Analysis of Breakthrough Curves – Sorption Equilibria and Kinetics

Andreas Möller
• Introduction

• Sorption Equilibria
  • Theory
  • Basics of dynamic experiments
  • Information from breakthrough curves
  • Planning an experiment
  • Examples
  • Summary Part I – Mixture Equilibria

• Kinetics
  • Influence shape of isotherms and heat effects on kinetics
  • Model for calculation of transport parameter
  • Examples for evaluation of breakthrough curves
  • Application of a well-calibrated model
  • Summary Part II – Kinetics
Application of Porous Materials as Adsorbents

Fine cleaning of gases (i.e. purification of H$_2$, natural gas, bio methane...)

Waste air treatment, respiratory protection, solvent recovery, removal of pollutants...

Gas separation (i.e. Air separation...)

Modern and effective materials should have high sorption capacities, high selectivities, and a good kinetic performance.

For such applications, one must consider gas mixtures and their sorption properties in any case.
Introduction – Characterization of Adsorbents

Synthesis and First Characterization
- Chemists
  - BET
  - Pore Volume
  - Pore Size Distribution

Determination of Thermodynamic Data
- Chemists, Physicists
  - Isotherms
  - Heat of Adsorption

Basic Process Design, Granulation of Adsorbents
- Chemical Engineers
  - Techn. Useable Sorption Capacity
  - Gas Mixtures
  - Selectivities
  - Kinetics
  - Cycle Stability

Detailed Process Design, Application
- Engineers
  - Bench scale, Pilot plants, Industrial Plant
  - Process Optimization
  - Production

Number of Samples
- Application Progress
- Chemists
- Physicists
- Chemical Engineers
- Engineers

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Textural Properties of Adsorbents:

• BET-Surface
• Pore Size Distribution
• Micropore Volume

Textural properties allow only limited qualitative statements regarding:

• expected saturation capacity (i.e. from micropore volume)
• rough assessment of general sorption properties from pore size distribution

Textural properties do not allow quantitative statements regarding:

• sorption affinity
• selectivity
• No information of kinetics
Dependence of partial and total adsorption amounts

General:

\[ n_{CO_2,CH_4,\text{total}} = FKT(Y_{CO_2}, Y_{CH_4}, P) \]

Investigation along:

THE READ LINE – Case A

\[ n_{CO_2,CH_4,\text{total}}(p = \text{const.}) = FKT(Y_{CO_2}, Y_{CH_4}) \]

THE BLUE LINE – Case B

\[ n_{CO_2,CH_4,\text{total}}(Y_{CO_2}, Y_{CH_4} = \text{const.}) = FKT(p) \]
Typical presentation of sorption capacities for binary mixtures

Case A – variable gas composition

\[ X_{CO_2} / \text{-} Y_{CO_2} / \text{-} \]

\[ p=\text{const. (1 bar), } CO_2, CH_4 \text{ on D55-1.5 (calc.)} \]

Case B – variable pressure

\[ \text{adsorbed amount / mmol g}^{-1} \]

\[ Y=\text{const. (50:50), } CO_2, CH_4 \text{ on D55-1.5 (calc.)} \]

\[ \text{X-Y-Plot with statement to the composition of adsorbed phase at constant pressure} \]

\[ \text{N-p-Plot with statement to the adsorbed amount at constant gas phase composition} \]
Typical presentation of sorption capacities for binary mixtures

**Case A – variable gas composition**

- Adsorbed amount / mmol g\(^{-1}\)
- \(Y_{\text{CO}_2} / \text{bar}\)

\[ Y_{\text{CO}_2} \text{ (bar)} \]

<table>
<thead>
<tr>
<th>(Y_{\text{CO}_2})</th>
<th>Total Loading</th>
<th>(\text{CO}_2)</th>
<th>(\text{CH}_4)</th>
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</thead>
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<td>0.0</td>
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\(p=\text{const. (1 bar)}, \text{CO}_2, \text{CH}_4 \text{ on D55-1.5 (calc.)}\)

