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Petrophysical characterization of the Dolomitic Member of the Boñar Formation (Upper Cretaceous; Duero Basin, Spain) as a potential CO_2 reservoir

Caracterización petrofísica del Miembro Dolomítico de la Formación Boñar (Cretácico Superior; Cuenca del Duero, España) para su uso como potencial reservorio de CO_2

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ABSTRACT

Boñar Formation (Upper Cretaceous) is a mainly carbonate succession, which outcrops in the North of Duero Basin (Spain). According to the existing data, the Dolomitic Member of this formation appears to be the most suitable for geological storage of CO_2.

The main objective of this study is to find evidence to support, clarify and specify –at an initial level– the potential of the Dolomitic Member of the Boñar Formation as a geological reservoir.

The study covers density, porosity and permeability tests on samples obtained from the outcrop of the succession near the village of Boñar (León). According to the analysis and interpretation of the mentioned petrophysical properties, the porosity of the Dolomitic Member is within the acceptable range for CO_2 geological storage, but the permeability values are far too low. This minimizes the possibilities of the Dolomitic Member –and probably of the whole Boñar Formation– to become an appropriate CO_2 reservoir.

Keywords: CO_2 storage; Upper Cretaceous; Boñar Formation; density; porosity; permeability

RESUMEN

La Formación Boñar (Cretácico Superior) es una sucesión carbonática que aflora al Norte de la Cuenca del Duero (España). Según datos previos, el Miembro Dolomítico de esta formación es el que muestra características petrográficas más favorables para almacenamiento geológico de CO_2.

El principal objetivo de este trabajo es el aporte de elementos de juicio que apoyen, clarifiquen y concreten –a un nivel de estudio preliminar– la potencialidad del Miembro Dolomítico de la Formación Boñar como roca almacén.

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Se han realizado un conjunto de ensayos de densidad, porosidad y permeabilidad a partir de muestras de dolomías recogidas en superficie en las proximidades de la localidad de Boñar (León). La cuantificación e interpretación de estas propiedades petrofísicas muestra que la porosidad de las rocas del Miembro Dolomítico es adecuada para el objetivo buscado, si bien sus valores de permeabilidad son bastante bajos, lo que reduce las posibilidades de este miembro y muy probablemente de toda la formación de convertirse en reservorio de CO_2.

Palabras clave: almacenamiento de CO_2; Cretácico Superior; Formación Boñar; densidad; porosidad; permeabilidad

Introduction

During the past few decades a continuous increase has been registered in atmospheric CO_2 concentration (Le Quéré *et al*., 2013), which may be one of the main factors enhancing global warming.

Nowadays, fossil fuels are the main energy source and they are expected to remain so, representing around 70% –depending on the projection scenario– in the energy mix, by 2035 (International Energy Agency, 2012). Therefore, there is a need to implement measures in order to attenuate CO_2 emissions. These measures are focused on three fields: energy saving and efficiency strategies, renewable energy development and Carbon Capture and Storage technologies (CCS) (International Energy Agency, 2012).

CCS techniques have a great potential, expected to contribute with a 17% decrease on total CO_2 emissions by 2035 (International Energy Agency, 2013). Geological CO_2 storage is the last step of the CCS process. This fluid must be confined in a porous and permeable formation (reservoir rock) at more than 800 metres depth, sealed by an impermeable rock layer (cap rock) (Metz *et al*., 2005).

One of the most widespread reservoir formations are saline aquifers. Concerning Spain, some of these formations –like the Cretaceous of Duero Basin– have been designated by the Spanish Geological Survey (IGME) as suitable CO_2 reservoirs (García Lobón *et al*., 2010; Zapatero Rodríguez *et al*., 2009; Llamas *et al*., 2014). Hurtado Bezos (2010) provided an estimation of the regional storage capacity of the Upper Cretaceous Carbonate facies but, unfortunately, had limited access to quantitative values of porosity and permeability.

Petrographic and petrophysical characterization of outcrop samples is one of the first steps of CO_2 reservoir exploration. In this context, the main objective of this study is to provide real porosity and permeability values which may be used, in an initial study, to determine the potential of the Upper Cretaceous carbonate facies as CO_2 reservoir. For definitive and more reliable results, further studies based on borehole samples should be conducted.

