Amine-Modified Multiscale Materials for Reversible CO₂ Capture

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3rd Annual Conference on Carbon Capture and Sequestration
May 4, 2004

Acknowledgements
- Project Team: Richard Zheng, Leo Fifield, Glen Fryxell, Diana Tran, Shane Addleman, Daryl Brown, Tom Zemanian
- Project Support: PNNL’s Carbon Management Laboratory Directed Research and Development Initiative
- Helpful Discussions: Jon Gibbons, Imperial College; Ken Humphreys & Pete McGrail, PNNL

Carbon Capture with Solid Materials
- Goal: Explore and develop functional multiscale materials to serve as reliable & regenerable sorbents for the capture of CO₂ from industrial processes such as fossil fuel power plants.

- Issues:
  - Surface Chemistry/Capacity: Can a solid-based system be made that competes with traditional wet amine systems?
  - Thermal and Chemical Stability: Can the materials remain durable with high reversible capacity in flue gas conditions over long periods of time?
  - Cost: Can these materials be produced and implemented in process systems affordably on a life cycle basis?

Solid vs. Liquid Capture
- Pros:
  - Since all functional groups are at the surface, there is effectively no liquid side mass transfer resistance.
  - In ideal configuration, there is no downstream purification of CO₂ required after regeneration.
  - No liquid handling required.

- Cons:
  - Not possible to store captured CO₂ and regenerate at preferred times (e.g., when power demand is low).
  - No possibility for sorbent make up unless moving bed or fluidized bed system is developed.

Project Scope
- Synthesize new materials and new functional approaches
- Characterize materials in bench scale CO₂ capture apparatus to assess total and working capacity
- Characterize material structure and mechanism for adsorption (NMR, FTIR, Raman, TGA, electron microscopy)
- Understand durability of materials under repeated cycling and exposure to potential poisons: SO₂, H₂S, and NOₓ.
- Understand the impact of water vapor on CO₂ capture
- Develop process concepts and flowsheets for implementation
- Perform preliminary economic analysis

Temperature Swing Adsorption
- Use high surface area materials → inherently high capacity.
- Large pore volume and surface functionalization useful to reduce mass transfer resistances. This will increase operating capacity.
- Use material classes that allow facile chemical functionalization.
- Thermal integration with power plant is critical.
Functional Multiscale Materials
Ordered Mesoporous Oxides & Aerogels

Applications
- Catalysis
- Gas or liquid phase separations
- Chemical storage
- Sensors

Carbon Nanotube Composites, Carbon Fibers

EDA Functionalized Silica

Synthesis
Condensation of an EDA-alkoxysilane and silanols on silica surface.

Substrate: SBA-15 mesoporous silica
- pore diameter 5.5-7.8 nm, surface area 700 m²/g

NH₂
NH
Si(OCH₃)₃
NH₂
NH
SiOH
O O
3CH₃OH
OH OH
Silica
OH OH OH OH
Silica

Ref: Turbomolecular Roughing Pump
Power: 25°C
Meas. CO₂ level from RGA
△P & Isotherms measured

Absorbance (a.u.)
Wavenumbers (cm⁻¹)

(a) SBA-15
- 3476 cm⁻¹ free silanol OH
- 3432 cm⁻¹ associated OH
- 1629 cm⁻¹ adsorbed H₂O

(b) EDA-SBA-15
- 3362 cm⁻¹ N-H asym. stretch
- 3299 cm⁻¹ N-H sym. stretch
- 2931 cm⁻¹ C-H asym. stretch
- 2881 cm⁻¹ C-H sym. stretch
- 1601 cm⁻¹ N-H deformation
- 1457 cm⁻¹ CH₂ scissor
- 1410 cm⁻¹ (EDA-silane)
- 1346 cm⁻¹ CH₂ wagging

FTIR spectra confirm presence of EDA functional groups in sorbent.

