

# Coal as an unconventional reservoir for a CO<sub>2</sub> safe geological sequestration solution

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**Abstract** — In the last decade, the energy sector has suffered several changes related not only with the decrease of conventional hydrocarbons reserves, i.e. oil and associated natural gas, but also and especially with restrictions imposed by mechanisms in the scope of sustainable environment. The energy dependency is one of the major problems that all countries must deal nowadays, and all the international energy bodies agree that it will be impossible, to the most part of the countries, to become energetically independent. Some international entities advised either governmental parties, as well as, other energy players to develop strategies in different fields in order to reduce external dependency. Additionally, the sustainable energy plan developed by the European Commission is closely related to sustainable environment and consequently to all policies involved in reducing the greenhouse gases effect. In this perspective, and knowing that nowadays it is not yet possible to displace fossil fuels from the energy scenario, it is pertinent to apply new technologies, such as CCS (carbon capture and storage) technologies. One of the current main objectives in CCS technologies deals specifically with CO<sub>2</sub> geological storage/sequestration, mostly in depleted oil and gas reservoirs, saline aquifers and in unminable coal seams, the later taking into account the so-called hydrocarbons (CBM) enhanced production.

This paper deals with the study of different coal samples in what concerns their storage and gas circulation capacities. In fact, both processes are highly dependent on physical and chemical properties of coal, which are intimately related to its genetic conditions. As a matter of fact, to understand the mechanisms involved in coal formation process, it is crucial to study in detail the deposition environmental conditions, as well as, the incarbonization process. Moreover, the coal organic components evolution is also directly related to both deposition conditions and the incarbonization process. In terms of petrographic parameters and besides the inorganic components (mineral matter content), the organic compounds of coal correspond to three quite different maceral groups (vitrinite, inertinite and liptinite) and the incarbonization stage, or rank, can be determined by the mean random vitrinite reflectance. All these parameters strongly influence the storage and the gas circulation capacities of a coal, since they can change the pore sizes, as well as, the porous structure organization and therefore the internal surface area.

**Keywords** — CCS technologies, reservoir, gas storage, gas circulation, coal

## 1 INTRODUCTION

In the actual Energy new scenario the environmental sector plays an important and unavoidable role. In this context, the energy sector enters in a total new strategic cycle [1], [2], underpinned by the principle that it is vital to create a sustainable global energy supply, always seeking the reduction of Green House Gases (GHG) emissions [3], [4], [5], [6], [7]. Actually, the European 2020 Energy and Environment Plan has already established new environmental targets, the so-called “the three twenties for 2020” (20 20 20 to 2020). As a matter

of fact, the most relevant issue in the EU environmental proposed targets [8], [9] consists in reducing the CO<sub>2</sub> emissions, as well as other GHG, in 20% (in reference to 1990) until 2020. This corresponds to the Zero Emissions Strategies which is intimately related to the renewable energy implementation in replacement of fossil fuels. However, it is not yet demonstrated that this goal resolves *per se* the GHG, and particularly CO<sub>2</sub>, emissions program. Additionally, and due to the international energy sector demand, it is also well known that it is impossible to eliminate the fossil fuel utilization for power generation. In this perspective, and having full consciousness that the renewable energies, the so-called “environment-friendly energies”, have not yet reached the level of technological efficiency capable to respond to the global energy demand, it is well-known that this difficulty can only be overcome by using a power supply based on fossil fuels [10]. In fact, the only alternative energy, already technologically well developed and able to suppress or at least to reduce the energy dependency we face today, falls into the

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non-renewable energy domain, i.e., the nuclear energy. Nevertheless, for political, economic and mostly for social reasons, the nuclear energy is not up till now seen as a real alternative solution to the world energy supply. Consequently, the solutions which are technically and economically more feasible to reply to the energy demand are once again related to fossil fuels [11]. However, the fact that accumulation of fossil fuels are currently associated to increasingly complex structures, and therefore of difficult access, and simultaneously the need to implement solutions concerning the environment protection implies the development of new technologies that are able to make energy both economically viable and environmentally acceptable [12] e [13]. As a result, it is essential to promote, in a complementary way to the expansion of renewable energies, the most appropriate technologies to reduce CO<sub>2</sub> emissions in the atmosphere. These technologies are headed by CCS (Carbon Capture and Storage) technologies which comprise three distinctive main areas (capture, transport and storage).

All in all, international studies demonstrated that a more sustainable energy based on the environmental protection obliges the implementation of new technologies on the different issues: increasing energy efficiency, CCS programs, renewable energies, and nuclear energy.

