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TECHNICAL NOTE

On the interest of bulk conductivity measurements for hydraulic dispersivity estimation from miscible displacement experiments in rock samples.

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SUMMARY

The determination of the hydraulic dispersivity and effective fraction of porous medium contributing to transport on soil and rock sample in the laboratory is important to understand and model the evolution of miscible contaminant plumes in groundwater. Classical methods are based on the interpretation of the breakthrough curve, i.e., the evolution of the concentration in contaminant at the downstream end-face of a sample into which a front of contaminant is advected. Here we present an experimental device aimed at performing such measurements, but also allowing the bulk electrical conductivity of the sample to be measured. We show that the dispersivity and effective fraction can be inferred from this electrical measurement, and that the combined use of both out-flowing fluid conductivity and bulk conductivity allows the incertitude on the dispersivity and effective fraction to be significantly enhanced.

Keywords: miscible displacement, hydraulic dispersivity, breakthrough curve, electrical conductivity

1. Introduction

Miscible contaminants flowing through a porous medium by advection are mixing with the non-contaminated water, yielding to dilution of the plume. This so-called dispersion phenomenon originates from the fact that the fluid moves faster in larger pores than in smaller ones and faster in the centres of the pores than along the walls, and also that some pathways are longer than others (e.g., Fetter 2001). If we consider an isotropic and homogeneous soil or rock sample, and assume that i) the flow through it is purely one-dimensional and ii) the dispersion process is Fickian, the concentration field $C(x,t)$ (in mol m^{-3}) inside the sample, where x (in m) stands for the distance from the upstream-face of the sample and t (in s) for the elapsed time, obeys the transport equation:

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - v \frac{\partial C}{\partial x}, \quad (1)$$

Here D is the hydrodynamic dispersion coefficient (in $\text{m}^2 \text{s}^{-1}$) and v the linear average velocity of water flowing through the sample (in m s^{-1}). Provided that diffusion processes can be neglected, the dispersion coefficient in Eq. (1) can be written $D = \lambda v$, where λ is the hydraulic dispersivity (in m). Even though the dispersivity changes with the observation scale (e.g., Xu and Epstein 1995), it is often required to determine its value on soil or rock samples to understand and model the dynamics of contaminants at the field scale.

The classical way to perform such measurements in the laboratory consists in applying a straight front of salty solution at the entrance (i.e., the upstream face) of the sample subjected to permanent, laminar flow, and to measure the concentration at the outlet (i.e., the downstream face). The evolution of the concentration of the out-flowing fluid, or “breakthrough curve”, is generally sigmoidal, provided that the medium is homogeneous at the scale of the sample and

that no other processes occur, such as chemical reactions with the minerals. The spreading of the curve increases with the dispersivity. Knowing the theoretical formulation of the breakthrough curve, it is then possible to determine the value of the dispersivity by fitting methods.

The out-flowing concentration is an integrated value, which presents variations only when the salt front reaches the downstream face of the sample. Other methods, such as electrical measurements, can give information as soon as the salt front penetrates the sample. For example, Odling et al. (2007) used electrical impedance measurements on microfractured granite to determine its longitudinal dispersivity. They showed that such a technique provided supplemental information about the dispersion process inside the sample. Here we report on an apparatus allowing the bulk conductivity of a rock sample to be measured during miscible displacement experiments. We show that fitting the classical breakthrough curve to the measured electrical conductivity of the out-flowing fluid, combined to fitting the theoretical evolution of the bulk conductivity of the sample to the measured one, enables a more accurate determination of the hydraulic dispersivity and fraction of the porous volume effectively contributing to the transport.

2. Materials and method

2.1. Device and procedure

We devised, constructed and tested an experimental set-up (Fig. 1), aimed at measuring the bulk electrical conductivity σ_b (in S m^{-1}) of large-sized samples (i.e., about 5 to 10 cm in diameter and 10-40 cm or more in length), as well as the electrical conductivity of the fluid that is out-flowing from the sample, denoted σ_f . This device is usable to perform miscible displacement experiments and therefore infer the hydraulic dispersivity λ (in m) and the effective fraction of

the porous volume contributing to transport, denoted f (no unit).

