

CO₂ Geological Storage in Saline Aquifers: Paraná Basin Caprock and Reservoir Chemical Reactivity

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Abstract

Geological storage is considered one of the most promising solutions to reduce CO₂ emissions. The CO₂ captured from large stationary sources can be safely injected and stored in appropriate geological formations. Saline aquifers have great potential for CO₂ storage because they are found in appropriate depths for carbon storage in the supercritical phase; have widespread geographic distribution and bigger storage capacity than other geological reservoirs. The aim of this work is to investigate mineralogical alterations of possible reservoir and caprock samples in the presence of CO₂ and saline solution to assess the long term storage system. Two sets of experiments were performed with rock samples from Paraná Basin, Southern Brazil: (1) in pressurized cells with supercritical CO₂, and (2) in Teflon batch reactors with dissolved CO₂ at atmospheric pressure. The temperature of the experiments was set to 80°C and duration from 3 to 6 months. A 0.1 M NaCl solution was used. Reactions with dissolved CO₂ show dissolution of feldspars in the reservoir samples; and dissolution/re-crystallization of the argillaceous phase (Illite-Smectite and Illite) in the samples. Preliminary results demonstrated a higher reactivity of the dissolved CO₂ than the dry supercritical fluid, and significant mineralogical transformations in the Palermo caprock, particularly for the clay minerals.

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1. Introduction

Carbon Capture and Geological Storage (CCGS) is considered one of the most promising solutions to reduce CO₂ emissions. The CO₂ captured from large stationary sources can be safely injected and stored in appropriate geological formations, such as mature and depleted oil fields, unmineable coal deposits and deep saline aquifers [1]. Geological formations have naturally had retained gas/oil for millions of years, so they are believed to be stable reservoirs for CO₂ storage in geological time scale [1, 2].

Saline aquifers have great potential for CO₂ storage owing to long time CO₂ stability, large capacity of this reservoirs, and appropriate depth for storage in supercritical phase and also because their wide geographic distribution, especially close to main CO₂ stationary sources [3]. Saline

aquifers present higher storage capacity when compared to other reservoirs (petroleum reservoirs and coal seams). This type of reservoir has also been used for waste storage [4], and is considered a viable option for the CO₂ storage.

Chemical processes associated with CO₂ injection in saline aquifers are directly related to mineralogical composition (carbonated or siliciclastic context). Several authors have evaluated CO₂ dissolution and CO₂ mineral precipitation phenomena simulating geochemical conditions of the reservoirs and evaluating caprocks with potentials sealing mechanisms [5, 6, 7, 8].

The CO₂ dissolution in water depends of temperature, pressure and salinity conditions. Dissolution leads to formation of carbonic acid (H₂CO₃) which reduces the pH of the system and dissociates in proton (H⁺) and bicarbonate (HCO₃⁻) ions. Thus, carbonate ions can react with metals (i.e. calcium, magnesium) present in the system and form calcium and/ or magnesium carbonates [5]. At pH about 4, H₂CO₃ formation is favored, while at pH 6, HCO₃⁻ ions and at pH 9, CO₃²⁻ ions prevail. When the system becomes more acid, carbonate dissolution is favored and mineral carbonation prevails for high pH values [5]. Mineral dissolution can possibility enhances fragility in the rock and promotes important increase in porosity and permeability [9]. Effective CO₂ trapping can be achieved through pH setting at relatively high values (> 9) to neutralize H⁺ production during mineral precipitation and CO₂ dissolution [10].

Clay-rich materials contain specific clay minerals possessing sealing properties due to the small size and high tortuosity of the pores as well as very high specific surface area and the surface charge [11]. Clayey caprocks can prevent or at least delay for several tens of thousands of years the CO₂ migration towards the atmosphere as predicted by previous modeling work [7, 12, 13, 14]. Physicochemical reactivity of clayey caprock involves clay minerals and rock cements such as silicates or carbonates. The prediction of the behavior of such minerals in the presence of acidified deep underground waters is critical for safety assessment of CO₂ storage. However, fractures and faults occurrence through geological formations can decrease time migration drastically results as evidenced by numerical modelling [14, 15]. This reactivity covers large space and time scales, differing for silicates or carbonates. Experimental determination of caprocks reactivity [3, 7, 9, 16] for clays and carbonates provide reaction pathways and parameters for modeling studies on the long term.