## 2 OVERVIEW ON CCS IMPLEMENTATION

Actually, in the new energy scenario it is fundamental to promote the reduction of CO<sub>2</sub> emissions using Zero Emission (Carbon Free) Technologies – ZETs, which includes capture and geological sequestration/storage. These technologies are the only ones capable to conform to the ambitious European targets in the EU document entitled “Limiting Global Change to 2 degrees Celsius – The way ahead for 2020 and beyond” [14], [15], as well as, with the economic aspects of the European Directives [8], [9]. Additionally, according to the IEA, CO<sub>2</sub> capture and sequestration/storage alone could contribute up to 19% to the reduction of global emission in 2050 [16], [17], [18]. So, it is internationally accepted that in addition to the effort to reduce CO<sub>2</sub> emissions, it is essential to capture CO<sub>2</sub> wherever feasible, from gases produced by fossil fuel combustion, which means primarily at industrial sites, and then to compress, transport and inject the CO<sub>2</sub> into deep geologic formations for permanent and secure storage. Governments around the world are totally engaged on CCS implementation that have already started applying on legal aspects on CO<sub>2</sub> storing and consequently advise all pertinent entities to create regulatory frameworks to facilitate the large-scale commercialization of CCS over the long term. In this context, the European Parliament and the

Council of 23 April 2009 on the geological sequestration/storage of CO<sub>2</sub> have created the Directive 2009/31/EC in order to define a regulatory framework for geological sequestration/storage of CO<sub>2</sub> [19].

At this point, it seems pertinent to mention all the possibilities presented on CO<sub>2</sub> abatement subject. Lemos de Sousa and Rodrigues [20] proposed a general scheme to account all the potential solutions for CO<sub>2</sub> abatement, which was organized in two different sectors: biological fixation and geological sequestration/storage (Fig. 1).

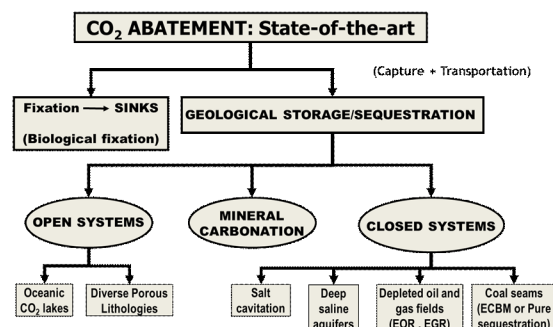


Fig. 1. CO<sub>2</sub> Abatement: State-of-the-Art [20].

Several studies [21], [22], [23] have been developed in the biological fixation domain, although major constraints lead this process to be considered a technological and economical unfeasible solution to the problem. Those constraints are mainly related to the flue gas produced from the industry, which has some unfavourable conditions, such as the high CO<sub>2</sub> concentration and toxic chemical compounds like SO<sub>x</sub> and NO<sub>x</sub>, for the cultivation of most microalgae, as well as the small amount of CO<sub>2</sub> capable to be fixed by microalgae. As shown in Fig. 1, several geological solutions have been considered for CO<sub>2</sub> sequestration/storage, yet the most technological and economical acceptable situations are: (i) depleted oils and gas fields (after production or during production with added benefit of helping to drain oil and gas from reservoirs (EOR/EGR)), (ii) deep saline aquifers, (iii) unminable coal seams (ECBM or pure sequestration), and (iv) mineral carbonation (storage in mineral form in ultrabasic rocks). In the authors opinion, from the different geological solutions available to the disposal of CO<sub>2</sub>, the “closed systems” (Fig. 1), and among them coal seams (deep unmineable coal seams and abandoned collieries), are considered to be the best long term option for CO<sub>2</sub> storage, despite some constraints related to the diversity of coal quality in different regions and mines [24], [25], [26]. Yet, some other authors [27], [28] do not agree with the previous statement. In fact, they defend that deep saline aquifers are the most feasible solution, on the basis of technical and economic reasons, to geologically store CO<sub>2</sub> and, eventually, other GHG. Additionally, the most part of

the energy companies believes that, for technical, political and mostly economic reasons, the only viable CO<sub>2</sub> geological sequestration/storage sites are the depleted oil and gas fields. At this stage, it is pertinent to emphasize the existing gap between the projects already developed or under development in the most part of the European countries [29], [30] and even in USA [31] and Canada. Some authors [27], [28], [32] have already developed a general methodology to study the CO<sub>2</sub> geological sequestration/storage issue, as well as, and in the particular topic of saline aquifers CO<sub>2</sub> storage also a Best Practice Manual [33] was also established. In conclusion, the development of a CCS industry at a commercial scale implies a number of technological and mainly economic challenges. In fact, it is essential to develop technologies capable to reduce the costs associated with the CO<sub>2</sub> capture process and at the same time capable to increase the energy efficiency. In terms of CO<sub>2</sub> transport, it is crucial to develop appropriate infrastructures taking into account the flue gas produced in the industry and the distance between the CO<sub>2</sub> capture place and the CO<sub>2</sub> geological sequestration/storage site. And finally, the CO<sub>2</sub> geological sequestration/storage represents the most complex section of the entire CCS chain, since the CO<sub>2</sub> sequestration/storage must be secure, in both health care and environment domains, in the short term (over a few decades of injection and storage monitoring) and the long term (several hundred to thousands of years) in order to be established as a viable permanent solution [34].

