GHGT-9

Experimental and modeling study of geochemical reactivity between clayey caprocks and CO_2 in geological storage conditions

Anthony Credoz[1], Olivier Bildstein, Michel Jullien, Joël Raynal, Jean-Claude Pétronin, Michel Lillo, Claudine Pozo, Guy Geniaut

Laboratory for Modeling of Transfers in the Environment, CEA Cadarache, 13108 Saint Paul-lez-Durance, France

Abstract

The capture and geological CO_2 storage (CCGS) in deep aquifers, depleted oil and gas fields and coal seams appears to be one of the main solutions to reduce greenhouse gases release to the atmosphere (IPCC, 2005). The geochemical reactivity between the mixed fluids (supercritical CO_2 and brine) and the clayey caprock formations under physicochemical conditions of geological storage remain largely under-investigated. The caprock is characterized by inherent properties notably supported by a high clayey content such as low reactivity, low permeability and high elasticity/plasticity. This study presents experimental and modeling results regarding the geochemical reactivity of two caprock samples under CO_2 storage conditions: a rock sample from the Chinle formation in Moab (Utah – USA) and a sample from the Comblanchien formation in Charmotte (Paris Basin – France). Experiments were conducted in pressurized cells where fluids (CO_2 and brine) are maintained at constant temperature (80 to 150°C) and pressure (1 to 150 bar). The duration of the experiments ranged from 30 to 360 days. The brine was synthesized as a representative solution of a saline aquifer. In the experiments, carbonate minerals (dolomite, calcite) dissolve partially or totally in the short term. In the long-term experiments, a new form of complex carbonate precipitates. To evaluate clay minerals reactivity, the same series of experiments were performed with a purified mixed-layer illite/smectite mineral (I/S), illite and smectite. The I/S reveals a clear stability towards CO_2 whereas illite and smectite tend to be destabilized in the long-term. Kaolinite is the most reactive clay mineral as it dissolves totally in the long-term experiments. To predict and compare the geochemical reaction pathways, reactive transport modeling was performed focusing on the behavior of the cap-rock at the timescale of the experiments (30 to 365 days). Calculations were also extended to duration up to 10,000 years which is the relevant timescale for the long term safety assessment of CO_2 storage.

© 2009 Elsevier Ltd. Open access under CC BY-NC-ND license.

Keywords: Carbon dioxide; geological storage; cap-rock; clay minerals; carbonates

1. Introduction

The capture and geological CO2 storage (CCGS) in deep aquifers, depleted oil and gas fields and coal seams appears to be one of the main solutions to reduce the industrial CO_2 emissions to the atmosphere. In a special report

---

[1] Corresponding author. Tel.: +33-442-253-724; fax: +33-442-256-272.
E-mail address: anthony.credoz@cea.fr.

on CCGS, , the expert of the International Panel on Climate Change detailed the concept of geological CO_2 storage defining the cap-rock as a rock of very low permeability that acts as an upper seal to prevent fluid flow out of a reservoir (IPCC, 2005). A caprock is considered as an impermeable layer of shale or clayey rock overlying the selected reservoir. The first phenomena occurring at the caprock interface is the CO_2 physical trapping forcing a lateral migration of the fluid beneath the sealing layer. Clay minerals are the main components of the caprock with a minimum mass fraction of about 40% (Kaszuba et al., 2003; Kaszuba et al., 2005; Gaus et al., 2005; Kohler et al., 2006; Gherardi et al., 2007). Variable proportions of quartz and carbonated minerals (among other accessory minerals) can also be found depending on the geological context of the storage site : limestone or silicoclastic context which may be crucial to understand the hydrogeochemical phenomenology in the short, medium and long-term reactivity. The geochemical alteration occurring along the reservoir-caprock interface with mixed CO_2 fluids and brine may lead to potential pathways for CO_2 leakage through the sealing layer. The injection takes place at depths below 800 m excluding the injection in coal beds (IPCC, 2005). At these depths, CO_2 reaches a supercritical state ($CO_{2(SC)}$) since the temperature and pressure exceed the critical point (37°C, 73 bars) and becomes partially immiscible in aqueous solution (Takenouchi and Kennedy, 1964). After the injection, CO_2 is driven by buoyancy forces which lead to an upward migration through the porous medium of the reservoir until it reaches the caprock. Although the first mechanism implied by the clayey caprock is the physical or structural trapping due the low permeability of the sealing layer, the most effective trapping on the longer timescale is the solubility and mineral trapping, when dissolved CO_2 is combined with a cation to form carbonate minerals such as calcite, dolomite, siderite and dawsonite (Kaszuba et al., 2003, 2005; IPCC, 2005; Gaus et a., 2005; Gherardi et al., 2007). In order to identify the different reactive pathways in the caprock components in storage conditions and to assess the performance and safety of the storage in various scales in time and space, a large panel of preliminary experimental and modeling studies needs to be performed. In the present paper, we identify the main geochemical phenomena (dissolution, precipitation) which may occur in the $CO_{2(SC)}$ – brine – caprock system focusing on clay and carbonated minerals reactivity, looking in particular at two cap-rock samples from a limestone context and from a sandstone context. The granulometry and solution to solid ratios in the experiments take much higher values than in the real geological system in order to accelerate the dissolution/precipitation processes and to anticipate the phenomenology that could take place in the long-term period at the basin scale. We simulate the behavior of each experiment at the laboratory duration and extrapolate the reaction path for a 10,000-year period of time which is required in a global safety assessment of the CO_2 injection site (Bildstein and al., *this issue*).

