Tema: Gestão de meio ambiente e recuperação e tratamento de rejeitos

EXPERIMENTAL STUDY OF CARBONATE REACTIVITY IN THE CONTEXT OF CO$_2$ GEOLOGICAL STORAGE*

Tiago de Abreu Siqueira[1]
Gabriela de Freitas Quandt[2]
Laura Kunz[3]
Anthony Credoz[4]
Rodrigo Iglesias[5]

Abstract

CO$_2$ geological storage is one of the current technologies developed worldwide to reduce industrial emissions of carbon dioxide to the atmosphere. Two main mineral types of deep geological reservoir could be contemplated for CO$_2$ storage: sandstone reservoirs and carbonaceous reservoirs. Geochemical reactivity of a dolomite-calcite mineral compound and magnesite pure mineral was studied with a set of nine experiments per crushed mineral phase with two saline solution and with mQ water and three temperatures: 50°C, 90°C and 150°C. Experiments were performed in batch reactors with 250 bar of CO$_2$ partial pressure during 24h to assess the effect of temperature and salinity in constant CO$_2$ pressure. Solid characterization was performed by XRD and solution analysis by ICP-OES. Acidification of solutions due to CO$_2$ dissolution in water is the main source of reactivity in the system. Proton concentration increases and causes partial dissolution of initial dolomite, calcite and magnesite and release of Ca^{2+} and Mg^{2+} cations in solution. Bicarbonate anion (HCO_3) concentration also increases due to CO$_2$ dissolution in water and carbonate minerals dissolution. Temperatures of 90°C and 150ºC increase the kinetic of reaction and the dissolution of minerals and cations release in solution. New carbonate crystalline phase precipitates as a Ca, Mg solid solution between dolomite and calcite pure poles.

Keywords: CO$_2$; Geological storage; Carbonate; Reactivity.

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[1] *Mestre em Engenharia de Materiais, Doutorando em Engenharia e Tecnologia de Materiais, CEPAC, IMA, PUC-RS, Porto Alegre, RS, Brasil.*
[2] *Graduanda em Engenharia Química, Bolsista de Iniciação Cientifica, CEPAC, IMA, PUC-RS, Porto Alegre, RS, Brasil.*
[3] *Graduanda em Química Industrial, Estagiaria, CEPAC, IMA, PUC-RS, Porto Alegre, RS, Brasil.*
[4] *Doutor em Geoquímica, Pesquisador, CEPAC, IMA, PUC-RS, Porto Alegre, RS, Brasil.*
[5] *Doutor em Química, Professor, CEPAC, IMA, PUC-RS, Porto Alegre, RS, Brasil.*

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1 INTRODUCTION

The capture and geological storage of CO_2 in suitable deep geological formations (> 800 m; e.g., Holloway, 1996; IEA, 2009), such as saline aquifers, depleted oil and gas fields or unexploited coal beds (fig. 1) (IPCC, 2005) is proposed as one of the main solutions to reduce CO_2 industrial emissions to the atmosphere (IPCC, 2005; Ketzer et al, 2011).

Once injected deep underground, CO_2 can be retained as supercritical fluid (physical trapping), fluid migrating very slowly in an aquifer (hydrodynamic trapping), dissolved $CO_2(aq)$ into groundwater (solubility trapping), and secondary carbonate minerals (mineral trapping) (Gunter et al., 1993, 2000), Among these sequestration processes, mineral trapping will be the most stable in the long-term. Since the geological media has been storing oil and gas for thousands of years, it can be assumed that these reservoirs could also store CO_2 in the geological time-scale (Holloway, 1997; Bachu and Adams, 2003; Kaszuba et al., 2003); Doughty and Pruess, 2004; Kumar et al, 2005).