### 3 COAL AS AN UNCONVENTIONAL RESERVOIR

As a general concept, it is now pertinent to mention that all type of reservoirs can be organized in two large groups: conventional reservoirs and unconventional reservoirs [35: 5], [36]. So, taking into account the three type of reservoirs more technological feasible for CO<sub>2</sub> geological sequestration/storage, previously stated, it is possible to conclude that both the depleted oil and gas reservoirs and the deep saline aquifers can be classified as conventional reservoirs, while unmineable coal seams fall into the unconventional reservoirs domain. Yet, since the CCS technologies implementation is intimately related to reservoir characteristics, it is essential to study the storage capacity and the gas circulation (flow) inherent of each type of reservoir. In fact, it is well known that both the gas storage and the gas circulation in coal seams reservoirs have a distinctive performance when compared with other unconventional reservoirs (such as fractured shales) and with conventional reservoirs. It means, that in coal seams, gases are stored in the adsorbed and desorbed/free states and, gas circulation obeys to two different processes, the diffusion and the laminar flow, respectively; and in other unconventional reservoirs

and in conventional reservoirs, gases are stored in the adsorbed and free states and, consequently, the dominant process, in terms of gas circulation, is the laminar flow.

After this small summary about the duality conventional and unconventional reservoirs and taking into consideration the main goal of the present work, it is fundamental to describe coal reservoir properties which lead the authors to consider the coal as one of the best technological solutions for CO<sub>2</sub> geological sequestration/storage. So, coal is an exclusive sedimentary rock, which plays different roles in the scope of the petroleum system, i.e., it is simultaneously a source rock and a reservoir rock, and due to its adsorbed inherent characteristics it also acts as an excellent trap to natural gas and, mainly to CO<sub>2</sub>. However, coal seams are highly heterogeneous in their composition and structure and, consequently, they can be characterized, at a large scale, by two typical and different porosity systems [37], [38], [39], [40]: the cleat system (natural fracture network); and the microporous structure (coal pores). The distinct coal storage processes, previously mentioned, are intimately related with these two porosity systems, i.e., the gas adsorption process occurs in the coal pores, which corresponds to over 95-98% of the gas storage, and the absorbed process (including the free gas) occurs in the network of natural fractures, corresponding to the rest (2-5%) of the gas storage [38], [41], [42]. Furthermore, coal seam is a porous medium reservoir characterized by a unique microstructure, which permits to store a volume of gas much higher than its pore volume capacity. In fact, due to its adsorbed inherent characteristics the gas in coal is stored in the pore internal surface areas in a condensed form, which is very close to a liquid state. Nevertheless, coal storage capacity is rather complex, largely beyond the simple measurement of the pore volume and understanding the condensed adsorption state, since it also depends on the pore size (consequently on the maceral composition and mineral matter content [43], [44]) and on the gas composition within the pores.

## 4 ANALYTICAL DATA

### 4.1 Coal samples

All experiments reported in this work were performed on four coal samples with different petrographic compositions (Table 1). Samples for petrographic analyses were prepared under ISO 7404-2 standard method [45], and petrographic determinations were performed under ISO 7404-3 and ISO 7404-5 standard methods [46], [47]. Samples A and B are of anthracite rank with the mean random vitrinite reflectance (*R<sub>r</sub>*) ranging from 4.68 to 5.58%, while samples C and D are of bituminous rank presenting a *R<sub>r</sub>* ranging from 0.62

to 0.72%, and the depositional environment conditions were more anaerobic during the formation of samples A and B than during the formation of samples C and D. Table 1 shows the maceral composition that presents pertinent variations in the four components measured, which will induce different gas storage and gas circulation capacities in the four analysed coals. Vitrinite content (*V*) presented a variation from a minimum of 68% for sample C to a maximum of 77% for sample A. Liptinite content (*L*) ranged from 0% for samples A and B to 5% for sample D. Inertinite content (*I*) and the mineral matter content (*MM*) presented a higher variation (10%) compared to the other two components, the former ranged from 8% for sample A to 18% for sample B, whereas the second component varied from 6% for sample D to 16% for sample C.

Table 1. Coal samples petrographic composition

Sample	<i>V</i> (%)	<i>L</i> (%)	<i>I</i> (%)	<i>MM</i> (%)	<i>Rr</i> (%)
A	77	0	8	15	4.68
B	72	0	18	10	5.58
C	68	4	12	16	0.62
D	75	5	14	6	0.72

#### 4.2 Sample Preparation

The four samples were crushed to less than 212 μm and were dried in an oven for at least 3 hours at a temperature of 105°C. Samples were then brought to a moisture state (corresponding to moisture in the analysis sample (*M*) as determined by ISO 11722 standard [48]) in order to exceed the equilibrium moisture value (*EM*) according to the standard ASTM D1412-04 [49] procedure [44], [50] (Table 2). In fact, the equilibrium moisture corresponds to the amount of water in equilibrium with the coal structure [50], [51], and the excess water remains free and does not compete with gas for the “void volume” in the coal porous structure [44], [52].

