NATIONAL ENERGY TECHNOLOGY LABORATORY

Solid Sorbent Modeling for the Carbon Capture Simulation Initiative

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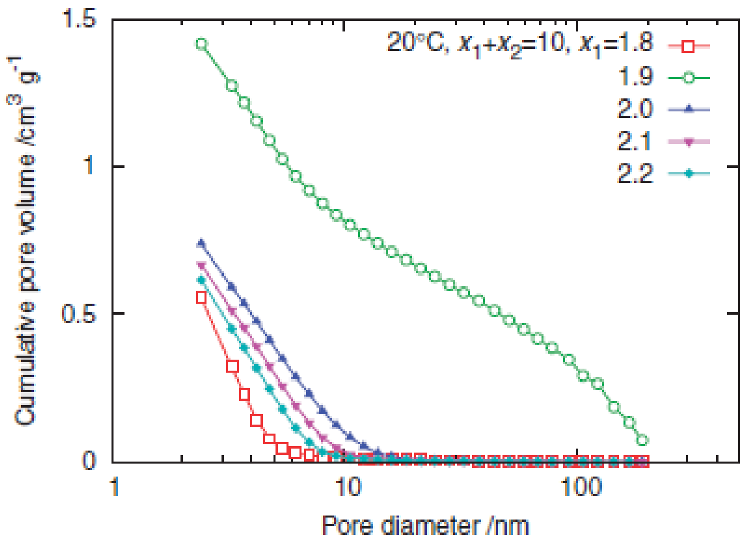
U.S. DEPARTMENT OF ENERGY

