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Experimental investigation of the influence of supercritical state on the relative permeability of Vosges sandstone



Étude expérimentale de l'influence de l'état supercritique sur la perméabilité relative d'un grès des Vosges

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ARTICLE INFO

Article history:

Received 30 January 2015

Accepted 26 June 2015

Available online 21 July 2015

Keywords:

Supercritical CO₂
Relative permeability
Sandstone
Steady-state
CCS
Darcy's law

Mots-clés :

CO₂ supercritique
Perméabilité relative
Grès
Régime permanent
CCS
Loi de Darcy

ABSTRACT

Measurements of relative permeabilities involve complex and long experiments, especially when dealing with supercritical carbon dioxide at high pressures and temperatures. However, the development of CCS (Carbon Capture and Storage) underlined the need of such experiments in order to carry-out the indispensable simulations of the behavior of deep saline aquifers or other geological formations subjected to carbon dioxide injection. In this article, we present the measurement of relative permeabilities of a sandstone with a new experimental set-up with the fluid pairs gaseous CO₂/water and supercritical CO₂/water. For highly permeable and non-reactive materials, the results are almost identical, showing little influence of the pressure, temperature, and physical state of the considered fluids on the obtained data.

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R É S U M É

Mesurer des perméabilités relatives implique des expériences lourdes et complexes, en particulier lorsqu'il s'agit de dioxyde de carbone supercritique à hautes pressions et températures. Cependant, le développement du CCS (capture et stockage du CO₂) a souligné l'importance de telles expériences afin de mener à bien les simulations indispensables du comportement des aquifères salins profonds ou autres formations géologiques soumises à injection de dioxyde de carbone. Dans cet article, nous présentons la mesure de perméabilités relatives d'un grès à l'aide d'un nouveau prototype expérimental, avec les couples de fluides CO₂/eau et CO₂ supercritique/eau. Pour des matériaux à haute perméabilité, les résultats sont pratiquement identiques, soulignant le peu d'influence de

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la pression, de la température et de l'état physique des fluides utilisés sur les données obtenues.

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1. Introduction

Reactive percolation simulations are an important part of the geological and geomechanical researches. In fields like Carbon Capture and Storage (CCS) or Enhanced Oil Recovery (EOR), numerical simulations of the behavior of supercritical carbon dioxide in geological formations are commonly used to obtain invaluable information on the temporal evolution of the reservoir, allowing one to anticipate the future of the injection [1,2]. In these simulations, the behavior of fluids in the porous volume is interpreted with Darcy's law: following their wettability with the pore wall, fluids can move more or less easily in the porosity, which is quantified by relative permeabilities [3].

The development of CCS and especially, the development of the research on coupled phenomena [4,5] has highlighted the strong lack in the literature of measurements of relative permeabilities with supercritical carbon dioxide. Indeed, considering the temperature and pressure state reigning in a deep saline aquifer, carbon dioxide will most certainly be in a supercritical state [6], which combines a low viscosity and a high density. The effect of this state on the relative permeability is ambiguous in the literature. Some studies show an influence of surface tension and viscosity on the behavior of fluids [7], while others claim that the relative permeabilities are actually an intrinsic characteristic of the porous medium and that the chosen fluid pair does not affect it [8,9].

In this article, we present an experimental set-up able to measure relative permeabilities under high temperature and pressure conditions and specially designed for the use of supercritical carbon dioxide. We use this set-up to measure and compare the relative permeabilities of a sandstone (from Vosges, France) with the fluid pairs gaseous carbon dioxide/water and supercritical carbon dioxide/water.

2. Multiphase flow and experimental method

2.1. Basic measurement principle

Intrinsic permeability characterizes the ability of a fluid to penetrate and move through the porosity of the considered rock. This parameter is defined by Darcy's law (for incompressible fluids), which relates, if gravity is not considered, the fluid pressure gradient to its flow rate through the rock:

$$\frac{Q}{A} = \frac{k^0}{\eta} \frac{\Delta P}{L} \quad (1)$$

with Q the flow rate of the fluid across a cylindrical core, A the cross-section of the rock core, k^0 the intrinsic permeability of the core, η the temperature-dependent viscosity of the fluid, L the length of the core and ΔP the pressure difference across the rock core. For compressible fluids (gaseous and supercritical CO_2), the integration of the generalized Darcy law leads to the replacement of $\frac{\Delta P}{L}$ with $\frac{p_1^2 - p_2^2}{2Lp_1}$, p_1 the inlet pressure and p_2 the outlet pressure [10]. However, considering the low pressure drops involved in our experiment, especially in the case of supercritical CO_2 , the difference between the two equations is of the order of magnitude of 1% and can be neglected.

