Sorption and Desorption Processes of Methane and Carbon Dioxide on Coals and Shales - Experiments and Theory*

Bernhard M. Krooss[1], Andreas Busch[2], Yves Gensterblum[1] and Dirk Prinz[1]

Search and Discovery Article #40376 (2009)
Posted January 20, 2009

*Adapted from oral presentation at AAPG Annual Convention, San Antonio, TX, April 20-23, 2008

[1]Institute of Geology and Geochemistry of Petroleum and Coal, RWTH Aachen University, Aachen, Germany. (krooss@lek.rwth-aachen.de)
[2]Shell International Exploration and Production B.V., Rijswijk, NL

Abstract

Physical sorption processes of hydrocarbon and non-hydrocarbon gases on coals and carbonaceous shales encounter increasing interest in the context of unconventional gas exploration and subsurface storage (sequestration) of CO_2.

During recent years experimental work has been performed in our laboratory to investigate sorption thermodynamics, kinetics, selectivity and fractionation processes of methane and CO_2 on coals of different type and rank and on shales of various compositions. Experiments have been conducted under high-pressure conditions (up to 25 MPa) at temperatures relevant for natural gas and coal basins. These studies have provided a database suitable for the development of numerical models on gas migration and storage. They have also revealed unexpected behaviour in terms of selectivity and relative sorption rates.

Generally, sorption and desorption of CO_2 to/from coals was found to proceed more rapidly than of methane. Although coals exhibit larger excess sorption capacities for CO_2 than for methane, certain coals showed preferential sorption of methane in the low-pressure range. Moisture content plays a crucial role in the sorption of gases on natural coals.

Selected results will be presented documenting the state of experimental work on gas sorption processes in sedimentary basins and implications for unconventional gas exploration.

SORPTION AND DESORPTION PROCESSES OF METHANE AND CARBON DIOXIDE ON COALS AND SHALES – EXPERIMENTS AND THEORY –

Bernhard M. Krooss, Andreas Busch, Yves Gensterblum, Dirk Prinz*

Institute of Geology and Geochemistry of Petroleum and Coal
RWTH Aachen University
Lochnerstr. 4-20, D-52056 Aachen, Germany

krooss@lek.rwth-aachen.de

Shell International Exploration and Production B.V., Rijswijk, NL

ACKNOWLEDGEMENTS

RWTH

- *Dieter Hanebeck*
- *Stefan Schlömer*
- *Alexandra Hildenbrand*
- *Sascha Alles*
- *Fengshuang Han*
- *Dongyong Li*

Physical sorption processes of hydrocarbon and non-hydrocarbon gases on coals and carbonaceous shales encounter increasing interest in the context of unconventional gas exploration and subsurface storage (sequestration) of CO_2

GAS SORPTION AND TRANSPORT IN COALS AND SHALES

RWTH

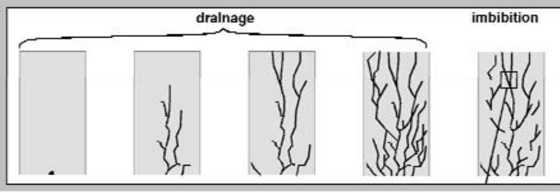
Mechanisms & Processes

- sorption/desorption
  - capacity
  - kinetics
  - selectivity

- transport processes
  - diffusion
  - Darcy flow (compressible)
  - capillary breakthrough
  - effective permeability
  - (relative permeability)

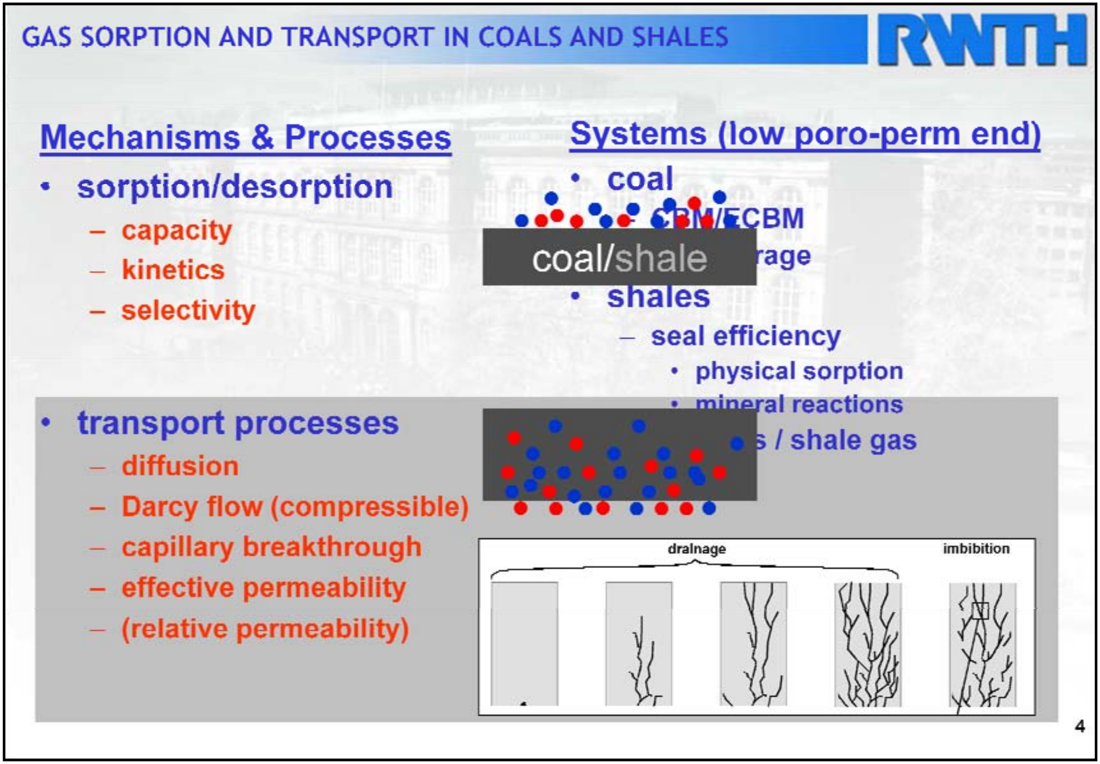
Systems (low poro-perm end)

