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An experimental approach to adsorption of CO_2 + CH_4 gas mixtures onto coal (European RFCS CARBOLAB research project)

Stéphane LAFORTUNE[a,*], Francis ADELISE[a], Gaëtan BENTIVEGNA[a], Christophe DIDIER[a], Régis FARRET[a], Philippe GOMBERT[a], Candice LAGNY[a], Zbigniew POKRYSZKA[a] and Noel CANTO TOIMIL[b]

[a]*French National Institute for Industrial Environment and Risks*
Institut National de l'Environnement Industriel et des Risques (INERIS)
Parc Technologique ALATA, BP2
60555 Verneuil-en-Halatte, France
[b]*HUNOSA (Grupo SEPI), Departamento Nuevos Desarrollos*
Av. Galicia 44
33005 Oviedo, Asturias, Spain

Abstract

Results from adsorption experiments of CO_2 + CH_4 gas mixtures onto coal show that adsorption capacities determined with pure gas phases cannot be added to determine the total adsorption capacity of a gas mixture; and that both CO_2 and CH_4 adsorption capacities for experiments performed with gas mixtures are lower than those determined for experiments with pure gases. These results confirm that gases compete to adsorb onto coal. Results also show that the extended Langmuir model that is often used to model sorption of binary gas mixtures does not fit our experimental data. Thus, authors propose here another model.

Keywords: ECBM ; CO_2 ; storage ; adsorption ; Langmuir ; modeling.

* Corresponding author. Tel.: +33-3-44-55-67-91; fax: +33-3-44-55-67-00.
E-mail address: stephane.lafortune@ineris.fr

1.1. The RFCS CARBOLAB research project

The main goal of the RFCS CARBOLAB research project was to fill the gap concerning the lack of data and comprehension of the physicochemical mechanisms that exist between laboratory experiments on gas adsorption properties of coal and full-scale CO_2 injection tests from the surface. This project was funded by European commission through the Research Fund for Coal and Steel from 2009 to 2013.

Gathering Spanish (HUNOSA, AITEMIN), French (BRGM, INERIS) and Polish (GIG) partners, the project contained three main actions: laboratory tests, numerical modeling and in-situ injection at a seam scale. The injection site was within an existing underground infrastructure, a crosscut of a coal mine located in Asturias (North of Spain) and owned by HUNOSA (project coordinator). This article details some of the results from laboratory tests. For further details on the injection test and monitoring at the seam scale, see [1] and [2].

1.2. Laboratory tests

Injection of CO_2 in coal can enhance methane recovery. This technique known as CO_2-ECBM (Enhanced coal bed methane recovery) can be used in conjunction with carbon capture and storage to mitigate anthropogenic CO_2 emissions. The mechanisms involved are known (injected CO_2 will flush the pore space, drive methane desorption and CO_2 will adsorb onto coal at approximately twice the sorption capacity of methane) but not well understood.

Thus, INERIS has performed adsorption experiments of gas mixtures onto a coal sample in order to (1) draw an experimental protocol to study the adsorption of gas mixtures; (2) characterize competitive processes between adsorption of CO_2 and adsorption of CH_4; and (3) determine mathematical equations to model the adsorption of gas mixture onto coal.

2. Coal sample

Coal sample was collected in situ using a hammer and a crow bar from the wall of the CARBOLAB crosscut. Sample was placed in a plastic bag which was sealed underground before carrying it to our laboratory. Proximate analyses have been done on sample (tab. 1; for further details refer to sample ES04 in [3]).

Table 1. Proximate analyses. DAF = dry and ash-free coal.

