Thirteenth Annual Conference on Carbon Capture, Utilization & Storage

*Post Combustion Capture Systems / Solid Sorbents*

# Post-combustion $CO_2$ Capture Using Metal Organic Frameworks

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April 28-May 1, 2014 • David L. Lawrence Convention Center • Pittsburgh, Pennsylvania

## Background

As part of GCEP-sponsored research:

- Develop preliminary systems-level performance and cost models for evaluation of new materials for $CO_2$ capture
- Incorporate these models in a broader power plant systems model such as the Integrated Environmental Control Model (IECM) to make comparative analyses

## Objectives

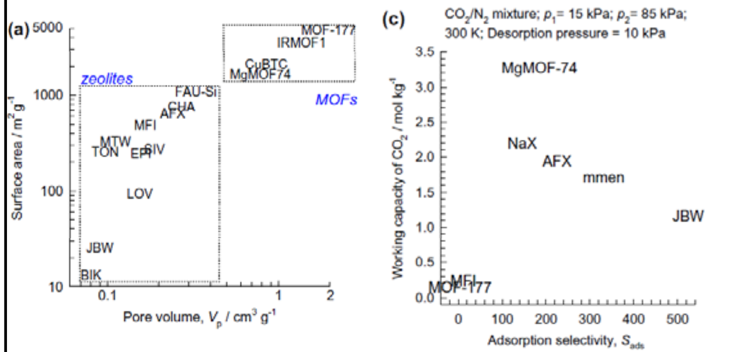
- Develop a preliminary performance model for evaluation of metal organic frameworks (MOFs) for post-combustion $CO_2$ capture
- Develop a preliminary thermodynamic model for pressure/vacuum swing adsorption (PSA/VSA)
- Compare the performance results with MEA-based $CO_2$ capture process

*Work in progress!*

## Sorbents for $CO_2$ capture

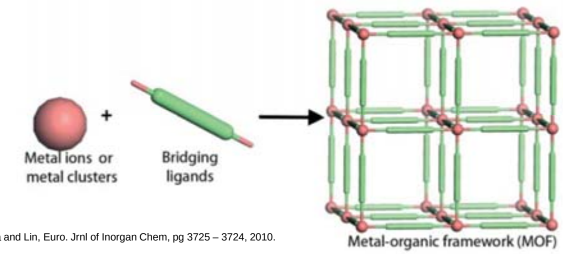
- Zeolites – porous crystalline aluminosilicates
  - Eg. Zeolite13X, NAX
- Amine-functionalized chemisorbents
  - Eg. PEI, NETL-32D
- Metal organic frameworks (MOFs)
  - MOF-5, MOF-177, Mg-MOF-74

## MOFs have better $CO_2$ capture properties than zeolites




Source: Krishna and van Baten, Separation and Purification Technology 87 (2012) 120–126

## Metal Organic Frameworks



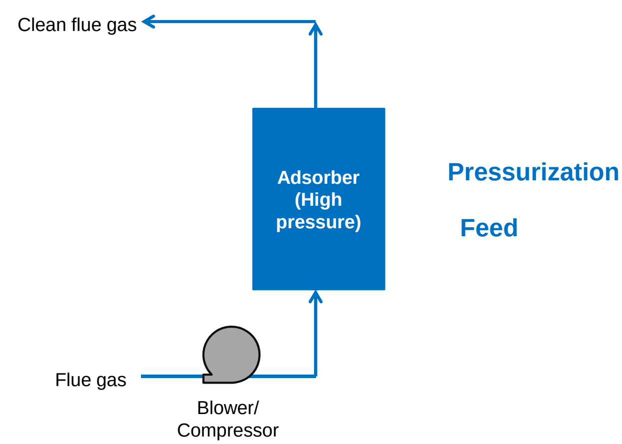

Source: Rocca and Lin, Euro. Jrnl of Inorgan Chem, pg 3725 – 3724, 2010.