2. Material and methods

2.1. Experimental approach

Two cap-rock samples were considered to evaluate the reactivity with CO_2 in two different geological contexts limestone and sandstone. Two types of experiments were performed to assess the potential reactivity of the clayey caprocks (1) close to the supercritical CO_2 plume, with brine and supercritical CO_2, and (2) further away from the plume, with brine and dissolved CO_2. The experiments were performed at 80°C (a representative temperature for deep storage conditions), and at 150°C in order to accelerate the reaction kinetics of clay minerals and assess geochemical evolution in the long-term. Two partial pressure of CO_2 (pCO_2) were used, 1 bar to 150 bar, corresponding to the two types of CO_2 experimental conditions (dissolved CO_2 and supercritical CO_2). To provide a basis of understanding for the effect of the two fluids in the experiment, separate reference experiments with brine only were also performed at 80°C and 150°C for 90 days. A special attention was given to clay minerals reactivity only interacting with supercritical CO_2 and supercritical CO_2 and brine, since these materials are considered as important components for reactivity control and caprock stability. The conditions and parameters for the experiments are reported in Table 1. At the end of the experiments, both the solids and the brine were analyzed.

2.2. Experimental devices

Two types of experimental apparatus were considered. The supercritical carbon dioxide-brine-rock experiments were conducted in a hydrothermal devices consisting of a Teflon cell contained within a 100 cm³ steel pressure autoclave (batch system). This equipment allows external control and monitoring of temperature and pressure, with

a maximal pressure of 180 bar and maximal temperature of 250°C. The set of experiments were performed with pCO_2 = 150 bar and temperatures of 80 °C and 150°C. In these conditions, carbon dioxide in the reaction cell is a supercritical fluid that is largely immiscible, but still partly soluble in brine (Takenouchi and Kennedy, 1964; Kaszuba et al., 2003; 2005). The crushed rock samples and solution were placed into the cell and reactied during various experimental durations: 30, 45, and 90 days, After reaction, the solutions and the solids were collected to be analyzed after 1 day of cooling and 6 hours of CO_2 purge.

The dissolved carbon dioxide-brine-rock experiments and the brine-rock experiments were conducted in smaller Teflon reaction cells contained in 50 cm³ steel reactors at 80°C and 150°C during 90 and 365 days. After reaction, the cells were cooled during 1 day before opening.

2.3. Materials

Two caprock series were considered for this study. In order to assess the reactivity in a sandstone context, a clayey caprock from the Chinle formation (Utah – USA) was selected. This reservoir-caprock system is a potential natural analog of geological CO_2 storage in the Colorado Plateau (Blanchet et al. 2008). The Triassic argillaceous formation of Chinle (250 million-year) was exposed to volcanic events and associated gas circulations 55 millions years ago. The sample (Colo) was collected from an outcrop close to Moab in 2006 during a campaign aiming at identifying preferential pathway of CO_2 leakage in the reservoir and the caprock at the long-term scale. It was sampled in a zone of the formation which a priori was not exposed to CO_2-rich fluids. In mass fraction, this sample is approximately composed of 40% mixed-layer illite/smectite (I/S), 40% quartz, 10% calcite A, 7% hematite and 3% calcite B (with a composition close to dolomite).

