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GHGT-12

# Assessing CO<sub>2</sub> adsorption capacities onto shales through gravimetric experiments: a first step in the feasibility study of coupling “fracking” with carbon storage

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## Abstract

Oil and gas production from shale formations stimulated by hydraulic fracturing (or “fracking”) is an abundant source of domestically available energy for the United States of America. Today, shale formations are mostly fracked using fresh water or brine which induces large volumes of water to manage. The use of CO<sub>2</sub> is an alternative fracking option and appears to have several benefits, as (1) it does not require water but carbon dioxide; as (2) injection of carbon dioxide could enhance the gas recovery; and as (3) carbon dioxide could be adsorbed onto the shale surface to be permanently stored in the formation. We performed adsorption experiments to assess the quantity of carbon dioxide that could be adsorbed onto shale.

*Keywords:* shale gas ; adsorption ; CO<sub>2</sub> ; storage.

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## 1. Introduction

Oil and gas production from shale formations stimulated by hydraulic fracturing (or “fracking”) is an abundant source of domestically available energy for the United States of America. Unconventional oil and gas development and more specifically shale gas and oil production should increase worldwide in the next years.

Today, shale formations are mostly fracked using fresh water or brine which induces large volumes of water to manage. Industry face issues related to containment, transport, recycling, reuse, treatment and disposal of wastewaters (wastewaters are defined as mixture of drilling fluids, hydraulic fracturing fluids and formation water). Some alternative fracking options are proposed by oil and gas companies to reduce the quantity of water that is used. Among these options, fracking with carbon dioxide appears to have several benefits compare to hydraulic fracking, as (1) it does not require water but carbon dioxide; as (2) injection of carbon dioxide could enhance the gas recovery; and as (3) carbon dioxide could be adsorb onto the shale surface to be permanently stored in the formation.

Here, we present and discuss results from laboratory experiments in order to assess adsorption capacities of carbon dioxide onto shales.

## 2. Shale samples

Rock used in this study was sampled from the Tounemire underground tunnel, which is located in a Mesozoic marine basin on the southern border of French Massif Central. The interest formation consists of three mainly levels of marls and shales of the Toarcian and Domerian ages. Toarcian layer is subdivided in three sublevels named upper, middle and lower. Our samples were taken from the lower and upper Toarcian. Average mineral composition of each layer can be determined from literature [1]. Samples from upper Toarcian are characterized by a predominance of clays (~60%) associated with quartz (15-20%) and calcite + dolomite (10-15%). Samples from lower Toarcian are characterized by a predominance of clays (~40%) and calcite + dolomite (~40%) associated with quartz (~10%). Other crystallized phases as feldspar and pyrite in minor quantities. Prior to experiments, shale samples were dried at 353 K (80°C) for at least 48 hours and crushed to obtain particles between 40 and 250  $\mu\text{m}$ .

## 3. Gravimetric experiment

Adsorption isotherms have been determined through a gravimetric experiment on a magnetic suspension balance. The balance measures the changes in mass which act on solid samples during gas adsorption process, under controlled pressure and temperature conditions. Quantities of gas that can be adsorbed or desorbed can thus be assessed (fig. 1 and [2]).

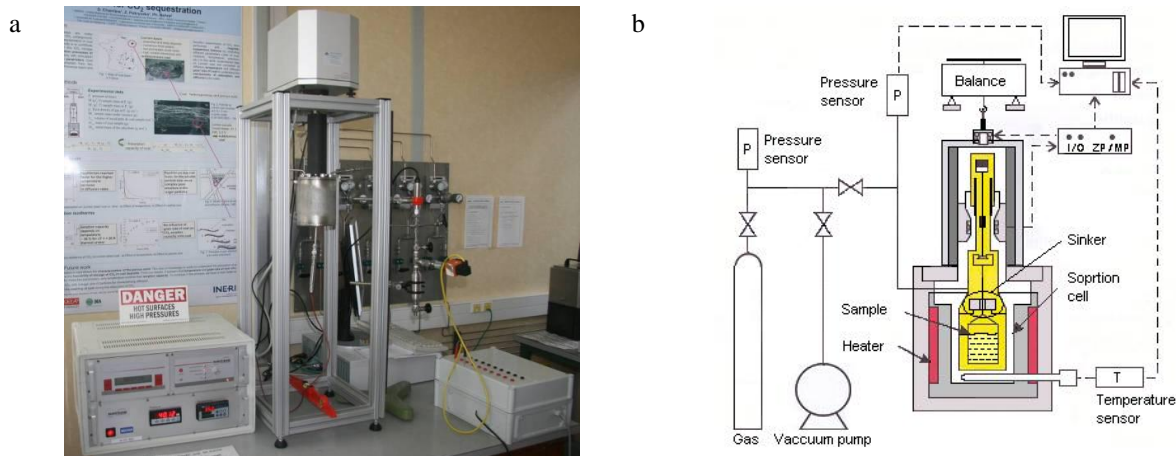


Fig. 1. Magnetic suspension balance: (a) photography of the equipment; (b) diagram of the equipment.

Adsorption experiments were performed with pure CO<sub>2</sub> on about 3 grams of dry and crushed shale sample. It is important to note that by crushing shale samples, kinetics of adsorption are sped up but sorption capacities are not modified. Carbon dioxide pressure ranged from 0.1 MPa (1 bar) up to 9 MPa (90 bar) and four temperatures have been investigated: 298 K (25°C), 313 K (40°C), 318 K (45°C) and 328 K (55°C). Mass of sample and gas phase density were continuously monitored during the experiments. The mass of the adsorbed gas can be monitored as a function of gas pressure or density to estimate adsorption capacities at equilibrium and as a function of time for kinetic purposes.