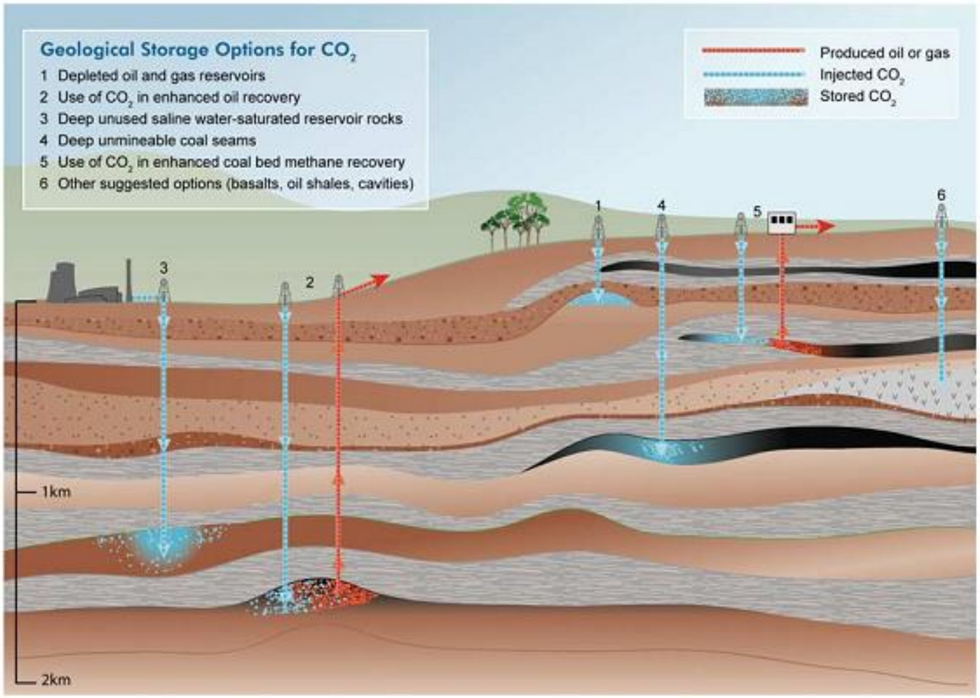

Figure 1. Options for geological storage of CO_2 (IPCC, 2005).

Carbonate reservoirs are attractive CO_2 sequestration sites as they provide both high capacity and potential storage integrity (Shukla et al., 2010). When combined with enhanced oil recovery (EOR) operations, water and CO_2 injection leads to disequilibrium of both fluid chemistry and pore pressures within the reservoir and caprock. In the vicinity of injection wells, CO_2 dissolves into resident reservoir fluids, which lowers the pH, resulting in mineral dissolution and alteration of porosity and permeability. Quantifying these coupled processes and their influence on the porosity and permeability of fractures is critical to understand the evolution of transport properties during CO_2 injection in connection with EOR and CO_2 sequestration efforts (Elkhoury et al., 2013).

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Previous experimental study of interactions between carbonate formations, saline solution and CO_2 at Weyburn field (Canada), reported that CO_2 injection in oil field decreases the pH causing the dissolution of carbonate minerals. The dissolution of carbonate increased the pH and bicarbonate production.

$$H^+ + CaCO_3 \rightarrow Ca^{2+} + HCO_3^- \qquad (1)$$

$$H_2O + CO_2 + CaCO_3 \rightarrow Ca^{2+} + 2HCO_3^- \qquad (2)$$

These reactions, as suggested by Emberley and collaborators (Emberley, Hutcheon et al., 2004), resulting in storage of CO_2 injected in the form of bicarbonate ions. Water chemistry suggests that reactive silicate minerals may influence the chemical composition and behavior of the formation water, possibly promoting the pH buffering. These reactions of formation and precipitation of bicarbonate caused by the variation of pH are possibly controlling the amount of CO_2 trapped geochemically in the oil field (Emberley et al., 2004).

