AVGas Transport and Sorption Processes in Coals and Shales: New Insights and Concepts from Laboratory Experiments*

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Abstract

Physical sorption is the key process in coalbed methane (CBM) and gas shale systems. Sorptive storage capacity, the principal thermodynamic parameter, is commonly expressed in terms of excess sorption isotherms and depends on pressure, moisture content, temperature, and type and maturity of the organic matter. It can be readily assessed by laboratory experiments at pressures and temperatures relevant for CBM and shale gas systems.

For both exploration and production purposes, the kinetics of sorption and desorption and the interrelation of sorption and transport processes are of crucial importance.

In coals, the cleat systems act as transport avenues while the microporous, polymer inter-cleat matrix system represents a source or a sink, depending on partial pressure (chemical potential). Rate and efficiency of mass transfer between the cleat and matrix system, and the transport and sorption rates within the coal matrix are therefore of prime interest for quantitative descriptions and modelling.

In carbonaceous shales, the connectivity of the pore and fracture systems determines the accessibility of the dispersed organic matter and its participation in gas transport. Capillary processes and two-phase (water/gas) transport appear to be relevant both in gas shale and CBM systems. Combined fluid flow and sorption experiments on cylindrical plugs under controlled temperature, pressure and stress conditions are being conducted in our laboratory to study the interaction of gas sorption and transport processes in coals and carbonaceous shales with a largely undisturbed fabric. The tests are performed with methane, CO_2, and non-sorbing inert gases (He, Ar). By systematic variation of the initial and boundary conditions, individual processes, such as compressible Darcy flow, diffusion, capillary breakthrough, sorption and

desorption kinetics, can be distinguished and described by numerical models. Selected examples for both, CBM and shale gas systems are presented to illustrate this approach.

References

Gensterblum, Y. P. van Hemert, P. Billemont, A. Busch, D. Charriere, D. Li, B.M. Krooss, G. De Weireld, D. Prinz, and K.-H.A.A. Wolf, 2009, European inter-laboratory comparision of high pressure CO_2 sorption isotherms, I: Activated carbon: Carbon, v. 47, p. 2958-2969.

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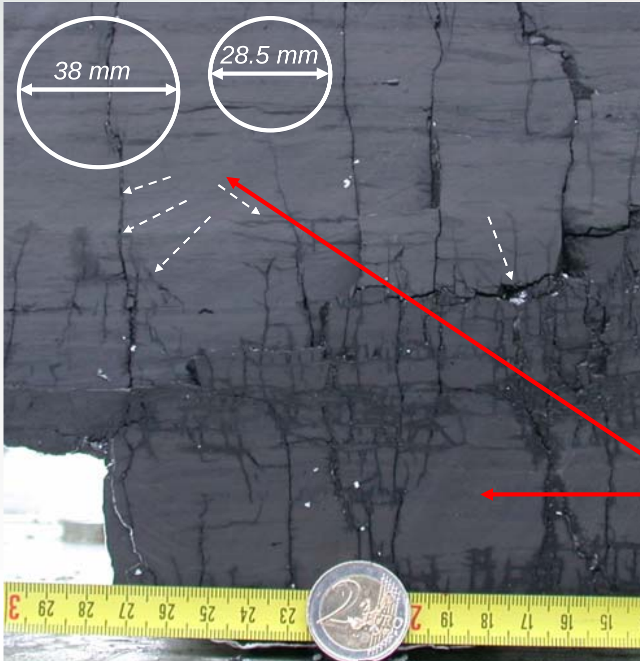
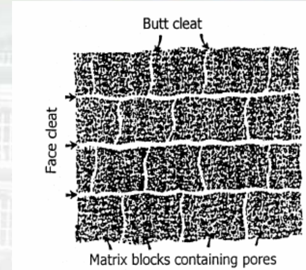
Gas sorption and transport in coals





cleat system
(transport avenues)

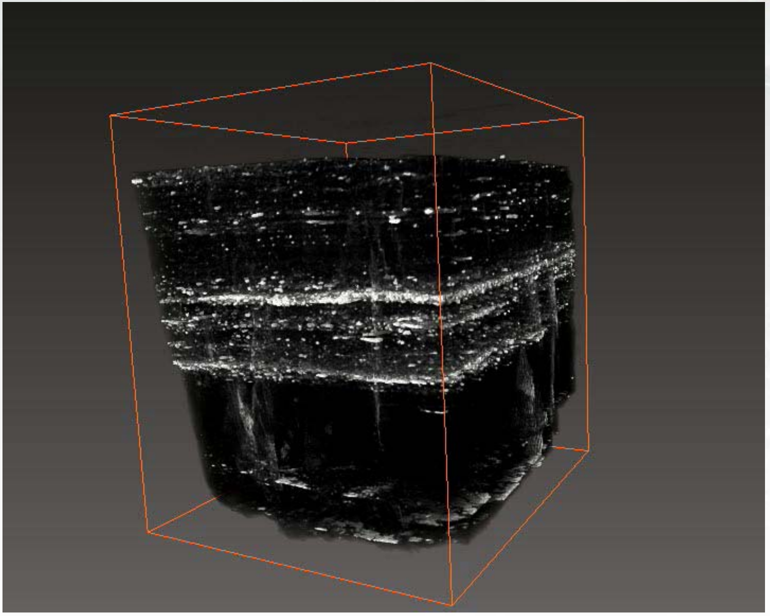
matrix volume
(storage capacity)

