchrotron Radiation Facility (Grenoble, France). Then, the sample is mounted inside the confinement cell and then saturated (following a vacuum period) with the rock-equilibrated brine which is injected at a constant flow rate to measure the initial permeability. At elapsed time $t = 0$, the brine- CO_2 mixture is injected at the same flow rate. At the end of the percolation-dissolution experiment the sample is stabilized in rock-equilibrated water and again scanned by XMT. For these experiments, time-resolved sample permeability $k(t)$ is directly deduced from monitoring the pressure difference ($\Delta P(t)$) between the reactor inlet and outlet using Darcy's law $k(t) = -\mu L Q / s \Delta P(t)$, where s is the cross-sectional area of the sample and μ is the dynamic viscosity of the fluid. Conversely, the time resolved sample-scale-averaged porosity $\bar{\phi}(t)$ is deduced from calcium concentration mass balance:

$$\bar{\phi}(t) = \bar{\phi}_f - \frac{Q v_{CaCO_3}}{V} \int_{\tau=t}^{t_f} (\Delta[Ca])(\tau) d\tau, \quad (2)$$

where $\bar{\phi}_f$ is the porosity measured at the end of the experiment, $[Ca]$ denotes the total calcium concentration, V is the total volume of the sample, v_{CaCO_3} is the calcite molar volume ($3.7 \times 10^{-5} \text{ m}^3 \cdot \text{mol}^{-1}$) and $\Delta[Ca] = [Ca]_{outlet} - [Ca]_{inlet}$.

2.3. Analysis of the experimental results

The results of Luquot and Gouze's experiments show non-uniform dissolution features (few localised wormhole-like structures) associated with transport-controlled mass transfers for experiment with the highest of P_{CO_2} (10 MPa; experiment D1), while surface-reaction-controlled uniform dissolution is observed for lowest value of P_{CO_2} (2.5 MPa; experiment D3). Experiment with the intermediate value of P_{CO_2} (6 MPa; experiment D2) displays the transition from transport-controlled dissolution to surface-reaction-controlled dissolution. For experiment D2 penetrative ramified wormholes

are observed (Fig. 1). The authors (op. cit.) showed that these distinctly different dissolution regimes are characterized macroscopically by the initial value of the sample-scale Damköhler number that is proportional to $\Delta[Ca]$ at the beginning of the experiment assuming that the homogeneous dissolution experiment (D3) allows determining the reference value $Da \equiv \bar{v}l/\bar{u} = 1$ with l the length of the sample.

These unanticipated results show that dissolution regime is forced by the initial conditions and persists over time, while the values of Pe and Da change with time due to changes in the sample-scale-averaged porosity $\bar{\phi}(t)$, permeability $k(t)$ and reactive surface area $S_r(t)$. Yet, porosity and reactive surface area are not independent parameters. In order to obtain a closed-form expression of the problem and determine the functional form of the sample-scale-averaged porosity $\bar{\phi}(t)$, Luquot and Gouze (2009) assumed a power law scaling between the reactive surface area and porosity:

$$\bar{\sigma}_r(t) = B_\sigma \bar{\phi}(t)^{-w}, \quad (3)$$

where $\bar{\sigma}_r(t)$ is the average reaction surface area per volume of fluid (reaction specific surface), w is a non-null positive coefficient that is fitted from time-resolved experimental data and $B_\sigma = \bar{\sigma}_r^{(0)}/\bar{\phi}^{(0)-w}$ with $\bar{\phi}^{(0)}$ and $\bar{\sigma}_r^{(0)}$ the initial value of porosity and reaction specific surface, respectively. With $\bar{\sigma}_r = S_r/(1 - \bar{\phi})V$, where V is the volume of the sample, equation (3) can be rewritten to obtain the total reactive surface area in the sample: $S_r(t) = B_\sigma \bar{\phi}(t)^{-w} (1 - \bar{\phi}(t)) V$.

