Mapping the Limitations of Breakthrough Analysis in Fixed-Bed Adsorption

James Clinton Knox
NASA Marshall Space Flight Center, Huntsville, AL, USA
Gas separation processes using fixed beds of adsorbents are important in many existing and emerging industries.

Adsorbent processes are typically cyclic, with adsorption and desorption steps that swing between high and low pressures, temperatures, or concentrations (PSA, TSA, CSA).

Computer simulations are typically used to select hardware and process parameters (adsorbent type, layer sizes, pressure and temperature set points, cycle time, flow rate, etc.).

A cyclic steady-state condition is only reached after many cycles.

Simulation execution speed is critical due to the large trade space and extensive number of cycles required for a single data point.
Skarstrom Patent

- Pressure swing adsorption process
- Air drying using silica gel beds
- Cyclic steady state only achieved after 6 days of operation
Introduction: Area of Concern

- Execution speed requirements dictate use of simplified one-dimensional model for cyclic process simulations.
- 1-D axially dispersed plug flow equation predominantly used in process simulations based on current literature.
- Simplifying assumptions include two lumped mass transfer terms requiring empirical determination.
- Mass transfer term determination is generally via breakthrough analysis in sub-scale fixed-beds with a low tube diameter to particle diameter ratio.

\[
\frac{\partial c}{\partial t} + \left(1 - \frac{\varepsilon}{\varepsilon} \right) \frac{\partial \bar{q}}{\partial t} - D_L \frac{\partial^2 c}{\partial x^2} = - \frac{\partial \bar{u}_i c}{\partial x}
\]

\[
\frac{\partial \bar{q}}{\partial t} = k_n(q^* - \bar{q})
\]
Introduction: Research Findings (1)

❖ Standard breakthrough analysis is based on measurement taken after mixing of two flow regimes: in the bed core, and channeled flow along the walls

❖ Resultant inaccuracies in mass transfer term cause errors during simulation-based design of full-scale separation process

❖ An improved approach was developed to use a centerline measurement in addition to the mixed measurement and determine terms individually

Introduction: Research Findings (2)

❖ Axial dispersion term derived based on Fickian (molecular) diffusion, but is used to model dispersion arising from flow around pellets and wall effects

❖ For strongly adsorbed species, interaction of a large dispersion term with the ill-posed Danckwerts boundary condition causes hidden nonphysical simulation result

❖ To prevent nonphysical behavior, limiting expressions for the mass transfer terms were derived for specific sorbent/sorbate pairs and inlet conditions

❖ A generalized expression was derived to limit the mass transfer terms for any sorbent/sorbate pair based on the strength of adsorption

Principle Equations in 1-D Model

\[
\frac{\partial c}{\partial t} + \left( 1 - \frac{\varepsilon}{\varepsilon} \right) \frac{\partial q}{\partial t} - D_L \frac{\partial^2 c}{\partial x^2} = -\frac{\partial u_c}{\partial x} \\
\frac{\partial q}{\partial t} = k_n (q^* - q) \\
\varepsilon a_f \rho_f c_{pf} \frac{\partial T_f}{\partial t} = -\varepsilon a_f \rho_f c_{pf} \frac{\partial^2 T_f}{\partial x^2} = a_f a_s h_s (T_s - T_f) + P h_i (T_w - T_f) \\
(1 - \varepsilon) \rho_c c_{pc} \frac{\partial T_c}{\partial t} = a_s h_s (T_f - T_s) - (1 - \varepsilon) a_f \lambda \frac{\partial q}{\partial t} \\
\varepsilon_s \rho_w c_{pw} \frac{\partial T_w}{\partial t} = a_w k_w \frac{\partial^2 T_w}{\partial x^2} = P h_i (T_f - T_w) + P h_i (T_s - T_w) \\
n = \frac{ap}{[1 + (bp)]}, \quad b = b_0 \exp(E/T); \quad a = a_0 \exp(E/T); \quad t = t_0 + c/T \\
\frac{1}{Pe} = \frac{20 \left( \frac{D}{2\nu r_f} \right)}{\varepsilon} + \frac{1}{2} = \frac{20}{Re Sc} + \frac{1}{2} \\
\frac{1}{Pe} = \frac{0.73 \varepsilon}{Re Sc} + \frac{1}{2 \left( 1 + 13 \cdot 0.73 \varepsilon \right) \frac{Re Sc}{Re Sc}} \quad 0.0377 < 2 R_p < 0.607 \text{ cm} \\
h_i = \frac{k_f}{2 R_i} Nu \quad \text{with} \quad Nu = 2.03 Re^{0.8} \exp \left( -6 \frac{R_c}{R_i} \right) \\
c_p = a_a + a_f T_f + a_2 T_f^2 + a_3 T_f^3 \\
Sh = 2 + 1.1 Sc^{0.5} Re^{0.6} \quad h_s = \frac{Sh D}{2 R_p} \\
k_c = k_f \left( \frac{k_s}{k_f} \right)^n \quad \text{with} \quad n = 0.280 - 0.757 \log_{10} \varepsilon - 0.057 \log_{10} \left( \frac{k_s}{k_f} \right) \\
k_{ef} = k_f \left( \frac{k_c}{k_f} + 0.75 Pr Re \right) \quad \text{where} \quad Pr = \frac{c_p \mu}{\rho_f k_f} \\
\text{All variables in Mass and Heat Balance Equations are determined except } D_L, k_n, \text{ and } h_o
Experimental Results