**Case B – variable pressure**

- Adsorbed amount / mmol g\(^{-1}\)
- Pressure / bar

\[ Y=\text{const. (50:50), CO}_2, \text{CH}_4 \text{ on D55-1.5 (calc.)}\)

- **N-Y-Plot** with statement to the partial loadings at constant pressure
- **N-p-Plot** with statement to the adsorbed amount at constant gas phase composition
Basics – Mixture Equilibria (Theory)

Models for mixture data

Extended langmuir-like equations

- Multi Component-Langmuir (MCLAI)
- Multi Component-Sips (MCSIPS)
- Multi Component-DSLAI (MCDSLAI)

\[ q_i = q_{m,i} \left( \frac{b_i p_i}{1 + \sum b_j p_j} \right)^{x_i} \]

MCSIPS

IAS-Theory

- IAST with Langmuir
- IAST with Toth
- IAST with DSLAI, DSLAISIPS
- IAST with UNILAN

\[ A \cdot \pi = \int_0^{p_i} \frac{n}{p} dp = \text{const.} \]
\[ n = \text{Isotherm}(p_{\text{eq}}) \]

Requirements:
- Knowledge of pure component isotherms

VS-Model

- VS-Model with Wilson

predictive calculations with 3P sim possible
Calculations of mixture data with 3P sim – Recommendations for pure components

1. Fitting of pure component data at **same temperature for all components**

2. All data as table - **pressure / bar** (mbar) and **adsorbed amount / mmol g⁻¹**

3. **All components** must be fitted with **same isotherm model**

![Diagram with various isotherm types](image)

**TYP I:** Langmuir, SIPS, Toth, DSLangmuir, DSLangmuirSIPS, UNILAN

**Typ II:** (Freundlich)

**Typ IV, V:** DSLangmuirSIPS, (DSLangmuir), (SIPS)
Relationship between loading – mole fraction – selectivity

1. Calculation of **mole fractions of adsorbed phase** from partial loading
2. Calculation of **mole fraction of gas phase** from partial pressures
3. Calculation of **selectivity**
4. Check **plausibility with** help of limit for selectivity (for IAST-Calculations)

\[
X_{CO_2} = \frac{n_{CO_2}}{n_{CO_2} + n_{CH_4}} \quad Y_{CO_2} = \frac{p_{CO_2}}{p_{CO_2} + p_{CH_4}}
\]

\[
\alpha_{CO_2,CH_4} = \frac{Y_{CH_4} X_{CO_2}}{Y_{CO_2} X_{CH_4}} \quad \alpha_{CO_2,CH_4}(p \to 0) = \frac{H_{CO_2}}{H_{CH_4}}
\]

**Limit of selectivity** can be used to check the results of IAST-Calculations or other models (only for models with Henry range)

Often **Limit of selectivity** do not reflect the **selectivity** for the real separation process, therefore a **single consideration is not enough**
Basics – Dynamic Gas Sorption a multi-scale Process

**Macroscopic**
- Size of Adsorber
- Shape of Adsorber

**Mesoscopic**
- Nature of the Fixed Bed
- Bed Porosity
- Shape of Particles

**Microscopic**
- Textural Properties
- Surface Characteristics
- Accessibility
Flow through the regenerated sample with a predefined gas mixture

Measurement of data at a specified pressure and gas mixture
Static Volumetric Measurements

- Sorption takes place in enclosed chamber
- Pressure is recorded over time
- Pure gases only

\[ n_{\text{ads},i} = n_{\text{dosed},i} - n_{\text{free},i} \]

\[ n_{\text{dosed},i} = \frac{p_{\text{Dose},i} V_{\text{Dose}}}{RT} \]

\[ n_{\text{free},i} = \frac{p_{\text{Cell},i} (V_{\text{Dose}} + V_{\text{Cell}})}{RT} \]

\[ n_{\text{ads}} = \sum_{i=0}^{i} n_{\text{ads},i} \]

