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Carbon Capture Simulation Initiative

The importance of transport processes in silica-supported, polyethyleneimine-impregnated CO_2 sorbents

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U.S. DEPARTMENT OF ENERGY

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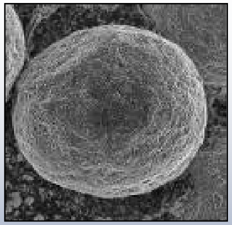
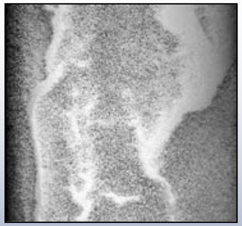
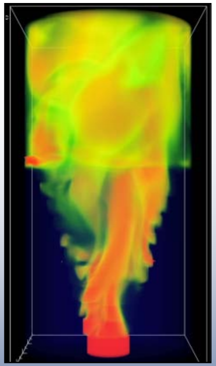


Identify promising concepts → Reduce the time for design & troubleshooting → Quantify the technical risk, to enable reaching larger scales, earlier → Stabilize the cost during commercial deployment

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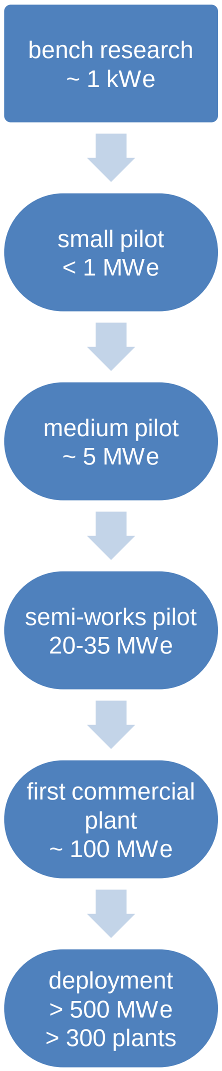
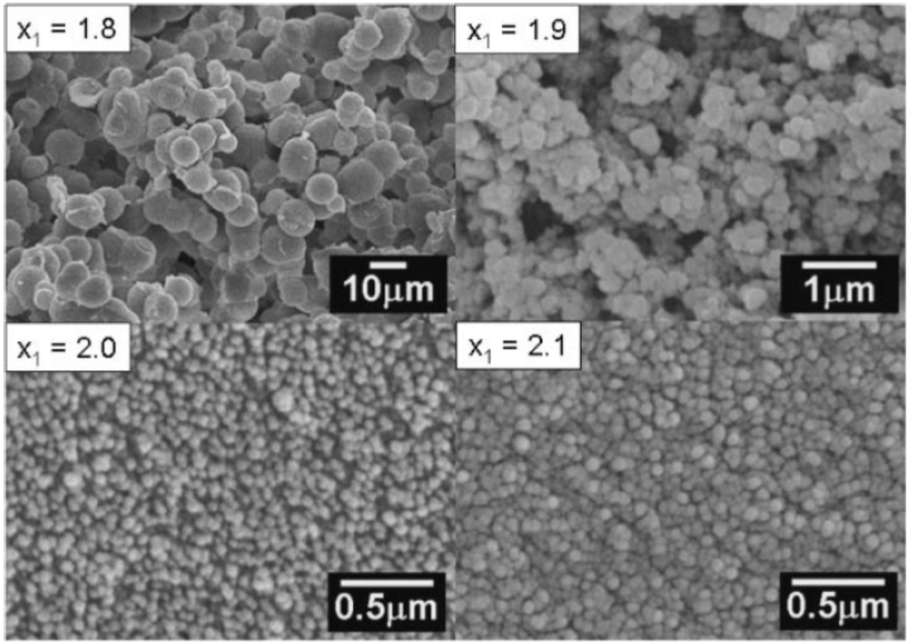
Carbon Capture Challenge

