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Coal laboratory characterisation for CO₂ geological storage

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Abstract

Geological storage of CO₂ in unmineable coal seams could be a very interesting option in the sustainable management of coal basins. However, the various chemical and physical parameters that determine the success or failure of this type of operation need to be clarified. The CHARCO project aims at developing methods and analysis techniques in order to define the major parameters enabling optimal CO₂ storage conditions. In this framework, 22 coals of different ranks were sampled in different locations and systematically characterized (coal ranks, macerals, porosities, CO₂ and CH₄ adsorption isotherms ...). The isotherms were modelled using the classical Langmuir formalism in order to obtain their adsorption capacities and their affinity for CO₂. The high number of coals and parameters considered in our study allow a statistical treatment using Principal Component Analysis. The sorption capacity can not be easily correlated with any other single parameter. On the other hand, CO₂ affinity is correlated with coal rank.

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Keywords: CO₂ storage; coal; ECBM; CO₂ sorption; modelling.

1. Introduction

Geological storage of CO₂ in unmineable coal seams has not yet reached operational maturity, although it could be a very interesting option in coal basins in order to limit the extension of CO₂ pipelines and related high costs. In coal basins, a virtuous cycle can be imagined, with the production of coal, the generation of electricity using local coal-fired power plants, the capture of CO₂ and the storage of CO₂ in the unmineable coal seams of the basin. In some cases, CO₂ storage could also be economically advantageous if it could be linked to CH₄ production in an

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Enhanced Coal Bed Methane (ECBM) operation (Figure 1) [1]. Considering the available volume, injection of CO₂ into coal seams could be a valuable option for storing CO₂ in geological formations. However, the various chemical and physical parameters that determine the success or failure of this type of operation need to be clarified. To address this objective, an intensive research program was undertaken by a French consortium (CHARCO) supported by ANR (French National Research Agency). This program aims at developing methods and analysis techniques in order to define the major parameters enabling optimal CO₂ storage conditions for numerous coal types.

The strong adsorption of CO₂ on the internal surfaces of coal means that the gas can be trapped with low reversibility, thus limiting the risk of leakage, which enhances the technical interest and societal acceptance of this type of storage [2, 3]. Moreover, due to the nature of the CO₂-coal affinity (adsorption) and the considerable internal surface area of coal (20 to 300 m²/g), coal seams can potentially store up to 40 m³ or even 60 m³ [STP] of CO₂ per tonne of coal at relatively low gas pressures of about 5 to 6 MPa. Coal seams can thus store at least 5 times (even 10 times for the most captive and porous layers) the quantity of gas that is a traditionally contained within a classical reservoir rock. As an example, a preliminary study carried out on two very limited areas, each of 50 km², respectively located in the Lorraine basin and in the Arc basin (France), resulted an estimation of the storage capacity at 30 millions tonnes of CO₂ in each area, considering an accessibility of 30% of the theoretical volume developed by the available layers between 500 and 1500 m depth [4].