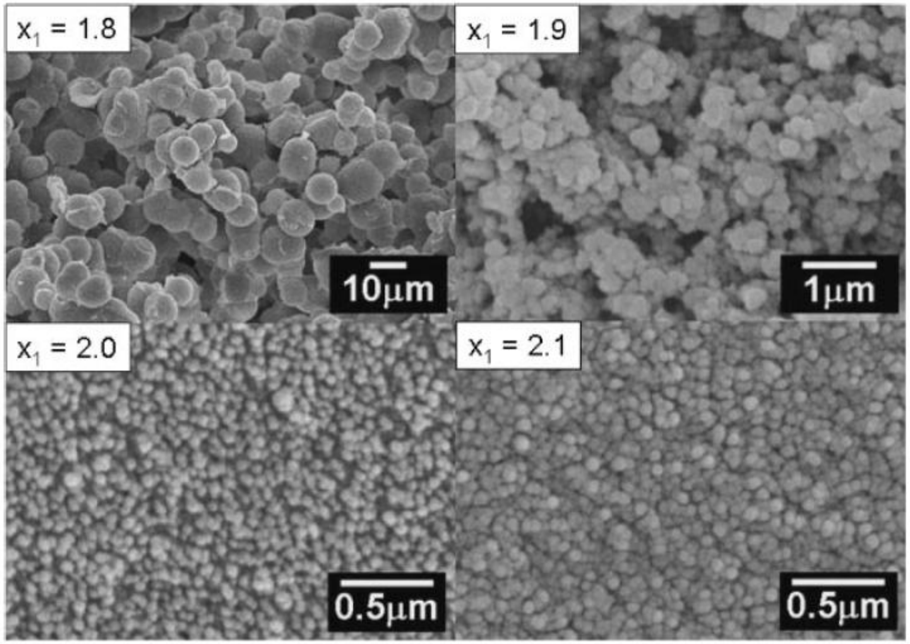
outline

- **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**



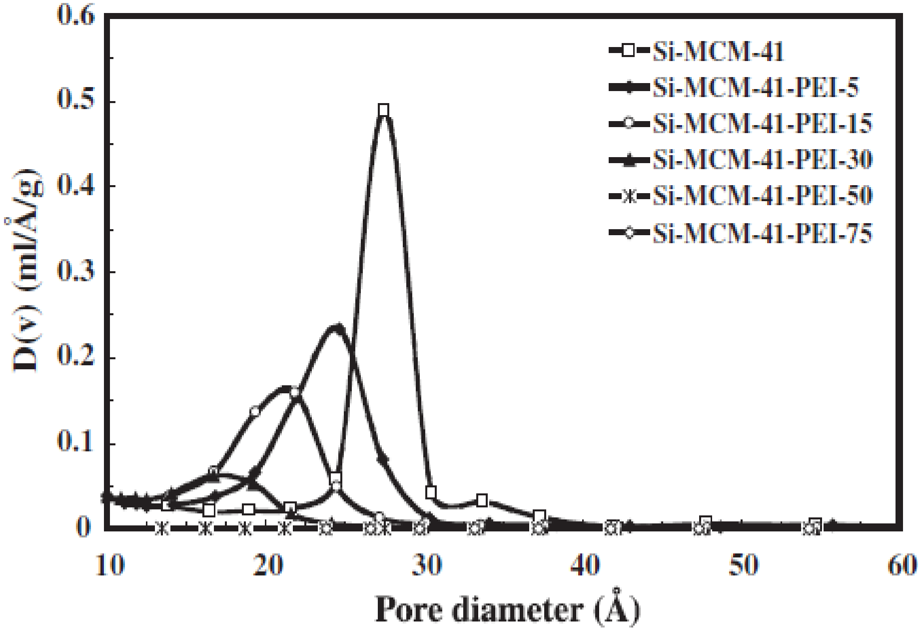


K. Kajihara, et al., Bull. Chem. Soc. Jpn. **82** (2009) 1470.

the sorbent: PEI loading

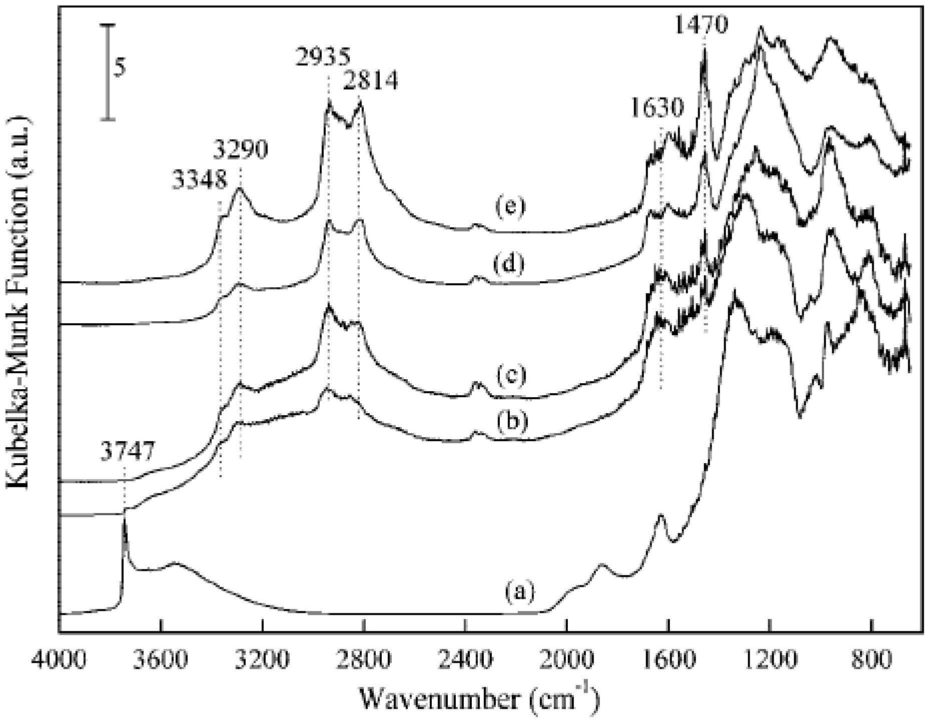
- **substrate impregnated with poly(ethyleneimine), or PEI**
- **PEI tends to fill the mesopores, reducing porosity and internal surface area**

X. Xu, et al., Micropor. Mesopor. Mat. **62** (2003) 29.



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**



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

X. Wang, et al., J. Phys. Chem. C **113** (2009) 7260.

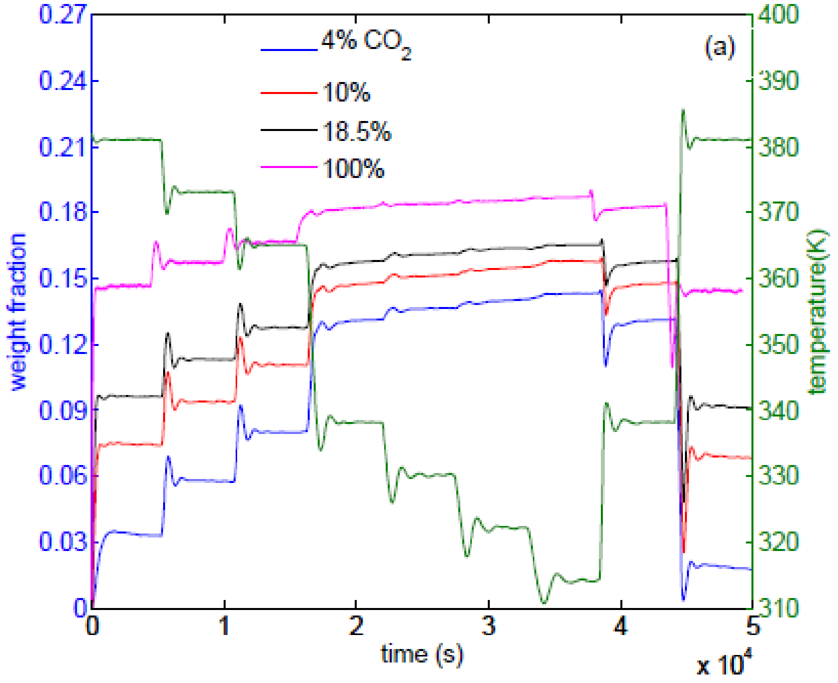
the sorbent: PEI loading

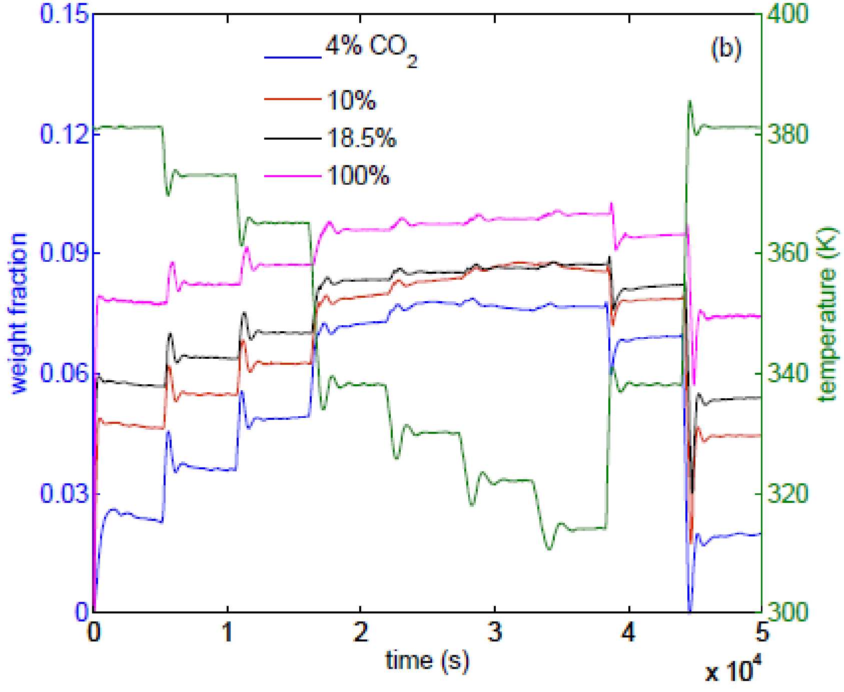
- **substrate impregnated with poly(ethyleneimine), or PEI**
- **PEI tends to fill the mesopores, reducing porosity and internal surface area**
- **some amines bind with silanol sites that cover the surface of the substrate**
- **capacity scales with internal surface area**

sample	BET surface area ($m^2\ g^{-1}$)	pore volume ($cm^3\ g^{-1}$)	pore diameter (nm)	CO_2 cap.[a] mg/g of sorb
MCM-41	1229	1.15	2.7	6.3
PEI(50)/MCM-41 (MBS-1)	11	0.03	0	89.2
SBA-15	950	1.31	6.6	5.0
PEI(50)/SBA-15 (MBS-2)	80	0.20	6.1	140