In Brazil one of potential sedimentary basins for CCGS is the Paraná basin. This basin has wide extension in southern and southeastern Brazil, where the largest amount of emission sources are located, presents potential to storage in coal seams and saline aquifers with an estimated capacity of 662,000 Mt CO₂ [17].

The Paraná basin presents geological formations which have potential for CO₂ injection: reservoirs such as the Rio Bonito Formation and caprocks such as the Palermo and Irati Formations. The Rio Bonito Formation is a promising reservoir for geological storage in saline aquifers in Brazil owing to reservoir quality (very porous and permeable sandstones), adequate burial depth (> 1000 m). On the other hand, Palermo Formation consists of siltstones, while Irati Formation presents representative content in shale, siltstone and limestone (upper section) [18].

The aim of this work is to present mineralogical transformations of rock samples in the presence of CO₂ to assess the persistence on the long term of the storage system confining properties and its impact on safety assessment.

2. Material and Methods

Caprock samples were collected from cores of the Palermo and Irati formations (marine shales) and reservoir rocks from cores of the Rio Bonito Formation (paralic sandstones) from the Paraná Basin (Lower Permian), Southern Brazil.

Samples were submitted to experiments in conditions that simulate geological storage conditions. Five representative levels were selected: two samples from Rio Bonito Formation (reservoir), a sandstone level (RB1) and a carbonaceous siltstone level (RB2), three caprock levels: a siltstone of Palermo Formation (PAL); and two levels of Irati Formation, a dark shale (IR1) and a

siltstone with bioturbation (IR2). Rock samples were crushed before experiment in order to accelerate and homogenise the global reactivity.

Two sets of experiments were performed: (1) in pressurized cells with supercritical CO₂ at 0-12 MPa, to simulate potential reservoir conditions and water-rock-CO₂ interactions; and (2) in Teflon batch reactors with dissolved CO₂ at atmospheric pressure to simulate reaction conditions when CO₂ is dissolved in the reservoir brines. All experiments were carried out with 0.1 M NaCl solution, at 80°C, to simulate the conditions of the deep geological formations. The duration of experiments ranged from 3 to 6 months.

Rock samples were characterized prior to and after reactions by X-Ray Diffraction (XRD). At the end of each experiment, the crushed rocks were collected and washed carefully twice with 50 mL ultrapure water. Slurry of the final suspension was deposited on XRD-dedicated glass slides and air-dried to enable a favourable orientation of the particles for an efficient diffraction. XRD scans were recorded between 2 and 40°2θ (counting time of 2s per 0.02°2θ step size) with a Bruker D8 diffractometer (Cu radiation at 40 kV and 40 mA) equipped with a Göbel mirror and a Sol-X detector.

Scanning Electron Microscopy (SEM) were performed using Philips® XL 30 and EDX analyses were performed with a large window Si-Li detector (Oxford Instrument). Semi-quantitative analyses were calculated with INCA®-Oxford Instrument software providing total atomic percentage for each analysis.

Transmission Electron Microscopy (TEM) was used to identify evolution of the initial mineral composition after interaction with CO₂. The structural and chemical evolution of rocks and some primary and secondary mineral phases was observed and analyzed. Slurry of the final suspension was deposited on TEM-dedicated 200 mesh carbon slides and air-dried during 24 h. The observations were performed on a JEOL 2000 FX Transmission Electron Microscope at 200 kV with a point by point resolution of 2.7 Å. EDX analyses were performed with a large window Si-Li detector (Oxford Instrument) and a super atmospheric thin window (SATW) slit of 30 mm². In convergent mode, spectra were acquired in one minute with a death time < 20% and a global count number of 500-2000. Semi-quantitative analyses were calculated with INCA®-Oxford Instrument software providing total atomic percentage for each analysis. Mean structural formulae have been built on set of selected crystallite analyses without any accessory mineral contamination.

Saline solutions were analyzed using Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES Jobin Yvon® ultra-trace) with an uncertainty of 5%, to determine cations concentrations initially existing in solutions and after reaction.