Breakthrough Experiments

- Sorption takes place in open system
- **Gas mixtures only**, constant pressure
- Outlet composition is recorded over time

\[ n_{\text{adsorbed}} = \int \dot{n}_{\text{in}}(t) dt - \int \dot{n}_{\text{out}}(t) dt \]

\[ n_{\text{adsorbed}} = \int \dot{V}_{\text{in}}(t) \frac{y_{\text{in}}(t)}{V_m} dt - \int \dot{V}_{\text{out}}(t) \frac{y_{\text{out}}(t)}{V_m} dt \]
## Basics – Experimental Possibilities of dynamic Method

<table>
<thead>
<tr>
<th>Simple Breakthrough Curves</th>
<th>Multicomponent Adsorption</th>
<th>Isotherms</th>
</tr>
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<td><img src="image" alt="Breakthrough Curves" /></td>
<td><img src="image" alt="Multicomponent Adsorption" /></td>
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</tr>
<tr>
<td>- Breakthrough time</td>
<td>- Competitive adsorption</td>
<td>- Saturation capacity</td>
</tr>
<tr>
<td>- Mass transfer</td>
<td>- Displacement</td>
<td>- Isotherms (single or mixture)</td>
</tr>
<tr>
<td>- Technically usable sorption capacity</td>
<td></td>
<td></td>
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<tr>
<td>- Modelling</td>
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<td>- Regenerability</td>
<td>- Emulation of PSA</td>
<td>- Chromatographic parameters</td>
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<td>- Cycle-Stability</td>
<td>- Down-Scaling</td>
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Basics - Different segments of a Breakthrough Curve

Unsaturated Zone

- Determination of technical usable sorption capacity
- Can be used as benchmark for separation performance of adsorbents

Mass Transfer Zone

- Mass transfer coefficient, axial dispersion, shape of isotherm
- Heat effects, heat dissipation
- The time interval of mass transfer zone has to be minimized

Saturated Zone

- Determination of saturation capacity
- By assuming of thermodynamic controlled system → Measurement of isotherms possible
Basics – Mixture Equilibria

• **binary mixture:**
  CO$_2$/He (non-adsorbable carrier gas)
  → Pure component equilibria
  CO$_2$/CH$_4$ (adsorbable carrier gas)
  → Preloading of sample with pure CH$_4$
  → **Incomplete determination** of the system
    (evaluation mostly simple)
  → Partial loading for CO$_2$ (mixture sorption data)

• **ternary mixture:**
  CO$_2$/CH$_4$/He (non-adsorbable carrier gas)
  Displacement of less adsorbed component
  → Partial desorption, role-up effects
  → **Complete determination** (evaluation complex)
  CO$_2$/CH$_4$/N$_2$ (adsorbable carrier gas)
  → Preloading of sample with pure N2
  → Incomplete ternary mixture data (CO$_2$, CH$_4$)
Basics – Schedule of a Mixed Gas Experiment

➢ Predictive calculation of mixture data desired (Y/N)?
  → Pure component isotherms necessary

➢ Is a complete determination of the system desired?
  → determination of all partial loadings, diluting with Helium-carrier gas (Y/N)

➢ Definition of total flow, concentration, measurement temperature etc.
  → Sample must be under „thermodynamic control“ (always)

➢ Depending on concentration range one should consider:
  → Calibration of suitable analytic technique (always)

➢ Sample preparation and definition of preparation conditions
  → Temperature, carrier gas (always)

➢ Build up of a measurement routine
  → pressurization, Helium or adsorptive 1 (Helium for complete determination)

➢ Evaluation of the experiment
Basics – Schedule of a Mixed Gas Experiment

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- Evaluation of the experiment

