ETH

Eidgenössische Technische Hochschule Zürich

Swiss Federal Institute of Technology Zurich

Study of adsorption-based CCS systems under wet conditions

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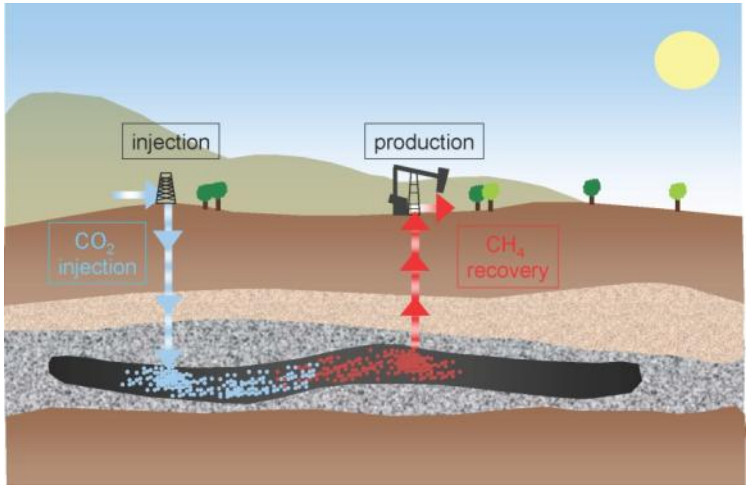
Motivation

Adsorption processes used in CO_2 capture and storage have to deal with the presence of moisture in the system. These include:

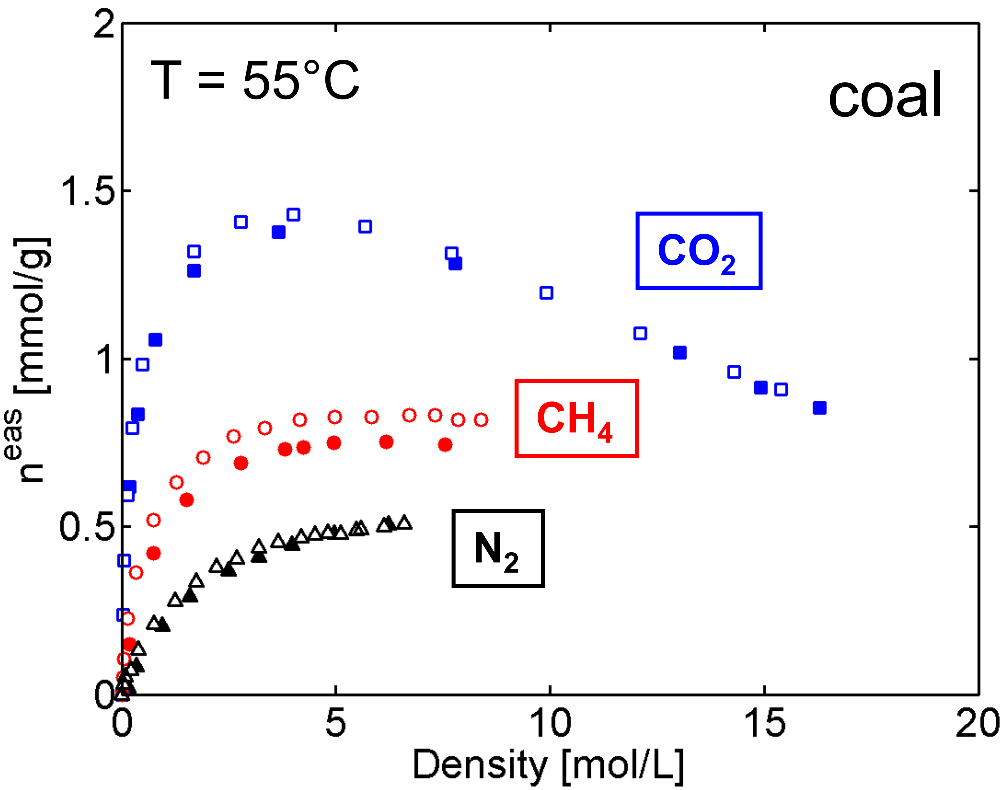
- Flue gases
- Gasification products
- Coal seams used for ECBM



Therefore it is important that we deal with wet sorbents.

Measurement of dry excess sorption

Dry adsorption-based separation systems are increasingly well studied

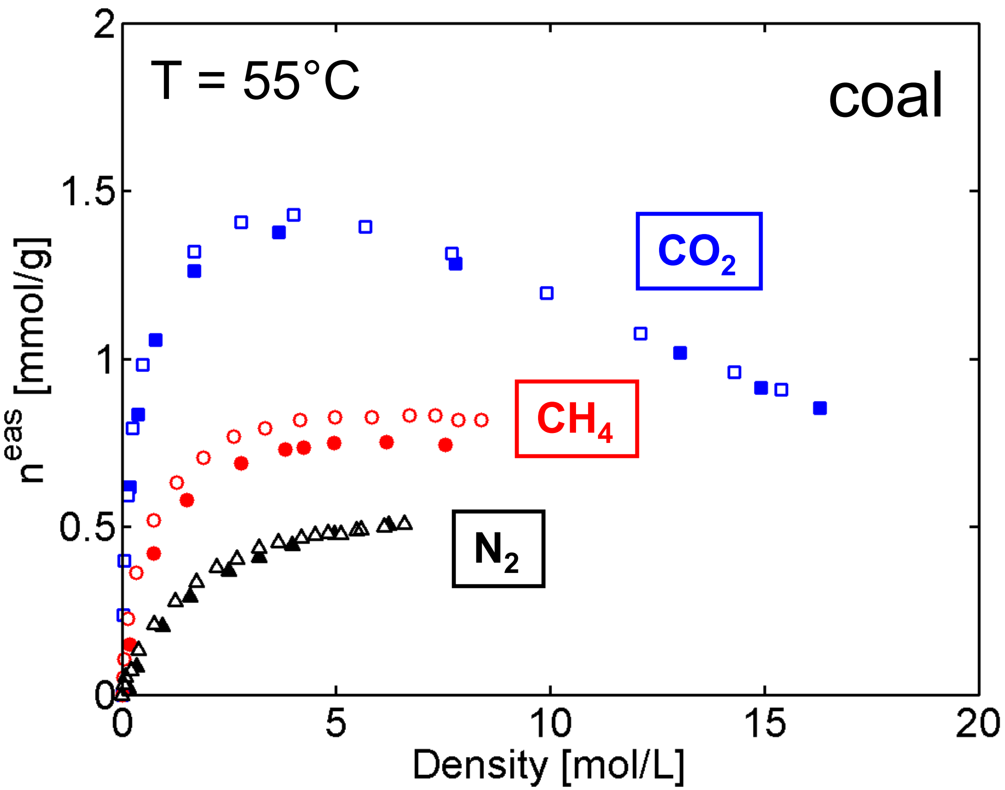


- Methods for measurement are reliable and consistent
- Plot on the left shows data from two separate laboratories
  - CSIRO
  - ETHZ

Sakurovs et al., *Energ. Fuel*. 21 (2007) 992-997
Mazzotti et al., J. Supercrit. Fluids 47 (2009) 619-627