3. Results

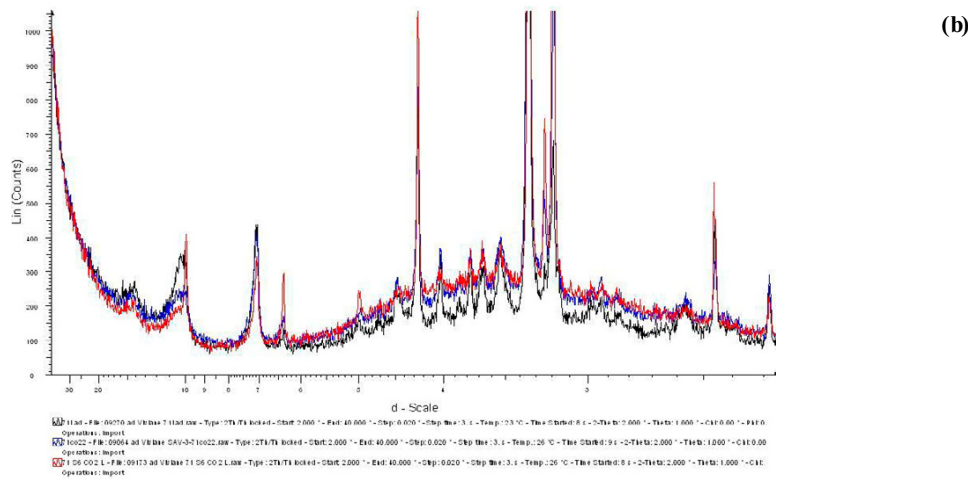
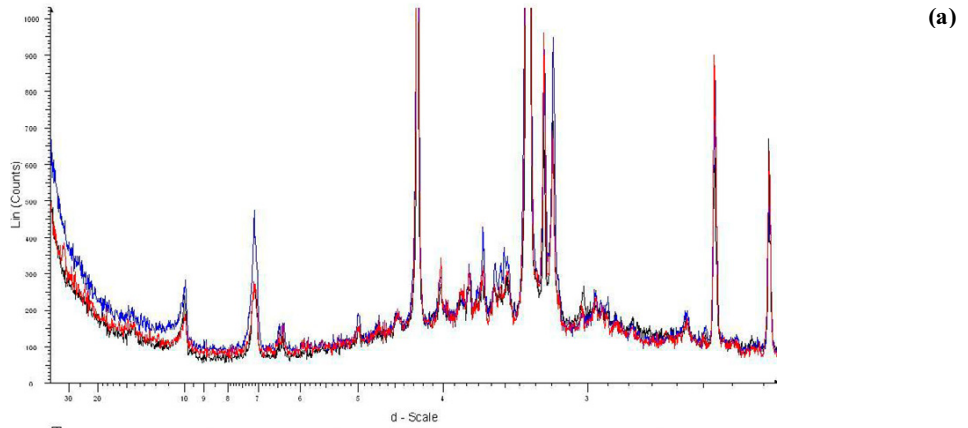
In this paper we will describe the experimental results obtained with RB1 reservoir and Palermo caprock.

3.1 Atmospheric pressure reactions

-XRD analysis

Initial diffractogram of reservoir level (RB1 sample) demonstrated sandstone content, constituted basically by quartz, other aluminosilicate minerals (albite and anorthite), carbonates (magnesium calcite) and clay minerals (illite, kaolinite and/or chlorite). Initial analyses of PAL caprock showed that this sample is formed by quartz, albite, dolomite, kaolinite and/ or chorite, illite and interstratified illite/ smectite (I/S). XRD analysis for RB1 sample after 3 months of reaction does not show any significant effect of reactions with CO₂, while RB1 analysis after 6 months showed probable attack on mixed-layer I/S with initial development of illite (Figure 1a).

PAL analysis after 6 months of reaction in the presence of CO₂ demonstrated significant alteration of I/S phase with changes in peaks at 10 and 5,02 Å, probably due to the development of an illite phase from interstratified phase (Figure 1b).



Initial - 3 months - 6 months

Figure 1: XRD spectrums for reactions at atmospheric pressure: (a) *RBI*, (b) *PAL*.

- SEM analysis

SEM analysis on reservoir (RB1) and caprock (PAL) samples after 3 and 6 months of reaction demonstrated mainly attack (dissolution) on feldspar phase and no precipitation of new phases.