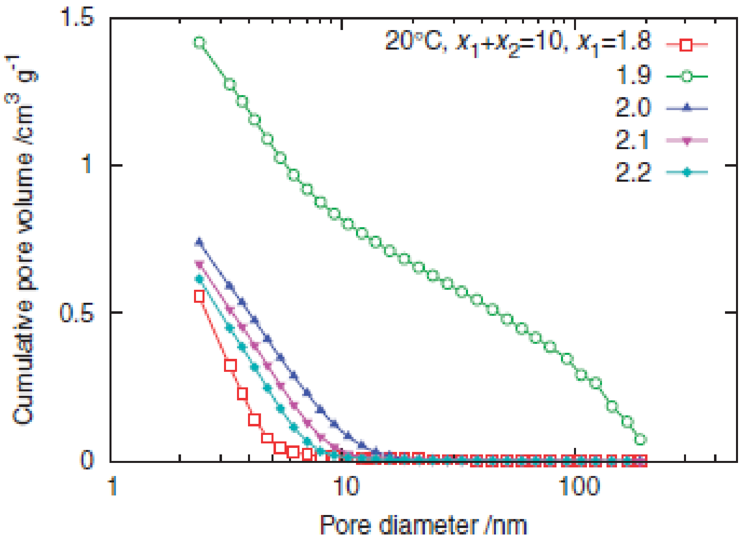
- The traditional pathway from discovery to commercialization of energy technologies can be quite long, i.e., ~ 2-3 decades
- President's plan requires that barriers to the widespread, safe, and cost-effective deployment of CCUS be overcome within 10 years
- To help realize the President's objectives, new approaches are needed for taking carbon capture concepts from lab to power plant, quickly, and at low cost and risk
- CCSI will accelerate the development of carbon capture technology, from discovery through deployment, with the help of science-based simulations



the sorbent: silica support

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

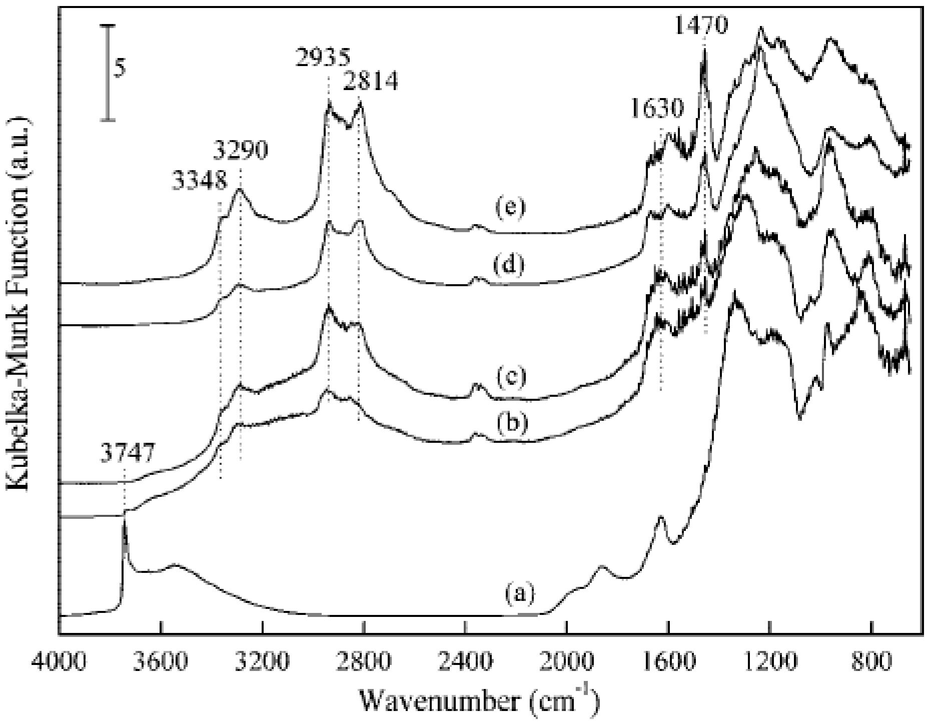




K. Kajihara, et al., Bull. Chem. Soc. Jpn. 82 (2009) 1470.

the sorbent: PEI loading

- substrate impregnated with polyethyleneimine, 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.

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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.