- Metal-containing nodes linked by organic ligand bridges
- "Tunable" properties to enhance $CO_2$ capture
- Over 100 MOFs reported in literature
  - Typical metals – Cu, Ni, Al, Sc, Co, Mn
- Pressure swing adsorption and regeneration

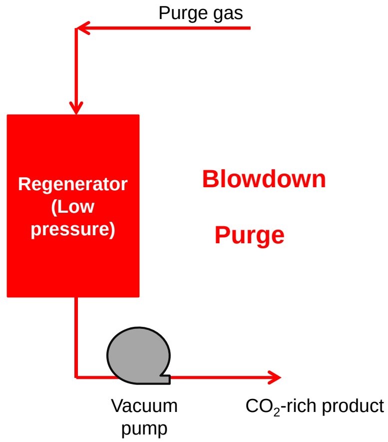
## Pressure/vacuum swing adsorption (PSA/VSA)

- Adsorption occurs at high pressure
  (*or at atmospheric pressure in VSA*)
- Desorption occurs when pressure is released
- Compared with thermal swing adsorption (TSA)
  - Shorter cycle times
  - Longer sorbent life, but …
  - Lower $CO_2$ product purity

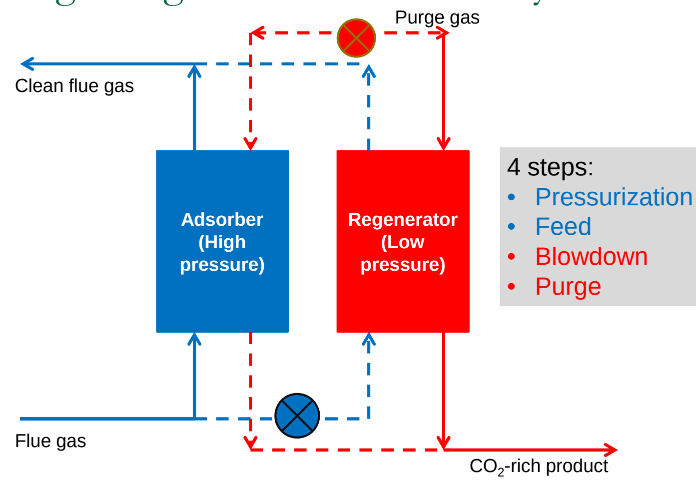
## Single-stage PSA – Skarstorm cycle



## Single-stage PSA – Skarstorm cycle




## Single-stage PSA – Skarstorm cycle



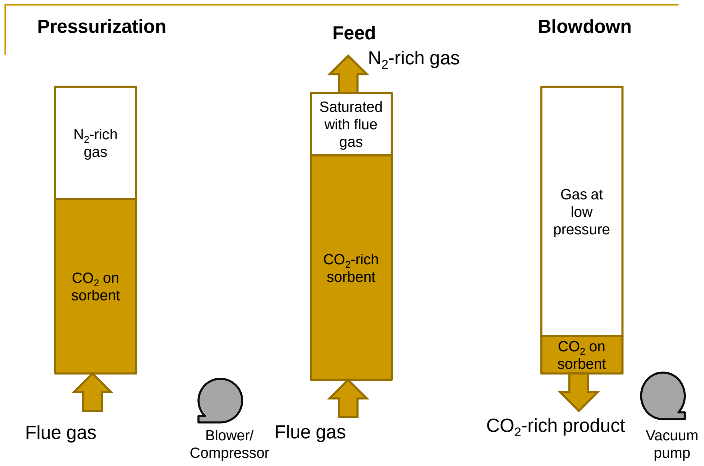

## Performance model

- For a given sorbent, desired $CO_2$ capture efficiency and operating conditions, estimate:
  - Amount of sorbent required
  - Amount of energy required
  - Purity of $CO_2$ product

## Simplified PSA/VSA model*

- Three steps:
  - Pressurization (adsorption)
  - Feed (adsorption)
  - Blowdown (desorption)
- Atmospheric pressure adsorption, vacuum pressure desorption
- Equilibrium conditions
- Cyclic steady state
- Single-stage operation

*Maring and Webley, Intl Jnl of Greenhouse Gas Control, 15, pg 16 – 31, 2013.




