Solid Sorbent Modeling for the Carbon Capture Simulation Initiative

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outline

• intro to silica-supported amine sorbents
• first-generation model
• high-fidelity approach
• outlook
  – statistical methods in model calibration
  – reduced-order modeling
the sorbent: silica support

- mesoporous silica forms the substrate
- silica xerogels (sol-gel process) most economical
- substrate particles agglomerates of micron-sized mesoporous particles

the sorbent: PEI loading

- substrate impregnated with poly(ethyleneimine), or PEI
- PEI tends to fill the mesopores, reducing porosity and internal surface area

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An IR peak associated with silanol (3747 cm\(^{-1}\)) disappears when PEI is loaded onto the substrate.

the sorbent: PEI loading

- substrate impregnated with poly(ethyleneimine), or PEI
- PEI tends to fill the mesopores, reducing porosity and internal surface area
- some amines bind with silanol sites that cover the surface of the substrate
- capacity scales with internal surface area

the sorbent: dry TGA behavior

(a) Sorbent NETL-196C, ~44.1 wt-% PEI (b) NETL-32D, ~22.5 wt-% PEI. Dry atmosphere. Sorbent synthesis: McMahan Gray, NETL; Sorbent characterization: Daniel Fauth, NETL.
the sorbent: wet TGA behavior

(a) Sorbent NETL-196C, ~44.1 wt-% PEI (b) NETL-32D, ~22.5 wt-% PEI. Humid atmosphere: ~9.1 mol-% H₂O. Sorbent synthesis: McMahan Gray, NETL; Sorbent characterization: Daniel Fauth, NETL.
first-generation model

\[
\begin{align*}
2R_2NH + CO_2(gas) & \rightleftharpoons R_2NCO_2^- + R_2NH_2^+ \\
R_2NH + H_2O(phys) + CO_2(gas) & \rightleftharpoons HCO_3^- + R_2NH_2^+ \\
H_2O(gas) & \rightleftharpoons H_2O(phys)
\end{align*}
\]

- **13 parameters fit to data sequentially**
  - dry (carbamate) kinetic and equilibrium (5)
  - water uptake kinetic and equilibrium (4)
  - bicarbonate kinetic and equilibrium (4)
first-generation model: fit for NETL-32D
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- heat of reaction in dry conditions: 65 kJ/mol calculated, vs. 67 kJ/mol measured by calorimetry\(^1\)

first-generation model

- **advantages**
  - quickly prepared
  - easy to implement at larger modeling scales
  - flexible

- **disadvantages**
  - accuracy
  - weak identification with actual physical processes
Multiphase Flow Workshop, 8-18-2011

high-fidelity approach

• carbamate formation is actually two-step:

\[
R_2NH + CO_2 \rightleftharpoons R_2NH^+ : CO_2^- \\
R_2NH^+ : CO_2^- + R_2NH \rightleftharpoons R_2NH_2^+ + R_2NCO_2^- 
\]

• three modes of mass transport:
  – gas phase bulk
  – gas phase Knudsen
  – solid state (zwitterion-mediated hopping)
high-fidelity approach

\[
\begin{align*}
&\left[ \epsilon_2 + RTn_s a_2 \frac{\kappa_z (1 - 2x_s)}{(1 + \kappa_z p)^2} \right] \frac{\partial p}{\partial t} = \frac{4\epsilon_2}{3\tau_2} K_o \left( \frac{8RT}{\pi M} \right)^{1/2} \nabla^2 p \\
&- RT a_2 n_s \left( \frac{1 - \kappa_z p}{1 + \kappa_z p} \right) \frac{\partial x_s}{\partial t} + RT q_{2,t}
\end{align*}
\]

\[q_{2,t} = -RTu_b n_s a_2 (n_v N_a)^{2/3} \left[ z_s (1 - 2x_1 - z_1) - z_1 (1 - 2x_s - z_s) \right]\]

\[
\epsilon_3 \frac{\partial z}{\partial t} = \frac{\epsilon_3}{\tau_3} RT u_b \nabla_3 \cdot \left[ (1 - 2x) \nabla_3 z + 2z \nabla_3 x \right] - \frac{\partial x}{\partial t}
\]

\[
\frac{\partial x}{\partial t} = \kappa_x \left[ (1 - 2x - z) z - x^2 / \kappa_x \right]
\]
high-fidelity approach

- line-by-line iterative method
- set of 12 unknown parameters
high-fidelity approach

(left) calculated output of the high-fidelity sorbent model (right) experimental TGA for NETL-32D
high-fidelity approach

(left) calculated output of the high-fidelity sorbent model (right) experimental TGA for NETL-196C
high-fidelity approach

![Graphs and tables showing multiphase flow dynamics and thermodynamic properties.](attachment:image.png)
high-fidelity approach

average cross-sectional site fraction of adsorbed CO$_2$ in the PEI bulk
outlook: parameter estimation

• **Bayesian statistical methodology for parameter estimation**
  – parameter set not a single, ‘true’ set of values, but a joint probability distribution
  – prior probability distributions arise from similar chemistries (e.g., aqueous amines), advanced microscopic measurements or *ab initio* calculations

• **model replaced by a Gaussian process emulator**
  – reduced order model for the process itself
  – normally distributed error includes inadequacy of the ROM and of the high-fidelity model itself, along with experimental error

• **Monte Carlo simulation for optimization**
  – analogous to genetic algorithm
  – leads to posterior probability distribution for parameters
outlook: reduced-order model

- proper orthogonal decomposition is homologous to a singular value decomposition
summary

• **first-generation model for silica-supported amine sorbents**
  – set of three nonlinear, ordinary differential equations
  – model parameters fit to data for two NETL sorbents

• **high-fidelity model for silica-supported amine sorbents**
  – hierarchical, microstructurally homogenized grain model
  – captures principal qualitative aspects of sorbent behavior
  – efficient vehicle for multi-scale modeling

• **Bayesian approach to multi-scale modeling**
  – microscopic data incorporated in statistically rigorous way
  – proper orthogonal decomposition looks promising
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