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Preliminary results from the experimental study of CO_2-brine-rock interactions at elevated T & P: implications for the pilot plant for CO_2 storage in Spain

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Abstract

A new experimental program has been carried out in order to study CO_2-brine-rock interactions susceptible to take place in conditions close to those expected in the pilot plant that is being developed in Spain (a carbonate reservoir located at more than 800 m depth, with 15% porosity, and a salinity of the native brine between 20 – 90 g/L). The combination of preliminary experimental and numerical modeling (PHREEQC) results suggests that the main geochemical processes are calcite dissolution and anhydrite precipitation.

Keywords: CO_2 storage; brine; experimental; modeling.

1. Introduction

One of the current European initiatives, in terms of research and development, on Carbon Capture and Storage (CCS) is the Experimental Platform “El Bierzo” which is supported by the Spanish Government through The *Fundacion Ciudad de la Energía (CIUDEN)*. One of the main objectives of CIUDEN project is the construction and operation of a Technical Development Plant that will be situated in Hontomin, municipality belonging to the province of Burgos (north of Spain), 30 Km north of the capital.

One of the objectives of this plant is the study of the geochemical processes taking place in the reservoir and seal rocks during and after the injection of CO_2. In this sense, geochemical reactions between injected CO_2, the host formation and its contained water, need to be studied in order to understand the geological trapping of CO_2 and the consequences on the petrophysical properties (porosity permeability and relative permeabilities) of the aquifer, potentially affecting its injectivity.

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This work presents the preliminary results using a new experimentation, designed to study (for conditions close to those expected in the Spanish pilot plant) all the key geochemical processes susceptible to develop between the main components of the CO_2 storage system.

2. Methodology

In several studies (e.g. [1]) brine-rock-CO_2 experiments were performed in autoclaves where the rock/brine ratio does not represent the real reservoir conditions. Here we present a complementary experimentation system in order to increase this ratio to build more relevant approach for real storage conditions. The experimentation was conducted in a small steel reactor designed in our laboratory, able to support high T&P conditions. To prevent the corrosion of the inside reactor due to the high reactivity of the dissolved CO_2, a Teflon sleeve has been used. Both the synthetic brine and CO_2 are injected using Gilson pumps and a heating mantle is placed around the reactor aimed to reach and stabilize the required temperature.

Moreover, if we compare the cost of this new desing with the commercial autoclaves it would be possible to work simultaneously with different reactors. Then, geochemical reactions at successive reaction times (dismantling each reactor separately) even at different T&P conditions could be studied.

The brine-rock-CO_2 experiment we present in this paper is the first that we have obtained. The experimental T&P conditions were 60ºC and 9 Mpa and the reaction time was 3 weeks. In order to have enough reactive surface area, which favors the reactivity of minerals, the rock sample was ground and sieved to a grain size less than 50 µm. After depressurizing and cooling, the reactor was dismantled and the soil fraction was separated from liquid product. The solid sample was dried in an oven at 60ºC for at least 48 hours before the chemical and mineralogical analysis were performed. The obtained brine After the Experiment (AE brine) was analyzed as soon as possible.

Natural brine, synthetic brine (synthetic brine before experiment), and the liquid product obtained after the experiment (AE Synthetic brine) were quantitatively analyzed for major dissolved ions (Ca, Na, Cl, Mg, K and sulfate), using ion chromatography (IC) Metrohm dual system 861.

The unreacted rock sample (B11.2) and the solid product after the experiment, were qualitatively analyzed with X-ray Diffraction (XRD) using a PANalytical X'Pert Powder Diffractometer. ICP-OES, after the solid digestion using EPA method 3052, has been used to the quantitative analysis.

3. Materials

With the purpose to synthesize representative brine of the native brine of selected Spanish test site, a total of eleven samples from the same well in Hontomin were analysed using ionic chromatography. All of these samples were sampled from well at 1355 meters depth but at different dates. It's supposed that the last sample brine is the most representative of the deep saline aquifer where CO_2 is going to be injected, as it is the closest to the storage structure. Then, this sample has been chosen to calculate the amount of salt needed to prepare the synthetic brine. Table 1 shows the composition of major elements presented in both brines.

Table 1. Natural brine composition (I.C) from the Spanish test site (Hontomin) and synthetic brine prepared in laboratory.

	pH	C.E (mS/cm)	Na^+	Cl^-	Ca^{2+}	Mg^{2+} (mg/L)	K^+	SO_4^{2-}	HCO_3^-
Natural brine	6.98	53.0	10384	20840	2058	1004	536	2242	336
Synthetic brine before experiment (BE brine)	7.26	54.5	10456	20855	1888	944	518	2600	317

The selected rock sample represents a potential reservoir (carbonate materials from the Jurassic; named B11.2) for the CO_2 storage in Spain. The mineral composition of rock is: 70% Calcite, 24% Quartz and <5% of Microcline. Fig 1b shows the XRD analysis of the reservoir rock (B11.2) as well as that of the solid collected after the experiment. Table 2 illustrates the chemical composition of major elements of the analyzed rocks (before and after the experiment) with ICP-OES.

Table 2. Major elements of solid samples (ICP-OES).