Pressurization and blowdown steps are done in 100 increments, with equilibrium reached at each step

## A few model equations

$$n_{CO2,total} = n_{CO2,ads} + n_{CO2,gas}$$

$$n_{CO2,ads} = \frac{m_{CO2} b_{CO2} P_{CO2}}{1 + b_{CO2} P_{CO2}} \quad b_{CO2} = b_0 e^{\frac{Q_{CO2}}{RT}} \quad n_{CO2,gas} = \frac{y_{CO2} PV}{RT}$$

(Loadings calculated using Langmuir equilibrium model)

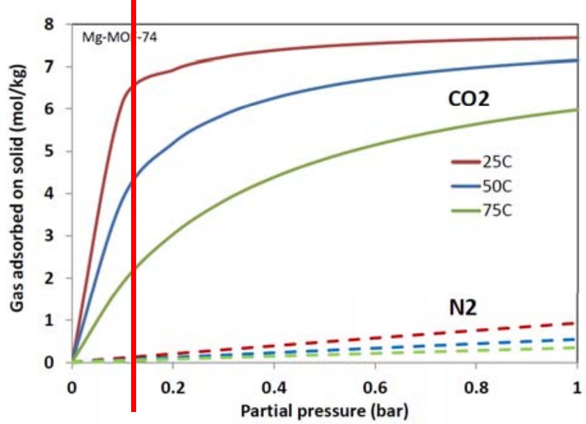
$$n_{CO2,product} = \sum_{1}^{Blowdown} y_{CO2,i} (n_{total,i} - n_{total})$$

$$Purity = \frac{n_{CO2,product}}{n_{CO2,product} + n_{N2,product}}$$

$$W_{vacuum} = \sum_{1}^{Blowdown} (n_{total,i} - n_{total}) \times \frac{1}{\eta} \left(\frac{k}{k-1}\right) T_{feed} \left( \left(\frac{P_1}{P}\right)^{\frac{k-1}{k}} - 1 \right)$$

$$Specific\ work = \frac{(W_{vacuum} + W_{blower})}{n_{CO2,product}}$$

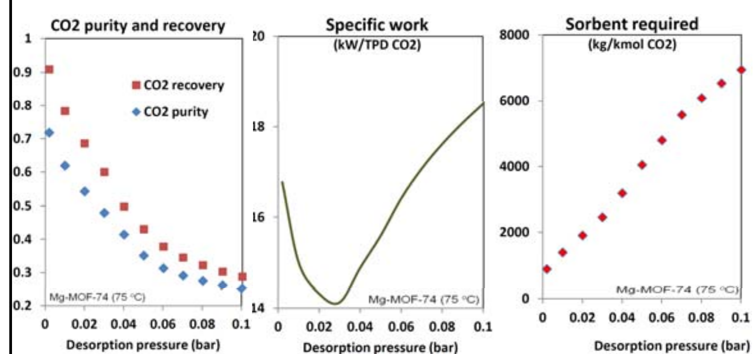
## Isotherms for $Mg_2$(dobdc) – MOF-74




$m_{CO2}$ = 7.9 mol/kg; $b_{0,CO2}$ = 1.56e-6 /bar; $Q_{CO2}$ = 42 kJ/mol
$m_{N2}$ = 14 mol/kg; $b_{0,N2}$ = 4.96e-5 /bar; $Q_{N2}$ = 18 kJ/mol

Mason et al. Energy and Environmental Science, 4, 3030 – 3040, 2011.

## Results from the single-stage VSA model




With single-stage VSA, high recovery and purity is possible only at very low desorption pressure.

## Preliminary case study

- Base plant (modeled using IECM 8.0.2)
  - 650 MWg, Appalachian Medium Sulfur coal
  - 11,310 kmol/hr $CO_2$ in flue gas (12% by volume)
- $CO_2$ capture using Mg-MOF-74 and VSA
  - 90% $CO_2$ capture
  - Desorption pressure 0.002 bar
  - Isothermal at 75°C
  - $CO_2$ product compressed to 135 bar

## Case study results

| | Base plant* | MOF-VSA $CO_2$ capture |
|---|---|---|
| Gross power out (MW) | 650 | 650 |
| Thermal energy input (MWth) | 1564 | 1564 |
| Net power out (MW) | 608 | 362 |
| Net plant efficiency (%HHV) | 39 | 23 |

Using a *single-stage* VSA process, energy penalty using MOFs is much higher compared to conventional MEA-based $CO_2$ capture

## Future work

- Improve the performance model
- Expand the model to incorporate multi-stage and advanced VSA cycles
- Explore better MOF materials
- Explore possibilities of combined PSA-VSA or TSA-VSA cycles
- Develop a cost model

## Acknowledgement

- This work is supported by Global Climate Energy Project (GCEP) at Stanford University

Thank you!

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