When several fluids are present in the porosity of the core, they will behave differently from the saturated case. In order to consider this effect, we use the relative permeability parameter, which is a function of the saturation of the considered fluid and is defined by the extended Darcy law (2):

$$\frac{Q_J}{A} = \frac{k_J^r k^0}{\eta_J} \frac{\Delta P}{L} \quad (2)$$

with Q_J the flow rate of phase J , k_J^r the relative permeability of phase J , and η_J the viscosity of phase J .

Measurement of intrinsic and relative permeabilities can be done with several methods, mainly transient methods (pulse-test) [11] or steady-state methods [12,9]. In our experiment, measurements have been carried out with a steady-state method: fluids are injected at a constant flow rate, while the outlet pressure is held constant. The pressure difference is recorded when the system has reached its steady state (constant flows at the outlet of the system and constant water saturation in the core).

2.2. Experimental device and procedure

2.2.1. Presentation of the equipment

The experimental set-up on which experiments have been performed is a classic relative percolation set-up with several improvements. A sketch of the set-up and its photography are presented in Figs. 1 and 2. It is composed of a triaxial cell,

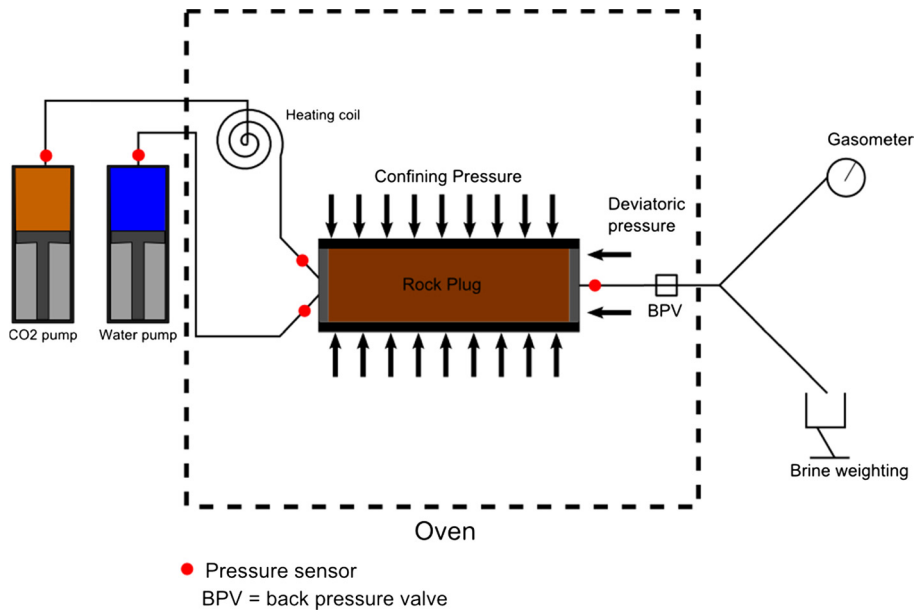


Fig. 1. (Color online.) Sketch of the experimental set-up.



Fig. 2. (Color online.) Picture of the experimental set-up.

a 3 L hastelloy bottle whose purpose is to allow the thermodynamical equilibrium of the two fluids before injection, and a back-pressure valve used to control the outlet pressure of the triaxial cell. The rock core to be tested is inserted in the triaxial cell within a Nitrile (CO₂ resistant polymer) jacket that allows the transmission of the confining pressure. At the inlet and the outlet of the rock core, two discs of sintered steel are placed in order to homogenize the flow of the two injected fluids. Injection of fluids is controlled by two pumps ST1000 from Sanchez Technologies whose precision is 0.1% of the specified flow rate. The body volume of the pumps is 1 L and their maximum working pressure is 300 bar.