X. Ma, et al., J. Am. Chem. Soc. **131** (2009) 5777.

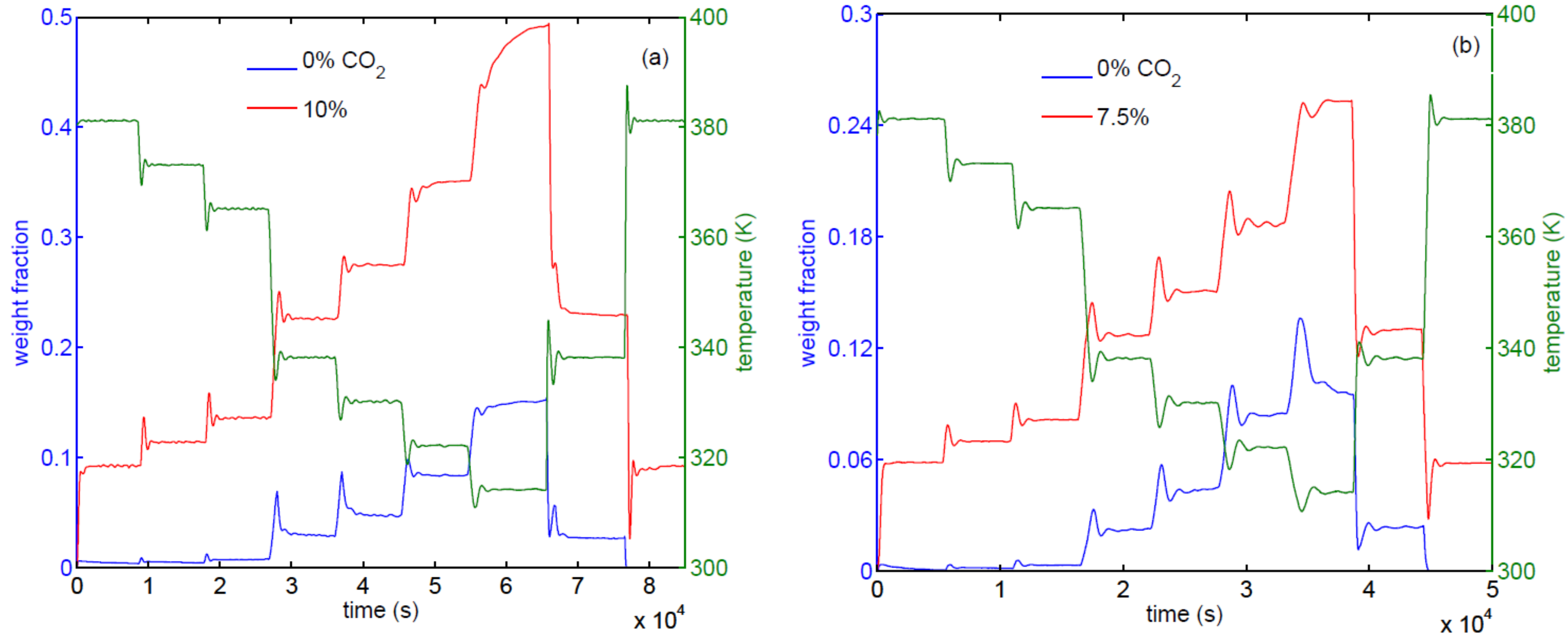
the sorbent: dry TGA behavior





(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-% H_2O. Sorbent synthesis: McMahan Gray, NETL; Sorbent characterization: Daniel Fauth, NETL.

first-generation model

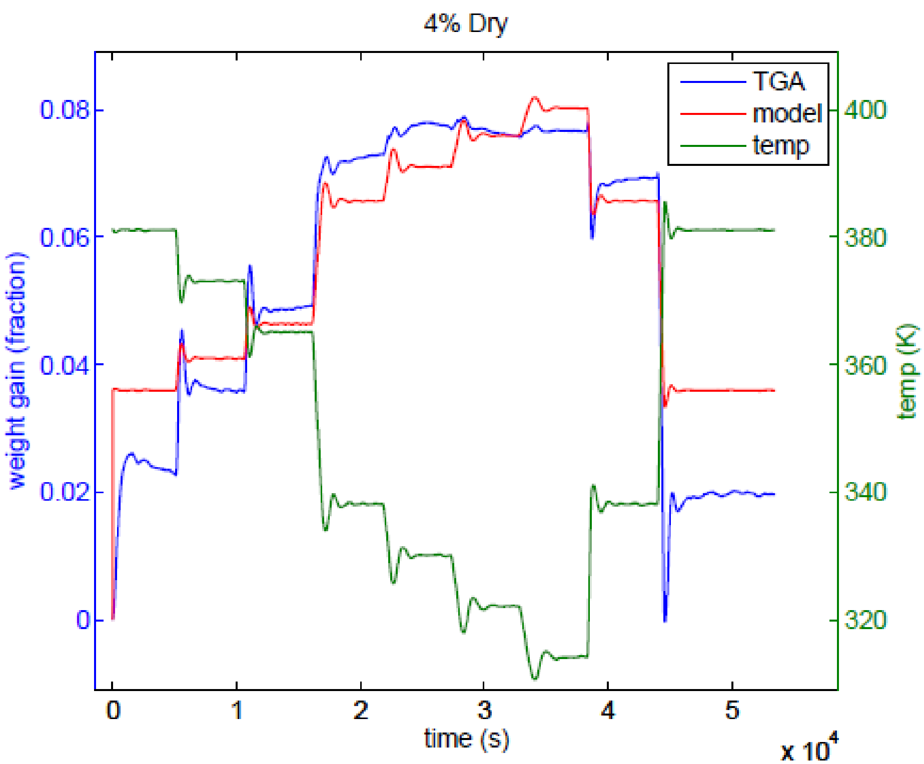
$$2R_2NH + CO_2(\text{gas}) \rightleftharpoons R_2NCO_2^- + R_2NH_2^+$$
$$R_2NH + H_2O(\text{phys}) + CO_2(\text{gas}) \rightleftharpoons HCO_3^- + R_2NH_2^+$$
$$H_2O(\text{gas}) \rightleftharpoons H_2O(\text{phys})$$