The upstream and downstream end-faces of the sample, which is placed horizontally to avoid the influence of gravity, are connected to a hydraulic circuit. They are also in perfect contact with stainless steel electrodes, whose external side is protected by a PVC cap to ensure electrical isolation. The conductivity of the out-flowing fluid is measured with a custom-made cell with four platinum electrodes that was calibrated with various brines at different frequencies. The fluid conductivity and the bulk conductivity of the sample are measured with an impedance-meter HP 4263A, at the frequencies of 120 and 1000 Hz. The optimal frequency, which minimizes the polarization effects, is equal to 1 kHz. Note that concerning the bulk conductivity, the measure is done with the two electrodes at the end-faces of the sample only, each electrode serving for both current injection and potential measurement.

To check its watertightness, the sample is first put under vacuum for a few hours. The sample is then saturated with distilled and de-aerated water. The porosity accessible by water under vacuum, which is close to the connected porosity, is deduced from the amount of injected water required to fill the connected voids, with an accuracy comprised between 0.3 and 3.5 percents. Then we let the fluid flowing through the sample from the upstream reservoir filled with distilled water. Once the chemical equilibrium is reached, i.e. when the conductivity of the out-flowing fluid is constant, the distilled water saturating the sample is flushed by NaCl brine at a concentration around 3 g L^{-1} , coming from the brine reservoir. This value of the concentration is large enough to consider the contribution of the surface conduction to the total electrical conductivity negligible, but small enough to neglect density-driven flow, at least for highly permeable samples. Brine is injected until the out-flowing solution has the same electrical conductivity. In practice, a given amount of brine is introduced in the sample. The electrical measurements are carried out rapidly enough to neglect the effects of pure diffusion and reduce

the density effects, if any. Afterwards we proceed to a new injection step, and so on.

2.2 Tested sample

To test our approach, we use a decimetric core of Saint-Maximin limestone (denoted SML). It is a bioclastic limestone, having a large macro-porosity, and a small amount of intraclastic porosity (Fig. 2a). The results of mercury injection carried out on a centimetric core (Fig. 2b) show that the distribution of the pore access radii is bi-modal with two modes at 13.6 and 0.13 μm respectively. However, the second mode, which corresponds to the intraclastic porosity, is clearly dominated by the first mode.

The sample was 309 mm in length, with a diameter of 97.90 mm. The volume of the sample (2326 cm^3) is therefore two orders of magnitude larger than the volumes of rock samples commonly studied in the laboratory for permeability estimation (i.e., 20 to 50 cm^3). This size was chosen to acquire measurements at a scale significantly larger than the representative elementary volume (e.g., Henriette et al. 1989). After machining, the sample was dried in an oven at 60 $^{\circ}\text{C}$ for several days, until its weight stabilized. Then the lateral surface was waterproofed by covering it with epoxy resin. The connected porosity value, determined from weighting, was equal to $36.6 \pm 0.5 \%$. From flow-rate measurement, the water permeability was estimated to be $1718 \pm 42 \text{ mD}$.

To check if advection is predominant over diffusion in our experiment, we estimated the Péclet number Pe . The classical formulation $Pe = v_{\text{DF}} d / D_m$ (e.g., Sahimi 1993), where v_{DF} is the Dupuit-Forchheimer velocity (in m s^{-1}), d the mean grain diameter (in m) and D_m the molecular diffusion coefficient ($1.5 \cdot 10^{-9} \text{ m}^2 \text{ s}^{-1}$ for NaCl), is not applicable for non-granular rocks. Therefore, we used the non-correlation radius r_{nc} , estimated from image analysis, instead of $d/2$.

This yields to $Pe = 2 v_{DF} r_{nc} / D_m$. For the highly permeable sample SML, v_{DF} was equal to 0.35 mm s⁻¹ during the experiment, and r_{nc} was estimated to 175 μm. The Péclet number is thus around 80, meaning that in this case advection can be neglected (power-law regime, e.g. Sahimi 1993).