Parameter	Sample
Moisture content [mass %, raw coal] (156h at 105°C)	0.31
Ash content [mass %, dry coal] (16h at 820°C)	17.18
Vitrinite reflectance [%]	1.16
Volatile matter content [mass %, DAF]	27.5

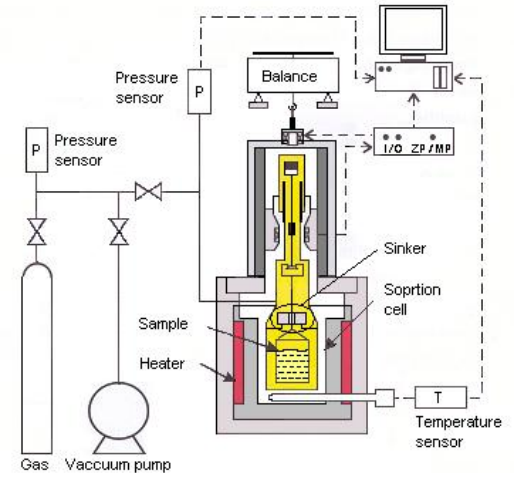
3. Adsorption isotherms determined through gravimetric experiment

Adsorption isotherms have been determined through a gravimetric experiment on a magnetic suspension balance, in order to assess quantities of gas that can be adsorbed or desorbed (fig. 1 and [4]). Adsorption experiments have been determined for pure gas phases (CO_2 and CH_4) and binary gas mixtures (tab. 2). All experiments have been performed at 298 K (25°C) and on dry crushed coal samples (40-250 µm).

The magnetic suspension balance has been coupled with a gas chromatography apparatus (GC; not shown on fig. 1) to determine the composition of the residual free gas phase when equilibrium between free and adsorbed gas

phases has been reached. Composition of the adsorbed phase at equilibrium is calculated from the measured composition of the residual free gas phase.

a



b



Fig. 1. Magnetic suspension balance: (a) diagram of the equipment; (b) photography of the equipment. Note that GC apparatus is not shown.

Table 2. Compositions of gas mixtures.

Mixture name (related to CO_2 concentration)	CO_2 concentration	CH_4 concentration
"100%"; pure CO_2	100%	0%
"90%"	90%	10%
"70%"	70%	30%
"50%"	50%	50%
"30%"	30%	70%
"10%"	10%	90%
"0%"; pure CH_4	0%	100%

Results are presented as adsorption isotherms giving sorption capacities at different values of pressure for a given temperature. Values are in mmol of sorbed gas per gram of dry and ash-free coal (DAF coal = pure organic matter). Results from adsorption experiments are given in the figure below (fig. 2).

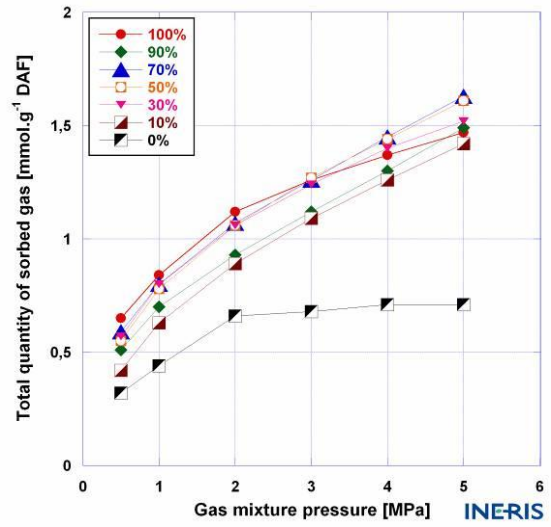


Fig. 2. Total adsorption isotherms (CO_2 + CH_4) determined for adsorption experiments of gas mixtures at 298 K.

By estimating the composition of the free gas phase at equilibrium, it is possible to estimate the quantity of CO_2 and CH_4 that has actually been adsorbed onto the sample and then to plot specific adsorption isotherms for CO_2 and CH_4 (fig. 3)