In a second step, to identify the geochemical phenomena of reactivity in a limestone system, a clayey limestone from Comblanchien reservoir/caprock transition area in Charmotte (Paris Basin - France) was chosen. This system is representative of a potential pilot project for CO_2 injection in a depleted oil field. The sample (Cha) was collected during a drilling campaign in the Charmotte oil field at ca. 1980m depth. The mineralogical composition (in mass fraction at +/- 10%) was determined by crossing XRD, STA and SEM-EDS analysis methods: 45% calcite, 15% mixed-layer illite/smectite, 10% kaolinite, 10% quartz, 5% gypsum, 5% pyrite and 5% other components (anatase, organic matter). The cap-rock samples were crushed and reduced to a fraction < 500 µm in order to maximize the reactive surface area and accelerate dissolution processes.

In addition to caprock sample, three types of purified clay minerals extracted from these rocks were also studied. First, a sample of the purified mixed-layer illite/smectite (80-90% illite / 10-20% smectite) extracted from Chinle material was selected (Cp). IThis caly material is representative of the major clay fraction found in the Chinle and Charmotte formations. Another sample of smectite and mixed-layer illite/smectite (Fp) coming from the reference area of Forez (France) and a sample of illite (Ip) from the reference area of Le Puy en Velay (France) were studied as they represent ubiquitous minerals found as a fraction of the I/S or as free clay components in some caprock.

The reference for the aqueous solution (V2) is the composition of the Dogger reservoir brine in the Paris Basin (Azaroual et al. 1997 – GLCIV2). The brine was synthesized using standard laboratory grade salts. It is essentially a Na-Cl dominated aqueous solution. The ionic strength of the brine is 0.25M and the pH of 6.3 was adjusted with 5 mL 0.1M HCl in 1 L of V2 solution. The V2 solution was not in initial equilibrium with the rock samples which implies some geochemical reactivity attributable only to the brine, not to reactions with CO_2. Although the interpretation of the results is more complicated, this initial non-equilibrium was also a way to investigate the interactions involved when a complex reservoir brine enters into the caprock. To perform the experiments with dissolved CO_2, $CO_{2(g)}$ bubbling was performed into V2 brine during 2 hours to reach a pH of 4.8. The V2 and V2-$CO_{2(aq)}$ chemical compositions are reported in Table 1. For the supercritical CO_2 brine-rock experiments were performed in the Teflon cell contained in the 100 cm³ steel autoclaves apparatus preliminary loaded with 1.25 g of solid sample powder (caprock or purified clay mineral) and 25 g of brine solution. After 5 min. of circulation of argon gas at 25°C to provide degassed conditions inside the cell, approximately 25 g of carbon dioxide was injected into the autoclave. This procedure resulted in an initial brine to rock mass ratio of 20:1 and the approximated initial brine to carbon dioxide mass ratio was ca. 1:1. For the experiments with CO2(aq) and brine only, the same rock mass ratio 20:1 was used. For all the experiments, it was not possible to control the redox state during or after reaction.

2.4. Analytical methods

After opening of the autoclaves and reactors, the suspension was centrifuged 5 min at 7000 r/min to separate the solid fraction. The brine was filtrated through a 0.45 μm Teflon membrane. To prevent precipitation, the aliquot was conserved at 5°C and acidified with nitric acid (pH 2). Dissolved Si, Ca, Na, Mg, K, Fe, Al were determined using an induced couple plasma coupled with an atomic electron spectroscopy (ICP-AES). Analytical results and uncertainties are reported in Table 1. The solid fractions were analyzed using simultaneous thermal analyzer (STA), X-ray diffraction (XRD), optical microscope and scanning electron microscope (SEM). Secondary and backscattered electron signals and qualitative X-ray analysis using Energy Dispersive Spectrometry (EDS) were used in SEM analysis.

Table 1: List of experiments and water chemistry (mmol/L)