- TEM analysis

TEM analyses were performed in order to describe initial PAL sample and for PAL sample after 6 months of reaction at atmospheric pressure. This sample was selected owing to the results obtained by XRD, where a significant reactivity was observed in the illite/smectite clay phase. Figure 2a and 2b corresponding to I/S mixed-layer phase in initial sample. The I/S exhibit common massive and thick crystals (a) with well developed stacking sequence (b) up to 150 nm. Mean

structural formulae (Equation 1) of initial massive I/S (Figure 1a), average of 17 analyses of isolated crystals without any accessory minerals as impurity was determined by EDX analysis.

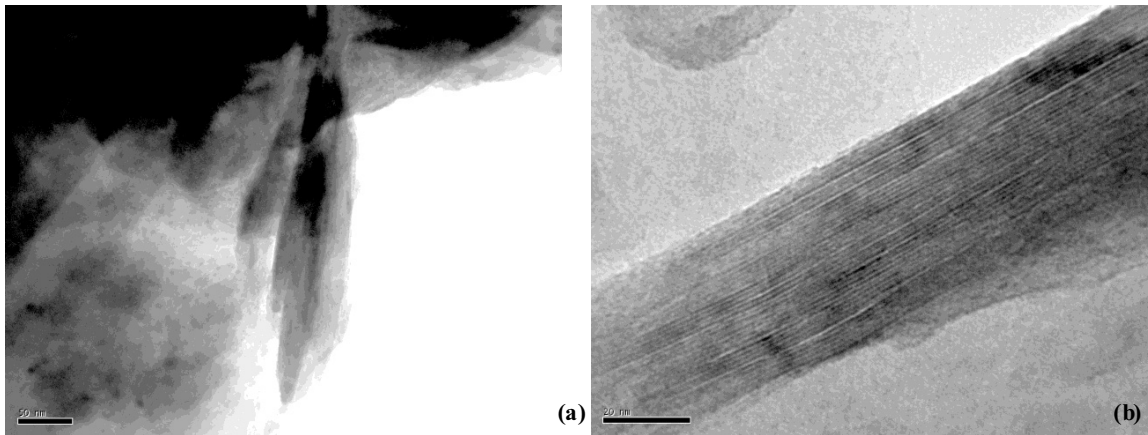
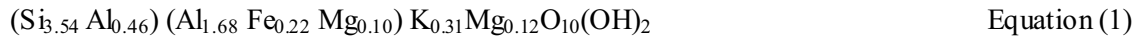


Figure 2: TEM analyses of PAL sample: (a) and (b) the thick I/S mixed-layer in initial sample.

Others images (Figure 3) illustrate the reaction products as new-crystallized minerals such pure illite after 6 months in presence of CO_2 : (a), (b) and (c) show the new crystallized acicular and thin illite with typical new sharpened aspect. TEM grids of this sample exhibit numerous crystals with this aspect never seen before in the initial material. Image (d) show I/S altered crystals with new crystallized illite. The clear transition area (d) between the mineral phases suggests probably a dissolution/recrystallization illitisation process.

