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Characterization of proposed reservoir and seal rocks for CO2 geological storage in the Asturian Mesozoic sedimentary basin (NW Spain)

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Abstract

This study is focused on the investigation of four lithostratigraphic units (two potential reservoir rocks and two potential seal rocks) for geological storage of CO\textsubscript{2} in the Mesozoic Asturian basin (NW Spain). Two systems reservoir-seal are studied both in the Jurassic (Liassic limestones and dolostones of the Gijón formation as reservoir rock and Sinemurian-Bajocian marly limestones of Rodiles formation as seal rock) and Cretaceous (Aptian greywackes and sandstones of the Pola de Siero formation as reservoir rock and Albian grainstone-type limestones with argillaceous horizons as seal rock) sequences. Detailed information of the mineralogical distribution and texture, geochemical composition, porosity and pore size distribution is provided for each rock. Compared to the Cretaceous system, the Jurassic reservoir shows a better net thickness and pore size distribution and the Jurassic seal has an already demonstrated low permeability. The Cretaceous reservoir presents better porosity values (7.96% against a 0.5% of the Gijón formation), but the seal permeability is yet to be proven as low.

Keywords: CO\textsubscript{2} geological sequestration; Asturian Mesozoic basin; reservoir and seal rock systems; mineral composition and texture; porosity

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1. Introduction

Geologic carbon dioxide (CO2) sequestration has already been worldwide considered as a viable technology to mitigate the effects of climate change. During the last decade, many important advances have been carried out in this field, mainly by means of pilot and full-scale operations of CO2 geological sequestration: pioneer countries are EEUU, Canada, Australia and Japan. Concerning Europe, up to now, some demonstration projects of capture and/or geological sequestration have been developed in Germany, United Kingdom, Norway, Poland, The Netherlands, Denmark, Ireland, France, Romania, Iceland, Italy and Czech Republic [1]. In Spain, only the OXYCFB300 Compostilla project (part of the European Carbon Capture and Storage –CCS- Demonstration Project Network) has been partially completed, without having performed the pilot-scale storage operation. On the other hand, National Public law 40/2010 directs the Spanish Geological Survey (IGME) to conduct an assessment of potential geologic storage sites for carbon dioxide [2] and to locate the suitable geological data (ALGECO2 project, [3]).

Asturias is a small-size (~10,000 km²) and moderate populated (~1,000,000 inhabitants) industrial region located in NW Spain (Fig. 1). Among others, five coal-based thermal power plants, two steel factories and two cement industries are currently in operation in Asturias, where a total of about 20 million of tons of CO2 are annually emitted [4]. Almost the entire surface of the region is constituted by sedimentary basins from Precambrian to Tertiary age. Some previous works concerning pre-selection and assessment of suitable reservoir rocks for CO2 geological storage were focused in: a) saline aquifers in thick sequences of limestones and dolostones of Devonian and Carboniferous ages [5] and b) non-economically recoverable coal beds [6,7,8].

Taking into account the main structural features of the Asturian Palaeozoic rocks, which were strongly fractured and deformed during the Variscan cycle [9,10 among others], and also the generally reduced thickness of coal layers (~1-2 m), in this paper a new alternative is presented. In the Central-North part of the region, the highly tectonized basement (Palaeozoic sequence) is discordantly overlain by a Mesozoic cover whose thickness, although irregular and variable, can reach several thousand meters. This Mesozoic cover includes a great variety of sedimentary facies and it was not very affected by the alpine cycle, remaining currently almost undeformed. From published data (mainly for hydrogeological applications) and field work, two different reservoir-seal systems were selected for an in-depth study: a Jurassic-age limestone-marlstone system and a Cretaceous-age sandstone-limestone+claystone system. The aim of this work is to provide a description of the geologic characteristics that influence the suitability of each system (reservoir thickness, depth, porosity, groundwater salinity and permeability).