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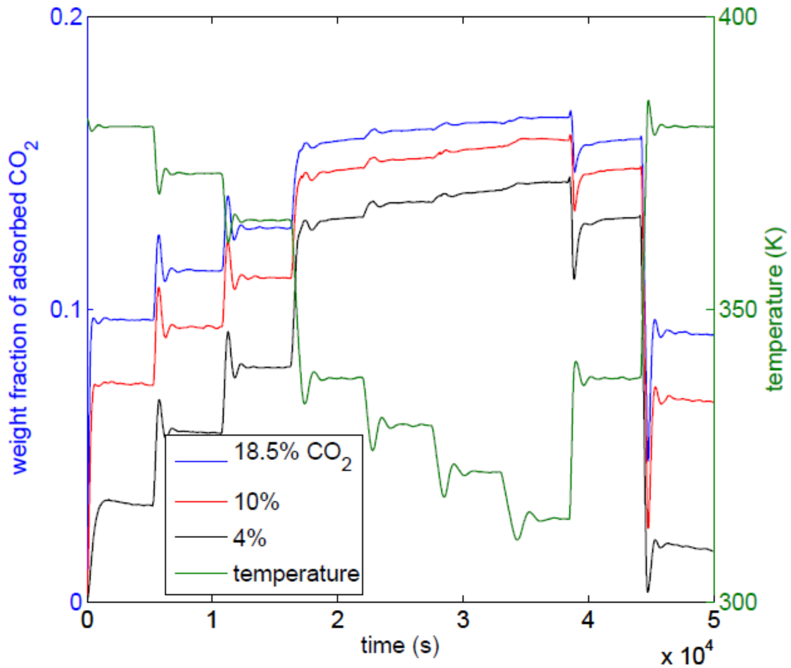
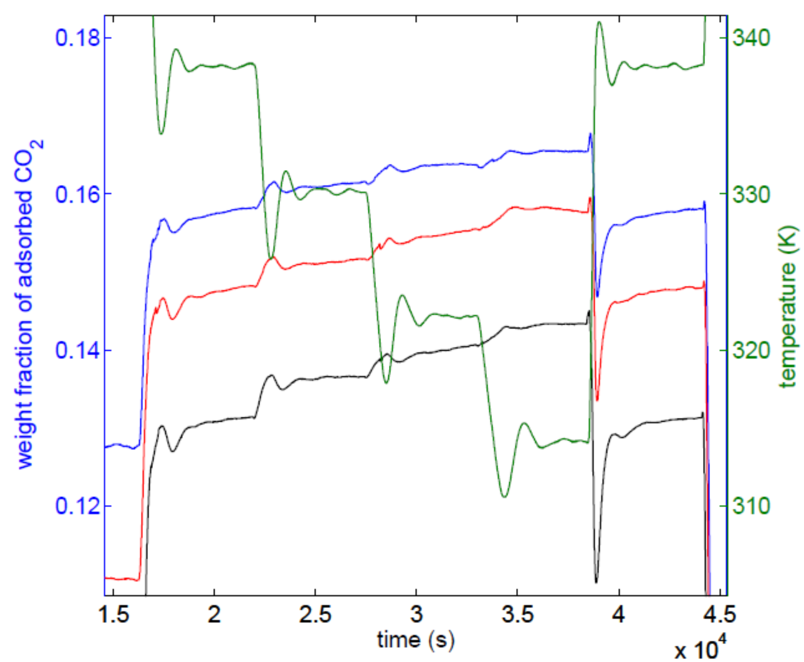
the sorbent: dry TGA behavior





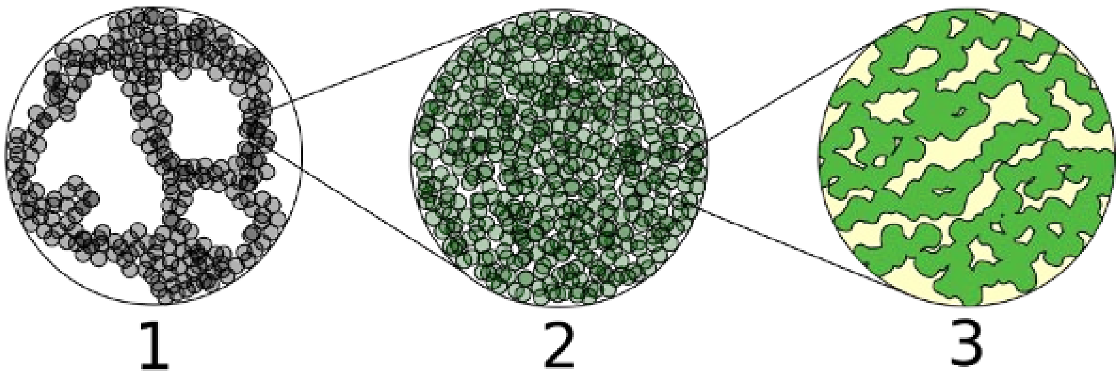
Sorbent NETL-196C, ~44.1 wt-% PEI, Dry atmosphere. Sorbent synthesis: McMahan Gray, NETL; Sorbent characterization: Daniel Fauth, NETL.

