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▶ **To cite this version:**

G. Radilla, M. Kacem, J.M. Lombard, M. Fourar. Transport Properties of Lavoux Limestone at Various Stages of CO2-Like Acid-Rock Alteration. Oil & Gas Science and Technology - Revue d'IFP Energies nouvelles, 2010, 65 (4), pp.557-563. 10.2516/ogst/2009081 . hal-01937552

HAL Id: hal-01937552
https://ifp.hal.science/hal-01937552

Submitted on 28 Nov 2018

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Oil & Gas Science and Technology – Rev. IFP, Vol. 65 (2010), No. 4, pp. 557-563
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DOI: 10.2516/ogst/2009081

Dossier

CO_2 Storage in the Struggle against Climate Change
Le stockage du CO_2 au service de la lutte contre le changement climatique

Transport Properties of Lavoux Limestone at Various Stages of CO_2-Like Acid-Rock Alteration

G. Radilla[1*], M. Kacem[1], J.M. Lombard[2] and M. Fourar[1]

1 LEMTA, UMR 7563, CNRS, Nancy Université, 2 avenue de la Forêt de Haye, BP 160, 54504 Vandœuvre Cedex - France
2 Institut français du pétrole, IFP, 1-4 avenue de Bois-Préau, 92852 Rueil-Malmaison Cedex - France
e-mail: giovanni.radilla@ensem.inpl-nancy.fr - mariem.kacem@ensem.inpl-nancy.fr - j-marc.lombard@ifp.fr - mostafa.fourar@ensem.inpl-nancy.fr

* Corresponding author

Résumé — Propriétés de transport d'un calcaire de Lavoux à différents stades d'altération acide-roche de type CO_2 — Depuis 2005, l'Agence Nationale de la Recherche (ANR) finance des projets scientifiques visant à sélectionner, valider et implémenter un site pour le stockage géologique du CO_2 sur le territoire français. Le travail présenté ici a été réalisé dans le cadre du projet Géocarbone Injectivité, dont l'objectif était d'étudier la possibilité d'injecter et de stocker du CO_2 dans un aquifère salin profond situé dans le bassin Parisien. Un analogue géologique de cette formation carbonatée a été choisi afin d'en effectuer une caractérisation des propriétés pétrophysiques et de transport. Les paramètres mesurés sont la perméabilité intrinsèque, le coefficient d'inertie, le coefficient de Klinkenberg, les perméabilités relatives ainsi que des propriétés de transport comme le coefficient de dispersion et le facteur de stratification. Des échantillons de calcaire de Lavoux ont été caractérisés dans leur état initial puis altérés par une attaque à l'acide retard à des niveaux d'altération différents selon les échantillons. Les résultats montrent des changements sensibles de porosité, de perméabilité et de coefficient d'inertie. En revanche, les perméabilités relatives et les deux coefficients de transport ne sont pas modifiés sensiblement. Ces résultats vont dans le sens d'un maintien, voire d'une amélioration de l'injectivité du CO_2 lors de son injection dans la formation considérée. Cependant, on peut imaginer qu'un déplacement de fines implique une réduction de mobilité du CO_2. Une étude complémentaire, à la fois expérimentale et de modélisation, prenant en compte ces possibles déplacements de fines est nécessaire.

Abstract — Transport Properties of Lavoux Limestone at Various Stages of CO_2-Like Acid-Rock Alteration — *Since 2005, the French National Research Agency supports several scientific projects intended to select, validate and implement a geological site for CO_2 storage in France. The work presented in this paper was carried out within the Geocarbone-Injectivity project, aimed to study the suitability of a carbonate deep saline aquifer located in the Paris basin for a geological CO_2 storage. A geological analog to the aquifer rock was chosen in order to perform several petrophysical and transport characterizations. Measured parameters were intrinsic permeability, inertia coefficient, Klinkenberg coefficient, relative permeabilities and transport properties such as the dispersion coefficient and the stratification factor. Samples of Lavoux limestone were characterized in their original state and also after a phase of CO_2-like acid-rock alteration. Results show sensible changes in porosity, permeability and inertia coefficient and almost no change in relative permeabilities, dispersion coefficient and stratification coefficient. These results mean that the CO_2 injectivity would be maintained and even enhanced during its injection in the considered Dogger formation. Nevertheless, to confirm this observation, additional experimental and modeling work should be performed, taking into account the potential fine migration. A permeability alteration could be expected due to these fine displacements.*

