

Ensaio de carbonatação mineral de CO₂ no gabro do maciço de Sines - dados preliminares do projeto InCarbon

Experiments on mineral carbonation of CO₂ in gabbro's from the Sines massif - preliminary data from project InCarbon

Moita, P.^{1*}, Berrezueta, E.², Pedro, J.³, Miguel, C.¹, Massimo B.¹, Galacho, C.¹, Barrulas, P.¹, Mirão, J.¹, Carneiro, J.³

¹ Laboratório HERCULES, IIFA, Universidade de Évora, Largo Marquês de Marialva, 2, Évora, Portugal

² Instituto Geológico y Minero de España (IGME), Oviedo, Espanha IGME, Espanha, Portugal

³ Instituto Ciências da Terra (ICT), IIFA Universidade de Évora, Rua Romão Ramalho, Évora Portugal

* pmoita@uevora.pt

Resumo: Portugal comprometeu-se com a neutralidade carbónica até 2050, mas o atual perfil de emissões do setor industrial indica a necessidade de recorrer a tecnologias de Captura e Armazenamento de CO₂ para atingir esse objetivo. De entre essas tecnologias, a carbonatação mineral, i.e. a capacidade de precipitar CO₂ sob a forma de carbonatos por reação com alguns dos principais cátions presentes em silicatos em rochas máficas (e.g. Ca²⁺, Fe²⁺), é uma das alternativas de sequestro de CO₂ mais estáveis e seguras. A eficiência da carbonatação mineral foi anteriormente demonstrada em rochas basálticas nos projetos CarbFix (Islândia) e Wallula (EUA). O projeto InCarbon pretende estudar a carbonatação mineral em rochas texturalmente mais grosseiras, nomeadamente em gabros e peridotitos que afloram no Alentejo, Portugal. Neste sentido o principal objetivo do projeto InCarbon é avaliar o potencial de carbonatação dessas rochas através de ensaios laboratoriais.

O gabro do maciço subvulcânico de Sines foi selecionado para o primeiro teste laboratorial atendendo às suas características geoquímicas e mineralógicas, bem como à sua proximidade com o principal foco de emissões de CO₂ na região do Alentejo. A metodologia global passou por mapear os provetes de gabro através de VP-SEM-EDS e ATR-FTIR, após o que foram submersos em salmoura natural com CO₂ dissolvido em períodos de 1, 4, 16 e 64 dias, a uma pressão de 80 bar e temperatura de 40°C. Posteriormente a estes ensaios os provetes de gabro foram novamente analisados por VP-SEM-EDS e ATR-FTIR. Simultaneamente, realizaram-se análises composicionais na salmoura e de XRD em amostra pulverizada de gabro. Os primeiros dados mostram essencialmente uma dissolução nos silicatos causando uma rugosidade textural, que se intensifica com o aumento dos dias de imersão em salmoura. O comportamento dos cátions na salmoura ao fim dos vários dias de ensaio é variável e não se detectou a precipitação de carbonatos.

Palavras-chave: CCS, Gabro, Sines, Salmoura, CO₂ supercrítico.

Abstract: Portugal has committed to achieve carbon neutrality by 2050, but the current profile of emissions from the industrial sector requires that CO₂ capture and storage technologies are deployed to accomplish that target. Amongst those technologies, mineral carbonation, i.e. the ability to precipitate carbonates by reacting the main cations present in silicates in mafic rocks (e.g. Ca²⁺, Fe²⁺) with CO₂, turns these rocks the most stable and safe reservoirs. Project InCarbon embraces the challenge of studying mineral carbonation in texturally coarser rocks, namely gabbros and peridotites that outcrop in Alentejo, Portugal. In this sense the main goal of InCarbon is to infer the carbonation potential of those rocks under laboratory controlled conditions.

The gabbro from Sines subvolcanic massif was selected for the first laboratory experiments, given its geochemical and mineralogical features as well its proximity with emission sources in the Alentejo region. As a global methodology, the specimens were mapped through VP-SEM-EDS and ATR-FTIR, after which they were submerged in a brine and CO₂ mixture in cycles of 1, 4, 16 and 64 days at 80bar and 40°C and later analyzed by the same two techniques. At the same time, compositional analyzes of brine and XRD were conducted. The first results show essentially a dissolution of silicates, causing an increase in surface roughness with contact time with the CO₂ enriched brine. The behaviour of cations within brine after experiments is variable and no carbonates precipitation were detected.