- coal
  - CBM/ECBM
  - CO_2 storage
- shales
  - seal efficiency
    - physical sorption
    - mineral reactions
  - tight gas / shale gas



Road show of experimental work performed in our laboratory with selected examples and varying focus of interest; combinations of processes depending on experimental conditions of selected examples.

Portfolio of experimental techniques that can be combined in a very flexible way; well-established understanding of processes (and open questions).



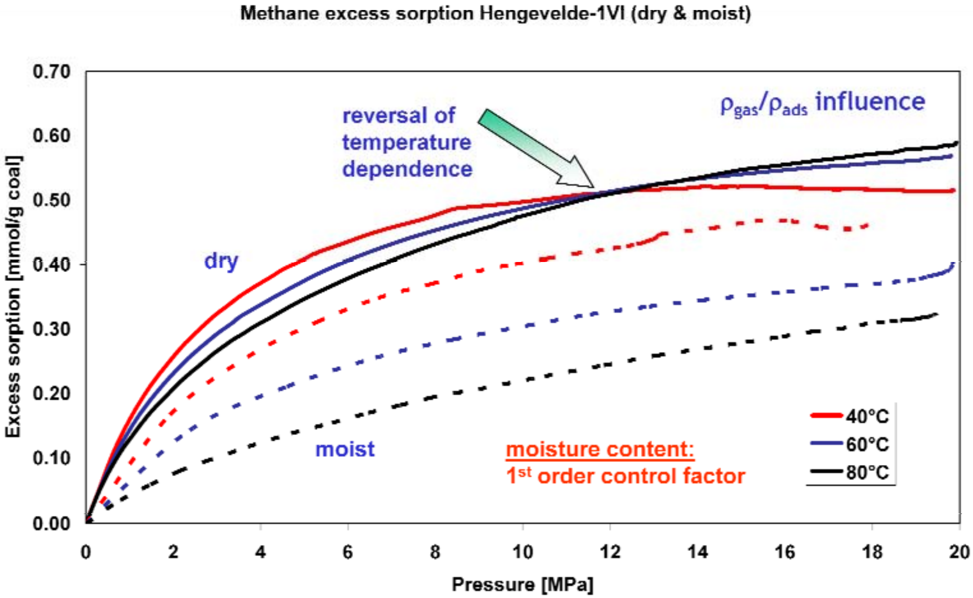
Road show of experimental work performed in our laboratory with selected examples and varying focus of interest; combinations of processes depending on experimental conditions of selected examples.

Portfolio of experimental techniques that can be combined in a very flexible way; well-established understanding of processes (and open questions).

- CH_4 excess sorption
- CO_2 excess sorption
- Selectivity (CH_4 vs. CO_2)
- Sorption kinetics (CH_4 vs. CO_2)
- Sorption on shales (CH_4 & CO_2)