INTRODUCTION

During the last decade, geological storage of carbon dioxide has become a serious mitigation possibility to greenhouse gases emissions in several countries (Bachu, 2000; Bachu and Adams, 2003; Holloway, 2005). The French government via the French National Research Agency (ANR) has funded several projects since 2005 intended to select, validate and implement and monitor a geological site for CO_2 storage in France. A crucial issue in geological storage of carbon dioxide is the long-term stability of the CO_2 within the geological formation. Chemical reactions between CO_2, brine and rock have been therefore studied in depth (Egermann *et al*., 2005; Egermann *et al*., 2006; André *et al*., 2007; Gaus *et al*., 2008) in order to investigate the effect of those reactions (*i.e*. rock dissolution or carbon precipitation) on the storage integrity.

The Geocarbone Injectivity project was aimed to study the suitability of the Dogger deep saline carbonate aquifer of the Paris basin in terms of it's capability to store large amounts of CO_2 injected at high flow rates. The second phase of this project was dedicated to the study of transport phenomena during a CO_2 injection.

In this paper we present results of CO_2-like acid-rock alteration experiments performed on Lavoux limestone samples. The impact of sample exposure to the acid alteration was measured in terms of porosity, permeability, inertia coefficient, relative permeabilities and tracer transport behaviour.

Samples are briefly described in Section 1. The alteration procedure is described in Section 2 while Section 3 presents all experimental results. Finally, the conclusions of this work are drawn.

1 SAMPLES

Lavoux limestone sister samples used in this work are shown in Figure 1. Their chemical composition is almost pure $CaCO_3$ (99%). Sample dimensions are 38 mm in diameter and 76 mm in length. The porosity of our samples was deeply studied by Grgic (Grgic, 2009). Samples appear to have a dual porosity distribution with peaks at 0.26 μm and 10 μm. Figure 2 shows the mercury porosimeter results.

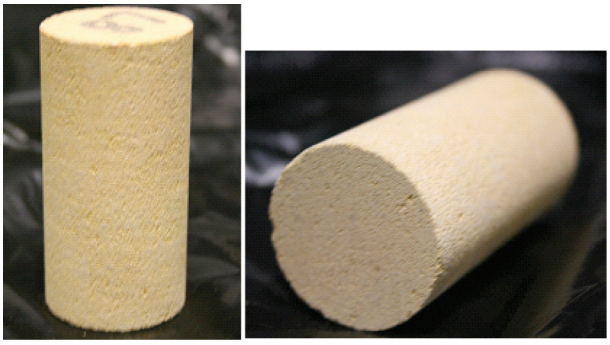


Figure 1

Samples used in this work.

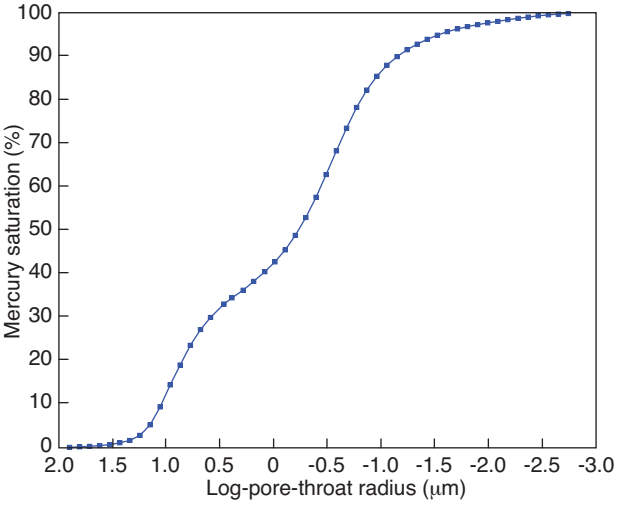


Figure 2

Mercury porosimeter results.

