A Solid Sorbent Technique to Capture CO_2 From Flue Gas

the ENERGY lab

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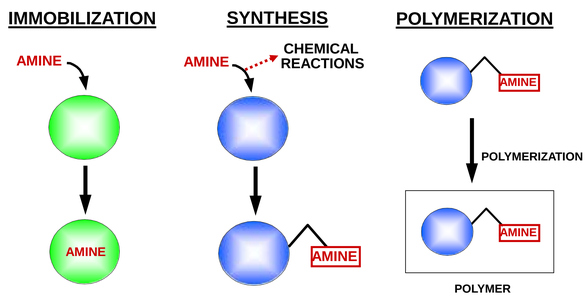
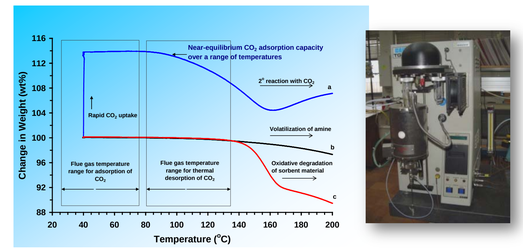
Overall Research Objectives

- **To develop solid, durable, regenerable sorbents that have a high selectivity and high adsorption capacity for CO_2 at conditions suitable for post-combustion capture.**
- **To ensure that engineering and reactor design issues are addressed in the sorbent development towards commercialization.**
- **To ultimately meet the programmatic goal for energy conversion systems that can remove 90% CO_2 while keeping the increase in cost of energy service below 35%.**

Pathways to Solid Amine Sorbents



Thermogravimetric Analysis Studies—Sorbent Evaluation



The rationale for examining dry, regenerable sorbent-based CO_2 capture processes lie in their potential of being more energy efficient as compared to traditional liquid amine scrubbing processes. Such energy reductions are envisioned in part from substantially higher CO_2 delta loadings (i.e., difference in loading at end of adsorption exposure to CO_2 and at the end of desorption).

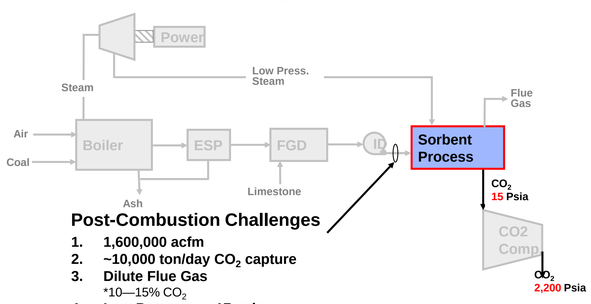
Candidate Reactor Designs*

- **Structured Bed Concept**
  - Fixed bed sorber, with internal heat removal
  - Internal heating of same bed for regeneration
- **Moving Bed Concept**
  - Moving bed sorber, with internal heat removal
  - Moving bed regenerator, with internal heating
- **Fluidized Bed Concept**
  - Fluid bed sorber, with internal heat removal
  - Moving bed regenerator, with internal heating
- **Fixed Bed Adsorber Concept**
  - Fixed bed sorber, adiabatic, multi-stage with interstage heat removal
  - Heating of same bed for regeneration with hot fluid stream
- **Transport Reactor**
  - Circulating fluid bed sorber
  - Circulating fluid or moving bed regenerator

Hoffman et al. "Factors in Reactor Design for Carbon Dioxide Capture with Solid, Regenerable Sorbents," Proceedings of the 33rd International Technical Conference Coal Utilization and Fuel Systems, 2008.

Postcombustion CO_2 Capture With Sorbent

Where does it fit?



Post-Combustion Challenges

1. **1,600,000 acfm**
2. **~10,000 ton/day CO_2 capture**
3. **Dilute Flue Gas**
   *10—15% CO_2
4. **Low Pressure —17 psia**
   *Decreased separation driving force
5. **High moisture content**
6. **Thermal need for regeneration**

NETL Immobilized Amine Sorbents

- **Polar liquid mixture containing polyethylenimine (or high molecular weight, linear ethylene amines) with additives**
- **Near-pore saturation of silica-based supports**
- **Advantages**
  - –Simplistic synthesis technique
  - – Materials are commercially available and low cost
  - – Fabrication of large batches easily performed
  - – Particle size adaptable to reactor design
- **U.S. Patent 7,288,136**