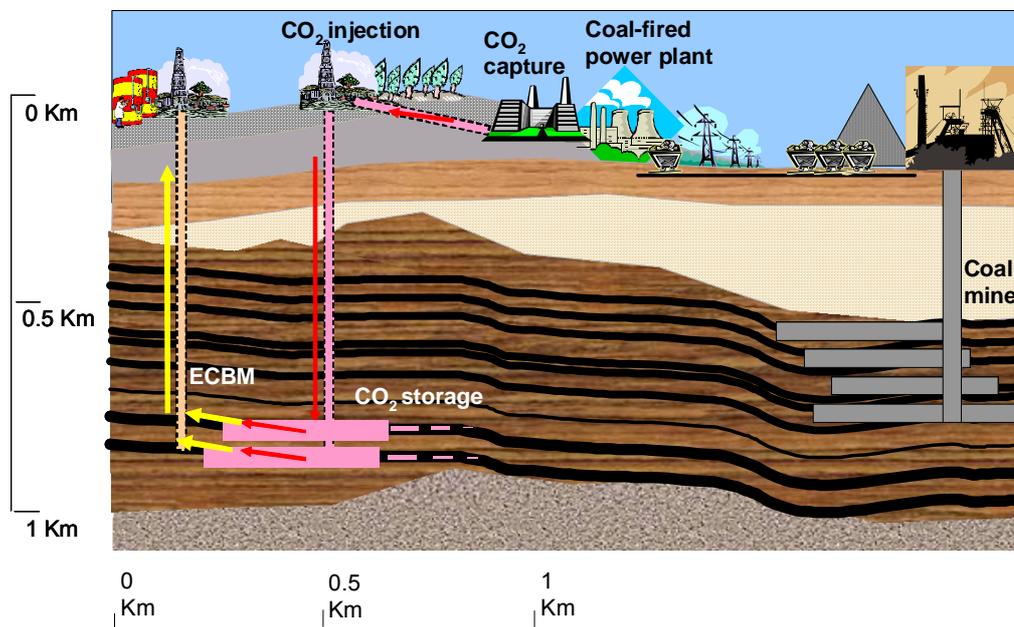


Figure 1 : The virtuous cycle of a coal basin: Coal mine, generation and exportation of electricity, CO₂ capture, CO₂ storage in the deepest seams of the basin and optional production of enhanced coal bed methane (ECBM).

The optimization of this storage depends primarily on the permeability of the layers (coal and surrounding strata), their behaviour during the injection of CO₂ and the quantity of methane likely to be recovered. As an example, coal seams in France classically contain methane concentrations ranging from 5 to 25 m³[STP]/tonne and it has been demonstrated [3, 5, 6] (and confirmed in our project) that one mole of methane can be replaced by two to five moles of CO₂. The displacement of CH₄ by CO₂ is obtained thanks to the preferential sorption of CO₂ under the pressure of injection. When the CO₂ pressure in the coal seam increases, the methane is partially replaced by the CO₂ and is transported by diffusion towards the cleat system (fractures) and then flows through cleats to the production wells.

In the framework of our project, 22 coals of different ranks were sampled in different locations and characterized. Firstly, the nature of the coal was determined:

- Coal rank
- Quantification of macerals (vitrinite (V), inertinite (In), exinite (Ex))

Secondly, the specific surfaces to $N_2(g)$ and $CO_2(g)$ were determined. The porosities (ultramicroporosity to macroporosity) were obtained using mercury injection and the numerical treatment of N_2 and CO_2 adsorption isotherms at low pressure. A quantification of the accessory minerals was also performed in order to avoid any misinterpretation due to the possible presence of clay minerals [7]

Gas adsorption isotherms for $CO_2(g)$ and $CH_4(g)$ on coal were systematically acquired at a gas pressure from 0.1 to 5 MPa. A study of the competition between gas sorption and water vapor sorption was also investigated. The isotherms were modelled using Langmuir, Freundlich, Tóth, or Temkin formalisms.

Since coal swelling capacity is a key issue for the long term injectivity of CO_2 into coal seams, the mechanical properties of the different types of coal were studied. However, only two samples in our collection were sufficiently hard to be cored. Consequently, an alternative approach was developed but will not be described in the present paper due to a pending patent.

2. Materials and methods

2.1. Coal samples

Table 1 details the different coals studied. An effort was made to obtain a wide range of maturities from lignite to the meta-anthracite.