For the miscible displacement experiment, the conductivity of the initial fluid after stabilization was equal to 4.7 mS m⁻¹. The conductivity of the injected fluid was 540 mS m⁻¹. (i.e., 54.3 mmol L⁻¹ or 3.17 g L⁻¹ NaCl). The bulk conductivity of the sample was equal to 1.4 mS m⁻¹ initially, and to 90.1 mS m⁻¹ at the end of the experiment, yielding to an electrical formation factor $F = \sigma_f / \sigma_b$ equal to 6.

3. Theory

3.1. Problem and solution for a 1D isotropic and homogeneous medium

Considering that Eq. (1) applies to our case, the initial condition is $C(x,0) = C_0$, where C_0 is the equivalent salt concentration of the solution initially saturating the pore space. The upstream boundary condition, corresponding to the injection of brine starting at $t = 0$, can be formalized as $C(0,t) = C_0 + (C_{brine} - C_0) H(t)$ where C_{brine} is the concentration of the brine and H the Heaviside step function. The solution is given by (e.g., Ogata and Banks 1961; Fried and Combarnous 1971; Gupta and Greenkorn 1974; Basak and Murty 1979):

$$C(x,t) = C_0 + \frac{C_{brine} - C_0}{2} \left[\operatorname{erfc} \left(\frac{x - vt}{2\sqrt{Dt}} \right) + \exp \left(\frac{vx}{D} \right) \operatorname{erfc} \left(\frac{x + vt}{2\sqrt{Dt}} \right) \right], \quad (2)$$

where erfc is the complementary error function. The second term in the brackets has an influence only if t is close to 0, and can be neglected otherwise (e.g., Ogata and Banks 1961; Pfannkuch 1963), yielding to the following approximation of Eq. (2):

$$C(x, t) \approx C_0 + \frac{C_{\text{brine}} - C_0}{2} \operatorname{erfc}\left(\frac{x - vt}{2\sqrt{Dt}}\right). \quad (3)$$

3.2. Non-dimensionalization of the solution

In order to compare the breakthrough curves for different samples, if any, it is convenient to use the normalized variation of the concentration δC (no unit) defined by

$$\delta C(x, t) = \frac{C(x, t) - C_0}{C_{\text{brine}} - C_0}. \quad (4)$$

Since the injection is not continuous but performed step by step (see end of section 2.1), it is convenient to consider δC as a function of the normalized injected volume of brine V_i^n , expressed in pore volumes, as (e.g., Pickens and Grisak 1981):

$$V_i^n = \frac{V_i}{V_{pc}}, \quad (5)$$

where V_i is the injected volume of brine and V_{pc} the total connected porous volume of the sample, equal to the total porosity times the volume of the sample. Following this way, the curves δC versus V_i^n for different samples are similarly scaled and therefore directly comparable. Indeed, the time required for the injection of a given volume of brine, which depends on the permeability of the rock, is eliminated from Eq. (3): considering that V_i^n is also equal to vt/L where L is the length of the sample (in m), and assuming that the molecular diffusion is negligible so that we can introduce the hydraulic dispersivity as $\lambda = D/v$, the combination of Eqs. (3) and (4) leads to:

$$\delta C(x, t) \approx \frac{1}{2} \operatorname{erfc}\left(\frac{1}{2} \sqrt{\frac{L}{\lambda}} \frac{\left(\frac{x}{L} - V_i^n\right)}{\sqrt{V_i^n}}\right). \quad (6)$$

The normalized variation of concentration of the out-flowing solution, denoted δC_{out} , is obtained

167 by taking $x = L$ in Eq. (6):

$$168 \quad \delta C_{out}(t) = \delta C(L, t) \approx \frac{1}{2} \operatorname{erfc} \left(\frac{1}{2} \sqrt{\frac{L}{\lambda}} \frac{1 - V_i^n}{\sqrt{V_i^n}} \right) \quad (7)$$

169 Classically, the λ/L ratio is inferred from the measured values of δC_{out} (i.e., the normalized
 170 breakthrough curve) by fitting the theoretical curve (Eq. (7)) to them. Note here that this
 171 theoretical curve passes through the point $M_{1,0.5} = (V_i^n, \delta C_{out}) = (1, 0.5)$, since the volume of brine
 172 required for the centre of mass of the front to arrive at the downstream end of the sample is equal
 173 to one pore volume.