(a) Breakthrough test apparatus and (b) cross-sectional view of a typical temperature measurement and gas sampling location. “T” indicates thermocouple probe location, and “S” indicates sampling tube location. Shading in (a) indicates location of sorbent packing.


Left panels: Experimental gas-phase concentration profile history breakthrough curves for CO2 (top) and H2O vapor (bottom) on zeolite 5A at 3 centerline locations in the bed (circles: 2.5%, squares: 50%, and diamonds: 97.5%) and just outside the bed (triangles). Right panels: Corresponding experimental temperature profile histories for CO2 (top) and H2O vapor (bottom) on zeolite 5A at 3 centerline locations in the bed (circles: 2%, squares: 50%, and diamonds: 98%). Error bars show experimental uncertainty.

Step 1: Wall to Ambient Heat Transfer Coefficient

$h_0$ is empirically derived via a Thermal Characterization Test
Step 2: Linear Driving Force Mass Transfer Coefficient

Fits of the 1-D axial dispersed plug flow model to the 97.5% location (diamonds) experimental centerline gas-phase concentration breakthrough curves for CO\textsubscript{2} (left) and H\textsubscript{2}O vapor (right) on zeolite 5A, and corresponding predictions from the model of the 2.5% (circles) and 50% (squares) locations. The saturation term in the CO\textsubscript{2}-zeolite 5A isotherm was increased by 15%. The saturation term in the H\textsubscript{2}O vapor-zeolite 5A isotherm was decreased by 3%. The void fraction was reduced to 0.33 based on the Cheng distribution (Cheng \textit{et al.}, 1991) with C = 1.4 and N = 5, as recommended by Nield and Bejan (1992)

\(k_{nh}\) is empirically derived via fitting to centerline concentration breakthrough curve. For this step, dispersion is taken to result from pellet effects only (no wall effects). Choice of dispersion correlation has a small impact on \(k_{nh}\)
**Step 3: Axial Dispersion Coefficient (CO$_2$ Case)**

$D_L$ term is fit to mixed gas concentration (far downstream), but requires value 7 times the correlation value to compensate for wall channeling. Fit is specific to the size of the column; for a much larger column wall channeling may be neglected and correlated values of $D_L$ used (but not for fixed beds with a tube to pellet ratio of 20 as in this case, or less).

CO$_2$ on zeolite 5A: Fit of the 1-D axial dispersed plug flow model to the outside bed (triangles) experimental breakthrough curve using a value of $D_L$ 7 times greater than that from the Wakao and Funazkri correlation and the fitted LDF $k_s = 0.0023$ s$^{-1}$ (left panel). The reported saturation term for the CO$_2$-zeolite 5A isotherm was used, along with the reported void fraction of 0.35. Predictions from the model (lines) of the gas-phase concentration breakthrough curves at 0, 4, 8, 12, ..., 92, 96 and 100% locations in the bed are also shown in the left panel, along with the 2.5% (circles), 50% (squares) and 97.5% location (diamonds) experimental center line gas-phase concentration breakthrough curves (left panel). The corresponding derivative (or slope) of the predicted gas-phase concentration breakthrough curves in the bed are shown in the middle panel. Predictions from the model (lines) of the 2.5% (circles), 50% (squares) and 97.5% location (diamonds) experimental center line temperature profile histories are shown in the right panel.
**Step 3: Axial Dispersion Coefficient (H₂O Case)**

The $D_L$ term is fit to mixed gas concentration (far downstream), but requires value 50(!) times the correlation value to compensate for wall channeling. However, the temperature profiles deviate increasingly from the test data with increasing $D_L$, indicating a breakdown of the axial dispersed plug flow model.
Step 3: Axial Dispersion Coefficient (H₂O Case)

