CONTRIBUTION OF THE STEADY STATE APPROACH FOR COMPLEX GAS TRANSFER IN UNCONVENTIONAL RESSOURCES

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ABSTRACT

Shale reservoirs represent the next challenge for oil and gas companies. In order to properly evaluate the potential of shale gas reservoirs, a 3D reservoir model is required. This model needs a complete understanding of the mechanisms involved in gas migration within such specific porous media and also relevant data. New models have been developed to add Knudsen diffusion, sorption isotherms or diffusivity in the gas transfer mechanisms but issues remain on how to measure them.

New experimental techniques, mainly based on transient experiments, are developed to assess unconventional resources. The present work aims to show by simulation how a simple steady state approach can be more effective to characterise shale reservoirs:

- An important aspect that is generally missed in the literature is that the steady state approach, especially in low porosity porous media like shales, can be faster than transient techniques such as pulse decay.
- If transient experiments are interpreted whereas pressure equilibrium is not reached, porosity and gas transfer parameters cannot be estimated separately. This problem is solved in steady state approach where the steady state fluxes provided the gas transfer parameters and the transient part of the experiment gives access to the porosity.
- For the steady state experiment, the experiment interpretation is straightforward in a Klinkenberg plot.
- The first three points were already discussed in a previous paper [1]. An innovative aspect of the present study is that sorption isotherms and diffusivity can be measured with the steady state approach. First, the diffusivity is assessed using methane and an inert gas [2]. Then, the transient part of the flux stabilization is studied. Since the isotherm impacts mass balance, the Langmuir parameters can be adjusted to fit the transient part of the experiment. The paper shows a simple way to proceed.

Further simulations at reservoir scale showed that, depending on the pressure regime of the reservoir, Klinkenberg effect and gas adsorption can have an impact or not in the gas production. Diffusivity, diffusion within the adsorption phase, has a limited impact even if its effect is significant in the experimental steady state approach.

INTRODUCTION

In the next years, the conventional gas production will decline and unconventional resources will play an important role in the oil and gas industry. Unconventional resources are shale gas, tight gas or coalbed methane (CBM). In order to properly evaluate the potential of shale gas reservoirs, a 3D reservoir model is required. This model needs a complete understanding of the mechanisms involved in gas migration within such specific porous media and relevant data. A great amount of research is now being conducted to set new models for gas migration in unconventional reservoirs [3, 4] and to establish innovative techniques for permeability measurements [5, 6]. Because we need models to be able to interpret properly the experimental results, both issues are related.

The main transport parameters in an unconventional reservoir matrix are the porosity, the permeability and the Klinkenberg coefficient due to its nanoporous structure [7]. Most of the authors dealing with very low permeability measurements use a transient method known as pulse decay. It consists in a sample bounded by two reservoirs that are initially at equal pressures [8]. A pressure rise is suddenly imposed in the upstream reservoir and the pressure evolution is recorded in both reservoirs. Determination of the permeability is made on the transient phase leading to pressure equilibrium in the reservoirs. Pulse decay is, in most cases, always preferred to the steady state method, which consists in imposing a pressure gradient over a sample and measuring the flow rate out of the sample. Many authors argue that the steady state method leads to long experimental durations compared to pulse decay tests, due to the long time required for the flow stabilization [9-12]. Steady state experiments are rare in the unconventional reservoirs literature [6]. In a pulse decay experiment both porosity and permeability can be obtained at the same time. To estimate other parameters, such as Klinkenberg effect, multiple steps are required [5]. However the analysis of the transient phase is not straightforward and it has to be interpreted with a model. Once the model is chosen, an inverse modeling tool will provide the parameters that fit the experimental data. Yet, some parameters can be strongly dependant and a careful sensitivity analysis should be performed [5]. For unconventional reservoirs, pulse decay interpretation is model dependant; and when the model has more than three parameters it becomes challenging [4, 13] to determine each of them individually.

To study low permeability porous media, it has been shown that for water the steady state techniques can be more effective than pulse decay to determine very low water permeabilities (range of 0.2 to 200 nD) [14]. The analysis is straightforward and actually Darcy's law can be verified on theses specific rocks such as claystones or shale reservoirs.

The study presents a simulation work which demonstrates that steady state method can be more effective than transient experiments to characterise unconventional reservoirs. The description is focused on the experimental duration and a protocol to get specific parameters inherent to gas sorption: Langmuir isotherm parameters and the diffusivity coefficient. Additional simulations were performed at the reservoir scale to check the importance of the different gas transport parameters.