2. Study area

From a geological point of view, Asturias is divided in two different units: the western part, constituted by Early Palaeozoic highly tectonized sequences of slates, sandstones and quartzites is known as “West Asturian-Leonese Zone” and it does not have any interest for geological sequestration purposes due to the lack of porous and permeable rocks. On the other hand, the eastern part (~2/3 of the region surface), known as “Cantabrian Zone” is the foreland of the Variscan chain of NW Iberia. This area, constituting the core of the Ibero-Armorican Arc, is the external part of the Variscan Orogen in the NW Iberian. From a structural viewpoint, the Cantabrian Zone corresponds to a thrust and fold belt developed during the Variscan cycle (Carboniferous).

Post-Variscan evolution in the Cantabrian Zone can be summarized as follows: firstly, an extensional episode led to the development of the Permian-Triassic basins, ending with an Early Jurassic sea transgressing over permo-triassic sediments. During the Late Jurassic-Early Cretaceous, a second extensional stage (related to the Vizcaya Gulf opening process) took place [11], resulting in the formation of the main Mesozoic basins, which remain stable from the Aptian until the tectonic inversion that took place during the Tertiary due to the alpine orogenesis. As it has been stated by previous works [10,12], the Cantabrian Zone was uplifted and exhumed during the Tertiary, as a result of a crustal thrust, giving rise to the Cantabrian Mountains. However, the alpine orogeny caused little internal deformation in the uplifted block.

These Mesozoic basins were partially filled during the Jurassic, Cretaceous and Tertiary, resulting in the formation of several sedimentary sequences where some lithostratigraphic units meet petrophysical properties to become both reservoir and seal levels suitable enough for carbon dioxide geological sequestration. Detailed stratigraphy of the Asturian Jurassic and Cretaceous sequences (Tertiary rocks stratigraphy knowledge is still
limited) is beyond the scope of this work and it can be consulted in the specialized bibliography [13,14,15, among others]. A synthetic geological map of this area in presented in Fig. 1.

In summary, in the Asturian Jurassic succession, two superposed sedimentary sequences can be distinguished: the lower one is mainly constituted by limestones, dolostones and marls of Hettangian-Bajocian age [13] and includes two different lithostratigraphic units, the Gijón and Rodiles formations. The upper Jurassic sequence is mainly composed by siliciclastic rocks and it is not of interest for the purposes of this study.

Concerning Asturian Cretaceous series, a total of 10 different lithostratigraphic units (about 650 m of thickness) were established by [14]: these sequences are constituted by silt and sandstones and carbonates, with many intermediate terms. The best porosity and permeability values in these series correspond to an Upper Aptian-Lower Albian sandstone known locally as “Pola de Siero formation”. At the top of this unit a bioclastic grainstone-type limestone level appears with some argillaceous decametric-metric thickness levels [16] of Upper Albian age: the Ullaga formation.

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**Fig. 1.** Synthetic geological map of the Cantabrian Zone northern part (adapted from [15]).
In the Asturian Mesozoic basin two reservoir-seal systems with potential interest as suitable sites for geologic CO2 sequestration purposes are considered. The first one is composed by the Gijón (reservoir) and Rodiles (seal) formations and the second one by the Pola de Siero (reservoir) and Ullaga (seal) formations.

The Gijón formation is formed by 100-170 m of micritic limestones and dolostones of Hettagian-Sinemurian age and it consists in a superposition of cyclic deposits that represents different sedimentary environments (shallow restricted lagoons and carbonate-evaporite microtidal flat environments [13]).

The Rodiles formation (90-160 m thick) is constituted by a marl-limestone rhythmic bedding of shallow marine environments, in which two different members were defined [13]: a lower nodular one (nearshore facies, called “Buerres member”) and an upper one (plane-parallel rhythmic, offshore facies called “Santa Mera member”).

The Pola de Siero formation has a variable thickness (60-100 m) and it is composed by sandstones with conglomeratic horizons in its lower part, interpreted [14] as alluvial fan deposits.

Finally, the Ullaga formation is represented by 40-50 m of bioclastic grainstone-type limestones with about 10 m of fine-grained detrital rocks distributed in several levels within the formation.

