New Adsorption Cycles for CO_2 Capture and Concentration

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Presentation Overview

- project origin and 2nd year status
- results: adsorbent materials research
- results: adsorption cycle research
- remaining work to be done in 3rd year

Presentation Overview

- project origin and 2^{nd} year status

Background

- capture and concentration of CO_2 from coal-fired power plants and coal gasification processes imminent
- viable separations technology yet to be identified
- promising results obtained during 04 IC Phase I Project: "Radically New Adsorption Cycles for CO_2 Sequestration"
  - showed possibility of pressure swing adsorption (PSA) for CO_2 capture and concentration at high temperature

New Project Objective

<u>Three Year Continuation Grant</u>

- continue study of new PSA cycles for CO_2 capture and concentration at high temperature
  - two key features of these new PSA cycles
    - use of hydrotalcite like (HTlc) adsorbent
      - captures CO_2 reversibly at high T simply by changing P
    - heavy reflux (HR) PSA concept
      - allows heavy component (CO_2) to be obtained in high purity

Questions Being Addressed

- definitive equilibrium and kinetic properties of the HTlc adsorbent
- type of HR PSA cycle configuration that should be used
- economics of resulting HR PSA-HTlc process (Air Products and Chemicals, Inc.)

Major Outcome

- definitive analysis and viability of a HR PSA-HTlc process for CO_2 capture and concentration at high T

Accomplishments

HTlc Materials Research

- devised mechanism to describe adsorption and desorption behavior of CO_2 on K-promoted HTlc
    - associated with completely reversible adsorption, diffusion and reaction phenomena
- developed non-equilibrium kinetic model
    - describes reversible adsorption and desorption behavior of CO_2 in a K-promoted HTlc
    - five times greater mass transfer coefficients validated
- validated non-equilibrium kinetic model using FTIR
    - observed rapid formation and depletion of carbonate species

Accomplishments

HR PSA Cycle Research

- modified stripping reflux (SR) PSA code
  - studied nine SR PSA cycle configurations with and without heavy and or light reflux steps
- determined light reflux step very important to process performance
  - made SR PSA cycle a dual reflux configuration
- determined mass transfer effects important
  - decreased mass transfer resistance allowed performance to exceed 90% CO_2 purity and 98% CO_2 recovery - first time
- including a recovery or feed plus recycle step, unequal step times, and equalization being analyzed
  - each expected to have impact on performance

Publications

- S. P. Reynolds, A. D. Ebner, and J. A. Ritter, "Stripping PSA Cycles for CO_2 Recovery from Flue Gas at High Temperature Using a Hydrotalcite-Like Adsorbent," *Ind. Eng. Chem. Res.*, **45**, 4278-4294 (2006).
- A. D. Ebner, S. P. Reynolds and J. A. Ritter, "Understanding the Adsorption and Desorption Behavior of CO_2 on a K-Promoted HTlc through Non-Equilibrium Dynamic Isotherms," *Ind. Eng. Chem. Res.*, 45, 6387-6392 (2006).
- S. P. Reynolds, A. D. Ebner and J. A. Ritter, "Carbon Dioxide Capture from Flue Gas by PSA at High Temperature using a K-Promoted HTlc: Effects of Mass Transfer on the Process Performance," *Environmental Progress*, 25, 334-342 (2006).
- A. D. Ebner, S. P. Reynolds and J. A. Ritter, "Non-Equilibrium Kinetic Model that Describes the Reversible Adsorption and Desorption Behavior of CO_2 in a K-Promoted HTlc," *Ind. Eng. Chem. Res.*, 46, 1737-1744 (2007).
- S. P. Reynolds, A. Mehrotra, A. D. Ebner and J. A. Ritter, "Heavy Reflux PSA Cycles for CO_2 Recovery from Flue Gas. Part I. Performance Evaluation," *Adsorption,* submitted (2007).

Presentations

- S. P. Reynolds, A. Mehrotra, A. D. Ebner, and J. A. Ritter, "Novel Heavy Reflux Cycles in Pressure Swing Adsorption Processes," Fundamentals of Adsorption FOA9, Giardini Naxos, Italy, May 2007.
- A. D. Ebner, S. P. Reynolds and J. A. Ritter, "Non-Equilibrium Kinetic Model for the Reversible Adsorption of CO_2 on a K-Promoted HTlc," AIChE 2006 Annual Meeting, San Francisco, CA, November 2006.
- S. P. Reynolds, A. D. Ebner and J. A. Ritter, "Novel Heavy reflux PSA Cycles for the Recovery of Carbon Dioxide at high temperature with K-Promoted HTlc," AIChE 2006 Annual Meeting, San Francisco, CA, November 2006.
- S. P. Reynolds, A. D. Ebner, and J. A. Ritter, "Non-Equilibrium Dynamic Adsorption and Desorption Isotherms of CO_2 on a K-Promoted HTlc," 4^{th} Pacific Basin Conference on Adsorption Science and Technology, Tianjin, China, May 2006.
- S. P. Reynolds, A. D. Ebner, and J. A. Ritter, "Capture of CO_2 from Flue gas by PSA using K-Promoted HTlc: Mass Transfer Effects," 4^{th} Pacific Basin Conference on Adsorption Science and Technology, Tianjin, China, May 2006.

