Chemical Geology 289 (2011) 98–113

Contents lists available at ScienceDirect

Chemical Geology

journal homepage: www.elsevier.com/locate/chemgeo

Dedolomitization as an analogue process for assessing the long-term behaviour of a CO_2 deep geological storage: The Alicún de las Torres thermal system (Betic Cordillera, Spain)

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A R T I C L E I N F O

Article history:
Received 18 February 2011
Received in revised form 22 July 2011
Accepted 23 July 2011
Available online 3 August 2011

Editor: J. Fein

Keywords:
Dedolomitization
Dissolved inorganic carbon (DIC)
Betic Cordillera Intramontane Tertiary Basin
CO_2 deep geological storage (DGS)
Natural analogues

A B S T R A C T

Carbon dioxide deep geological storage, especially in deep saline aquifers, is one of the preferred technological options to mitigate the effects of greenhouse gases emissions. Thus, in the last decade, studies characterising the behaviour of potential CO_2 deep geological storage sites along with thorough safety assessments have been considered essential in order to minimise the risks associated with these sites. The study of natural analogues represents the best source of reliable information about the expected hydrogeochemical processes involved in the CO_2 storage in such deep saline aquifers.

In this work, a comprehensive study of the hydrogeochemical features and processes taking place at the natural analogue of the Alicún de las Torres thermal system (Betic Cordillera) has been conducted. Thus, the main water/CO_2/rock interaction processes occurring at the thermal system have been identified, quantified and modelled, and a principle conclusion is that the hydrogeochemical evolution of the thermal system is controlled by a global dedolomitization process triggered by gypsum dissolution. This geochemical process generates a different geochemical environment to that which would result from the exclusive dissolution of carbonates from the deep aquifer, which is generally considered as the direct result of CO_2 injection in a deep carbonate aquifer. Therefore, discounting of the dedolomitization process in any CO_2 deep geological storage may lead to erroneous conclusions. This process will also influence the porosity evolution of the CO_2 storage formation, which is a very relevant parameter when evaluating a reservoir for CO_2 storage. The geothermometric calculation performed in this work leads to estimate that the thermal water reservoir is located between 650 and 800 m depth, which is very close to the minimum required to inject CO_2 in a deep geological storage.

It is clear that the proper characterisation of the features and hydrogeochemical processes taking place at a natural system analogous to a man-made deep geological storage will provide useful conceptual, semi-quantitative and even quantitative information about the processes and consequences that may occur at the artificial storage system.

1. Introduction

The increase of greenhouse gas emissions in the atmosphere during the twentieth century is generally considered to have contributed to global warming. In an attempt to mitigate the dangerous effects of rising temperatures, several important actions have been adopted, actions that were summarised, for the first time, in the so-called Kyoto Protocol. This was signed in December 1997, with the aim of mitigating global climate change by reducing the emissions of greenhouse gases that were identified as mainly responsible for this global process. Thus, in 2005, the greenhouse gases emissions market began operating and set the amounts to be paid for emissions exceeding the pre-assigned quota for each country. This measure gave an economic value to the CO_2 not emitted into the atmosphere and stimulated the development of technologies focused on reducing such emissions. One of these technological alternatives is CO_2 sequestration that includes three main research lines: capture, transport and storage (CCS). At present, deep geological storage (DGS) is the most accepted method for CO_2 sequestration, with the most natural systems envisaged for this purpose being the gas and oil depleted reservoirs, the methane-bearing deep non-mining coal seams, and the deep saline aquifers. In Spain, the absence of the first two types of system along with the abundance of deep saline aquifers, usually with high storage capacity, are the main reasons that

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doi:10.1016/j.chemgeo.2011.07.017

most studies in this country are currently focused on the characterisation of the hydrogeochemical interaction processes that can occur in deep saline aquifers, specifically hosted in carbonate formations, after the injection of supercritical CO_2. Due to the increasing interest in this alternative, which is presently being implemented in many other countries, the proper characterisation of the water-gas-rock interaction processes that take place in a natural CO_2-rich deep carbonate aquifers will allow a better understanding of those processes that may occur after the CO_2 injection into a deep saline aquifer hosted in a carbonate formation.

Although modelling exercises and experimental work, both in the field and in the laboratory, can provide valuable information about the processes involved in such storage (Gunter et al., 1997; Shiraki and Dunn, 2000; Johnson et al., 2001; 2004; Rochelle et al., 2002; Kaszuba et al., 2003; 2005; Cipolli et al., 2004; Pruess et al., 2004; Soong et al., 2004; Xu et al., 2004, 2005, 2007; Bateman et al., 2005; Emberley et al., 2005; Gaus et al., 2005; Knauss et al., 2005; Lagneau et al., 2005; Moore et al., 2005; Noiriel et al., 2005; White et al., 2005; Bertier et al., 2006; André et al., 2007; Audigane et al., 2007; Gherardi et al., 2007), the only reliable source of information to assess the long-term behaviour of a CO_2-DGS in deep saline aquifers are the natural analogue systems for CO_2 storage, with or without CO_2 leakage. Consequently, many works, mainly focused on the hydrogeochemical processes involved in these natural systems, characterised by high CO_2 partial pressures, have been recently performed (Anderson et al.;, 2006; Annunziatellis et al., 2008; Czernichowski-Lauriol et al., 2003; Gaus et al., 2005; Haszeldine et al., 2005; Lafortune et al., 2009; Lewicki et al., 2007; Oldenburg and Lewicki, 2006; Orlic et al., 2005; Pauwels et al., 2007; Quattrocchi et al., 2009; Stevens;, 2005; Summers et al., 2005; Worden, 2006).