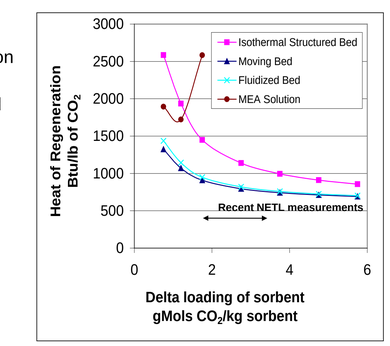
Summary for Basic Immobilized Amine Sorbent

- High delta loadings in the 3-4mol/kg range
- CO_2 regeneration improbable
- Stable at elevated temperatures
- Silica substrate candidate of choice
- Loading results confirmed by TVA and ADA-ES
- Moisture adsorption may impact energetics
- Susceptible to poisoning with SO_2 and NO_2; upstream cleaning required in process
- Kinetic study conducted

Schematic and actual pilot unit

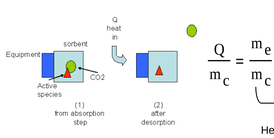
Regeneration Energy versus Sorbent Loading for Various Reactor Designs

- **Includes:**
  - Heat of sorption
  - Sensible heat of sorbent and equipment vessel walls
- **Excludes:**
  - Pumping, compression, cooling, conveying materials

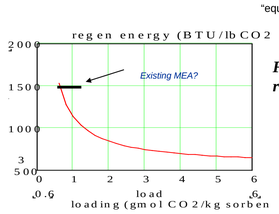


Results depend on the reactor to handle the sorbent

Regeneration Energy for Solid Sorbents TSA



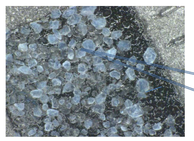
$$\frac{Q}{m_c} = \underbrace{\frac{m_e}{m_c}\cdot C_e\cdot\Delta T}_{\text{Heating the "equipment"}} + \underbrace{\frac{B}{L}\cdot C_s\cdot\Delta T}_{\text{Heating The sorbent}} + \underbrace{C_{p,c}\cdot T_2 - C_s\cdot T_1}_{\text{Enthalpy change Between gaseous } CO_2 \text{ and sorbent}} + \underbrace{\frac{Q_r}{m_c}}_{\text{Heat of reaction}}$$



For a given ΔT, regeneration energy may be reduced by:

1. *increasing CO_2 capture loading (L)*
2. *decreasing specific heat of the sorbent (C_S)*
3. *Find a sorbent with lower heat of reaction Q_r*

Supported Polyethylenimine (PEI) on Silica



Amine Deposition on Silica Support

$H—(HN—CH_2\ CH_2—)_n—NH_2$

CARiACT G and Q series (Silica)
50X magnification

- Surface Area—294 m^2/g, 300 m^2/g
- Pore Volume— 1.77 ml/g, 1.22 ml/g
- Pore Diameter—24 nm, 10 nm

Particle size distribution—75-500 microns

Support Characteristics
- High purity, readily available material
- Water and attrition resistant

Poly(ethylenimine) Linear, M_w ca. 423
- Linear, high molecular polymer compound having a high density of amines. High ratio of secondary to primary amines.
- Favorable physical characteristics, i.e., high boiling point, low vapor pressure, and low viscosity.
- High amine loading/g of material.

Reactor RD&D Challenges

Laboratory

- **0.1 ft^3 Reactor Volume**
- **0.27 scf per minute**

Technically possible?

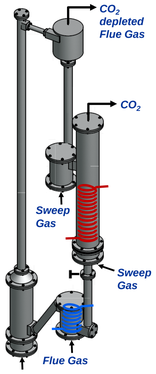
Scale-up

Economically feasible?

500 MW Commercial Power Plant

- **57,000 ft^3 Reactor Volume**
- **1,800,000 scf per minute**

Path Forward Towards Commercialization



- **Sorbent Development**
  - Conclude thermodynamic, physical, and kinetic information gathering and assure initial objectives met
- **Reactor Design Development**
  - Develop, apply, and validate computational fluid dynamics (CFD) models for solid sorbent-based CO_2 capture systems. Transport of sorbent between absorption and regeneration reactors desired
- **Systems Analysis**
  - Integrate sorbent and reactor development
  - Validate technical performance and economic advantages of sorbent process as compared to conventional techniques

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