3. Sampling and methodology

The four litostratigraphic units above described were sampled in different outcrops, taking about 10 kgs for each sample. Location of sampling points is detailed in Table 1.

<table>
<thead>
<tr>
<th>Formation</th>
<th>Site name</th>
<th>UTM coordinates (ERTS89 Datum)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gijón (Lower member)</td>
<td>La Cuesta</td>
<td>X=293,590; Y=4,810,276</td>
</tr>
<tr>
<td>Gijón (Medium member)</td>
<td>Obaya</td>
<td>X=307,441; Y=4,820,460</td>
</tr>
<tr>
<td>Gijón (Upper member)</td>
<td>Rodiles beach</td>
<td>X=293,590; Y=4,810,276</td>
</tr>
<tr>
<td>Rodiles (Buerres member)</td>
<td>Rodiles beach</td>
<td>X=307,858; Y=4,822,634</td>
</tr>
<tr>
<td>Rodiles (Sta Mera member)</td>
<td>Vega beach</td>
<td>X=308,124; Y=4,822,839</td>
</tr>
<tr>
<td>Pola de Siero</td>
<td>Pilofeta</td>
<td>X=327,516; Y=4,816,521</td>
</tr>
<tr>
<td>Ullaga</td>
<td>Cardes</td>
<td>X=309,717; Y=4,801,108</td>
</tr>
</tbody>
</table>

Samples were transported to the laboratory and prepared to be studied by means of the following techniques:
A) Optical polarizing microscopy: using a Leica MDLP petrographic microscope.
B) X-ray Diffraction (XRD): by means of a X-ray diffractometer Seifert XRD 300 T7T.
C) X-ray fluorescence (XRF): samples elemental composition was determined through a Niton XL3t portable XRF analyzer.
D) Hg intrusion porosimetry: porosity and pore size distribution of the samples were obtained using a Micromeritics Autopore IV Hg-injection porosimeter.

4. Results and discussion

4.1 Optical polarizing microscopy

Jurassic reservoir (Gijón formation): from a petrographical point of view, three different typologies of carbonate can be distinguished: i) micritic mudstone-type and homogeneous limestones and dolostones with poor fossil record (mainly fragments of bivalves). This lithofacies contains moderate to scarce quantities of detrital quartz silt-sized (Fig. 2a); ii) Pellesparitic grainstone-type limestones without carbonate matrix, being pellets (200-300 μm) the only type of grain (Fig. 2b); iii) micritic-mudestone type limestones without bioclasts and with poor quantities of silt-sized detrital quartz.

Figs. 2, 3, 4 and 5 are taken with plane-parallel light.
Jurassic seal (Rodiles formation): it is constituted by marly limestones from mudstone to wackestone-type and biomicritic texture (Fig. 3). Matrix is formed by very dark calcitic micrite, presumably with certain content in argillaceous mineral phases. Bioclasts are again the only type of grain (predominantly fragments of bivalves, but echinoderms and foraminifera were also observed). This unit contains an approximate 2% of opaque minerals.

Cretaceous reservoir (Pola de Siero formation): in this case, two different lithofacies can be described. The lower unit is composed by siliceous conglomerates (heterometric and well-rounded particles) with a silt-sandy matrix. The upper unit is classified as a well-sorted (250 μm) quartzitic greywacke (Fig. 4). Within the matrix, weathered muscovite sheets and glauconite can be observed.
Cretaceous seal (Ullaga formation): grainstone-type silicified limestones. The main components are large carbonate crystals (mean diameter about 360 μm) that provide a subhedral equigranular texture to the rock. Rounded monocry stalline quartz grains are commonly found disseminated within carbonate crystals (Fig. 5).

4.2 XRD

XRD analyses were solely carried out in seal samples, as they contain fine-grained material that can be mineralogically identified by optical microscopy procedures.

Jurassic seal (Rodiles formation): four different minerals were identified: calcite (60.87%), quartz (30.87%), muscovite (5.78%) and ankerite (2.47%).