Measurement of dry excess sorption

Excess sorption is the truly measurable quantity



- At high gas densities, the adsorbed phase experiences a buoyancy

$$n^{ex} = n^a - V^a \rho^b$$

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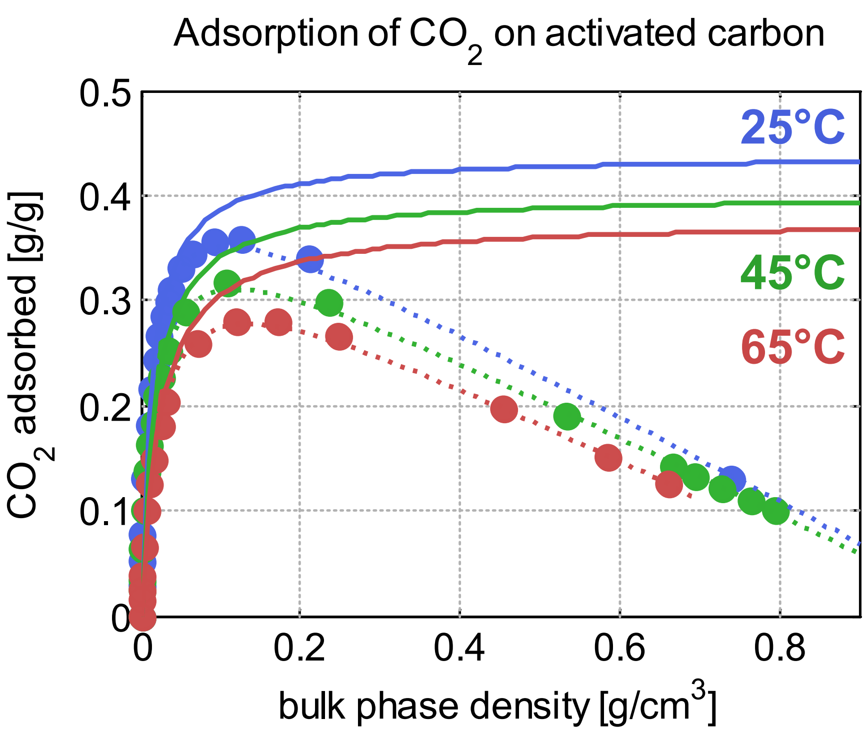
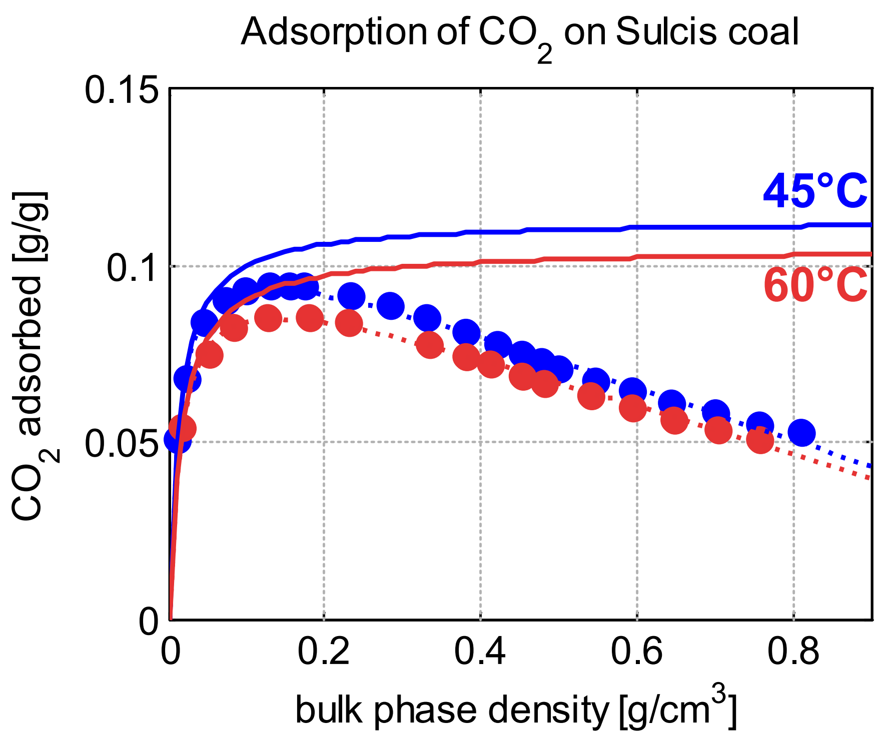
Modeling dry gas adsorption on AC and coal





Langmuir model

$$n^{ex} = \left(\frac{N_{\max} k \rho_b}{1 + k \rho_b}\right)\left(1 - \frac{\rho_b}{\rho_a}\right)$$

Research on wet sorbents

		AC	Zeolites	Silica	coal
ETHZ	This work	CO_2	CO_2	CO_2	CO_2 on wet sorbent
CSIRO	Day et al. 2008				CO_2 on wet sorbent
Okla. State University	Fitzgerald et al. 2005				CO_2 on wet sorbent
RWTH Aachen	Kroos et al. 2002				CO_2 on wet sorbent
Monash	Li et al. 2009		CO_2 on wet sorbent	CO_2 on wet sorbent	
Univ. of Maine	Brandani et al. 2004		CO_2 on wet sorbent		
Univ. of Queensland	Do et al. 2009	water			
Univ. of Illinois	Qi et al. 2000	water			
Vanderbilt University	Qi et al. 2005	water	CO_2 on wet sorbent		
Univ. of Porto	Ribeiro et al. 2008		water		
Univ. of Stuttgart	Gorbach et al. 2004		water		
Univ. de Mons	Billemont et al. 2011	CO_2 on wet sorbent			

CO_2

water

CO_2 on wet sorbent

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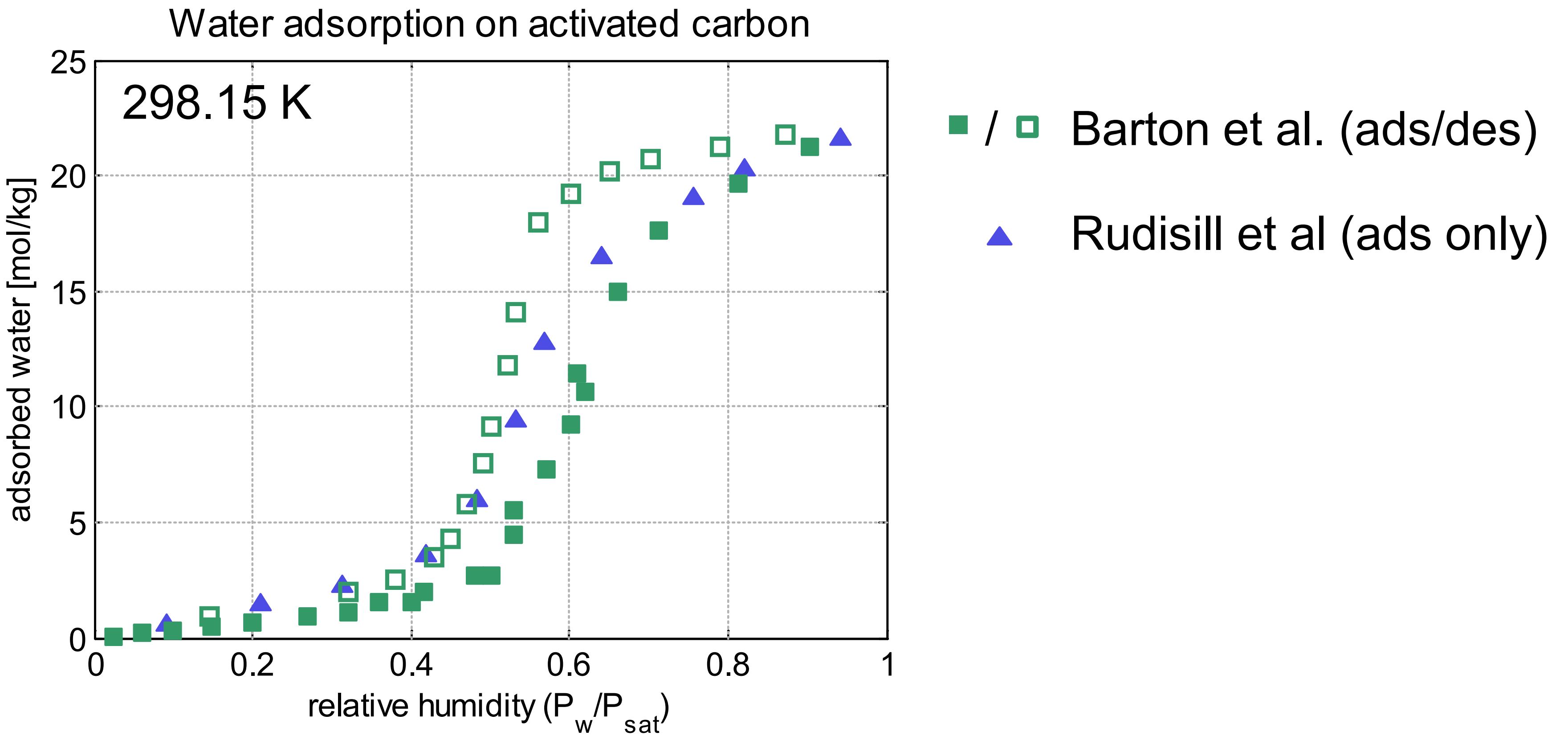
CO_2

