Experimental Simulation of the Impact of a Thermal Gradient on a Clayey Caprock Submitted to the Combined Action of Water and CO₂

Jérôme Sterpenich, Emmanuel Jobard, Jacques Pironon, Aurélien Randi
Université de Lorraine, CNRS, CREGU, GeoRessources laboratory, BP 70239, F-54506 Vandœuvre-lès-Nancy, France
jerome.sterpenich@univ-lorraine.fr

Keywords: Caprock, clay, CO₂, saline solution, experiment, high pressure, thermal gradient, metals

ABSTRACT
This paper aims at studying the effect of a thermal gradient on a clayey caprock in the framework of a coupled system implying CO₂ injection (as supercritical or dissolved in a brine) and heat recovery.

We investigated the reactivity of a typical caprock represented by a Callovo-Oxfordian clay submitted to a high CO₂ pressure (100 bar) and a thermal gradient (100 to 35°C in a 78 cm long tubular reactor) for 30 days. The original COTAGES experiment used in this paper was carried out with a saline aqueous solution (4 g·L⁻¹ NaCl) initially in equilibrium with calcite at 100°C. A mass transfer was observed from the cold area of the reactor (35-55°C) to the warmest area (100°C). Dissolution and precipitation processes are responsible for a mass transfer representing approximately 6% of the initial mass of the most reactive sample. The petrographical analyses showed that the dissolution has mainly affected the carbonated minerals because the clay minerals didn’t show any important mineralogical transformation. However, the dissolution of the carbonate fraction didn’t lead to a loss of mechanical cohesion of the rock while the samples from the hot zone are completely disaggregated despite the precipitation of secondary carbonate minerals. The analyses of major and trace elements confirmed the important mass transfers during the experiment. As expected, carbonate precipitation was linked to strontium trapping. However, transition elements and especially Co, Ni, Cu and Zn showed a significant enrichment in the hot zone implying that mobilization of potential toxic elements has to be taken into account when the caprock undergoes the combined action of water, CO₂ and a thermal gradient.

1. INTRODUCTION
Within the framework of the geological storage of CO₂, it is necessary to ensure the preservation of the confinement properties of the caprock covering the reservoir. A degradation of the caprock could cause a leakage of the sequestrated fluid and lead to an inefficiency of the storage as well as to a possible contamination of the surrounding aquifers. For small CO₂ emitters, a solution coupling CO₂ sequestration and geothermal heat recovery is studied (Kervévan et al., 2013, 2014). The goal is to dissolve CO₂ in water and inject the solution in an injection well. The brine is then pumped from a production well to form a classical geothermal doublet. In these conditions the caprock of the geothermal reservoir will be submitted to the attack of the acid brine with temperatures varying between the injection point and the production well. Several experimental studies investigated the reactivity of clayey caprocks in presence of CO₂. Angelli et al., (2009) showed that a CO₂ flow could cause the reopening of microcracks which could play a role of drains leading to the leakage of the stored CO₂. Credoz et al., (2009) highlighted from batch experiments the apparition of drains due to the dissolution of carbonated minerals of the caprock matrix. These results were also confirmed by numerical simulations (eg. Bildstein et al., 2009, Luo & Bryant, 2011). Rutqvist & Tsang, (2002) showed that only the basal part of the caprock submitted to 10 years of CO₂ exposure was subjected to physico-chemical transformations such as the reopening of old microcracks.

Concerning the behavior of clayey minerals under geological storage conditions of CO₂, the main phenomenon described in the literature was the ilitization of I/S occurring in acidic solution with alkaline ions such as sodium or potassium (Credoz et al., 2011).