THEORY AND MODEL DESCRIPTION

Gas migration within shales in production can be divided in three different processes: 1- Gas desorption from the matrix; 2- Gas migration from the matrix to the fractures; 3- Gas migration from the fractures to the production well. The transport parameters measured on shale plugs are characteristic of processes 1 and 2. Gas will migrate to the fractures by different transport processes:

- Permeation, controlled by Darcy's law, which is the result of pressure gradient within the shales;
- Effect of interaction (collision) between gas molecules and the pore walls. The correction required can be introduced through the Klinkenberg effect (modification of the Darcy's law), or by the Knudsen diffusion;
- Surface diffusion. It corresponds to gas migration in its adsorbing phase;
- Diffusion of dissolved gas in the water.

The study of those mechanisms is difficult due to two main issues:

- The matrix is a complex structure of pores, each pore having a different affinity to gas (as organic matter which is part of the matrix has a strong affinity to gas sorption);
- Transport processes can be mixed up. In one hand, those phenomena occur simultaneously. On the other hand, terms employed in the literature are similar (diffusion and permeation) which could be confusing [3, 15].

Theory on gas migration has been discussed in many papers [3, 4, 13, 15]. Most of the different models discussed have never been compared to any experiments on shale and some of them may be misleading. The experience on shale is too limited to get a straight idea on which model should be used. Shale gas reservoirs are characterized by pore diameter in the nanometer scale and a part of their porosity, especially in the organic matter, has an affinity to gas. Gas can adsorb and migrate through the organic matter. This configuration is close to catalysts membrane which has been intensively studied in the chemical engineering literature [2, 17, 18]. It corresponds to porous membrane of 1 to 40 nanometer pore diameters; the surface can be functionalised to have affinity with specific gases. In such "mesoporous" membrane experiments were performed and models were confronted. The results have been used in this study to have new insight on gas migration in unconventional reservoirs and how to model them.

When pore size is close to nanometer, the gas molecules do not interact any more among themselves other but interact as well with the pore walls. It is the Knudsen regime controlled by the Knudsen number K_n which is equal to the ration between the mean free path of the molecule λ and a representative length such as the pore diameter. In the petrophysical literature, Knudsen regime has been studied through the Klinkenberg effect. Gas migration results of advection and Klinkenberg effect [7]:

$$N^{\mu} = -\frac{P}{R \times T} \cdot \frac{k_{\infty} \times (1 + \frac{b_k}{P})}{\mu} \nabla P \tag{1}$$

In equation (1), N^{μ} is the molar flux (mol/m^2/s), P the gas pore pressure (Pa), R the gas constant, T the temperature (K), k_{∞} the intrinsic permeability (m^2), μ the gas viscosity (Pa.s) and b_k the Klinkenberg coefficient (Pa). The mass balance within the rock is written as follows:

$$\frac{\partial(\Phi \cdot \frac{P}{R \cdot T})}{\partial t} = -\nabla . N^{\mu} \tag{2}$$

Where Φ is the porosity. In fact, Klinkenberg effect can be seen as diffusion. Indeed, when the advection part is neglected, the mass balance equation (2) is a diffusion equation. It is the Knudsen diffusion, the effective Knudsen diffusion coefficient D_k is equal to [19]:

$$D_k = \frac{b_k \cdot k_{\infty}}{\mu} \tag{3}$$

Several authors [20, 21] showed that Knudsen diffusion model, as expressed with equation (1), is valid in mesoporous glass of 2 to 5 nm pore diameters. There is no need to add second order Knudsen diffusion as theory suggests [3, 4]. Discrepancies between model and experiment arises when pore diameter of 1 nm are involved [22]. The pore size is in the order of magnitude of the gas molecule size and the biggest molecules are blocked by the porous network, it is called configurational diffusion.

When the pore surface have an affinity with the gas, migration occurs in the adsorption phase or within the rock structure itself likewise gas diffusivity in polymers [23]. The total flux is part of the flux in the gas phase and part of surface diffusion [2]:

$$N^T = N^{\mu} - D_S \times \nabla q_s \tag{4}$$

where D_S is the diffusivity coefficient (m^2/s) and q_s is the molecular concentration in the adsorption state (mol/m3 of rock, porosity is already accounted inside). q_s can be described by a Langmuir isotherm:

$$q_s = q_{sat} \times \frac{bP}{1 + bP} \tag{5}$$

where q_{sat} and b are the Langmuir parameters. Since, gas migration implies pressure change, the adsorbing layer q_s change as well. The mass balance becomes:

$$\Phi \cdot \frac{\partial(\frac{P}{R \times T})}{\partial t} + \frac{\partial(q_s)}{\partial t} = \Phi \times \frac{\partial(\frac{P}{R \times T})}{\partial t} - \frac{\partial(P)}{\partial t} \times q_{sat} \times \frac{b}{(1+bP)^2} = -\nabla.N^T \qquad (6)$$

The simulations of the next chapter were performed with equation (4) and (6) using the finite element method software COMSOL Multiphysics [23].