anhydrous model

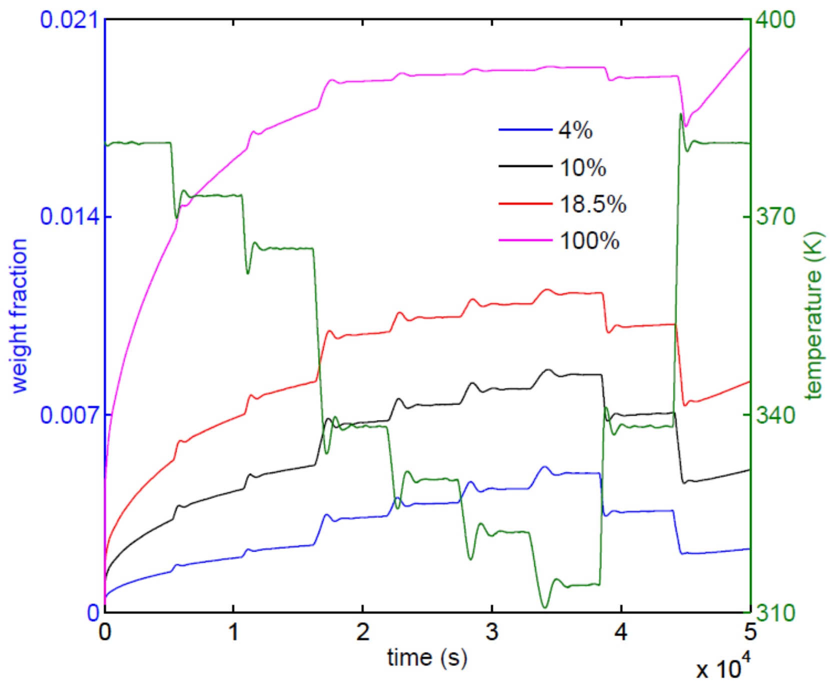
- two-step formation of carbamic acid:

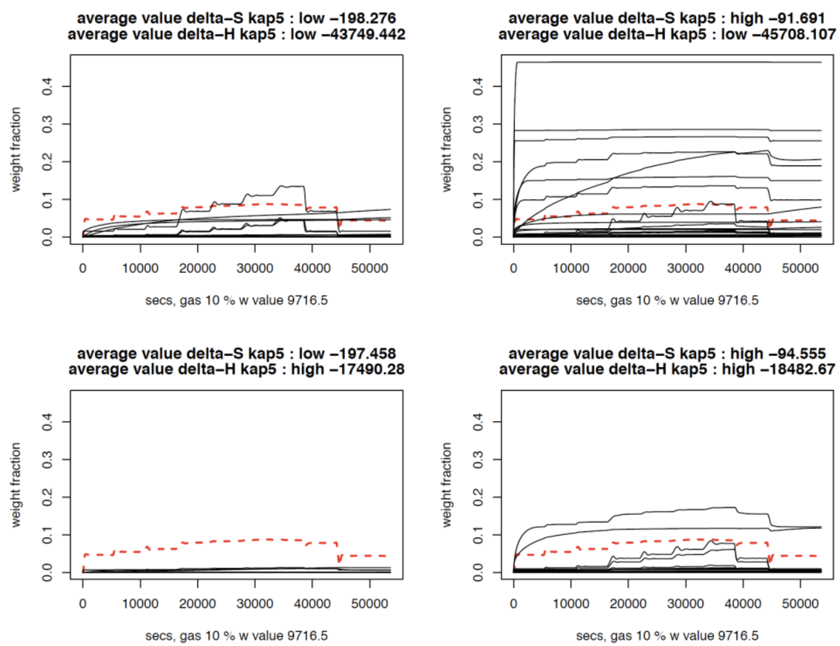
$$\mathrm{R_2NH + CO_2(g) \rightleftharpoons R_2NH^+ - CO_2^-}$$
$$\mathrm{R_2NH^+ - CO_2^- + R_2NH \rightleftharpoons R_2NCOOH : R_2NH}$$

- three modes of mass transport:
    - gas phase bulk
    - gas phase Knudsen
    - solid state (zwitterion-mediated hopping)