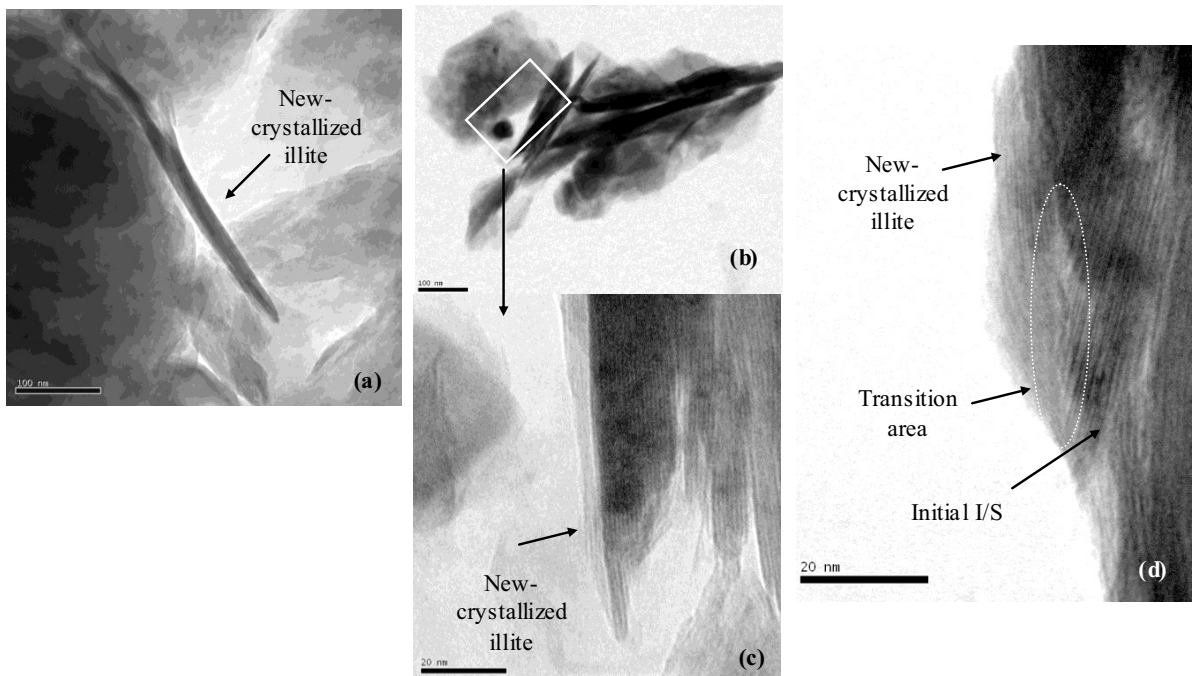
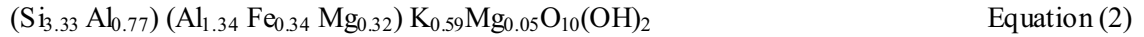


Figure 3: TEM analyses of PAL sample after 6 months of reaction in the presence of CO_2 ; (a), (b) typical sharpened crystals of new crystallized illite, (c) new crystallized illite (detail), (d) altered I/S versus pure illite).

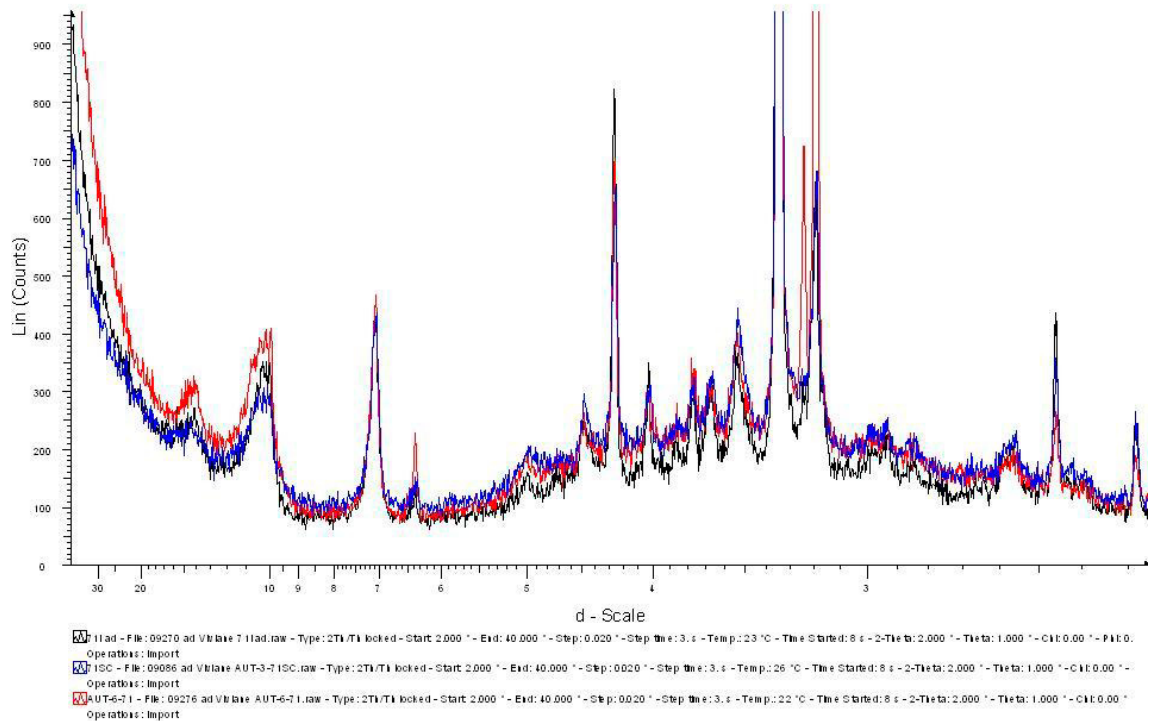
Illite recrystallization was confirmed by EDX analysis and the mean structural formulae (Equation 2) of new crystallized illite (Figure 3c), average of 10 analyses of isolated acicular thin crystals without any accessory minerals as impurity was determined.