Experiment reference	T(°C)	pCO2(bars)	Time (d)	pH (a)	Ca	Si	Mg	Al	Fe	Na	K
Initial brine											
V2	25	atm	-	6,3	22,22	0,82	9,40	0,00	0,00	205,20	5,02
V2 + CO2(aq)	25	1	-	4,8	23,58	1,13	9,92	0,00	0,00	211,44	5,30
Rock + brine experiments											
ColoV280C90	80	atm	90	7,76	23,95	0,25	7,96	0,00	0,00	194,87	6,87
ColoV2150C90	150	atm	90	8,59	41,92	1,31	0,02	0,00	0,00	276,21	10,05
ChaV280C90	80	atm	90	7,11	30,44	0,26	0,01	0,00	0,00	196,39	4,99
ChaV2150C90	150	atm	90	7,26	38,17	1,45	0,09	0,00	0,00	242,28	5,54
Rock-CO2(aq) brine experiments											
ColoV2CO280C90	80	1	90	7,4	25,95	0,53	9,88	0,01	0,00	198,35	6,49
ColoV2CO2150C90	150	1	90	7,23	34,43	1,81	0,17	0,00	0,00	217,49	8,99
ColoV2CO2150C365	150	1	365	7,58	-	-	-	-	-	-	-
ChaV2CO280C90	80	1	90	7,22	33,68	0,15	0,01	0,00	0,00	221,40	5,28
ChaV2CO2150C90	150	1	90	7,09	37,67	1,36	0,13	0,00	0,00	228,80	6,32
ChaV2CO2150C365	150	1	365	7,53	-	-	-	-	-	-	-
Rock-CO2(SC) experiments											
ColoCO2SC80C150B30	80	150	30	-	-	-	-	-	-	-	-
ChaCO2SC80C150B30	80	150	30	-	-	-	-	-	-	-	-
Rock-CO2(SC) brine experiments											
ColoV2CO2SC80C150B30	80	150	30	-	33,81	0,88	13,42	0,00	0,00	245,15	7,85
ColoV2CO2SC150C150B30	150	150	30	-	37,12	1,01	11,13	0,00	0,30	244,24	7,17
ChaV2CO2SC80C150B30	80	150	30	-	49,90	0,96	15,35	0,00	0,45	301,70	8,03
ChaV2CO2SC80C150B90	80	150	90	-	52,89	0,81	10,51	0,00	0,00	218,36	6,02
Clay-CO2(SC) experiments											
CpCO2SC150C150B45	150	150	45	-	-	-	-	-	-	-	-
FpCO2SC150C150B45	150	150	45	-	-	-	-	-	-	-	-
IpCO2SC150C150B45	150	150	45	-	-	-	-	-	-	-	-
Clay-CO2(SC) brine experiments											
CpV2CO2SC80C150B45	80	150	45	6,38	26,26	0,86	11,29	0,00	0,00	47,89	3,62
CpV2CO2SC150C150B45	150	150	45	6,58	-	-	-	-	-	-	-
FpV2CO2SC80C150B45	80	150	45	5,26	27,86	1,41	9,91	0,00	0,00	47,67	3,87
FpV2CO2SC150C150B45	150	150	45	5,65	-	-	-	-	-	-	-
IpV2CO2SC80C150B45	80	150	45	5,06	27,02	1,65	13,27	0,00	0,01	57,53	4,72
IpV2CO2SC150C150B45	150	150	45	5,57	-	-	-	-	-	-	-
Maximum 2σ uncertainty (b)				3%	2%	2%	2%	30%	30%	3%	2%

[a] pH reported in this table is the stabilized value at standard temperature (25°C) and after partial degassing

[b] Maximum 2σ uncertainty is the analytical uncertainty

2.5. Modeling tools

The coupled reaction-transport code Crunch (Steefel, 2001) was used to calculate the dissolution rate of the minerals from each caprock and to identify the main geochemical phenomena. The code uses a kinetic formulation for all mineral dissolution and precipitation reactions. The generic formulation of the kinetic law is based on the theory of the transition state law which was developed by Aagaard and Helgeson (1982) and Lasaga (1981, 1984). Data for the equilibrium calculations in the aqueous phase are taken from the EQ3/EQ6 database (Wolery, 1992). Kinetics data for each are taken from the compilation of Palandri and Kharaka (2004). The experimental

composition of the Colorado and Charmotte capro ck, and the V2 solution we re introduced in the model. I/S were modeled as an assemblage of illite and Ca-montmorillonite. To take into account the substitutions in the calcite B mineral from the Colorado sample and in the Fe-dolomite from the Charmotte sample, dolomite and disordered dolomite were used respe ctively. The simulations were performed for each material: the "rock -brine experiment", the "rock-$CO_{2(aq)}$ brine experiment" and the "rock-$CO_{2(SC)}$ brine" experiment at 80°C.
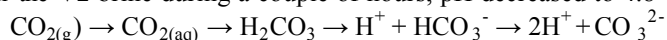
3. Results