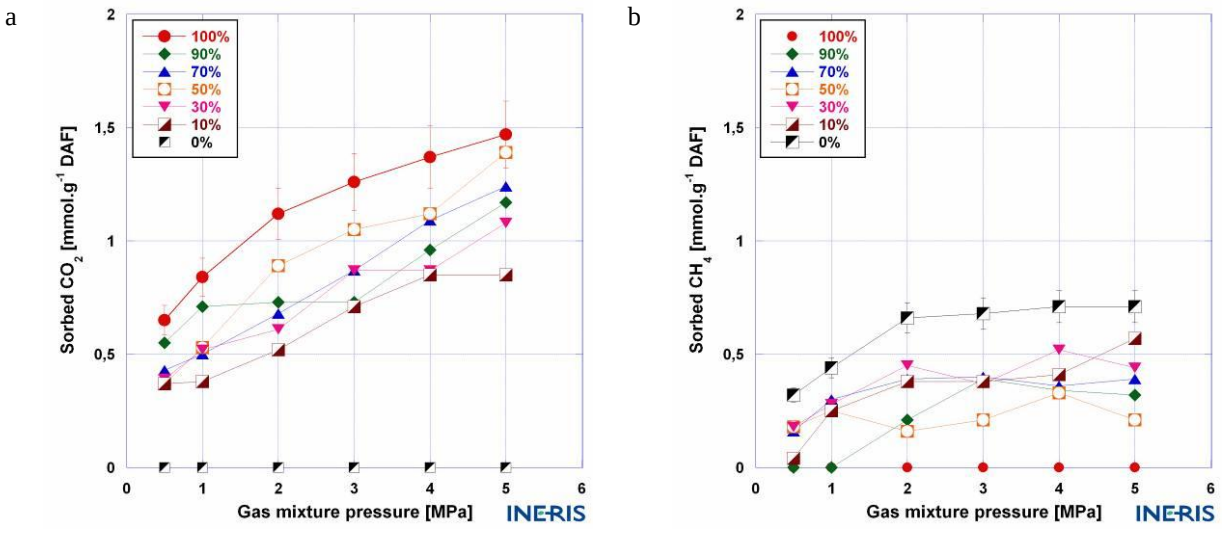


Fig. 3. Adsorption isotherms determined for adsorption experiments of gas mixtures at 298 K: (a) CO_2; (b) CH_4.

The coupling between the magnetic suspension balance and GC is not optimal. Errors on the determination of the composition of the free gas phase at equilibrium are high (>10%) because the quantity of free gas is very important compare to the quantity of gas that can be adsorbed on the sample. Thus, adsorption that occurs during experiments has a very low impact on the composition of the free gas phase (change are very small and are not easily detected by GC). Note that errors have not been precisely calculated and will not be plotted on the figures. Experimental results are detailed in the following tables (tab. 3 and 4).

Table 3. CO_2 adsorption capacities measured during adsorption of gas mixtures. Color scale: highest values in red, lower values in green. Values in $mmol.g^{-1}$ of dry and ash-free coal.

Gas mixture pressure [MPa]	Gas mixtures						
	"100%"	"90%"	"70%"	"50%"	"30%"	"10%"	"0%"
0.5	0.65	0.55	0.43	0.37	0.39	0.37	-
1.0	0.84	0.71	0.50	0.53	0.52	0.38	-
2.0	1.12	0.73	0.68	0.89	0.61	0.52	-
3.0	1.26	0.73	0.87	1.05	0.87	0.71	-
4.0	1.37	0.96	1.09	1.12	0.87	0.85	-
5.0	1.47	1.17	1.24	1.39	1.08	0.85	-

Table 4. CH_4 adsorption capacities measured during adsorption of gas mixtures. Color scale: highest values in red, lower values in green. Values in $mmol.g^{-1}$ of dry and ash-free coal.

Gas mixture pressure [MPa]	Gas mixtures						
	"100%"	"90%"	"70%"	"50%"	"30%"	"10%"	"0%"
0.5	-	0.00	0.16	0.18	0.18	0.04	0.32
1.0	-	0.00	0.30	0.25	0.28	0.25	0.44
2.0	-	0.21	0.39	0.16	0.45	0.38	0.66
3.0	-	0.39	0.40	0.21	0.37	0.38	0.68
4.0	-	0.34	0.36	0.33	0.52	0.41	0.71
5.0	-	0.32	0.39	0.21	0.44	0.57	0.71

Adsorption experiments that have been performed with binary gas mixtures allow highlighting the following conclusions:

- CO_2 and CH_4 adsorption capacities determined with pure gas phases cannot be summed to determined the total adsorption capacity of a gas mixture (see fig. 2).
- Respective CO_2 and CH_4 adsorption capacities for experiments performed with gas mixtures are lower than those determined for experiments with pure gases (see fig. 3).
- CO_2 adsorption capacities seem to be higher when gas pressure and CO_2 volume fraction in the mixture increase (see tab. 4). CH_4 adsorption capacities increase with gas pressure, but no clear relation can be stated with the CH_4 volume fraction (see tab. 5).