Table 2. Moisture in the analysis sample and equilibrium moisture values

Sample	<i>M</i> (%)	<i>EM</i> (%)
A	16.3	~ 2.0
B	20.0	~ 2.0
C	6.6	5.1
D	4.6	4.3

#### 4.3 Experimental setup for sorption isotherms

The experimental data were produced using a sorption isotherm apparatus. Sorption isotherm measurements were carried out using a volumetric method, using the single component Langmuir Model to fit the data. This model describes the existing equilibrium between the stored gas and the absorbed/free gas in microsporous structures, such

as the one presented in coal [53]. The apparatus (Fig. 2) consists of a stainless steel sample cell, a stainless steel reference cell, a set of valves (connection, safety, purge) and thermocouples, and two high precision pressure transducers (maximum pressure 17 MPa, with a precision of 0.05% of the full-scale value).

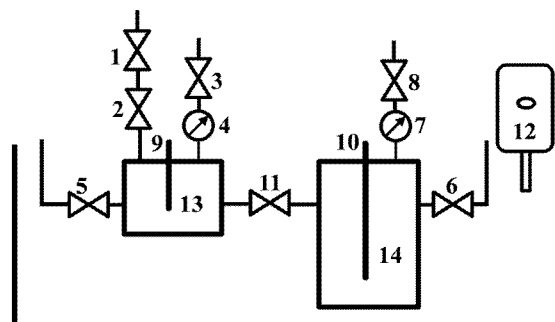


Fig. 2. Apparatus for sorption isotherm determinations: 1- CO<sub>2</sub> supply valve; 2 - Helium supply valve; 3, 8 - Safety valves; 4, 7 - Pressure transducers; 5, 6 - Purge valves; 9, 10 - Thermocouples; 11 - Connection valve; 12 - Thermostatic head; 13 - Reference cell; 14 - Sample cell.

The experimental procedure starts by purging the system and calibrating the reference cell and the sample cell volumes using the helium expansion. The powdered coal samples were placed into the calibrated sample cell, and the void volume in sample cell, the coal sample volume and the coal density were calculated using the helium expansion. The reference cell was then charged with CO<sub>2</sub> (sorption gas (*SG*)) and the connection valve between both cells was opened, thereby allowing the pressure stabilization, i.e., the adsorbed phase and the absorbed/free phase must be in kinetic equilibrium. The pressure decay curves were monitored as a function of time, in both cells, at each pressure step during sufficient time [54]. Sorption measurements were carried out at 5 or 7 different pressure steps. All sorption experiments were performed with CO<sub>2</sub> only, at a constant bath temperature of 35°C (*BT*), using coals with a sample mass (*SM*) ranging from 84 and 90 g (Table 3).

Table 3. Experimental conditions

Sample	<i>SG</i> composition (% of CO <sub>2</sub> )	<i>BT</i> (°C)	<i>SM</i> (g)
A	99.999	35	88.60
B	99.999	35	87.84
C	99.999	35	89.27
D	99.999	35	84.63

#### 4.4 Gas Storage Data

The gas storage process in coal is mainly controlled by physical mechanisms, specially the so-called adsorption process. Additionally, coal is a unique microporous reservoir characterized by a high

storage capacity, which is intimately related to the energy of interaction between the pore system structure of coal and the properties of the stored gas. The coal porous structure comprises a combination of micro-, meso- and macropores, although gas in coal is mainly stored in the adsorbed state on the internal surface area of the coal micropores, i.e., the volume of micropores in coal structure is small and consequently the great amount of stored gas in coal consists of adsorbed gas within the internal surface areas of micropores. In fact, these micropores are characterized by an enormous surface area which associated to the high affinity presented between the CO<sub>2</sub> and the coal structure and, finally to CO<sub>2</sub> high compressibility properties, enable a much greater amount of CO<sub>2</sub> to be stored than other gases [55], [39]. Therefore, CO<sub>2</sub> geological sequestration/storage in coal seams has been considered as a successful technological solution to the effective reduction of CO<sub>2</sub> emissions.

The gas adsorption property of coals is measured at isothermal conditions; consequently the most common technique used to study this mechanism is the adsorption isotherm. In fact, adsorption isotherms represent the experimental measurements of the amount of gases adsorbed on pore internal surface area, such as the case of coal micropores. Additionally, the adsorption isotherm consists in the technique capable of quantitatively characterize the relationship between the free/adsorbed gas and the gas stored (adsorbed gas) in the coal porous structure at a constant temperature. These experimental measurements were conducted as a function of pressure and temperature, which generally correspond to the *in situ* coal reservoir conditions. Adsorption isotherms data depend directly on the nature of the gas, in this particular case of CO<sub>2</sub> properties, the coal petrographic composition, the nature of interactions developed between the CO<sub>2</sub> and the coal micropores and the characteristics of the pore internal surface areas.