TRANSIENT Vs STEADY STATE EXPERIMENTS

The first drawback of the steady state method cited in the literature is the time required to reach steady state in a very low permeability rocks. With equations 1 and 2, the validity of this assumption can be checked. Simulations were done to describe pulse decay and a steady state approach on a hypothetic porous media with a permeability of 10 nD (10^{-20} m^2) with nitrogen. Its porosity was set to 2%, 5 %, 10% and 20%. Its length was 2 cm and its diameter 4 cm. The size chosen for the upstream and downstream reservoir is 10 cc. The sample is initially at 10 bar. The pressure at the upstream reservoir is increased instantaneously to 20 bar for the pulse decay experiment (Figure 1). In the steady state approach, the upstream pressure is increased by steps of 40h. The pressure steps are 12.5 bar, 15 bar, 17.5 bar and 20 bar (Figure 2).
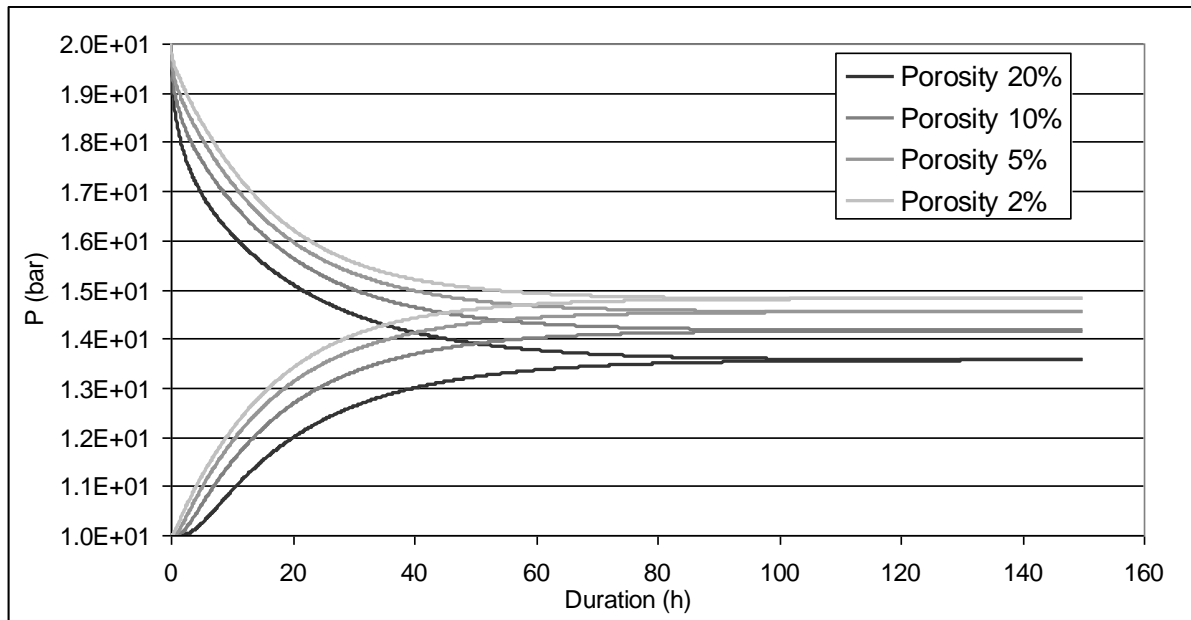