4. Modeling adsorption of gas mixtures onto coal

Modeling the adsorption of gas mixtures onto coal cannot be done by using the Langmuir's model applied on partial pressures:

$$\frac{q_i}{q_{m,i}} = \frac{\alpha_{L,i} P_i}{1 + \alpha_{L,i} P_i}$$

Where:

Subscript i refers to gas component i in the mixture;

P_i is the partial pressure of gas component i;

q_i is the adsorbed quantity of gas component i at Pi;

$q_{m,i}$ is the maximum quantity of gas component i that can be adsorbed onto the surface (known as "first Langmuir's parameter");

$\alpha_{L,i}$ is the second Langmuir's parameter for gas component i.

This model doesn't fit our experimental data (see fig. 4 for an example with experimental data from experiment performed with mixture "10%"). Thus, we must use other models. Two models will be presented and discussed below for the adsorption of binary gas mixtures onto coal.

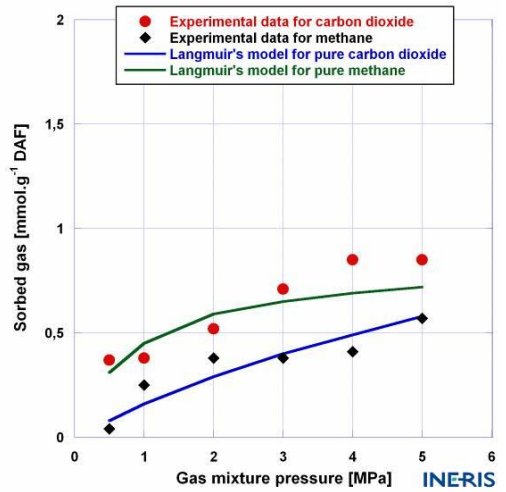


Fig. 4. Misuse of Langmuir's models for pure gas adsorptions to model the adsorption of a gas mixture. Experimental data from experiment performed with gas mixture "10%".

4.1. Models

4.1.1. Extended Langmuir's model

Extended Langmuir's model (EL model) is an improvement of the Langmuir's model for adsorption of binary gas mixtures [5,6,7]:

$$\frac{q_i}{q_{m,i}} = \frac{\alpha_{L,i} P_i}{1 + \alpha_{L,i} P_i + \alpha_{L,j} P_j}$$

With:

Subscript i refers to the first gas component in the mixture and subscript j refers to the second gas component;

P_i and P_j are the partial pressures of gas components i and j;

q_i is the adsorbed quantity of gas component i at P_i;

$q_{m,i}$ is the maximum quantity of gas component i that can be adsorbed onto the surface (known as "first Langmuir's parameter");

$\alpha_{L,i}$ and $\alpha_{L,j}$ are the second Langmuir's parameters for gas components i and j.

Note that parameters q_m and α_L are here the same than those determined for pure gas adsorption.

4.1.2. Empirical model proposed by INERIS

INERIS proposes an empirical model which was fitted from experimental data for adsorption of CO_2 + CH_4 mixtures. This model lies on the Langmuir's theory:

First equation to model the adsorption of CH_4:

$$q_{CH4} = q_{m,CH4}\ x_{CH4}\ \frac{\alpha_{L,CH4} P}{1 + \alpha_{L,CH4} P}$$

Second equation to model the adsorption of CO_2:

$$q_{CO2} = q_{m,CO2}\frac{\alpha_{L,CO2}P}{1+\alpha_{L,CO2}P} - q_{CH4}$$

With:

P is the total gas mixing pressure;

x_{CH4} is the volume fraction of CH_4 in the mixture;

q_{CH4} and q_{CO2} are the adsorbed quantities of each gas at P;

$q_{m,CH4}$ and $q_{m,CO2}$ are the maximum quantities of each gas that can be adsorbed onto the surface (known as "first Langmuir's parameters");

$\alpha_{L,CH4}$ and $\alpha_{L,CO2}$ are the second Langmuir's parameters for each gas.