The studies about the caprock reactivity in presence of CO₂ are usually performed under isothermal conditions. However the CO₂ or the CO₂ rich brine injection implies a thermal gradient due to the injection of a cold fluid in a rock submitted to the natural geothermal gradient. This thermal gradient leads to a physico-chemical disequilibrium of the system. Similarly to the investigations by Jobard et al. (2013) on a carbonated reservoir rock, the purpose of this study is to observe the reactivity of the Callovo-Oxfordian (COX) caprock under the influence of a thermal gradient and in presence of supercritical CO₂ and brine. The COTAGES (Colone Thermorégulée à Grains pour Gaz à Effet de Serre) model is used to submit a clayey caprock to the combined actions of supercritical CO₂, a saline solution and a thermal gradient. The experiment carried out at 100 bar of CO₂ pressure reproduces the conditions occurring in the vicinity to the injection well during CO₂ or CO₂ rich brine injection.

2. EXPERIMENTAL SET UP
2.1. Material and samples preparation
The clayed rock of Callovo-Oxfordian age (COX) was selected as the caprock for this experiment. This geological stratum is intensively studied within the framework of the geological storage of nuclear wastes in France (ANDRA, eg. Descostes et al., 2007). XRD analyses of the Callovo-Oxfordian clay rock revealed dominant clayed minerals (45% illite and interstratified illite/smectite), a calcium carbonate phase, mainly calcite (25%) and a siliciclastic phase (mainly quartz 25%). Other phases (feldspar, pyrite) and organic matter were detected but in quantities of less than a few percent in mass.

The initial material was crushed into grains which were separated with sieves as a function of their grain size. A total of twelve samples were made with 2.5 g of each grain size (4-3.15, 3.15-2.5, 2.5-2, 2.1-1.41, and 1.41-1 mm) representing a total of 12.5 g per sample. Grains were then wrapped in a fiber glass-braided tissue covered with Teflon. This microporous tissue is inert to CO₂ and
allows mass transfer of aqueous species between the different samples. Twelve samples (representing a total mass of 150 g) were placed in the reactor for the ageing experiments.

2.2. Experimental set up and protocol
The COTAGES device (Figure 1) was composed of an a horizontal tubular reactor made of stainless steel (type 316) with an inner diameter of 22 mm and a length of 780 mm, representing a total volume of 1.2 l. A complete description of the experimental device is given in Jobard et al. (2013). The reactor was placed on a block composed of three separate ovens which allowed heating independently three areas of the reactor up to required temperatures. The gas and the aqueous solution were injected with a pneumatic pump. The temperatures in the middle of the three areas and the confining pressure were monitored every 20 seconds during the experiment. The thermocouple used was a T type (with Cu/Cu-Ni electrodes) and allowed the measurements of temperatures with a precision close to 0.5°C. In these experiments, only the area located at the right extremity of the device was warmed to 100°C. The experiments were carried out with an aqueous solution initially pre-equilibrated at 100°C with a powder of limestone in order to avoid the sample dissolution during the first time of the experiments and before the gas was added. Experiments were carried out with N₂ or CO₂ as the gas phase. N₂ was used as a nonreactive gas in order to help dissociate the action of CO₂ and the only thermal effect which occurred in the reactor.

![Figure 1: Schematic view of the COTAGES experimental device.](image)

In both experiments, the protocol followed was the same. After placing the rock samples in the reactor, an initial gas sweep (N₂ or CO₂) was performed in the reactor under 20-30 bar of pressure (equilibrium between gas bottle pressure and gas flow through the opened reactor) to sweep away the air trapped in the reactor and between the grains of the samples. The exit valve was then closed and the system reached an equilibrium pressure imposed by the gas bottle pressure (close to 55 bar for CO₂). This first pressurization lasted 15 minutes. The reactor was then depressurized and the same procedure was performed a second time. In the N₂ and CO₂ experiments, 270 and 257 g of saline solution were injected respectively with the pneumatic pump. The right area of the reactor was then warmed up to a temperature of 100°C leading to a thermal gradient imposed by the thermal conductivities of the rock, of the aqueous solution and of the reactor (steel). At thermal equilibrium, temperatures at the middle of the three areas were respectively (from the left to the right extremity of the reactor) of 35, 55 and 100°C. As soon as the temperature of the warmed area reached 100°C, the gas (N₂ or CO₂) was injected to get a final pressure close to 100 bar. The experiments lasted 842 hours with N₂ and 787 hours with CO₂. At the end of the experiments, the samples were removed and dried at room temperature for 48 hours.