water

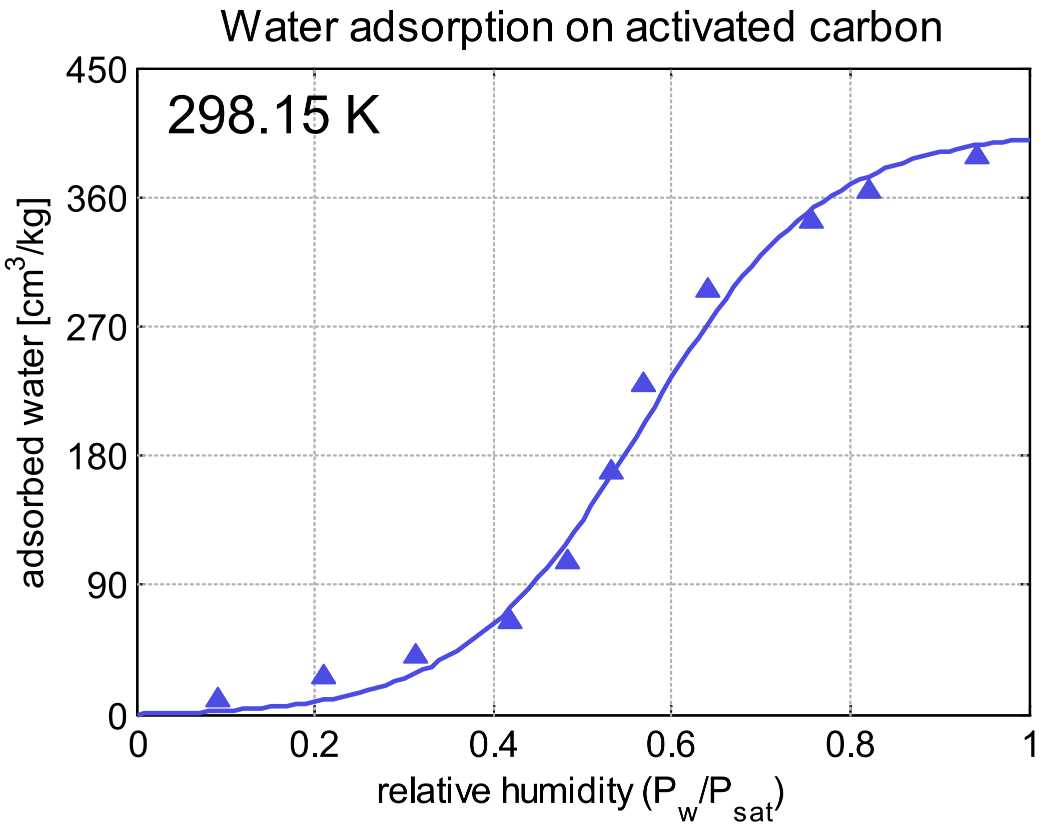
CO_2 on wet sorbent

Pure water data and isotherm on activated carbon



Sources: Barton et al., *Carbon* 22 (1984) 265-272
Rudisill et al., *Ind. Eng. Chem. Res.* 31 (1992) 1122-30

Pure water data and isotherm on activated carbon



$$V_w = \frac{V_0}{1+\exp\left[k\left(\frac{P_{1/2}}{P_{sat}} - \frac{P_w}{P_{sat}}\right)\right]}$$

where:

- V_w – pore volume filled with water [cm^3/kg sorbent]
- V_0 – specific pore volume [cm^3/kg sorbent]
- P_{sat} – saturation pressure of water
- P_w – partial pressure of water
- k, $P_{1/2}$ – model parameters

Sources: (data) Rudisill et al., *Ind. Eng. Chem. Res.* 31 (1992) 1122-30
(model) Qi et al. *J. Env. Eng.* 126. (2000) 267-271

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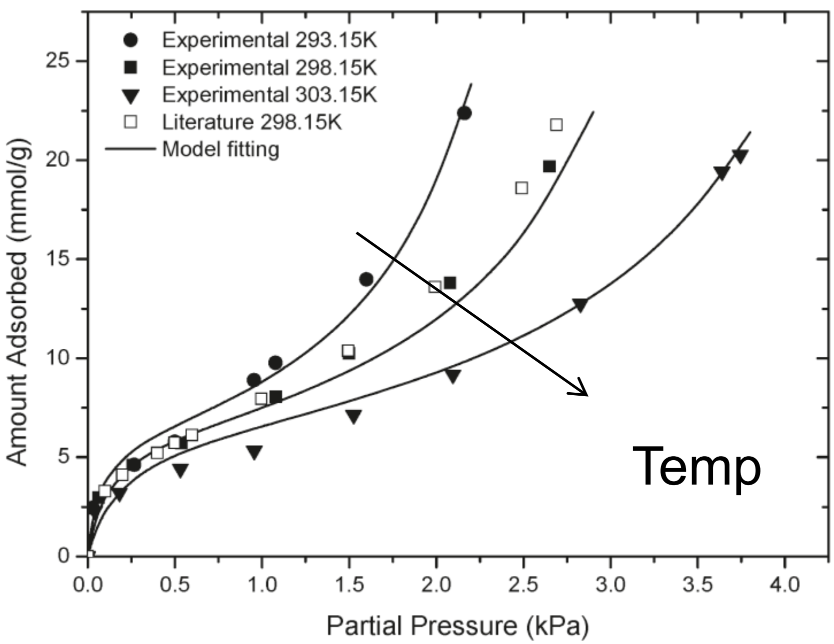
CO_2