Keywords: CCS, Gabbro, Sines, Brine, Supercritical CO₂.

1. Introduction

The potential of mafic rocks for CO₂ storage rests in their ability to stabilize CO₂ via mineral carbonation (Andreani et al., 2009; Klein and McCollom, 2013). The feasibility of this process was demonstrated for mafic volcanic rocks in the CarbFix (Iceland) and Wallula (USA) projects. InCarbon project aims to assess the potential of using mafic and ultramafic plutonic rocks in Alentejo for storage of CO₂ captured in large stationary sources, such as those in the Sines industrial cluster. It focuses on “in situ” mineral carbonation, where CO₂ is injected into mafic rocks saturated with high salinity groundwater, promoting fast mineral carbonation and trapping the CO₂ in solid phase. CO₂-brine-rock interaction experiments represent a useful method to understand and explore the mechanisms and processes of geological storage (Kaszuba et al., 2005; Ketzner et al., 2009) and to design safe underground CO₂ storage operations.

This work presents preliminary data of laboratory tests on the CO₂-brine-rock interaction, on samples of gabbro's from the Sines subvolcanic massif. A multianalytical approach was applied resorting to VP-SEM-EDS (Variable Pressure – Scanning Electron Microscope – Energy Dispersive X-ray Spectroscopy), XRD (X-ray Diffraction), OM (Optical Microscopy) and ATR-FTIR (Attenuated Total Reflection - Fourier - Transform Infrared Spectroscopy) techniques.

2. Methodology

A coarse-grained gabbro was sampled at a cliff near Praia do Norte (Sines) and cut in 50 subsample cubes with 27cm³ each and 4 with 1cm³, divided in 4 test sets and one reference set (0 day set). The specimens - 8 at a time - were put in contact with a high salinity brine and CO₂ within a hyperbaric chamber simulating CO₂ injection conditions in a geological reservoir (40°C and 80bar) for 1, 4, 16 and 64 days (Fig. 1). One cube of each set was mapped with VP-SEM-EDS and ATR-FTIR before and after contact with the brine and CO₂ solution. Concomitantly XRD and OM was performed on a cube from each experiment set and on the reference set (0-day). The

chemical composition of the brine was also analyzed before and after the experiment.

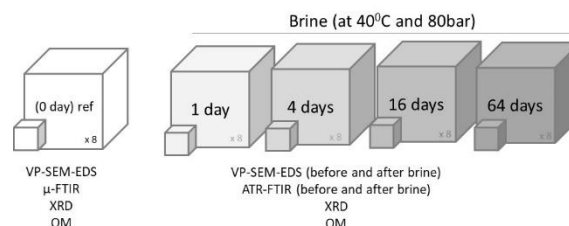


Fig. 1 – Methodology adopted for this work.

The X-ray powder and in-situ diffractograms were produced using a Bruker AXS-D8 Advance (Bruker Corp, Billerica, Mass. USA), with Cu-K α radiation ($\lambda = 0.1540598$ nm), under the following conditions: scanning between 3° and 75° (2 θ), scanning velocity of 0.05° 2 θ /s, accelerating voltage of 40 kV, and current of 40 mA. In order to evaluate the mineralogical composition of the specimen surface, in-situ grazing incidence geometry experiments was conducted, with incidence of 1° and 2 θ scanning from 8 to 60°.

A Hitachi S-3700N SEM (Hitachi High Technologies, Berlin, Germany) coupled with a Bruker XFlash 5010 SDD detector (Bruker Corp, Billerica, Mass. USA) was used for the surface sample analysis. The analysis was performed under low vacuum, i.e. 40 Pa, with a current of 20 kV.

An infrared spectrometer Bruker Hyperion 3000 equipped with a single point MCT detector cooled with liquid nitrogen and a 20x ATR objective with a Ge crystal of 80 μ m diameter was used. The infrared spectra were acquired with a spectral resolution of 4 cm⁻¹, 32 scans, in the 4000-650 cm⁻¹ of the infrared region.

The brine analyses were performed at IGME (Madrid) by atomic absorption spectrometry. Fe was analysed by ICP-MS at HERCULES.

3. Results and discussion

3.1 Gabbro

The gabbro reveals a preserved igneous texture although showing a variable degree of alteration products (e.g. chlorite, actinolite). Clearly preserve the ferromagnesian phases (olivine, pyroxene, amphibole and biotite), plagioclase as well as primary ilmenite (Fig. 2).