Table 1 presents values of average porosity of all samples of this study. Values show a good homogeneity of the rock in which our samples were drilled.

TABLE 1

Porosity of the samples in their original state

Sample	Density	Water porosity	Total porosity
L4	2.07	23.3	24.2
L5	2.01	25.0	26.4
L6	1.99	25.7	27.0
L7	1.99	26.2	27.3
L8	2.01	25.4	26.6
L9	2.02	24.8	25.9

2 ALTERATION PROCEDURE

Alteration of three samples at different stages was performed using the following procedure (Egermann *et al*., 2006):

- saturate sample with brine;
- inject the retarded acid solution (*Acidgen© Cleansorb Ltd*.) until complete saturation with an initial pH of 6.3 at 17°C;
- activation of the acid with temperature (60°C) and soaking;
- flooding of the sample with fresh brine.

The procedure was repeated to achieve the desired number of alteration cycles. The permeability of the sample was measured in its initial state and after each alteration cycle. Table 2 presents the number of cycles and the total alteration time applied to samples L4, L5 and L6.

TABLE 2

Alteration of samples L4, L5 and L6

Sample	L4	L5	L6
Alteration cycles	6	4	2
Total alteration time (h)	242	571	48

CT-scan porosity profiles for the three altered samples were measured before and after the alteration. Figure 3 presents the porosity profiles obtained before and at the end of the alteration procedure for samples L4, L5 and L6. Figure 3 shows clearly that the alteration procedure leads to a uniform alteration of the samples which is suitable for using JBN theory for the experimental determination of relative permeability curves. After the alteration, porosity increases up to 10%.

Both pore body and throat radii are increased during the acid injection. The NMR T2 profiles (Godefroy *et al.*, 2001) before and after the alteration show this porosity increase *(Fig. 4)*. The mean T2 value of the small pore population is higher for the altered samples, indicating larger pore bodies (11 ms for LJ6 after alteration, 8 ms before alteration – This difference of 3 ms is well larger than the method accuracy which is below 1%).

Remark: In order to check the representativity of this acid alteration technique, a complementary study is still in progress. This alteration process will be compared to a direct alteration by a CO_2 saturared brine, in terms of geochemical and petrophysical parameters.

3 EXPERIMENTAL RESULTS

3.1 Petrophysical Properties

Permeability and Inertia Coefficient

Geological storage of carbon dioxide involves very high flow rates injected through a single well. Therefore, near injection wells, flow velocities are high enough to generate inertia effects. It is important to take those effects into account when it comes to calculate the injection pressure. Forchheimer's law (Forchheimmer, 1901) is commonly used in such flow configuration as a generalization of Darcy's law (Darcy, 1854) and it is given for an incompressible fluid as:

$$-\frac{\Delta P}{\Delta x} = \frac{\mu}{k}\frac{Q}{A} + \beta\rho\left(\frac{Q}{A}\right)^2 \quad (1)$$

where $\Delta P/\Delta x$ is the pressure gradient in the flow direction, μ and ρ are respectively the dynamic viscosity and density of the fluid, Q is the volumetric flow rate, A is the cross sectional area, k and β are the intrinsic permeability and inertia coefficient of the porous medium. For a compressible fluid, Forchheimer's equation is:

$$\frac{MA}{2rT}\left(\frac{P_1^2 - P_2^2}{\Delta x}\right) = \frac{\mu}{k}Q_m + \frac{\beta}{A}Q_m^{\,2} \quad (2)$$

where M is the molar weight of the gas, T the temperature, r the universal gas constant, P_1 and P_2 are pressures at two different sections, and Q_m is the mass flow rate.