water

CO_2 on wet sorbent

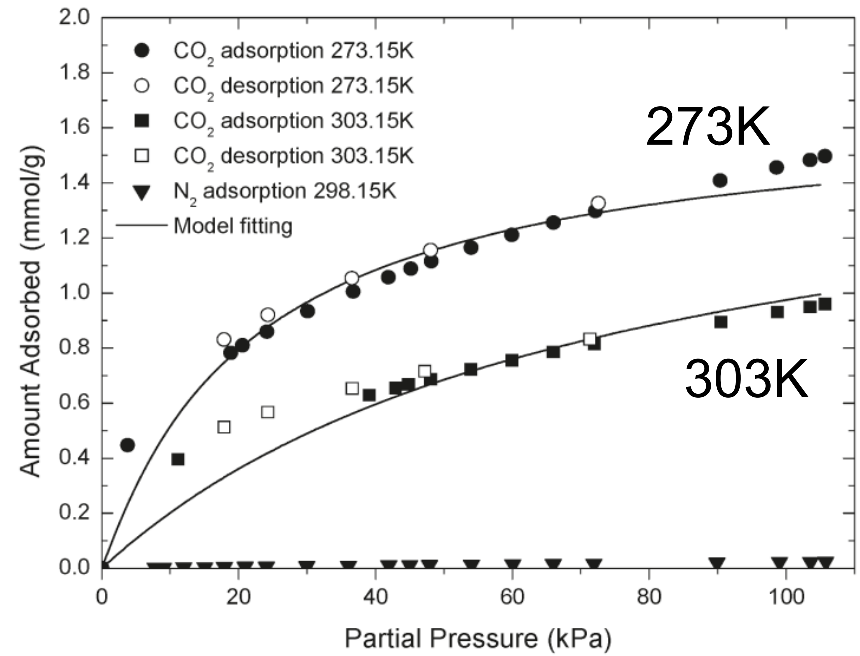
Data from Li et al. on activated silica

Pure water isotherms



Water adsorption described by modified BET model

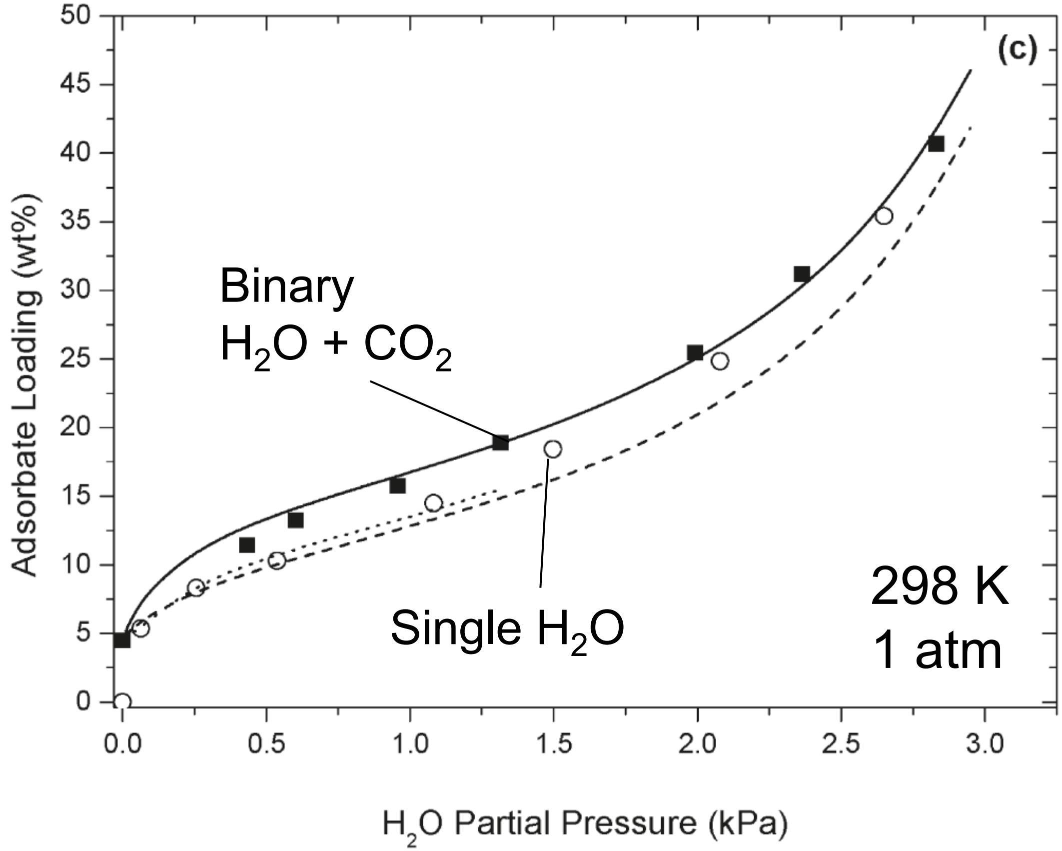
CO_2, N_2 isotherms



CO_2 adsorption described by Langmuir model

Li et al. *Langmuir* 25 (2009) 10666-10675

Data from Li et al. for CO_2/water isotherm



For a good description, it is necessary to fit parameters for the interaction of water and CO_2

Li et al. *Langmuir* 25 (2009) 10666-10675

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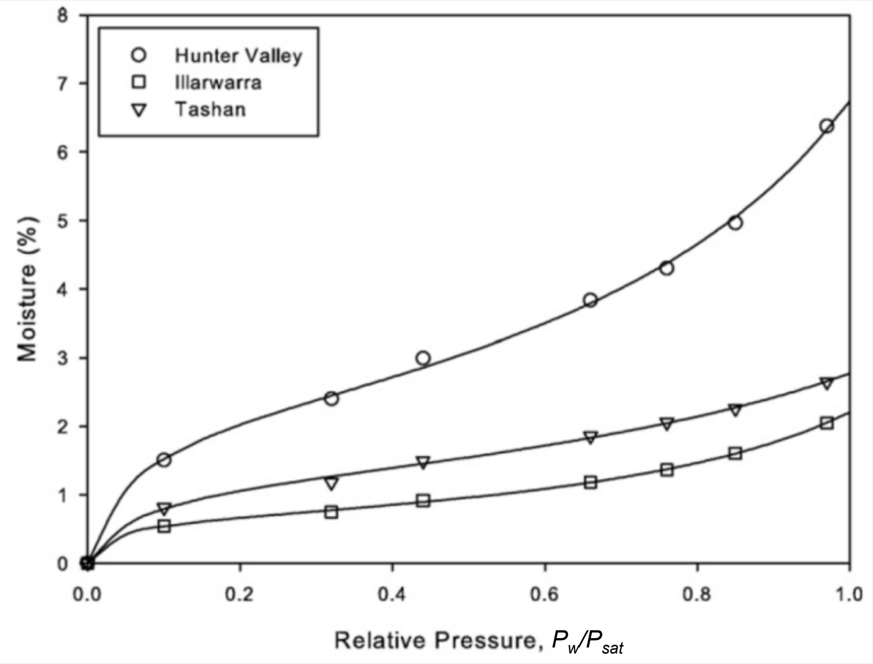
CO_2