Cretaceous seal (Ullaga formation): the tested sampled was composed by ankerite as predominant phase (56.3%), calcite (35.7%) and quartz (8%).

4.3 XRF

Representative samples of each reservoir and seal rock were analyzed by XRF to determine geochemical composition. Although the content in major elements can be approximately determined by means of mineralogical
composition (known through optical polarizing microscopy and XRD), interesting information about minor and trace elements is provided in Table 2:

Table 2. Ranges of elemental composition of selected samples of each lithostratigraphic unit (all results in mg/kg). Elements with a molecular weight below 32 uma (S) are not detected.

<table>
<thead>
<tr>
<th>Element</th>
<th>Gijón formation</th>
<th>Rodiles formation</th>
<th>Pola de Siero formation</th>
<th>Ullaga formation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mo</td>
<td>4.7-5.5</td>
<td>&lt;3</td>
<td>6.1-9.7</td>
<td>5</td>
</tr>
<tr>
<td>Zr</td>
<td>5.2-7.9</td>
<td>159.8</td>
<td>156.7-277.5</td>
<td>20.7</td>
</tr>
<tr>
<td>Sr</td>
<td>206.4-795.1</td>
<td>215.2</td>
<td>0-6.2</td>
<td>&lt;3</td>
</tr>
<tr>
<td>Rb</td>
<td>2.5-4.9</td>
<td>133.8</td>
<td>8.5-11.7</td>
<td>3.7</td>
</tr>
<tr>
<td>Pb</td>
<td>&lt;3</td>
<td>13.7</td>
<td>&lt;3</td>
<td>&lt;3</td>
</tr>
<tr>
<td>Se</td>
<td>&lt;2</td>
<td>&lt;2</td>
<td>0-4.3</td>
<td>5.7</td>
</tr>
<tr>
<td>As</td>
<td>&lt;4</td>
<td>6.7</td>
<td>12.6-31.6</td>
<td>23.1</td>
</tr>
<tr>
<td>Hg</td>
<td>0-9.7</td>
<td>&lt;4</td>
<td>&lt;4</td>
<td>&lt;4</td>
</tr>
<tr>
<td>Zn</td>
<td>0-9.8</td>
<td>84.1</td>
<td>8.1-13.4</td>
<td>13.1</td>
</tr>
<tr>
<td>Cu</td>
<td>20-34.4</td>
<td>39.2</td>
<td>46.3-70</td>
<td>&lt;4</td>
</tr>
<tr>
<td>Fe</td>
<td>591.4-1,298.3</td>
<td>10,302.9</td>
<td>12,422.6-29,413.3</td>
<td>222,609.1</td>
</tr>
<tr>
<td>Mn</td>
<td>49.4-80.3</td>
<td>76.7</td>
<td>408.2-509.1</td>
<td>223.9</td>
</tr>
<tr>
<td>Cr</td>
<td>28.7-36.3</td>
<td>155.8</td>
<td>64.2-93.7</td>
<td>&lt;7</td>
</tr>
<tr>
<td>V</td>
<td>&lt;5</td>
<td>256</td>
<td>75.1-76.2</td>
<td>28.1</td>
</tr>
<tr>
<td>Ti</td>
<td>&lt;11</td>
<td>7,000.2</td>
<td>706.9-816.2</td>
<td>&lt;10</td>
</tr>
<tr>
<td>Sc</td>
<td>0-379.7</td>
<td>&lt;8</td>
<td>0-223.6</td>
<td>550.9</td>
</tr>
<tr>
<td>Ca</td>
<td>204,212.5-431,733.3</td>
<td>213,935.4</td>
<td>903.3-2,802.9</td>
<td>136,335.3</td>
</tr>
<tr>
<td>K</td>
<td>997.7-5,230.2</td>
<td>25,467.1</td>
<td>3,208.7-4,694.1</td>
<td>1,061.3</td>
</tr>
<tr>
<td>S</td>
<td>&lt;20</td>
<td>671.3</td>
<td>&lt;19</td>
<td>&lt;20</td>
</tr>
</tbody>
</table>

Jurassic reservoir (Gijón formation): only Ca (related to calcite, main mineral component) is a major element. Minor elements are Fe and K. None specific Fe or K mineral were detected by optical polarizing microscopy. Fe can be present as carbonate and/or oxide and K could be linked to the presence of argillaceous minerals.