H₂O vapor on zeolite 5A: Predictions from the model (lines) shown in Figure 9 of the gas-phase concentration breakthrough curves at 0, 4, 8, 12, ..., 92, 96 and 100% locations in the bed (left panels). The 2.5% (circles), 50% (squares) and 97.5% location (diamonds) experimental centerline gas-phase concentration breakthrough curves are also shown for comparison in the left panels. The corresponding derivatives (or slopes) of the gas-phase concentration breakthrough curves in the bed are shown in the right panels. (a) $D_L = \text{Wakao-Funazkri correlation}$, and (b) $D_L = 7$, (c) 30 and (d) 50 times greater than Wakao and Funazkri correlation.

At 7X, internal concentration history slope matches mixed concentration just as for CO₂ case. This indicates that same dispersive mechanism occurs regardless of sorbate. To overcome non-physical breakthrough sharpening, $D_L$ must be increased by 50X to decrease breakthrough slope. Expected CPB is lost entirely for this condition.
Breakthrough tests with tube diameter to pellet diameter ratios of around 20 (or less), are subject to wall channeling, a mechanism not captured in standard dispersive correlations. Breakthrough tests are generally sub-scale to conserve sorbent materials and gas flow equipment costs and thus frequently in this range.

The typical breakthrough measurement is taken far downstream, after mixing. Fitting the mass transfer coefficient to this measurement will provide erroneous results for a larger (or smaller) diameter column due to the influence of channeling.

A method has been demonstrated where a centerline measurement is used to derive a mass transfer coefficient that captures physics free of wall effects and thus appropriate for scale-up to large diameter columns.

Using the mass transfer coefficient derived above, this method uses the mixed concentration data for fitting of a dispersion coefficient $D_L$ specific to the tube diameter, as needed for processes that utilize small diameter tubes.

However fitting $D_L$ blindly to the breakthrough curve (as apparent in many published breakthrough analyses) can, in specific cases, result in a complete breakdown of the axially dispersed plug flow model, and result in fitted coefficients that are incorrect.

Thus it is important to map the set of conditions where significant breakthrough sharpening occurs in order to avoid nonphysical and non-predictive simulation behavior.
Mapping the Sensitivity of Sorbate/Sorbent Systems to $D_L$ and $k_n$

Mass Balance Equations

$$\frac{\partial c}{\partial t} + \left(1 - \frac{\epsilon}{\varepsilon}\right) \frac{\partial \bar{q}}{\partial t} - D_L \frac{\partial^2 c}{\partial x^2} = -\frac{\partial \nu c}{\partial x}$$

$$\frac{\partial \bar{q}}{\partial t} = k_n (q^* - \bar{q})$$

CO2 and H2O Capacity Isotherms

Equilibrium adsorption isotherms for CO2 (top) and H2O vapor (bottom) on zeolite 5A at temperatures from 0°C to 100°C as indicated. Symbols represent experimental data; Toth isotherm fits are shown as lines (Wang and LeVan, 2009)

$$n = \frac{ap}{[1 + (bp)^n]^{1/n}}; \quad b = b_0 \exp(E / T); \quad a = a_0 \exp(E / T); \quad t = t_0 + c / T$$

Slope ratio provides metric for breakthrough sharpening and departure from constant pattern behavior
Threshold parameter determination for H$_2$O on 5A
(similar analysis for CO$_2$ on 5A, H$_2$O on 13X, and CO$_2$ on 13X)

Contour plot of slope ratio for H$_2$O/5A system based on 100 breakthrough simulations

Curve fit of $k_n = f(D_L)$ for simulation runs with slope ratio values between 1.13 and 1.16 for H$_2$O on 5A. Coefficient of determination ($R^2$) is 0.998.

For this system, the simulation will result in a slope ratio limit below the threshold if $k_n (1 + \theta D_L) - 1 < 0$
Generalization to any sorbent/sorbate system

\[ K_d = \frac{q^*}{q_0 - q^*} \frac{c_0 - c}{c} \]  
Distribution Factor

\[ q^* = \frac{bc}{q_m} \]  
Langmuir Isotherm

\[ K_d = 1 + bc_0 \]  
Distribution Factor for Langmuir Isotherm

Threshold parameter values and distribution factor values

<table>
<thead>
<tr>
<th>Sorbate/Sorbent System</th>
<th>( \theta )</th>
<th>( K_d ) (fitted)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO(_2) on zeolite 5A</td>
<td>10241</td>
<td>5.213</td>
</tr>
<tr>
<td>CO(_2) on zeolite 13X</td>
<td>11713</td>
<td>4.862</td>
</tr>
<tr>
<td>H(_2)O on zeolite 5A</td>
<td>522353</td>
<td>33.106</td>
</tr>
<tr>
<td>H(_2)O on zeolite 13X</td>
<td>679013</td>
<td>75.309</td>
</tr>
</tbody>
</table>