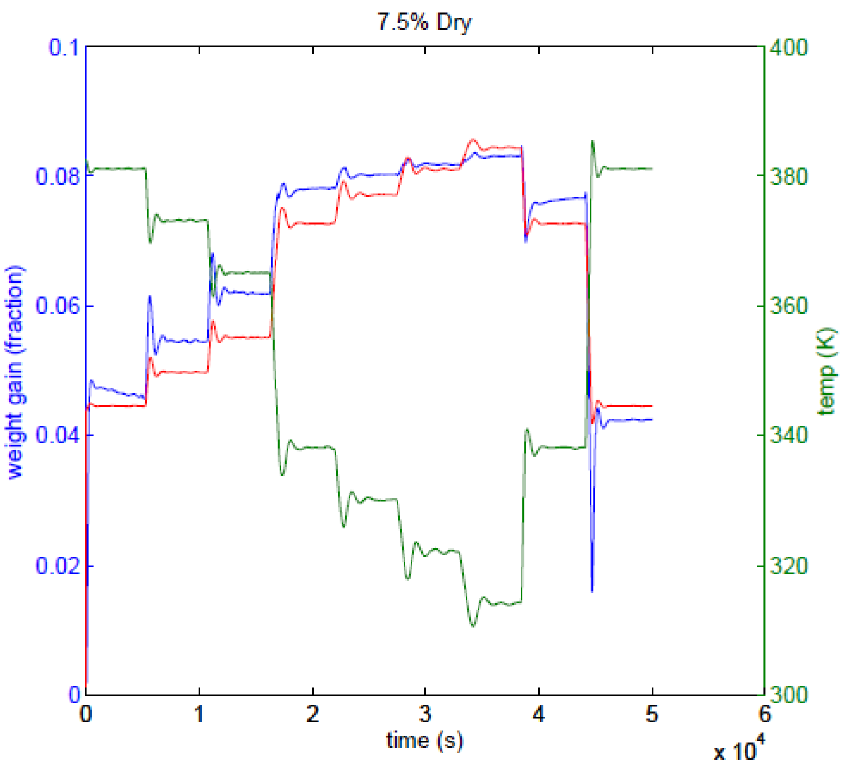
$$\frac{\partial x}{\partial t} = k_c\left(s^2 p_c^m - xw/\kappa_c\right)$$
$$\frac{\partial b}{\partial t} = k_b\left(sap_c - bw/\kappa_b\right)$$
$$\frac{\partial a}{\partial t} = k_h\left(p_h - a/\kappa_h\right)$$