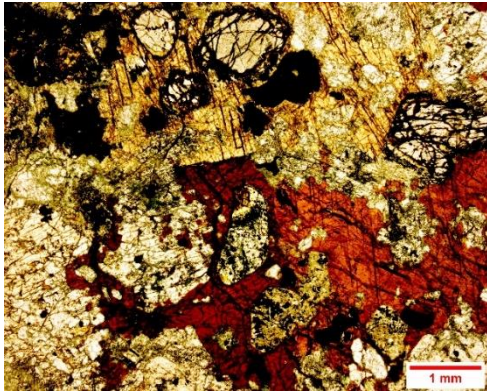


Fig. 2 – Gabbro under Polarized Light Microscope

After interaction of the rock specimens with the CO₂ + brine in the hyperbaric chamber, an increase in dissolution of gabbro can be perceived (Fig.3).

Petrographic analysis and powder-XRD on gabbro before and after the brine reveals no mineralogical differences besides salts. Moreover, XRD on the surface of specimen (Fig. 4) after 64-day experiments reveals only the presence of salts, halite and gypsum and clay minerals.

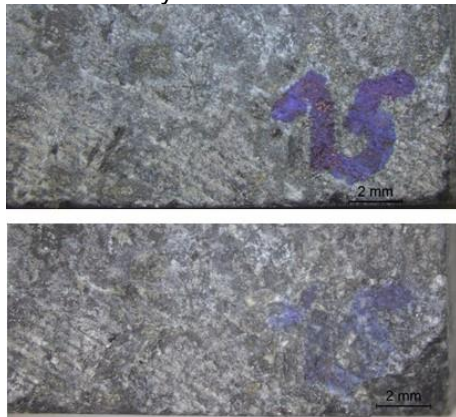


Fig.3 – Stereozoom microscope of specimen (#15) before and after 16 days within brine at 40°C and 80 bar.

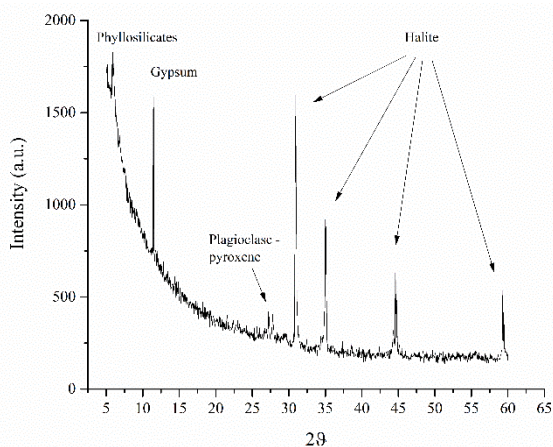


Fig. 4 – Diffractogram on the surface of gabbro after 64 days within brine.

The mappings performed on the specimens with VP-SEM-EDS after the experiments essentially shows an increase in the dissolution of silicates, translated by a greater surface roughness (Fig. 5) and a strong enrichment in Na, Cl, S and Ca in the form of halite and gypsum.

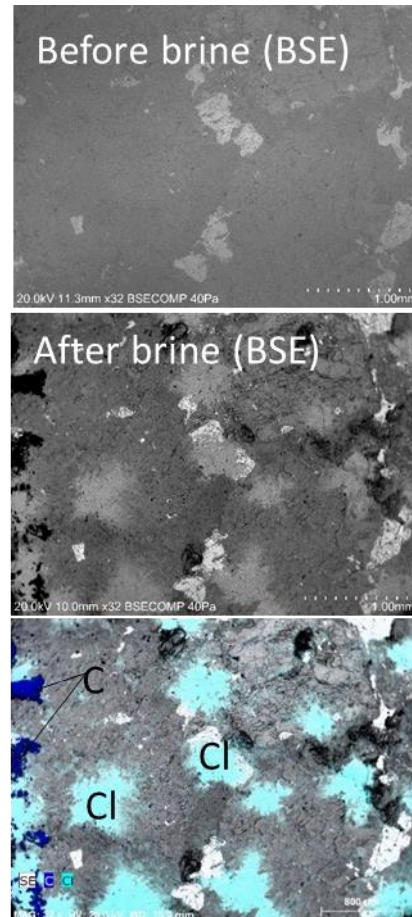


Fig. 5 – VP-SEM-EDS results comparison of samples before and after 16 days within brine.