The whole set-up (cell, bottle and back-pressure valve) is inserted in an oven (MEMMERT) in order to control the temperature. The circuit of CO₂ includes a coil, which allows to heat the carbon dioxide that is stored outside the oven in the pump and thus allows its phase change (from liquid to supercritical) before the penetration in the rock core. The tempera-

ture can be set up to 150 °C and the precision on temperature is 0.5 °C from ambient to 100 °C. Temperature is measured at two different places: by the oven itself, and by a thermocouple inserted in the triaxial cell.

2.2.2. Intrinsic permeability

Measures of intrinsic permeabilities have been performed using with pure water. Water has been injected at several flow rates and the resulting pressure differences have been recorded. The slope of the $\Delta P/Q$ curve obtained gives the intrinsic permeability, knowing the viscosity and the geometry of the core sample of the considered rock. The equilibrating time for the pressure difference at each flow rate depends on the permeability of the medium: the smaller the permeability is, the longer it takes to reach the equilibrium value.

2.2.3. Relative permeabilities

Measures of relative permeabilities are much more difficult to carry out than intrinsic permeability because of the presence of the two fluids in the porosity and the necessary measurement of the water saturation. However, the principle is the same: injection of the two fluids at constant flow rate and measure of the pressure difference between the inlet and the outlet. The values of the two pumps flow rates are chosen in order to cover the whole range of water saturations. Let us remark that in the case of supercritical carbon dioxide, the fluid in the pump is actually liquid and the transformation into a supercritical state occurs in the coil in the oven. As a result, the pump flow rate is not the actual flow rate that is injected in the sample. To get this flow rate, a density correction is applied, taking into account the density of liquid and supercritical carbon dioxide (i.e. 800 kg/m³ for the liquid (100 bar, 20 °C), and 290 kg/m³ for the supercritical fluid (100 bar, 60 °C) [13]).

Experimental protocol In function of the target saturation, the experimental protocol varies.

For high water saturations, the rock core is initially saturated with water and its desaturation is obtained following the drainage curve, through an increase of the ratio between gas and liquid flow rates. In this case, desaturation is easy and is obtained in a relatively short time.

When the target water saturation is close to the residual value (defined as the minimum saturation that is possible to be reached by following the drainage curve), this simple method is not efficient anymore. Indeed, because of the wettability of the medium, the wetting fluid will be trapped by capillary forces while the non-wetting one will flow between the pockets of the wetting fluid [14]. Accordingly, reaching water saturations close to the residual saturation needs a very high ratio between the two flow rates (1000 or more), which is not compatible with the technical limitations of the experimental set-up (mainly the limited volume of the pumps bodies). A way to overcome this problem is to reach the target saturation following the imbibition curve: both fluids were injected on a dry sample. We then consider that we can neglect the hysteresis between the imbibition and the drainage curve.

Finally, even starting with a dry sample, the simultaneous injection of both fluids does not allow reaching the lowest saturations. Indeed, as a wetting fluid, water will imbibe spontaneously the rock core before breaking through. In order to avoid this problem and to reach very low water saturations, a small and precise quantity of water is injected in the core before the experiment. Carbon dioxide is then injected alone. In this case, because the low water saturation is far below its percolation value, the water mobility can be estimated as zero and thus the loss of information on the water relative permeability by not injecting water is not an issue.

Water saturation measurement The water saturation values at each step have been obtained by two different methods: for the measurement with gaseous carbon dioxide, water saturation was measured by dismantling and weighing the sample. This method allows us to obtain an accurate value of the water saturation as soon as the pressure and the temperature are close to the ambient ones. On the other hand, when supercritical carbon dioxide is used, this dismantling and weighing cannot be proceeded as it has to be preceded by a stage of depressurization and temperature decrease that modifies the saturation of the core. Indeed, this stage changes the solubility of water in the carbon dioxide phase [15,16], but also the phase change between supercritical and gaseous carbon dioxide triggers fluid movements within the rock core. Because of these reasons, we chose to get the water saturation by the comparison of the water input and output volumes, taking into account the dead volumes and phase changes within the different parts of the set-up.