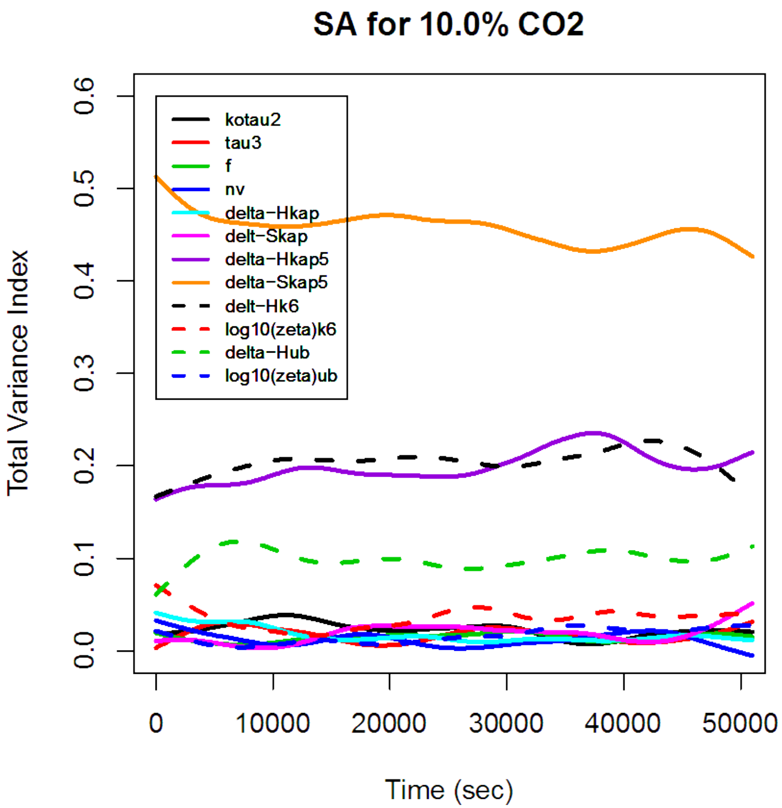
anhydrous model

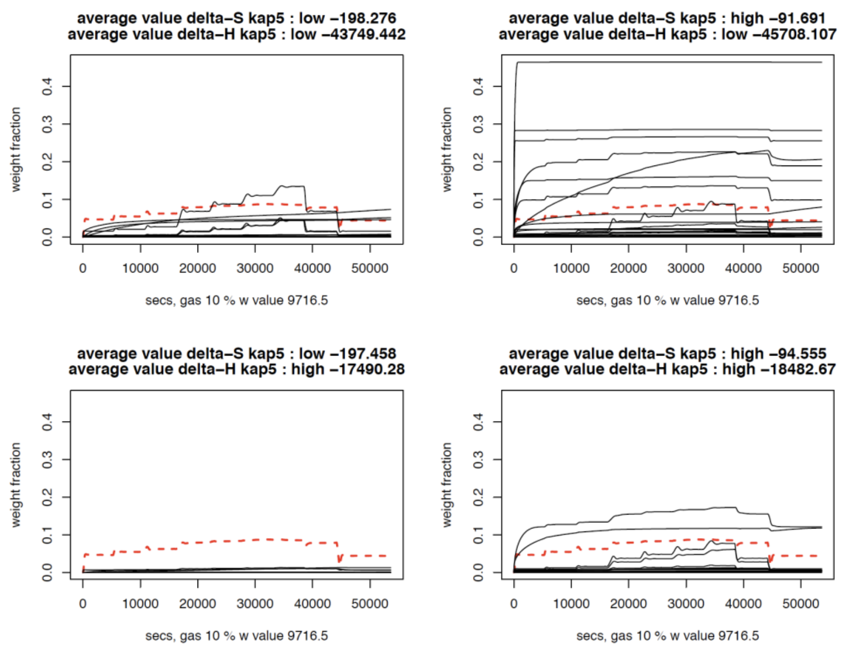




(left) sample calculated output of the sorbent model showing diffusion effects
(right) average model response for different entropies and enthalpies of zwitterion formation:
bot.-left: low-high; top-left: low-low; bot.-right: high-high; top-right: high-low