3.1. Evolution of brine chemistry during reactions

Rock-brine experiments

  Initially, the pH value of the V2 brine was 6.3 and was not at equilibrium with the rock. After 90 days of rock-brine interactions, the pH reached a value of 7.76 and 8,59 (measurement at 25°C) for Colorado cap -rock experiments at 80°C and 150°C respect ively (representing an increase of 23% and 36%). For the Charmotte sample, the same phenomena occurred: the pH reached respectively 7.11 and 7.26, which represents an increase of 11% and 15%, for the experiments at 80 and 150°C .This adjustment of brine composition to rock evolution was very significant and led to various geochemical changes for the solid phases. Indeed, changes appeared for cations concentrations for the two rock-brine experiments. For the Colorado sample, after 90 -day exposure, Ca and K concentrations increas ed by 20-30% at 80°C to reach 100% at 150°C. Na concentration only increased at 150°C whereas Mg concentrations strongly decreased at this temperature (a 1000-fold decrease). Si concentration revealed a inverse behavior with respect to temperature: it decreases at 80°C and increases at 150°C. For the trace elements Al and Fe no significant changes were recorded. In the Charmotte rock case study, the similar t rends were recorded for all the major cations after 90-day of rock-brine experi ments. Ca concentrations increased significantly by 50% at 80°C and 90% at 150°C. Na and K concentrations only increased at 150°C. Mg concentrations again decreased strongly at 80 and 150°C. As it was observed in Colorado case study, Si concentrations reve aled distinct behaviors, decreasing at 80°C and increasing at 150°C. Trace cations Al and Fe concentrations remained stable.

Rock-$CO_{2(aq)}$ brine experiments

  After $CO_{2(g)}$ circulation in the V2 brine during a couple of hours, pH decreased to 4.8 according to :
$$CO_{2(g)} \rightarrow CO_{2(aq)} \rightarrow H_2CO_3 \rightarrow H^+ + HCO_3^- \rightarrow 2H^+ + CO_3^{2-}$$
  After 90 days of rock -$CO_{2(aq)}$ brine interactions, the pH of the solution reached 7,4 and 7,23 (measurement at 25°C) which represented an increase of 54% and 51% respectively for the Colorado caprock for the experiments at 80 and 150°C. For the Charmotte rock, the same phenomen on is observed: the pH reached respectively 7.22 and 7.09, which represented an increase of 50% and 48%, for the experiments at 80 and 150°C. The pH was buffered at a value of 4.8 which led to various geochemical changes for the solid phases and for the cation concentrations in solution in the two rock-brine experiments. The two cap -rock samples have a strong buffering capacity due to their mineral composition which will be discuss ed in the next sections . For the Colorado sample, after 90 -day of exposure, Ca and K concentrations increased at 80°C and at 150°C by 46% and 70% respectively. Na concentration remained stable at 80°C and 150°C whereas Mg concentrations decreased by a fact or of 50 at 150°C. Si concentration decreased at 80°C and increased at 150°C. For the trace elements Al and Fe no significant changes were observ ed. In the Charmotte rock case study, similar t rends were observed for all the major cations after 90 -day of rock-brine experiments. Ca concentrations increased significantly by 43% at 80°C and 60% at 150°C. K concentrations only increased at 150°C by 20%. Mg concentrations strongly decreased by a factor of 1000 at 80°C and by a factor of 100 at 150°C . Again, Si co ncentrations decreased at 80°C and increased at 150°C. Trace cations Al and Fe concentrations remained stable.

Rock-$CO_{2(SC)}$ brine experiments

  The rock -$CO_{2(SC)}$ brine experiments were performed in different conditions (temperature and duration) with the Colorado and the Charmotte samples. In-situ pH measurements were not available but can be inferred from data from Duan et al. (2003), knowing the solubility of CO2 in brine : for a solution ionic strength of 0.2, a pCO 2 of 150 bars, the CO2(aq) concentrations reaches 0.98 molal and 0.90 molal , respectively at 80°C and 150°C . The pH of the brine in equilibrium with $CO_{2(SC)}$ can be calculated with Crunch, giving a pH of 3,19 at 80°C and 3.52 at 150°C. In

the 30-day Colorado-CO$_{2(SC)}$ brine experiments, Ca, K and Mg concentrations increased by 52%, 56% and 43% at 80°C and by 67%, 43% and 18% at 150°C respectively. Na concentrations increased by 20% at 80°C and 150°C. Si concentrations remained steady at the two temperatures. For the Charmotte-CO$_{2(SC)}$ brine experiments at 80°C, Ca, K and Mg concentrations increased by 125%, 60% and 63% after 30 days and by 138%, 20% and 12% after 90 days respectively. Na concentrations increased by 44% after 30 days. Si concentrations remained stable after 30 and 90 days. The evolution of Fe concentrations in all the experiments were difficult to interpret. Some CO$_{2(SC)}$ experiments were conducted in anhydrous conditions. The results are presented in the next paragraph.