174 It is assumed here that the whole connected pore volume contributes to the transport, but
 175 it is rarely expected. For example, dead-end pores do not contribute to the transport processes. If
 176 the pore volume contributing to transport (or “efficient porosity”), denoted V_{pc}^* , is smaller than
 177 V_{pc} , the experimental curve δC_{out} versus V_i^n is shifted to the left. In other words, the injected
 178 volume, normalized using Eq. (5), for which δC_{out} is equal to 0.5, is smaller than 1. In this case,
 179 one should also find the best V_{pc}^* to be used in place of V_{pc} in Eq. (5). To do so, we define the
 180 effective fraction of the porous volume contributing to the transport as $f = V_{pc}^*/V_{pc}$. Equation (5)
 181 must thus be rewritten as:

$$182 \quad V_i^n = \frac{V_i}{V_{pc}^*} = \frac{V_i}{f V_{pc}}. \quad (8)$$

183 The problem then involves two parameters, λ/L and f , to be found using Eqs. (7) and (8).

184 It should be noted here that if no theoretical curve can explain the data, it means that the
 185 medium is not homogeneous, and/or that retardation processes occur such as trapping in small
 186 pores, or that molecular diffusion is not negligible, or that density-driven flow occurs, or even
 187 chemical reactions with the reactive mineral phases happen.

Finally, note that for the calculation of V_i^n , the measured injected volume of brine was corrected from the volume of the tube between the T-valve (Fig. 1) and the upstream end of the sample for the bulk sample conductivity, and from the same volume plus the volume of the tube between the downstream end of the sample and the conductivity cell for the conductivity of the out-flowing fluid.

3.3. Conversion of conductivity to concentration

As previously stated, we do not measure the salt concentration directly, but the electrical conductivity of the fluid. To transform the concentration C into conductivity σ_f , and reciprocally σ_f into C , we use the empirical relations established by Sen and Goode (1992) for NaCl brine:

$$\sigma_f = \left(5.6 + 0.27T - 1.5 \cdot 10^{-4} T^2\right) M - \frac{2.36 + 0.099T}{1 + 0.214M} M^{\frac{3}{2}} \quad (9)$$

where T is the temperature (in °C) and M is the molality (in mol kg⁻¹). To convert the concentration C_f into molality, we use the CRC Handbook Table at 20°C (Lide 2008).

For coherence, we also normalized the conductivity of the out-flowing fluid, σ_{out} , as:

$$\delta\sigma_{out}(t) = \frac{\sigma_{out}(t) - \sigma_{out,0}}{\sigma_{out,max} - \sigma_{out,0}}, \quad (10)$$

where $\sigma_{out,0}$ and $\sigma_{out,max}$ are the initial and maximal (i.e., the plateau value at the end of the experiment) conductivities of the effluent solution, respectively. We proceeded similarly for the bulk conductivity of the sample σ_b :

$$\delta\sigma_b(t) = \frac{\sigma_b(t) - \sigma_{b,0}}{\sigma_{b,max} - \sigma_{b,0}}, \quad (11)$$

where $\sigma_{b,0}$ is the initial and $\sigma_{b,max}$ the maximal (i.e., the plateau value at the end of the experiment) value of the bulk conductivity.

4. Estimation of the dispersivity

To estimate the dispersivity λ , we first use the classical method, which consists in fitting a straight line in Henry's space to the experimental points of the out-flowing fluid concentration. Secondly we systematically explored the parameter space. This second method allows the effective fraction f to be taken into account, and the sample conductivity to be also considered.

4.1. Cost-function

To evaluate the agreement between the data (i.e., the normalized measured conductivity variations) and the model (i.e., the normalized predicted conductivity variations), a cost-function R as meaningful as possible has to be defined. We used the determination coefficient r^2 , which quantifies the mean deviation of the N experimental points (vector $\mathbf{d}^{\text{obs}}$) from the predictions (vector $\mathbf{d}^{\text{pred}}$):

$$r^2 = 1 - \frac{\sum_{i=1}^N (d_i^{\text{obs}} - d_i^{\text{pred}})^2}{\sum_{i=1}^N (d_i^{\text{obs}} - \langle \mathbf{d}^{\text{obs}} \rangle)^2} \quad (12)$$