This model lies on hypotheses drawn from the adsorption experiments of gas mixtures performed at INERIS. During the adsorption of a gas mixture, sorption sites for CO_2 and CH_4 are considered to be the same and we suppose that (fig. 5):

- CH_4 is adsorbed onto a number of sites that is smaller than the number of sites that the gas occupies during adsorption experiments of pure methane. The number of sites that are occupied is considered to be proportional to the volume fraction of CH_4 in the mixing;
- CO_2 is adsorbed onto a number of sites that equals the number of sites that the gas occupies during adsorption experiments of pure carbon dioxide minus the number of sites which are occupied by CH_4.

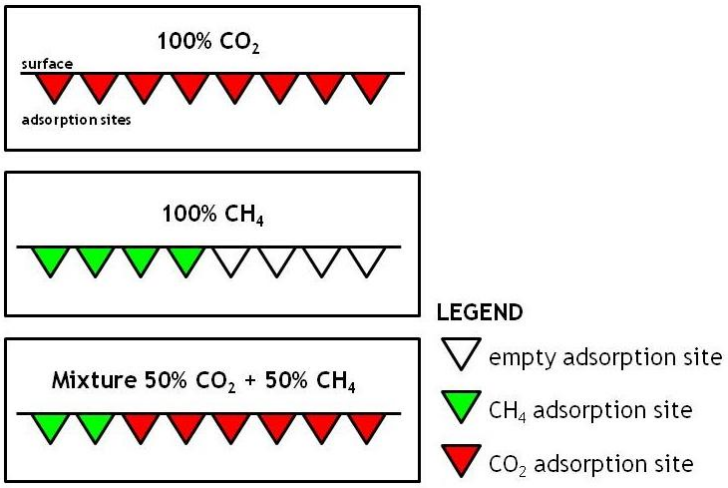


Fig. 5. Empirical model proposed by INERIS for the adsorption of CO_2 + CH_4 gas mixtures. Example with mixture "50%".

4.2. Comparison of models and discussion

Results for CO_2 + CH_4 adsorption experiments are plotted on the following figure (fig. 6). Theoretical isotherms from EL model and model proposed by INERIS are also plotted to determine which model ensures the better fit of the experimental data.