Definition of measurement task
Definition of measurement conditions
Selection and calibration of analytics
Measuring and evaluation
Task: Investigation of a binary system

Activated Carbon, CO₂ (25%), CH₄ (75%), complete determination at 5 bar

1. Weighting the sample and sample preparation at 120°C, He-flow 200 ml min⁻¹ (STP)
2. Definition of partial pressures: 1.25 bar CO₂; 3.75 bar CH₄; 5 bar He; Σ10 bar
3. Gas flows: 0.25 l min⁻¹ (STP) CO₂, 0.75 l min⁻¹ (STP) CH₄, 1 l min⁻¹ (STP) He
4. Pressurization with Helium up to 10 bar
5. Start of measurement by simultaneous dosing of CO₂ and CH₄ in Helium
6. Recording of effluent gas composition via MS (all components!)
7. After breakthrough, regeneration of sample for determination of activated mass
Task: Investigation of a binary system

Activated carbon, CO₂ (25%), CH₄ (75%), complete determination at 5 bar

Result of experiment:

Breakthrough curve with “role-up” effect

➢ Includes all partial loadings
➢ Reference on $p_{CO_2}=1.25$ bar and $P_{CH_4}=3.75$ bar
➢ Mole fraction: $y_{CO_2}=0.25$; $y_{CH_4}=0.75$
➢ Helium will not be considered!

Integration of areas:

➢ $n(CO_2)$; $n(CH_4)$; total; $\alpha$
Mixture Equilibria – Examples of a Mixed Gas Experiment

5% CO\(_2\) 15% CH\(_4\) in He at 20°C, 5 bar, 2500 ml min\(^{-1}\) (STP) on D 55/1.5

Dynamic experiment (determination of all partial loadings)

\[ n_{\text{CO}_2} = 0.86 \text{ mmol g}^{-1} \]
\[ n_{\text{CH}_4} = 0.71 \text{ mmol g}^{-1} \]

\[ \alpha_{\text{Experiment}} = 3.63 \]

System is complete determined, all partial loadings were measured (points).

Data can be used to confirm predictive models for mixture sorption (lines).
Mixture Equilibria – Examples of a Mixed Gas Experiment

5% CO$_2$ in N$_2$ at 20°C, 5 bar, 2500 ml min$^{-1}$ (STP) on D 55/1.5

System is incomplete determined.

A thermodynamic model is necessary to get all data!

This simple technique is widely used in practice (i.e. only the separation of a harmful component is of interest)
Sequence of several breakthrough curves on activated carbon D 55-1.5

**Conditions:**
- 20°C, 2 L min$^{-1}$
- 10 bar (pressurization with N$_2$)
- Concentrations: 5% CO$_2$ - 80% CO$_2$ in N$_2$

**Procedure:**
- Start further breakthroughs after equilibrium before
- **Integration** and **summation** results in partial loading data of CO$_2$
- Volume ratio and total pressure defines the partial pressure of CO$_2$
- Mixed isotherm data of CO$_2$ in N$_2$
- Always less adsorbed component as carrier (here: N$_2$)
Mixture Equilibria – Examples of a Mixed Gas Experiment

Measured partial loading data for CO$_2$ on activated carbon D 55-1.5 at 10 bar

- Dynamic measured data (red)
- IAST-Model (Ideal Adsorbed Solution Theory) based on pure component isotherms (lines)
- Mixture of CO$_2$ and N$_2$ shows ideal behavior on AC

A thermodynamic model is necessary to get all data!