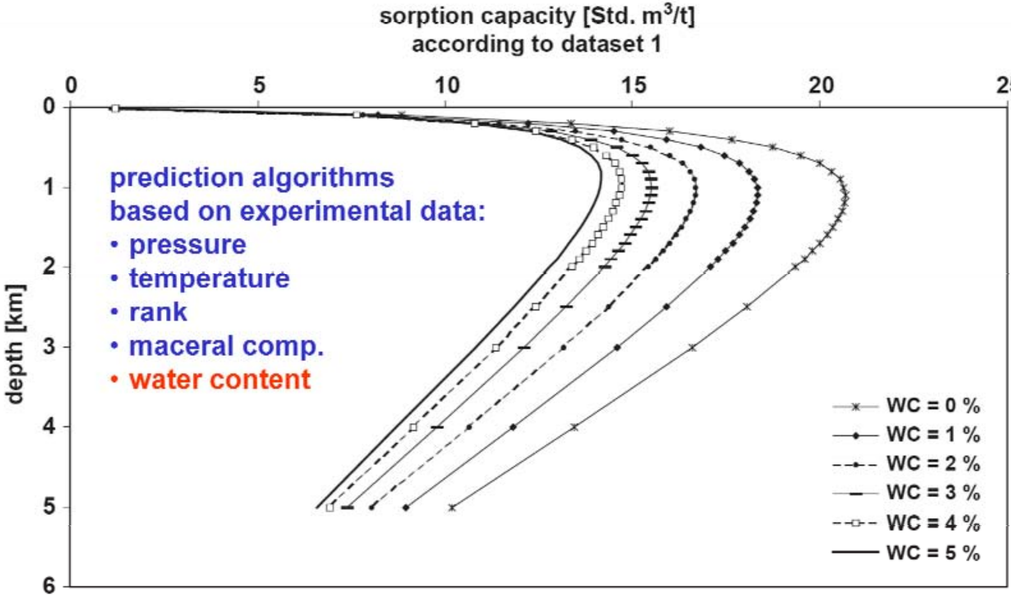
- **CH_4 excess sorption**
- CO_2 excess sorption
- Selectivity (CH_4 vs. CO_2)
- Sorption kinetics (CH_4 vs. CO_2)
- Sorption on shales (CH_4 & CO_2)

CH_4 SORPTION: TEMPERATURE AND MOISTURE EFFECTS



Krooss et al. (2002)

CH_4 SORPTION CAPACITY MODEL



A. Hildenbrand et al. / International Journal of Coal Geology 66 (2006) 179–203

- CH_4 excess sorption
- **CO_2 excess sorption**
- Selectivity (CH_4 vs. CO_2)
- Sorption kinetics (CH_4 vs. CO_2)
- Sorption on shales (CH_4 & CO_2)

High-pressure CO_2 sorption

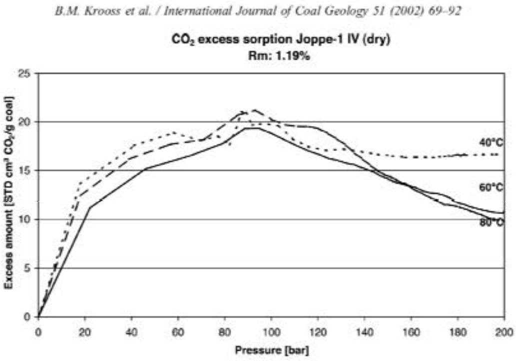
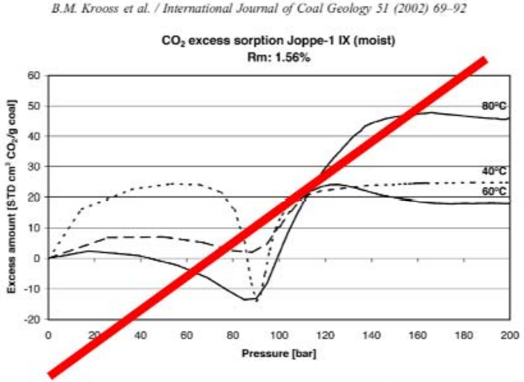


Fig. 9. Excess sorption isotherms for CO_2 on dry Joppe-1 IV coal at 40, 60 and 80 °C.