Data recorded during the sorption (comprising adsorption and desorption processes) isotherm experiments were pressure and time, which were the fundamental basis for all calculations. In practical terms, sorption isotherm data were established, at a given temperature and pressure, and after sufficient time, when the adsorbed phase and adsorbed/free phase are in dynamic kinetic equilibrium, i.e. the rate of adsorption and desorption from coal pore internal surface areas is equal. The Langmuir model is used to establish the adsorbed volume kinetic equilibrium, expressed by the following equation:

$$V_g = (V_L \times P)/(P + P_L) \quad (1)$$

where  $V_g$  is the gas volume per unit mass of coal (m<sup>3</sup>/ton);  $P$  is the equilibrium pressure (MPa);  $V_L$  is the maximum gas storage capacity of coal known as

Langmuir Volume (m<sup>3</sup>/ton) and  $P_L$  is the pressure at which coal adsorbs a volume of gas equal to half of its maximum capacity, known as Langmuir Pressure (MPa).

Adsorption isotherm measurements were performed at 5 different pressure steps (Table 4).

Table 4. Pressure steps used in sorption isotherms

Pressure step	Pressure (MPa)			
	Sample A	Sample B	Sample C	Sample D
1	0.67	0.76	0.88	0.84
2	1.46	1.79	1.72	1.96
3	2.59	2.83	3.06	2.99
4	3.62	3.81	4.04	4.04
5	4.81	4.72	5.09	4.91

The experimental sorption isotherm results show that the gas concentration ( $Q_{\text{residual}}$ ) is not constant during each adsorption pressure step but it decreases with time due to adsorption on the coal pore internal surface areas. Additionally, the general trend of the gas concentration decrease changes in the five pressure steps within the same adsorption isotherm and when comparing with the other adsorption isotherms (Fig. 3).

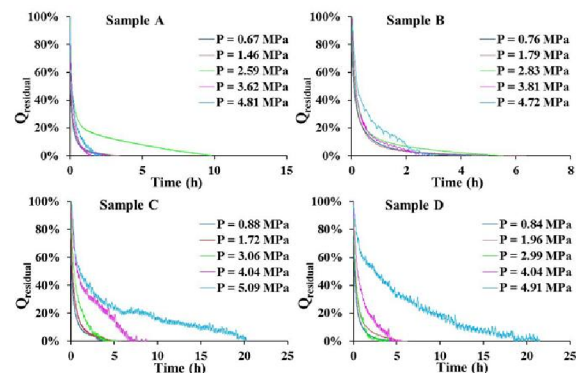


Fig. 3. CO<sub>2</sub> pressure equilibration curves for the five pressure steps in samples A, B, C and D.

Fig. 4 shows the CO<sub>2</sub> isotherms measured at 35°C for the four different coal samples. It is pertinent to mention that variations exist between the four CO<sub>2</sub> isotherm curves. In general, the higher adsorption capacity is exhibited by the sample B, while the lower adsorption capacity is reported by sample C. This is due to the fact that sample B is characterized by the higher  $Rr$  value (5.58%) and, at the same time, presents a high vitrinite content (72%); on the contrary the lower  $Rr$  value (0.62%) and vitrinite content (68%) are determined in sample C.

In fact, in general terms, the increase of both parameters in coal petrographic composition contributes to the increase of gas storage capacity by coal. Nevertheless, the understanding of the gas storage capacity presented by the different selected coal samples is more complex than analysing the



two parameters previously mentioned. In fact, accordingly to several authors [37], [41], [53], [55] the three maceral groups are characterized by different pore sizes, which will induce different gas storage capacities in coal. The vitrinite group is mainly characterized by micropores, the inertinite group is predominantly represented by meso- and macropores and finally the liptinite group does not present any relevant pores in their structure.

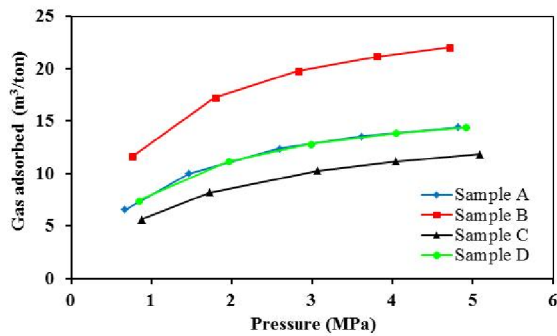


Fig. 4. CO<sub>2</sub> adsorption isotherms for samples A, B, C and D.