Moreover, considering that the concentration break-through curves (Eq. (7)) are similar to cumulative Gaussian distributions, we combined r^2 with the Kolmogorov-Smirnov (KS) test (e.g., Press et al. 1997), usually used as an estimator of the semblance between two distributions, given by:

$$\begin{cases} \mu = \left(\sqrt{N} + 0.12 + \frac{0.11}{\sqrt{N}} \right) \max |\mathbf{d}^{\text{pred}} - \mathbf{d}^{\text{obs}}| \\ KS = 2 \sum_{j=1}^{\infty} (-1)^{j-1} e^{-2j^2\mu^2} \end{cases} \quad (13)$$

228 We thus used the function $R = KS r^2$; an optimal fit is obtained when $R = 1$.

229

230 4.2. Fitting method in Henry's space

231 Defining the two parameters α (no unit) and Γ (no unit) as:

$$232 \quad \begin{cases} \alpha = \frac{1}{2} \sqrt{\frac{L}{\lambda}} \\ \Gamma = \frac{1 - V_i^n}{\sqrt{V_i^n}} \end{cases}, \quad (14)$$

233 Eq. (7) can be rewritten as:

$$234 \quad \delta C_{out}(t) = \frac{1}{2} \operatorname{erfc}(\alpha \Gamma). \quad (15)$$

235 Therefore the curve Γ versus δC_{out} plotted in linear arithmetic probability paper (in ordinates)
236 forms a straight line (e.g., Brigham 1974), also called Henry's line. The slope of this line,
237 denoted p , is theoretically given by:

$$238 \quad p = -\frac{1}{\alpha \sqrt{2}} = -\sqrt{2} \sqrt{\frac{\lambda}{L}}. \quad (16)$$

239 We did not apply the classical two-point Taylor's (1953) method to determine λ (e.g., Fried and
240 Combarous 1971; Gupta and Greenkorn 1974; Pickens and Grisak 1981). Instead, we
241 determined the straight line fitting the data in the least-square sense, as suggested by Gupta and
242 Greenkorn (1974), considering that this method provides more accurate values for the slope p .
243 Note that in this case it is necessary to restrict the data to the interval for which the conductivity
244 variation is linear, i.e., generally for δC_{out} comprised between 0.1 and 0.9. The dispersivity is then
245 deduced using Eq. (16) as $\lambda = L p^2 / 2$.

246 The observed normalized conductivity $\delta \sigma_{out}$ and deduced normalized concentration δC_{out}
247 of the out-flowing fluid as a function of the volume of injected brine V_i^n , expressed in fraction of

porous volume, are shown in Fig. 3a for SML sample. The concentrations δC_{out} are distributed along a sigmoid, which seems to pass very close to the point $M_{1,0.5} = (V_i^n, \delta C_{out}) = (1, 0.5)$, meaning that the whole pore volume contribute to the transport. The associated Γ values computed using Eq. (14), versus normalized experimental concentration δC_{out} , are distributed along a straight line (Fig. 3b). The line fitting the best the data, in the least-squares sense, passes through the point $(\delta C_{out}, \Gamma) = (0.5, 0)$, meaning that indeed the effective fraction f is equal to 1. The slope of the fitting line gives a value of 4.018 mm for the dispersivity λ_{HL} . The modelled curves δC_{out} (continuous line in Fig. 3a, obtained with Eqs. (7) and (5)) and $\delta \sigma_{out}$ (dotted line) versus the volume of injected brine, expressed in fraction of porous volume, explain the data rather well (the cost-function R^{HL} is close to 1.0).