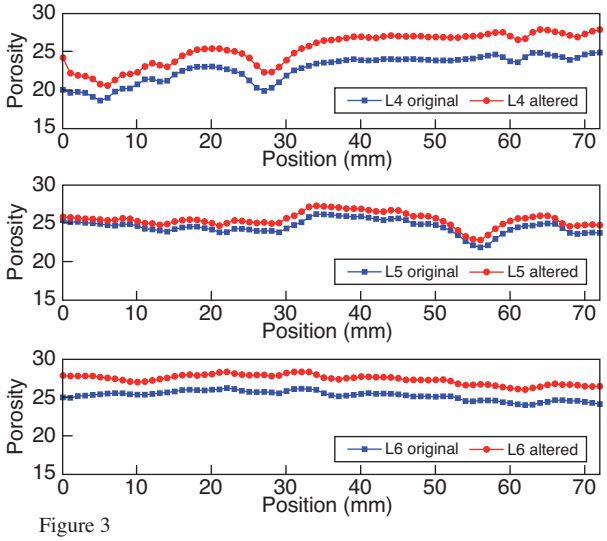


Figure 3

Porosity profiles of initial and altered samples.

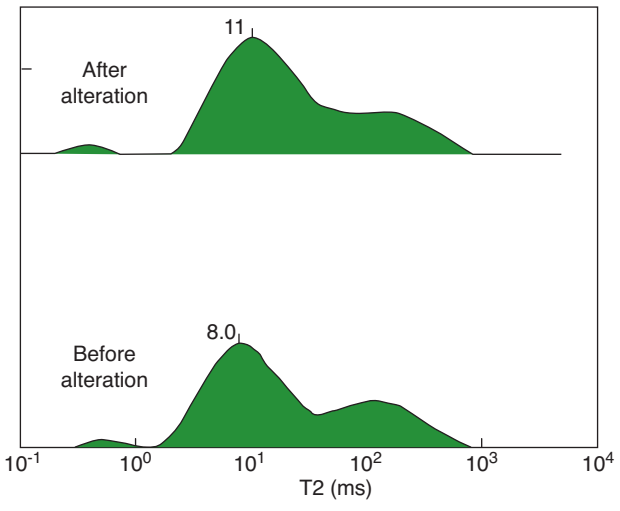


Figure 4

NMR T2 distribution of sample LJ6, before and after the acid alteration.

