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A combined methodology using electrical resistivity tomography, ordinary kriging and porosimetry for quantifying total C trapped in carbonate formations associated with natural analogues for CO_2 leakage

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ABSTRACT

Currently, carbon deep geological storage is one of the most accepted methods for CO_2 sequestration, being the long-term behaviour assessment of these artificial systems absolutely essential to guarantee the safety of the CO_2 storage. In this sense, hydrogeochemical modelling is being used for evaluating any artificial CO_2 deep geological storage as a potential CO_2 sinkhole and to assess the leakage processes that are usually associated with these engineered systems. Carbonate precipitation, as travertines or speleothems, is a common feature in the CO_2 leakage scenarios and, therefore, is of the utmost importance to quantify the total C content trapped as a stable mineral phase in these carbonate formations.

A methodology combining three classical techniques such as: electrical resistivity tomography, geostatistical analysis and mercury porosimetry is described in this work, which was developed for calculating the total amount of C trapped as $CaCO_3$ associated with the CO_2 leakages in Alicún de las Torres natural analogue (Granada, Spain).

The proposed methodology has allowed estimating the amount of C trapped as calcite, as more than 1.7 Mt. This last parameter, focussed on an artificial CO_2 deep geological storage, is essential for hydrogeochemical modellers when evaluating whether CO_2 storages constitute or not CO_2 sinkholes. This finding is extremely important when assessing the long-term behaviour and safety of any artificial CO_2 deep geological storage.

1. Introduction

Currently, CO_2 Deep Geological Storage (CO_2-DGS) is one of the preferred technological options to mitigate the effects of greenhouse gas emissions and the most accepted method for CO_2 sequestration. The increasing interest in this alternative, which is presently being implemented in many countries, is stimulating numerous studies in order to elucidate the long-term behaviour of a potential CO_2-DGS, along with a thorough safety assessment (Anderson et al., 2006; Hansen et al., 2013; Keating et al., 2013; Lafortune et al., 2009; Lewicki et al., 2007; Quattrocchi et al., 2009; Summers et al., 2005). Gas and oil depleted reservoirs, methane-bearing deep, non-mining coal seams, and deep saline aquifers are the most natural systems envisaged for this purpose. Accordingly, many research works focussed on the interaction processes between saline aquifers and supercritical CO_2 have been recently performed on some natural analogues (NNAA) characterised by their high pCO_2 (Annunziatellis et al., 2008; Chopping and Kaszuba, 2012; Harvey et al., 2013; Haszeldine et al., 2005; Li et al., 2013; Oldenburg and Lewicki, 2006; Orlic et al., 2005; Pauwels et al., 2007; Stevens, 2005; Worden, 2006). These studies have greatly contributed to the prediction and assessment of the long-term behaviour and safety of any CO_2-DGS hosted in deep saline aquifers.

The abundance of deep saline aquifers in Spain, usually with high storage capacity, is the main reason that most studies are currently focussed on the characterisation of the abovementioned geochemical processes, as well as other physical and physico-chemical events occurring in some NNAA of a CO_2-DGS, such as leakages and carbonate precipitation (Auqué et al., 2009; Auque et al., 2013; Prado-Pérez and Pérez del Villar, 2011; Rodrigo-Naharro et al., 2013; Trippetta et al., 2013; Vaselli et al., 2010). In this regard, hydrogeochemical modelling and reactive transport modelling are necessary to investigate long-term CO_2 injection in deep saline aquifers and can solve many problems related to: i) fate and transport of injected CO_2; ii) storage safety and iii) impact of potential leakage on the groundwater quality (Xu, 2009). To properly assess the long-term safety of these sites is of utmost importance quantifying all the hydrogeochemical processes implied during the CO_2 injection and storage. Accordingly, the total amount of C precipitated as calcite,

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which is associated to any CO_2 leakage, is one of these processes that need to be correctly estimated prior to perform any direct or inverse modelling. Moreover, several studies show that it is possible estimating the total C input into a closed system from the carbonate amount precipitated as travertine (Pentecost and Coletta, 2007; Spiro and Pentecost, 1991).

One of the main physical processes occurring in any CO_2-DGS is the CO_2 leakage usually associated with carbonate precipitation, either as travertine or speleothems (Auqué et al., 2009; Prado-Pérez and Pérez del Villar, 2011). During the last decades, travertine formations have been mainly studied in relation to their mineralogical, petrographic, petrophysical, geochemical and isotopic features, in order to obtain data on their genesis, dating, palaeoclimatic and even seismic implications (Auler and Smart, 2001; Faccenna et al., 2008; Frank et al., 2000; Horowitz, 1987, 1989, 2001; Liu et al., 2006; Menking et al., 2004; Ortiz et al., 2006; Pentecost, 1995, 2005; Prado-Pérez, 2012; Prado-Perez et al., 2013a, 2013b; Soligo et al., 2002). However, only few studies focussed on the CO_2-DGS technologies have been found. Only those carried out by Moore et al. (2005), in the frame of the USA NACS programme; and Prado-Pérez and Pérez del Villar (2011), in the frame of the PSE-CO_2 Spanish Project, consider these carbonate formations as external manifestations of CO_2 leakage from a deep CO_2–water reservoir.