Pokrovsky *et al*. () investigated the effect of temperature (25 to 150°C) and pCO_2 (1 to 55 atm) on the rate of dissolution of calcite, dolomite and magnesite at far from equilibrium in slightly acidic and circumneutral solutions pertinent to conditions of CO_2 geological sequestration. For the three minerals, the effect of pCO_2 has been found to be of second order importance compared to that of pH and bicarbonate/carbonate ion concentrations. Above 60–100 °C, the effect of both temperature and pCO_2 on far from equilibrium calcite dissolution rates becomes negligible. The effect of pH is clearly pronounced up to pH~4, but in the presence of HCO_3^- produced by calcite dissolution, pH-independent surface metals hydration controls calcite reactivity. At these conditions, dissolved carbonate and bicarbonate ions are the only major variables, and the higher the solution pH, the larger the inhibiting effect of CO_2. Dolomite and magnesite follow the same trend with dissolved carbon dioxide inhibition at pH=5–6 being approximately ten times stronger than that for calcite. At both acidic and circumneutral pH's, dissolution rates measured at 150°C are equal or lower than those measured at 100°C and even 60°C which yields a sharp drop of the apparent activation energy of carbonate mineral dissolution at t>100°C.

When the pH is higher than 5, carbon dioxide will act as an inhibitor of dissolution and, as a result, the stability of carbonate confining reservoir may be higher than it is usually expected. Therefore, these results suggest the efficiency of CO2 sequestration in Mg-bearing carbonate sedimentary rocks. The following optimal conditions of CO_2 storage can be recommended: 1) dolomite- or magnesite-bearing carbonates, especially at far from the front of CO_2 injection; 2) the presence of calcite at the beginning of injection in order to provide high HCO_3^- concentration and pH above 5; 3) the temperature range from 100°C to 150°C; 4) a CO_2 partial pressure of 50 atm or higher.

Nevertheless, all the studies reported were performed at pressure and temperature of the on-shore and off-shore current reservoirs of CO_2. Average depth does not exceed 2000 m. The aim of this study was to verify the geochemical reactivity of a dolomite-calcite mineral compound and magnesite pure mineral aiming to understand the effects of CO_2 injection in carbonate formations deeper than current geological reservoirs.

2 MATERIAL AND METHODS

The laboratory experiments aimed at simulating the interactions between CO_2, two solutions (milliQ water and saline solution) and two samples of carbonate minerals (dolomite-calcite and magnesite) in reservoir conditions with a constant pressure of 250 bar and three different temperatures: 50, 90, 150°C. All the reactions were performed in a batch stainless steel reactor of 100 mL equipped with a teflon (PTFE) internal cup, manometer and automatic temperature controller, connected to an electric heating apparatus (Figure 2). In batch reactions, samples of the crushed carbonate minerals and aqueous solution are added to the reactor, which is subsequently sealed, filled with CO_2 and heated until the desired pressure and temperature during 24 h.

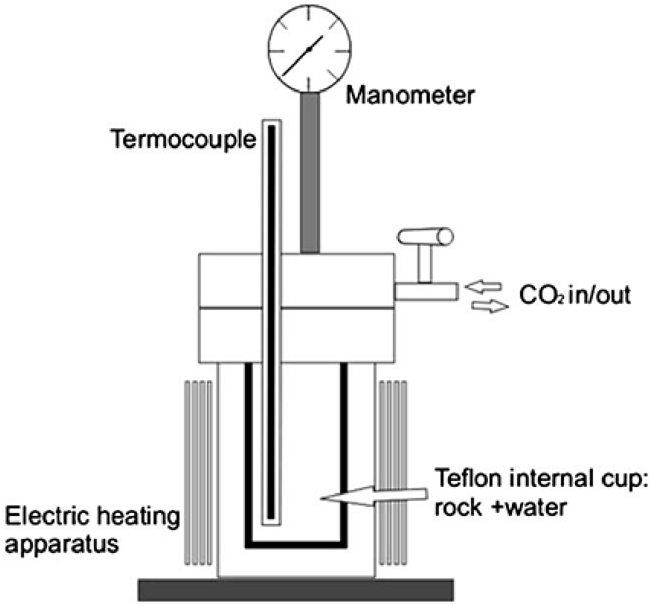

Figure 2. Scheme of equipment used for water-rock-CO2 reactions (Ketzer et al. 2009).

For the simulation of reservoir conditions, the reactions followed the conditions described in the Table 1 where DC stands for dolomite-calcite experiment and M stands for magnesite experiment.

Table 1. Reaction conditions for all samples.