Notes of Presenter:

Gas shale work (GASH Project) started in 2009; and first results have been obtained.

Cooperation with University of Queensland.

Prosper Haniel #3 plug CT scan (cementation and mineralization)



15 cm (~6 inch)

14 cm (5.5 inch)

Notes of Presenter:

This XRD tomogram of a MVB coal from the German Ruhr area shows that pervasive cementation and mineralization add to the anisotropy and heterogeneity of coals.

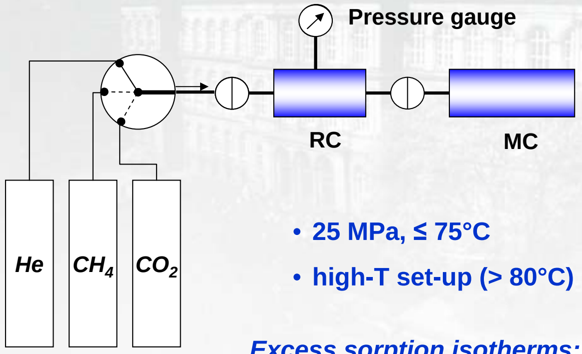
This coal has been investigated in the True Triaxial Coal Permeameter at the University of Queensland.

- **EXCESS SORPTION ISOTHERMS**
  - Pressure, moisture content, temperature
  - Type and maturity of coal/organic matter
  - Quality control (Inter-laboratory tests)
- **SORPTION/DESORPTION KINETICS**
- **TRANSPORT PROCESSES**
  - Pressure-driven volume flow (Darcy flow)
  - Capillary effects (two-phase fluid system)
  - Diffusion and sorption
- **CONCLUSION**

Excess sorption isotherms

- *powdered coal or shale samples*
- *grain-size fractions*
- *cuttings*

High-pressure sorption of CO_2, CH_4 on coals and shales



- **25 MPa, ≤ 75°C**
- **high-T set-up (> 80°C) under construction**

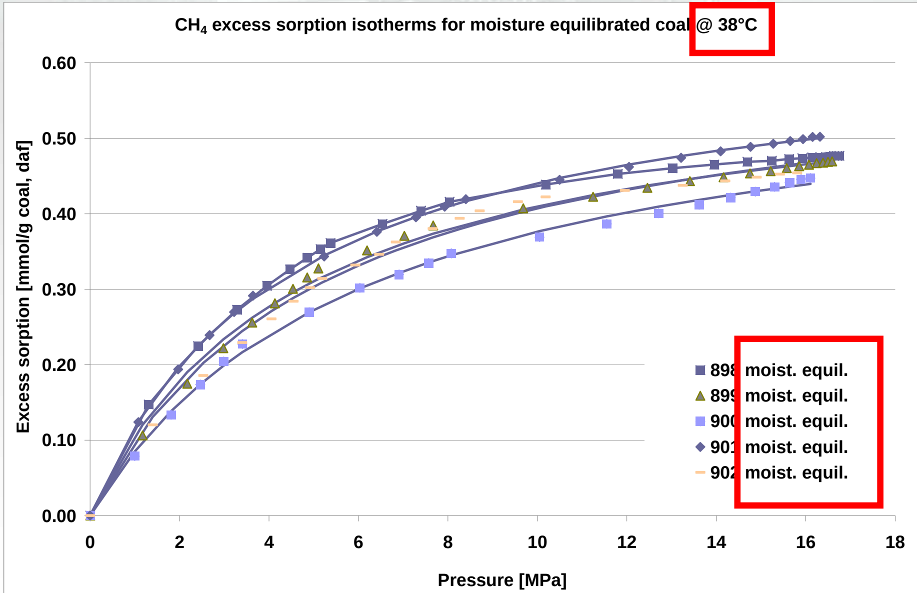
Excess sorption isotherms:

$$m_{excess}(p) = m_{adsorbed}(p) \cdot \left(1 - \frac{\rho_{free}(p)}{\rho_{sorbed}}\right)$$

Langmuir-type sorption function: $$m_{adsorbed}(p) = m_{\infty} \cdot \frac{p}{K_L + p}$$

Methane sorption (coal)

samples from one well; variability due to composition, rank, ...