4.3. Parameter space exploration

The previous procedure takes into account the conductivity variation of the out-flowing fluid only. Moreover, it does not provide a confidence interval for the dispersivity or the effective fraction of porous volume. We hereafter estimate the dispersivity directly from the curves of the out-flowing fluid conductivity variations $\delta \sigma_{out}$ or/and the variations of the bulk conductivity $\delta \sigma_b$ versus the injected volume V_i^n by exploring the parameter space

To estimate the sample bulk conductivity σ_b , we apply the generalized Reuss average, since the measurement is performed in the direction of the concentration gradient. We assume that i) the concentration front is one-dimensional along the axis of the sample (i.e., the sample is homogeneous and the front is straight, i.e., the density effect are negligible), and ii) the formation factor F does not depend on the value of the local fluid conductivity. Therefore, σ_b can be written as (Odling et al. 2007):

$$\frac{1}{\sigma_b(t)} = \frac{F}{L} \int_0^L \frac{dx}{\sigma_f(C(x,t))} \quad (17)$$

where $\sigma_f(C(x,t))$ corresponds to the fluid conductivity distribution inside the sample (computed using Eqs. (3) and (9)). It is important to note that the knowledge of the formation factor is not required, since it vanishes in the computation of the normalized variation of the bulk conductivity using Eq. (11).

The application to limestone SML is shown in Figs. 4, 5 and 6. We explored the dispersivity values in the interval comprised between 0 and 20 mm (based on the value previously determined for λ_{HL}) with a spacing of 0.1 mm, and the values of the effective fraction in the interval comprised between 0.85 and 1 with a spacing of 0.001.

When the exploration method is applied to the fluid conductivity only (Fig. 4a), the maximal value of the cost-function $R_{\max}^f$ is equal to 0.99951 (with a Kolmogorov-Smirnov value equal to 100 %) and corresponds to a dispersivity λ_f (subscript "f" standing for "fluid") of 4.0 mm and an effective fraction f_f of 0.982. The value of the dispersivity is very close to the value determined previously using Henry's line (4.018 mm). The value of the effective fraction is very close to 1, but is slightly smaller. The predictions computed with Eqs. (7), (8) and (10) explain very well the data (Fig. 4b).

We proceeded similarly for the bulk conductivity only (Fig. 5). As for the fluid, the normalized bulk conductivity of the sample is sigmoidal, but the bulk conductivity evolves as soon as brine is injected in the sample (Fig. 5b). The dispersivity λ_s (subscript "s" standing for "sample") is equal to 3.3 mm, a value slightly smaller than λ_f . The effective fraction f_s is equal to 0.987. The prediction, computed using Eqs. (3), (9), (11) and (17), explains here again rather well the data, with a cost-function $R_{\max}^s$ equal to 0.99954. However, it seems that the dispersivity may

be slightly underestimated for injected volume above 1, the prediction being systematically higher than the experimental points.

We finally apply the same methodology to find the best dispersivity and effective fraction explaining both fluid and sample conductivities simultaneously (Fig. 6). In this case, we defined the cost-function as the product of the two cost-functions for the fluid and the sample, i.e. $R = R^f R^s$. Doing so, the best dispersivity value λ is equal to 3.5 mm and the best effective fraction f to 0.986 (Fig. 6a). The predictions explained rather well the fluid conductivity (Fig. 6b) and the bulk conductivity of the sample (Fig. 6c).

5. Discussion

First of all, a coherent estimation of the dispersivity and of the effective fraction is provided by the interpretation of the evolution of the bulk conductivity of the sample.

Secondly, when performing sensitivity analysis, it can be seen that the ranges of dispersivity and effective fraction which produce high values of the cost-function for the out-flowing fluid conductivity are quite large (red area in Fig. 4a). For instance, values of dispersivity between 1.5 and 8.1 and effective fraction between 0.941 and 1 produce a cost-function value superior to 0.99, sufficiently high to produce satisfactorily predictions. A way to estimate the error interval on the determined values of dispersivity and effective fraction may be to consider their values which produce cost-function values higher than a certain threshold value. Here we can consider $R^f = 0.998$. In this case, the dispersivity λ_f is comprised between 3 and 5.4, and the effective fraction f_f between 0.966 and 0.998. From the exploration of the parameter space for the bulk conductivity of the sample, it can be concluded that the bulk conductivity is more sensitive to the variations of the dispersivity (the red area in Fig. 5a is less extended in the λ -direction than

in Fig. 4a), but is less sensitive to the variations of the effective fraction (the red area is more extended in the f -direction). Considering again the threshold value of 0.998 for R^s , the dispersivity λ_s is comprised between 2.2 and 4.5, and the effective fraction f_f between 0.955 and 1. The dispersivity is thus best determined by the bulk conductivity and the effective fraction by the out-flowing fluid conductivity. This illustrates the fact that using the bulk conductivity of the sample provides supplemental information, compared to the use of the out-flowing fluid conductivity alone. Finally, when considering the exploration on both out-flowing fluid conductivity and bulk conductivity of the sample, the area producing high values of the cost-function R is much restrained than in the previous two cases. Indeed, the $R = 0.998$ threshold gives an interval of [3.2,3.9] for the dispersivity λ and an interval of [0.978,0.994] for the effective fraction f .