Among the main hydrogeochemical processes that can occur in both natural and artificial CO_2 storages in carbonate formations, dedolomitization should be highlighted. This geochemical process, involving dissolution of dolomite and precipitation of calcite, has been extensively studied in both thermal and environmental hydrological systems in relation to: i) hydrochemistry, groundwater origin, palaeohydrogeology, evolution and water quality of carbonate aquifers (Al-Ruwaih et al., 2005; 2007; Back et al., 1979, 1983; Capaccioni et al., 2001; Carroll et al., 2008; Hanshaw and Back, 1985; Leybourne et al., 2009; Lopez-Chicano et al., 2001; Moral et al., 2008; Plummer and Back, 1980; Wang and Jaffe, 2004); ii) tectonic brecciation and porosity occlusion (Katz et al., 2006); and iii) anthropogenic activity on sediments (Pacheco and Szocs, 2006); and iv) CO_2 geological storage and natural and artificial analogue systems (Romanak and Smyth, 2008; Assayag et al., 2009; Auqué, et al., 2009; Romanak et al., 2009; Casteleyn et al., 2010; Prado et al., 2010a, 2010b; Romanak et al., 2010). As a preliminary conclusion extracted from all of these research works, it can be stated that dedolomitization process should be taken into consideration since it is a very important geochemical process that can occur in any hydrogeochemical environment similar to a CO_2-DGS after CO_2 injection, considering the existence of a Ca source, which is the main triggering mechanism of this process. Regarding this input of Ca several scenarios have been invoked, such as: dissolution of gypsum or anhydrite within a carbonate aquifer (Lopez-Chicano et al., 2001); sulphate-rich fertilisers (Pacheco and Szocs, 2006); and mixing of fresh and Ca-SO_4^{2-} waters, accompanied by the infiltration of Na-Cl brines (Romanak et al., 2010).

In this work, a comprehensive study of the Alicún de las Torres thermal system has been conducted since, according to Pérez del Villar et al. (2009), the site is characterised by the existence of: i) a carbonate aquifer with high dissolved inorganic carbon (DIC) located between 650 and 800 m deep; ii) a fluvial-lacustrine sedimentary formation over 800 m thick acting as a sealing formation for the deep aquifer; iii) an artesian well that intersects the above mentioned carbonate aquifer at about 800 m deep, from which DIC-enriched water is being used for agricultural purposes; iv) 5 thermal springs at a temperature of about 34 °C with evidences of degassing processes; v) meteoric springs close to the thermal ones without evidence of significant degassing processes, indicating that they are not hydraulically connected with the previous thermal springs; vi) high ^{222}Rn concentrations in the thermal springs without any evidence of U-rich rocks in the site and vii) present and fossil travertine deposits directly related to the degassing processes of the thermal waters. For these reasons, it represents a natural system with many similar characteristics to those of an artificial CO_2-DGS. Thus, most of the hydrogeochemical processes taking place in this system would be expected to be analogous to those in a CO_2-DGS with or without CO_2 leakage processes.

The main objectives of this work are the following: i) to characterise the hydrogeological and hydrogeochemical features of the Alicún de las Torres thermal system in order to better understand its overall behaviour, by refining the pre-existing hydrogeological model, identifying the water types and determining the temperature and depth of the thermal reservoir; ii) to identify the main water/gas/rock interaction processes which determine the hydrogeochemical evolution of the thermal system, by means of hydrogeochemical modelling, emphasising the hydrogeochemical environment generated by the dedolomitization process, and comparing it to the expected environment driven by the CO_2 injection in a DGS; and iii) to assess this thermal system as a potential sink for C and/or CO_2 by studying the behaviour of C alongside the hydrogeochemical evolution of the system.

Furthermore, the extrapolation of these three objectives to other locations with similar geological and hydrogeological features can be carried out, which is the main objective of any study performed on a particular natural analogue (Miller, 1994). Finally, some conclusions arising from this work can be used to: i) assess the long-term safety and behaviour of any CO_2-DGS in carbonate aquifers; ii) generate public confidence in the CCS technology; and iii) supply technical and scientific information to corresponding national institutions to assist in decision making.

2. The Alicún de las Torres site

The Alicún de las Torres thermal system is located in the southeast of the Iberian Peninsula, at the contact zone between the two main domains of the central sector of the Betic Cordillera: the External and Internal Zones (Fig. 1). This contact is fossilised by the filling materials of the Guadix-Baza Basin that is the main intramontane Neogene basin in the Betic Cordillera. Therefore, the basement of this thermal system includes Triassic metamorphic materials, which outcrop to the south (Internal Zones), and Mesozoic carbonate materials, outcropping to the north (External Zones). In the Internal Zones, materials from the Alpujárride complex are well represented. This complex is the largest of the Betic Cordillera that, in the studied area, particularly in the Sierra de Baza, overlies the Nevado-Filábride Complex. The Alpujárride materials were affected by a moderate to severe Alpine metamorphism, and lithologically are characterised, from the bottom to the top, by: i) a metapelitic formation, mainly formed by Paleozoic shales; and ii) a second Permo-Triassic unit of the same nature, with interlayer limestone, dolomite and quartzite levels. Finally, towards the top of the Alpujárride Complex, a middle-upper Triassic formation appears, constituted of both calcite and dolomite marbles, with frequent interbedded gypsum levels that have been frequently identified in the field.

In turn, materials that outcrop to the north belong to the External Zones and are characterised by sediments aged between the upper Triassic and the Eocene, and mainly formed by evaporitic-bearing marls from Keuper; dolomitic limestones from the Jurassic Milanos formation; and the interbedded marls belonging to the Fardes and Lechos Rojos formations, aged between the Cretaceous and Paleogene (Viseras et al., 2004).

The Tertiary materials, consisting of the infill of the Guadix-Baza Basin, are mainly characterised by sandstones and conglomerates, as well as marls, clays and gypsum.