$$1 = s + w + x$$
$$w = x + b/n_v$$

- **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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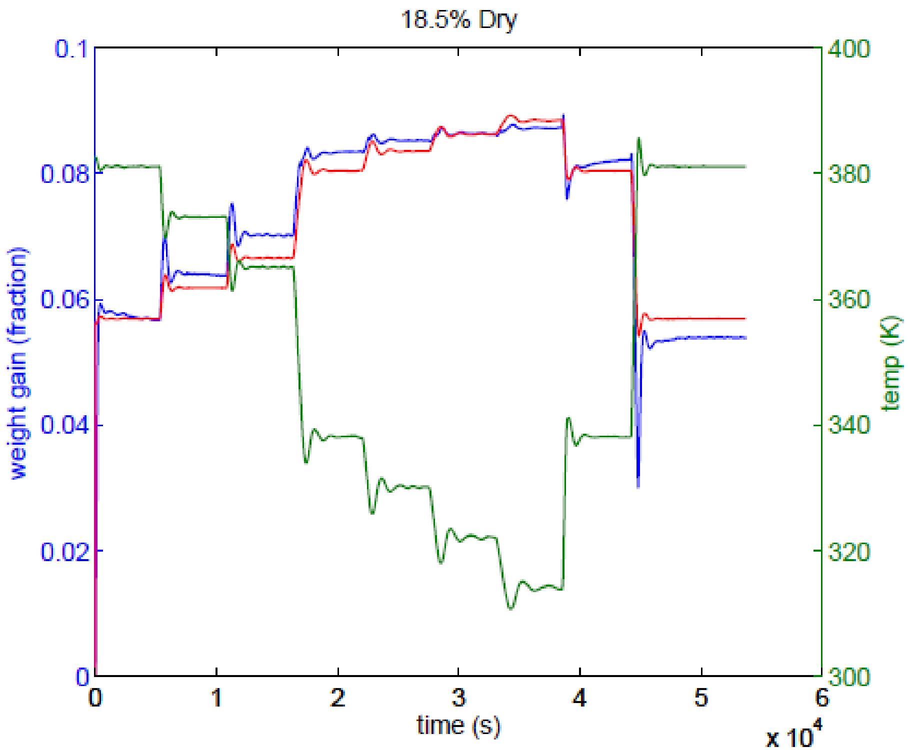
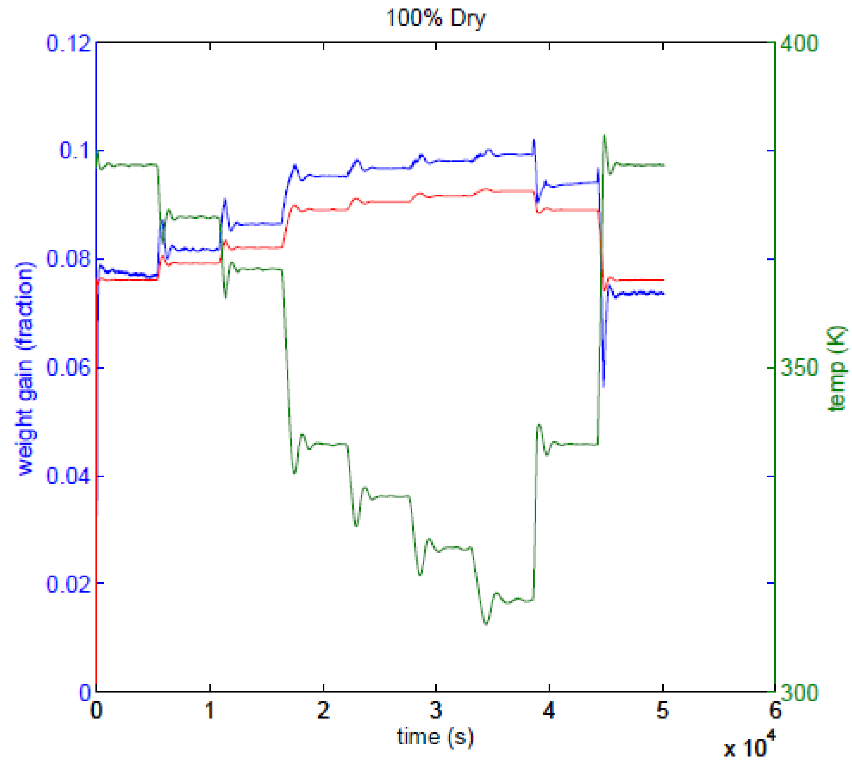
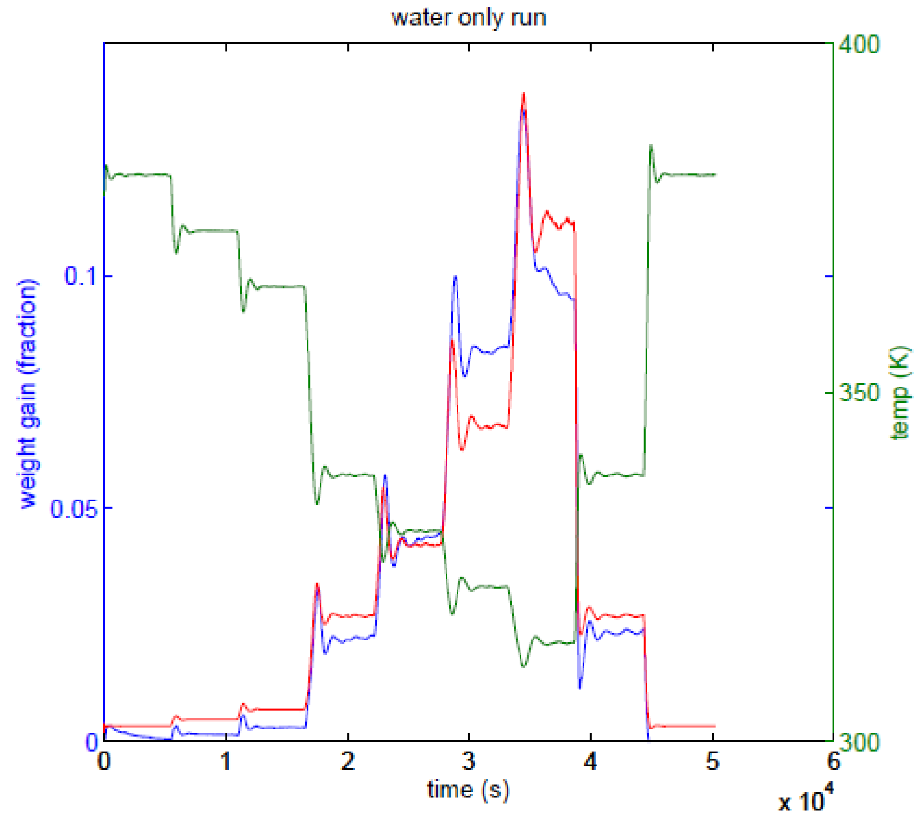
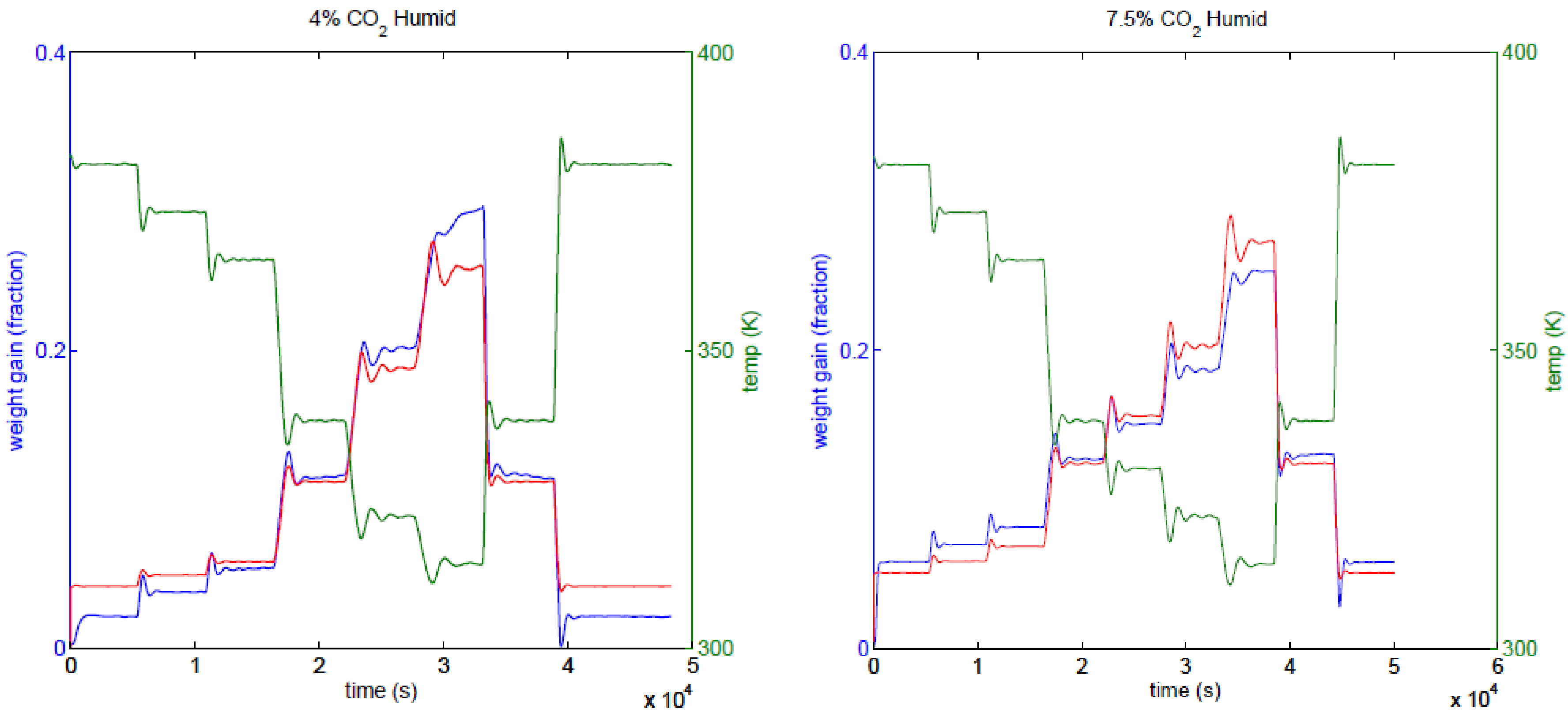




first-generation model: fit for NETL-32D



first-generation model: fit for NETL-32D



- **heat of reaction in dry conditions: 65 kJ/mol calculated, vs. 67 kJ/mol measured by calorimetry[1]**

[1]R. Serna-Guerrero and A. Sayari, Chem. Eng. J. 161 (2010) 182.

first-generation model

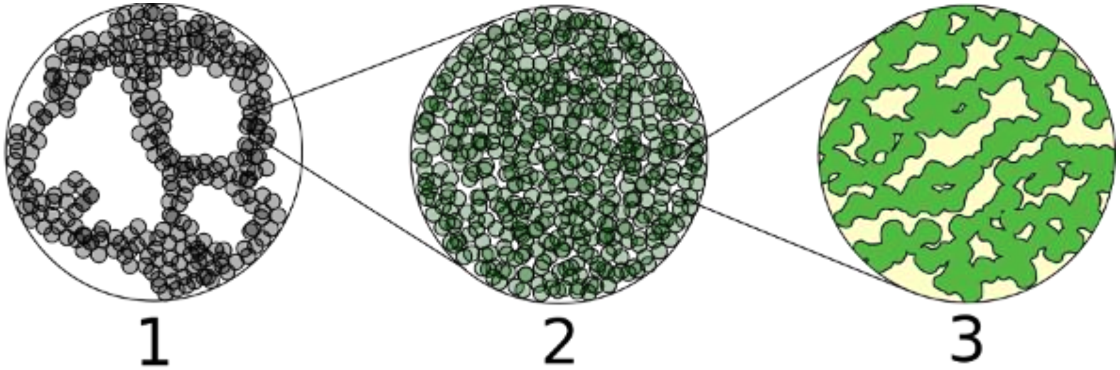
- **advantages**
  - quickly prepared
  - easy to implement at larger modeling scales
  - flexible
- **disadvantages**
  - accuracy
  - weak identification with actual physical processes