Jurassic seal (Rodiles formation): three major elements are present, which are Ca (calcite), Fe (ankerite) and K (muscovite). Ti appears as a minor element and its presence is assumed to be related to non-observed Ti or Ti/Fe oxides. Although in trace element concentrations, S is present (671.3 mg/kg): some euhedral opaque grains seen in thin section showed cubic morphologies, so the presence of pyrite can be probable.

Cretaceous reservoir (Pola de Siero formation): as a siliciclastic rock, only Si and O should be major elements. Fe concentration is remarkable (1.24-2.94%) and this element seems to be related to matrix or opaque components. Minor elements are Ca and K: the first one is supposed to be in calcite form, in the form of chemical cement and the latter is expected to be in the argillaceous components of the matrix.

Cretaceous seal (Ullaga): XRD stated that mineral composition was Fe and Ca carbonates, so it is not surprising to find Fe and Ca as major elements. K appears as minor element, probably in the form of K-phyllosilicates.

4.4 Hg intrusion porosimetry

Jurassic reservoir (Gijón): Table 3 summarizes the main properties of the Hettagian limestone porous system.
Table 3. Hg injection porosimetry results for samples of the Gijón formation

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Lower member</th>
<th>Medium member</th>
<th>Upper member</th>
<th>Mean</th>
</tr>
</thead>
<tbody>
<tr>
<td>Porosity (%)</td>
<td>0.77</td>
<td>0.19</td>
<td>0.51</td>
<td>0.49</td>
</tr>
<tr>
<td>Pore mean diameter (μm)</td>
<td>1.35</td>
<td>34.83</td>
<td>42.16</td>
<td>26.11</td>
</tr>
<tr>
<td>Pore mean length (μm)</td>
<td>27.13</td>
<td>46.34</td>
<td>26.73</td>
<td>33.40</td>
</tr>
<tr>
<td>Tortuosity</td>
<td>4.78</td>
<td>3.48</td>
<td>4.96</td>
<td>4.41</td>
</tr>
</tbody>
</table>

This potential reservoir rock presents a moderate porosity value and its pore size ranges from 100 to 0.1 μm (samples from middle and upper members hardly have pores below 10 μm). In Fig. 6, the intrusion diagram for a sample from the lower member is presented. Pores between 1-100 μm are associated to intergranular voids, while pores below 1 μm are supposed to be due to surface grain irregularities. Published data [17] indicates a high-very high permeability for this limestone.

![Cumulative Intrusion vs Pore size](image)

Fig. 6. Intrusion diagram for the lower member of the Gijón formation.

Jurassic seal (Rodiles formation): results are presented in Table 4.

Table 4. Hg injection porosimetry results for samples of Rodiles formation.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Mean</th>
</tr>
</thead>
<tbody>
<tr>
<td>Porosity (%)</td>
<td>11.20</td>
</tr>
<tr>
<td>Pore mean diameter (μm)</td>
<td>0.03</td>
</tr>
<tr>
<td>Pore mean length (μm)</td>
<td>7.97</td>
</tr>
<tr>
<td>Tortuosity</td>
<td>12.01</td>
</tr>
</tbody>
</table>

Marly limestones from Rodiles formation have a great porosity value (Table 4) with a very small pore size (1 μm-10 nm, Fig. 7). Then, a very low intergranular porosity can be deduced, whereas it has a matrix with fine-
grained surface rugose particles. A low permeability for the Rodiles formation is known for previous works focused in the Mesozoic Asturian basin hydrogeological aspects [18].