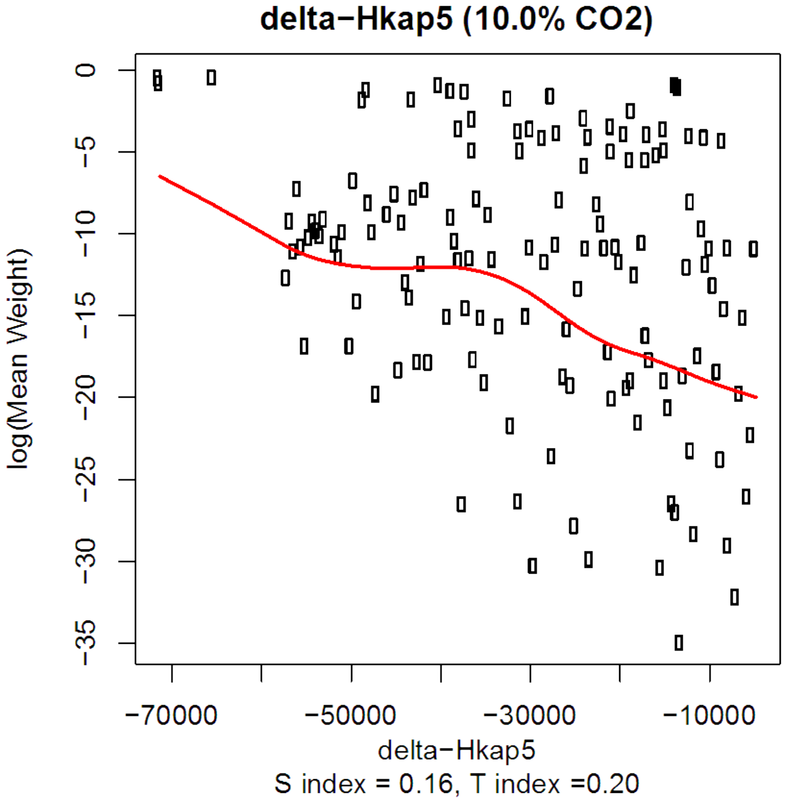
anhydrous model

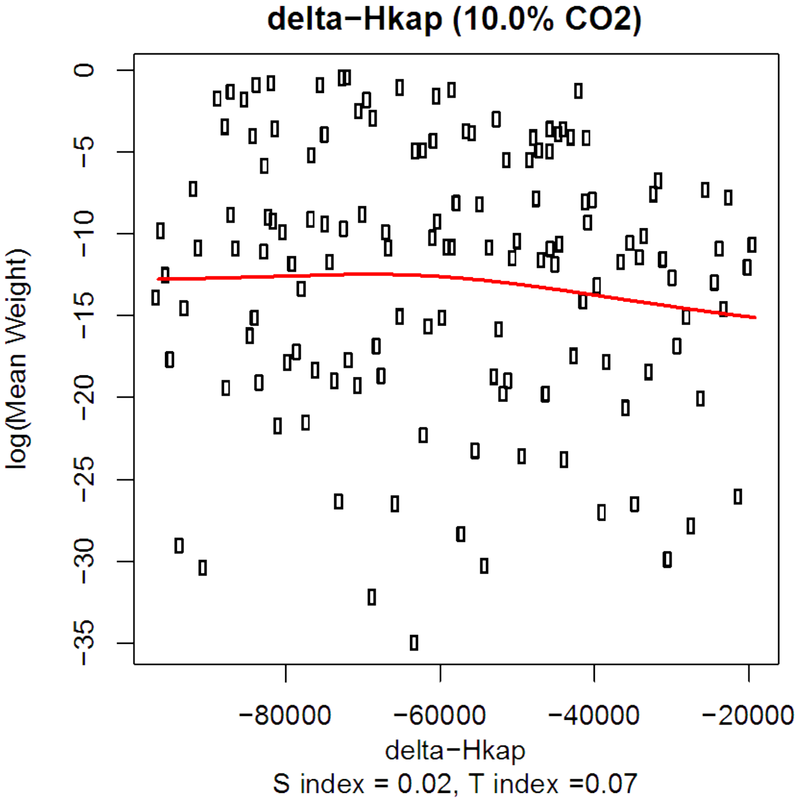




(left) total variance metric for all model parameters
(right) average model response for different entropies and enthalpies of zwitterion formation:
bot.-left: low-high; top-left: low-low; bot.-right: high-high; top-right: high-low

anhydrous model





(left) scatter plot of model sensitivity to formation enthalpy of zwitterions
(right) scatter plot of model sensitivity to formation enthalpy of carbamate