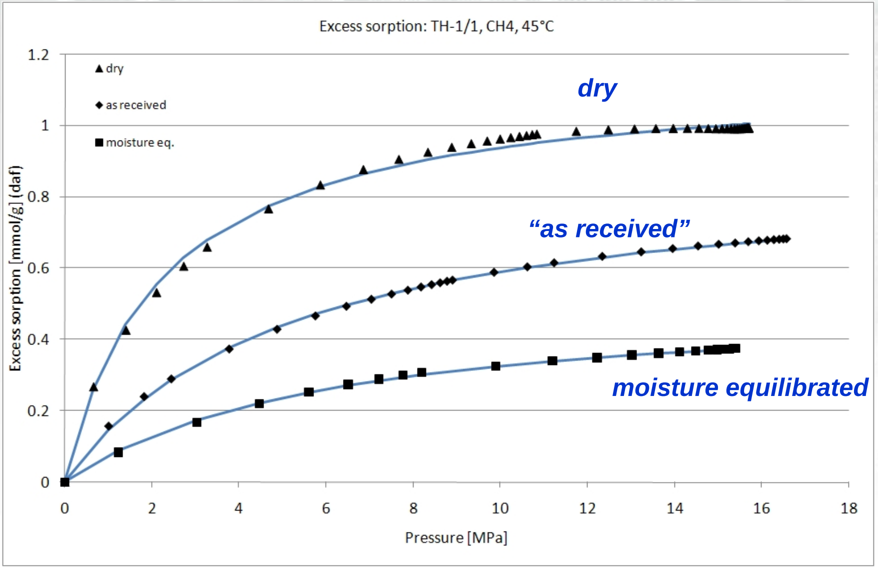


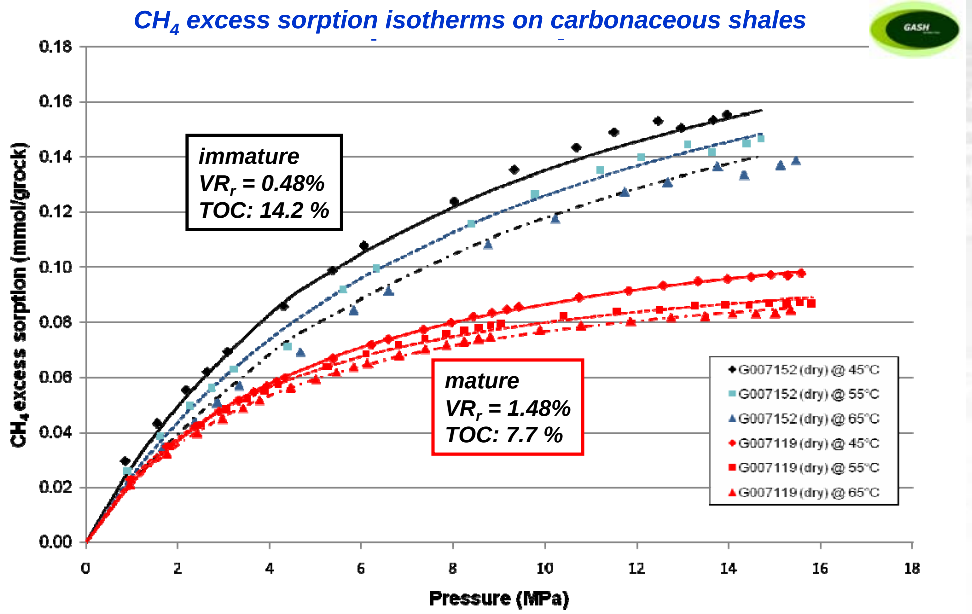
Note of Presenter:

Performed measurements on a routine basis; our recommendation is to perform measurements on moisture-equilibrated samples; temperature dependence is of lesser importance.