The fact that the effective fraction is not equal to 1, but close to it, means that a small part of the porous volume does not contribute to the transport. This non-contributing volume may be the intraclastic porosity associated with the second mode in the pore access radius distribution (Fig. 2b). Moreover, the fact that the predictions are slightly higher than the observations for injected volume greater than 1 (Figs. 4b, 5b and 6bc) may be results from retardation processes of small intensity – maybe the penetration of salt in this intraclastic porosity.

Finally, the fact that all the estimated dispersivities λ_{HL} , λ_f , λ_s and λ , as well as the effective fractions f_f , f_s and f are close one to the other, and that the data are rather well explained by these values, means that all the assumptions made here (mainly: the sample is homogeneous and the diffusion and the density effect can be neglected) are reasonable. For less permeable samples with lower Péclet number, and/or for higher brine concentration, more complicated models have to be implemented, but this is beyond the scope of this study.

339

340 **6. Conclusions**

341 We added to the classical measurement of the breakthrough curve (evolution of the
342 conductivity of the out-flowing fluid) during miscible displacements experiments the
343 measurement of the evolution of the bulk conductivity of the sample. A methodology based on
344 the exploration of the possible values for the hydraulic dispersivity and for the effective fraction
345 of total connected porous volume contributing to the transport was developed, which also provide
346 confidence intervals. The values obtained on a sample of limestone using the out-flowing fluid
347 conductivity only or the bulk conductivity of the sample only are coherent with those determined
348 by the classical method of Henry line. The most interesting point is that the combined use of out-
349 flowing fluid and bulk conductivities also produces coherent values, but with significantly
350 reduced confidence intervals. This underlines the interest of systematically including the
351 measurement of the bulk conductivity during laboratory measurements of the dispersivity on rock
352 samples.

353

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356 This is IPGP contribution n°3744.

357

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Fig. 1. Scheme of the experimental device for miscible displacement. Explanation in the text.

Fig. 2. (a) Thin section of Saint-Maximin limestone SML, where the blue areas correspond to the void space filled by the resin; (b) histogram of pore access radius distribution inferred from mercury injection.

Fig. 3. Determination of the dispersivity by fitting the conductivity of the outflowing fluid in Henry's space for Saint-Maximin limestone SML. (a) Observed fluid conductivity and deduced fluid concentration (squares and circles), as a function of the injected volume of brine expressed in fraction of total porous volume; (b) concentration in Henry's space (see text for detail). The dispersivity value $\lambda_{HL} = 4.018$ mm, deduced from the slope of the line, is then used to model the fluid concentration and conductivity shown by the lines in (a). R^{HL} is the value of the cost-function.

Fig. 4. Exploration of the parameter space to model the evolution of the outflowing fluid conductivity for Saint-Maximin limestone SML. (a) isocontours of the cost-function R^f as a function of the dispersivity and the effective fraction; (b) optimal solution ($\lambda_f = 4$ mm and $f_f = 0.982$).

Fig. 5. Exploration of the parameter space to model the evolution of the bulk conductivity of the SML sample. (a) isocontours of the cost-function R^s as a function of the dispersivity and the effective fraction; (b) optimal solution ($\lambda_f = 3.3$ mm and $f_f = 0.987$). Note that the cost-function R^s is more sensitive to the variations of the dispersivity than R^f , but globally less sensitive to the variations of the effective fraction (compare to Figure 5).

Fig. 6. Exploration of the parameter space to model simultaneously the evolutions of the outflowing fluid and bulk conductivities for the SML sample. (a) isocontours of the cost-function R as a function of the dispersivity and the effective fraction; (b) and (c) optimal solution ($\lambda = 3.5$ mm and $f = 0.986$).