3. Experimental test on a Vosges sandstone

3.1. Material characterization and preparation

The core used was made of Vosges sandstone from the Rothbach quarry (France). It is a cylinder of 3.81 cm in diameter (1.5 in) and 7.62 cm (3 in) in length, with a porosity of 18.05% [17]. Only one core is used for all the experiments described here. We consider that the different experiments carried out did not alter it. The chosen confining pressure is 50 bar above the inlet pressure of the rock core.

Intrinsic permeability measurements have been processed at 60 °C and 100 bar (same temperature and pressure as for the measurement of relative permeability with supercritical carbon dioxide and water).

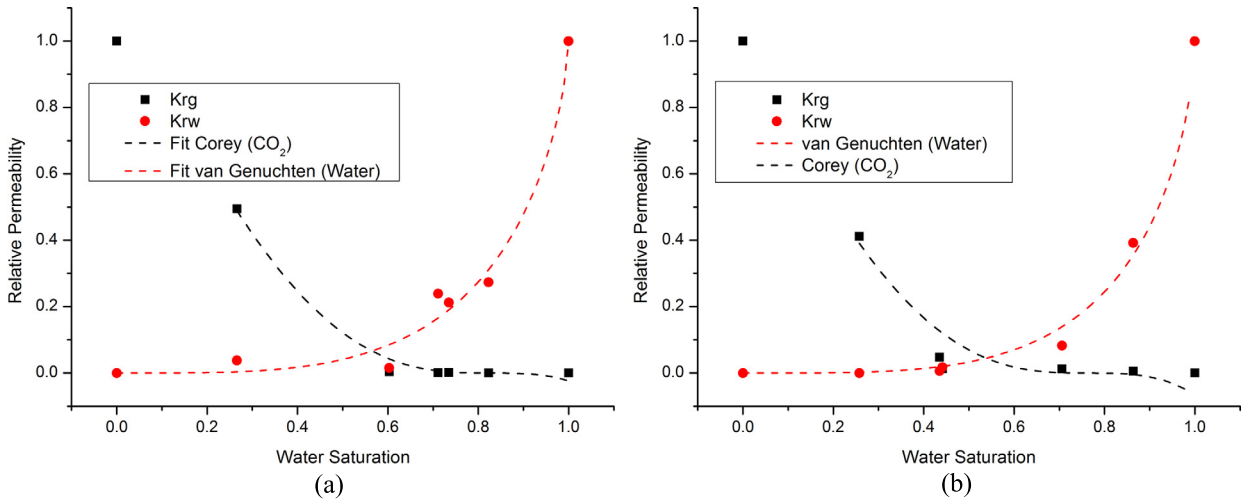


Fig. 3. (Color online.) Relative permeability of Vosges sandstone to supercritical (a) and gaseous (b) carbon dioxide and water (60°C and 100 bar for supercritical carbon dioxide, 2 bar and 25°C for gaseous carbon dioxide).

Table 1
Summary of the obtained results and comparison with the literature.

	[18]	Gaseous CO ₂	Supercritical CO ₂
S_{lr}	0.19	0	0.05
S_{gr}	0	0.23	0.17
m	0.675	0.62	0.65

Relative permeability experiments for gaseous carbon dioxide and water have been proceeded at low pressure (outlet pressure set to 2 bar) and ambient temperature (25 °C), while the experiment with supercritical carbon dioxide and water needed high temperatures and pressures to remain in the supercritical domain (outlet pressure set at 100 bar and temperature set at 60 °C).

3.2. Results and data analysis

The results of the measurement of intrinsic permeability show that the presented experimental set-up yields accurate values of pressure difference under a constant flow rate (the obtained curves are linear). Considering Darcy’s law (1) for a saturated case with no gravity effect, the slope Q versus ΔP provides a value of intrinsic permeability of about 150 mD, which is in the range of permeabilities measured for the Vosges sandstone (from 50 mD to 500 mD) [18].