The experimental results are summarized in Fig. 2, where $\bar{\phi}(t)$ and $S_r(t)$ are reported. We observe that the rate of increase of porosity is higher for the localized dissolution regime (D1) where wormholes-like features are observed, while the reactive surface area decreases weakly compared to the strong decrease of the reactive surface area calculated for the homogeneous dissolution regime (D3) that conversely displays a weak increase in porosity. Using equation 3, Luquot and Gouze (2009) showed that these macroscopic observations are well explained by a single non-linear model:

$$\bar{\phi}(t) = \bar{\phi}^{(0)} [1 + \bar{v}^{(0)} wt]^{1/w} \quad (4)$$

where $\bar{v}^{(0)}$ is the initial sample-scale averaged reaction velocity. As the value of $\bar{\phi}^{(0)}$ can be easily determined by independent measurements, the model has two degrees of freedom: w and $\bar{v}^{(0)}$. Luquot and Gouze (2009) fitted the values w and $\bar{v}^{(0)}$ for each of the experiments from the porosity versus time

curves. Nevertheless, the remaining question is whether this model (using equations 3 and 4) is just a practical way to fit $\bar{\phi}^{(0)}$ curves or whether $\bar{\vartheta}^{(0)}$ and w are effective parameters that can be used in predictive models. To address this problem, it is important to verify the assumption that S_r scales with $\bar{\phi}$, and therefore to perform independent measurement of S_r (or $\bar{\sigma}_r$) and $\bar{\phi}$.

Conversely, Fig. 6a shows that the permeability increase with porosity is much higher for the intermediate regime (D2) than for the fully localized and the fully homogeneous dissolution regime. Comparable observations were reported by Cohen et al. (2008) using a 2D modeling approach for computing the optimal procedure for well acidification assuming a fully homogeneous initial porosity distribution. For instance, Cohen et al. (2008) observed that the dissolution regime, characterised by a dense network of thin unramified wormholes, allows minimizing the volume of acid to be used for increasing the well performance. Still, the origin of this optimal permeability increase is difficult to settle using the sample-scale averaged porosity and permeability data only and requires independent measurements of the parameters controlling the permeability.

3. XMT Data Analysis

XMT is a non-invasive visualization technique producing 3D maps of the X-ray attenuation of the material. For a given energy of the incident X-ray beam (here 40 keV), attenuation depends on the chemical composition of the rock, which is related closely to the atomic number of its components, and their mass fraction per volume (i.e. the density). In mono-crystalline rock, such as the sample studied here, XMT images provide simply the density distribution in the rock, or in other words, the 3D porosity maps. The imaging technique consists in performing 1500 X-rays at different angles, which are subsequently processed to obtain a matrix of 2048^3 values, each representing the porosity of a cube (a voxel) of size $5.06 \mu\text{m}$. Then, raw data are transformed in a binary 3D image, where each voxel belongs either to the rock matrix or to the pore space (void). For that, a segmentation technique based on region growing is applied (Gonzalez and Woods (1992); Noiriél, Bernard, Gouze, and Thibault (2005)). Following the segmentation procedure, the total porosity $\bar{\phi}_T$ of the sample is simply the ratio of the pore space to the total number of voxels. The next step consists in determining the percolation clusters, or sample-spanning clusters, which are the networks of

pores connected to the boundaries of the sample, and the unconnected pores, using a cluster-labeling algorithm (Stauffer, Adler, and Aharony (1994)). For our samples, there is only one single percolation cluster defining the connected porosity $\bar{\phi}$. Furthermore, the fraction of unconnected porosity (for pores larger than 5 μm) appears to be negligible ($\bar{\phi} \approx \bar{\phi}_T$).

Both tortuosity (τ) and fluid-rock interface area (S_{XMT}) can be deduced from numerical simulations of time-dependent effective diffusion coefficient $D(t)$ in the porosity of the rock. These parameters can be measured for the entire rock sample or for any sub-volume of characteristic size larger than some tens of pores. Segmented XMT images are used to perform these simulations. For a large ensemble of P particles, initially evenly distributed in the pore space (the void-labelled voxels), the diffusion coefficient $D(t) \equiv \sigma^2/6t$ is computed from the recording of the mean square displacement $\sigma^2(t) = P^{-1} \sum_{i=1}^P \left(\mathbf{x}_i(t) - \mathbf{x}_i^{(0)} \right)^2$ of the diffusing particles (Einstein (1956)), where $\mathbf{x}_i^{(0)}$ denotes the initial ($t = 0$) position of the i^{th} particle. The diffusion coefficient characterizes the ability of these particles undergoing random Brownian motion to disperse in the connected pore domain confined by the solid phase. In such confined geometry, $D(t)$ probes the structure that restricts the motion of the particles. At long time (i.e. $t \rightarrow \infty$) $D(t)$ reaches an asymptotic value $D(t \rightarrow \infty) \equiv d_0/\tau$, where d_0 is the diffusion coefficient in an unbounded domain (free diffusion). Conversely, the short-time diffusion is controlled by the pore surface to pore volume ratio $S_{XMT}/\phi V$ (Sen (2004)):

$$D(t \rightarrow \epsilon) = d_0 \left(1 - (4\sqrt{d_0 t} S_{XMT}) / (9\phi\sqrt{\pi}V) \right) \quad (5)$$