Determination of partial loading data of CO$_2$ on AC D 55-1.5 by performing sequentially experiments along constant total pressure.

\[ n_{CO_2,N_2,\text{total}}(p = \text{const.}) = FKT(Y_{CO_2}, Y_{N_2}) \]
• Using Helium as one component and assuming that it is not adsorbed allows measurement of pure component isotherms

• Using other gases than Helium yields in mixture isotherms
Breakthrough Experiments - Comparison

15% Propane 45% Propylene in He at 25°C, 5 bar, 1000 ml/min on AC1, AC2, AC3

Sample: AC1
\[ Y_{\text{Propane}} = 0.25 \]
\[ Y_{\text{Propylene}} = 0.75 \]
\[ n_{\text{Propane}} = 0.03 \text{ mmol g}^{-1} \]
\[ n_{\text{Propylene}} = 0.06 \text{ mmol g}^{-1} \]
\[ \alpha_{\text{Propylene}} = 0.67 \]

Sample: AC2
\[ Y_{\text{Propane}} = 0.25 \]
\[ Y_{\text{Propylene}} = 0.75 \]
\[ n_{\text{Propane}} = 0.2 \text{ mmol g}^{-1} \]
\[ n_{\text{Propylene}} = 1.7 \text{ mmol g}^{-1} \]
\[ \alpha_{\text{Propylene}} = 2.83 \]

Sample: AC3
\[ Y_{\text{Propane}} = 0.25 \]
\[ Y_{\text{Propylene}} = 0.75 \]
\[ n_{\text{Propane}} = \text{ca. 0 mmol g}^{-1} \]
\[ n_{\text{Propylene}} = 2.1 \text{ mmol g}^{-1} \]
\[ \alpha_{\text{Propylene}} = \text{not determined (>20)} \]

Selectivity

Statements on selectivity also possible without thermodynamic models
Determination of sorption capacities and selectivities, recording of kinetic
Summary Part I - Mixture Equilibria

- With **breakthrough experiments mixture sorption data** with He also pure component are **accessible**.
- By assumption of a non-adsorbable carrier (i.e. He) a complete determination of mixture system is possible (adsorptive 1+adsorptive 2+He).
  - Investigation of **role up effects**
  - Determination of **all partial loadings** and calculation of thermodynamic **selectivity α**

For the **investigation of role up effects and α → selective analytical devices necessary (Mass Spec)**

- Simple breakthrough data can also contain mixture equilibria (i.e. for carrier gas as second adsorptive)
  - **No role up effect** can be observed, thermodynamic model necessary for whole description
  - **No** experimental determination of **selectivity α** possible
  - Carrier gas should be the less adsorbed component

**Unselective analytical devices are enough for binary systems (i.e. TCD)**
Kinetics from Breakthrough Experiments

Breakthrough curves of 5% CO₂ in N₂ on zeolites 13X, 5A, 3A (1 bar, 5 l/min (STP), 20°C)

Qualitative observation of Mass Transfer Zone:
- Zeolite 3A have a spontaneous breakthrough due too narrow pores (kinetic-steric exclusion)
- Zeolite 5A exhibits a broad mass transfer zone
  → indicates lower kinetic for 5A as 13X
- Both zeolites, 5A and 13X have quite unsymmetrical breakthrough curves
  → indicate a big influence of temperature effects and shape of isotherms
Question:

• Is it possible to get reliable kinetic data from such experiments?
• How is the influence of the isotherm shape and temperature effects?

Answer:

• Yes, but associated with high effort (model of mass- and energy balances is necessary)
  → Simple comparison of slope can be erroneous
• For quantification of temperature effects also a model must be used!
  → I.e. in some cases heat effects can be control nearly the whole curve
Parametric study - Influence of isotherm shape (favored isotherm)

Calculation of breakthrough with same $k_{LDF}$ value and different isotherm shapes

- Slope of breakthrough curves strongly depends on isotherm shape!
  - simple comparison of slope at $C/C_0=0.5$ only for materials with similar or same isotherm shapes
  - Shape of isotherms cannot be neglect, view on desorption curves can be helpful
Parametric study - Influence of non-isothermal effects

Increasing of heat effects

Flattening with stronger heat effects

5% CO$_2$ on NaMSXK (zeolite 13X)

Calculation of breakthrough with same $k_{LDF}$ value and different heat transfer coefficients