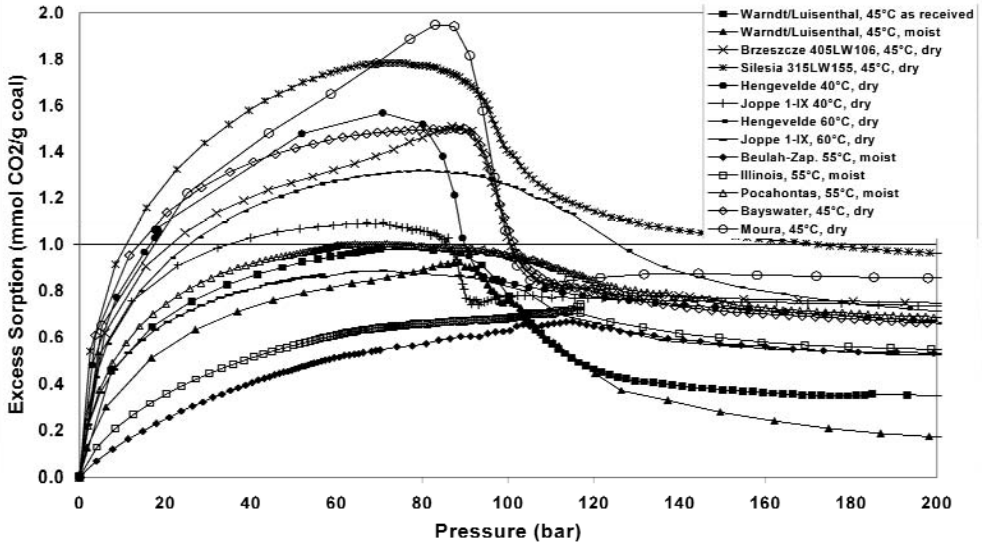


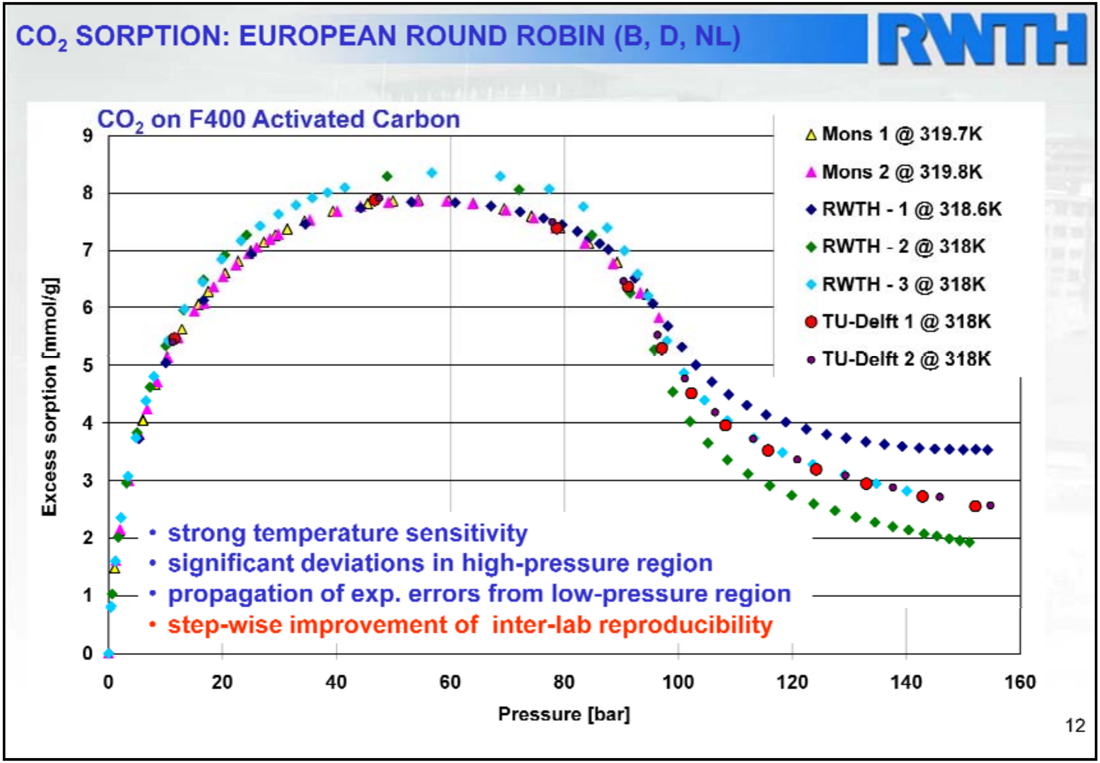
ig. 13. Excess sorption isotherms for CO_2 on moisture-equilibrated Joppe-1 IX coal at 40, 60 and 80

Krooss et al. (2002)

DOE/NETL Round Robins on high-pressure CO_2 sorption: Goodman et al. (2004, 2007)

CO_2 SORPTION ISOTHERMS (COALS)

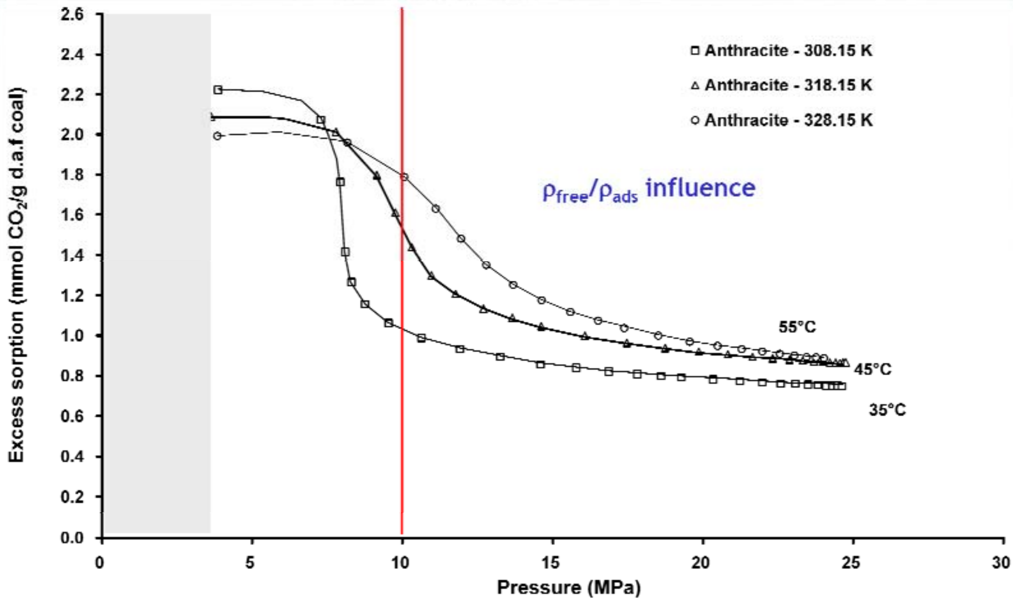




We teamed up with laboratories in Belgium and The Netherlands for inter-laboratory comparison on selected samples (activated carbon and natural coals).