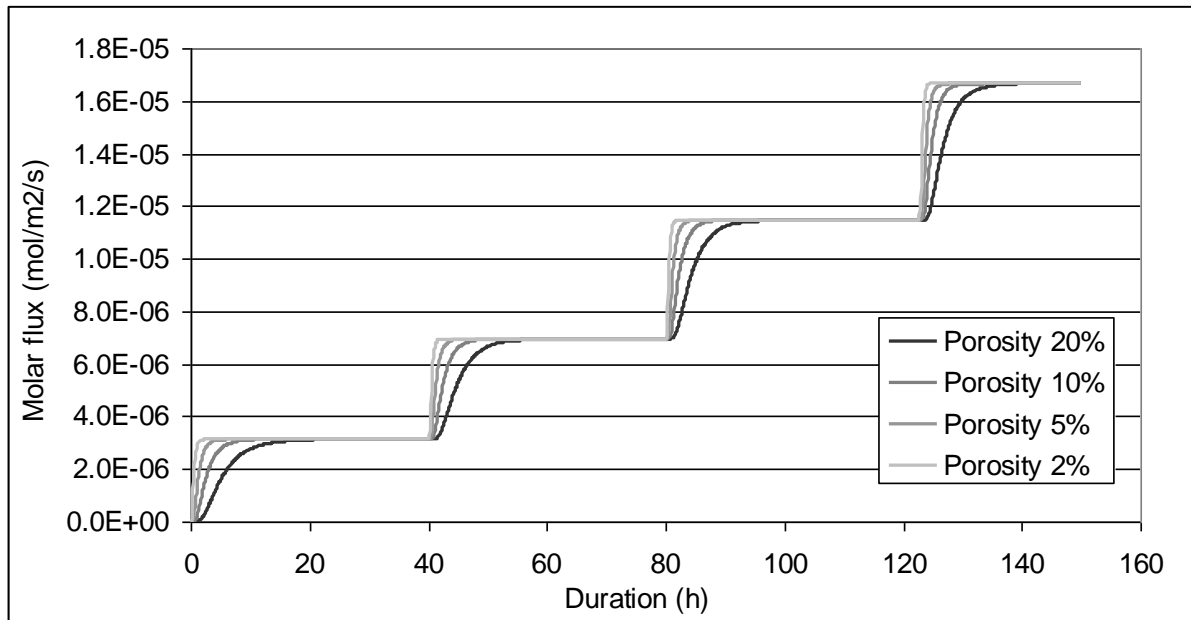Figure 1. Numerical pulse decay experiment at 10 nD for different porosities

Figure 2. Numerical steady state experiment at 10 nD for different porosities. Evolution of the gas flux for the different pressure steps

The pulse decay is completed after 100 hours. The duration of pulse decay can be shortened with smaller volumes or higher sample diameters. The porosity has no effect on the duration of the experiment. The porosity is a short time effect [5] and impacts the pressure equilibrium within the sample at the beginning of the pulse decay experiment. It would have been different if the reservoirs were much smaller (0.1 cc). For very small reservoir volumes, the pressure variations are mainly controlled by the pressure equilibrium within the sample porosity and thus controlled by the ration Φ/k. In this case, permeability cannot be easily estimated without a previous measurement of the sample porosity.

The steady state method is in the same order of duration as pulse decay. As previously demonstrated on water [14], there is no reason for the steady state method to be much longer than pulse decay experiment. The gas flux equilibrium is controlled by the pressure equilibrium within the sample porosity. As explained earlier it is a short term effect, Brace *et al.* even considering it instantaneous [8]. The duration of this equilibrium is proportional to Φ/k. For the 2% porosity sample, the flux is stabilized within three hours, an extra 3 hours is required to establish that the flux is constant and to measure it. In pulse decay, prior to test, pressures need to be equilibrated within the sample, it delays the experiment.

The steady state method can be performed in very low porous media. The method is more efficient in low porosity experiment as it shortens the gas flux stabilization. It is also interesting for partially saturation sample where the porosity accessible to gas is small. For example, Billiote *et al.* have estimated permeability of 3 nD in partially saturated Callovo-Oxfordian claystone in 1 day while the pulse decay that was only 20% completed [25]. On similar samples, Boulin *et al.* measured permeabilities lower than 1 nD by the steady state method within one day with more than eight different pressure gradients [1].

The main difficulty associated to the steady state techniques is the measurement of the gas flux that goes out of the sample. This value can be too small to be measured with classical gas flow meter. There are several ways to improve this measurement:

- Measure indirectly the gas flux by: pressure accumulation (pseudo steady state [26]), or piston displacement [6]. Nevertheless, it is a very long process in order to get sufficient gas accumulation to measure the flow rate properly.
- Increase the average pore pressure. As well as it shortens the experiments it increases the flow rate. However it is possible to miss the Klinkenberg effect when mean pore pressure is to high.
- Use tracers to measure the permeability. This method was first introduced by Falconneche *et al.* to measure very low flow rate though polymers [27]. It was then adapted to porous rocks by Boulin *et al.* [28, 29]. The main drawback of using tracers is the necessity to take into account diffusion processes. In some cases, a clear Klinkenberg plot without diffusion interference can be obtained [1].