Geological setting

Cretaceous rocks crop out in the North of the Duero Basin in a narrow band of East-West orientation, bordering the Cantabrian Zone and lying with unconformity above Paleozoic rocks (Figure 1). The lower part of the Cretaceous succession – Voznuevo Formation (Evers, 1967) – is mainly composed of sandstones, whereas the upper part – Boñar Formation (Evers, 1967) – has mainly a carbonate composition. Nevertheless, the Boñar Formation presents a significant lithological diversity, according to which it can be divided into four members (Gómez-Fernández *et al*., 2003; Figures 1 and 2). From base to top, these members are: (1) Calcarenitic Member (BM1), mainly consisting of bioclastic grainstones, (2) Argillaceous and Sandy Member (BM2), composed of claystones and marls in the lower part and of poorly consolidated sandstones in the upper part, (3) Heterolithic Member (BM3), composed of alternations of marls, micritic limestones, calcarenites and sandstones, and (4) Dolomitic Member (BM4), consisting of dolomites, which alternate with marls on the top. Figure 2 shows the thickness of the Boñar Formation and its members in the studied section, in a graphic form.

The sandstones of the top of BM2 and the dolomites of BM4 are the rocks of highest porosity within the Boñar Formation (Gómez-Fernández *et al*., 2003) and therefore, theoretically, the most suitable as reservoir rocks. This study, however, only addresses the dolomites of BM4 due to the following reasons: a) According to the criteria established by Chadwick *et al*. (2008), the thickness of the sandstones in BM2 (<25 m in the Boñar-Las Bodas series) is not considered a positive indicator for storage site suitability (Table 2) and, b) the sandstones are poorly consolidated in outcrop and, thus, they are not appropriate for preparation of

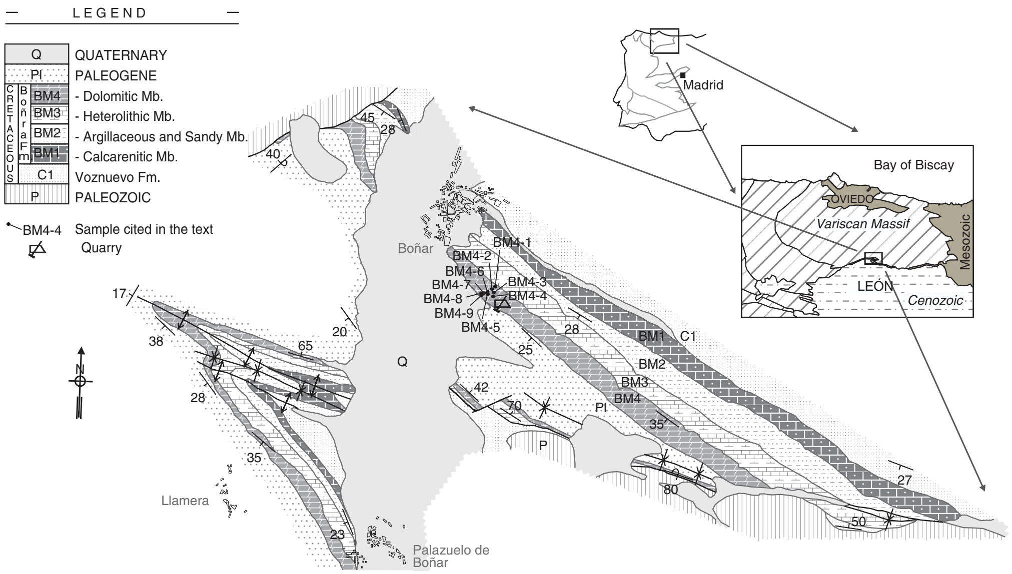

Figure 1.—Geological map of Boñar Formation in the studied area, with the samples' location.