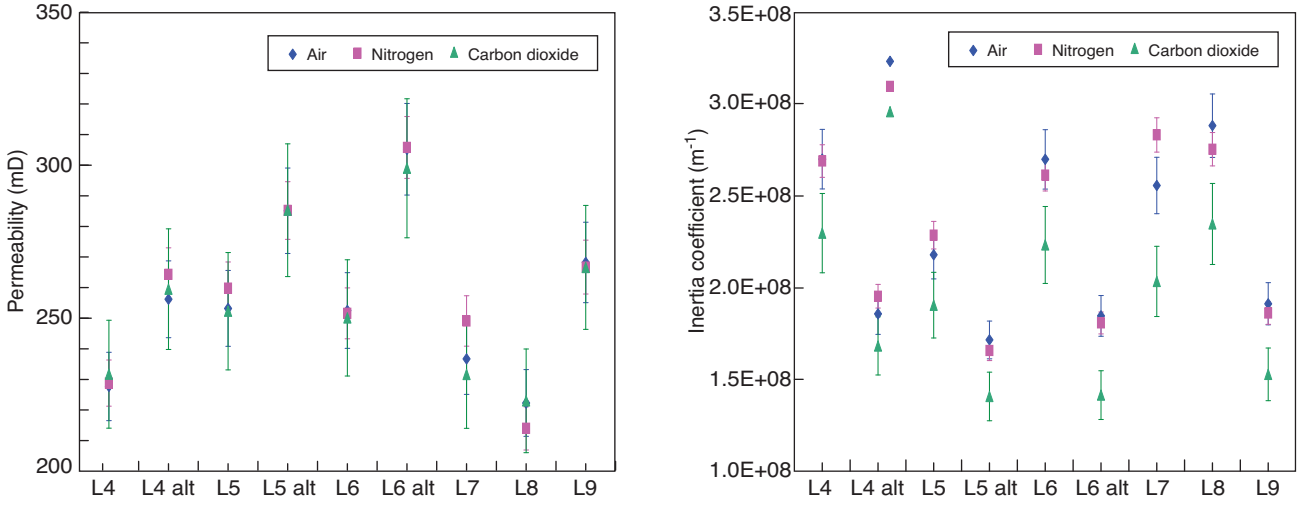


Figure 5

Permeability and inertia coefficient.

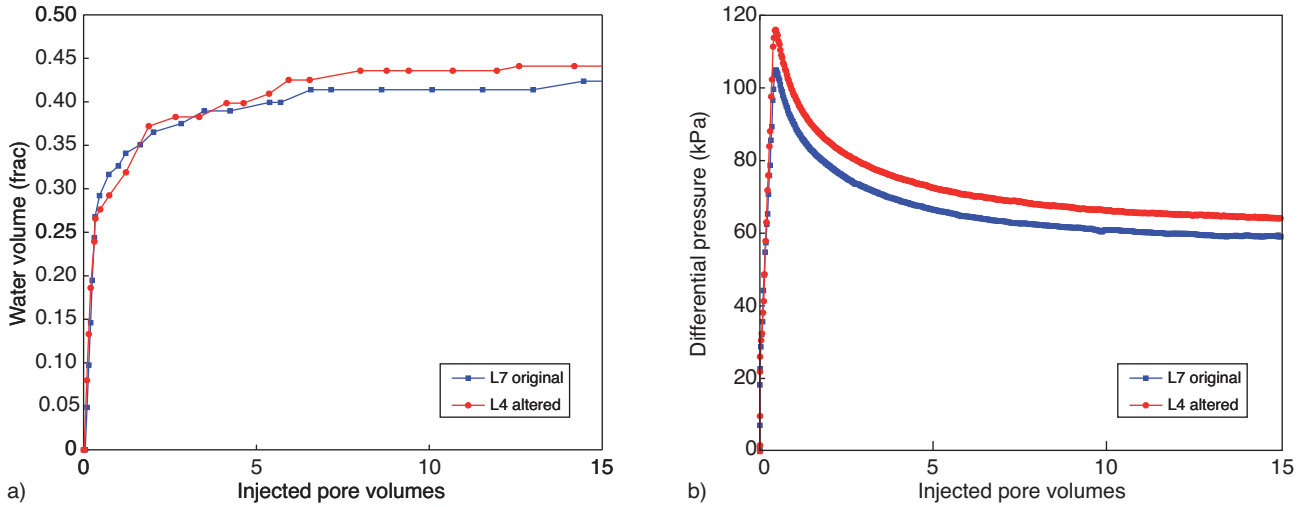


Figure 6

a) Water volume production during drainage experiment on samples L4 and L7 altered. b) Pressure drop during drainage experiment on samples L4 and L7 altered.

Figure 5 shows the effect of acid alteration on both permeability and inertia coefficient. Equation (2) was used to calculate both parameters and experiments were conducted using three different gases (N_2, Air and CO_2). Permeability of the samples is in the range of 200 to 300 mD, inertia coefficient is in the range of 1×10^8 to 3×10^8 m^{-1}.

After alteration, a 20% permeability increase and a 30% inertia coefficient decrease were observed. In addition to the observed porosity increase, these results indicate that CO_2 injectivity would be enhanced during the acid injection. But with the adopted experimental procedure, no fine displacements was produced. This is contrary to what was measured during the CO_2/brine injection performed within the Phase 1 of the project (Lombard *et al*., 2007). This conclusion has thus to be considered carefully and would need further investigations.

Klinkenberg Effect

Klinkenberg effect (Klinkenberg, 1941) was not observed in the samples neither in their original state nor in their altered state. This is attributed to quite high permeability value (> 200 mD).