STEADY STATE EXPERIMENT WITH METHANE

The steady state method can be analysed towards Klinkenberg effect with the plot of the apparent permeability k_{app} versus the inverse of the mean pore pressure [30]. k_{app} (apparent permeability) is obtained from the stabilized flux N (mol/m^2/s):

$$k_{app} = N \times \frac{2 \times RT \times \mu \times e}{(P_2^{\,2} - P_1^{\,2})} \tag{7}$$

Where e is the sample length and P_1, P_2 are the pressures applied at both sides of the sample. The analysis is straightforward for an inert gas, the plot is a straight line:

$$k_{app} = k_\infty (1 + b_k \left. 1 \middle/ P_m \right.) \tag{8}$$

The slope is directly proportional to D_k x μ. To obtain the diffusivity parameter D_s, the protocol described in [2] for porous glass membrane can be used. It consists in a three phase process:
- First, determine the parameter k_∞ and b_k in a steady state experiment with an inert gas such as nitrogen or helium
- Estimate the Klinkenberg coefficient for methane with the equation:

$$b_{k,CH4} = b_{k,inert} \sqrt{\frac{M_{inert}}{M_{CH4}}} \cdot \frac{\mu_{CH4}}{\mu_{inert}} \tag{9}$$

Relationship (9) is due to Knudsen theory validated experimentally by Higgins *et al.* [21] with methane and in other papers [17] [20] [31] for other simple gases.
- Finally , the steady state experiment is done with methane. The diffusivity flux is deduced from the total flux minus the advective flux estimated from the previous step. The pressure along the sample is strongly non linear due to adsorption [2] and simulations

are required to quantify advection and surface diffusion fluxes for different value of the surface diffusion coefficient D_S.

For example, Figure 3 shows the shows a model calculation of a hypothetical steady state experiment. From the nitrogen experiment an intrinsic permeability of 2 nD and a Klinkenberg coefficient of 34 bar can be deduced. The methane apparent permeability without diffusivity can be calculated ($b_{k,CH4}$ = 25 bar). The difference between the total methane flux and the theoretical advective flux is due to the diffusivity flux (Figure 3).

The flux is proportional to D_S and to the concentration gradient within the adsorbed phase (equation 4):

$$N^D = -D_S \cdot \frac{b}{(1+bP)^2} \nabla P \tag{10}$$

The parameter D_S in equation (10) can be estimated if the Langmuir parameters q_{sat} and b are known. It was chosen for this simulation Langmuir parameters from Zhang *et al.* data on shale [32]. It is b=1.5 $\cdot 10^{-7}$ Pa^{-1} and q_{sat} = 1.5 mmol/g TOC. In a rock with a solid density of 2.7, 4% weight of TOC and a porosity of 5%, q_{sat} = 154 mol/m^3 of rock (almost 70 scf/ton). An interesting point is that the gas represents in the porosity 300 mol/m^3 (almost 105 scf/ton) at 150 bar. Theses values are consistent with Wang and Reed study on shale [33].

Figure 4 shows the simulations performed for different D_S. The D_S that was used for illustration is 5 $\cdot 10^{-9}$ m^2/s.