Sample	US/FR Classification	Origin	Ro%	VM%	Corg%
JER01	Meta-anthracite	Jerada, Morocco	3.65	10.7	90.9
CO03	Anthracite	El Cerrejon, Columbia	2.54	5.6	87.3
AL03	LVB / 3/4 gras	Alès, France	1.68	13.9	84.5
AL02	MVB / Gras à coke	Alès, France	1.44	15.2	79.9
GR02	MVB / Gras à coke	Graissessac, France	1.42	18.5	83.0
GR01	MVB / Gras à coke	Graissessac, France	1.42	19.4	82.8
GR03	MVB / Gras à coke	Graissessac, France	1.27	22.6	79.2
ES02	MVB / Gras à coke	Monsacro, Spain	1.24	27.9	83.2
ES03	MVB / Gras à coke	Monsacro, Spain	1.19	25.6	83.2
BHS01	MVB / Gras à coke	Boleslaw Smialy, Poland	1.18	23.5	87.7
AL01	MVB / Gras	Alès, France	1.16	14	86.0
ES04	MVB / Gras	Monsacro, Spain	1.16	27.5	82.4
ES01	HVB / Gras	Monsacro, Spain	0.98	26.7	80.8
BHP01	SB / Lignite dur	Gardane, France	0.79	54.7	47.6
CO04	HVB / Flamb.	El Cerrejon, Columbia	0.76	46.4	76.1
CO02	HVB / Flamb.	El Cerrejon, Columbia	0.75	36.1	74.02
BHL01	HVB / Flamb.	La Houve, France	0.74	33	73.0
BHL02	SB / Lignite dur-Flamb.	La Houve, France	0.73	32.5	66.2
TH01	SB / Lignite dur-Flamb.	La Houve, France	0.70	34.9	70.5
SA01	HVB / Lignite dur	Carbosulcis, Sardinia	0.54	44.9	59.4
CO01	SB / Lignite dur	El Cerrejon, Columbia	0.49	33.6	74.4
BHS02	HVB / Flamb.	Zofowka, Poland	0.31	37.7	76.2

Table 1: Coal samples origin and rank (US and French classification). The maturity of the coals was determined coupling different parameters: Vitrinite reflectance Ro, Volatile matter VM%. SB: Sub Bituminous Coal; HVB: High Volatile Bituminous Coal; MVB: Medium Volatile Bituminous Coal; LVB: Low Volatile Bituminous Coal.

2.2. Methods

The analytical and experimental methods listed above are not described in this paper. The petrographical, textural and chemical analyses can be found in Défossez et al. [8]. Coal rank was determined by combining different techniques: Volatile matter (VM%), Oxygen index (Oi), Hydrogen index (Hi), and Vitrinite reflectance (Ro). The Ash content (Ash%) was measured and a mineralogical characterization by X-ray diffraction was performed. The moisture fractions were obtained before (W%) and after correction of the mineral (“ash”) fraction (WAF%). The different coals were also assayed for: Total carbon (C_{tot}), Organic carbon (C_{org}), Mineral carbon (C_{min}), Total sulphur (S), and Iron (II) (Fe_{II}).

Three techniques were used to characterize the microtexture of the different coals. Classical gas monolayer adsorption at low pressure was performed with $\text{N}_{2(\text{g})}$ (BET at 77 K) and $\text{CO}_{2(\text{g})}$ (BET at 298 K). Since the shape and size of the two molecules are different, they do not “explore” the same porosities of the coal. $\text{CO}_{2(\text{g})}$ is adsorbed on a larger surface than $\text{N}_{2(\text{g})}$, thus making it possible to quantify the microporosity of the coal, i.e. pores of diameter less than 2 nm. $\text{N}_{2(\text{g})}$ enables the mesoporosity of the coal, i.e. pores of diameter between 2 and 50 nm, to be quantified. The last technique, mercury injection enables the macroporosity of the coal, i.e. the pores larger than 50 nm, to be quantified.

The adsorption isotherms were performed with a gravimetric method at pressure up to 5 MPa; details in Charrière et al. [9].