3.2. Evolution in mineral composition

Rock brine experiments

In the Colorado-brine and Charmotte-brine experiments, carbonate minerals presented superficial features of dissolution, especially for the Fe-dolomite from Charmotte, but the destabilization was not significant enough to be detected by XRD analysis. Gypsum (CaSO$_4$, H$_2$O) precipitated, but this phenomenon was interpreted as an artifact of experiment where sulfates from the solution combine with calcium during cooling and opening of the reactor. No significant changes were identified on clay minerals.

Rock-CO$_{2(aq)}$ brine experiments

In the Colorado cap-rock sample, two different calcite compositions, more or less substituted were identified using XRD analysis and STA. The first calcite (CaCO$_3$), referred to as calcite A, is close to a pure calcite with some Ca substitution by Fe or Mg. The second calcite, referred to as calcite B, shows approximately 20% of substitution. Generally speaking, the substitutions are thought to imply some weakness of the mineral crystalline network. However, after 365-day Colorado-CO$_{2(aq)}$ brine experiment at 150°C, the calcite A was totally dissolved whereas calcite B was not destabilized. The substituting cation (Fe, Mg) could be at the origin of the contradictory reactivity of substituted minerals. At the end of the reaction, a new form of mixed carbonated minerals also precipitated whose composition was not yet determined. XRD shows that the substituted phase probably integrates Ca, Fe and Mg ions in the mineralogical structure.

The dissolution of carbonated minerals allows acidic solution to be buffered from pH 4.8 to neutral pH. For the clay fraction, the evolution of the I/S phase was not clearly identified. The formation of halite was interpreted as an experimental artifact, i.e. precipitation of Na and Cl coming from the solution since the solid was not rinsed with deionized water before lyophilization. In the Charmotte cap-rock sample, two different carbonated minerals were identified, a pure calcite and a substituted Fe-dolomite (Fe-CaMg(CO$_3$)$_2$). After 365-day Charmotte-CO$_{2(aq)}$ brine experiment at 150°C, the calcite began to be destabilized whereas the initial Fe-dolomite was almost totally dissolved. This dissolution is in agreement with the assumption that the crystalline network of a substituted mineral is weaker than for a pure phase. Ca substitution by Fe ions (for Fe-dolomite and probably for Fe-calcite) could be at the origin of this carbonated crystalline network weakness. At the end of the reaction, a new form of mixed carbonated minerals precipitated whose composition was not yet determined (Figure 1).

Concerning clay minerals, the most relevant change is the smectitisation of the mixed-layer illite/smectite at 150°C. The destabilization of the I/S was especially focused on the smectite phase initially present, as inferred using XRD. The destabilization of the smectite phase and the dissolution of kaolinite provided elements in solution to form a new 15.5A smectite:

$$I/S + Kaolinite \rightarrow illitic\ I/S + Fe\text{-}Mg\text{-}Smectite$$
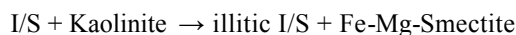
This new mineral was identified more precisely as a Mg-Fe-smectite using results from STA measurements, showing a thermal signal close to a saponite signal. Finally, the destabilization of pyrite (FeS$_2$) observed after 90-day Charmotte-CO2(aq) brine experiment were confirmed in 365-day experiment at 150°C as the pyrite was massively dissolved (as shown by XRD) and "pseudomorphization" of a new carbonated minerals at the expense of pyrite (FeS$_2$). This reaction was identified by the texture of the surface characterized by SEM and analyzed by EDS showing that S^{2-} ions are substituted by HCO$_3^-$.

Rock-CO$_{2(SC)}$ experiments

No effect of the supercritical carbon dioxide on the cap-rock samples from Colorado and Charmotte was observed clearly in the 30-day experiment. However, additional experiments performed in parallel on purified illite

from Le Puy and on I/S and free smectite from Forez, show that a dissolution of the illite fraction in small amounts after 45 days at 150°C . This result has to be confirmed in long term experiments.