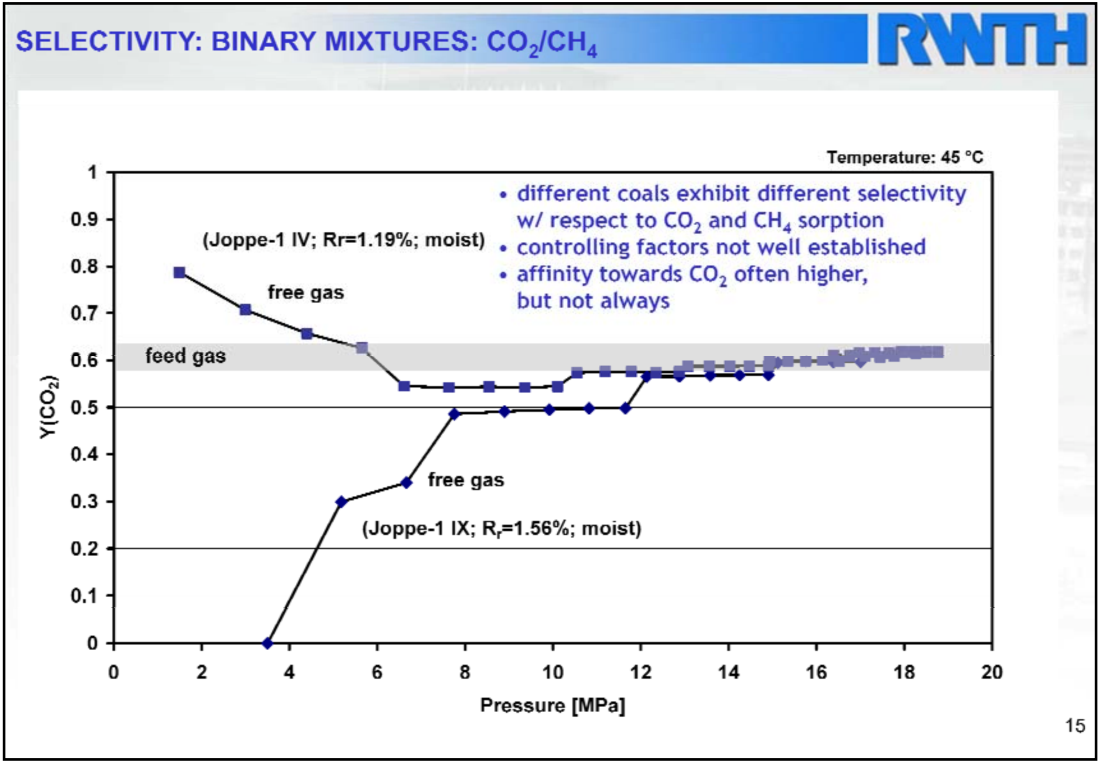
Our aim: improve overall quality of high-pressure CO_2 sorption measurements.