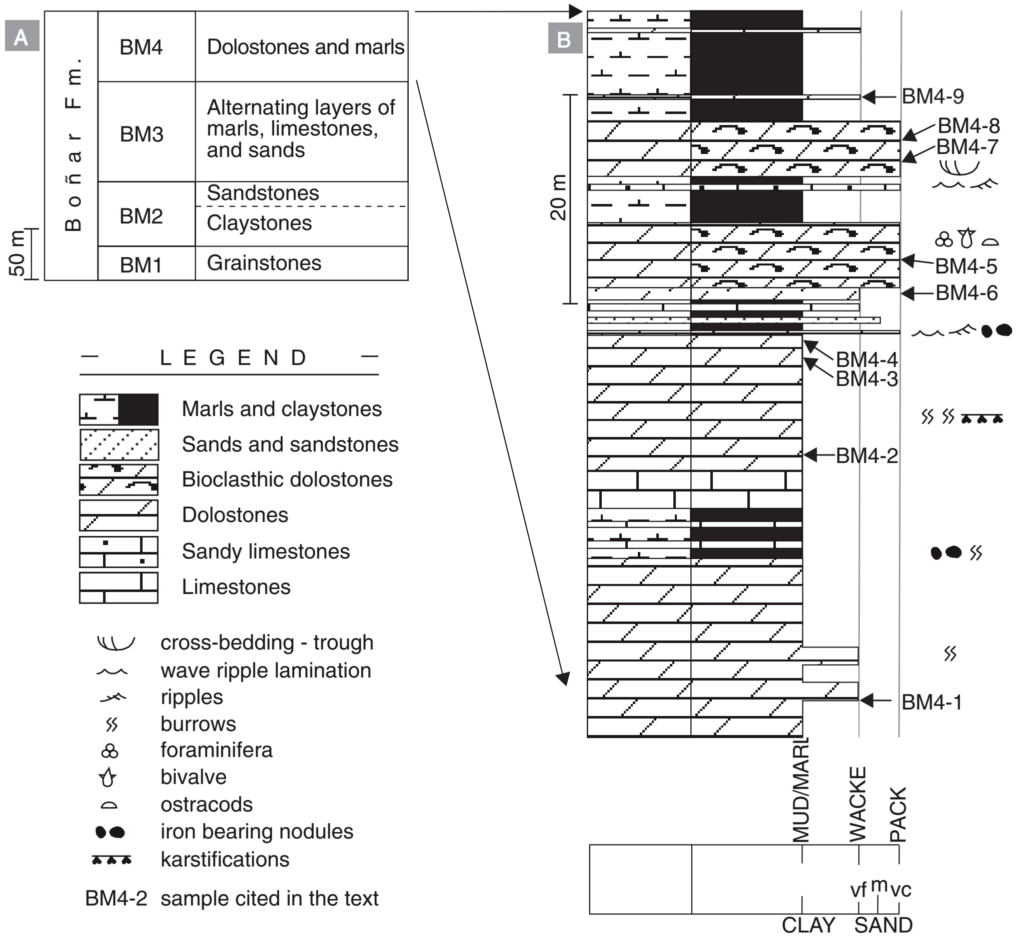

Figure 2.—Synthetic stratigraphic column of the Boñar Formation (A) and detailed column of member BM4 (B). A=modified from Gómez-Fernández *et al*., (2003).

the sample type (cylindrical plugs) required by the methodology and resources available for the study.

Methods and materials

A detailed stratigraphic column of the BM4 member was constructed and sampled at the outcrop along the slope of Boñar-Sabero road (Figure 1). Nine samples of 5 kg, each, were taken (BM4-1 to BM4-9; Figures 1 and 2) and used for preparation of thin sections of 30 µm and for microscopic studies. For the petrographic characterization of carbonate minerals, staining method of alizarin red and potassium ferricyanide was used during the sample preparation (Lindholm & Finkelman, 1972). An Olympus BX51 petrographic microscope equipped with an Olympus Camedia C-5050 Zoom camera was applied for the petrographic study and the microphotography.

For petrophysical studies, five representative samples were selected of the dolomitic BM4 member, each of them representing one of the five lithofacii detailed below (BM4-1 to BM4-5; Figure 2). 1,5” diameter plugs were prepared of each of these samples and were named correlatively by adding a hyphen to their origin sample (i.e. BM4-1-1 is the first plug obtained from BM4-1). Owing to equipments' operational conditions, every plug out of the 3 to 7 centimetres range of length were discarded. For the petrophysical characterization, the *helium density* of each plug was quantified using a helium pycnometer (ULTRAPYC 1200e, Quantachrome Instruments); the *open porosity* was calculated from the difference between apparent and skeletal volumes; and the *Klinkenberg permeability* values were obtained using a nitrogen permeameter (GasPerm 2 flow series v6.30, Vinci Technologies).

Stratigraphy and petrography

The synthetic stratigraphic sequence of the BM4 member, from bottom to top, is the following (Figure 2):

17.3 m Beige dolomicrites in beds of up to 1.5 m of thickness (Sample BM4-1).
These are diagenetic dolomicrites formed by the replacement of mudstones (Figure 3A) and, in some cases, wackestones (Figure 3B). Occasionally, dolosparite crystal zones surround the secondary open pores. Most of the fossils are ghosts but some of them were cemented by calcite before the dolomite deposition.

9 m Alternation of sandy marls and light grey mudstones.