Such structural formulae is close to classical diagenetic illite and results in our experiment of dissolution/crystallization processes.

3.2 High pressure reactions

We chosen PAL and IR1 samples for high pressure reactions. Here we present XRD analyses for the PAL sample after of 3 and 6 months reactions (Figure 4). Analysis for PAL sample after 3 months does not present any significant mineralogical alterations, while at 6 months probable I/S alteration were observed, as described above for PAL reactions at atmospheric pressure reactions.



SEM analysis of PAL sample demonstrated the same results that for samples submitted to atmospheric pressure reactions, i.e., attack on feldspar phase.

4. Discussion

Samples submitted to atmospheric and high pressure reactions in presence of CO₂ demonstrated dissolution on feldspar minerals and dissolution/re-crystallization or transformation of the argillaceous phase. XRD analyses of both RBI and PAL samples showed evidences of these mineral transformations on I/S mixed-layer and Illite phases. TEM analyses on PAL sample after 6

months reaction with CO₂ at atmospheric pressure confirm the alteration of the I/S and its conversion to a new illitic phase supported by a dissolution/crystallization process.

These results demonstrated higher reactivity of dissolved CO₂ compared to dry supercritical fluid CO₂. It is well established [19] that the CO₂ is able to react in the aqueous phase with the minerals inside geological formations to promote dissolution and precipitation processes.

These preliminary results demonstrated a mineralogical transformation from illite-smectite to illite in Palermo caprock. It has also been observed elsewhere that smectites can be slowly transformed to illite upon heating. This process leads to destruction of smectite and a release of Si which may precipitate as SiO₂ cement (Equation 3) [20].



Smectites formed from high temperature silicates in low temperature environments such as marine sediments (this the case for the Palermo Fm.) or in hydrothermal systems, when submitted to higher temperatures can be transformed into more stable silicate phases such as illite/smectite mixed layers, illite, chlorite, etc [21]. Diagenetic or sedimentary series has been studied using illitisation from smectite approach [22]. Smectite to illite transition is defined by XRD as transformation of mixed-layer illite-smectite (smectite rich) to highly ordered minerals (illite rich).

Mineral dissolution and/or crystallization in geological means are important parameters involved in safety assessment processes of the CO₂ geological storage process. Mineral transformations can affect the surface area, quantity of sorption sites, can change the porosity and concentration of dissolved species, and in fine have direct impact on sealing properties of caprocks. These changes may in turn modify permeability and effective diffusion coefficients affecting flow rate and transport of dissolved species [23, 24].

5. Conclusions

We present in this work experimental studies developed to assess Paraná Basin rocks as potential host for CO₂ in Brazil. Potential Formations of this basin were studied in order to determine their function as reservoir and/ or caprock. Samples were tested in presence of CO₂ in geological storage conditions in laboratory scale experiments. The results presented here demonstrated some reactivity of feldspars in Rio Bonito sample (RB1), while for Palermo sample a significant reactivity of I/S phase with re-crystallization of illite was observed. These results demonstrate the reactivity of the Paraná Basin samples, providing a preliminary assessment of the reactivity of these Formations in the presence of CO₂.

The re-precipitation of new phases in Palermo sample represents an important aspect that have to be assessed, because this mineral transformation may cause significant changes of rock properties. These changes can influence porosity filling which is an important parameter for reservoir capacity, while in the caprocks such alteration could induce rock fragility and decrease of the global seal capacity.

The results and the determination of reaction processes represent an important help for modeling studies by the supplying of basic data. This work will be also complemented through numerous modeling studies in order to simulate experiments and in fine to assess the reactivity and stability of the potential geological formations up to representative time scale (10.000 years), to achieve the safety assessment of the CO₂ geological storage process.

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