

Contribution of Applied Mineralogy Group to Capture and Storage of CO₂

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INTRODUCTION

The increase in average global temperatures since the mid-20th century may be ascribed to increased emission of anthropogenic greenhouse gases (Metz *et al.*, 2005). One mean for reducing net greenhouse gas emissions is "Capture and Storage of CO₂" (CCS). The storage of CO₂ may be affected through a number of mechanisms, including ex-situ mineral carbonation, oceanic storage, underground injection for enhanced fossil fuel recovery, and injection into saline aquifers or other geological reservoirs.

Geological CO₂ 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, CO₂ gas must first be compressed to a dense fluid state known as "supercritical" (31°C, 7.4 MPa). 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 CO₂ is permanently "fixed" (as stable carbonate minerals) in relatively deep geological formations, preventing its return to the atmosphere. When CO₂ 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 CO₂ dissolves in water, a solubility trapping occurs. The primary benefit of solubility trapping is that once CO₂ 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, 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.

The aim of this contribution is to evaluate the contributions to CCS of the Research Group "Applied Mineralogy", which was focus to: a) the role of clays as sealing materials in the geological storage of carbon dioxide, and b) the evaluation of carbonation capacity by wastes.

THE ROLE OF CLAYS AS SEALING MATERIALS IN THE GEOLOGICAL STORAGE OF CARBON DIOXIDE

Sepiolite and palygorskite were studied by Galán *et al.* (2011). They noted that, the BET-N₂ surface area of palygorskite decreased with treatment following with CO₂, possibly because the carbonic acid produced led to the formation of amorphous phases, partial destruction of the structure, and reduction in micropore volume. The exchangeable cations and the Mg ions released

into solution induce precipitation of dolomite. However, the behaviour of sepiolite could be different because this mineral would decompose within a short time.

Galán *et al.* (2011) suggested that sepiolite and palygorskite are capable of sequestering CO₂ through both a physical and mineral mechanism. At the same time, these minerals can be cannibalized by CO₂ 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 CO₂ loss. In the case of palygorskite, however, the carbonates formed during reaction with CO₂ can precipitate and become chemically-bound (trapped). More importantly, the structural integrity of palygorskite is largely preserved, and CO₂ release is inhibited.

Galán & Aparicio (2014) provides experimental data on the reactive behavior of saponite (Mg-smectite), kaolin and Common Clay (composed of illite with minor montmorillonite) samples with CO₂ in presence of water or under dry conditions.

The Mg ions released into solution induced the precipitation of dolomite. The reaction of saponite with CO₂ could be summarized through the following reaction:

Saponite + H₂CO₃ → saponite + "amorphous saponite" + amorphous silica + dolomite

The prolonged attack by carbonic acid can lead to: (a) a reduction in the volume of structural micropores

palabras clave: Captura y Secuestro de CO₂, arcillas, residuos construcción.

key words: CO₂ capture and storage, clays, construction and demolition waste.

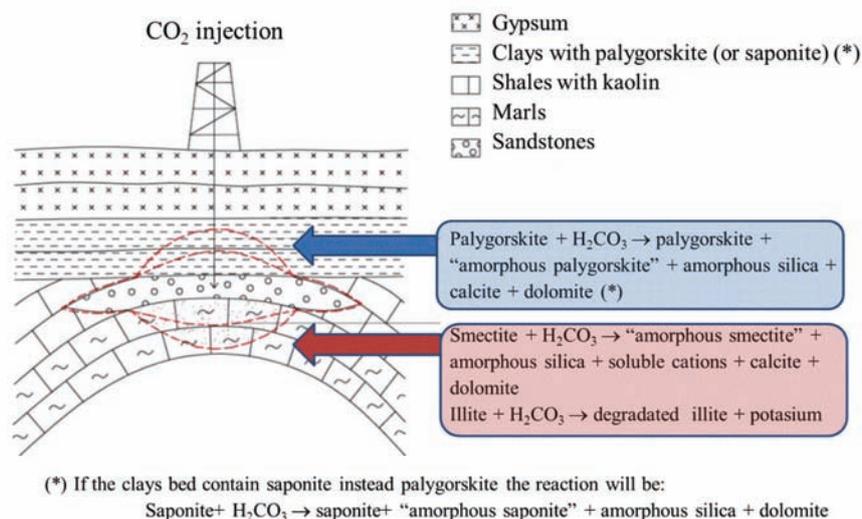


Fig. 1. Chemical and mineralogical conceptual model for a sandstone reservoir on marls and topped by kaolinite shales and clays with Mg-bentonite.