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

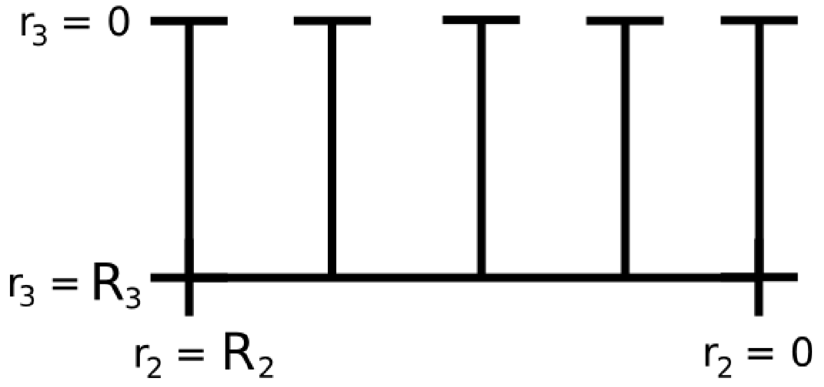
$$\left[\epsilon_2 + RTn_\mathrm{s}a_2\frac{\kappa_\mathrm{z}(1-2x_\mathrm{s})}{(1+\kappa_\mathrm{z}p)^2}\right]\frac{\partial p}{\partial t} = \frac{4\epsilon_2}{3\tau_2}K_o\left(\frac{8RT}{\pi M}\right)^{1/2}\nabla_2^2 p - RTa_2n_\mathrm{s}\left(\frac{1-\kappa_\mathrm{z}p}{1+\kappa_\mathrm{z}p}\right)\frac{\partial x_\mathrm{s}}{\partial t} + RTq_{2,t}$$

$$q_{2,t} = -RTu_b n_\mathrm{s} a_2 (n_\mathrm{v}N_\mathrm{a})^{2/3}\left[z_\mathrm{s}(1-2x_1-z_1) - z_1(1-2x_\mathrm{s}-z_\mathrm{s})\right]$$

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

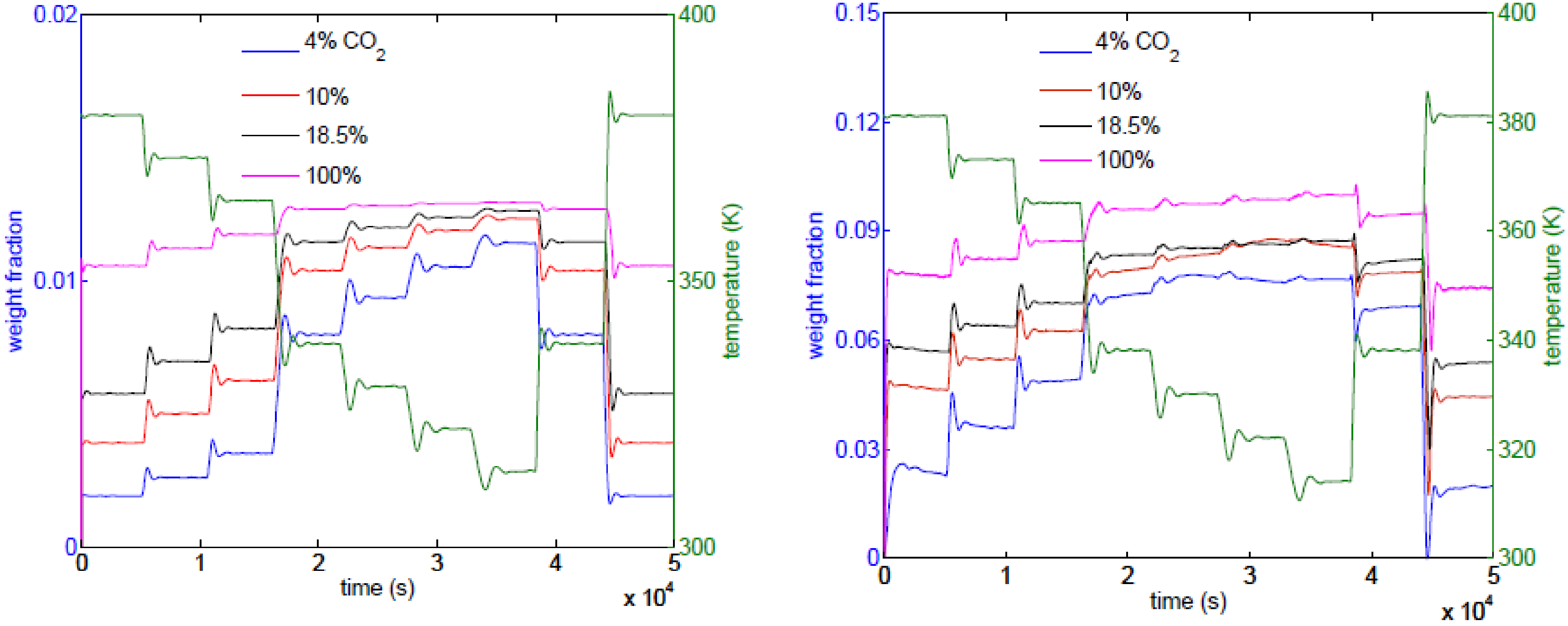
$$\frac{\partial x}{\partial t} = k_\mathrm{x}\left[(1-2x-z)z - x^2/\kappa_\mathrm{x}\right]$$