water

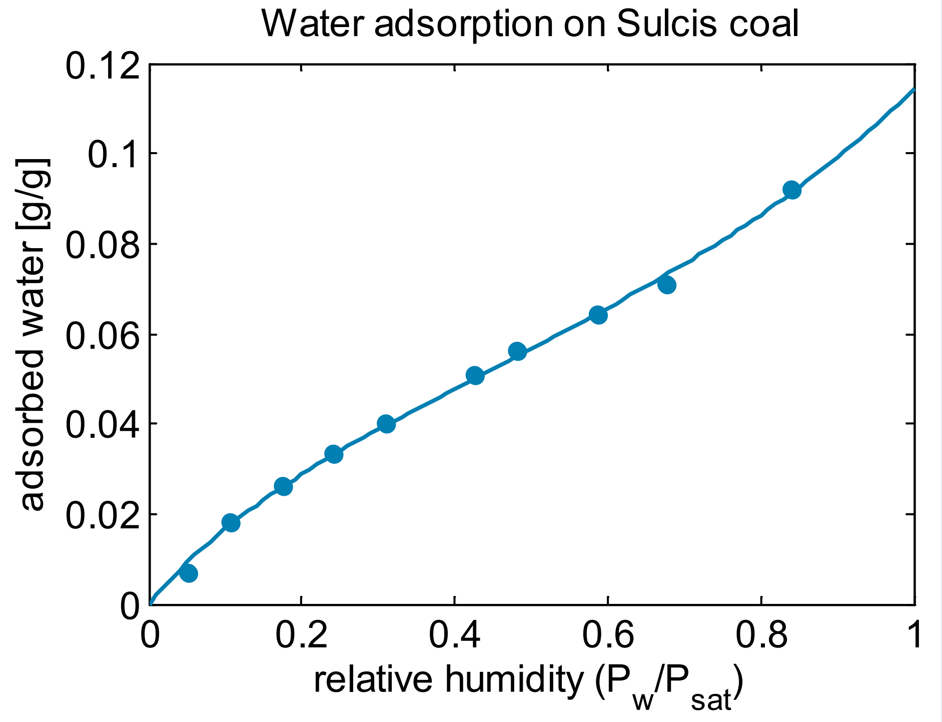
CO_2 on wet sorbent

Work on coal – CSIRO and ETHZ

CSIRO



ETHZ

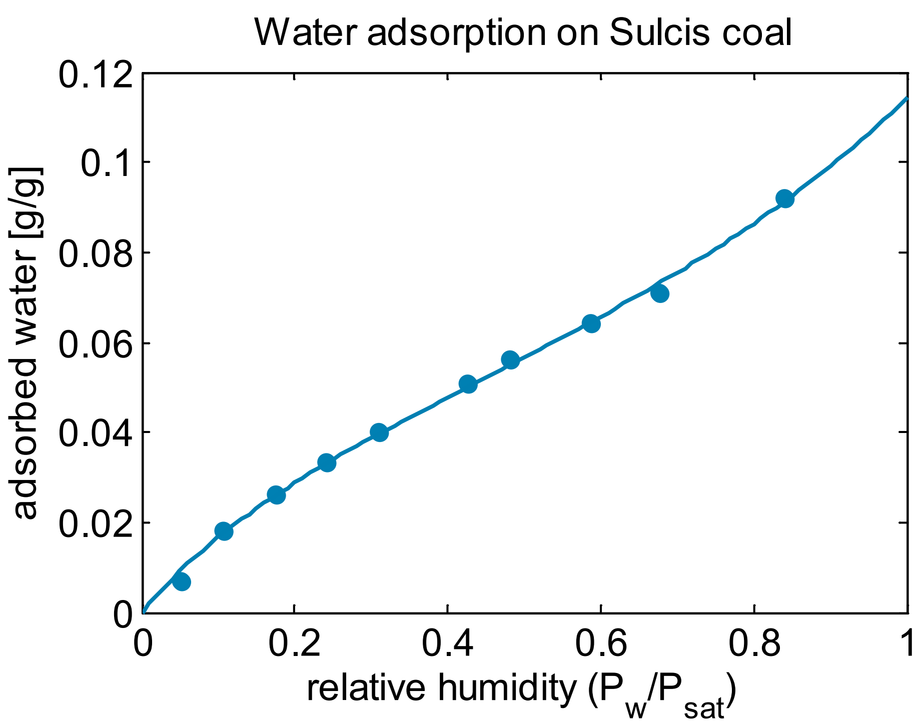


Pure water adsorption data, described by the Guggenheim-Anderson-de Boer model (GAB)

Day et al., Int. J. Coal Geol. 74 (2008) 203-214

Model for adsorption of water on coal

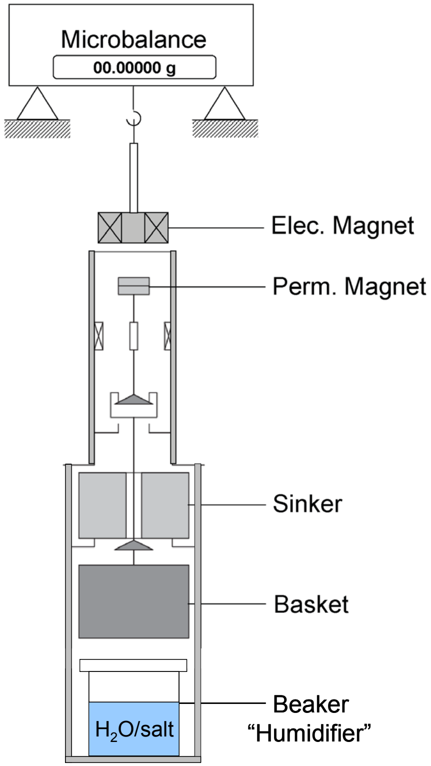
Adsortion of pure water vapor onto coal has been described using the Guggenheim-Anderson-de Boer (GAB) model.



$$W = \frac{W_m C_G \frac{P_w}{P_{sat}}}{\left(1 - K\frac{P_w}{P_{sat}}\right)\left(1 + (C_G - 1)K\frac{P_w}{P_{sat}}\right)}$$

model parameters	
W_m [g/g]	0.032
C_G [-]	6.43
K [-]	0.55

Measurements of sorption on wet coal



MSB slightly modified to ensure constant humidity during the adsorption experiments.

Procedure:

- Saturated salt solutions used to control relative humidity.
- Beaker with saturated salt solution inserted at the bottom of the cell.
- Coal sample let saturate under a constant humidity atmosphere for 2 days.
- Coal sample exposed to the high pressure CO_2.

Interpretation of the results

- Total excess sorption (CO_2 and water) with respect to dry sample

$$\boxed{\begin{aligned} m^{\text{eas}}(\rho^{\text{b}},T) &= M_1(\rho^{\text{b}},T) - M_1^0 + \rho^{\text{b}}(V^{\text{met}} + V_0^{\text{coal}}) \\ &= m^* - \rho^{\text{b}}\Delta V^* \end{aligned}}$$

  - $m^* = m^{\text{a}}_{CO_2} + m_w$ → total sorption
  - ΔV^* → total volume increase due to adsorption

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  - $m^* = m_{\mathrm{CO_2}}^{\mathrm{a}} + m_w$ → total sorption
  - ΔV^* → total volume increase due to adsorption

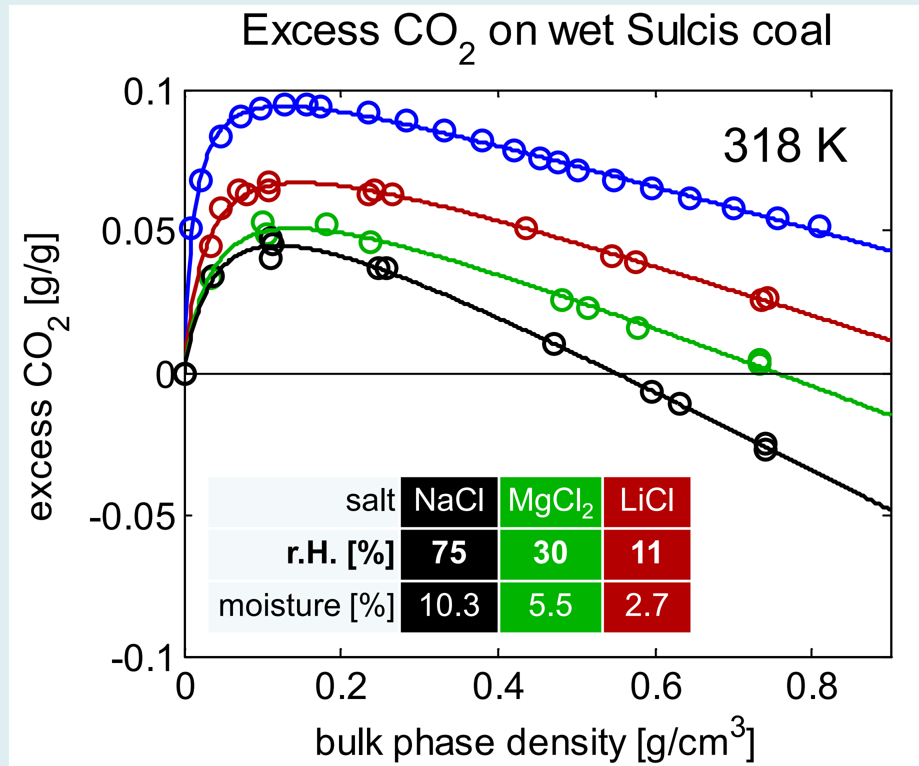
m_w is constant

- CO_2 excess sorption

$$\boxed{\begin{aligned} m_{\mathrm{CO_2}}^{\mathrm{eas}}(\rho^{\mathrm{b}},T) &= M_1(\rho^{\mathrm{b}},T) - (M_1^0 + m_{\mathrm{w}}) + \rho^{\mathrm{b}}(V^{\mathrm{met}} + V_0^{\mathrm{coal}}) \\ &= m_{\mathrm{CO_2}}^{\mathrm{a}} - \rho^{\mathrm{b}}\Delta V^* \end{aligned}}$$