3. Results

3.1. Specific surfaces and porosities

	Ro	SSBET	SS μp	V μp	Vmp	VMp	VPT
Sample	%	m ² .g ⁻¹	m ² .g ⁻¹	cm ³ .g ⁻¹	cm ³ .g ⁻¹	cm ³ .g ⁻¹	%
JER01	3.65	6.8	218.4	0.080	0.004	0.077	10.1
CO03	2.54	1.1	175.1	0.064	0.002	0.071	9.47
AL03	1.68	2.1	111.6	0.041	0.004	0.085	8.67
AL02	1.44	3.8	91.4	0.033	0.007	0.104	8.67
GR02	1.42	2.0	118.1	0.043	0.004	0.106	10.7
GR01	1.42	2.5	117.1	0.043	0.004	0.112	11.4
GR03	1.27	4.8	76.2	0.028	0.006	0.081	6.46
ES02	1.24	1.6	98.8	0.036	0.003	0.084	8.64
ES03	1.19	2.2	111.9	0.041	0.004	0.084	9.20
BHS01	1.18	2.1	117.9	0.043	0.003	0.112	11.5
AL01	1.16	2.0	119.0	0.043	0.003	0.074	8.67
ES04	1.16	2.4	92.3	0.034	0.004	0.110	10.2
ES01	0.98	1.6	110.1	0.040	0.003	0.061	7.30
BHP01	0.79	4.4	74.9	0.027	0.009	0.126	9.44
CO04	0.76	1.2	120.7	0.044	0.003	0.041	6.47
CO02	0.75	2.8	120.6	0.044	0.007	0.062	8.47
BHL01	0.74	1.9	267.5	0.097	0.003	0.119	16.1
BHL02	0.73	1.6	132.7	0.048	0.003	0.101	11.2
TH01	0.70	1.1	127.4	0.046	0.002	0.102	11.6
SA01	0.54	2.1	86.9	0.032	0.006	0.081	8.24
CO01	0.49	5.3	117.9	0.043	0.013	0.091	10.9
BHS02	0.31	3.7	96.8	0.035	0.008	0.054	6.39

Table 2: Specific surfaces obtained using the classical monolayer adsorption of $\text{N}_{2(\text{g})}$ (SSBET method) or $\text{CO}_{2(\text{g})}$ (SS μp). The microporosity (V μp) and the mesoporosity (Vmp) were obtained by calculation from the $\text{N}_{2(\text{g})}$ and $\text{CO}_{2(\text{g})}$ isotherms. The macroporosity (VMp) was directly measured using the mercury injection technique. VPT is the total porosity obtained as the sum of the three fractions expressed as a percentage of the total volume of the samples.

Table 2 shows the analytical results concerning specific surfaces and porosities. These results are dispersed and cannot be correlated with any rank parameter. The decrease in total porosity observed for coals of Ro lower than 1.0% by Rodrigues and Lemos de Sousa [10] is not observed in our experiments. However, for coal of Ro higher than 1.0%, an increase in the total porosity is observed. The macroporosity is not linked to any rank parameter. This porosity seems clearly linked to the specific geology of the coal basins. The mesoporosity is not strongly correlated with any rank parameter. However, the highest values are obtained for the lowest ranks and the lowest for the anthracites. The microporosity is clearly linked to maturity and can be double for anthracites in comparison with lower ranks.

3.2. Adsorption isotherms

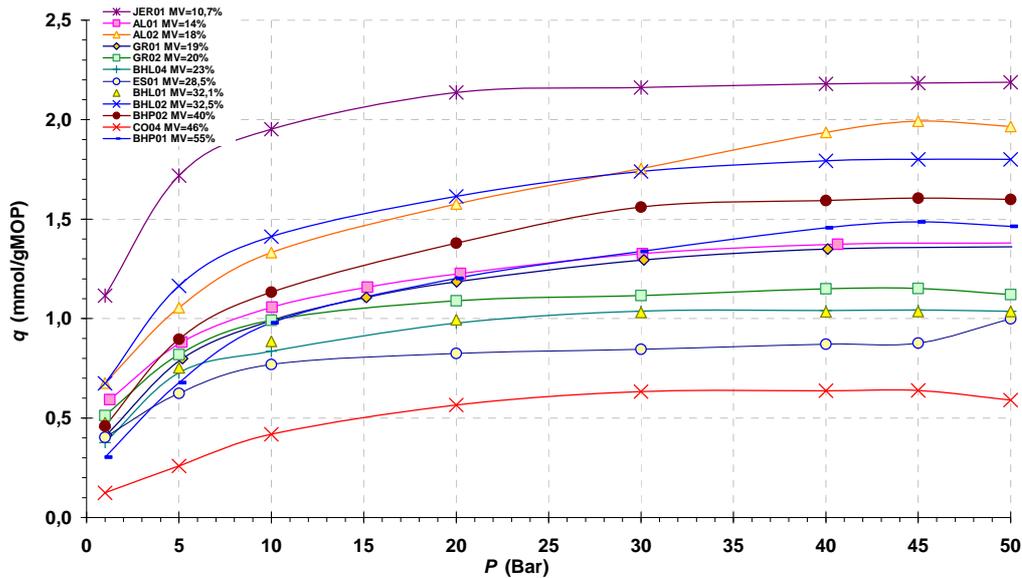


Figure 2: Selection of adsorption isotherms of CO₂ of our collection of coal. The samples were dried. The maximum pressure was 5.5 MPa. The quantity of CO₂ is expressed in mmol/g of pure organic matter (MOP).