The diffusion computations are performed as follows. After being randomly positioned ($\mathbf{x}_i^{(0)}$) at $t = 0$ in the porous space, random walk is performed for each particle i . For any particle the position increment is $\mathbf{x}_i^{(t+\Delta t)} = \mathbf{x}_i^{(t)} + \xi_i$, where $\Delta t \ll \lambda^2/6d_0$ is the time step, λ is the characteristic size of the pores and ξ_i is a zero mean random Gaussian vector increment defined by its variance $\langle \xi_i^2 \rangle = 6d_0\Delta t$. At each jump try, there are two possible movements: (i) the particle hits a solid-pore interface; in this case the jump is not performed and a new random position is selected, and (ii) the move is successful and a new particle position is recorded. Note that S_{XMT} can be also measured by simply summing the pixel area at the pore-solid interface. Results show that the difference between the values of S_{XMT} evaluated from diffusion simulation (equation 5) and those measured by summing the pore-

solid interface area is less than one percent. Examples of computed curves $D(t)$ are given in Fig. 3.

4. Dissolution features and surface area of reaction

The XMT data are used to characterize the dissolution patterns and compare fluid-rock interface area measured by XMT with the surface area of reaction inferred from fluid composition (Fig. 2). The water-rock interface area deduced from the XMT data does not measure the surface area of reaction directly. However, the difference between the water-rock interface areas obtained from XMT acquisitions before and after dissolution, $\Delta S_{XMT} = S_{XMT}^{(f)} - S_{XMT}^{(0)}$, is proportional to the difference in the reactive surface area $\Delta S_r = S_r^{(f)} - S_r^{(0)}$ because changes in the fluid-rock interface area can be due to dissolution processes only. The coefficient of proportionality is controlled by the resolution of the XMT data acquisition. Specifically, the oolithe grain roughness as well as grains smaller than the XMT resolution ($5.06 \mu\text{m}$) cannot be measured and the water-rock interface area is a priori underestimated. Scanning electron microscope (SEM) measurements shows that oolithes surface roughness decreases from the beginning to the end off the experiment for experiment D3, emphasizing that a different coefficient of correction should be applied for the XMT images taken before and after the dissolution experiment. The coefficient of correction for the rock at the beginning of the experiment and after dissolution can be simply evaluated from comparing $S_r^{(0)}$ and $S_{XMT}^{(0)}$, and $S_r^{(f)}$ and $S_{XMT}^{(f)}$, respectively, for experiment D3 for which dissolution is assumed homogeneously distributed within the sample. We obtain $\alpha^{(0)} = S_r^{(0)}/S_{XMT}^{(0)} = 1.22$ and $\alpha^{(f)} = S_r^{(f)}/S_{XMT}^{(f)} = 1.05$. For experiments D1 and D2, the initial and final surface areas calculated by XMT technique do not represent the true water-rock interface area because part of the sample have not been dissolved due to dissolution localization processes. It follows that the fraction undergoing dissolution at the beginning and the end of the experiment are $\psi^{(0)} = S_r^{(0)}/\alpha^{(0)}S_{XMT}^{(0)}$ and $\psi^{(f)} = S_r^{(f)}/\alpha^{(f)}S_{XMT}^{(f)}$, respectively. By definition, $\psi^{(0)} = \psi^{(f)} = 100\%$ for experiment D3 (homogeneous dissolution). For experiment D2 displaying ramified dissolution patterns diffusely distributed across and along the sample $\psi^{(0)} = 61\%$ and $\psi^{(f)} = 13\%$. For experiment D1, where we observe the formation of few conical penetrative wormholes associated with a large increase of porosity localized in the vicinity of the inlet, $\psi^{(0)} = 12\%$ and $\psi^{(f)} = 1\%$. These values are similar to those deduced from the observations

discussed in Luquot and Gouze (2009). For each of the experiments, ΔS_r is given by

$$\Delta S_r \approx S_{XMT}^{(f)} \alpha^{(f)} \psi^{(f)} - S_{XMT}^{(0)} \alpha^{(0)} \psi^{(0)}. \quad (6)$$

For experiment D3, D2 and D1, the sample-averaged values are $\Delta S_r = -5.4 \text{ m}^2$, -1.9 m^2 and -0.9 m^2 , respectively. However, the value of ΔS_r is not uniformly distributed along the flow direction axis (z) for D1 and D2 denoting the transport-controlled regime with higher decrease of the reactive surface area corresponding to the higher dissolution (wormholes) in the vicinity of the inlet (Fig. 4).