CO₂ Sorption Bench
- CO₂ levels of 1-50% possible
- SO₂ examined using mixtures
- CO₂ level measured with RGA
- △P & Isotherms easily measured

CO₂ Sorption Cell
- CO₂ mix
- N₂
- Ar
- Adsorption Cell
- Turbomolecular Pump
- RGA
- Roughing Pump
- Vent

Breakthrough Testing
Type of Measurements:
- Adsorption capacity
- Adsorption kinetics
- Desorption temperature

CO₂ mass spec signal (a.u.)
Wavenumbers (cm⁻¹)

Breakthrough curve data
- Measured breakthrough curve data
- Best-fit breakthrough using the Wheeler equation

Amount of CO₂ adsorbed at complete breakthrough
Amount of CO₂ adsorbed when CO₂ concentration in the eluted gas averages 1 vol%
Amount of CO₂ eluted at complete breakthrough

Data:
- Wheeler Eqn (Wood, 2002)

\[ w_c = \frac{W_c}{W_i} = \frac{Q_L}{K_v} \left( \frac{C_C - C}{C} \right) \]

Capacity and Rate Coefficient Data:
- \( w_c \) = 12.1 mg/g (Wheeler equation)
- \( K_v \) = 414.2 min⁻¹ (Wheeler equation)
- \( w_c \) = 19.3 mg/g (by integration at complete breakthrough)
- \( w_c \) = 10.2 mg/g (by integration at 1% breakthrough)
FTIR – Reaction with CO₂

Free amine groups are abundant in regenerable sorbent. 1602 cm⁻¹ NH₂ deformation vibrations 1449 cm⁻¹ CH₂ deformation vibrations 1576 cm⁻¹ NH₂ deformation vibrations

Upon exposure to CO₂ at room temperature, the sorbent forms an intramolecular carbamate ammonium salt. 1688 cm⁻¹ CH₂ stretch (Amide I band)
1416 cm⁻¹ Amide II band

IR band assignments are tentative. Experiments to confirm urea formation in progress.

Mechanism (Ethylene Diamine)

Stability of Zwitterionic compound (intramolecular carbamate) governs ease of regeneration and working capacity

FTIR – Effect of SO₂ exposure

(a) Sample exposed to ambient air
1576 cm⁻¹ NH₂ deformation
1484 cm⁻¹ unassigned
1416 cm⁻¹ unassigned
1320 cm⁻¹ CH₂ wagging
795.6 cm⁻¹ Si–O–Si sym. stretch

(b) Sample exposed to 500ppm SO₂, 21% CO₂, and balance N₂
Band structure same as (a) except for one new band:
619.7 cm⁻¹ SO₂ bending in -NH-SO₂ complex

It is believed that SO₂ reacts with secondary amine to form a charge-transfer complex. Determination of the fate of the SO₂ adduct upon heating is likely reversible based on Diaz, Garcia, and Beckman (1994).

Performance – Dry vs. Wet

- 100% indicates capacity to full breakthrough. 1% indicates working capacity for total equivalent slip of 1% CO₂
- Data pertain to CO₂ in N₂
- Wet corresponds to 2% H₂O in gas mixture
- Little difference in capacity when water is added to the stream indicates good selectivity.

TGA-MS Analysis: Thermal Stability

- Mass loss indicates significant desorption events.
- Mass spectrometry indicates what comes off sorbent.
- In He, EDA decomposes above 400°C.
- In air, EDA decomposes above 200°C.

Parallel Bed: Thermal Swing

Stack Gas
Heat for Regen.
Unit 2
Stack Outlet

Regeneration
Sorption

Condenser
Dryer
Compressor

CO₂ Injection

Unit 1

Equilibrium bed:
- High CO₂ concentration

Equilibrium bed:
- Low CO₂ concentration

Inlet
Outlet
Economics
It is essential to perform economic analysis in tandem with technical discovery and development in order to guide work in direction of commercial viability.
- Preliminary economics suggest approach could be attractive with future expected improvements.
- Preliminary model is based on adaptation of carbon adsorber model available from EPA for VOC capture.
- Expecting posting of a new solid-based capture model from NETL soon.

Future Work
- Continue to develop additional amine-modified materials.
  - Fill in operating temperature gaps in order to make applicable to many streams.
- Complete economic analysis and use as a basis for R&D targets.
- Look at steam regeneration.
  - Trend of higher working capacity
  - Also trend of more difficult regeneration

Various Approaches Possible
- Target ligands result in facile proton transfer during H uptake
- Multifunctional ligands also attractive.
- Polymeric and dendrimeric functionality are being examined

Immediate Targets
- Propyl Amine (verify comparison to NETL literature)
- Piperazine (determine impact of ligand rigidity and amine degree)
- Propylene Diamine (determine impact of carbamate ring size)

Aminomethyl Imidazole (examine cyclic compounds with potential multifunction)
Various Polymeric Species (multifunctional approach)