Methane sorption on coal (moisture effect)

same sample; different moisture content




CH4 excess sorption isotherms on carbonaceous shales
immature
VRr = 0.48%
TOC: 14.2 %
mature
VRr = 1.48%
TOC: 7.7 %
G007152 (dry) @ 45°C
G007152 (dry) @ 55°C
G007152 (dry) @ 65°C
G007119 (dry) @ 45°C
G007119 (dry) @ 55°C
G007119 (dry) @ 65°C
CH4 excess sorption (mmol/grock)
Pressure (MPa)
0.00
0.02
0.04
0.06
0.08
0.10
0.12
0.14
0.16
0.18
0
2
4
6
8
10
12
14
16
18

CARBON 47 (2009) 2958–2969

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European inter-laboratory comparison of high pressure CO_2 sorption isotherms. I: Activated carbon

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Gensterblum et al. (2009)

Part II (natural coals): submitted in March 2010

Excess sorption isotherms

- ***moisture content is the most important (but least controlled) parameter!***
- ***holds for coals***
- ***probably also for shales***

Sorption kinetics

- ***powdered coal or shale samples***
- ***grain-size fractions***
- ***cuttings***

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High-pressure sorption isotherms and sorption kinetics of CH_4 and CO_2 on coals

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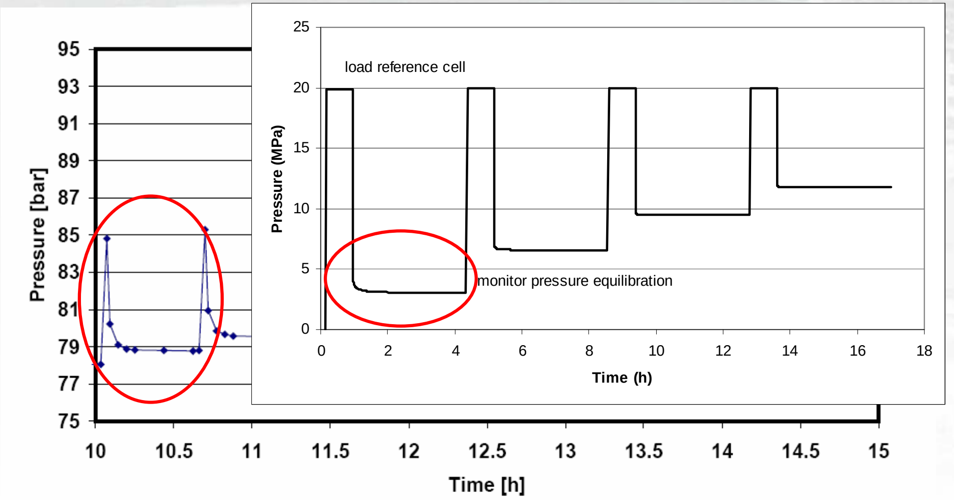
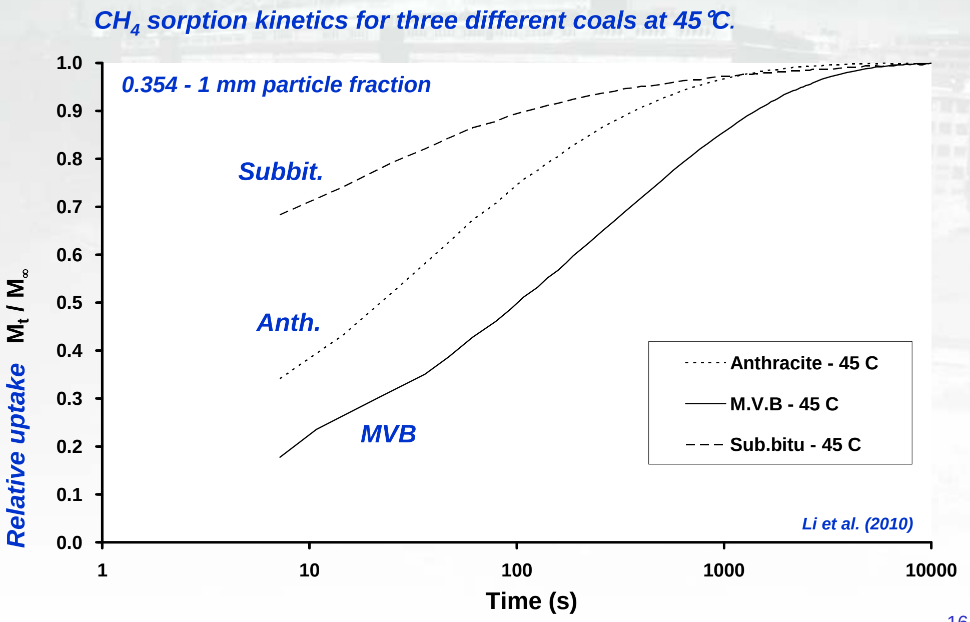
Li et al. (2010)

Pressure equilibration times (ranging from minutes to hours)