In Fig. 3 are presented the relative permeability curves for the Vosges sandstone with supercritical carbon dioxide and pure water (Fig. 3a) and with gaseous carbon dioxide and pure water (Fig. 3b) that reveal to be mostly the same. In order to analyze their difference, we use the classical fit of relative permeabilities by the van Genuchten/Mualem model [12,19] for the liquid phase (wetting phase) and the Corey equation [20] for the gas or the supercritical (i.e. non-wetting) phase:

$$k_l^r = \sqrt{S^*} \left(1 - \left(1 - [S^*]^{1/m} \right)^m \right)^2 \tag{3a}$$

$$k_g^r = (1 - S_h)^2 \left(1 - S_h^2 \right) \tag{3b}$$

with k_g^r the relative permeability of the gaseous (or supercritical phase), k_l^r the relative permeability of the liquid phase, $S^* = \frac{S_l - S_{lr}}{1 - S_{lr}}$, S_l the water saturation, S_{lr} the residual water saturation, m the van Genuchten/Mualem exponent, $S_h = \frac{S_l - S_{lr}}{1 - S_{lr} - S_{gr}}$, S_{gr} the residual gas saturation (other semi-empirical expressions of the relative permeabilities for the wetting and the non-wetting phase can be found in the literature [12], but equations (3a) and (3b) are the most widely used and fit accurately our results).

The results for the fits are shown in Fig. 3 and are summarized in Table 1. For supercritical carbon dioxide, the fitting parameters are $m = 0.65$, $S_{lr} = 0.05$ and $S_{gr} = 0.17$, while for gaseous carbon dioxide, the fitting parameters are $m = 0.62$, $S_{lr} = 0$, and $S_{gr} = 0.23$.

There are numerous issues in the measurement of relative permeabilities. The most important issue is the so-called “capillary end effect” [21]. Indeed, experiments are proceeded with a finite rock core. At the outlet, both fluids follow the same tubing and thus have the same pressure. As capillary pressure is continuous, this means that there is a nil capillary

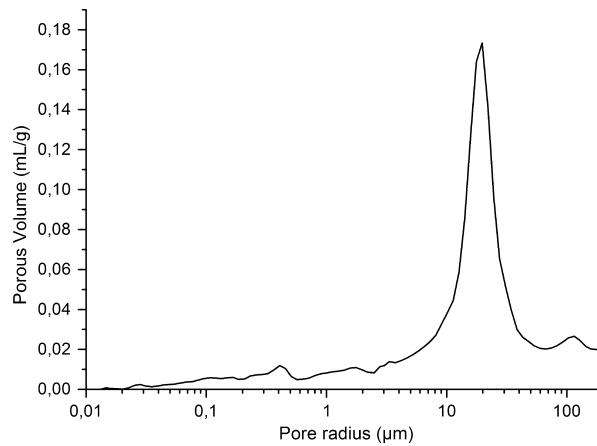


Fig. 4. Pore size distribution as measured by Mercury Intrusion Porosimetry.

pressure at the outlet surface of the rock core and thus the water saturation is not completely homogeneous along the rock core.

Despite this problem and the difficulty to obtain an accurate value of the water saturation, along with the difficulty to reach extreme values of low water saturation, the measurement of relative permeabilities with carbon dioxide and water gave interesting results. First of all, the accuracy of the measure can be compared to data from the literature. For example, in [18] is presented a curve of relative permeability for a sample of Vosges sandstone calculated from the capillary pressure curve fitted with the Van Genuchten/Mualem expression. They found a residual water saturation $S_{lr} = 0.19$, which is higher than ours. However, their determination of the coefficient $m = 0.675$ is close to our value (relative difference of 8%), which confirms our measurement. The discrepancy between their estimation of the water residual saturation and ours comes from the difficulty to measure extreme values of water saturation: the low water saturations are difficult to reach as described in the experimental procedure part, which explains an imprecision on the residual water saturation. We were only able to obtain one experimental point below a water saturation of 40%, which decreases the accuracy of the carbon dioxide fit and thus forbids any accurate determination of the residual water saturation by this mean. Moreover, this difficulty to obtain the right slope of the supercritical/gas curve at low water saturation impacts also mathematically the fit at high water saturations as we can see in Fig. 3a, the fit giving negative values between 0.9 and 1.

Nevertheless, from Fig. 3 and the fitting curves, it is clear that the two curves are nearly identical, especially the two water relative permeabilities. This similarity can be explained by the fact that the relative permeabilities are governed by the geometry of the pore space within which the fluid flows. The impact of the fluid nature on the flow rate is, for its part, rather captured by its dynamic viscosity in the generalized Darcy law (2). Then, since the type of non-wetting fluid, the pressure and the temperature do not affect the pattern of residual water saturation, which is true if we consider similar capillary numbers and viscosity ratio [22,9], they should also not affect the shape of the relative permeability curve.