	Ca (mg/g)	K (mg/g)	Mg (mg/g)	Na (mg/g)
B11.2 / **B11.2 after experiment**	365.48 / **347.17**	9.66/ **9.59**	4.35/ **4.43**	0.29 / **2.22**

4. Results and discussion

Figure 1a illustrates the chemical composition variation between the synthetic brine before being injected in the reactor (BE brine), and final brine (AE brine) after its interaction with the limestone rock (B11.2) and the dissolved CO_2 during 3 weeks. The results reveal an increase of Ca^{2+} in AE brine that might be due to calcite dissolution because of CO_2 injection. CO_2 dissolution in brine causes its acidification (pH decrease) because of proton liberation. This acidification favours the carbonates dissolution, such as calcite, inducing in some experimental conditions, the precipitation of other mineral phases. In our experiment, this phase could be anhydrite (more likely at higher temperatures than gypsum stability domain) because of the sulfate ion decrease (43%) in the final reacted brine (AE brine). The anhydrite formation reduces the total content of disolved calcium from calcite dissolution.

Another highlight is the removal of Mg^{2+} from final solution, which could be justified with an incorporation process of this cation in the initial calcite. Finally, Na^+ and Cl^- decrease might be explained by a formation of a soluble salt crust on the solid surface (these stipulations needs to be corroborated by observations using for example SEM).

The chemical variations observed in the brine composition should be confirmed with chemical and mineralogical changes in the solid collected after the experiment. ICP-OES analysis of the solid after the experiment is shown in Table 2. It can be observed that calcium concentration has decreased compared to the initial concentration of B11.2 rock sample. This is coherent with the dissolution process of calcite and the subsequent anhydrite precipitation, which leads to a net increase of 6% of Ca^{2+} in AE brine.

In XRD (Fig. 1b) it is observed the general trend of calcite dissolution. In the initial sample (B11.2) the characteristic peak 104 ($2\theta = 29.42^{\circ}$) of calcite is more intense than the reacted sample. This may be due to a lower concentration of calcite in the reacted sample. On the other hand, there is a displacement of this peak as the reaction time is progressing which could be an indicative of Mg^{2+} incorporation in the structure of calcite crystals [2]. This incorporation could be justifiable with the analysis of total Mg concentration in the final solid (Table 2), which increases compared with the initial rock sample (B11.2).

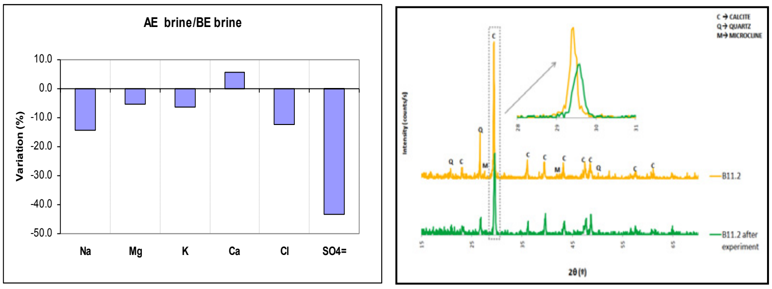

Fig. 1. (a) Chemical variations in synthetic brines (I.C) and (b) chemical variations in rock samples (XRD).

Regarding the anhydrite precipitation, and assuming that this mineral is the only sink of sulfate in the system, it could be estimated by chemical calculations, that throughout the experiment, less than a 0.5% of this phase had been formed, which is not enough to be observed by XDR.

4.1. Geochemical modeling

Finally, a preliminary modeling was carried out to evaluate the geochemical processes susceptible to be developed inside the reactor due to the interaction of CO_2-brine-rock in the experimental conditions. The geochemical code used for this purpose was PHREEQC. The main geochemical processes suggested from modeling, among others, are the calcite dissolution and the subsequent precipitation of anhydrite (Fig. 2).

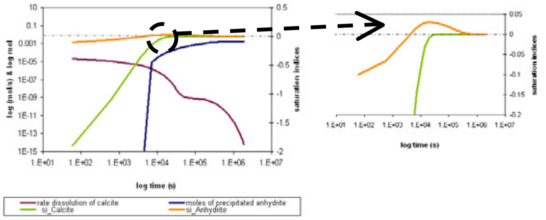

Fig. 2. Preliminary modeling of calcite dissolution and anhydrite precipitation. The rate of calcite dissolution (mol/s) can be observed together with the precipitated anhydrite number of moles and the saturation indices of both phases.

Initially, the brine is unsaturated with respect to calcite, leading to its dissolution, and it is almost in equilibrium with respect to anhydrite. It is noted that as the dissolution rate of calcite decreases, an increase on moles of anhydrite is predicted, resulting in tendency to a supersaturation of the brine with respect to the anhydrite. These obtained results are consistent with the geochemical interactions supposed above to justify chemical variations of the brine and the rock, as a consequence of CO_2 injection.

5. Conclusions

An experimentation device has been designed in order to approach to real reservoir conditions of brine/rock mass ratio. This new design allows working with different reactors simultaneously. The most significant compositional variations observed in brine after the experiment have been an increase of Ca^{2+}, as well as a Mg^{2+} and sulfate decrease. The main geochemical processes highlighted by those changes could be the calcite dissolution, the magnesium incorporation within calcium carbonate and the anhydrite precipitation. These processes should be carefully studied in successive experiments, as they involve a direct effect on reservoir rock. Anhydrite precipitation is kinetically rapid and may reduce porosity when CO_2 is injected into a deep aquifer. The introduced model is in agreement with the chemical variations observed.

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