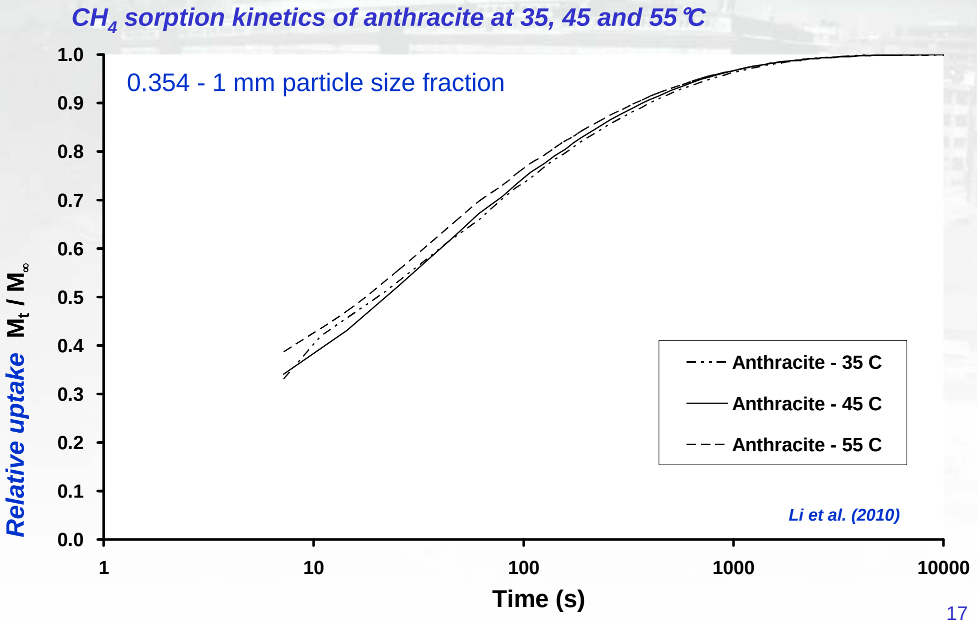


Analysis of pressure decay curves during the 1st sorption step

CH_4 sorption kinetics (rank effects)



CH_4 sorption kinetics (temperature dependence)



Transport processes

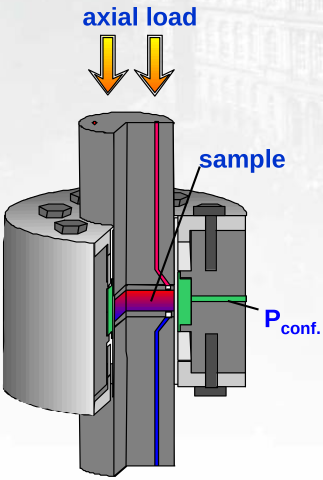
- *cylindrical plugs (28.5 and 38 mm diameter)*
- *controlled stress conditions*

Fluid transport experiments

Multi-purpose high pressure triaxial flow cells:

F_{axial} (max) = 100 kN, $P_{conf.}$ (max) = 50 MPa

Cylindrical samples: Δx(max) = 3.5 cm, ∅ = 2.85 & 3.85 cm



Experiments:

(a) Single phase system:

- **Gas permeability on dry samples**
  - **Steady state**
  - **Non-steady state**

  → $k_{abs(gas)}$
- **Water permeability/saturation**

  → $k_{abs(water)}$

(b) Two-phase system:

- **"gas breakthrough"**

→ $p_{c(entry,\ breakthrough)}$
→ $p_{c(snap\text{-}off)}$
→ $k_{eff(gas)}$ f(Δp)
→ D_{eff}

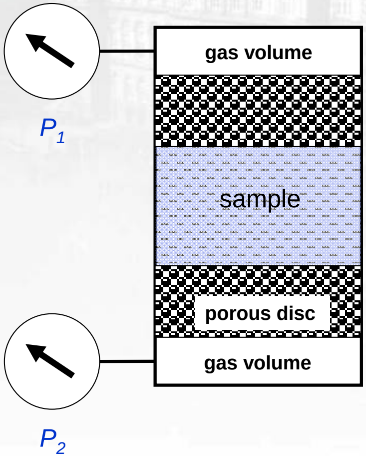
Notes of Presenter:

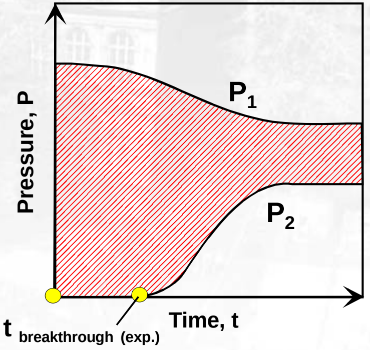
Schematic – assembled -- individual parts/components.

The sample is placed between two stainless steel pistons.