CO_2 adsorption on wet coal

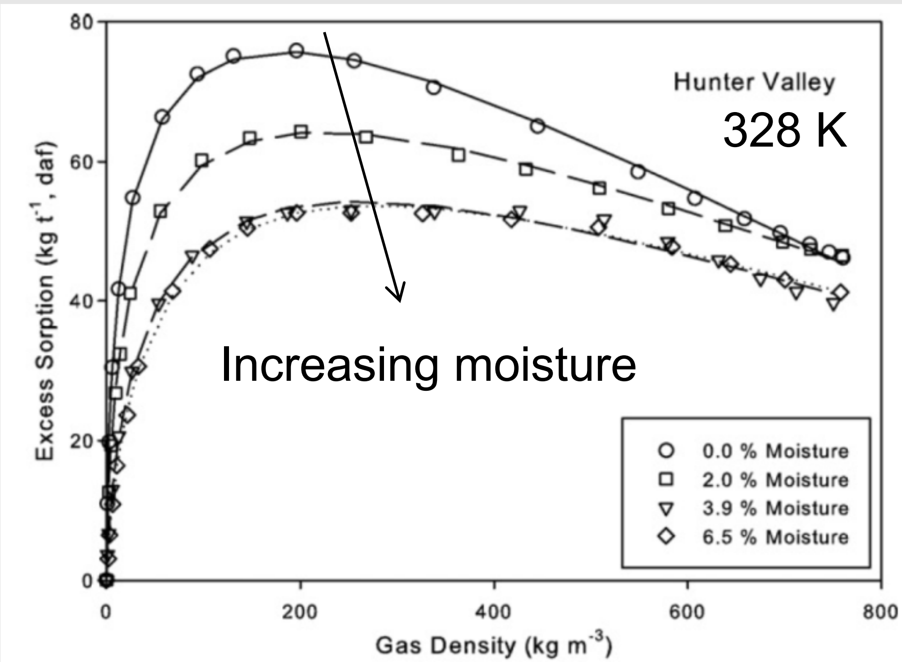
ETHZ



excess calculated with respect to *dry* sample

CO_2 adsorption on wet coal

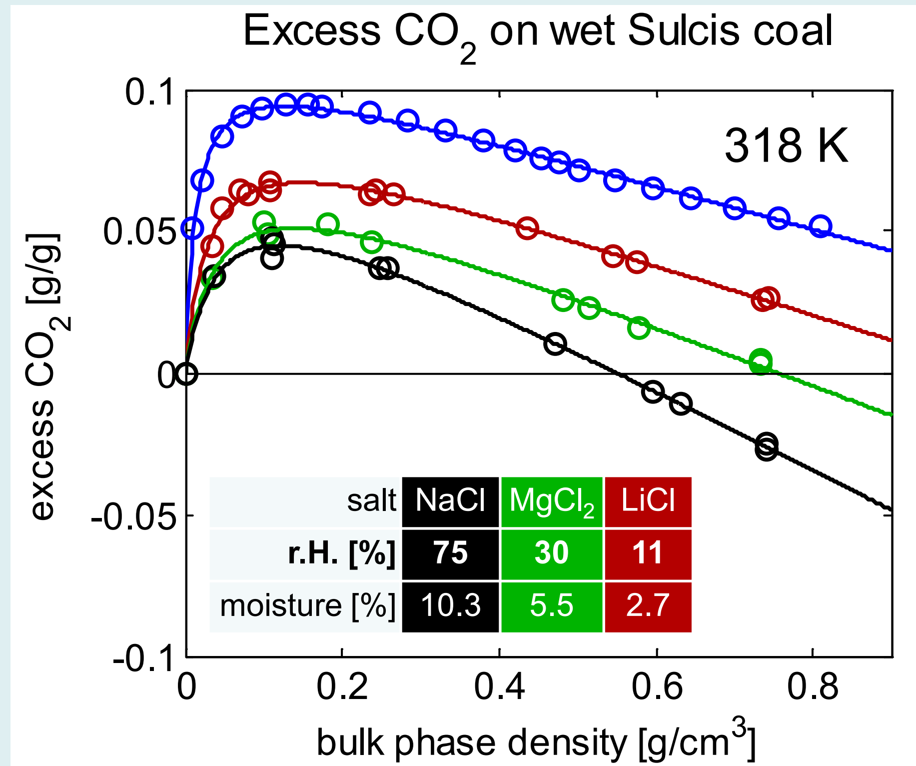
CSIRO



excess calculated with respect to *wet* sample

Day et al., Int. J. Coal Geol. 74 (2008) 203-214

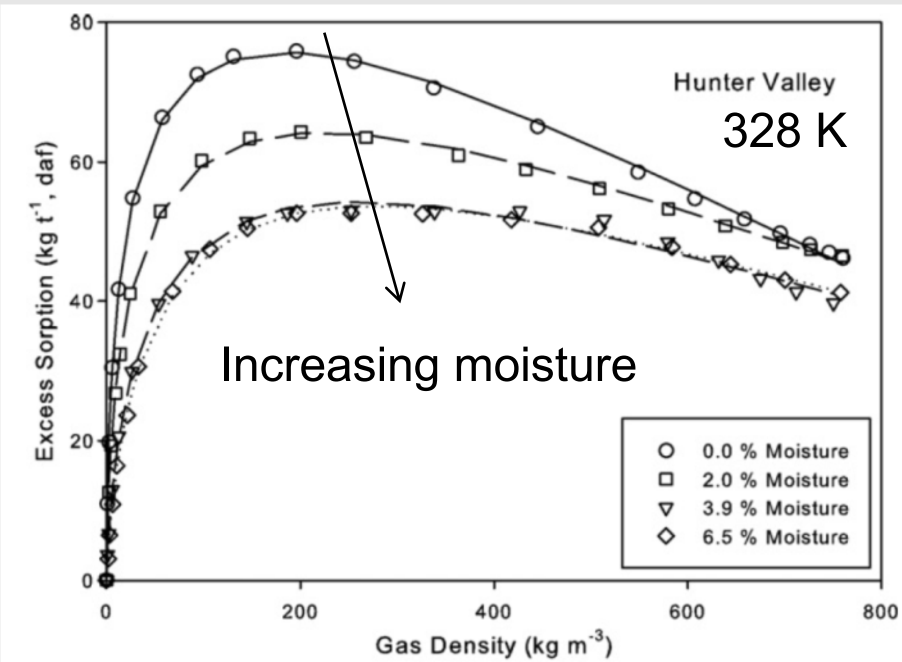
ETHZ



excess calculated with respect to *dry* sample

CO_2 adsorption on wet coal

CSIRO



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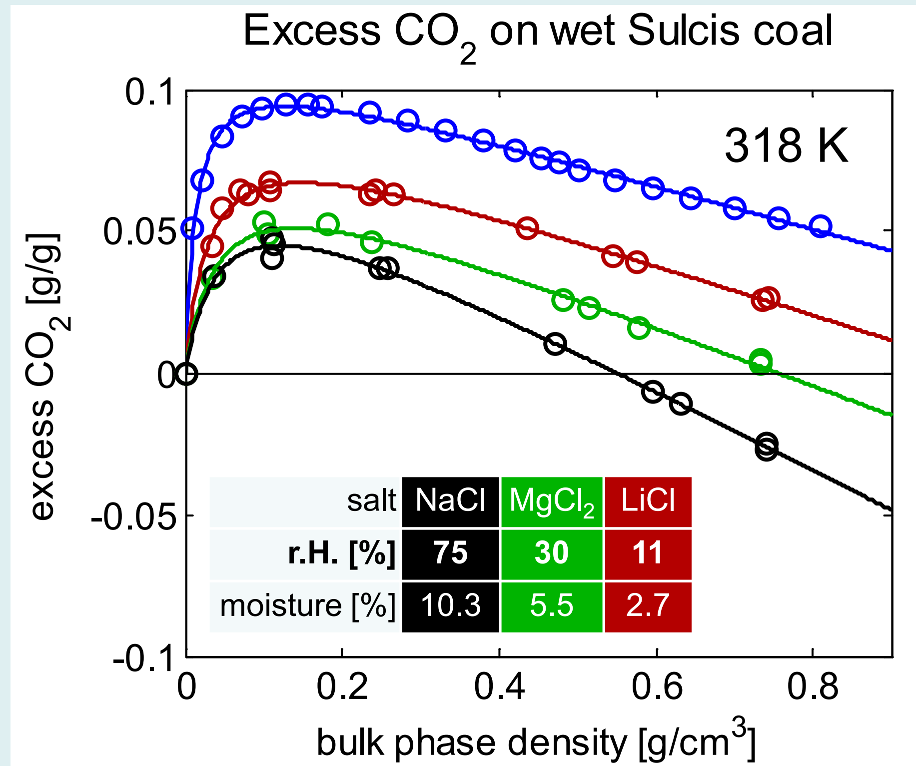
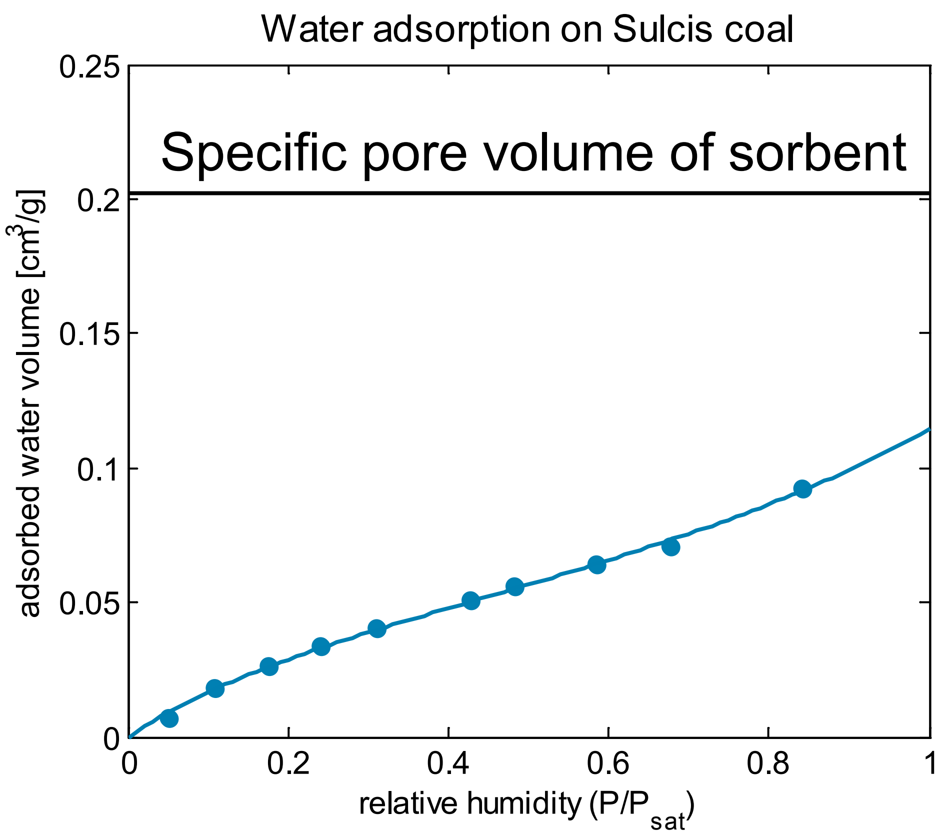