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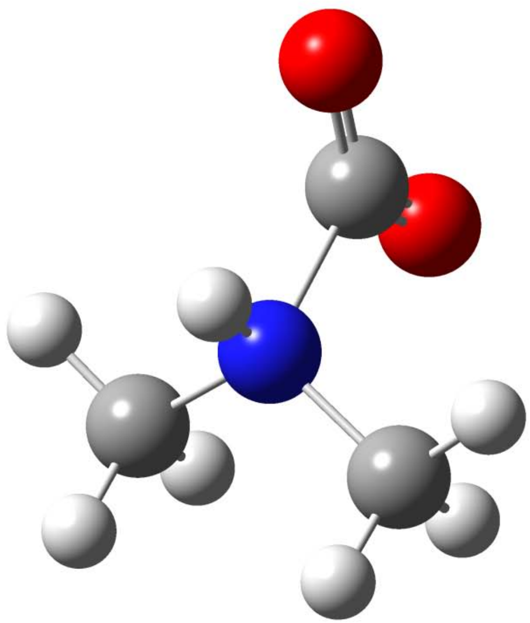
quantum chemistry



CO_2-DMA zwitterion

zwitterion stability (DFT-B3LYP)

ε_r = 1	ΔE = +147.0 kJ/mol
ε_r = 3 (DPA)	ΔE = +96.6 kJ/mol
ε_r = 80 (H_2O)	ΔE = -12.6 kJ/mol

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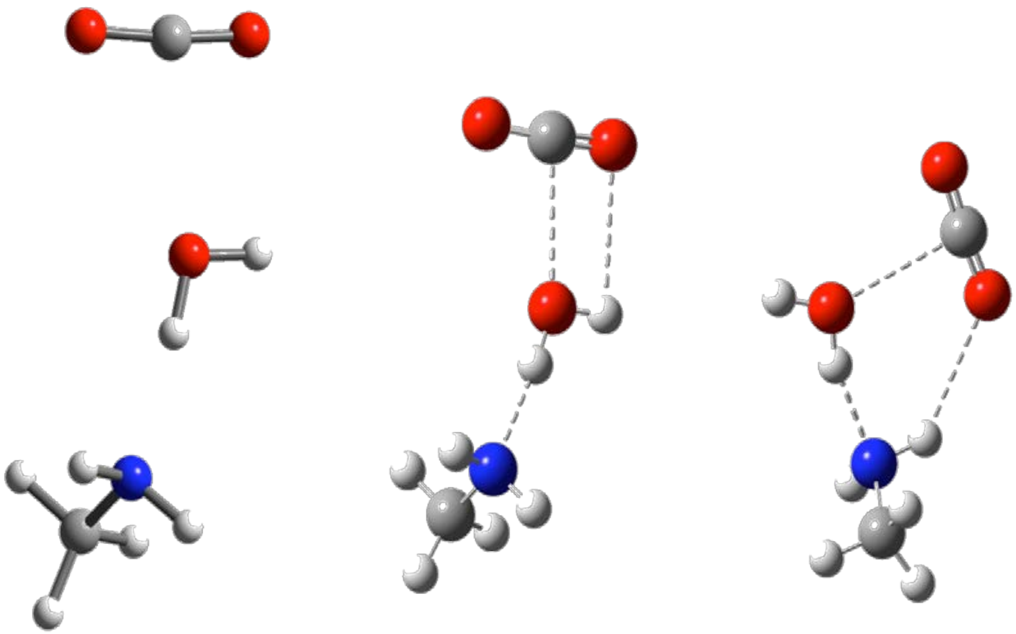
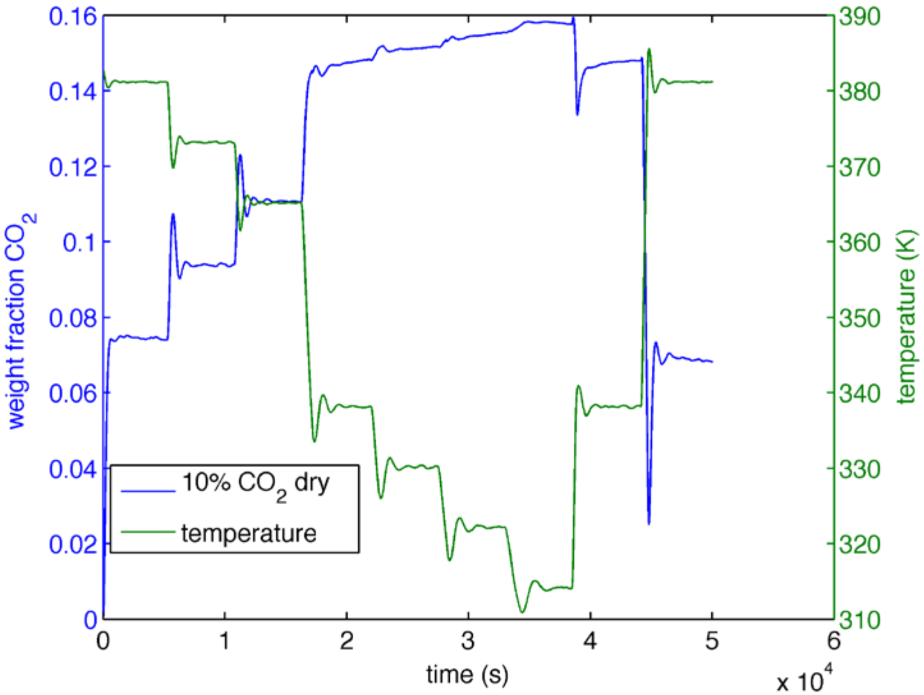
quantum chemistry