Besides this, hydrogeochemical modelling, geophysics and geostatistical methodologies are currently being used to support other geological data. Thus, many papers applying geophysics to CO_2 storage have been published (Bergmann et al., 2012; Hovorka et al., 2011; Jafargandomi and Curtis, 2012; Kiessling et al., 2010; Kim et al., 2011; Le Roux et al., 2013; Schmidt-Hattenberger et al., 2011, 2012; Streich et al., 2010; White, 2011; Wuerdemann et al., 2010).

The Alicún de las Torres thermal system, comprehensively studied by Prado-Pérez (2012), Prado-Pérez and Pérez del Villar (2011) and Prado-Perez et al. (2013a, 2013b) 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 sealing formation; iii) 5 thermal springs at a temperature of about 34 °C, with evidence of degassing processes; iv) high ^{222}Rn concentrations in the thermal waters without any evidence of U-rich rocks in the site; and v) present and fossil travertine deposits directly related to water degassing processes. All of these features allow considering this natural system as a good NNAA of an artificial CO_2-DGS affected by natural processes of CO_2 leakages with associated thermogene travertine.

This work is aimed to quantify the total C trapped in any carbonate formation associated with CO_2 leakages from NNAA of CO_2-DGS. This parameter is essential to hydrogeochemical modellers when performing any direct or inverse modelling, which are currently used to assess the storage/leakage system as a potential C sinkhole. This fact is extremely important when evaluating the long-term behaviour and safety of a CO_2-DGS, since it gives support to reactive-transport and hydrogeochemical modelling.

To meet this objective, the geology of the Alicún de las Torres was complemented with 2 ERT campaigns, obtaining a dataset that was analysed by using ordinary kriging and a comprehensive porosity study in order to: i) determine the geological features of each travertine unit; ii) establish the thickness of each unit; iii) define the spatial relationships among them; iv) estimate the total volume of travertine in the site and v) estimate the total C retained as $CaCO_3$.

2. Geological background

The Alicún de las Torres thermal system and the associated travertine formation are located to the southeast of the Iberian Peninsula, at the contact 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 Cordilleras. 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). Geological formations that predominate in the Internal Zones are mainly represented in the Alpujárride Complex, which is the largest geological complex of the Betic Cordilleras. This Complex overlies the Nevado-Filábride Complex that outcrops in the Sierra de Baza, located in the studied area. 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 interbedded limestone, dolomite and quartzite beds. Finally, to the top of the Alpujárride Complex appears a middle-upper Triassic formation constituted by both calcite and dolomite marbles, with frequently interbedded gypsum seams.

The materials outcropping to the north belong to the External Zones, are dated between the Upper Triassic and Eocene, and they are mainly formed by gypsum and evaporitic materials, from Keuper; limestone and dolomite, 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., 2005).

From a tectonic view point, the Negratín fault, also known as Cádiz–Alicante fault, and the Baza normal fault are the most important structures in this area. The first consists of a NE–SW dextrose strike-slip fault system, which outcrops only to the northern margin of the basin. Along this fault system, several thermal springs, including Alicún de las Torres, Sierra Elvira and Zújar are aligned. The Baza fault, with 37 km in length, divides the tertiary Basin into two sub-basins: the Guadix basin, located to the west, and the Baza basin, situated to the east (García-Tortosa et al., 2008).

The thermal springs aligned on the Cádiz–Alicante strike-slip fault have been exploited since the 18th century for medical and therapeutic purposes. Important travertine formations are always associated with these springs, as in the case of the Alicún de las Torres. This last travertine formation is located in the central-western zone of the Guadix–Baza sedimentary basin, just in the contact between the post Miocene materials from the Guadix–Baza Tertiary basin and the Mesozoic materials from the External Zones (Subbetic Zone) of the Betic Cordilleras (see Fig. 1). Furthermore, this travertine formation is unconformable over Cretaceous and Paleocene materials and the contact is defined by a discontinuous, strongly-cemented and polygenic conglomerate bed, as well as sands with typical sedimentary structures of fluvial terraces. The formation of the travertines in the site is mainly due to CO_2 leakage processes that take place in the thermal springs, and consists of three partially overlapping units (Diaz-Hernandez and Julia, 2006; Prado-Pérez, 2012; Prado-Pérez et al., 2013b), known as Lower, Intermediate and Upper Units (Fig. 2).

The Lower Unit is about 40 m thick and consists of several sigmoid subunits that overlap each other towards the Fardes River. These sigmoid subunits are typically found in prograding deposits, resulting in dam and cascade morphologies. The Intermediate Unit overlies the Lower Unit and the Cretaceous–Palaeocene basement. Its total thickness is similar to the Lower Unit (40 m) and contains abundant tufa. Finally, the Upper Unit is approximately 60 m thick and it is directly in contact with the Subbetic substrate. It is structured in 3 strata that prograde to cascade morphologies towards the Fardes Valley (Prado-Pérez, 2012; Prado-Perez et al., 2013b).

3. Methodology

3.1. Electrical resistivity tomography

A total of 21 ERT profiles were performed during two consecutive field campaigns. Eleven profiles were performed during the first campaign and characterised by a distance among electrodes of 10 m. With this configuration the exploration depth is around 150 m in depth. The second campaign consisted of 10 profiles characterised by a distance among electrodes of 5 m, leading to a higher resolution and to a lesser exploration depth (≈80 m) (Table 1, Fig. 3).