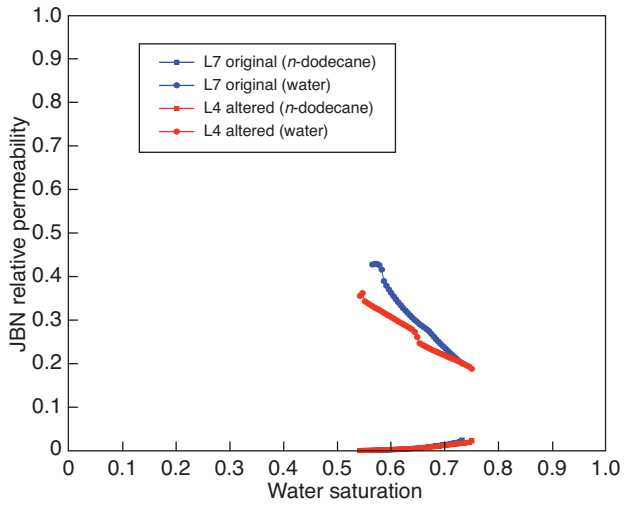


Figure 7

Relative permeabilities of samples L7 (original) and L4 (altered).

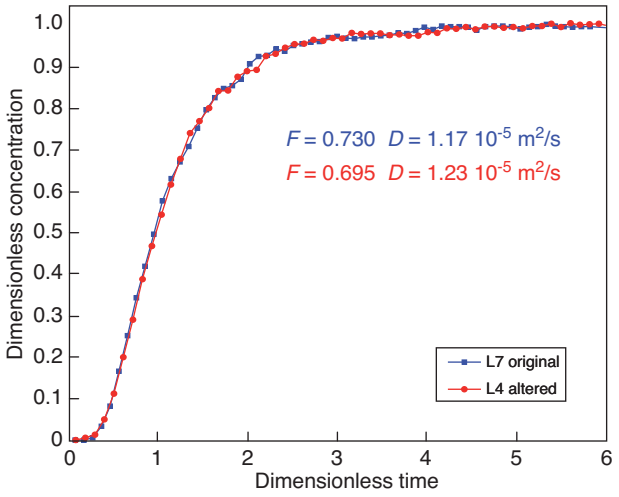


Figure 8

Tracer breakthrough curves for samples L7 (original) and L4 (altered).

Relative Permeabilities

We used the JBN approach (Johnson *et al*., 1959) to estimate the relative permeabilities of our samples for a two-phase flow of water–*n*-dodecane. Typical plots of the water volume production and pressure drop within the sample during drainage are presented in Figure 6. The corresponding JBN relative permeabilities are presented in Figure 7.

The explored range of relative permeabilities in terms of water saturation is very narrow. This is due to the homogeneity of our samples and to the fact that the JBN approach allows the calculation of relative permeabilities only when the two fluids flow together. While water relative permeability is almost not affected by the alteration, a sensible decrease of the *n*-dodecane relative permeability is observed.

Although relative permeability curves for the CO_{2SC}/brine system are unknown, our experiment seems to indicate that the alteration of our samples has limited influence on relative permeabilities. Additional experiments would be required to study the wettability modifications induced by the retarded acid solution. However, for such a water-wet sample, only slight changes in relative permeabilities are expected for CO_{2SC}/brine two-phase flow, CO_{2SC} as oil being the non wetting phase (Chalbaud *et al*., 2009).

3.2 Transport Properties

Step injections of tracer (KCl) were performed on samples in their original state and on altered samples. Figure 8 shows tracer breakthrough curves for sample L7 in its original state and for sample L4 after alteration. As expected from the mercury porosimetry, the dual porosity of the samples is reflected by the non symetrical breakthrough curves.