2.3. Analytical processes
Mass balance calculations were performed for both the CO₂ and N₂ experiments by weighing the samples before and after the experiments. Changes in the mass of the samples allow the mass transfers between the different thermal zones to be quantified. After drying, the samples were weighed with a precision of 0.01 g.

A petrographical study was performed on the samples after the experiment to evaluate changes in the initial mineral phases by dissolution and/or precipitation. A SEM study was carried out on fresh samples and on samples after experiment. The secondary electron (SE) mode was used on a HITACHI S-4800 SEM with field effect (Service Commun de Microscopies Electroniques et de Microanalyses, SCMEM, laboratory of Université de Lorraine, Vandoeuvre lès Nancy, France). Images were acquired with a current of 3 kV.

Rock samples 3 and 11 of the N₂ experiment and 4 and 7 of the CO₂ experiment were analyzed for major elements using inductively coupled plasma optical emission spectroscopy (ICP-OES) and for trace elements using inductively coupled plasma mass spectroscopy (ICP-MS). All of these analytical details (detection limits and procedures) were described by Carignan (2001).

3. RESULTS AND DISCUSSION
Concerning the N₂ experiment, the initial pressure was close to 110 bar (Figure 2). Then, the pressure decreased to a value of 105 bars until the depressurization occurred 842 hours after the N₂ injection. This pressure decrease was due to N₂ solubilization in the...
aqueous solution. During all the experiment, the temperatures in the three zones were stable once the thermal gradient was established (50 hours after the gas injection).

Concerning the CO$_2$ experiment, the initial pressure was close to 120 bar. Then the establishment of the thermal gradient resulted in the raise of T2 and T3 temperatures (not regulated) and simultaneously caused a raise of the pressure to a value of 150 bar. Then the pressure decreased in an irregular way to reach a constant value close to 80 bar 50 hours after the CO$_2$ injection. The pressure was then stable until the depressurization which occurred 787 hours after the gas injection. The temperatures of the three zones were stable during all the experiment once the thermal gradient was established.

![Figure 2: Variations of the pressure and temperatures during the COTAGES experiment with COX caprock and with N$_2$ (blank experiment, left side) or CO$_2$ (right side). T1, T2 and T3 correspond to the temperatures recorded in the cold, middle and hot zones of the reactor respectively.](image)

The decrease of the pressure can be explained by the CO$_2$ solubilization in the aqueous solution and/or by its consumption to precipitate carbonated minerals. A similar experiment performed with a limestone on the same device revealed that the solubilization of the CO$_2$ firstly governed the decrease of pressure, but a few hours after the injection the carbonate precipitation had to be taken into account (Jobard et al., 2013). This study also showed that the constant pressure had to be interpreted as a dynamical equilibrium since chemical gradients occurred between the warmed and the non-warmed zones implying mass transfers during all the experiment. These chemical gradients can be compared to a chemical pump. Each mole of CO$_2$ released by carbonate dissolution in the cold zone was counterbalanced by the precipitation of one mole of newly formed calcite. The same dynamic mechanism can be evoked in this experiment since the carbonate phase of the COX caprock seems to be the only one controlling the reactions involving CO$_2$.

In order to quantify the mass transfers during experiment, a mass balance was performed by weighing the initial and the aged samples after drying at room temperature during 24 hours (Figure 3).