5. Porosity versus permeability relationship

To predict the CO_2 mass transfers and their implications for long-term storage of CO_2 , numerical models introduce empirical relations between permeability and porosity. In the experiment, porosity is obtained using equation 2 where $\bar{\phi}_f$ is the value of the porosity measured by XMT after dissolution. This value is assumed to be the best evaluation of the true porosity because most of the structures smaller than few microns are dissolved (see section 4). The curves $\bar{\phi}$ versus k are presented in Fig. 6a. The $k - \phi$ function can be modeled by a power law equation with a single exponent coefficient that is fully determined by the effective reactivity $\bar{\vartheta}$ of the fluid percolating the sample and the flow pattern:

$$k(t) = k_0(\phi(t) - \phi_c)^n, \quad (7)$$

where ϕ_c is the value of the porosity (assumed the same for the 3 samples) below which the pore network is unconnected at the scale of the sample (percolation threshold). Experiment D2 displays the larger value of the power law coefficient, which is the most favorable situation for increasing permeability, i.e. higher value of $\partial k / \partial \phi$. To interpret these results we now focus on the relation between the permeability, the porosity, the pore diameter and the tortuosity, with the help of the XMT images.

The permeability is a macroscopic parameter that measures the energy loss of the viscous fluid along the connected pore cluster in the sample. In first approximation, permeability is controlled by the effective hydraulic diameter θ of the throats in the sample and the average length λ of flow paths within the connected pore cluster (de Marsily (1981)). Both θ and λ are viewed here as macroscopic parameter. Defining the tortuosity $\tau = \lambda/L$ (i.e. $\tau \geq 1$), its

value is often related to porosity by the empirical relationship $\tau = B_\tau(\phi - \phi_c)^{-\beta}$, where B_τ is a dimensionless geometrical parameters. The origin of this relation based initially from the Archie's law (Archie (1942)) is discussed in Dullien (1992) and Ben Clennell (1997), for examples. Consequently, the permeability versus porosity law (equation 7) is now:

$$k(t) = k_0(\phi(t) - \phi_c)^\alpha \left(\frac{B_\tau}{\tau} \right), \quad (8)$$

where $\alpha = n - \beta$ and the constant $k_0 = k^{(0)}/(\phi^{(0)} - \phi_c)^n$ is easily determined from figure 6a with $\phi_c = 5.9\%$ evaluated experimentally by Luquot and Gouze (2009). For heterogeneous porous media the effective hydraulic diameter is a complex function of the porosity and pore space structure. Yet, assuming that permeability depends only on θ and τ , and that θ and τ are independent parameters, equation (eq. 8) tells us that $\theta(t)$ scales with $\phi^\alpha(t)$, i.e. $\theta = B_\theta(\phi - \phi_c)^\alpha$, where B_θ is the scaling constant. Consequently the values of α and β are weighting coefficients denoting the differential importance of the effective hydraulic diameter and the tortuosity for controlling the $k(\phi)$ relationship:

$$\log \left(\frac{k}{k_0} \right) = \log \left(B \frac{\theta}{\tau} \right) = \alpha \log(\phi - \phi_c) + \beta \log(\phi - \phi_c) \quad (9)$$

with $B = B_\tau/B_\theta$ a geometrical coefficient (independent of time) that characterizes the rock type. In the following, we will investigate which of these parameters controls the $k(\phi)$ relationship for homogeneous (experiment D3) and heterogeneous dissolution (experiment D1).

The tortuosity τ before and after dissolution is obtained by computing the diffusion of randomly distributed particles in the rock pores following the method describe in section 3, where the connected pore cluster is obtained from the segmented XMT at $t^{(0)}$ and $t^{(f)}$ (Gouze, Melean, Le Borgne, Dentz, and Carrera (2008)). The initial value of the tortuosity measured for sub-volumes of the sample is homogeneous along the sample. Unsurprisingly, for this highly heterogeneous low-porosity medium the sample-averaged value is high; $\bar{\tau}^{(0)} \approx 4.8, 4.6$ and 4.9 for D1, D2 and D3 respectively (Fig. 5). At the end of the percolation experiments, tortuosity decreases for each experiment. This decrease is more important for the experiment D1 than for D2 and D3 respectively, moreover the tortuosity change is not homogeneous along the sample but more important at the inlet for experiment D1 and, to a

lesser extent, for experiment D2 (Fig. 5). For experiment D1, the tortuosity decreases to a mean value of 3.9 and 4.4 for $z < 2.5$ mm (i.e. in the vicinity of the inlet) and for $z > 2.5$ mm, respectively, due to the wormhole-like dissolution (Fig. 5).