Figure 2 shows a selection of the adsorption isotherms for our collection of coals. The shape of the isotherms is of type I (IUPAC Classification), corresponding to the formation of a monolayer of molecules or/and the filling in of the microporosity. The isotherms show a rapid increase in adsorption capacity over a low pressure range (<10 bar). An asymptotic tendency is observed for higher pressures corresponding to the saturation of the adsorption capacity. The maximal capacity for our collection of coals is between 0.6 and 2.5 mmol/g_{MOP}. These results are in the classical range obtained for coals [11, 12]. A careful observation of the isotherms shows that the concavity of the isotherms is very variable. The strongest concavities provide evidence of a strong affinity of the coal for CO₂. On the other hand, some isotherms have a very “flat” shape, showing low affinity for the CO₂ (for example: CO04).

4. Modelling of CO₂ isotherms.

In the framework of our CHARCO project, different treatments were performed on the CO₂ isotherms. The classical approach of Langmuir was applied (Figure 3). To increase the precision of the fits, two more modern models from Tóth and Temkin were also tested. This work is detailed in Garnier et al., [13]. In the present paper, we have only exploited the results obtained with the Langmuir formalism (Table 3).

Sample	Ro	qmL	αL
	%	mmol/gMOP	
JER01	3.65	2.25	0.79
CO03	2.54	1.66	0.77
AL03	1.68	1.60	0.22
AL02	1.44	2.15	0.20
GR02	1.42	1.18	0.58
GR01	1.42	1.47	0.24
GR03	1.27	2.06	0.12
ES02	1.24	1.68	0.11
ES03	1.19	1.04	0.25
BHS01	1.18	1.07	0.43
AL01	1.16	1.47	0.30
ES04	1.16	1.13	0.23
ES01	0.98	0.97	0.36
BHP01	0.79	1.67	0.15
CO04	0.76	0.71	0.17
CO02	0.75	1.38	0.24
BHL01	0.74	1.08	0.57
BHL02	0.73	1.91	0.34
TH01	0.70	1.10	0.42
SA01	0.54	2.70	0.14
CO01	0.49	2.26	0.12
BHS02	0.31	1.31	0.21

Table 3: Langmuir parameters obtained by a systematic calculation on the CO₂ isotherms: $\theta = \frac{q}{q_{mL}} = \frac{\alpha_L P}{1 + \alpha_L P}$ qmL is the quantity of CO₂ adsorbed at saturation of the porosity. αL is the Langmuir constant .

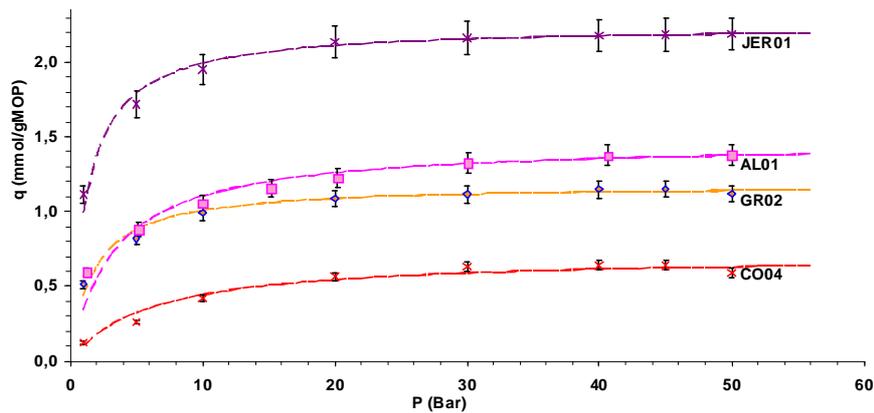


Figure 3: Example of modelling of CO₂ isotherms using the Langmuir formalism after [13]. .