11.9 m Mostly beige, in some cases grey, dolomicrites (samples BM4-2 to BM4-4; Figure 3C and D), in beds of up to 1 m thickness. They were formed by the replacement of mudstones. Dispersed quartz grains are present. The ornamental stone type called “Piedra de Boñar”, used as construction material in several monuments of the region, is extracted from this level of BM4.

4.1 m Alternation of grey marls, sandy limestones, sandstones and marly limestones.

17.3 m Mostly beige dolosparites (samples BM4-5 to BM4-8), alternating with nodular marls, dolomicrites and sandy limestones. These lithologies have moldic and fracture porosity often cemented by different phases: Fe rich dolomite, calcite and Fe rich calcite (Figure 3E). The dominant protoliths are bioclastic packstones with minor micritic matrix and dispersed quartz grains.

10.8 m Green nodular marls with dolomite intercalations of up to 0.35 m (sample BM4-9) and with partially calcite cemented secondary porosity (Figure 3F). The protolith of the dolomites are wackstones, in which the textural elements were replaced by dolomicrite and dolosparite.

The microscopic study confirms that most of the samples are secondary dolomites originated by diagenetic dolomitization (Figure 3). In the bottom half of BM4, the replacement of the dominant mudstones formed dolomicrites, in which the evolution of the dolomitization led to the formation of some dolosparite crystals. A secondary open porosity is connected to these crystals (Figures 3A and D*)*.

In the top half of BM4, the dolomitization of the dominantly bioclastic dolomites was selective, replacing sceletic fragments with dolosparite crystals of homogeneous size, often, with powdery residues in the interior and clean borders (Figure 3E). At the

