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CO₂ storage from blast furnace in the Triassic sandstones of Lorraine, (Eastern Paris Basin, France): an experimental study

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Abstract

A core flow test autoclave has been designed in order to reproduce an injection well at a scale of 1/20. This autoclave allows the CO₂ injection into a steel tube cemented to a core sample of red sandstone from the Triassic formations of Lorraine (France). Temperature and pressure gradients can be recorded between the injection point and the confining water phase. Such gradients imply solubility gradients of CO₂ and mineral species into the water phase as permeability changes with time. Some chemical reactions can be observed from collected sample at the end of the experiment. Precipitation and dissolution are suspected both into the cement and rock phases. No fracturing is observed. Cement-rock interface is not opened.

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1. Introduction

ArcelorMittal, through the ULCOS-BF program, is involved in a research program about the feasibility of geological sequestration of the CO₂ produced in a blast furnace. This project, first CCS demonstrator devoted to Steel primary production, aims at storing CO₂ from new generation TGR (Top Gas Recycling) blast furnace in open dipping saline aquifer at supercritical conditions. Sandstones and Limestones are the most common potential reservoir rocks for carbon sequestration projects. The Lorraine lower and middle Buntsandstein sandstones formation constitutes a good candidate for carbon dioxide sequestration in terms of capacity, injectivity and trap efficiency. It outcrops in the Vosges massif and dips westward in the Paris Basin. This formation reaches depths higher than 800 meters allowing CO₂ storage at supercritical conditions. Lower and middle Buntsandstein sandstones are constituted (from the bottom to the top) by the “Grès Vosgiens” formation, the “Conglomérat Principal” formation, the

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“Couches Intermédiaires” formation and the “Grès à Voltzia” formation. The “Grès Vosgiens” formation may offer the best capacity of storage. These rocks have good petrophysic properties (porosity, permeability) and are mainly made of quartz, which is a mineral highly resistant to mechanical and chemical stresses induced by CO₂ injection. Because CO₂ injection causes an acidification of porous water, it may induce mineral dissolutions and precipitations together with mechanical/hydrodynamic stress due to CO₂ flow and pressure increase in the reservoir. However, other common minerals in sandstones, like aluminosilicates, micas and clays, can be supposed to be more sensitive to the mechanical and/or chemical impact of supercritical CO₂ [1], [2], [3], [4], [5], [6]. Water chemistry of target formations for storage is poorly known. However, porous water of targeted reservoir rocks display a wide range of salinities from values of 1g NaCl/l to 250g NaCl/l. More targeted studies have investigated reactivity of iron bearing minerals in redbeds and have concluded that red sandstones did not show any change in iron mineralogy during flow-through experiment [7]. Reactivity of red sandstones was only observed for hematite [8] and ferrihydrite [9] in the presence of aqueous sulfides. The well cement can also be considered as a reactive component in the system. Indeed, it is important to understand how CO₂ may escape via active or abandoned wells, especially at the interface between the well cement and the geologic formation, which would constitute the first potential pathway for CO₂ leakage. Although numerous papers were addressed to study geochemical reactivity of cement in presence of CO₂ or carbonated brine [10], [11], a few studies were focused on composites cement-reservoir rock reactivity to investigate cement/reservoir behavior in presence of CO₂. To guarantee operation success, it is essential to anticipate well-cement and reservoir behavior in presence of supercritical CO₂ flow and its consequences on well integrity and reservoir injectivity. Although numerous papers were addressed to study geochemical impact of CO₂ exposure on each component separately, accurate prediction of carbon dioxide injection impact must consider co-interactions between each component and injected gas. The aim of this study is to experimentally assess the supercritical CO₂ flow mechanical and geochemical impact on a complex system constituted by the well cement, the reservoir rock and interacting porous water. For that, a new experiment concept has been developed to mimic an injection well at the reduced scale of around 1/20.