Separate model parameters fit to each moisture level

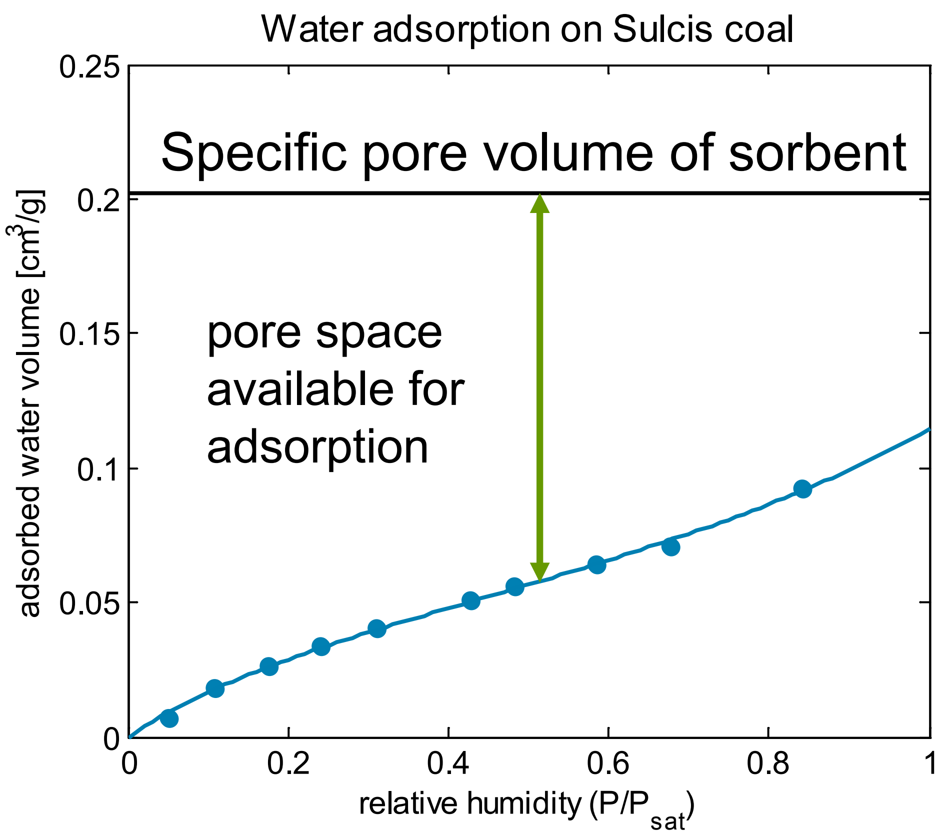
Day et al., Int. J. Coal Geol. 74 (2008) 203-214

Proposed modeling approach



$$V_w = \frac{W_m C_G \dfrac{P_w}{P_{sat}}}{\left(1 - K\dfrac{P_w}{P_{sat}}\right)\left(1 + \left(C_G - 1\right)K\dfrac{P_w}{P_{sat}}\right)\rho_w}$$

Proposed modeling approach



$$n_{CO_2,L} = \frac{N_{CO_2} k \rho_{CO_2}}{1 + k \rho_{CO_2}}$$

$$V_w = \frac{W_m C_G \frac{P_w}{P_{sat}}}{\left(1 - K \frac{P_w}{P_{sat}}\right)\left(1 + \left(C_G - 1\right) K \frac{P_w}{P_{sat}}\right) \rho_w}$$

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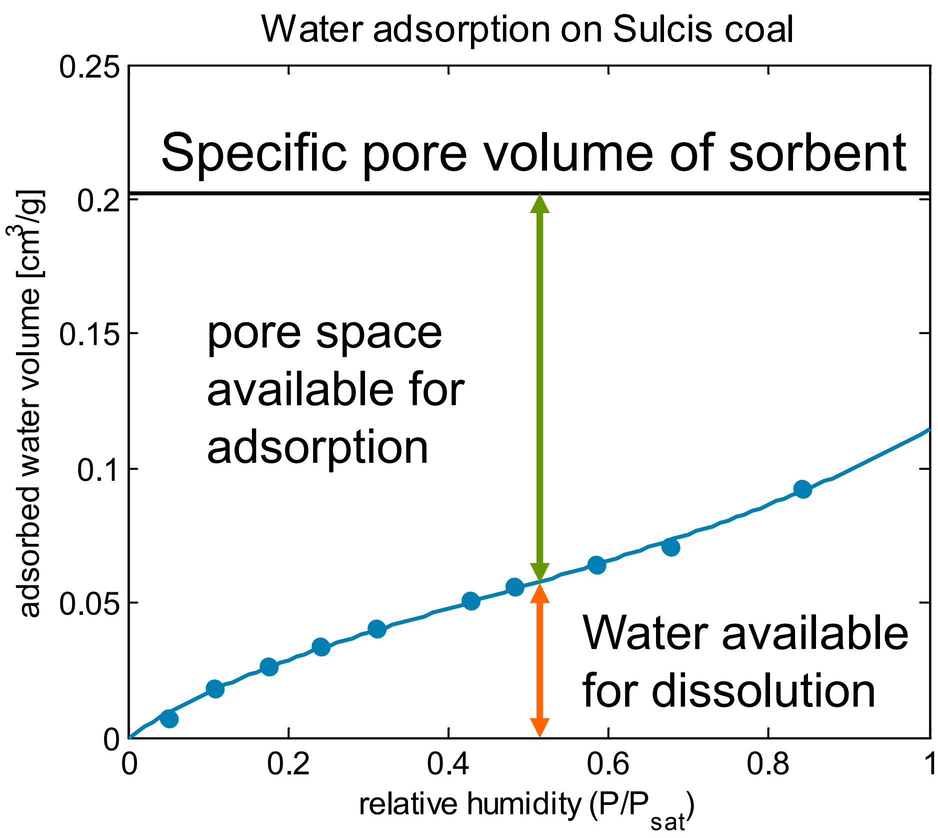