As a result, it is possible to conclude that the values of the relative permeabilities measured with gaseous carbon dioxide can be used for supercritical CO_2 with good accuracy, the supercritical state having little or no influence on the relative permeabilities of this non-reactive rock with a high intrinsic permeability (150 mD). This conclusion must now be checked on cores with small to very small permeabilities, for which differences in behavior may occur between the gaseous state and the supercritical state. However, such experiments are even more time consuming, as the time needed to reach the steady state might be very long.

The results of the fits also allow us to obtain the capillary pressure curve. Indeed, the Van Genuchten coefficient m is also a parameter of the Van Genuchten semi-empirical expression for capillary pressure:

$$P_{\text{cap}} = p_0(T) \left([S^*]^{(-1/m)} - 1 \right)^{1-m} \quad (4)$$

with $p_0(T)$ the pore entry pressure i.e. the capillary pressure at which the non-wetting fluid (here carbon dioxide) can start to penetrate the pores of the considered rock. Experimentally, we have obtained a value of $p_0(25^\circ\text{C}) = 0.06$ bar with an outlet pressure of 2 bar and gaseous carbon dioxide. This value depends on the injected fluid considered and particularly on its surface tension. Knowing this value and the relative permeability curves allows then to infer the capillary behavior of the rock, and thus also its poromechanical behavior [23].

Interestingly, the value of the non-wetting fluid relative permeability is close to zero until a water saturation of 0.5–0.6 is reached. This can be explained by the pore-size distribution as measured by Mercury Intrusion Porosimetry (AutoPore IV, MicroMeritics) and presented in Fig. 4. Indeed, the rock exhibits a pore-size distribution centered around 20 μm , but with a strong presence of very large pores. The very small values of the non-wetting relative permeability within the range [0.5–1] can be explained by the fact that these large pores do not create a continuous and percolating path through the sample. The desaturation of these large pores will lead to a decrease in the water saturation, but without increasing

significantly the capacity of the non-wetting phase to flow through the sample. However, once we start to desaturate the main pore size (i.e. 20 μm) the non-wetting phase relative permeability increases then drastically because of the opening of the different percolation paths and the connection between already emptied large pores. Let us underline that, assuming a surface tension between water and CO_2 of 60 mN/m [24], a perfect wetting of the solid surfaces by water (nil contact angle), and a spherical geometry of the interface, the Young–Laplace law gives a capillary pressure of 0.06 bar for this radius, which is consistent with the air entry pressure, $p_0(25^\circ\text{C})$ obtained experimentally.

4. Conclusion

Measurements of relative permeabilities of rock cores involve long and difficult experiments. It is worse when the measurements are made with carbon dioxide in a supercritical state because of the high temperature and pressure needed in the experiments. This accounts for the lack of experimental measurements of relative permeabilities with supercritical carbon dioxide in the literature and explains why the numerical simulations—particularly in the CCS area—are carried out with relative permeability measures obtained with the couple nitrogen/water (or even through the measurement of capillary pressure solely, as in [18]). In this article, we have presented a new experimental prototype capable of measuring relative permeabilities, allowing to handle carbon dioxide in its supercritical state. Using this experimental set-up, we have been able to obtain, for a sample of Vosges sandstone, the relative permeability curves for the two pairs gaseous carbon dioxide/water and supercritical carbon dioxide/water. The comparison of the measurements of the relative permeabilities with gaseous and supercritical carbon dioxide have shown very little difference on the obtained curves, which allows us to conclude that the effect of the supercritical state on the relative permeability curves can be neglected in the case of high-porosity non-reactive materials: this result agrees with those in [8,9]. Moreover, it means that the relative permeability curves can be obtained with experiments performed at ambient temperature and low pressures, which makes the measurements much easier and faster to proceed. Additionally, the van Genuchten fitting parameter m also allows us to determine the shape of the capillary pressure curve if the pore entry pressure is known for the considered fluid and the considered rock.

Acknowledgements

The present work has been supported by the French Environment and Energy Management Agency (ADEME) through the Project SALTCO No. 1094C0013 and the Chaire “Captage Transport Stockage du CO_2 ”.

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