- Slope of breakthrough curves strongly depends on non-isothermal effects!
  - simple evaluation of slope at $C/C_0=0.5$ leads to wrong interpretation
  - Temperature profiles can’t be ignored, lower concentrations and desorption can be helpful
Kinetics from Breakthrough Experiments

### Input Parameters

- **Isotherms**
- **Kinetics (start values)**
- **Heat of adsorption and heat capacities**
- **Co-adsorption**
- **Adsorber dimensions**
- **Heat transfer**
- **Feed flow, Feed pressure**
- **Product purity**
- **Kinetics, cycle duration, pressure range...**

**Red:** properties of adsorbent/adsorptive system

**Black:** properties of adsorber and adsorber wall

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Kinetic considerations - Mass Transfer coefficient $k_{\text{LDF}}$
Example breakthrough calculation with isothermal SIPS model

- No knowledge of script language
- Simple input form for parameter
- Overview of used isotherm model
- No knowledge of solver necessary
- Usage of own $\Delta z$, $\Delta t$ values possible
- Output of stoichiometric values
- Comparison of calculations with Experiment
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Example breakthrough calculation with isothermal SIPS model

- No knowledge of script language
- Simple input form for parameter
- Overview of used isotherm model
- No knowledge of solver necessary
- Usage of own \( D_z, D_t \) values possible
- Output of stoichiometric values
- **Comparison of calculations with Experiment**
Example breakthrough calculation with **nonisothermal** SIPS model

**Observation**

- $k_{LDF}$ value (isothermal model) $\rightarrow \sim 4\,\text{min}^{-1}$
- $k_{LDF}$ value (nonisothermal model) $\rightarrow \sim 13\,\text{min}^{-1}$
- approx. 3 times higher $\rightarrow$ Heat effect should not be neglected
Kinetics from Breakthrough Experiments (one Adsorptive)

Determination of LDF-constant

Input Isotherms

- CO₂ at 20°C
- CO₂ at 40°C
- CO₂ at 60°C
- SIPS

CO₂ isotherms on D 55/1.5

Input Heat Transfer

- Bed/Wall ~ 50 W m⁻² K⁻¹
- Wall/Liquid ~ 400 W m⁻² K⁻¹

5% CO₂ in He at 40°C, 5 bar, 1000 ml/min on D 55/1.5

Finding of Mass Transfer Coefficient $k_{LDF}$:

- Start value for $k_{LDF}$ 1 min⁻¹
- Best fit with $k_{LDF}$ 13 min⁻¹

Iterative recalculation!
Kinetics from Breakthrough Experiments (two Adsorptives)

**CO₂ isotherms on D 55/1.5**

- Input pure component isotherms
- Determination of \( k_{\text{LDF}} \) only for CO₂

**N₂ isotherms on D 55/1.5**

- Adsorption and desorption of \( \text{CO}_2 \) in \( \text{N}_2 \)

- 5% \( \text{CO}_2 \) 95% \( \text{N}_2 \) at 40°C, 5 bar, 2 L/min on D 55/1.5
Kinetics from complex Breakthrough Experiments (two Adsorptives)

Input pure component Isotherms

Determination of $k_{LDF}$ for CH$_4$ and CO$_2$

Fitting $k_{LDF}$

Heat Transfer Coeff.

Breakthrough of a mixture CO$_2$/CH$_4$ in He

5% CO$_2$ 15% CH$_4$ in He 20°C, 2500 ml/min, 5 bar on D 55/1.5
Kinetics from Breakthrough Experiments

High effort to calculate breakthrough due to shape of isotherm, good isotherm model fit necessary!

