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Research paper

Experimental study on the role of clays as sealing materials in the geological storage of carbon dioxide

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ABSTRACT

The aim of this work is to further the knowledge of reactions that can occur between carbon dioxide, diffused or escaped from a geological storage, and the sealing rock (e.g. clay-rich sediments). This research provides experimental data on the reactive behaviour of saponite (Mg-smectite), kaolin and Common Clay (composed of illite with minor montmorillonite) samples with CO_2 in the presence of water or under dry conditions. The mechanisms for physical and chemical retention of CO_2 were determined, and the influence of pressure, temperature and relative humidity on the effective sealing of the rock was examined. Firstly, the saponite did not physically adsorb CO_2, and an amorphous phase was formed due to carbonic acid attack. Nevertheless, the Mg-smectite exchange cations, lead to the precipitation of dolomite and increase the mineral CO_2 trapping. Secondly, the smectite and illite of the Common Clay sample were partially destroyed and the smectite destruction leads to the precipitation of some carbonates. Thirdly, kaolin did not physically trap CO_2 nor any chemical reaction. This paper has demonstrated that the cannibalization of saponite and Common Clays is not total and the precipitation of carbonates may occur, which could avoid the progressive destruction of the sealing rock.

1. Introduction

Geological storage of anthropogenic CO_2, as a greenhouse gas mitigation strategy, was first proposed in the 1970s. However, no significant research was done until the early 1990s, when the idea gathered momentum by work of individuals and research groups (Bachu et al., 1994; Baes et al., 1980; Gunter et al., 1993, 1997; Kaarstad, 1992; Koide et al., 1992; Korbol and Kaddour, 1994; Marchetti, 1977; van der Meer, 1992).

Geological CO_2 storage in sedimentary basins may be achieved within a variety of geological settings, the most suitable formations being oil fields, depleted gas fields, deep coal seams, and saline formations. To this end, CO_2 gas must first be compressed to a dense fluid state known as “supercritical” (31 °C, 7.4 MPa) (Metz et al., 2005).

Marini and Accornero (2009) have identified several drawbacks in the geochemical modelling of reactions occurring during the geological storage of CO_2. The main target of the geological storage of CO_2 is represented by sedimentary basins where brines are commonly present. Thus, it is necessary to describe specific interactions among solute species at the pertinent salinities, compute correct activity coefficients, and extrapolate these interaction parameters to the temperature and pressure conditions of the aquifer of interest.

According to Hitchen (1996), the geological storage of CO_2 through injection into deep reservoirs, involves three different processes: (i) hydrodynamic trapping as a gas or supercritical fluid below a cap-rock of low permeability; (ii) solubility trapping, through dissolution of CO_2 in aqueous solutions; (iii) mineral trapping, through the precipitation of secondary carbonates formed by dissolution of primary silicates and Al-silicates upon injection of CO_2 into aquifers.

Metz et al. (2005) have differentiated between physical and geochemical trapping. Physical trapping includes comprising both the stratigraphic and the residual trapping. The former occurs below low-permeability seals or cap-rocks, whereas the latter takes place in saline formations, where fluids migrate very slowly over long distances even in the absence of closed traps. Geochemical trapping encompasses solubility trapping and mineral trapping. Mineral trapping is especially attractive because CO_2 is permanently “fixed” (as stable carbonate minerals) in relatively deep geological formations, preventing its return to the atmosphere.

When CO_2 is injected in a sedimentary basin, it has a strong tendency to react with the enclosing rocks. Carbon dioxide in the subsurface can undergo a sequence of geochemical interactions with the rock and with water that will further increase storage capacity and effectiveness. First, when CO_2 dissolves in water, a solubility trapping occurs. The primary benefit of solubility trapping is that once CO_2 is dissolved, it no longer exists as a separate phase, thereby eliminating the buoyant forces that drive it upwards. Next, it will form ionic species as the rock dissolves, accompanied by a rise in the pH. Finally, some fraction may be converted to stable carbonate minerals (mineral trapping) (Gunter et al., 1993). Mineral trapping is believed to be a comparatively slow process, potentially taking a thousand years or longer. Nevertheless,

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the permanence of mineral storage, combined with the potentially large storage capacity present in some geological settings, makes this a desirable feature of long-term storage.

Dissolution of CO_2 in formation waters can be represented by the chemical reaction:

$$CO_2(g) + H_2O \leftrightarrow H_2CO_3 \leftrightarrow HCO_3^- + H^+ \leftrightarrow CO_3^{2-} + 2H^+.$$

The CO_2 solubility in formation water decreases as temperature and salinity increase. Dissolution is rapid when formation water and CO_2 share the same pore space, but once the formation fluid is saturated with CO_2, the rate slows and is controlled by diffusion and convection rates (Metz et al., 2005).

CO_2 dissolved in water produces a weak acid, which reacts with the sodium, calcium and potassium silicates or calcium, magnesium and iron carbonates in the reservoir to form bicarbonate ions by chemical reactions approximating to:

$$3\ \mathrm{K-feldspar} + 2H_2O + 2CO_2 \leftrightarrow \mathrm{Muscovite} + 6\ \mathrm{Quartz} + 2K^+ + 2HCO_3.$$

The reaction of the dissolved CO_2 with minerals can be rapid (days) in the case of some carbonate minerals, but slow (hundreds to thousands of years) in the case of silicate minerals. The formation of carbonate minerals occurs from continued reaction of the bicarbonate ions with calcium, magnesium and iron from silicate minerals such as clays, micas, chlorites and feldspars present in the rock matrix (Gunter et al., 1993, 1997).