2. Experimental procedure

2.1. A new design to simulate CO₂ injection in a reservoir at bottom hole conditions: The MIRAGES core-flow experiment.

The core-flow test autoclave MIRAGES (Radial Model for Greenhouse Gas Injection) was designed to reproduce accurately supercritical CO₂ injection in aquifer under bottom hole conditions of temperature and pressure. The experiment consisted in injecting supercritical CO₂ through a core plug immersed in water (fig.1, 7) during fifty days under reservoir thermodynamic conditions of 60°C and 100 bar pressure reached in a 2l volume autoclave composed of stainless steel (316L-X2CrNiMo17-12-2) (fig.1, 31). Distilled water was used rather than brine to create more severe conditions because CO₂ is more soluble in water than in brine [12], and because it avoids corrosion of the experimental device. Same water composition was chosen in the studies carried out by [10] and [11]. Volume of water used during the experiment was 1.3l. Several studies have buffered reactive mixture pH at 2.5 or 5 to be in accordance to down hole chemical conditions in case of CO₂ injection. This choice was not retained in our case. To simulate injection in the near-well zone, a stainless steel tube (length = 136.5 mm, internal diameter = 4.5 mm, external diameter = 6.3 mm) (fig. 1, 5) was screwed to a Teflon ring (diameter = 28 mm, thickness = 2 mm) (fig. 1, 4) and cemented to the core plug (fig. 1, 2). Confinement pressure in the autoclave was regulated using a clipping valve (Fig.1, 29) and temperature in the autoclave was reached thanks to a

ceramic heater band (fig. 1, 27). The autoclave was equipped with electronic sensor for pressure and temperature linked to a pressure and temperature recording station (fig. 1, 26). Such equipment allowed measuring temperature and pressure in the confining zone (fig. 1, 8-14) and in the part of the core plug where CO₂ was injected called injection zone (fig 1, 30-15). Injection was performed at constant mass rate of 200 g/h for an injection pressure of 100 bar using an ISCO type pump (fig. 1, 21). This pump, linked to a CO₂ tank (fig. 1, 22), allows injection pressure from 0 to 200 bar. Injected CO₂ flow was controlled by a computer assisted mass flowmeter linked (Fig1, 18) to a needle valve (fig. 1, 17). This device (fig. 1, 23) allowed recording injection flow data in time. Liquid samplings, using a sampling valve (fig. 1, 20) were performed regularly during experiment to measure pH of the water from the reaction mixture. pH was measured at atmospheric pressure after sampling using a Metler Toledo pH probe. A pneumatic pump (fig. 1, 28) allowed to re-inject the equivalent mass of sampled water in the reaction mixture to maintain the core sample fully saturated by water.