Several models allow to take into account for dual porosity during tracer dispersion experiments in porous media. Some are numerical, others are probabilistic, and also there are models based on Fractionnal Brownian motion (Carlier, 2008). As our samples present no major heterogeneities besides their dual porosity, and also because we focus on quantifying the effect of the alteration, we preferred to analyse breakthrough curves using two robust and straightforward models: the classical advection-dispersion equation, and the equivalent stratified porous media approach.

All breakthrough curves were modeled by the Ogata-Banks solution (Ogata and Banks, 1961) to the well-known advection-dispersion equation (Bear, 1972):

$$C(x,t) = \frac{1}{2}\left[\operatorname{erfc}\left(\frac{x-t}{2\sqrt{Dt}}\right) + \exp\left(\frac{x}{D}\right)\operatorname{erfc}\left(\frac{x+t}{2\sqrt{Dt}}\right)\right] \qquad (3)$$

where C is the dimensionless tracer concentration, D is the dimensionless dispersion coefficient, t is the dimensionless time and x is the dimensionless position.

Also, we used the stratification factor approach (Fourar, 2006; Fourar and Radilla, 2009). In this approach, a given porous medium is replaced by an equivalent stratified medium in which, each stratum is perfectly homogeneous and has its own intrinsic permeability. The stratification factor characterizes the permeability distribution of all the strata. The higher the stratification factor, the higher the heterogeneity of the medium.

For our boundary conditions, the stratification factor approach leads to the following concentration equation:

$$C(x,t) = \frac{1}{2}\operatorname{erfc}\left(\frac{\ln\left(\frac{x}{t}\sqrt{1+F^2}\right)}{\sqrt{2\ln\left(1+F^2\right)}}\right) \quad (4)$$

where F is the stratification factor.

As suggested by the porosity profiles in Figure 3, samples remain homogeneous after alteration and therefore, the dispersion coefficient and the stratification factor are almost unchanged. Table 3 summarizes the experimental results on tracer dispersion.

TABLE 3

Experimental results on tracer dispersion

Sample	Flow rate (cc/h)	Peclet number	Porosity	Dispersion coefficient (m^2/s)	Stratification factor
LJ4N1	600	12.12	0.24	1.23E-05	0.695
LJ5N2	594	9.02	0.267	0.91E-05	0.679
LJ6N3	570	9.22	0.269	1.25E-05	0.834
L7	600	9.39	0.26	1.17E-05	0.730
L8	600	11.34	0.245	1.11E-05	0.820
L9	582	11.24	0.242	0.70E-05	0.567

Table 3 shows that the dispersion coefficient and the stratification factor of altered samples are very close of those of the samples in their original state. Moreover, the variability of the values of those parameters is the same for the samples in their original state and for those that where altered.

CONCLUSIONS

Porosity, intrinsic permeability, inertia coefficient, Klinkenberg effect, JBN relative permeabilities, dispersion coefficient and stratification factor were measured on samples of Lavoux limestone in their original state and after being altered by exposure to a retarded acid.

In their original state, samples appear to be issued from a very homogeneous rock sample. Samples appear to have a dual porosity distribution with peaks at 0.26 μm and 10 μm which explains the non symetrical breakthrough curves. The alteration procedure allows preserving samples homogeneity in order to apply the JBN method for calculating the relative permeabilities.

Altered samples show sensible changes of the porosity, the intrinsic permeability and the inertia coefficient. Little changes were observed in relative permeabilities and almost no change was observed in tracer transport behavior.

These results indicate that CO_2 injectivity would be enhanced during the acid injection in the Dogger formation. But with the adopted experimental procedure, no fine displacements was produced. This is contrary to what was measured during the CO_2/brine injection performed within the Phase 1 of the project. This conclusion has thus to be considered carefully and would need further investigations.

ACKNOWLEDGMENTS

Authors acknowledge financial support for this work funded by the French National Research Agency (ANR) within the frame of the Geocarbone Injectivity project. Authors also acknowledge *LAEGO Laboratory* for performing the mercury porosimetry and average porosity measurements of all samples.

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Final manuscript received in September 2009
Published online in June 2010

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