CO_2 HIGH-PRESSURE SORPTION, TEMPERATURE DEPENDENCE

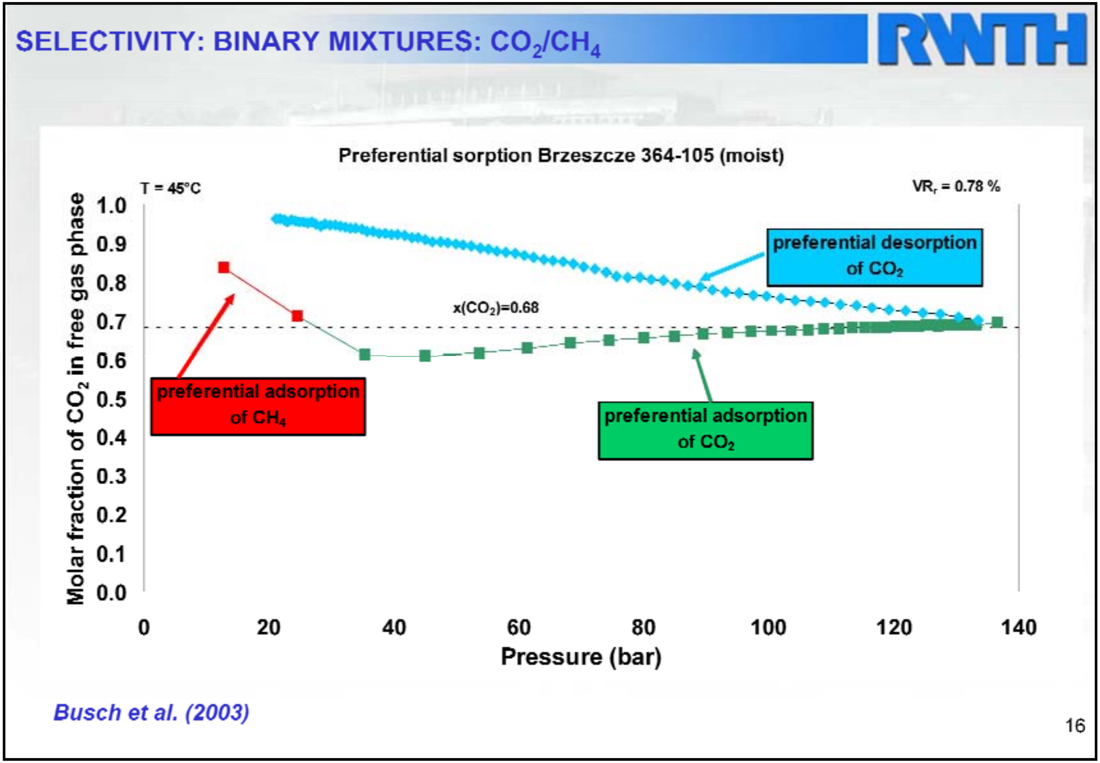


data from PhD project of Dongyong LI

- CH_4 excess sorption
- CO_2 excess sorption
- **Selectivity (CH_4 vs. CO_2)**
- Sorption kinetics (CH_4 vs. CO_2)
- Sorption on shales (CH_4 & CO_2)



Take-home message: different coals exhibit different selectivity with respect to CO_2 and CH_4 sorption. Not yet clear what is the controlling factor.

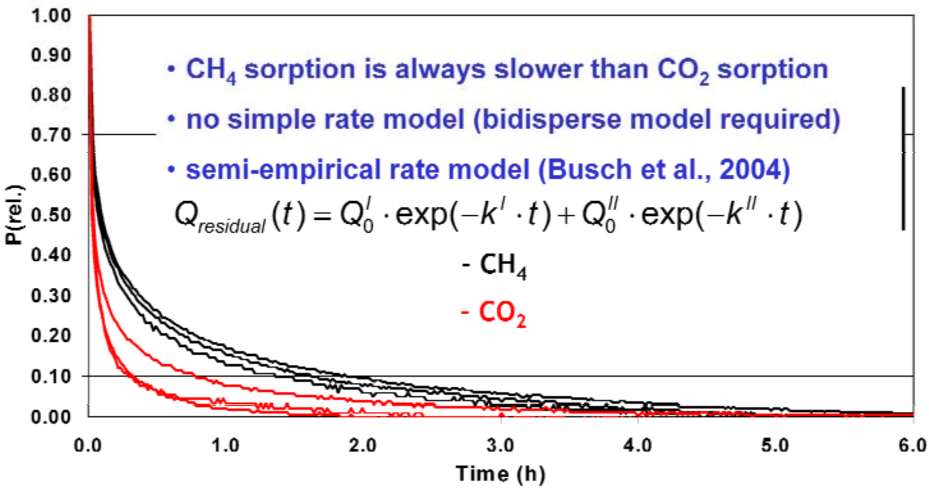


When a coal is exposed to a gas mixture, selective sorption is likely to occur; this will manifest itself in the composition of the free gas phase. An enrichment of the gas phase in one component indicates the selective or preferential sorption of the other compound. A series of measurements was performed in our lab on a variety of coals.

- CH_4 excess sorption
- CO_2 excess sorption
- Selectivity (CH_4 vs. CO_2)
- **Sorption kinetics (CH_4 vs. CO_2)**
- Sorption on shales (CH_4 & CO_2)