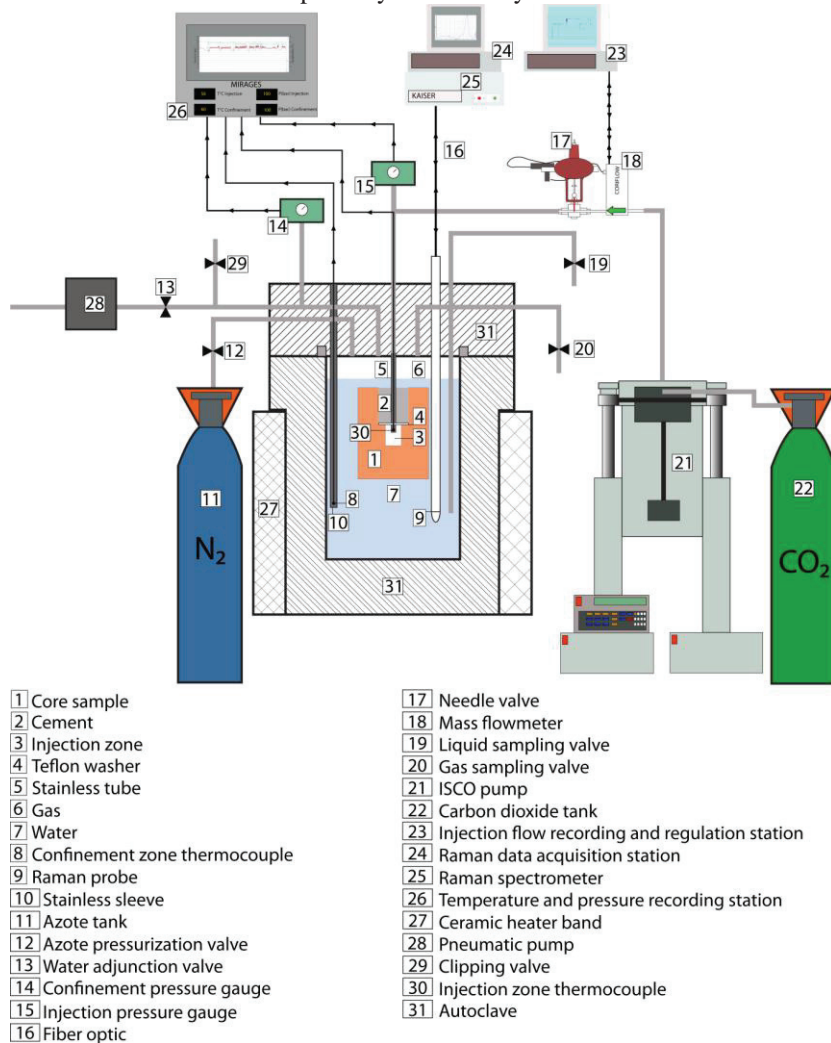


Fig. 1: Schematic diagram of MIRAGES core-flow experiment.

2.2. Materials

The reduced model of injection well is constituted by a core plug drilled in the center for the introduction of a stainless steel tube for CO₂ injection, sealed to the core plug by adding of well cement (fig. 2). A Teflon ring allows avoiding cement seepage down to the hole. The cement height is 30 mm, the cavity of injection below the Teflon ring is a cylinder of 15 mm height and 10 mm diameter. A first temperature probe is inserted inside the injection “well” whereas a second one is placed into the confining water phase.

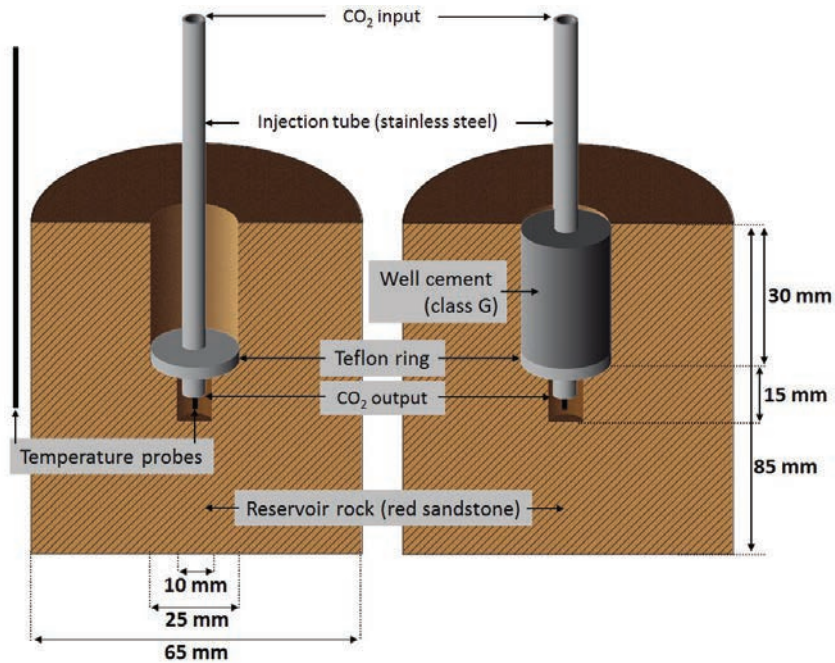


Fig. 2: The equipped core plug before (left) and after (right) cement filling.