![Figure 3: Results of the mass balance performed on initial and on aged samples dried for 24 hours at room temperature. The temperature corresponds to the mean value of each sample and shows the thermal gradient applied during the experiment.](image)

The mass balance revealed a mass loss for the samples from the non-warmed area during both the N$_2$ and CO$_2$ experiments. Nevertheless, the mass loss was more important for the samples aged with CO$_2$ (4% of mass loss against 2% for the N$_2$ experiment). The greatest mass loss was reached for the sample number 7 with a value close to 5% of the initial mass. Concerning the samples aged with N$_2$, the mass loss was generally of 1% except for the sample number 11 (in the coldest area) for which the value was close to 2%. The samples of the warmed zone presented a mass gain close to 0.5% for the samples aged with N$_2$ whereas...
it reached values up to 6% for the samples aged with CO₂. The mass balance study clearly revealed a mass transfer from the cold areas to the warmed zones. This mass transfer was clearly enhanced with CO₂.

From a petrographical point of view, the most important effect of the thermal gradient was highlighted from the study of the warmed samples. The observation of the samples at the macroscopic scale showed the disaggregation of the grains from the warmed zone (Figure 4b) whereas both the mass balance and the SEM observations (Figure 5) showed an important carbonate precipitation. The mechanical cohesion of the sample seemed to be controlled here by the clayey fraction which was affected by the highest temperatures when CO₂ was present. On the contrary, carbonate dissolution didn’t seem to affect the caprock in the coldest zones.

![Figure 4](image1.png)

**Figure 4:** Observation at the macroscopic scale of samples from the cold area (sample 10, a) and from the warmed area (sample 4, b) after ageing with CO₂.

![Figure 5](image2.png)

**Figure 5:** SEM picture (SE mode) of the sample 4 (warmed area) from the experiment performed with CO₂ and showing a newly formed aggregate of carbonate crystals.

ICP-MS analyses were performed on rock samples from cold and warmed areas in order to follow the behavior of trace elements during the experiment. Both samples from N₂ and CO₂ experiments were analyzed (Figure 6). For both experiments, most of the elements from the cold samples had a concentration close to that of the pristine rock. Cu seemed to be enriched in samples from N₂ and CO₂ experiments whereas Sr and Co are systematically impoverished. Concerning the warmed area, Sr showed a strong enrichment for the CO₂ experiment which could be related to the carbonate precipitation. This is also the case for Co, Ni, Cu, Zn and Cd even if the bearing phases were not clearly identified. This enrichment could be up to 60% superior than the initial value for the sample aged with CO₂. For most of the trace elements and especially Rare Earth Elements, an impoverishment was observed for the samples in the warmed areas with a more pronounced effect for the CO₂ experiment. If considering that carbonate minerals are stable in the hot zone, the release of such potential toxic elements could be attributed to the clay minerals. Two mechanisms could be evoked: the dissolution of clay minerals and/or mechanisms of ionic exchange of interfoliar cations.

Whatever the mechanism involved and the possible nature of the metal bearing phases, this study suggests that the mobilization of potential toxic elements has to be taken into account when the caprock undergoes the combined action of both CO₂ and a thermal gradient.
4. CONCLUSION
This work has described the impact of a thermal gradient on a clayey caprock within the framework of the geological storage of CO₂, both supercritical and combined with geothermal heat recovery. The innovative COTAGES experimental simulation limestone showed that the thermal gradient caused by the injection of a cold CO₂ or CO₂ rich brine in a hot reservoir could enhance the mass transfers from the cold to the hot areas. These mass transfers in the COX argillite were confirmed by mass balance calculation and petrographical evidence. The samples from the warmed area showed a loss of mechanical cohesion despite the precipitation of secondary calcium carbonate. The analyses of trace elements showed that some potential toxic elements have migrated during experiment. The transport of such trace elements was enhanced in the CO₂ experiment and should be submitted to further investigations, in particular concerning the metal bearing phases.

5. ACKNOWLEDGMENTS
This study was financially supported by the French agency ANR (ANR-08-PC02-006)

REFERENCES