Dolomite-calcite sample			*Magnesite sample*		
Ref	Fluid	Temperature	Ref	Fluid	Temperature
DC1	miliQ water	50 °C	M1	miliQ water	50 °C
DC2	miliQ water	90 °C	M2	miliQ water	90 °C
DC3	miliQ water	150 °C	M3	miliQ water	150 °C
DC4	Saline solution	50 °C	M4	Saline solution	50 °C
DC5	Saline solution	90 °C	M5	Saline solution	90 °C
DC6	Saline solution	150 °C	M6	Saline solution	150 °C

Saline solution composition is reported in Table 2.

Table 2. Reaction conditions for all samples.

Component	Mass (g)
NaCl	57,8832
KCl	1,6855
$CaCl_2.2H_2O$	0,5495
$MgCl_2.6H_2O$	1,1919
$NaHCO_3$	0,1849

The characterization of aqueous phase was performed by standard techniques such as water analysis measurements of pH and Optical Emission Spectroscopy Inductively Coupled Plasma (ICP-OES) to quantify ions. These analyses, which allow quantifying the major ions in solution should be performed before and after the experiments, allowing to identify the presence or variations in the amount of elements due to the dissolution and precipitation of minerals during reaction (Iglesias et al., 2009).

Analyses of minerals were made by x-ray diffraction before and after experiments, so that you can view the non-existent before and after the reaction mineral phases, and dissolution of constituents (Iglesias et al., 2009).

1 RESULTS AND DISCUSSIONS

After experiments, analysis of x-ray diffraction (X-RD) was performed, which shows that the characteristic peaks of dolomite and calcite in Figure 3. Characteristic signs of dolomite can be observed in 2,881Å this is the main sign of dolomite, other distinctive signs can be observed in 1,785 Å and 2,190 Å. some characteristic signs of calcite could be observed in the region of 3,035 Å, 2,285 Å and 2,095 Å.

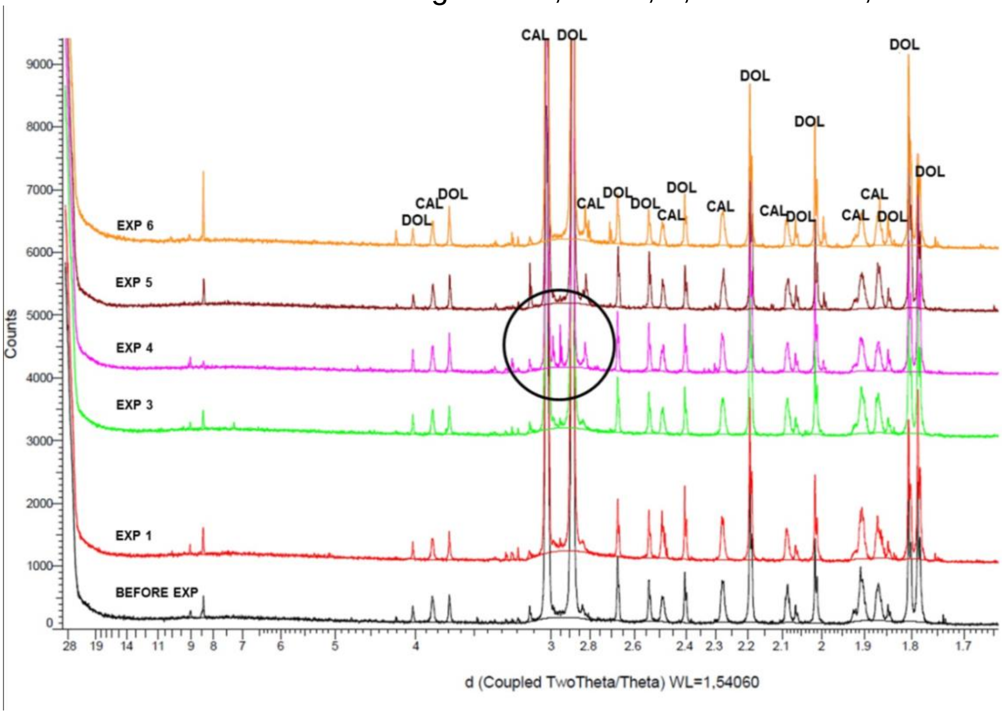

Figure 3. XRD patterns of the mineral fraction before and after the 6 experiments with dolomite-calcite (DOL: Dolomite, CAL: Calcite).