Much research effort has been focused on the mineral trapping of CO_2 through carbonate precipitation. A prerequisite for carbonate precipitation is the availability of aqueous metal cations, derived from non-carbonate minerals, and their ability to combine with dissolved CO_2. The dissolution of metal-bearing silicate minerals is a very important potential source of these cations. The dissolution rate of such minerals is mainly controlled by the pH and temperature of the medium in contact with the mineral surfaces, whereas the influence of hydrodynamic conditions is nil, at least for surface-controlled processes.

Galán et al. (2011) suggested that sepiolite and palygorskite are capable of sequestering CO_2 through both a physical and mineral mechanism. At the same time, these minerals can be cannibalized by CO_2 in either a dry or wet environment, leading to partial decomposition of their structure together with a reduction in volume and mechanical resistance. This attack may lead to the partial destruction of the cap-rock, if those minerals are major components of the cap-rock, and possible CO_2 loss. In the case of palygorskite, however, the carbonates formed during reaction with CO_2 can precipitate and become chemically-bound (trapped). More importantly, the structural integrity of palygorskite is largely preserved, and CO_2 release is inhibited.

Espinoza and Santamaría (2012) studied the changes in electrical and capillary forces which are expected when CO_2 invades the water saturated pore space, and showed that the volume contraction and crack initiation are consistent with the sediment response within an effective stress framework. According to these authors the advection of CO_2 after breakthrough promotes further water dissolution in CO_2, the dehydration of the seal layer and increased suction.

The aim of this work is to obtain a fundamental understanding of the reactions that occur between carbon dioxide, diffused or escaped from a geological storage, and the sealing rock (i.e. clay-rich sediments). The research provides experimental data on the expected reactive behaviour of saponite-rich and kaolinite-rich rocks, and Common Clay (mainly composed of illite, with secondary smectite) with CO_2 in the presence of water or under dry conditions. The effect of pressure, temperature and relative humidity on the physical and chemical retention of CO_2 was investigated. The behaviour of these clays will be compared with the results obtained for sepiolite and palygorskite by Galán et al. (2011).

2. Materials and methodology

The samples selected for this study were two special clays and a Common Clay: a) Saponite (SAPO) supplied by TOLSA, S.A.; b) Kaolin (NM) from NW Iberian massif (Galicia, Spain); and c) Common Clay (CC1-3) from the Guadalquivir Basin (Spain).

In order to evaluate the reactions of the selected clays with CO_2, several experiments were carried out in a high-pressure and high-temperature Parr reactor. Depending on the water content of the material, temperatures between 80 and 100 °C were used to obtain high pressures close to CO_2 supercritical conditions (Table 3). The reaction time was during a period of ≥ 40 days, taking into account the result obtained by Galán et al. (2011) for sepiolite and palygorskite.

The mineralogical composition of the raw materials was determined by X-ray diffraction (D8 Avance model, Bruker) and the chemical composition performed by X-ray fluorescence (Axios model, Panalytical). The elemental carbon content was measured using an elemental analyzer (LECO CHNS 932).

A profile-fitting peak decomposition program, part of MacDiff 4.1.2 by Petschick (2004), was used to assess changes in the main representative peaks in the XRD patterns. A Pearson VII function was used to obtain the following parameters: peak position, height above the baseline, full width at half height, and the mixing parameter for the function. The initial fit results were iterated until the difference between the experimental and decomposed patterns was <5%.

The specific surface area of the samples (before and after reaction with CO_2), were determined by adsorption of N_2 and applying the BET equation (Gemini 2360 equipment). In addition soluble ions were measured by ICP-OES (Horiba Jobin Yvon, mod ultima2). The mineralogical composition of reacted materials and total elemental C was determined as noted above.

Mineralogically the saponite sample is a pure Mg-smectite, whereas the kaolin sample is comprised of kaolinite, quartz and muscovite. The Common Clay sample contains major calcite and illite with minor smectite and dolomite. The chemical composition of the samples is consistent with their mineralogy (Tables 1 and 2). Elemental C contents for saponite, kaolin and Common Clay samples are 0.355, 0.244 and 3.865 wt.% respectively. The higher C content measured in the Common Clay sample corresponds to its abundant calcite (43 wt.%) and minor dolomite (<5 wt.%) (Table 2).

3. Results

Table 4 shows BET-N_2 surface area results obtained in this study. Kaolin and Common Clay specific surface areas did not change with CO_2 treatment under dry or wet conditions. The BET values for saponite increased suggesting mineral decomposition by carbonic acid.

The changes produced on total pore volume are shown in Fig. 1. The presence of water during the CO_2 reaction produces an increment in the total pore volume mainly for saponite and only slightly for the Common Clay sample. However, the total pore volume of kaolin is not affected by the treatment with CO_2.

Thus, in relation to the physical trapping of CO_2 by these clays, the Common Clay sample showed a slight retention of CO_2, whereas saponite results suggest mineral decomposition by carbonic acid. No significant change was observed for kaolin.

Table 1
Mineralogical composition of selected clays (wt.%).

Sample	Quartz	Calcite	Dolomite	Feldspar	Illite	Smectite	Kaolinite
Saponite	Traces	–	Traces	–	–	98	–
Kaolin	35	–	–	tr	26[a]	–	38
Common Clay	15	43	<5		27	6	Traces

[a] Muscovite.