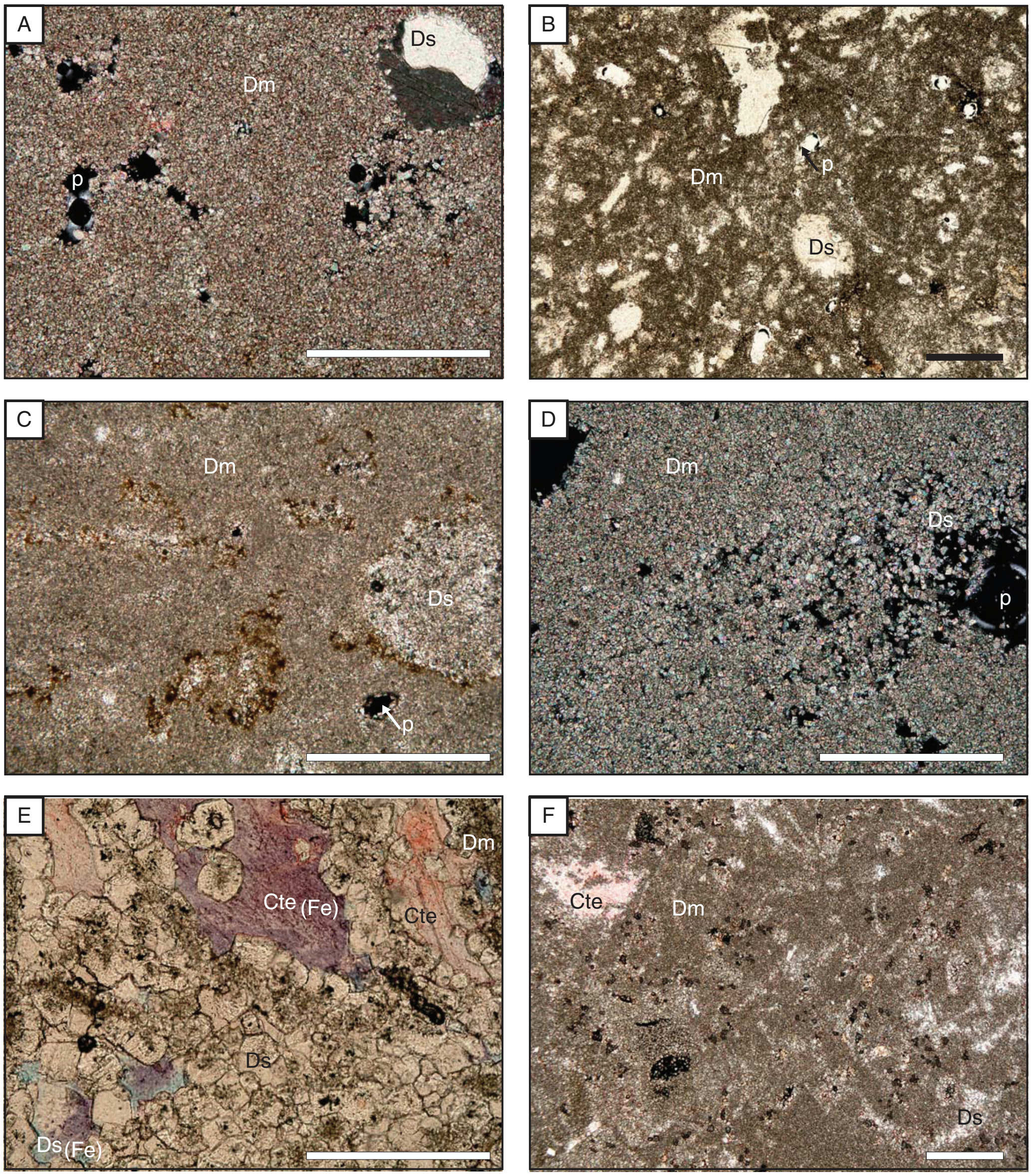

Figure 3.—MOP images showing representative microtextures of dolostones of BM4. A, C and D/Dominantly dolomicrite samples with secondary porosity connected to dolosparite crystals. Occasional ghost fossils sometimes replaced by dolosparite. B and F/Dolomicrite and dolosparite replacing preferentially and respectively matrix and fossil fragments. E/Dolostone composed of (1) dolosparite replacing fossil fragments, (2) dolomicrite replacing matrix, and (3) Fe rich dolomite, calcite and Fe rich calcite cementing secondary porosity. Abbreviations: Dm=dolomicrite; Ds=dolosparite; $Ds_{(Fe)}$=iron rich dolosparite; Cte=calcite; $Cte_{(Fe)}$=iron rich calcite; p=porosity. Relation of image/sample number and macroscopic colour: A and B/BM4-1, beige; C/BM4-3, beige; D/BM4-4, grey; E/BM4-5, beige; F/BM4-9, grey. A, C and D: crossed polars. B, E and F: plane polarized light. Scale bar=500 μm.

same time, the matrix was mostly replaced by dolomicrite. Moldic porosity was formed, which was usually cemented by Fe rich dolomite, calcite and Fe rich calcite after the main dolomitization.

Finally, the carbonates of the uppermost level of BM4 member are similar to the facies of the bottom half of the member, again (Figure 3F).

The dominant colour of the rocks of BM4 is light beige to yellowish-beige (such as samples BM4-1, BM4-2, BM4-3, BM4-5, BM4-6, BM4-7 and BM4-8). However, residues of grey coloured rocks can be found in several outcrops (such as samples BM4-4 and BM4-9). These colour changes are associated to the oxidation state of Fe in the rock (Gómez-Fernández *et al*., 2003), thus the beige colour appears when the rock is exposed to the atmospheric oxidative processes. The same authors confirm that some of the beige dolomites have higher secondary porosity than their grey counterparts.

Petrophysical study

The petrophysical study was conducted on representative samples of the lithofacii present in BM4 (Figure 2): a) three samples of beige dolomicrites (BM4-1 to BM4-3, Figure 3A to C) and one sample of grey dolomicite (BM4-4, Figure 3D), all of which has a secondary open porosity connected to dolosparite crystals, and b) one dolosparite sample (BM4-5; Figure 3E) with moldic porosity filled with calcite and dolomite cement.

Once the petrophysical properties were determined for each plug, mean values for each unit and for the Dolomitic Member of the Boñar Formation were calculated (see Table 1).

Hence,

- Helium density values vary between 2.80 g/cm^3 and 2.85 g/cm^3 with a mean value of 2.82 g/cm^3, and a standard deviation of 0.02 (Table 1).
- Open porosity values vary between 10.38% and 20.62% with a mean value of 16.10%, and a standard deviation of 4.09 (Table 1).
- Klinkenberg permeability values vary between 0.01 mD and 0.52 mD with a mean value of 0.20 mD and a standard deviation of 0.19 (Table 1).

Discussion

The petrophysical homogeneity of the Dolomitic Member was confirmed: density, porosity and permeability values are quite similar in each plug. There are, however, slight variations in the petrophysical properties due to petrographical differences between the beige dolomicrites (BM4-1 to BM4-3), the grey dolomicrite (BM4-4) and the dolosparite (BM4-5).