Figure 4 shows an enlargement of the region between 2.0 Å and 5.0 Å, where it is possible to observe that in the experiment at 50°C there was an evolution of the precipitation of a mineral intermediary between the poles of pure calcite and dolomite. That may indicate the formation of a solid solution of calcite and dolomite ($Ca_{2-x}Mg_x(CO_3)_2$).

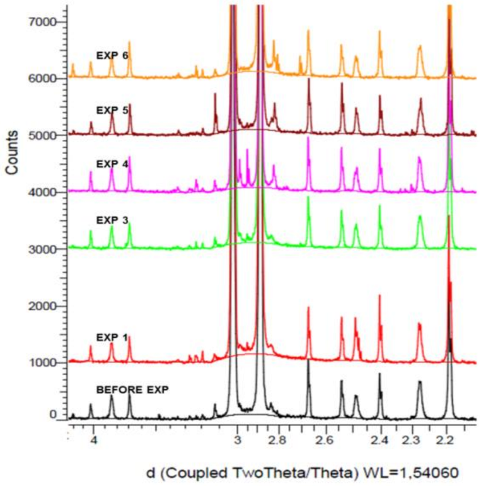

Figure 4. Expansion of the region between 2,0 Å and 5,0 Å of the XRD pattern of dolomite-calcite.

In the experiments with magnesite, it was not observed any reaction and gradual precipitation of carbonate minerals, but it is possible to identify the characteristic signs of magnesite in 2,741 Å, 2,102 Å and 1,701 Å (Figure 5). In reactions performed with saline solution, there was a precipitation of halite evidenced by signals at 2,820 Å and 1,628 Å, possibly formed from saline solution. In all reactions with magnesite, it has also been observed the presence of calcite indicated by the signal at 3,035 Å, which is the characteristic sign of this mineral which may be present as impurity in the initial mineral sample.

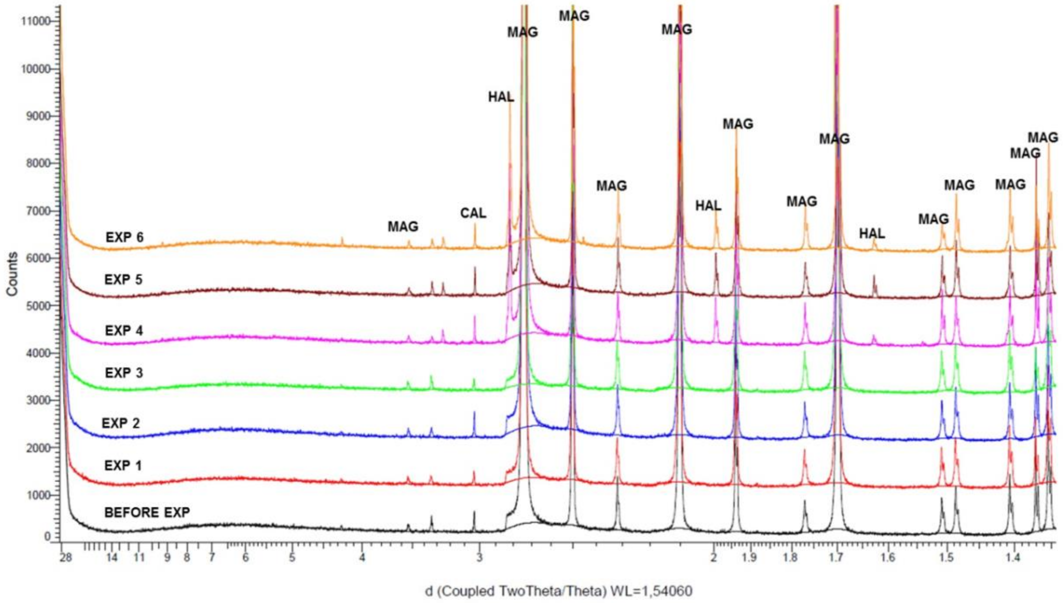

Figure 5. Diffractograms of the mineral fraction before and after the 6 experiments with Magnesite (MAG: Magnesite, CAL: Calcite, HAL: Halite).