Fig. 7. Intrusion diagram for marly limestones of Rodiles formation.

Cretaceous reservoir (Pola de Siero formation): the obtained data is shown in Table 5:

Table 5. Hg injection porosimetry results for Pola de Siero formation samples.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Lower member</th>
<th>Upper member</th>
<th>Mean</th>
</tr>
</thead>
<tbody>
<tr>
<td>Porosity (%)</td>
<td>11.18</td>
<td>4.75</td>
<td>7.96</td>
</tr>
<tr>
<td>Pore mean diameter (μm)</td>
<td>0.11</td>
<td>0.05</td>
<td>0.08</td>
</tr>
<tr>
<td>Pore mean length (μm)</td>
<td>9.01</td>
<td>9.24</td>
<td>9.12</td>
</tr>
<tr>
<td>Tortuosity</td>
<td>8.44</td>
<td>10.16</td>
<td>9.30</td>
</tr>
</tbody>
</table>

Porosity values for sandstones of the Pola de Siero formation are high and, as it can be seen in Fig. 8, the vast majority of its pores are located in the 10-0,1 μm (intergranular porosity), with minor contributions in the nm-unit scale.
Fig. 8. Intrusion diagram for greywackes of the Pola de Siero formation (lower member).

Cretaceous seal (Ullaga formation): the main properties of Ullaga formation porous system are detailed in Table 6.

Table 6. Hg injection porosimetry results for samples of the Ullaga formation.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Mean</th>
</tr>
</thead>
<tbody>
<tr>
<td>Porosity (%)</td>
<td>0.44</td>
</tr>
<tr>
<td>Pore mean diameter (μm)</td>
<td>0.29</td>
</tr>
<tr>
<td>Pore mean length (μm)</td>
<td>47.22</td>
</tr>
<tr>
<td>Tortuosity</td>
<td>3.43</td>
</tr>
</tbody>
</table>

This grainstone limestone shows a moderate porosity value and a curious pore size distribution, with three well-defined intervals of pore size at 50, 30 and 0.2 μm (Fig. 9). Permeability values for this rock between $10^{-1}$ (limestone levels) and $10^{-4}$ m·d⁻¹ (argillaceous levels) for this formation have been reported in previous works [19].
5. Conclusions

Four lithostratigraphic units (potential reservoir and seal rocks) have been sampled and analyzed to reach a better understanding of their suitability to configure adequate CO2 geologic sequestration systems. Selected rocks belong, from a geological point of view, to the Mesozoic Asturian basin (NW Spain).

The first unit considered as a potential reservoir rock (Gijón formation) is constituted by Liassic limestones, mudstone and grainstone-type and generally with a micritic or biomicritic texture. Mean porosity value for this reservoir is about 0.5%, with pore sizes between 1 and 100 μm.

The suprayacent level to the above cited reservoir is a rhythmic sequence (Rodiles formation) of mudstone to wackestone limestones and marls (calcite-quartz-muscovite-ankerite) with a high porosity (11.2%, although a reduced permeability has been cited for this rock) with a very low pore mean size (<1 μm).

The second potential reservoir rock are Aptian greywackes and sandstones of sandy texture (Pola de Siero formation) with interesting porosity values (7.96%) and adequate pore sizes (0.1-10 μm), suitable for CO2 geological sequestration.

Finally, the proposed seal for this second reservoir is composed by grainstone-type limestones of biosparitic texture with interbedded argillaceous horizons (Ullaga formation). These limestones show a moderate porosity value (0.44%) and pore size distribution within tens to tenths of μm.

Jurassic system (Gijón + Rodiles formations) has a thicker reservoir rock with better pore sizes and the low permeability of its seal has already been stated by previous works. On the other hand, the Cretaceous system (Pola de Siero + Ullaga formations) shows a much better porosity value for its reservoir rock, but its seal quality has not yet been demonstrated. Future work would be focused on the evaluation of the permeability of each unit and the injectivity into the reservoir rocks.

Acknowledgements

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References