The core plug (65 mm diameter, 85 mm height) was sampled in a drilling at 650 m depth in the “Grès Vosgiens” Triassic Buntsandstein sandstones formation, 50 km to the East of the expected injection well, possible target for CO₂ storage. Before experiment, petrographic observations were collected from thin sections in which a detailed point counting was performed to get relative proportions of minerals in the rock. Reservoir rock contains monocristalline (26,9 %) and polycristalline quartz (23,6 %), quartz overgrowths (0,5 %), potash feldspars (11,7 %), lithic elements (11,5 %), traces of iron oxides (0,2 %), iron carbonates and sulphides and a significant amount of authigenic clays represented as illite associated to microcrystalline iron oxides (6,2 %), kaolinite (2,8 %) and interlayered illite/smectite. The porosity determined by this method was estimated to 15%. The sandstone used in this experiment is reddish in color with hematite and siderite as most abundant iron-bearing minerals. Iron oxides occurs as detrital, automorph and microcrystalline crystals associated to authigenic illite coating. Siderite occurs as altered patchy cements associated to microcrystalline hematite. The mass of rock used during experiment was 568.7 g.

The cement was obtained by curing slurry at atmospheric pressure and room temperature of 20°C during 24h. The slurry was composed of Portland cement, silica flour (35% by weight of cement) and

water (water-to-cement ratio = 0.55). The Portland cement is of class G, type high sulfate resistant, defined on API specification 10, similar to the ISO 10426-1 specification, and similar to the ASTM II type [13], [14]. The same type of cement and W/C was used in the study carried out by [15]. Used cement during experiment contained mainly calcium and silicium and potassium, sodium, titanium and phosphorous in a minor part. The mass of cement used for experiment was 48.97g. The colour of unreacted cement was grey. XRD analysis carried out on unreacted cement detected intense reflections of Portlandite which constituted the main crystalline phase. Before CO₂ injection, a phase of curing was carried out: in a first time, the cement was cured at atmospheric pressure and 21°C in a vessel during 24 hours. Then, the sandstone cemented to the stainless tube remained immersed in water for around 12 days in the autoclave, under 100 bar of N₂ and 60°C to equilibrate water with cement and to saturate rock with water.

3. Results

Temperature was recorded into the well and into the confining water phase all along the experiment each 30 seconds. Fig. 3 shows the evolution of confining temperature in blue. The temperature remains constant at 60°C because it is fixed by the oven temperature. The injection temperature (red curve in fig. 3) is equal to the confining temperature during the curing of cement under 100 bar of N₂. As soon as the CO₂ is injected, the injection temperature strongly decreases (the CO₂ tank is maintained at the room temperature). Then a slow decrease is observed during one week probably explained by a water sweeping effect. Injection temperature stabilizes during the rest of the experiment around a mean value of 52°C. Periods of increase of injection temperatures are correlated to stops of the injection pump. The green curve of fig.3 shows the evolution of the ΔT between confining and injection temperatures. It reaches 8°C after one week of CO₂ injection.