Normalized concentration vs. normalized bed loading for six sorbate/sorbent systems for conditions of 10°C and 1.0 kPa. Solid lines: Langmuir isotherms; Dashed lines: Toth isotherms.
Correlation between threshold parameter and distribution factor

\[ \ln(\theta) = d + \frac{e}{K_d} \]

\[ d = 13.682 \]

\[ e = -18.020 \]

Threshold parameter values and distribution factor values

<table>
<thead>
<tr>
<th>Sorbate/Sorbent System</th>
<th>( \theta )</th>
<th>( K_d ) (fitted)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO(_2) on zeolite 5A</td>
<td>10241</td>
<td>5.213</td>
</tr>
<tr>
<td>CO(_2) on zeolite 13X</td>
<td>11713</td>
<td>4.862</td>
</tr>
<tr>
<td>H(_2)O on zeolite 5A</td>
<td>522353</td>
<td>33.106</td>
</tr>
<tr>
<td>H(_2)O on zeolite 13X</td>
<td>679013</td>
<td>75.309</td>
</tr>
</tbody>
</table>

Estimated threshold value \( q \) vs. distribution factor \( K_d \) for four sorbate/sorbent systems (filled circles) and fitted relationship shown in Equation 5.6 (line). Coefficient of determination (R\(^2\)) is 0.997.
One-page text content:

Three-step process to prevent excessive breakthrough sharpening

1. Determine distribution factor ($K_d$) for sorbent/sorbate system of interest by fitting to Langmuir isotherm

2. Calculate threshold parameter:

\[
\ln(\theta) = d + \frac{e}{K_d}
\]

3. Map limits on $D_L$ vs. $k_n$ plot based on:

\[
k_n = \frac{1}{(1 + \theta D_L)}
\]

For values where $k_n(1 + \theta D_L) - 1 < 0$ excessive breakthrough sharpening and breakdown of the constant pattern behavior will be avoided.
Conclusions for Parameter Mapping

- The axially dispersed plug flow equation and the Danckwerts boundary condition works well for values of dispersion within bounds of accepted correlations.

- However, for specific combinations of $K_d$, $D_L$ and $k_n$ this model breaks down due to the elimination of dispersion at the outlet boundary. In these cases, significant breakthrough sharpening occurs as well as distortion of the internal concentration, deviating from the accepted CPB for these systems.

- This work presents a methodology where a threshold parameter may be calculated based on $K_d$, $D_L$ and $k_n$, and applied to avoid non-physical model distortion.
Overall Conclusions

❖ The separation of gases through adsorption plays an important role in the chemical processing industry, where the separation step is often the costliest part of a chemical process and thus worthy of careful study and optimization.

❖ This work developed a number of new, archival aspects on the computer simulations used for the refinement and design of these gas adsorption processes:

1. Presented a new approach to fit the undetermined heat and mass transfer coefficients in the axially dispersed plug flow equation and associated balance equations

2. Examined and described the conditions where non-physical simulation results can arise

3. Presented an approach to determine the limits of the axial dispersion and LDF mass transfer terms above which non-physical simulation results occur
Backup
Gas Separation Processes

- Separation processes are defined as those that transform a mixture of substances into two or more product streams (King, 1980)
- The study of separations is of critical importance as they are the costliest step in many chemical processes, as they reverse the mixing of substances and thus require a decrease in entropy (Yang 2003)

Table 2.1 Common Commercial and Industrial Uses for Sorbents (Keller, 1983; Yang, 2003)

<table>
<thead>
<tr>
<th>Component to be adsorbed</th>
<th>Other components</th>
<th>Adsorbent(s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas purification</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H₂O</td>
<td>Olefin-containing cracked gas, natural gas, air, synthesis gas, etc.</td>
<td>Silica, alumina, zeolite (3A)</td>
</tr>
<tr>
<td>CO₂</td>
<td>C₃H₄, natural gas, etc.</td>
<td>Zeolite, carbon molecular sieve</td>
</tr>
<tr>
<td>Hydrocarbons, halogenated organics, solvents</td>
<td>Vent streams</td>
<td>Activated carbon, silicalite, others</td>
</tr>
<tr>
<td>Sulfur compounds</td>
<td>natural gas, hydrogen, liquefied petroleum gas (LPG)</td>
<td>Zeolite, activated alumina</td>
</tr>
<tr>
<td>SO₂</td>
<td>Vent streams</td>
<td>Zeolite, activated carbon</td>
</tr>
</tbody>
</table>