On Figure 3, the apparent permeability with methane is linear with the inverse of the mean pressure. It means that, in some cases, a mix of advection and diffusivity can become confused with a simple Klinkenberg effect. However the slope of the Klinkenberg plot is different from the one provided by the Knudsen theory. In this case, $b_{k,CH4}$ = 38 bar. Furthermore, the simulations done for the three different D_S show that the apparent Klinkenberg coefficient is proportional to D_S, at D_S=0, $b_{k,CH4}$ = 25 bar. Therefore, only one simulation for one D_S is necessary. The D_S that will fit the experimental data can be deduced from the apparent Klinkenberg coefficient.
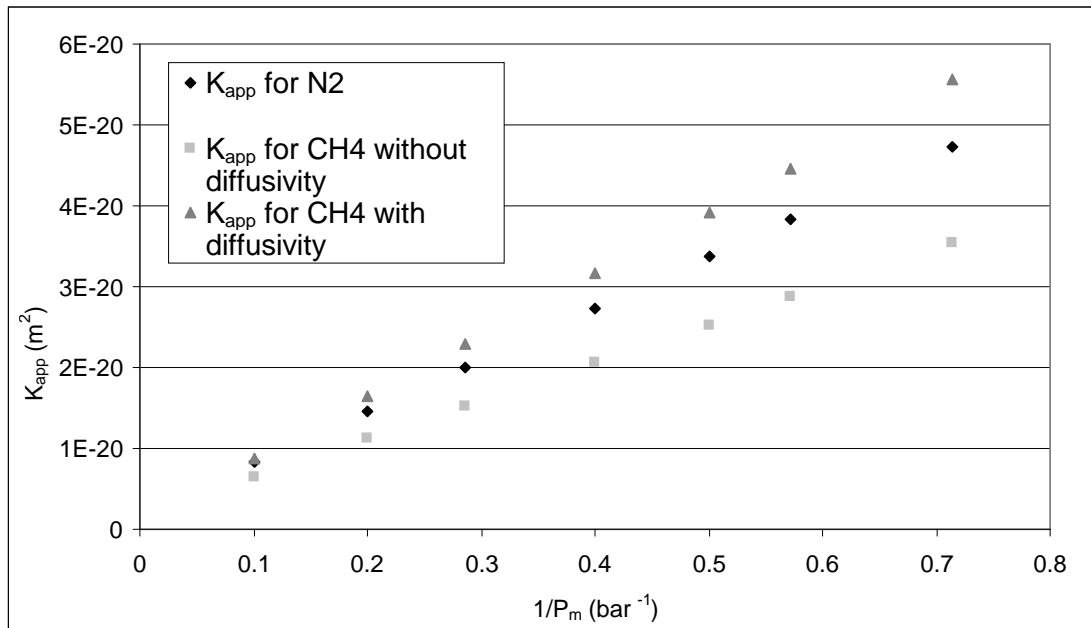
Figure 3. Evolution of the apparent permeability from nitrogen to methane experiment. Without or with diffusivity.
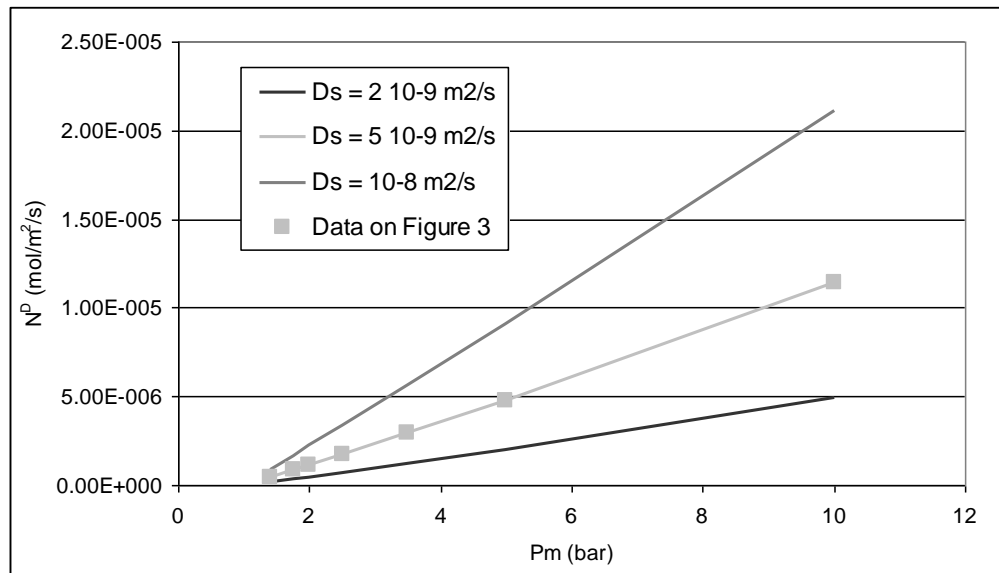

Figure 4. Evolution of the diffusivity flux with pressure for different value of D_S.

To determine *Ds* the Langmuir isotherm parameters are necessary. Theses values can be obtained from isotherm experiments made on crushed rocks. Those values may not be representative of gas migration and adsorption at an bigger scale like on plugs. The protocol proposed here aims checking the validity of the Langmuir isotherm parameters to model the migration of gas in unconventional reservoirs.

First, [1] show the possibility to get the porosity accessible to gas on steady state experiments.

This determination is made on the transient part of the steady state experiment as on figure 2. Time required for flow stabilization is proportional to (equation (1) and (2)):

$$T = \frac{\Phi \times e^2 \times \mu}{P_m \cdot k_{app}} \tag{11}$$

More porosity means more pore volume where pressure need to be increased. In high porosity rocks, the flux is controlled and limited by the permeability, and therefore pressure stabilisation is longer. When methane adsorption is involved the gas flux helps to increase pressure in the pore volume in two ways: compression of gas within the pore volume and increasing the amount of methane adsorbed on the pore surface. Time required for flow stabilisation is proportional to (equation (1) and (6)):

$$T = \frac{e^2 \times \mu}{P_m \times k_{app}} (\Phi + q_{sat} \frac{b \times RT}{(1 + bP_m)^2})$$

$$\begin{cases} P << 1/b, \quad T = \frac{e^2 \times \mu}{P_m \cdot k_{app}} (\Phi + q_{sat} \times b \cdot RT) \\ \\ P >> 1/b, \quad T = \frac{e^2 \times \mu}{P_m \cdot k_{app}} (\Phi + q_{sat} RT / bP_m) \end{cases} \tag{12}$$

Both parameters (b and q_{sat}) affect the flow stabilisation process. If the Langmuir parameters used in the model doesn't help to fit the transitional part of the flux stabilisation in the steady state experiment with methane then they can be adjusted

-   If in the experiment the pressures are lower than 3-5 bar (P << 1/b) then b should be adjusted (equation (7)). If the flux stabilisation is slower than the experimental data then b should be decreased. It means that adsorption is not so important to slow down gas migration into the sample.
-   If pressure is higher than 20-30 bar (P >> 1/b) then q_{sat} should be adjusted (equation (7)).