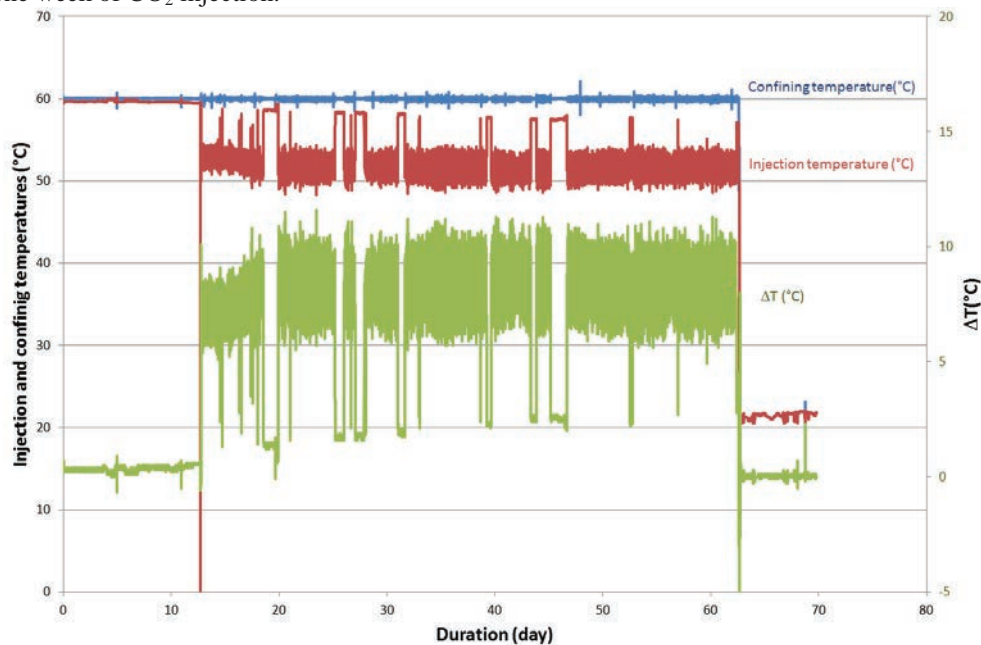


Fig. 3: Evolution of confining and injection temperatures into the MIRAGES core flow test autoclave with time. CO₂ injection started day 12 and autoclave was opened day 62.

The evolution of pressures is presented fig. 4. The injection pressure, in red, is centered around 100 bar. Variations are due to dissolution of N_2 into water and re-injection of N_2 to compensate the decrease of pressure during the curing period till day 12. During CO_2 injection period, pressure variations are produced by the exhaust valve. This valve insures the confining pressure does not increase above 120 bar. The confining pressure variations follow those of the injection pressure. The ΔP , in green in fig. 4, equals 0.2 to 0.3 bar during the cure and the first 20 days of CO_2 injection. After, ΔP increases with a change of rate in the last 15 days. Such behavior indicates a change in petrophysical properties of the sample. Permeability decreases by chemical reaction (dissolution and precipitation) or by reorganization of porosity by displacement of fine particles. These changes can be of local or general extension through the sample.