high-fidelity approach



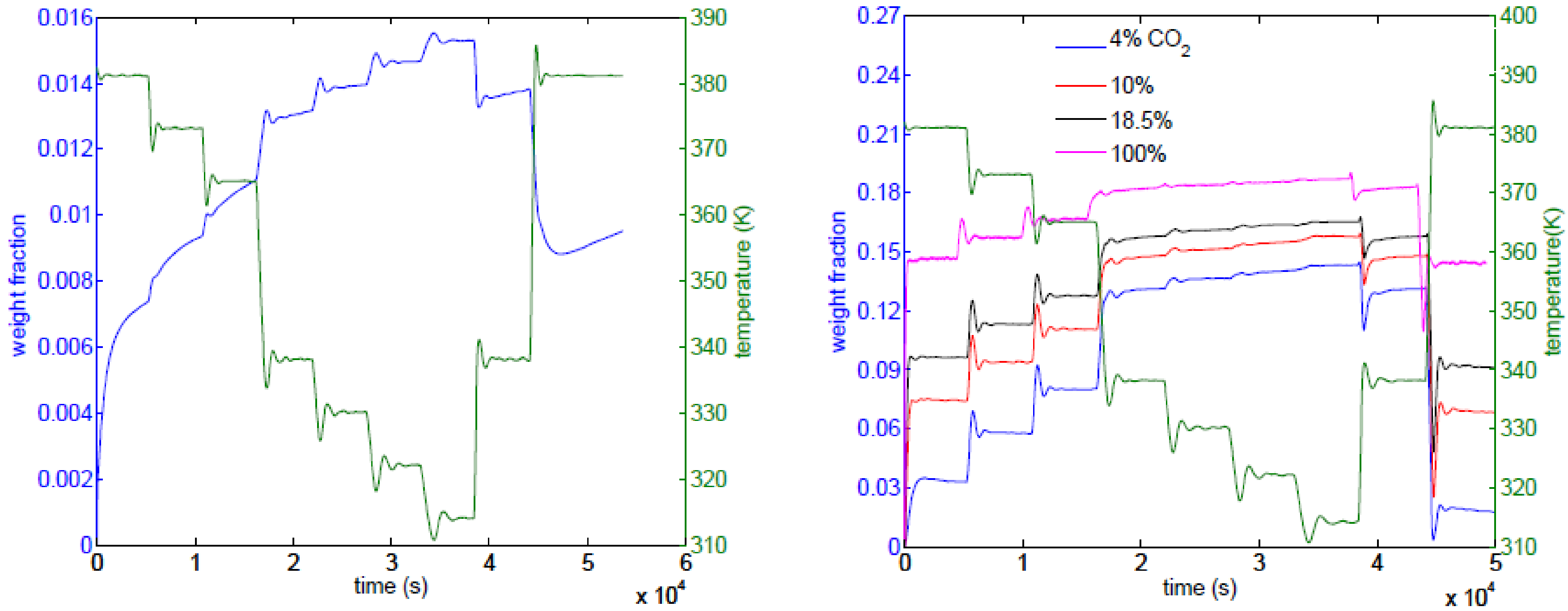
- **line-by-line iterative method**
- **set of 12 unknown parameters**

high-fidelity approach



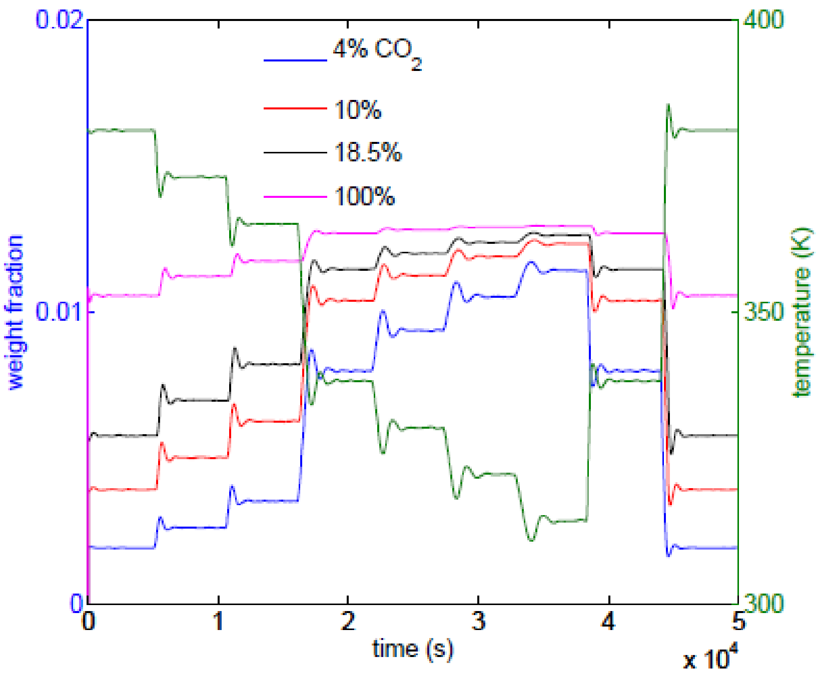
(left) calculated output of the high-fidelity sorbent model (right) experimental TGA for NETL-32D