Rock-CO$_{2(SC)}$ brine experiments

At 80°C and 150°C, Color ado-CO$_{2(SC)}$ brine experiments revealed a major reactivity of the calcite A which is massively dissolved after 30 days. For the Charmotte-CO$_{2(SC)}$ experiments, the Fe-dolomite was significantly dissolved at 80°C after 30 days and 90 days and the pyrite was destabilized. Concerning the clay fraction, the I/S remained stable but the kaolinite is partially dissolved after 90 days. The experiments performed with purified clay minerals revealed some evidence of different I/S evolution with the temperature: after 45 days, the relative illite fraction increased in the Forez I/S phase at 80°C due the decrease of smectite fraction in the mixed-layer. At 150°C, the Forez smectite dissolved and I/S remained stable.

3.3 Numerical simulations of the experiments wit h Crunch

In the simulation of the Colorado -brine experiment at 80°C, the pH increased from 6.22 to 7.54 after 90 and 365 days. The pH of the solution was buffered by calcite dissolution (-1%) after some hours which precipitated after 90 and 365 days (+0.5%). No significant precipitations of kaolinite and Na-montmorillonite o ccurred due to little destabilization of the initial Ca-montmorillonite and illite after a few days of reaction. It is thus diffi cult to interpret the mineralogical changes. The system remained stable in 1 -year simulations. For the Charmotte-brine simulation at 80°C, the pH increased from 6.22 to 7.35 after 90 days and 7.07 after 365 days. The disordered dolomite was dissolved (-20%) and the calcite dissolved initially and then precipitat ed (+2% at the end). Montmorillonite, illite and kaolinite, which are the most sensitive clay minerals , were a little bit destabilized. For the Colorado -CO2(aq) brine simulation at 80°C, the pH increased from 4.77 to 5.55. The acidification of the solution due to CO2 dissolution was buffered by calcite dissolution (-8%) after some days and remained stable until 365 days. Precipitation of kaolinite and of a small amount of montmorillonite -Na were also observed due the destabilization of Ca-montmorillonit e and illite (-0,1%). The same kind of reactivity was observed in Charmotte-CO$_{2(aq)}$ experiments with a pH increase from 4.77 to 5.53 , buffered by dolomite dissolution (-27%).Illite was also a little bit destabili zed. For the Colorado -CO$_{2(SC)}$ brine simulation at 80°C, the pH increased from 3.23 to 4.69 after 90 and 365 days. In Colorado-CO$_{2(aq)}$ brine simulation, calcite dissolution (8%) was simulated after some days and then remained stable after 90 and 365 days. The same evolution of the clay fraction reactivity were observed, in the some order of magnitude. In Charmotte -CO$_{2(SC)}$ brine simulations, the same conclusions were reached with a pH increase from 3,24 to 4,69 due to dolomite and calcite dissolution (-34% and -8% respectively) in a few days and for the one-year simulation.