Therefore, pores in the vitrinite group present a higher internal surface area comparing to the other two maceral groups and consequently a higher gas storage capacity. So, when comparing the gas storage capacity by coals with extremely different ranks and similar vitrinite contents, such as samples A ( $Rr = 4.68\%$ ,  $V = 77\%$ ) and D ( $Rr = 0.72\%$ ,  $V = 75\%$ ), it is also important to take into account the inertinite and mineral matter contents and coal porous structure changes induced by the depositional environment conditions and the incarbonization process. To better understand the effect produced by petrographic composition on the gas storage capacity, taking into consideration that  $V_L$  for coals corresponds to the maximum gas sorption capacity, the parameter  $V_L$  was plotted against the most relevant petrographic characteristics ( $Rr$ ,  $V$ ,  $I$ ,  $MM$ ). Fig. 5, and specifically when comparing data from samples A and D, clearly demonstrates that the increase on adsorption capacity does not depend exclusively on the  $Rr$  increases, i.e., in this case both samples present similar gas adsorption capacities ( $V_L = 17.89 \text{ m}^3/\text{ton}$  in sample A;  $V_L = 17.91 \text{ m}^3/\text{ton}$  in sample D) due to the fact that the  $MM$  content in sample A is 2.5 times higher than in sample D, and the  $I$  content in sample A is 1.75 times lower than in sample D. In fact, both trends reduce the pore structure medium and consequently the gas storage capacity. In addition, the most relevant effect is related to the incarbonization process. Several authors [55], [56] defended that between the boundary of the bituminous coal rank and the anthracite rank, coals develop progressive changes in their molecular structure, i.e., the molecular structure became highly aromatized and pores start collapsing, reduction the gas storage capacity.

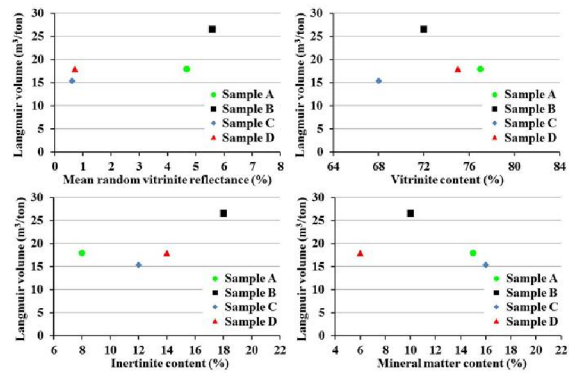


Fig. 5. CO<sub>2</sub> Langmuir volume *versus* petrographic characteristics (mean random vitrinite reflectance, vitrinite content, inertinite content and mineral matter content) for samples A, B, C and D.

#### 4.5 Gas Diffusion Data

Diffusion is the predominant process in gas circulation (flow) in coal microporous structure, i.e. that diffusion is the process responsible for gas molecule movements through voids and micropore spaces present in the coal, allowing to fill the micropore system as a function of a specific rate. Taking into consideration that coals, in underground conditions, are isothermal reservoirs, the diffusion process depends on coal properties, the gas composition and the pressure gradient. Diffusion in this paper is measured by the diffusion coefficient using data produced during sorption isotherms, assuming that a monolayer adsorption/desorption occurs at the coal pores and gas interface. The diffusion coefficient determination stand in the fundamental principle, that this parameter measures the coefficient of proportionality between the gas flux and the concentration gradient of a given gas. Diffusion coefficient measurements are rather complex than sorption isotherm determinations. In the second data set only the final equilibrium pressure and the gas concentration (gas content) were required, whereas the diffusion coefficient data set requires precise and continuous monitoring of changes in pressure and gas concentration in sample and reference cells, during the whole sorption process. This procedure is repeated for all pressure steps during the adsorption and desorption processes, and the calculated change in gas concentration *versus* the square root of elapsed is plotted for each pressure step. Nevertheless, it is pertinent to mention that for the diffusion coefficient calculation the initial sorption period, i.e. when the gas sorbs at an extremely fast way, play a crucial and fundamental role. In fact, the slope of the first linear part of the data curve, expressed as the parameter  $b$ , when incorrectly determined will introduce significant uncertainties in the calculation of diffusion coefficient values. Therefore, the diffusion coefficient is calculated taking into consideration the

slope of the first linear part of the data sorption curve, the radius of spherical particles and the gas content change using the following equation:

$$D = \left[ \frac{br_s}{3.3851(V_i - V_{i-1})} \right]^2 \quad (2)$$

where  $D$  is the diffusion coefficient ( $\text{cm}^2/\text{sec}$ );  $b$  represents the slope (first linear part of the data curve);  $r_s$  is the spherical particle radius (cm);  $V_i$  is the gas content at the end of step  $i$  ( $\text{cm}^3/\text{ton}$ ) and  $V_{i-1}$  represents the gas content at the end of step  $i-1$  ( $\text{cm}^3/\text{ton}$ ).

Diffusion coefficients were calculated for the four samples in each pressure step of the adsorption and desorption processes. Figs. 6, 7, 8 and 9 show the same general trend in what concerns the evolution of diffusion coefficient values *versus* pressure changes, i.e. that figures show a negative correlation between diffusion coefficient and pressure, both for increasing (adsorption process) as well as decreasing pressure steps (desorption process). This general behavior is intimately related to the increase and decrease of kinetic mechanisms induced by pressure increase and decrease, respectively. Additionally, all studied samples show higher diffusion coefficient values for the adsorption process than the desorption process.