The parameters qmL and αL allow a classification of the coals as a function of their adsorption capacities and their affinity for CO₂, respectively. The highest capacity (qmL) is obtained for the coal from the Carbosulcis mine in Sardinia (SA01), which is a low rank coal. The second highest value is obtained with the meta-anthracite of Jerada (JER01). The lowest value is found in the El Cerrejon mine (Columbia) for a coal of HVB type (CO04). However, this tendency to find the lowest capacities for the coal of intermediate rank is not systematic in our collection of coals. One explanation could be linked to the presence of accessory minerals such as clays or palygorskite (detected by X-ray diffraction), which could increase the sorption capacities of the coals. The meta-anthracite of Jerada (JER01) also shows the highest affinity for CO₂. The coal (CO04) is clearly the worst case with a very low affinity for CO₂ coupled with a very low adsorption capacity.

5. Multivariable correlations

The high number of coals and parameters considered in our study allow a statistical treatment using Principal Component Analysis (PCA). The graphic representation of the multiple correlations helps to understand how the data is organized and hence clarifies the relation between parameters. When two parameters are strongly correlated, they are very close. When they are anti-correlated, they are at opposite ends in the figure. An angle of around 90° between two parameters indicates that no correlation exists between them.

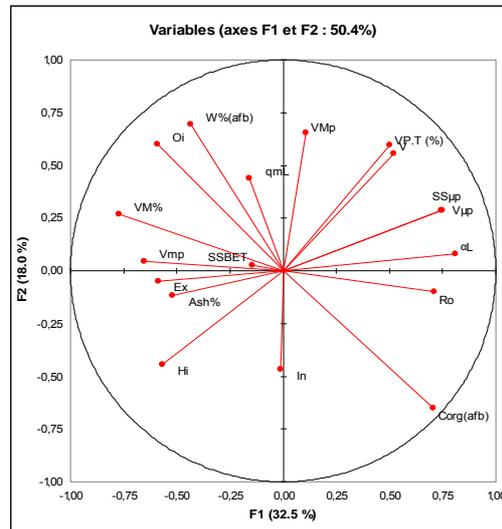


Figure 4 : Principal Component Analysis (PCA) of the major chemical and physical parameters for 22 coals.

Variables	VM%	Ro	SSμp - Vμp
qmL	-0.005	0.113	-0.085
αL	-0.56	0.70	0.75

Table 4: Results of the Pearson correlation matrix for the whole collection of coals for two parameters: qmL and αL.

No statistical correlation can be found for the adsorption capacity (qmL) with any parameter of rank or porosity for the whole collection of coals (Figure 4 and Table 4). On the other hand, the affinity (αL) is clearly correlated (values > 0.5) to the parameters of rank and microporosity (Vμp).

6. Conclusions

The analysis of a significant number of coals of various ranks with the same techniques and the same modelling methods allows some noticeable progress in the parameter discrimination involved in the sorption and storage of CO₂ in coal. The sorption capacity can not be easily correlated with any other single parameter. Even if some tendencies can be detected with a lower capacity for coals of intermediate ranks, no systematic correlation can be found. On the other hand, CO₂ affinity is correlated with coal rank. A recommendation can thus be formulated from this study: anthracites seem to combine the highest capacity with the highest affinity and thus research work in the perspective of CO₂ storage in this type of coal can be recommended. However, Durucan et al., [14] have found that a correlation exists between the rank increase and the swelling capacity of the coals during gas adsorption. This result, if it is confirmed, could exclude the higher ranks from future pilot sites for CO₂ injection into coal seams. In the work in progress developed by our CHARCO consortium, the question of the intensity of the swelling of coals

as a function of the other intrinsic parameters is under focus. The better understanding of this problem, using our systematic approach, would help to increase the probability of successful implementation of future pilots for CO₂ injections into coal seams.

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