The exponent β is now calculated for $t = t^{(f)}$ by solving $\bar{\tau} = B_\tau(\phi - \phi_c)^{-\beta}$ with the condition $\tau = 1$ for $\phi = 1$:

$$\beta = \log(\bar{\tau}^{(f)}) / [\log(1 - \phi_c) - \log(\phi^{(f)} - \phi_c)]. \quad (10)$$

Calculation shows that β is higher for the experiment D1 than for D2 and D3, or in others words that the tortuosity change associated with porosity change is higher for D1 than for D2 and D3. Yet, the asymptotic $k(\phi)$ relationship (i.e. the n coefficient) is controlled by both the hydraulic diameter changes (which rate $\partial\theta/\partial\phi$ is controlled by α ; $\partial\theta/\partial\phi = \alpha B_\theta(\phi - \phi_c)^{\alpha-1}$) and the reorganisation of the flow paths that is modeled by the tortuosity change rate $-\partial\tau/\partial\phi$ controlled by β ($\partial\tau/\partial\phi = -\beta B_\tau(\phi - \phi_c)^{\beta-1}$), with $n = \alpha + \beta$. The results displayed in Fig. 6b show that for experiment D1, where heterogeneous dissolution is observed during all the experiments, the changes in permeability are due to both changes in the hydraulic diameter and tortuosity, while for experiment D3, where dissolution is homogeneous, the increase of permeability is only due to the decrease of the tortuosity of the porous media. However, for experiment D2, $\alpha > \beta$, and thus we conclude that the change in the effective hydraulic diameter during the dissolution is the dominant process for D2. For this experiment, the $k(\phi)$ relationship is controlled by the radial dissolution of the wormhole-like porosity clusters that occupy only a portion of the sample and resulting in high permeability channels, which are induced by minor changes in porosity.

6. Conclusion

Luquot and Gouze (2009) proposed that macroscopic observation of $\partial k/\partial t$ and $\partial\phi/\partial t$ can be used to characterize, at the scale of the sample, the average dissolution regime and to define the functional $k(\phi)$ relationship from homogeneous dissolution to localized dissolution regimes. However, complementary structural parameters deduced from processing XMT data are essential to determine the reaction surface area and consequently validate the model for calculating the sample-scale averaged rate of change of the reactive surface as a function of the porosity:

$$\partial\bar{\sigma}_r(t)/\partial\bar{\phi}(t) = -w\bar{\phi}^{-w-1}, \quad (11)$$

where w (fitted on the experimental data) characterizes the dissolution regime and can be related to the Damköhler number as suggested by Luquot and Gouze (2009). Because of the large variations of the reactive surface area occurring during CO₂-enhanced dissolution (Fig. 2), the use of dissolution-regime specific phenomenological relations, such equation 11, in simulation tools is certainly an important improvement for modeling accurately mass transfers in the vicinity of the CO₂ injection well, while, so far, modelers used mainly a constant value for reactive surface area or power relations, based on surface to volume ratio, assuming that the reactive surface area is taken as proportional to the total fluid-rock interface.

Furthermore, the analysis of XMT data gives physical meaning to the constitutive relationships that relate porosity to permeability. Specifically, XMT data allowed us to determine the relative importance of tortuosity and pore enlargement that rules the $k - \phi$ law for the different regimes of dissolution. Results show that the intermediate dissolution regime (moderate positive value of Da) where multiple thin unramified wormholes develop, gives the higher value of n (i.e. the optimal regime to increase permeability with small changes in porosity) due to a large increase in the mean effective hydraulic diameter in the sample. Conversely for homogeneous dissolution, results show that the increase of permeability is only due to the spatially homogeneous decrease of the tortuosity. The increase of the effective hydraulic diameter in the sample observed for heterogeneous dissolution regimes (D1 and D2) is certainly at the origin of the memory effect displayed by the $\log(k) - \log(\phi)$ linearity of the curves that denotes a single dissolution regime whereas the Da number for each of these experiments decreases with time. Yet further experimental and theoretical investigations are required for integrating these processes, described here for finite size rock samples, into reservoirs models.