Fluid transport experiments ("gas breakthrough")

- ***Closed volumes, separated by the (water-saturated) sample***
- ***Monitoring of the evolution of upstream and downstream pressure with time***





used by Hildenbrand et al (2002, 2004) for assesment of capillary sealing efficiency*

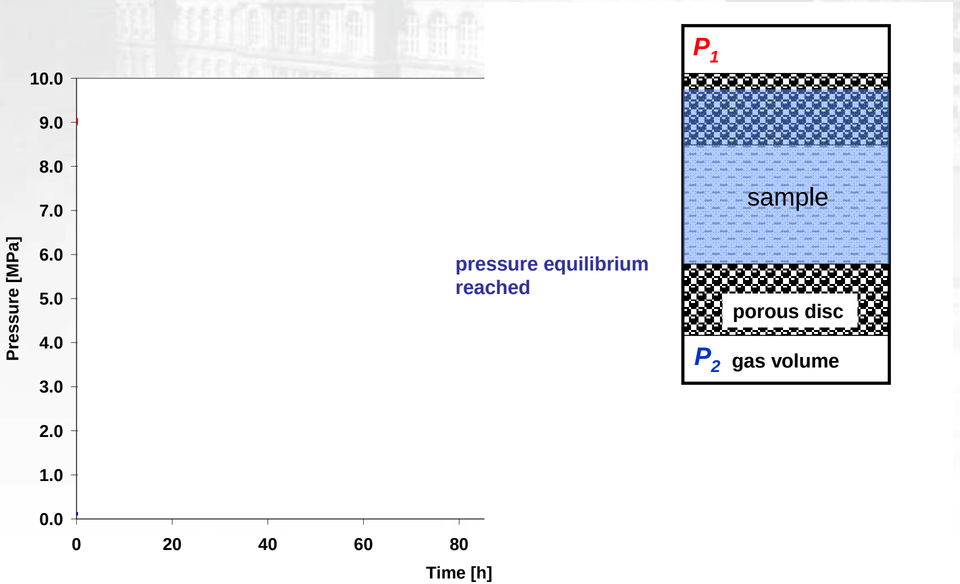
**now Amann*

Note of presenter:

Pressure equilibrium between upstream and downstream compartments is achieved before the gas/water interface reaches the sample surface.

Fluid transport experiments

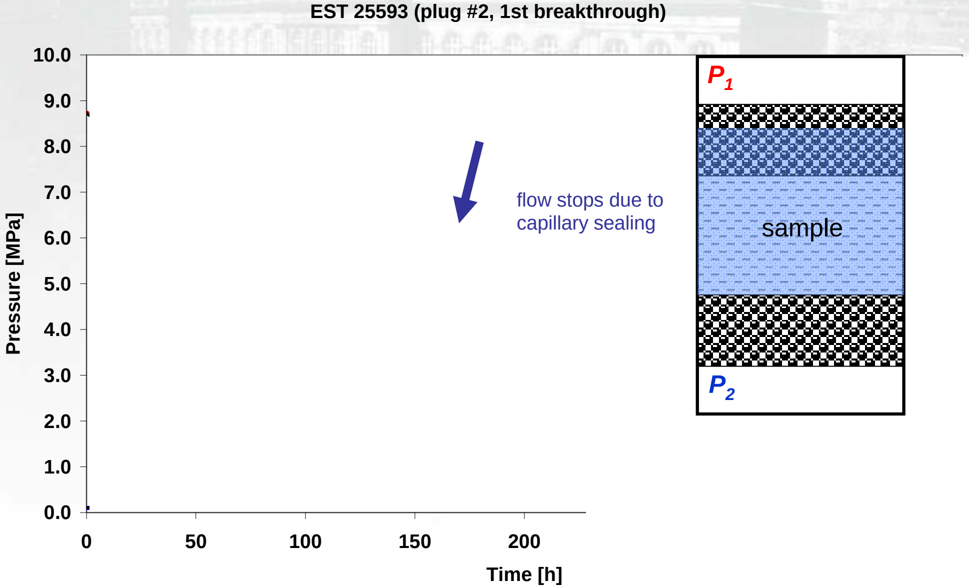
Water displacement between two gas-filled reservoirs (up to pressure equilibrium)



Note of Presenter:

