

## High pressure adsorption of natural gas on coal as a possible fractionation mechanism

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Among hydrocarbon reserves, natural gas is the most abundant. A better understanding of its origin requires the study of the possible fractionation phenomena occurring during its migration through the sediments: diffusion through sediments, adsorption, oil-gas equilibrium.

Our goal is to study the adsorption of natural gas on coal (type III kerogen): especially the isotopic and molecular segregation with and without water.

For years, the carbon isotopic ratio ( $\delta^{13}\text{C}$ ) of methane has been used as gas origin signature. In fact, methane is the only gas issued from two different processes: (1) by bacterial action in the shallower zones, yielding  $\delta^{13}\text{C}$  between  $-75$  and  $-55\%$ , and (2) by thermal cracking in deeper zones, yielding mostly  $\delta^{13}\text{C}$  between  $-40$  and  $-20\%$  (Tissot and Welte, 1984). Intermediate values of  $\delta^{13}\text{C}$  are often attributed to a mixture of gas from both sources (Schoell, 1983), assuming implicitly that there is no fractionation during migration.

However isotopic fractionation could occur during migration, either by diffusion if the transport mechanism is significant, or by adsorption. Indeed, Colombo (1967) found an isotopic shift of  $\delta^{13}\text{C}$  on methane desorbed from coal.

Methane, nitrogen and carbon dioxide show classical type I adsorption isotherms at high pressure (Chaback *et al.*, 1996) whereas water shows a type II or type III adsorption isotherm, depending on coal rank (Mahajan and Walker, 1978). These differences are explained by the different interactions between chemical species and the internal coal surface. However these data cannot answer to the basic questions related to geochemical problems, i.e. (1) is the isotopic composition of methane adsorbed at high pressure significantly different from the gas phase? (2) are C2+ gases more adsorbed than methane? (3) in the presence of water, is methane adsorption significant on coal?

Our intention is to answer these questions by an experiment

To that end, an original piece of equipment has been designed by IFP, with working conditions corresponding to that of gas fields and source rocks ( $200^\circ\text{C}$ , 1000 bar). This high pressure adsorption equipment consists of two piston cells ( $300\text{ cm}^3$ ) containing the gas, a container ( $147\text{ cm}^3$ ) with the powdered coal and a sampling loop ( $1\text{ cm}^3$ ). These components are enclosed in a constant temperature air bath.

Adsorption equilibrium is reached with the two piston cells by a back and forth circulation of the fluid through the powdered coal. A computer controls the process (Fig. 1). The gas can be sampled at constant pressure and temperature. Gas phase is analysed by GC (Gas Chromatography) and GC-C-IRMS (Gas Chromatography-Combustion-Mass Spectrometry). Information about the adsorbed phase is obtained from the variations in volume and composition of the gas phase during adsorption.

The sample used is a Carboniferous coal from

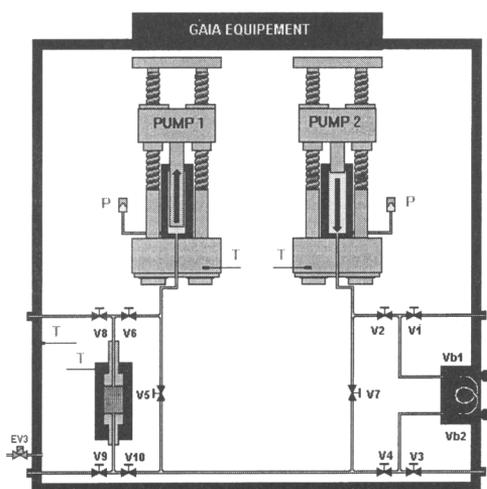


FIG. 1. Adsorption equipment (GAIA).

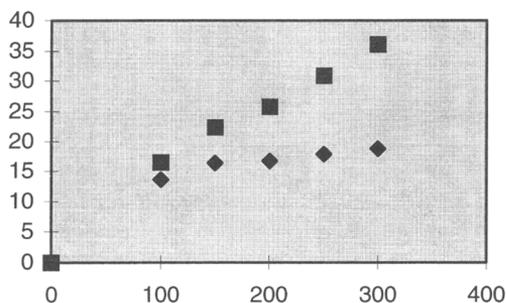


FIG. 2 Adsorption isotherm on coal at 35° C.