As a further remark, it is worth noticing that the approach presented in this paper, not only explains the origin of the distinctly different values of the exponent of the heuristic law $k(t) = k_0(\phi(t) - \phi_c)^n$ depending on the dissolution regime, but gives the foundations for relating this expression to those developed by several authors on the basis of the pioneering works of Kozeny (1927) and Carman (1937), who derived the functional equation $k = \phi/2\sigma^2\tau$ assuming that the porous structures behave as a bundles of cylindrical smoothly tortuous capillaries such as clean high porosity sandstones. Actually, defining $\alpha = iw + j$ and introducing equation (3) in equation (7) gives $k = (k'_0\phi^j)/(\tau\sigma^i)$, where $k'_0 = k_0B_\sigma^iB_\tau$ is a rock-dependent scaling coefficient. For instance, a similar relation, called the PARIS-equation,

$k = (k_0''\phi)/(\tau\sigma^m)$, was derived by Pape, Riepe, and Schopper (1982). In this model, which appears to be useful to model sandstones (Pape, Clauser, and Iffland (2000)), the value of m ($2 < m < 3$) is controlled by the fractal dimension of the fluid-rock interface. This model is characterised by a strong control of the specific surface changes on the permeability changes. Conversely, for low porosity carbonates it is not surprising that the porosity variation plays a more important role ($j > 1$) in ruling the $k(\phi)$ law.

The next step for enhancing the capacity of laboratory experiment to produce directly usable parameters for reservoir scale modeling is to perform long term dissolution experiments with recurrent XMT data acquisitions during the experiment in order to determine the time-resolved changes and explore the memory effect discussed previously. Precisely, the main question posed by associating the results of Luquot and Gouze (2009) and the microscale analysis presented here concerns the sustainability of the memory effect that controls the distinctly different $k(\phi)$ relationship. The results presented in this paper indicate that this memory effect is certainly linked to the macroscopic structural rearrangement of the connected permeable paths and to the properties (e.g. tortuosity and pore throat diameters) of these paths, independently of the changes in reactive surface area as long as the memory effect holds.

As a general conclusion we emphasize that the experimental approach presented here, combining macro- and micro-scale determinations of the hydrochemical parameters, is essential to give physical meaning to the constitutive relationships that relate porosity to permeability and quantify the effective reaction rate for highly reactive systems, for which extrapolation from homogeneous dissolution theories is impractical. The experimental effort is important, but it is certainly critical to improve significantly our understanding of CO₂ migration in reservoirs and produce reliable models for risk assessment.

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Table 1: Water composition for experiments D1, D2, and D3.

Species (mmol.l ⁻¹)	D1	D2	D3
Na	1000	1000	1000
Ca	8.25	9.37	10.0
Mg	0.16	0.19	0.21
Cl	1 000	1 000	1 000
CO ₂ (mol.l ⁻¹)	0.8	0.5	0.2
pH	3.21	3.51	4.02

Figure 1: X-ray micro-tomography data acquired before (left) and after (right) dissolution for experiment D2. The cross-section (bottom) is displayed in grey scale corresponding to the X-ray absorption; the cubic sub-volume displays segmented data (voids in black, calcite in white); the medial axis skeleton of the pore space, in red, shows the increase of the pore space connectivity and anisotropy. The water flows from the top to the bottom.

Figure 2: Reactive surface area in the sample (S_r , plain symbols) and sample-scale averaged porosity ($\bar{\phi}$, empty symbols) versus time during the percolation experiments (D1 - circles, D2 - squares and D3 - diamonds).

Figure 3: Measuring tortuosity and S/V using diffusion probes computation.

Figure 4: XMT-computed specific surface change ($\Delta\sigma_{XMT} = \left(\left(S_{XMT}^{(f)} \right) / (1 - \bar{\phi}^{(0)}) V \right)$) along the sample for experiment D1, D2 and D3. The CO₂-enriched brine is injected at $z = 0$.

Figure 5: XMT-computed tortuosity along the sample. Plain and empty symbols denote the values of the tortuosity measured before ($\tau^{(0)}$) and after ($\tau^{(f)}$) the dissolution experiments, respectively.

Figure 6: a) Sample-scale averaged porosity versus permeability for experiments D1, D2 and D3. b) Values of exponent α (indicator of hydraulic diameter increase) and β (indicator of tortuosity increase), with $n = \alpha + \beta$, for experiments D1, D2 and D3.