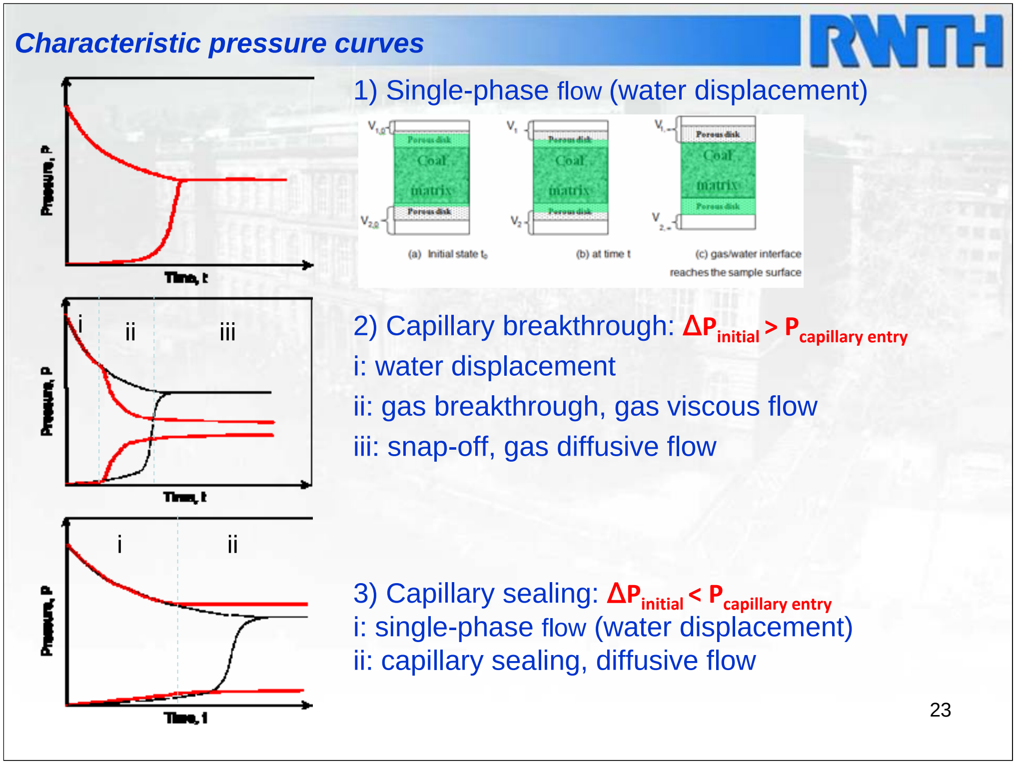
Pressure equilibrium between upstream and downstream compartments is achieved before the gas/water interface reaches the sample surface.

Water displacement between two gas-filled reservoirs (with capillary sealing)



Note of Presenter:

Black curves are measured; red and blue curves are calculated.



Notes of presenter:

These experiments are performed by imposing an initially high gas pressure gradient across the sample.

On both sides of the samples there are two closed reservoirs with known volume.

The pressure on each side is measured continuously by pressure transducers.

In the left plot, where the absolute pressure is plotted versus the exp. time we observe that

after a certain time the pressure on the inflow side will start to decrease,

while the pressure on the outflow side will increase;

here gas flow becomes possible;

pressure difference will decrease until a constant pressure difference is maintained.

This data can be used to calculate the keff using Darcy's for compressible media.

We observe that after breakthrough keff will increase, run through a max., decline again and ending in zero keff, when constant pressure gradient is reached.

Transforming the characteristic steps into the conventional Pc/Sw plot, where Pc equals DP between both sides of the sample,

we start with the initially high pressure difference.

After a certain time, breakthrough of gas takes place; thus capillary pressure will decrease.

This Pc is still high enough to displace water from pore space until we reach a certain Pc-value, with max. gas saturation.

Lower Pc-values are not high enough to displace water, which is then re-imbibed again, shutting more and more pores until the last interconnected pore is shut off.

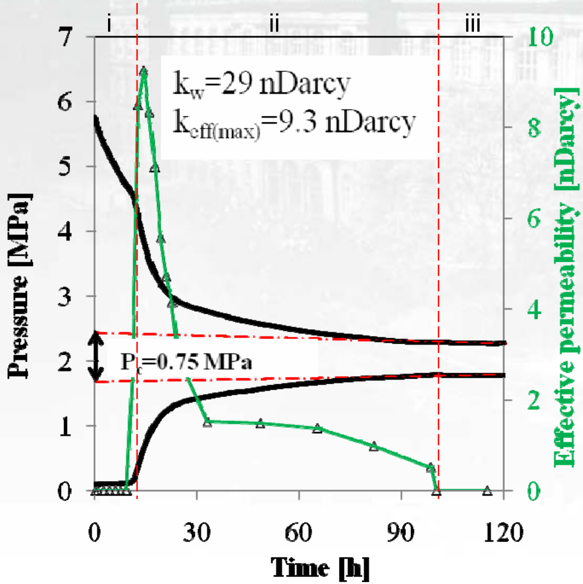
Here the residual pressure diff. is reached, which we interpret to be equal to the Pbreakthrough of the slow drainage process (here plotted in grey).

So key parameters are.

this final capillary pressure is the pressure for which a seal starts to leak

and keff as a function of pressure decay, thus gas saturation.