In the interaction between dolomite-calcite and CO_2 with milliQ water (Table 3), dolomite and calcite dissolved partially releasing Ca and Mg in solution for the three

temperatures performed due to pH decrease. Ca release increased at 150°C whereas Mg release increased at 90 °C. The main result was that Ca concentration is 50 times higher than Mg realease which would be related to higher dissolution of calcite ($CaCO_3$) than dolomite ($CaMg(CO_3)_2$).
In the experiments with saline solution, Na and K remained constant for the three different temperatures. Ca was released in solution significantly whereas Mg concentration decreased. Precipitation of Mg-enriched carbonate mineral could lead to Mg trapping from the solution.

Table 1. Results of analyzes by ICP-OES of cations in post-experiment solutions with dolomite-calcite (mol/kg).

Ref. Experimento	Ca	Na	K	Mg
Água mQ	*<DL*	<DL	*<DL*	*<DL*
1	1,57E-02	<DL	*<DL*	6,42E-04
2	1,32E-02	<DL	*<DL*	1,82E-03
3	2,11E-02	<DL	*<DL*	4,58E-04
Solução salina	*3,50E-02*	*1,40E+00*	*1,68E-02*	*1,87E-02*
4	5,06E-02	1,29E+00	1,73E-02	8,73E-03
5	5,19E-02	1,37E+00	1,78E-02	9,70E-03
6	5,16E-02	1,37E+00	1,74E-02	8,44E-03

**DL stands for detection limit*

In the interaction between magnesite and CO_2 with milliQ water (Table 4), magnesite dissolved partially releasing Mg in solution for the three experiments performed due to pH decrease. Mg concentration remained constant during the three experiments. Release of Ca at 50°C could be related to dissolution of calcite impurities in the initial material.
In the experiments with saline solution, Na and K remained partially constant. Precipitation of halite could imply the drop of Na concentration at 150 °C. Ca concentration increased due to potential calcite impurities dissolution and Mg was probably trapped by Mg-enriched carbonate precipitation.

Table 4. Results os analyzes by ICP-OES of cations in post-experiment solutions with dolomite-calcite (mol/Kg

Ref. Experimento	Ca	Na	K	Mg
Água mQ	*<DL*	*<DL*	*<DL*	*<DL*
1	8,60E-03	<DL	*<DL*	2,50E-03
2	<DL	<DL	*<DL*	2,60E-03
3	<DL	<DL	*<DL*	1,90E-03
Solução salina	*3,50E-02*	*1,40E+00*	*1,68E-02*	*1,87E-02*
4	4,01E-02	1,62E+00	1,36E-02	2,87E-03
5	8,25E-02	1,96E+00	1,52E-02	3,08E-03
6	2,46E-02	1,08E+00	1,57E-02	1,01E-02

**DL stands for detection limit*

4 CONCLUSIONS

Two series of experiments have been performed to study the reactivity of carbonate minerals in deep CO_2 geological storage (250 bar and temperature from 50°C to 150°C). Two kinds of solutions were used: a pure water (milliQ) and saline solution and it has been observed that the ionic strength of the solution has a relevant effect on solubility of carbonates in this context of reactivity. Nevertheless, the main effect of was the acidification of the solution due to CO_2 dissolution in solution and proton attack on mineral crystal. From the aqueous species released in solution, new products could form only after 24 h of reaction resulting of solid solution from calcite and dolomite minerals. In a large scale geological storage in limestone, calcite would be the first mineral to react, dissolving and buffering the pH, whereas carbonate minerals enriched in Mg would be the main stable minerals in the system. Further studies need to be done to confirm these assumptions increasing the duration of experiments and keeping the system far from equilibrium as it could be performed with flow-through system.

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