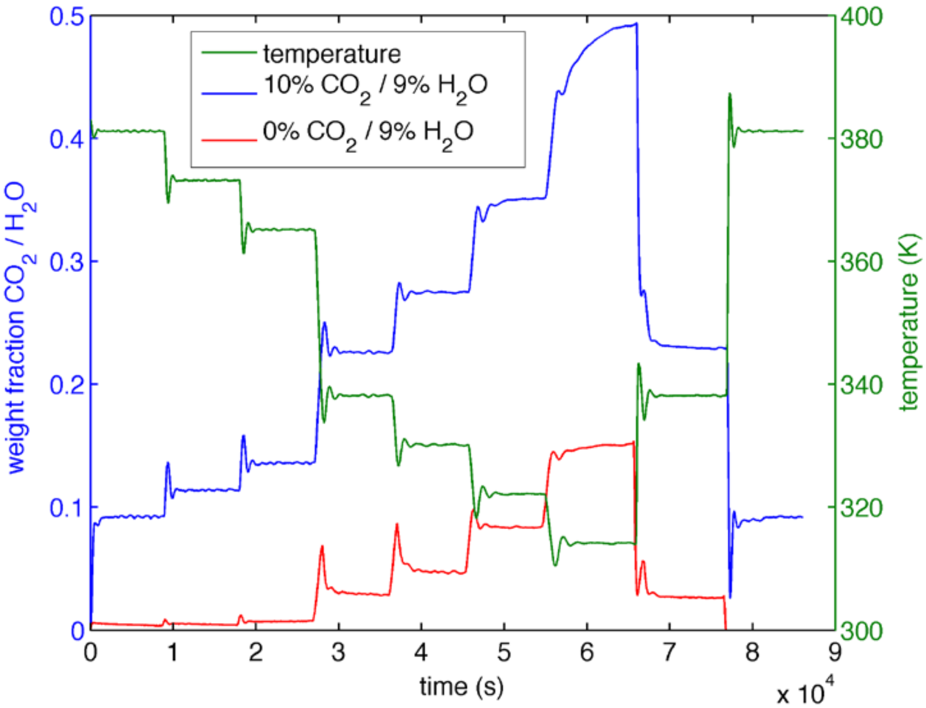


(left) MMA + H_2O + CO_2
(middle) linear topology
(right) ring topology

- linear topology:
  ΔE = -16.2 kJ/mol
- ring topology:
  ΔE = -34.4 kJ/mol

anhydrous model





(left) TGA data for NETL-196C in 10% CO_2 and **nominally** dry conditions
(right) TGA data for NETL-196C in 10% CO_2 (blue) and 0% CO_2 (red) with 9% H_2O

conclusions

- Transport of CO_2 within the amine bulk controls not only the kinetics but the apparent capacity of PEI-impregnated silica sorbents.
- These sorbents depend on water to open up the bulk amine sites for CO_2 adsorption.
- Adsorption measurements in nominally dry conditions will therefore be misleading, significantly underestimating the capacity for carbamate formation in H_2O-saturated flue gas.

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- Joanne R. Wendelberger, LANL
- Greg Ball, NETL

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