He breakthrough test on Yangquan anthracite plug #1



Starting with fully water-saturated (matrix) samples

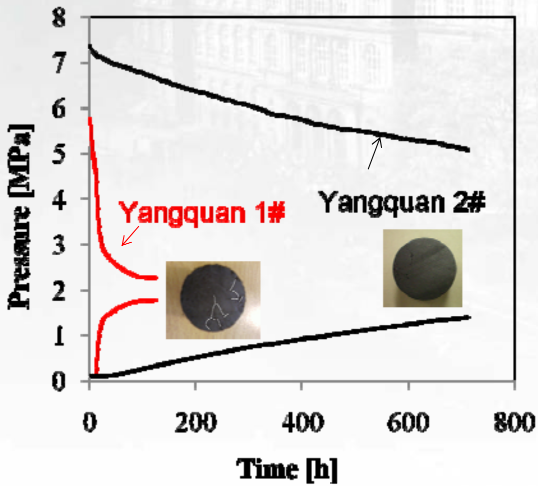
⇨ non-sorbing gases

(i) Single phase flow

(ii) Gas breakthrough, gas flow, snap-off

(iii) diffusion

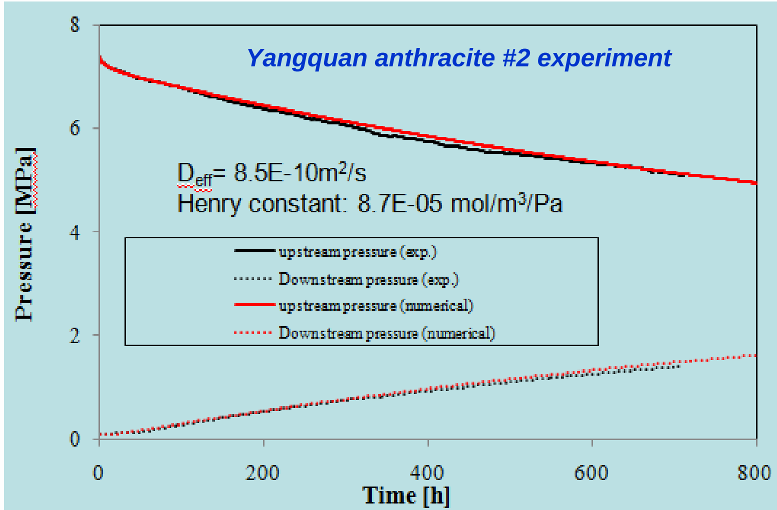
He "breakthrough" tests at 45°C, $P_{conf.}$=20MPa



Breakthrough characteristics

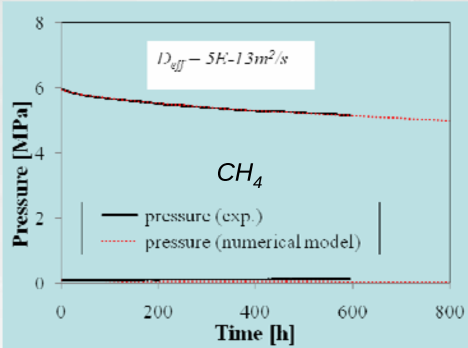
Yangquan #1	Yangquan #2
cleated	cleat-free (matrix)
"standard" breakthrough	No breakthrough
capillary pressure controlled	diffusion-controlled
k_w=29 nDarcy	k_w: sub-nDarcy

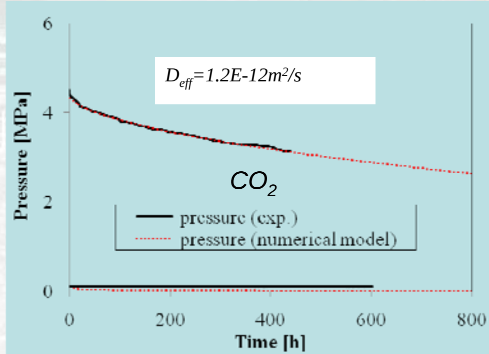
Numerical model (He diffusion in coal)



Upstream and downstream pressure curves can be explained by a diffusion model with a Henry-type constant for He "dissolution" in coal

Yangquan anthracite #2 CH_4 and CO_2 tests





Results of numerical (finite difference) model:

Gas	C_∞ [mol/kg]	K_L [MPa]	D_{eff} [m²/s]
CH_4	1.01	1.79	**5.0E-13**
CO_2	1.60	0.82	**1.2E-12**

- *Essentially no gas transport across the sample (all gas is taken up)*
- *Effective diffusion coefficient of CO_2 2.4 times larger than CH_4*

Conclusion

Combination of experimental techniques for sorption and fluid transport measurements provides improved insight into processes relevant for CBM and shale gas systems

Simple numerical models were successfully used for interpretation and consistency-testing of experimental results

Thank you!