In both cases, if b and q_{sat} are modified *Ds* is likely to be changed in order to get the same diffusivity flux (equation (10)). The most important is to make the experiment close to in situ condition to adjust the Langmuir isotherm parameter properly.

RESERVOIR SIMULATIONS

The experiments on unconventional reservoir should provide information that can be useful for reservoir simulation. An important point raised in the experiments is that a Klinkenberg effect observed with methane on plugs can be more than that at reservoir scale and may require an adequate model to describe gas production. Very Simple reservoir simulations were performed to check what could be the effect of the Klinkenberg effect, the methane sorption and the diffusivity flux on gas production.

The model is based on the equations and the parameters proposed before. The reservoir studied is an infinite plane of 1 m thickness. Both surfaces produce gas. The model is run for two cases: the reservoir is initially at 80 bar and is connected at 5 bar on its boundaries (low pressure scenario); the reservoir is initially at 250 bar and is connected at 100 bar on its boundaries (high pressure scenario). First, a simulation was performed with a simple Darcy equation with a permeability of 2 nD and 52 nD which corresponds on equation (8) to the permeability at atmospheric pressure. It may be representative of permeability obtained on crushed samples like the GRI methods [34]. Then the simulation was performed with the Klinkenberg effect from equation (7). For each simulation adsorption was then added on the gas transport equation. The diffusivity flux was added afterward. On each figure are reproduced the mean pressure within the reservoir throughout the gas depletion (Figure 5) and the associated production rate (Figure 6).
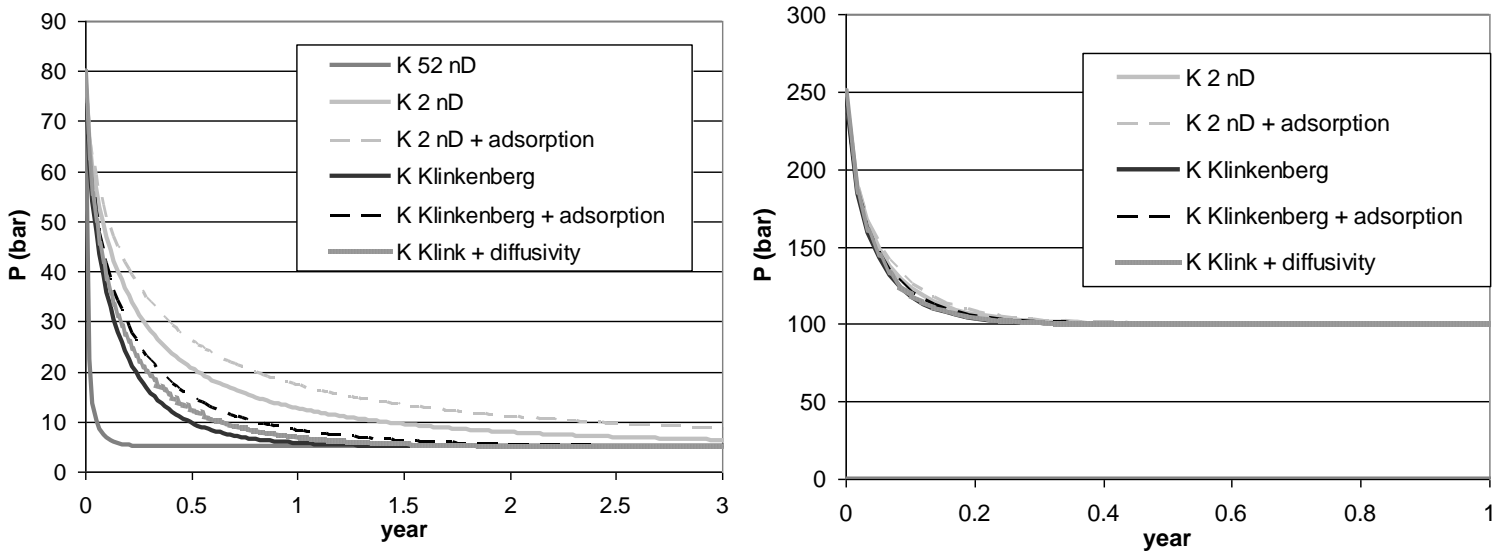