Comparison of pressure decay curves for CH_4 and CO_2

- different grain-size fractions
- different pressure steps

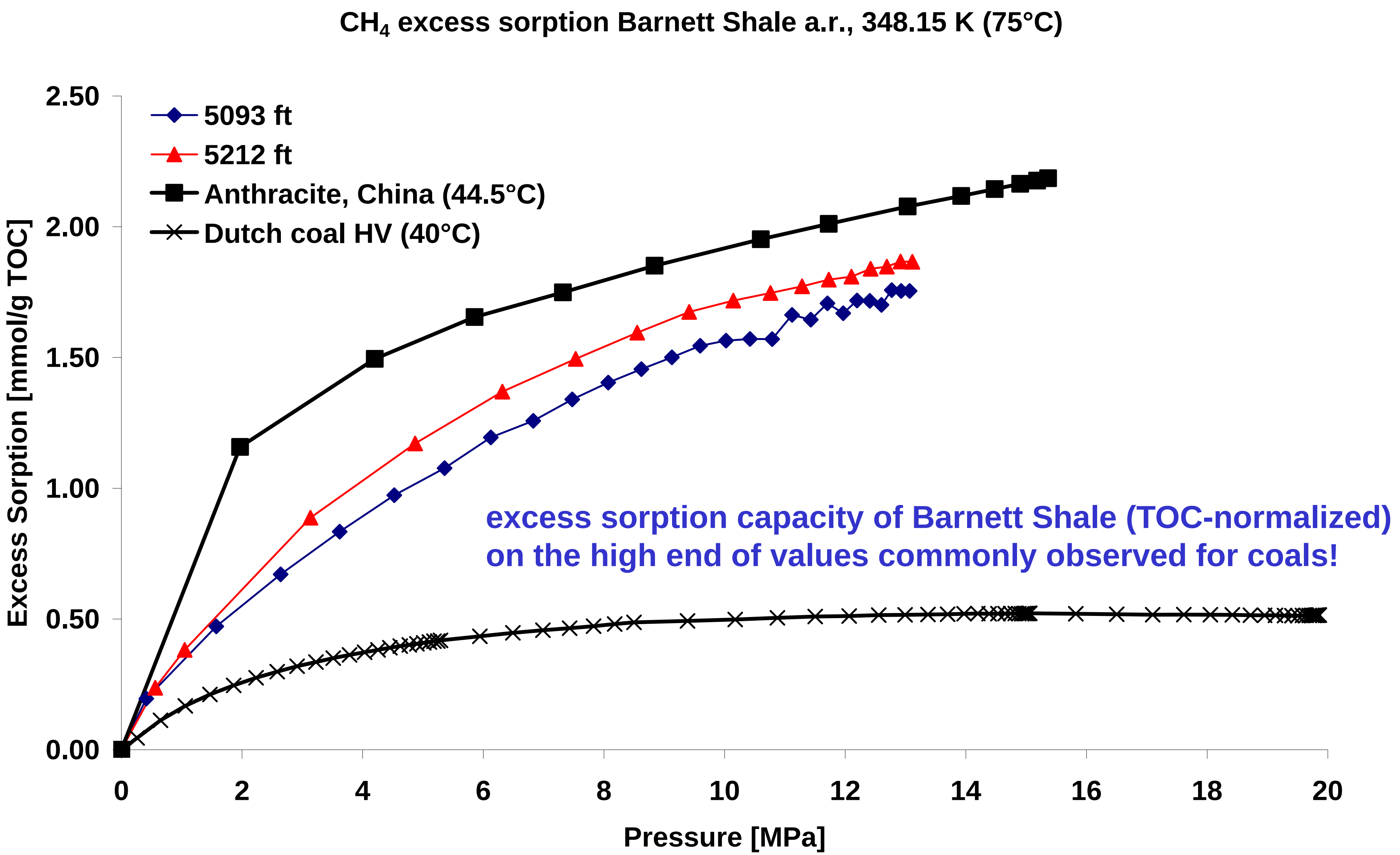


- CH_4 sorption is always slower than CO_2 sorption
- no simple rate model (bidisperse model required)
- semi-empirical rate model (Busch et al., 2004)

$$Q_{residual}(t) = Q_0^{I} \cdot \exp(-k^{I} \cdot t) + Q_0^{II} \cdot \exp(-k^{II} \cdot t)$$

- CH_4 excess sorption
- CO_2 excess sorption
- Selectivity (CH_4 vs. CO_2)
- Sorption kinetics (CH_4 vs. CO_2)
- **Sorption in shales (CH_4 & CO_2)**

METHANE SORPTION ON BARNETT SHALE (TX)



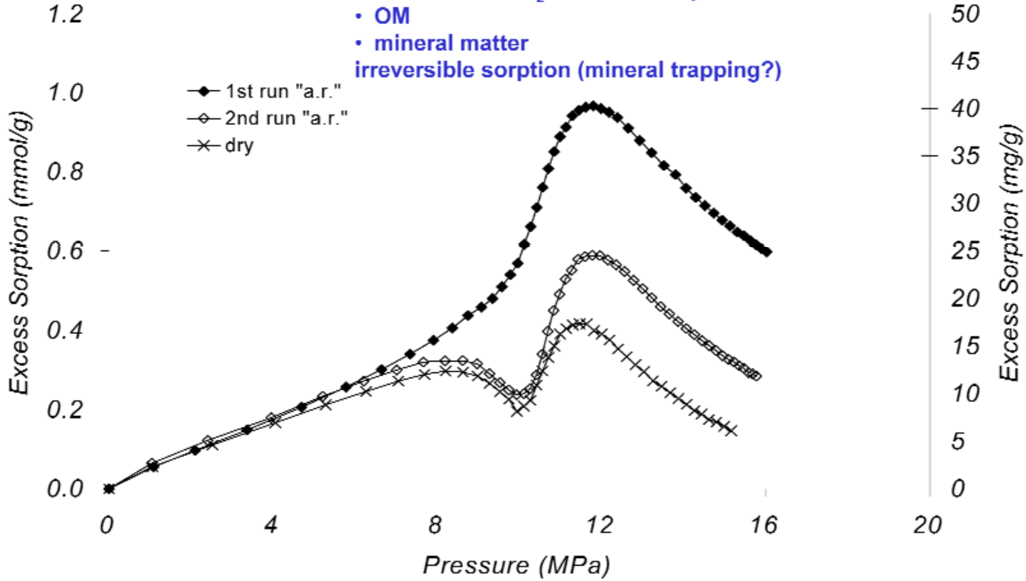
Anthracite data from PhD project of Fengshuang HAN

CO_2 SORPTION ON MUDERONG SHALE (AUS)