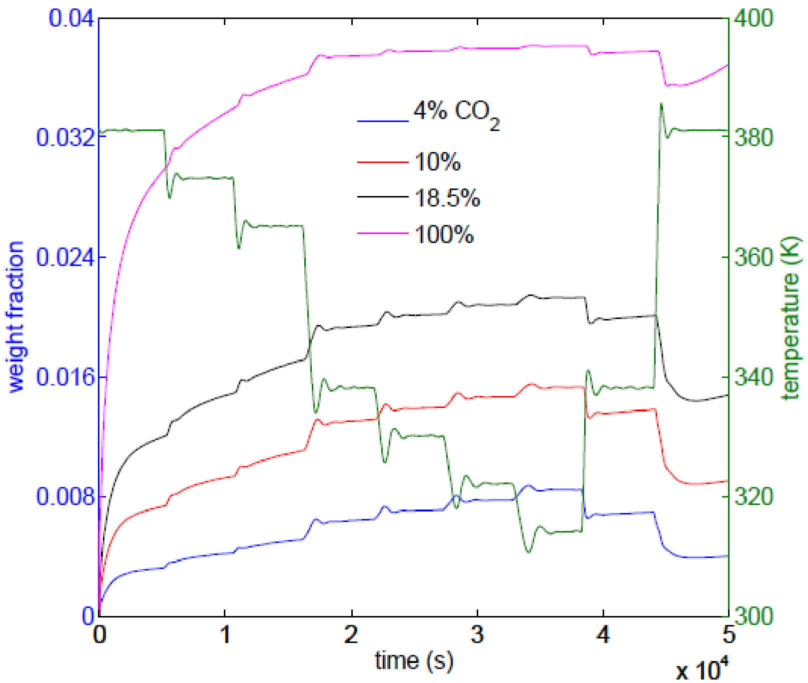
high-fidelity approach



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

high-fidelity approach

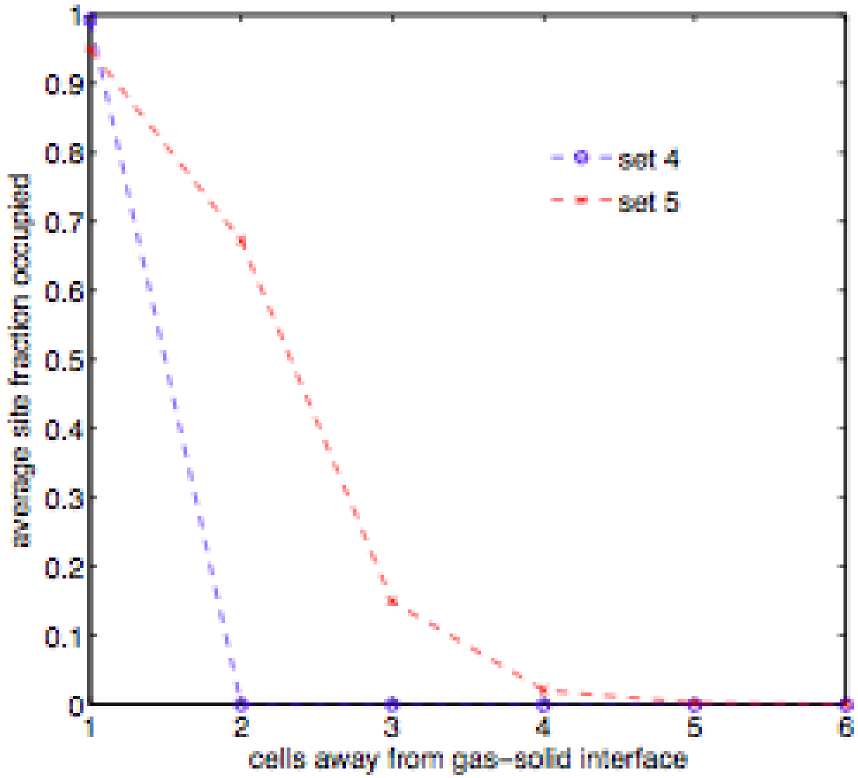




set	K_o/τ_2	τ_3	f	n_v	ΔH_{tot}	ΔS_{tot}	ΔH_5	ΔS_5	$\Delta H_6^{\ddagger}$	ζ_6'	$\Delta H_b^{\ddagger}$	ζ_b'
4	$10^{-8.57}$	3.98	3.26	2.31×10^4	-0.61	-35.0	-0.57	-16.0	0.39	$10^{3.87}$	1.20	$10^{-10.1}$
5	$10^{-9.40}$	2.35	1.78	2.44×10^4	-0.51	-38.9	-0.40	-11.5	0.35	$10^{4.20}$	1.25	$10^{-4.7}$

high-fidelity approach

average cross-sectional site fraction of adsorbed CO_2 in the PEI bulk

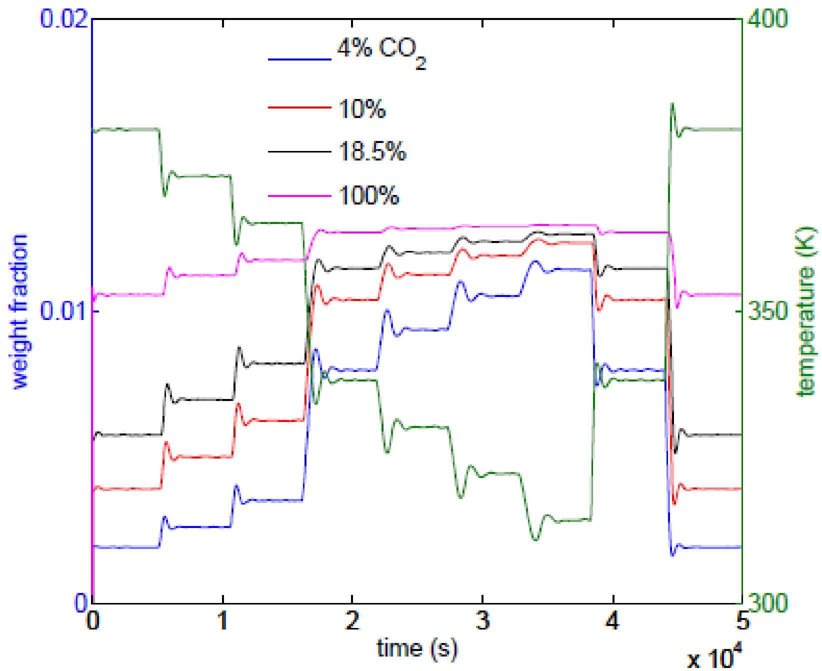


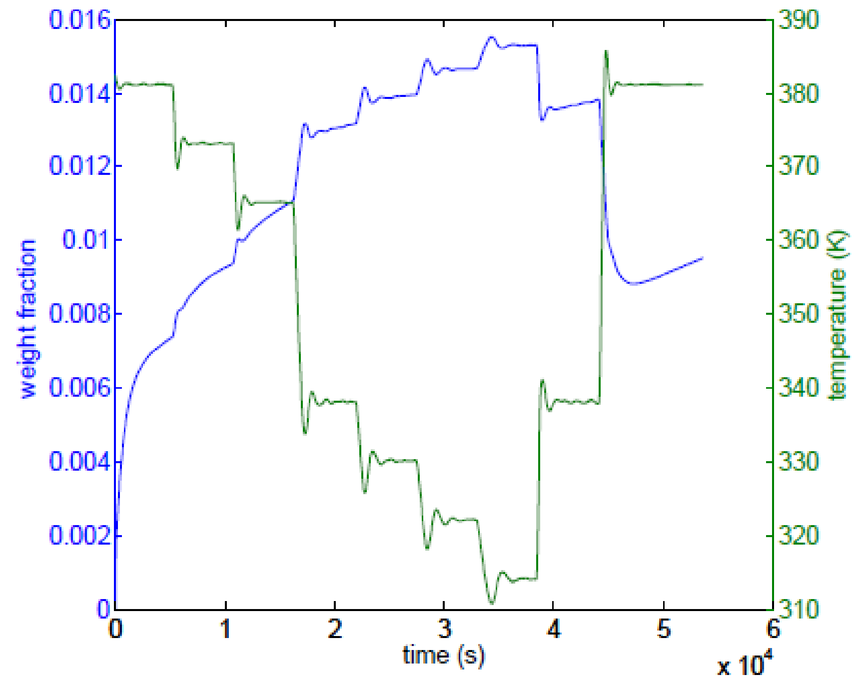
outlook: parameter estimation

- **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

acknowledgements

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