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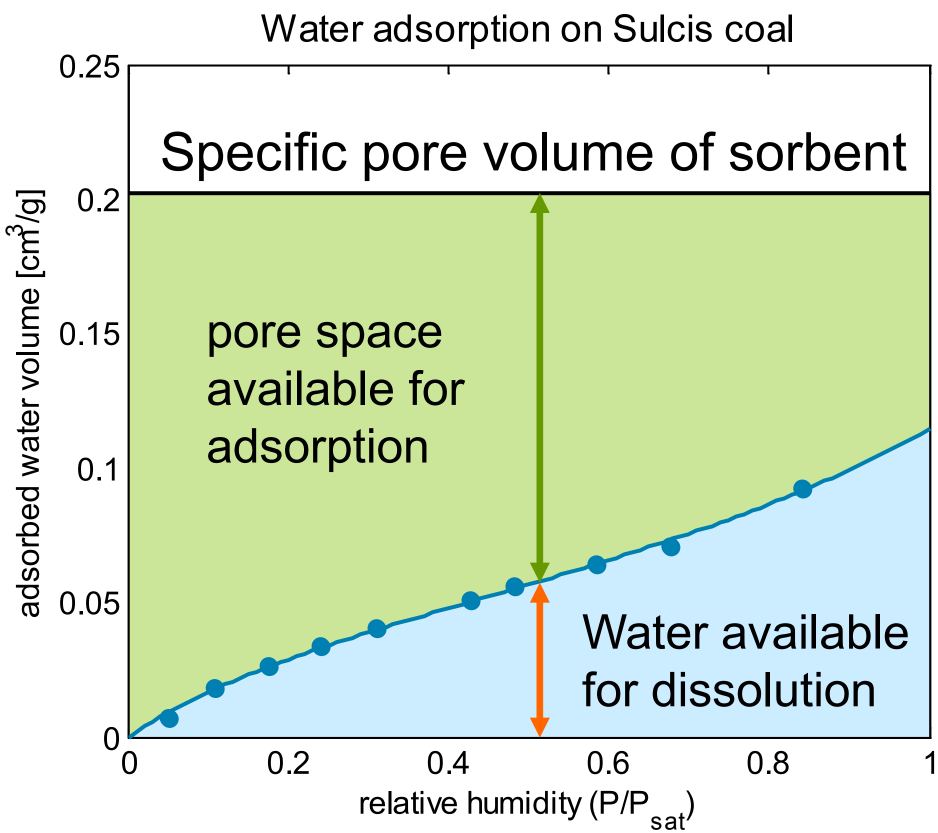
$$C^{diss} = \left[CO_{2(aq)}\right] = k_H(T) f_{CO_2}$$

Proposed modeling approach



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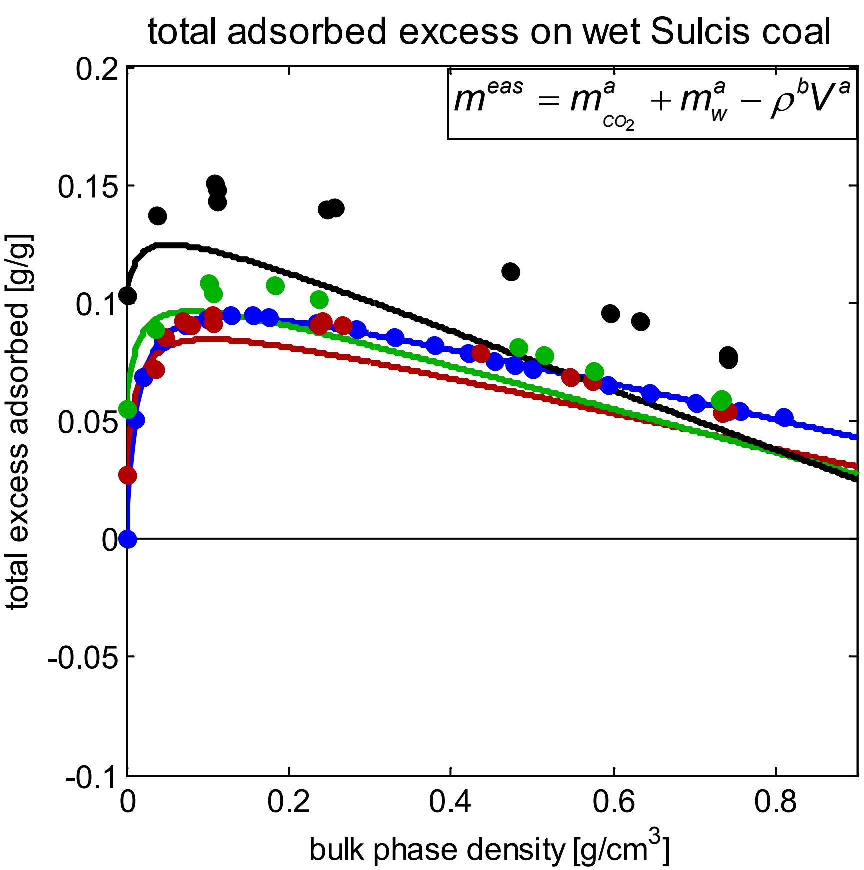
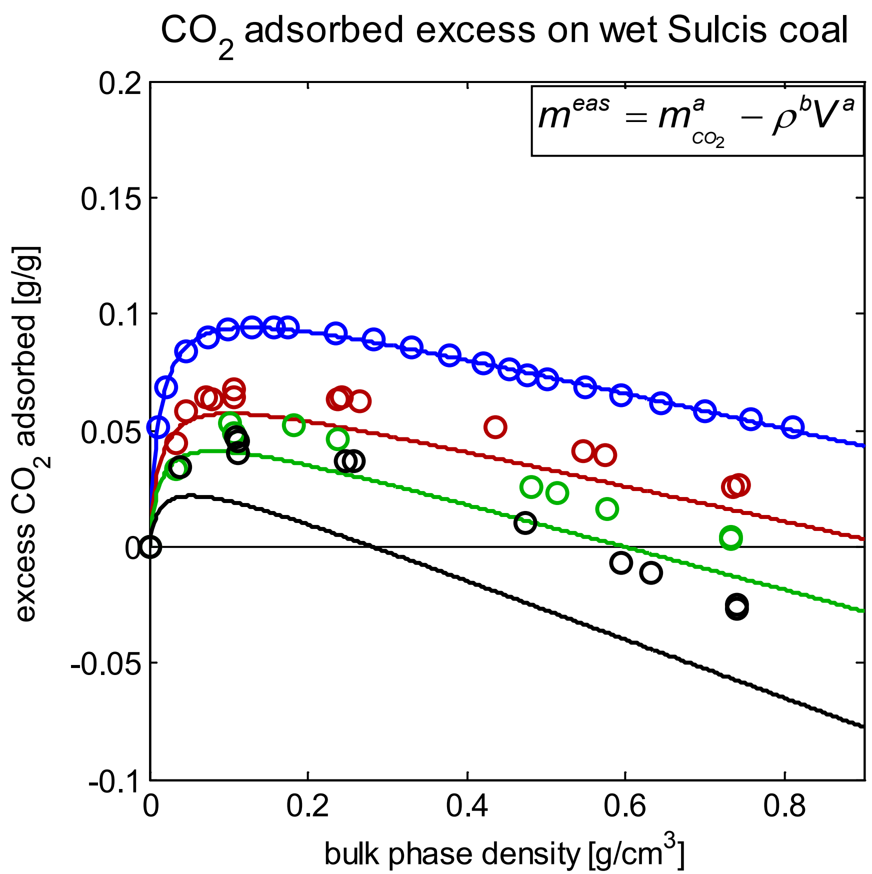
$$C^{diss} = \left[CO_{2(aq)}\right] = k_H(T) f_{CO_2}$$

$$\boxed{n_{CO_2} = V_w C^{diss} + \left(\frac{V_0 - V_w}{V_0}\right) n_{CO_2,L}}$$

Results of the proposed model





Conclusions

- Proposed model delivers encouraging results
  - Extension to other adsorbent materials
- Model is simple enough to have low computational requirements
  - Use in simulation software for separation columns
- Water/gas interactions still need to be better understood
- Assumption of constant water content needs testing
  - Modified experimental procedure
  - Monitoring of gas phase composition