The carbon observed at the surface is not related with the crystallization of carbonates. The ATR-FTIR spectra (Fig. 6) of these carbon-enriched areas present the characteristic infrared absorption bands of a *cutting oil* (Fig.6, fuxia spectrum), namely the triglyceride pattern of the carbonyl stretching of the ester (C=O, 1736 cm⁻¹) and the infrared profile bands related to the C-H absorptions from the fatty acid chain due to the methylene stretching at circa 2918 cm⁻¹ and 2851 cm⁻¹ (ν_{asym}(CH₂) and ν_{sym}(CH₂), respectively), and to the methyl stretching at 2955 and 2874 cm⁻¹ (ν_{asym}(CH₃) and ν_{sym}(CH₃), respectively). However, despite these infrared

fingerprints pointing to the presence of tryglicerides-enriched areas, its origin is still to be clarified.

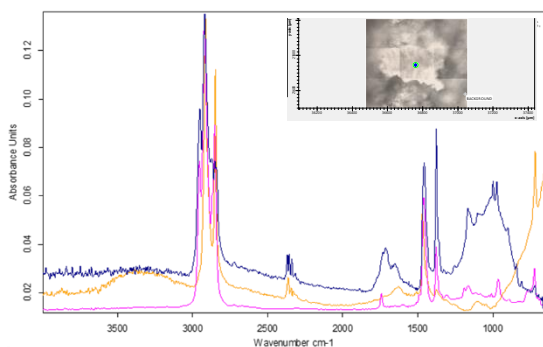


Fig. 6 – ATR-FTIR spectra of carbon-enriched areas (blue) and of a standard spectrum of a cutting oil (fúxia spectrum). The inset, the spot of analysis on specimen after 16 days.

3.2 Brine

The natural brine used in the experiments is highly saline as expected at depths usually considered for CO₂ injection (e.g. more than 800m deep)

The chemical composition of the brine was analyzed before and after the testing period and the results are shown in Table 1. The injection of supercritical CO₂-rich brine induced an evolution of pH conditions into system. During the experiments, pH varied from 6.85 (brine without CO₂) to 4.5, 4.87, 5.1 and 5.5, for the 1, 4, 16 and 64-day for the brine and CO₂ mixture, respectively (Tab. 1).

Table 1 – Brine characterization.

days->	Brine before CO ₂	Brine after CO ₂ and experiment			
	0	1	4	16	64
Na ⁺ (ppm)	85450	67105	86015	84050	79680
K ⁺ (ppm)	260	260	305	310	415
Ca ²⁺ (ppm)	2050	1900	1890	1860	1650
Mg ²⁺ (ppm)	630	660	680	730	630
Fe (ppm)	5,158	6,024	11,249	18,882	27,369
Cl (ppm)	133500	104000	133000	124000	119000
SO ₄ ²⁻ (ppm)	5400	5400	5600	5700	5300
HCO ₃ ⁻ (ppm)	40	35	38	35	33
NO ₃ ⁻ (ppm)	0	0	0	0	0
SiO ₂ (ppm)	11,5	20	24,9	39	37
pH	6,85	4,5	4,87	5,1	5,5
Conductivity (μS/cm)	80000	85000	80000	75000	75000

In general, the behavior of cations in solution is variable, with the concentration Na⁺ and Ca²⁺ decreasing, while K⁺, Mg²⁺ as well total-Fe, shows an increasing trend. This variability reflects the complexity imposed by the composition of the high salinity brine, with silicates dissolution and crystallization of halite and gypsum. The HCO₃⁻ does not present significant changes due to loss of CO₂ (depressurization) when

the test is completed and the chamber is open. During the four experiments the pH remained always low (<5.5), limiting the formation of carbonates.

4. Final remarks

After interaction of gabbro and brine for 1, 4, 16 or 64 days, no carbonate formation was observed. However, it was noticeable an increase in the dissolution of the silicates testified by the roughness of the surface of specimens. This mechanism of dissolution is in agreement with the increase of silica and iron concentration in solution. Nevertheless, the behaviour of cations within the brine after experiment is complex and needs to be better understood. The results obtained should be complemented with analyzes of elementary geochemistry and TGA. Future experiments will evaluate the relevance of the rock/brine/CO₂ relative proportions.

Acknowledgments

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