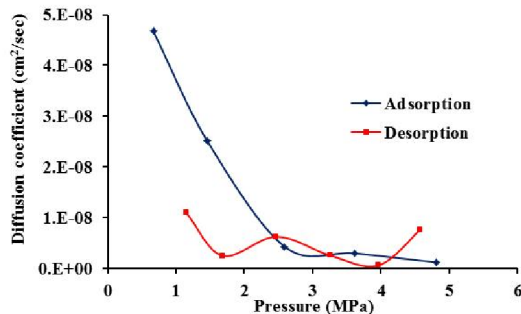


Fig. 6. Diffusion coefficients for adsorption and desorption pressure steps for sample A.

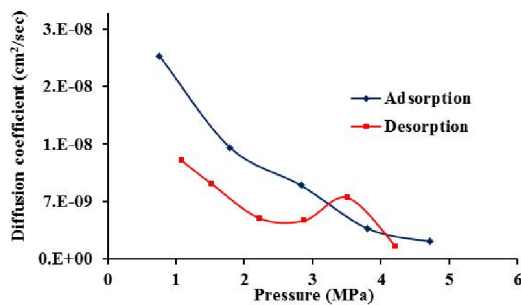


Fig. 7. Diffusion coefficients for adsorption and desorption pressure steps for sample B.

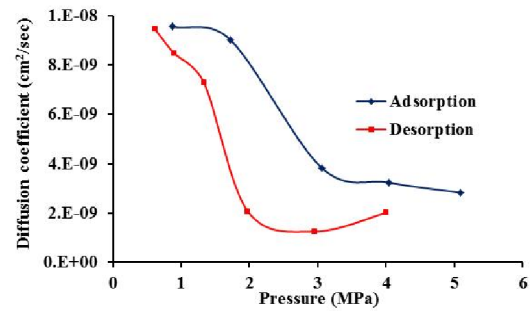


Fig. 8. Diffusion coefficients for adsorption and desorption pressure steps for sample C.

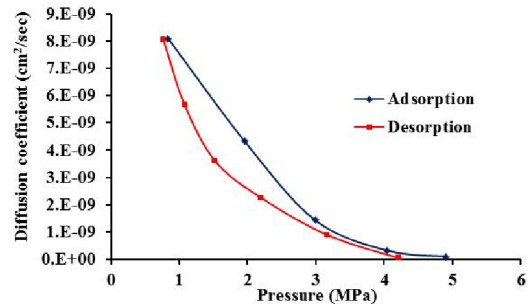


Fig. 9. Diffusion coefficients for adsorption and desorption pressure steps for sample D.

When comparing diffusion coefficient values determined for the four samples, it is possible to identify an identical general trend in both adsorption (Fig. 10) and desorption (Fig. 11) processes. However, analysing the entire four adsorption data sets plotted along with the variation in diffusion coefficient values suggest that the variation in diffusion coefficient values with pressure present a high dependency on pressure evolution. The same response to the entire four desorption isotherm data sets were detected. In fact, both diffusion coefficient data sets, adsorption and desorption data, show two distinct behaviours depending on pressure: at low pressures (below c. 2 MPa) and at high pressures (above c. 2 MPa). At low pressures and during the adsorption process, the diffusion coefficient values determined for the four samples decrease with pressure increase, suggesting that adsorption behaviour is responsible for the decrease in the diffusion coefficient values, while during the desorption process, the diffusion coefficient values show a general increase with pressure decrease suggesting that desorption behaviour controls the increase in the diffusion coefficient values. At high pressures the diffusion coefficient values remain almost constant in all samples in both adsorption and desorption processes. Yet, at low pressures, the decrease rate with pressure increase identified on diffusion coefficient values determined during the adsorption data and the increase rate with pressure

decrease detected during the desorption process is significantly different between samples A/B and samples C/D. In fact, at low pressures, samples A and B show higher diffusion coefficient values than samples C and D, i.e. the activation energy for diffusion of CO<sub>2</sub> is higher for samples A and B (anthracite coals) than for samples C and D (bituminous coals), which suggests that the samples A and B are characterized by a smaller average micropore size than samples C and D.

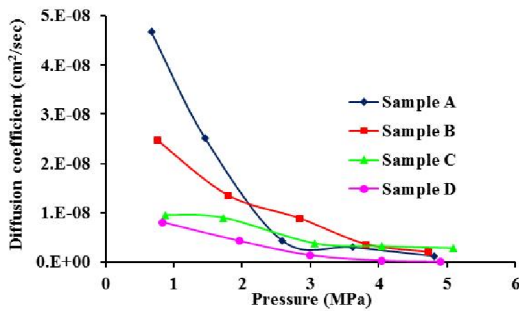


Fig. 10. Diffusion coefficients for adsorption pressure steps for samples A, B, C and D.