5. Conclusions

Different physicochemical conditions were considered to assess the reactivity of caprock and transition area (reservoir/caprock) using samples from the sandstone and limestone geological contexts respectively. Two main mineralogical family, carbonates (calcite, dolomite in this study) and clay minerals (illite, smectite, I/S, kaolinite in this study), had been studied in details to describe caprock reactivity after interaction with mixed CO$_2$-brine fluids.The most import ant effect of CO$_2$ is the acidification of brine. The primary carbonate minerals are the most reactive minerals, with partial or total dissolution (depending on experimental conditions), providing an effective pH buffering in solution. Morever, it provides el ement (Fe, Mg) in solution for the formation of new minerals, i.e. mineral trapping, as carbonated aqueous species (HCO$_3^-$, CO$_3^{2-}$) are associated to cation also coming from silicates dissolution. Clay minerals are sensitive to acidic conditions but their association with carbonates prevents from a significant destabilization at least in the short -term which tends to confirm the persistence of the elasticity/plasticity,properties involved in the geomechanical integrity of the caprock. "Long term" 365 -day experiments were required to clearly identify the partial dissolution of kaolinite and a preferential destabilization of the smectite fraction the mixed -layer illite/smectite component in agreement with purified minerals experiments. A newly formed smectite was interpreted to be the result of an hydrothermal type of alteration, which is typically found in these conditions of temperature (150ºC) and brine composition.
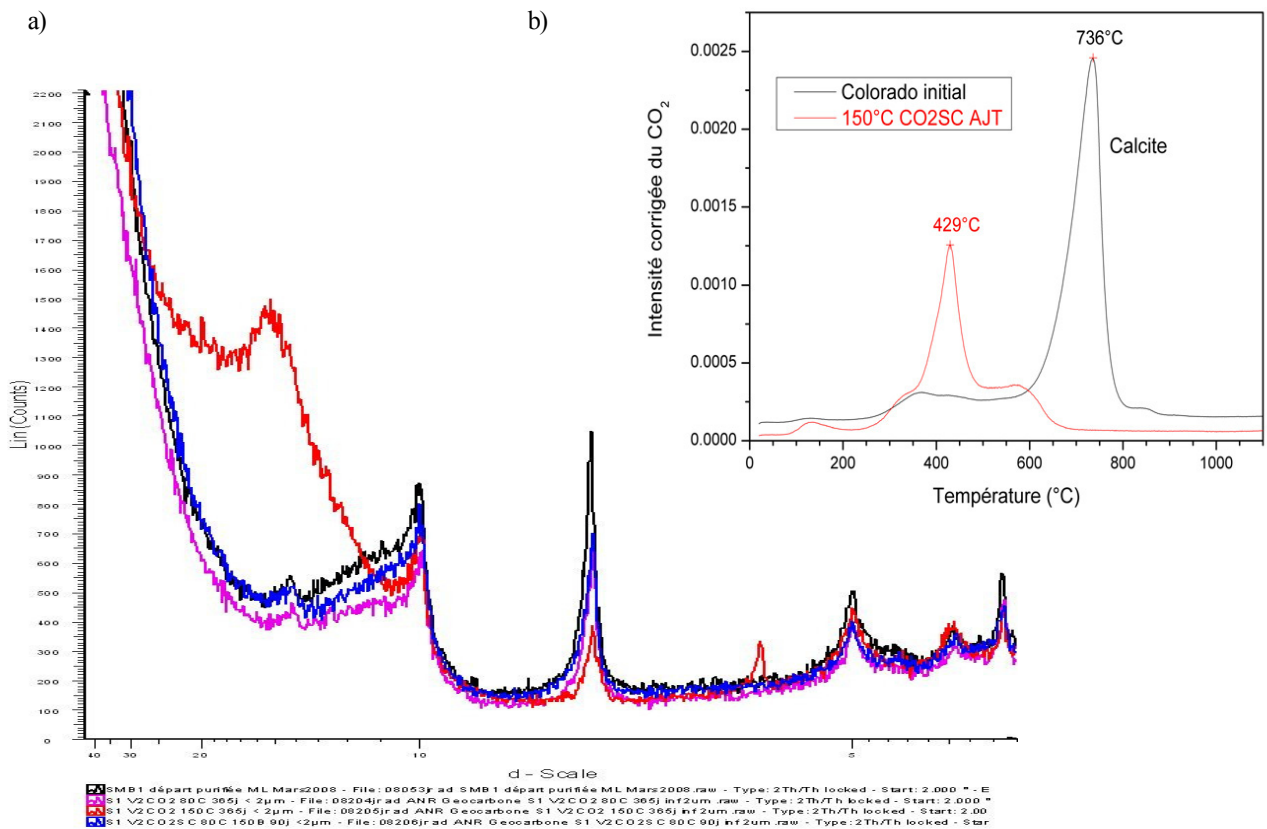
a)   b)

Figure 1. (a) Evidence for the formation of a mixed Mg-Fe-smectite on XRD diffraction (red curve at 15A) , and (b) "low temperature" carbonate (429°C) on t he AGE curve in the Colo experiments at 150°C with CO2 (SC)

The dissolution of carbonated minerals, which often is the cementing material in the caprock, can create preferential pathways for CO_2 migration through the caprock. At the opposite, the buffering capacity of carbonates, the potential mineral trapping and the geochemical and geomechanical properties of clay minerals favor long-term storage safety. (Bildstein et al., *this issue*). Therefore, during the injection site selection, the characterization of caprock composition in carbonates and clay minerals considering their substitutions and arrangements and the identification of the main geochemical phenomena during their reactivity with mixed CO_2-brine fluids will be one of the key point for CO_2 storage safety assessment.

Acknowledgments

References

[1] Kaszuba et al., 2003
[2] Kaszuba et al., 2005
[3] Gaus et al., 2005
[4] Kohler et al., 2006
[5] Gherardi et al., 2007
[6] Takenouchi and Kennedy, 1964
[7] Blanchet et al. 2008
[8] C.I. Steefel, UCRL -MA -143182, Livermore , California, 2001.
[9] T.J. Wolery, Lawrence Livermore Nat. Lab. Report UCRLMA -110662 PT IV, Livermore California, USA, 1992.
[10] O. Bildstein et al., this iss ue