- Isotherm fit with an empiric dual-site Langmuir-SIPS equation
- Heat of adsorption 60 kJ mol\(^{-1}\) assumed
- Heat for condensation 40.8 kJ mol\(^{-1}\) (at 100°C)

\[ \Rightarrow k_{LDF} = 1.2 \text{ min}^{-1} \]

\( \text{H}_2\text{O} \) isotherm on D 55/1.5 at 25°C

2.5% \( \text{H}_2\text{O} \) in \( \text{N}_2 \) at 25°C (RH 80%), 1 bar, 4000 ml min\(^{-1}\) on D 55/1.5

- Description of the curve is possible
- Isothermal calculation failed for this example
- Stronger deviations for condensation part
Kinetics from Breakthrough Experiments – how to use?

Parameter from experiment:

- Adsorption time 5.78 min
- Adsorption pressure 5 bar
- Feed flow 2000 ml min\(^{-1}\)
- Purge flow 2000 ml min\(^{-1}\) pure \(N_2\)

General requirements for PSA:

- Purge flow 500 ml min\(^{-1}\) pure \(N_2\)
- Desorption in counter current flow
- Max. \(CO_2\) content in product 1%

Question concerning:

1) Desorption pressure in Pressure Swing Processes (PSA)?

Known model parameter after fitting

- Isotherms (MCSIPS)
- Kinetic parameter \((k_{LDF})\)
- Heat transfer parameter

→ Model can consider slower desorption due to curved isotherm
Kinetics from Breakthrough Experiments – how to use?

Cycle times for modeling:

- Adsorption time 5.78 min
- Desorption time 5.03 min
- Calculating 5 cycles

Cycle times for experiment:

- Adsorption time 5.78 min @ 5 bar
- Blow down time ~ 0.25 min
- Desorption time 4.75 min
- Pressurization to 4.6 bar with N₂
- Pressurization from 4.6 bar to 5 bar with feed
- Measurement of 5 cycles

Calculations with $p_{\text{DES}} = 1$ bar

Predictions by modeling:

Regeneration conditions not strong enough

$\rightarrow \text{CO}_2$ impurity in effluent flow increases from cycle to cycle to ~ 3 %
Kinetics from Breakthrough Experiments – how to use?

Cycle times for modeling:
- Adsorption time 5.78 min
- Desorption time 5.03 min
- Calculating 5 cycles

Cycle times for experiment:
- Adsorption time 5.78 min @ 5 bar
- Blow down time ~ 0.25 min
- Desorption time 4.75 min
- Pressurization to 4.6 bar with N₂
- Pressurization from 4.6 bar to 5 bar with feed
- Measurement of 5 cycles

Calculations with $p_{\text{DES}} = 1$ bar

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Calculations with $p_{\text{DES}} = 0.5$ bar

Predictions by modeling:

Regeneration conditions good enough

$\rightarrow$ CO₂ impurity in effluent flow increases from cycle to cycle, but still below target (<1%)
Kinetics from Breakthrough Experiments – how to use?

**Cycle times for modeling:**
- Adsorption time 5.78 min
- Desorption time 5.03 min
- Calculating 5 cycles

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Modeling differs from experiment!

- Cycle steps in modeling strongly simplified
- Variations experiment from model mainly in desorption part

→ Modeling can help to reduce experimental effort
→ final evaluation only by experiment!
Summary Part II - Kinetics

- Comparison of breakthrough slope only qualitative → can lead to wrong interpretation
- Strong nonisothermal effects must be considered for evaluation of kinetics → influence of dissipation of heat
- Measurement of desorption part is helpful → influence of isotherm, heat dissipation etc.
- Model is necessary to get reliable transport parameter → $k_{\text{LDF}}$ value
- $k_{\text{LDF}}$ values depend on concentration, total pressure etc. → measurements under same conditions like technical process

- With well-known model parameter set predictive calculations possible
  - Results: technical useable sorption capacity, optimization of regeneration, cycle times etc.
    → reducing experimental effort in bench scale
    → helpful for upscaling
- But: Validation by some experiments necessary
Thank you for your attention!

Please visit our website for further information

www.dynamicsorption.com