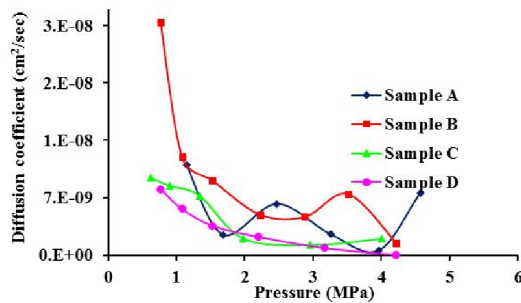


Fig. 11. Diffusion coefficients for desorption pressure steps for samples A, B, C and D.

Nevertheless, several authors [54], [55] stated that the activation energy for diffusion of CO<sub>2</sub> is less for anthracites than for the bituminous coals. So, to study the diffusion coefficient behaviour implies a carefully analysis because of the uncertainties in the interpretation of determined values, which are mainly related with coal properties. In fact, the anthracite coals (sample A and B) selected to the present study show higher diffusion coefficient values than bituminous coals (samples C and D) due to their different genetic conditions. The depositional environment conditions for Samples A and D were mainly characterized by anaerobic processes when compared to samples C and D, which allows the production of a secondary cell infillings in the vitrinite group and consequently an increase in the average of micropore size and therefore in the pore internal surface areas. So, in this case, the genetic conditions specific of both sample sets (samples A/B and samples C/D) were able to mask the rank effect. In conclusion and in general terms, sample D presents the lower diffusion coefficient values and

sample A the higher coefficient values during the adsorption process, and during the desorption process the lower diffusion coefficient values are once again determined in sample D, but the higher diffusion coefficient values are calculated for sample B.

## 5 CONCLUSIONS

In the scope of the main goal proposed for the present work, i.e. to study the coal as an unconventional reservoir for a CO<sub>2</sub> safe geological sequestration/storage solution, results must be analyzed in two distinct components: to study the CO<sub>2</sub> storage capacity presented by the four selected coals and to study the viability to perform a permanent and secure CO<sub>2</sub> storage in short term (few decades) and long term (several hundred to thousands of years). In this perspective, results related to gas storage (adsorption) data can be mainly used to understand the different CO<sub>2</sub> storage capacities by coals, and gas diffusion data can be set a fundamental tool to study the permanent and secure CO<sub>2</sub> storage viability.

Four coal samples were selected to the present investigation, two of them from anthracite rank (samples A and B) and the others two from bituminous rank. Sorption isotherm measurements were carried out at a temperature of 35°C and at CO<sub>2</sub> pressures below 6 MPa.

As a general conclusion, in what concerns pressure changes, results show for all four samples an increase of CO<sub>2</sub> sorption capacities and a decrease of diffusion coefficient values with pressure increases.

The maximum CO<sub>2</sub> adsorption capacity of these coals varies from about 15 to 27 m<sup>3</sup>/ton. The higher CO<sub>2</sub> adsorption capacity is reported by sample B, due to the high mean random vitrinite reflectance value of 5.50%, high vitrinite content of 72%, and mainly to his depositional environment conditions. In fact, the anaerobic conditions, which are representative in the coal sample B formation, are the most pertinent parameter responsible for the production of a secondary microporous structure and consequently an increase on pore internal surface areas, which finally will increase diffusion coefficient values. On the contrary, sample C presents the lower diffusion coefficient values, which is mainly related to the low mean random vitrinite reflectance value (0.62%) and low vitrinite content (68%). So, in terms of CO<sub>2</sub> geological sequestration/storage sample B appears as the best solution.

In general terms, the diffusion coefficient values show significant changes at low pressures, although at high pressures the diffusion coefficient values remain almost constant, in both adsorption and desorption processes. In addition, the higher diffusion coefficient values are calculated for sample



A and the lower values are determined for sample D, during the adsorption process. However, the desorption process reports the higher diffusion coefficient values for sample B and the lower values for sample D. As a result, and taking into account the CO<sub>2</sub> geological/sequestration scope, which implies a CO<sub>2</sub> injection first phase and a CO<sub>2</sub> leaks control at short and long terms second phase, the diffusion coefficient values calculated during the adsorption process are more relevant to understand the CO<sub>2</sub> injection and CO<sub>2</sub> leaks are more easily interpreted by analysing data calculated during the desorption. In this context, the most suitable diffusion coefficient values to CO<sub>2</sub> injection phase were determined for sample A, and sample D presents the most appropriate diffusion coefficient values for the CO<sub>2</sub> leaks control phase.

In conclusion, and considering that a CO<sub>2</sub> geological sequestration/storage programme implies a CO<sub>2</sub> injection pressure value near from the *in situ* pressure conditions, i.e. high pressures, the sample D shows the most suitable diffusion coefficient values. In fact, this is due to the fact that during the adsorption process at high pressures, the diffusion coefficient values for sample D are similar to the ones determined for the other three samples, and at the same time this sample shows the lower diffusion coefficient values during the desorption process. In fact, this last statement will contribute strongly to the permanent and secure CO<sub>2</sub> storage required for a suitable geological sequestration/storage solution.

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