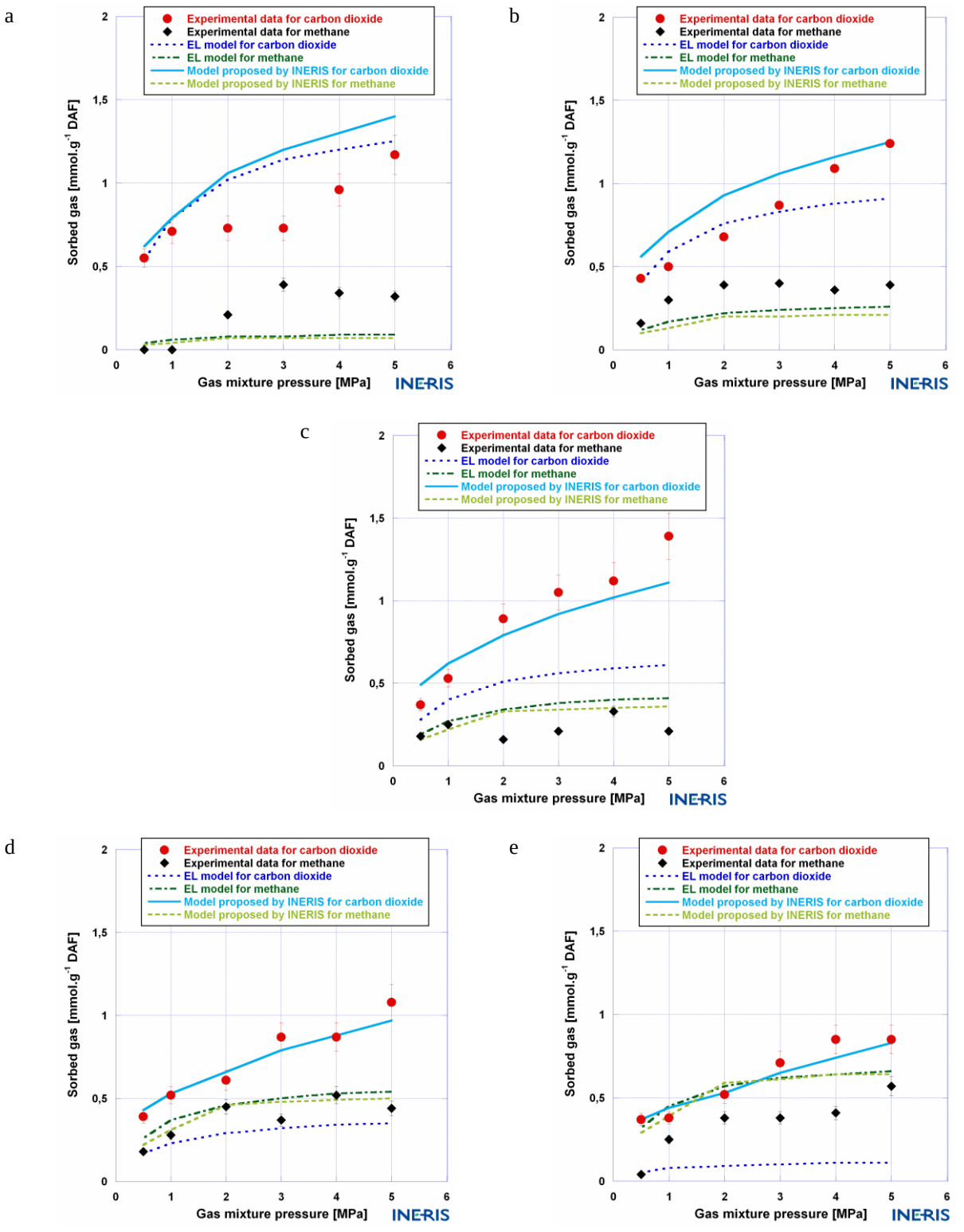


Fig. 6. Experimental results and theoretical isotherms for adsorption experiments of gas mixtures: (a) 90% CO_2 + 10% CH_4; (b) 70% CO_2 + 30% CH_4; (c) 50% CO_2 + 50% CH_4; (d) 30% CO_2 + 70% CH_4; (e) 10% CO_2 + ç0% CH_4.

The two models don't fit well all the data obtained for the different experiments that have been done with gas mixtures. But one can note that:

- EL model underestimates the adsorption capacities of CO_2 for experiments performed with mixtures having a CO_2 concentration $\leq 50\%$;
- EL model underestimates the adsorption capacities of CH_4 for experiments performed with mixtures having a CO_2 concentration $> 50\%$;
- EL model overestimates the adsorption capacities of CH_4 for experiment performed with mixture "10%";
- Model proposed by INERIS is quite in good accordance with experimental data concerning the CO_2 adsorption capacities. But the model overestimates the CO_2 adsorption capacities for experiment performed with mixture "90%";
- Model proposed by INERIS gives the same results as the EL model concerning the CH_4 adsorption capacities.

5. Conclusion

INERIS has performed adsorption experiments of CO_2 + CH_4 gas mixtures onto a coal sample from a Spanish mine. Results show that CO_2 and CH_4 adsorption capacities determined with pure gas phases cannot be added to determine the total adsorption capacity of a gas mixture; and that both CO_2 and CH_4 adsorption capacities for experiments performed with gas mixtures are lower than those determined for experiments with pure gases. Thus, these results confirm that both gases compete to adsorb onto coal.

In this study, the Extended Langmuir model that is often used to model sorption of binary gas mixtures appears to not fit the experimental data. Indeed, this model underestimates the adsorption capacities of CO_2 for experiments performed with binary gas mixtures having a CO_2 concentration $\leqslant$ 50 vol. %; and underestimates the adsorption capacities of CH_4 for experiments performed with binary gas mixtures having a CO_2 concentration $>$ 50 vol. %. Thus, INERIS has proposed a new empirical model that better fits experimental results and that can be used in numerical codes.

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