#### 4. Results: CO<sub>2</sub> adsorption isotherms

Results are presented as adsorption isotherms giving sorption capacities at different values of pressure for a given temperature (fig.2 and fig.3). Values are in mmol of sorbed CO<sub>2</sub> per gram of dry shale.

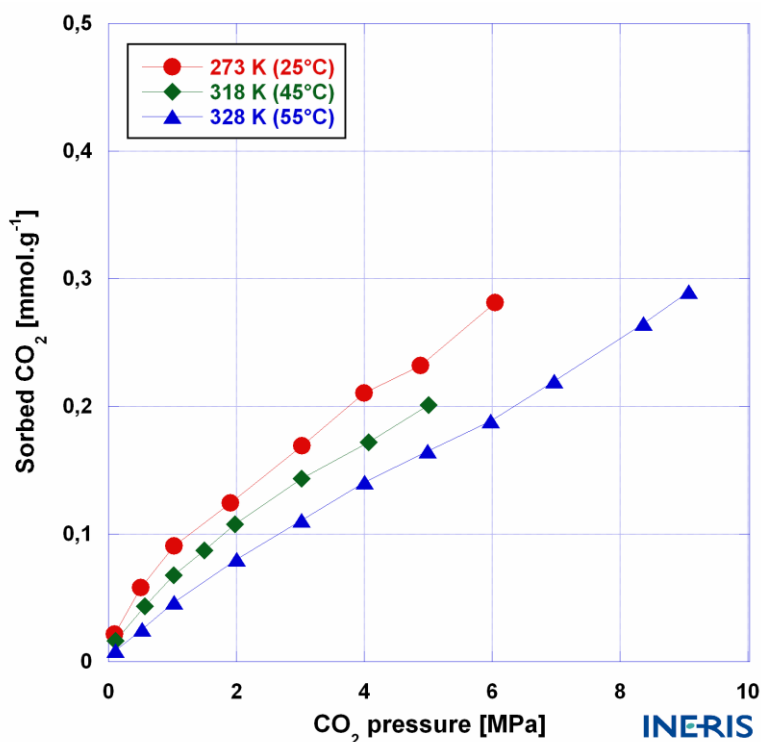


Fig. 2. CO<sub>2</sub> adsorption isotherms on lower Toarcian shale at 3 different temperatures.

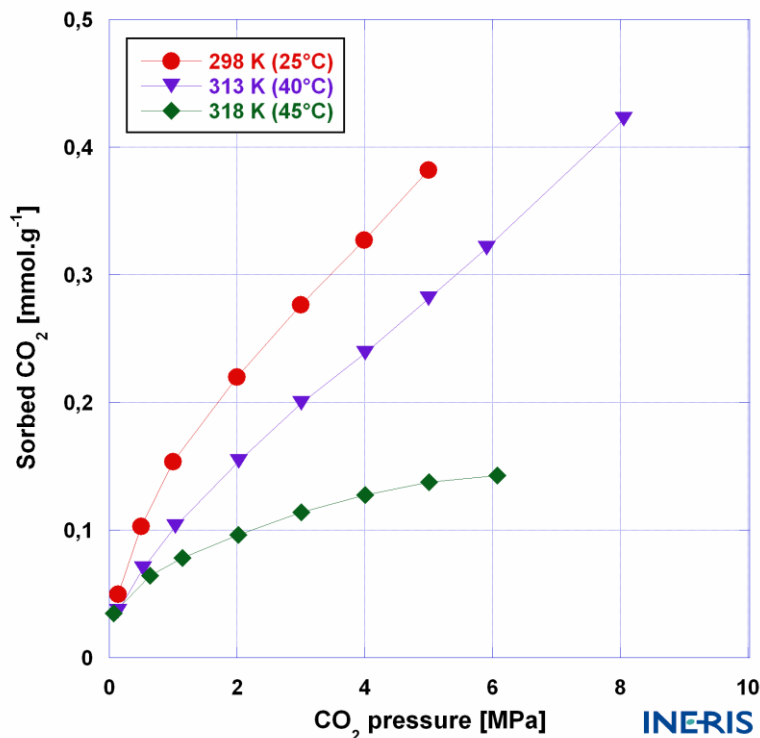


Fig. 3. CO<sub>2</sub> adsorption isotherms on upper Toarcian shale at 3 different temperatures.

Adsorption experiments highlight the following conclusions:

- The increase in temperature induces a decrease of the adsorbed CO<sub>2</sub> quantity. This is a well-known result, already observed for coal samples [2].
- Adsorbed CO<sub>2</sub> quantities are lower than those observed for coal samples. At 298 K and 5 MPa, the adsorbed CO<sub>2</sub> quantity onto shale is about 0.3 mmol/g, where as it is between 0.45 to 2.0 mmol/g onto raw coal, depending the coal sample [3].
- The results are not the same for the 2 shale samples, which is not surprising because the samples do not have the same mineral composition.

## 5. Conclusion

We performed adsorption experiments to determine the quantity of carbon dioxide that can be adsorbed onto shale. Results show that CO<sub>2</sub> adsorption onto shale is significant even if it is lower than adsorption onto coal. This work is a first step in the feasibility study of coupling “fracking” with carbon storage during shale gas exploitation.

But beyond the assessment of the adsorption/storage capacities, other topics should be discussed in further details as: What could be the impacts of changes in shale nanoporous structure through CO<sub>2</sub>/water/rock interactions on gas adsorption or methane production [4]? Is there any competitive adsorption between carbon dioxide and methane onto shale as it is the case of gas adsorption onto coal? How can we model replacement of adsorbed methane by adsorbed carbon dioxide onto shale? Future studies will help to answer these questions.

## Acknowledgements

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