RWTH

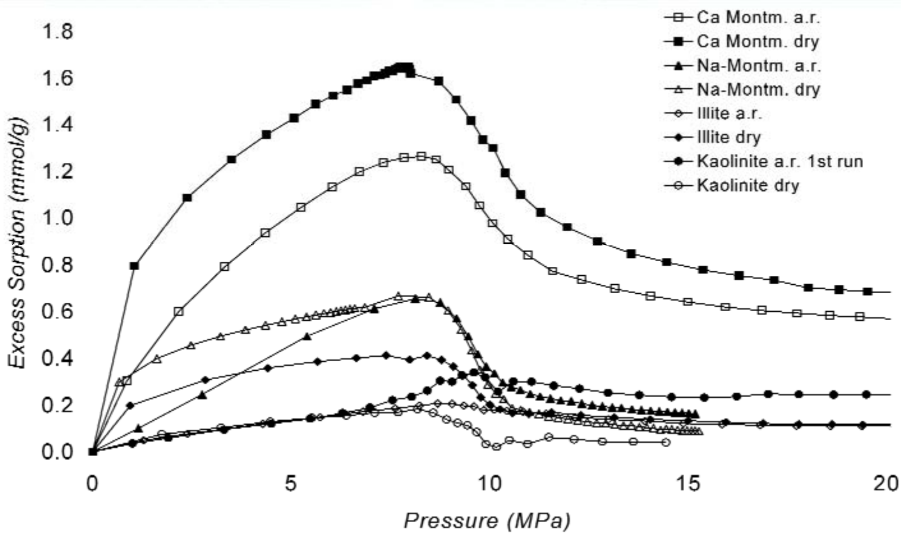
interaction of CO_2 with shale caprocks
- OM
- mineral matter

irreversible sorption (mineral trapping?)



CO_2 SORPTION ON PURE CLAY MINERALS

mineral alteration effects due to exposure to CO_2?!



clay samples from "source clay" (CMS)

IJGGC 93 1–12

ARTICLE IN PRESS

INTERNATIONAL JOURNAL OF GREENHOUSE GAS CONTROL XXX (2008) XXX–XXX

available at www.sciencedirect.com

ScienceDirect

journal homepage: www.elsevier.com/locate/ijggc

ELSEVIER

Greenhouse Gas Control

Q1 Carbon dioxide storage potential of shales

Andreas Busch[a,], Sascha Alles[a], Yves Gensterblum[a], Dirk Prinz[a], David N. Dewhurst[b], Mark D. Raven[c], Helge Stanjek[d], Bernhard M. Krooss[a]*

[a] *RWTH Aachen University, Institute of Geology and Geochemistry of Petroleum and Coal, Lochnerstr. 4-20, D-52056 Aachen, Germany*
[b] *CSIRO Petroleum, Australian Resources Research Centre, Western Australia, Australia*
[c] *CSIRO Land and Water, Urrbrae, South Australia, Australia*
[d] *RWTH Aachen University, Clay and Interface Mineralogy, Aachen, Germany*

INTERACTION OF GASES WITH COALS AND CARBONACEOUS SHALES

- significant progress has been made in sorption research
- practically useful relationships are emerging
- research issues:
  - high-pressure CO_2 isotherms
  - selectivity
  - sorption kinetics
  - physical sorption vs. mineral reactions (CO_2)
  - relationship sorption - transport processes

References

Busch, A., S. Alles, Y. Gensterblum, D. Prinz, D.N. Dewhurst, M.D. Raven, H. Stanjek, and B.M. Krooss, 2008, Carbon dioxide storage potential of shales: International Journal of Greenhouse Gas Control, v. 2, p. 297-308.

Busch, A., Y. Gensterblum, and B.M. Krooss, 2003, Methane and CO_2 sorption and desorption measurements on dry Argonne premium coals; pure components and mixtures: International Journal of Coal Geology, v. 55/2-4, p. 205-224.

Goodman, A.L., et al., 2004, An Inter-laboratory comparison of CO2 Isotherms Measured on Argonne Premium Coal Samples: Web accessed 2 December, 2008 (http://204.154.137.14/technologies/carbon_seq/refshelf/articles/ef034104h.pdf).

Goodman, A.L., et al., 2007, Inter-laboratory comparison II; CO_2 isotherms measured on moisture-equilibrated Argonne premium coals at 55 degrees C and up to 15 MPa: International Journal of Coal Geology, v. 72/ 3-4, p. 153-164.

Hildenbrand, A., B.M. Krooss, A. Busch, and R. Gaschnitz, 2006, Evolution of methane sorption capacity of coal seams as a function of burial history; a case study from the Campine Basin, NE Belgium: International Journal of Coal Geology, v. 66/3, p.179-203.

Krooss, B.M., F. van Bergen, Y. Gensterblum, N. Siemons, H.J.M. Pagnier, and P. David, 2002, High-pressure methane and carbon dioxide adsorption on dry and moisture-equilibrated Pennsylvanian coals: International Journal of Coal Geology, v. 51/2, p. 69-92.

THANK YOU!