Lorraine Basin (France), La Houve vein ground to 53–710  $\mu\text{m}$ . Its atomic composition (H/C = 0.747 and O/C = 0.136) and Rock-Eval Tmax (436°C) correspond to the end of the diagenesis zone. Gases (methane, ethane, propane, butane and carbon dioxide) were obtained from Air Liquide: purity 99.99%.

Prior to an experiment the coal is weighted and heated at 130°C under vacuum. Gas is then introduced in the piston cells, isolated from coal, at the desired pressure and temperature. Gas is sampled and analysed to obtain its composition before adsorption. Then coal is contacted with gas, which is transferred repeatedly across solid at constant pressure. When equilibrium is reached (global volume constant) we measure the apparent volume change defined by Gibbs as the surface excess. Finally we obtain the adsorbed volume at pressure and temperature of the experiment as a difference of initial and final gas in the bulk phase. This volume can be converted to the absolute adsorption using the specific volume of adsorbed phase (equation 1).

In a first series, we studied isotopic segregation during adsorption of pure methane on dry coal from 100 to 300 bar at 50 and 35°C. Adsorption isotherms show a shape in agreement with literature (Ruppel *et al.*, 1972). The volume capacity of Langmuir equation (equation 2) is 20.7  $\text{cm}^3$  STD/g at 50°C and 22.7  $\text{cm}^3$  STD/g at 35°C, also in agreement with Ruppel. We obtain a variation of +5% in  $\delta^{13}\text{C}$  between bulk phase and desorbed gas. This allows us to conclude that the heavier component is adsorbed preferentially.

In a second series we studied the chemical

segregation during adsorption of a synthetic gas (methane 66.7%, ethane 15%, propane 9%, normal butane 3.3%, iso butane 2.2% and carbon dioxide 3.8%) from 150 to 400 bar at 75 and 100°C. The adsorption of synthesised gas shows a preferential adsorption of carbon dioxide, which is slight but significant.

We conclude that isotopic and molecular segregation due to adsorption on coal at high pressure and temperature can induce some compositional variations in natural gas. Further investigation is required to improve quantification of these phenomena.

## Appendix:

Equation 1. Adsorbed volume

$$V_{\text{absolute}} = V_{\text{Gibbs}} \frac{1}{1 - \frac{P_{\text{bulk}}}{P_{\text{ads}}}}$$

$V_{\text{absolute}}$	absolute volume adsorbed ( $\text{cm}^3$ STD/g)
$V_{\text{Gibbs}}$	lump volume ( $\text{cm}^3$ STD/g)
$P_{\text{bulk}}$	specific volume of bulk phase ( $\text{g}/\text{cm}^3$ )
$P_{\text{ads}}$	specific volume of adsorbed phase ( $\text{g}/\text{cm}^3$ )

Equation 2. Langmuir equation

$$V = V_m \frac{kP}{1 + kP}$$

$V$	adsorbed volume ( $\text{cm}^3$ STD/g)
$V_m$	saturation volume ( $\text{cm}^3$ STD/g)
$k$	equilibrium constant ( $\text{bar}^{-1}$ )
$P$	pressure (bar)

## References

- Chaback, J.J. *et al.* (1996) *Fluid Phase Equilibria*, **117**, 289–96.
- Colombo, U. *et al.* (1967) *Org. Geochem.*, 279–92.
- Mahajan, O.P. and Walker, P.L. (1978) *Technical report 7- The Pennsylvania State University*.
- Ruppel, T.C., Gein, C.T. and Bienstock, D. (1973) *Fuel*, **53**, 152–62.
- Schoell, M. (1983) *Amer. Assoc. Petrol. Geologists Bull.*, **67**, 2225–38.
- Tissot and Welte (1984) *Petroleum Formation and Occurrence*, Springer, 699p.