Figure 5. Pressure depletion (average pressure in the reservoir) in the low and high pressure scenario
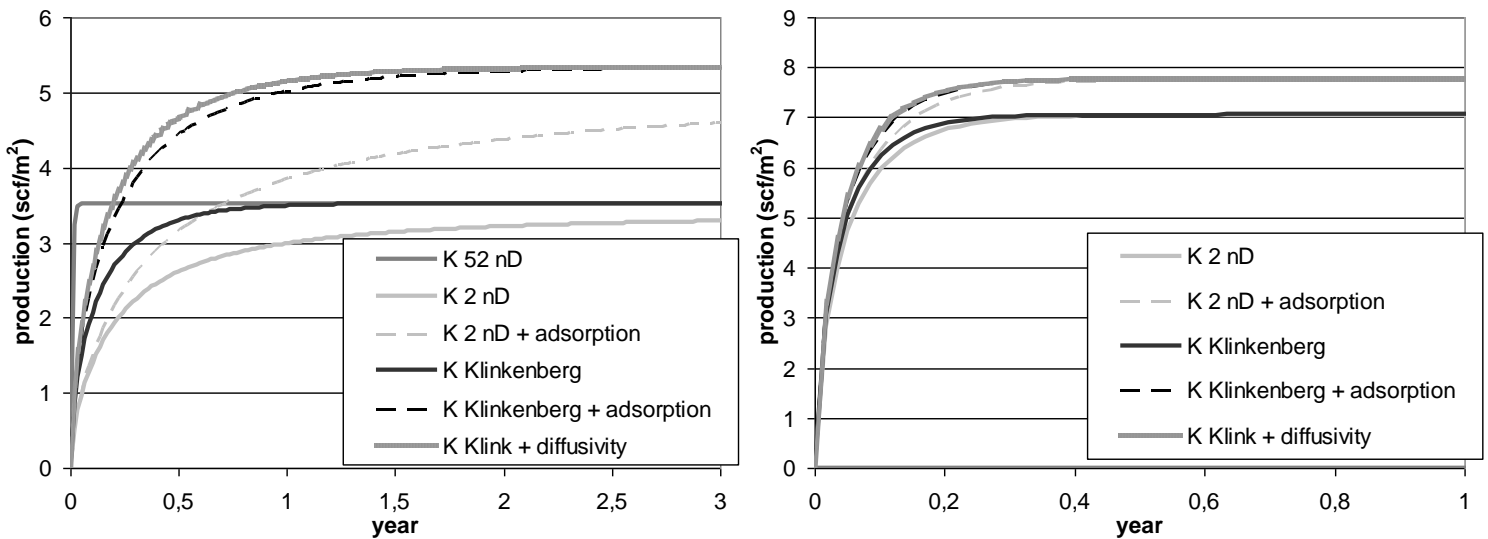
Figure 6. Gas production in the low and high pressure scenario

In the low pressure scenario, the Klinkenberg effect simulation lies between the two simulations at 2 and 52 nD. The shapes of the curves are almost similar even if the Klinkenberg effect is more a diffusive process. The sorption has two effects in the reservoir: more gas is produced, and it slows down the pressure depletion. Adding diffusivity has a slight impact on the production.

In the high pressure, all the simulations are almost similar. Due to high pressure the apparent permeability is close to the intrinsic permeability of 2 nD. In addition, between 100 and 250 bar the Langmuir isotherm is close to a plateau. Thus, the gas mobilised by the pressure drop is small. Furthermore, diffusivity has no impact.

The parameters used for the simulation were hypothetical and may be different from unconventional reservoirs to another by one or two order of magnitude. Therefore, the observation made here may differ. Even with a diffusivity coefficient D_S of $5 \cdot 10^{-9}$ m^2/s which can affect the experimental data (Figure 3), the simulations shows that it has a limited impact on reservoir simulation. In addition, in the high pressure scenario, Klinkenberg effect has a low impact in production whereas the pressure drops from 250 to 100 bar. It may be interesting at this point to look at the permeability variation mechanically induces by the pore pressure reduction. This impact may be more important than the gas transport phenomenon in shale [35].

CONCLUSION

Basin or reservoir modelling required accurate data and a complete understanding of gas migration within the rock. The steady state approach is an effective method to measure gas transport properties of unconventional reservoirs: the experimental time is as long as a transient approach and the analysis is simple and straightforward.

Furthermore, based on the literature on chemical engineering, a new methodology has been developed to handle Knudsen regime with adsorption in nanopores. First, the Knuden regime is characterized with an inert gas. After that, diffusivity is assessed using methane. Finally, the transient part of the flux stabilization is then studied to adjust the Langmuir isotherms.

Further simulations at reservoir scale showed that, depending on the pressure regime of the reservoir, Klinkenberg effect and gas adsorption can have an impact or not in the gas production. Diffusivity, diffusion within the adsorption phase, has a limited impact even if its effect is significant in the experimental steady state approach.

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