Samples BM4-1 to BM4-3 show similar density values, which is in accordance with their similar petrography. Density values of the other two samples (BM4-4 and BM4-5) are lower, however. The higher concentration of calcite in BM4-5 may account for the lower density of this sample. In case of the BM4-4 sample, the lower density may be due to some variation in the mineralogy – also responsible for the different colour. This hypothesis, however, must be confirmed by further research.

We can observe a similar tendency in porosity as in the density values. In this case, the lowest porosity belongs to the BM4-5 sample. This can be explained by the textural difference (i.e. dolosparite vs. dolomicrite), also confirmed by the microscopic observation. On the other hand, the grey variety of dolomicrite (BM4-4) shows lower porosity than the beige, as described by previous studies (Gómez-Fernández *et al*., 2003).

The comparison of the permeability values of each sample is not practical given that all of them fall in the poor permeability class (k<1 mD), according to Tiab & Donaldson (2015). The high standard deviation values further complicate the interpretation. The highest permeability value was obtained for the BM4-1 sample, which also shows the highest porosity among the samples. For the other samples, however, no correlation between the porosity and permeability values can be established.

Taking into account research data from CO_2 storage studies in saline aquifers from all over the world, CO2Store Project has established some geological selection criteria to be fulfilled, including reservoir depth, thickness, porosity, permeability, seal integrity and salinity (Table 2) (Chadwick *et al*., 2008).

Table 1.—**Results of petrophysical characterization**

	Density		Porosity		Permeability	
Sample	g/cm^3	St. dev.	%	St. dev.	mD	St. dev.
BM4-1 (beige)	2.85	0.0008	20.62	0.41	0.52	0.0088
BM4-2 (beige)	2.83	0.0009	18.10	0.17	0.10	0.0072
BM4-3 (beige)	2.84	0.0070	17.87	0.44	0.17	0.0027
BM4-4 (grey)	2.80	0.0114	13.53	1.06	0.01	0.0027
BM4-5 (beige)	2.81	0.0072	10.38	2.38	0.13	0.1847

Table 2.—**Key geological indicators for storage site suitability (Chadwick *et al*., 2008)**

Parameter	Positive indicators	Cautionary indicators
Depth	>1000 m <2500 m	<800 m >2500 m
Thickness	>50 m	<20 m
Porosity	>20%	<10%
Permeability	>500 mD	<200 mD

The Dolomitic Member of the Boñar Formation is 1000 to 2000 metres deep in the Duero Basin (Hurtado Bezos, 2010). Thus, according to Table 2, it is within an acceptable range. Thickness is another accomplished parameter, up to 95 metres in some places (Gómez-Fernández *et al*., 2003), and at the sampled outcrop it is more than 50 metres.

Porosity values (between 8% and 20%) are broadly adequate, being within the allowable limits. Nevertheless, permeability is the main limiting factor of the Dolomitic Member of the Boñar Formation to be used as a reservoir rock. Maximum values obtained barely reach 0.5 mD while the minimum level to be achieved is 200 mD, according to Table 2.

This also proves that high porosity values are not necessarily related to high permeability values. Therefore, volumetric expressions for capacity calculation in saline formations –such as the one proposed by the US Department of Energy (2007)– are not enough to completely define the suitability of a formation to become a CO_2 storage site, as they don't take into account permeability influence. However, these equations have often been used in regional and basin scale studies and numerical simulations (e.g. Lee *et al*., 2014 or Hurtado Bezos, 2010).

The Dolomitic Member was selected by the authors as the potentially most suitable level of the Boñar Formation for CO_2 storage according to the criteria described under *Geological setting*. This allows us to draw some general conclusions concerning the potential of the whole Boñar Formation as a geological reservoir.

Conclusions

The dominantly carbonate Upper Cretaceous succession of the Duero basin has been considered as a suitable CO_2 reservoir, on a regional scale (Zapatero Rodríguez *et al*., 2009; Hurtado Bezos, 2010).

This study assesses the outcropping rocks of the Dolomitic member of the Boñar formation (North Duero basin), which, in theory, is the most suitable level of the mentioned formation for CO_2 storage (Gómez-Fernández *et al*., 2003). However, according to the analysis and interpretation of the petrophysical properties obtained in this study, permeability of this member is far too low for CO_2 geological storage, although the porosity values are sufficient.

In all, results obtained are considered representative enough to conclude that the Dolomitic Member, and probably the whole Boñar Formation, are not appropriate CO_2 reservoirs. However, a local study of outcrop rocks should be considered as a preliminary approach; hence, further studies based on borehole samples are suggested to definitely confirm this main conclusion.

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