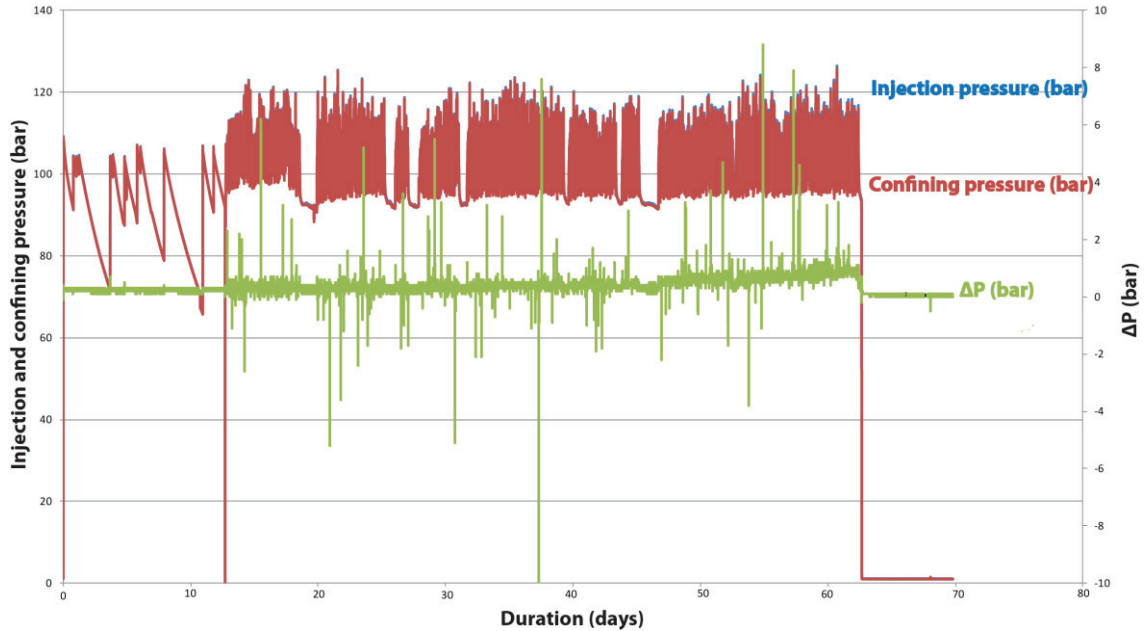


Fig. 4: Evolution of confining and injection pressures into the MIRAGES core flow test autoclave with time. CO_2 injection started day 12 and autoclave was opened day 62.

A first observation of sandstone before and after experiment did not highlight a significant change in the color of reservoir rock. Indeed, sandstone had the same reddish color before and after experiment. However, careful observation shows some crystallization into the sandstone porosity near the injection point. Cement before experiment displayed a grey color. After 50 days of supercritical CO_2 injection, an orange color is observed on the top of sample, which strongly differed from the greyish inner part of cement. Study of transverse view of sawed core plug after experiment, highlighted a continuous yellowish fringe in cement. Those fringes, considered as the reacted part of cement, are both developed in cement which was directly in contact with water in the reaction mixture and at cement/sandstone interface. However, this fringe did not display a homogeneous thickness within cement. No open space is observed at the boundary between rock and cement.

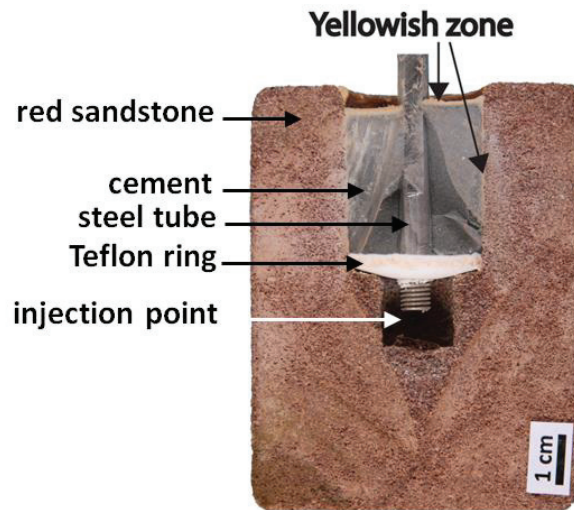


Fig: 5: Photography of a transverse view of sawed core sample after experiment.

4. Conclusions

The new core test flow device has shown its ability to reproduce an injection well at a reduced scale of around 1/20. The equipment mimics an injection process controlling the rate of injected CO₂, the temperature and pressure into the injection tube as into the confining water phase. An experiment onto a sandstone core sample from Triassic formation of Lorraine (France) equipped with cemented injection steel tube has shown:

- Important temperature variation between the injection point and the confining water phase. Such gradient implies, by consequence, solubility gradients of CO₂ and mineral species into water. This chemical gradient is of great importance on the modification of the petrophysical properties of reservoir rocks in the neighborhood of the injection point,
- Some ΔP evolutions between confining and injection pressures are probably due to petrophysical change of the sample. Dissolution and precipitation, reorganization of fine particles can be suspected to have affected the permeability of the rock.
- Observations of sample petrography show intense recrystallization into the cement phase. Some dissolution and precipitation of minerals are suspected into the rock.
- Such device allows us to follow the behavior of cement-rock interfaces. It is proved that the injection of CO₂ has not created drains along the rock-cement interface during 50 days of experiment.
- No fracturing is observed into the rock as the cement phase.

Careful sample characterization is in progress and should give us new quantitative arguments to precisely describe the effect of CO₂ injection in a red sandstones aquifer.

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