Gas bulk separations

<table>
<thead>
<tr>
<th>Component</th>
<th>Other components</th>
<th>Adsorbent(s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Normal paraffins</td>
<td>iso-paraffins, aromatics</td>
<td>Zeolite</td>
</tr>
<tr>
<td>N₂</td>
<td>O₂</td>
<td>Zeolite</td>
</tr>
<tr>
<td>O₂</td>
<td>N₂</td>
<td>Carbon molecular sieve</td>
</tr>
<tr>
<td>CO</td>
<td>CH₄, CO₂, N₂, Ar, NH₃/H₂</td>
<td>Zeolite, activated carbon</td>
</tr>
<tr>
<td>Acetone</td>
<td>Vent streams</td>
<td>Activated Carbon</td>
</tr>
<tr>
<td>C₃H₄</td>
<td>Vent streams</td>
<td>Activated Carbon</td>
</tr>
</tbody>
</table>

Table 2.2 Gas Separation and Purification Applications Enabled by New Sorbents (Yang, 2003)

<table>
<thead>
<tr>
<th>Application</th>
<th>Sorbent and Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>N₂/CH₄ separation for natural gas upgrading</td>
<td>Clinoptilite, tinanosilicates by kinetic separation, single-wall carbon nanotubes</td>
</tr>
<tr>
<td>CO removal from H₂ to &lt; 1 ppm for fuel cell applications</td>
<td>π-complexation sorbents such as CuCl/γ-Al₂O₃, CuY, and, AgY</td>
</tr>
<tr>
<td>NO₃ removal</td>
<td>Fe-Mn-Ti oxides, Fe-Mn-Zr oxides, Cu-Mn oxides, multi-wall carbon nanotubes</td>
</tr>
<tr>
<td>C₃H₄/C₃H₆ (+hydrocarbons) separation</td>
<td>π-complexation sorbents such as CuCl/γ-Al₂O₃, AgNO₃/SiO₂, AgNO₃/clays, aluminophosphate</td>
</tr>
<tr>
<td>C₃H₄/C₃H₆ (+hydrocarbons) separation</td>
<td>π-complexation sorbents such as CuCl/γ-Al₂O₃, AgNO₃/SiO₂, AgNO₃/clays</td>
</tr>
</tbody>
</table>

Table 2.3 CO₂ Capture Technologies Funded Under DOE (Vora, 2013)

<table>
<thead>
<tr>
<th>Project Name</th>
<th>Project Focus</th>
<th>Sorbent Materials</th>
<th>Process Approach</th>
<th>Technology Maturity</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low-Cost Sorbent for Capturing CO₂ Emission Generated by Existing Coal-Fired Power Plants</td>
<td>Low-Cost Solid Sorbent</td>
<td>Alkalized Alumina sorbent</td>
<td>Simulated Moving Beds</td>
<td>Bench-Scale Using Actual Flue Gas</td>
<td>Elliot, 2012</td>
</tr>
<tr>
<td>CO₂ Removal from Flue Gas Using Microporous Metal Organic Frameworks</td>
<td>Microporous MOFs</td>
<td>Alumina and Mg/DOBDC</td>
<td>VPSA</td>
<td>Laboratory-Scale, Simulated Flue Gas</td>
<td>Benin, 2012</td>
</tr>
</tbody>
</table>
Adsorbents and Fixed Beds

Figure 2.3 (a) Pelletized zeolite pellets, (b) crystals, and (c) framework structure.  See http://www.grace.com/engineeredmaterials/productsandapplications/InsulatingGlass/Siev eBeads/Grades.aspx

Figure 2.4 SEM images of pelletized zeolite 5A used in the ISS CDRA. Individual zeolite crystals are evident in the 1kx views (Radenburg, 2013).

Figure 2.7 Packed (or fixed) bed of zeolite 13X beads. Photo taken by author.

Figure 2.8 Depiction of fixed bed and zeolite mass transfer mechanisms (Shareeyan et al, 2014)
Criteria for inclusion:

- Published in 2000 or later
- Includes description of experimental data used for validation

1-D model used in 16 publications

Tube to particle diameter ratio ≤ 20 for 16 (most much lower)

LDF used in 12 publications

Axial dispersion used in 14 publications

Breakthrough curve only shown in 14 publications