(radius < 1.5 nm), that are contributing to generate a higher specific surface; (b) an increase in the concentration of surface silanol (SiOH) groups through rupture of Si-O-Si bonds on the saponite surface, which accept either a proton or a hydroxyl ion (protonation and hydroxylation) to compensate their residual charge; and (c) a progressive destruction of the saponite structure.

Saponite is capable of sequestering CO₂ through mineral reactions. At the same time, this mineral is subject to attack by CO₂ in either a dry or wet environment, leading to partial decomposition of its structure together with a reduction in volume and mechanical resistance. This attack may lead to the partial destruction of the cap-rock containing this smectite as major component, and possible CO₂ loss. However, the carbonates formed during reaction with CO₂ can precipitate. Thus, a portion of the CO₂ is chemically bound ("trapped"). More importantly, the structural integrity is largely preserved, and CO₂ release is inhibited.

The behaviour of saponite could be compared with those obtained by Galán *et al.* (2011) in the case of sepiolite, except that in the latter the precipitation of Mg carbonate is inhibited by kinetic reasons. After the experiment with saponite the dolomite precipitation is evident in presence of water, including interlayer water of the saponite structure.

The formation and relative stability

of dolomite will offset problems related to volumetric variations or mechanical resistance of the cap rock overlaying the geological reservoir of CO₂. This might be because the carbonic acid produced led to the formation of amorphous phases, partial destruction of the structure, and reduction in micropore volume. The exchangeable cations and the Mg ions released into solution induce precipitation of dolomite.

It can therefore be predicted that when Common Clay-rich rocks (mainly illitic marls) are sealing materials, these rocks would slightly decompose, at least in the very first few metres of the cap-rock overlaying the geological reservoir where CO₂ is stored under supercritical conditions. The resultant variations in volume and the consequent decreasing of mechanical resistance of the cap-rock would cause operational problems.

Kaolin is not capable of sequestering CO₂ through both a physical mechanism and mineral reaction, but has the advantage that it is inert to chemical degradation by carbonic acid.

According to the results presented a possible model for the mineralogical evolution of a reservoir in sandstone is presented in figure 1. According to this research and the behaviour of clays in acid media, the sealing of a CO₂ reservoir could be advisable using clays rich in kaolinite, palygorskite and saponite, in this preferential order. However, a mathemati-

cal model needs to be developed to describe the sequence of reactions between CO₂ and clay rocks (reaction path and reactive transport) and then validated by experimental measurements for long-term reactive effects.

REACTIVITY OF WASTES WITH CO₂

Reactivity of construction and demolition waste with carbon dioxide

The aim of this research is to assess the possibilities of CO₂ sequestration on ceramic building materials and other construction and demolition waste, in order to propose the injection of CO₂ in these waste used for mined reclamation Galán and Aparicio (2010). Raw materials with suitable composition to prepare porous red wall tile, porous light-weight bricks and porous light-coloured wall tiles were heating between 800 and 900°C. The reactivity of those heating bodies with CO₂ was followed in situ using an X-ray diffractometer equipped with a temperature chamber, and a reactor to work with different pressure range. The reaction products were evaluated in function of relative humidity and reaction temperature for a constant pressure of CO₂.

The principal conclusions are that: a) calcite was the main product formed in any experimental conditions, b) the presence of water is essential for the carbonation reaction; c) those formulations heating at 850°C presented a higher reactivity than the others, because of the mineralogical composition of the starting materials. The amount of calcite increased until five times the original amount in function of the experimental conditions.

The principal advantages of the carbonation of building ceramic materials could be: a) it is not necessary to use CO₂ in critical conditions for the storage; b) it is not necessary 800 m depths; c) the volume of construction materials waste is high and usually are employed for mining reclamation.

Reactivity of other wastes with carbon dioxide

The research group Applied Mineralogy have developed a patent

(Moriña et al., 2013) to synthesize calcium silicates appropriate to sequester CO₂. The calcium silicates are obtained using sub products or industrial wastes rich in calcium and silica.

During the synthesis process from wastes the aim has been to reduce the energetic cost to maximize the efficiency on the capture of CO₂. The temperature of the reaction has been reduced from 1000°C to 600-800°C.

The sub product obtained from the carbonation of calcium silicates presents an appropriate particle size distribution and abrasivity to be employed at the industry (filler of plastic).

ACKNOWLEDGMENTS

This research was granted by Instalaciones Inabensa SA. Diffraction patterns and chemical analysis were performed using the facilities of the General Research Centre at the University of Seville (CITIUS).

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