Students Supported

- Steven P. Reynolds, PhD, USC. Steven, while being supported through this grant, and a MeadWestvaco Fellowship, worked on PSA code development, and has carried out thousands of simulations and corresponding analyses of nine different SR PSA cycle configurations. He graduated with his PhD in May 2007 and is currently working for Fluor.
- Hai Du, PhD candidate, USC. Hai, as a relatively new PhD student in the group and while being supported through this grant and a MeadWestvaco Fellowship, recently began working on the synthesis and characterization of K-promoted HTlcs for high temperature CO_2 capture and concentration. Results from his work are forthcoming.
- Amal Mehrotra, PhD candidate, USC. Amal, as a new PhD student in the group that joined in August 2006 was brought in to take Steven's place. He is being supported through this grant and a MeadWestvaco Fellowship. Amal has been coming up to speed very quickly on PSA code development and has been carrying out simulations of novel PSA cycle configurations that include recovery and feed plus recycle steps. He will remain on this project until its completion.
- Shubhra J. Bhadra, new PhD Candidate, USC. Shubhra will join the group in August with an MS from Singapore in PSA.

Presentation Overview

- results: adsorbent materials research

Adsorption and Desorption of CO_2 at High Temperature on K-Promoted HTlc

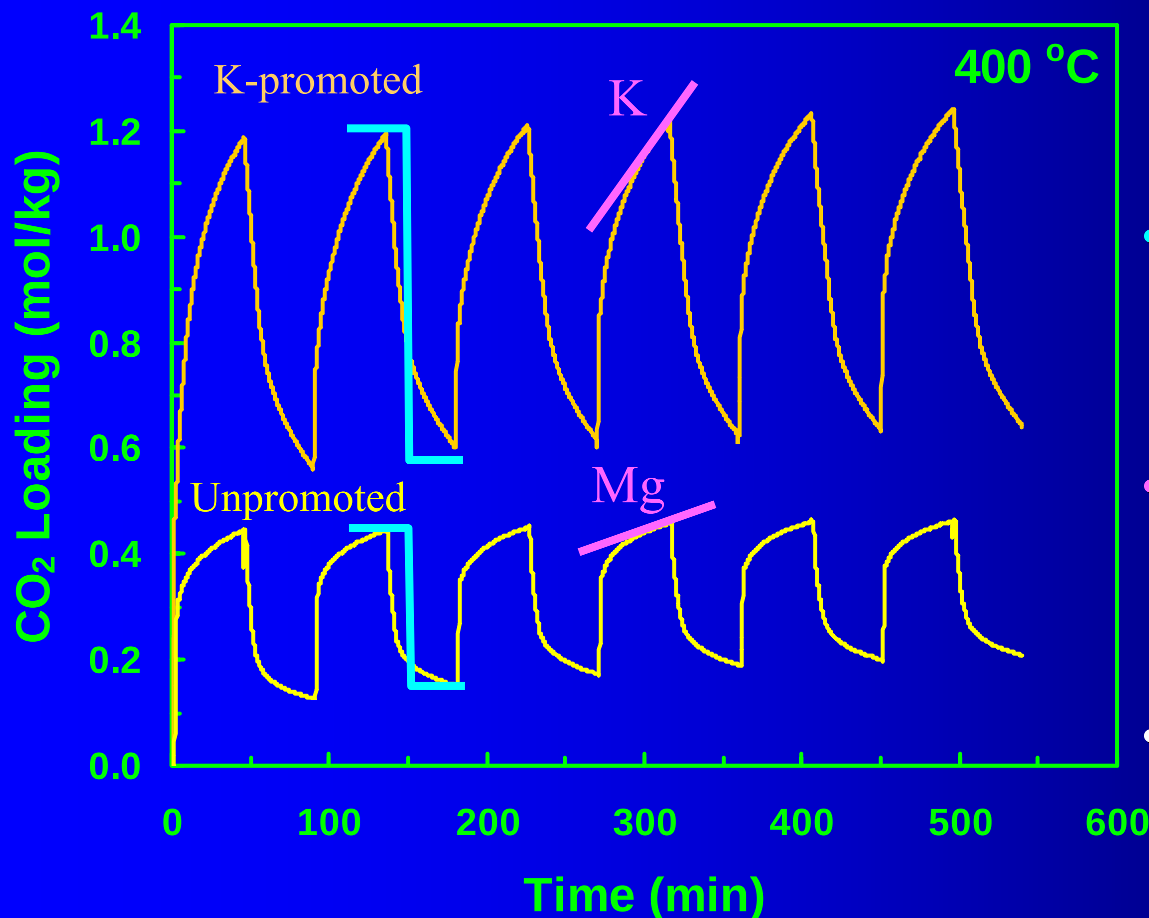
Objectives

…..Based on two key sets of experiments carried out with a K-promoted HTlc that provided clues on the controlling mechanism for CO_2 uptake and release:

- discuss dynamic thermo-gravimetric cycling experimental studies
- introduce non-equilibrium kinetic mechanism that describes the reversible uptake and release of CO_2 on a K-promoted HTlc at high Ts
- describe model combining adsorption, diffusion and reaction processes consistent with a Langmuir-Hinshelwood approach
- show FTIR results that validate the kinetic model

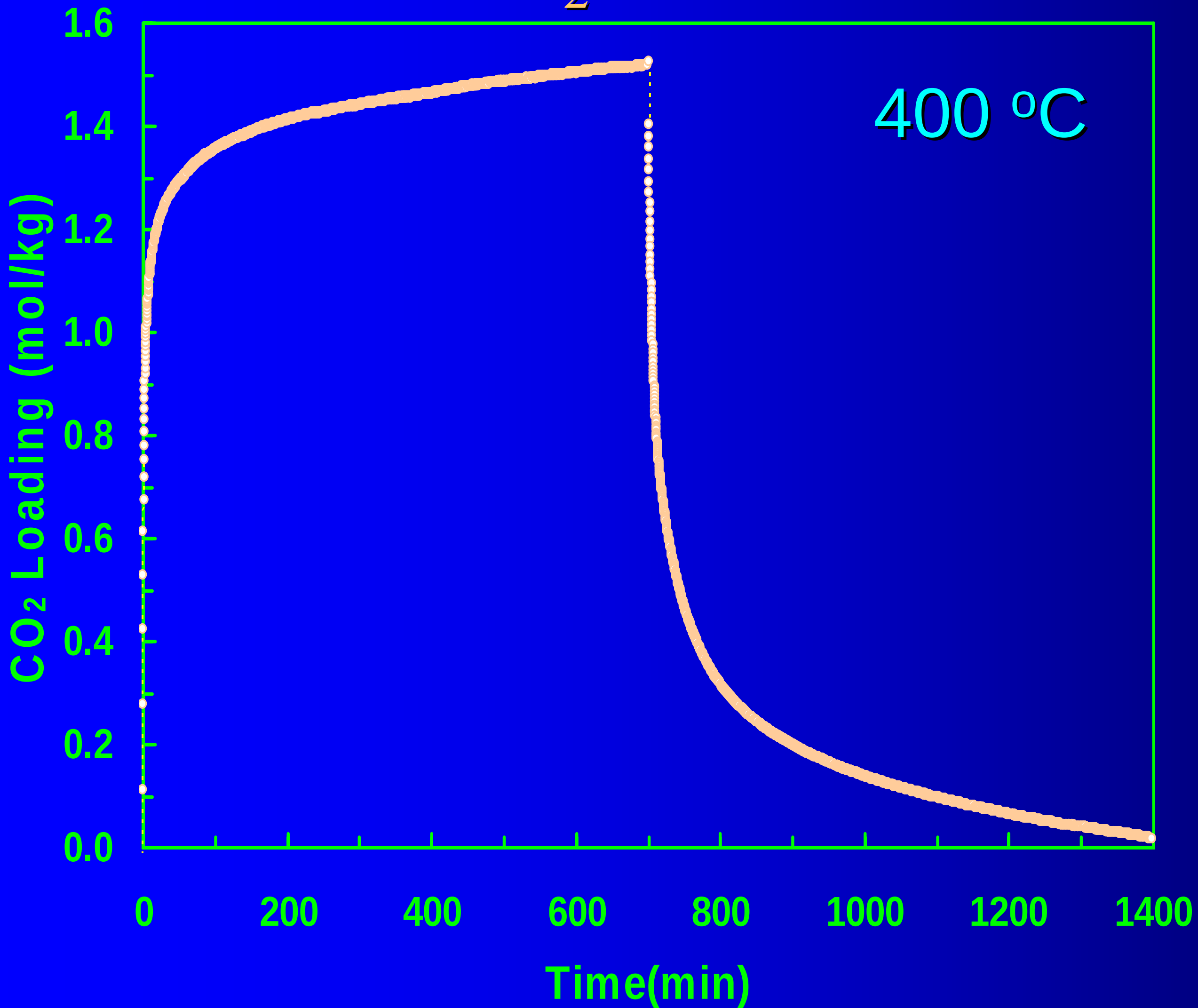
TGA: Promoted vs Unpromoted HTlc

$$[Mg_3Al(OH)_8]_2(CO_3)\cdot K_2CO_3\cdot nH_2O$$



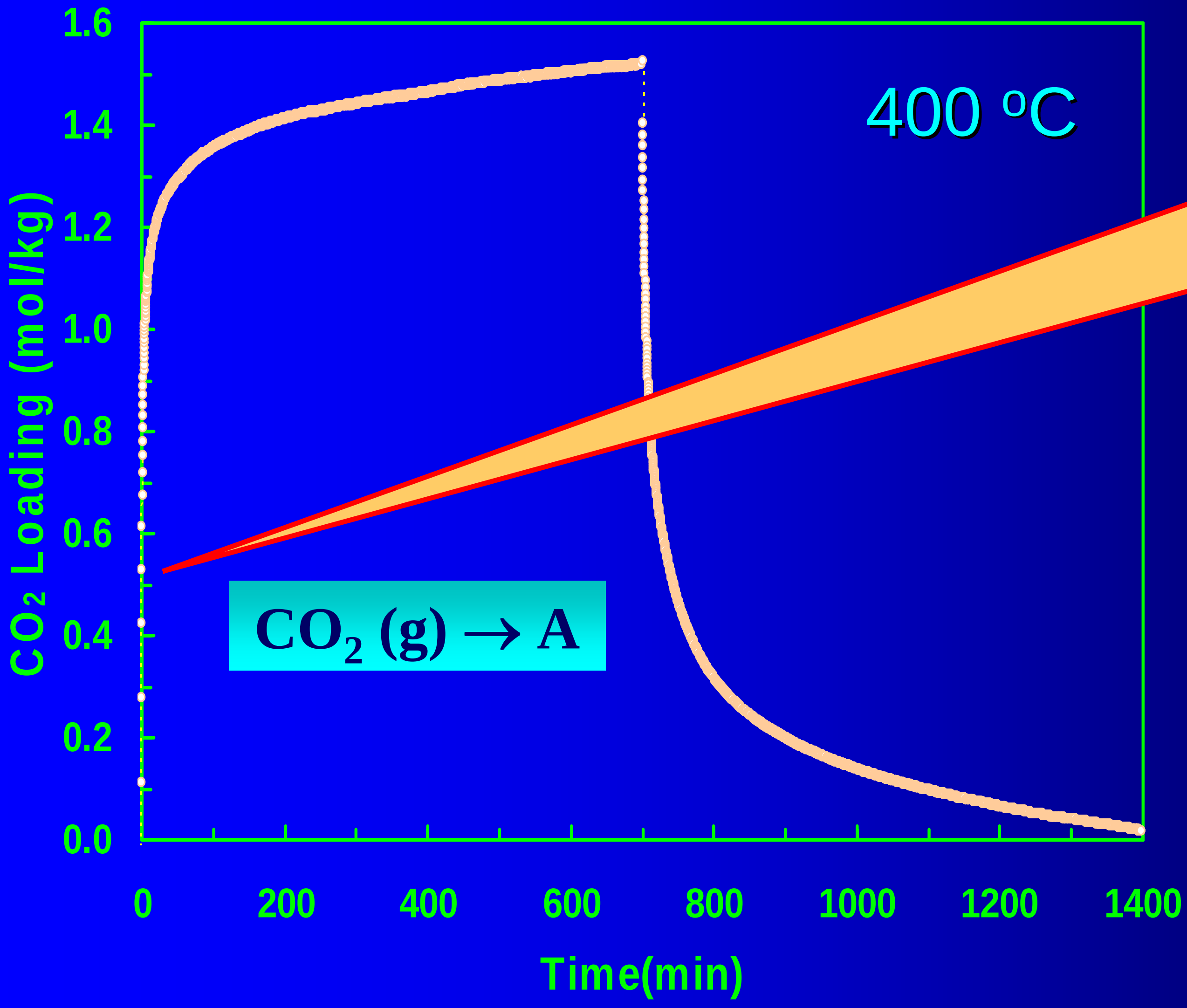
- TGA adsorption/desorption experiments at 400 ^oC clearly show the significant effect of K-promotion on HTlc.
- improvement possibly due to opening of crystal inter-layering spacing by potassium carbonate, and
- activation of a 2nd reaction mechanism (slow kinetics) barely perceived in pristine HTlc
- may be explained by replacement or addition of active K_2CO_3 for inactive $MgCO_3$ in the crystalline HTlc structure

Adsorption and Desorption of CO_2 on K-Promoted HTlc



Typical TGA result obtained just after activation, showing long term completely reversible behavior of CO_2 on K-promoted HTlc.

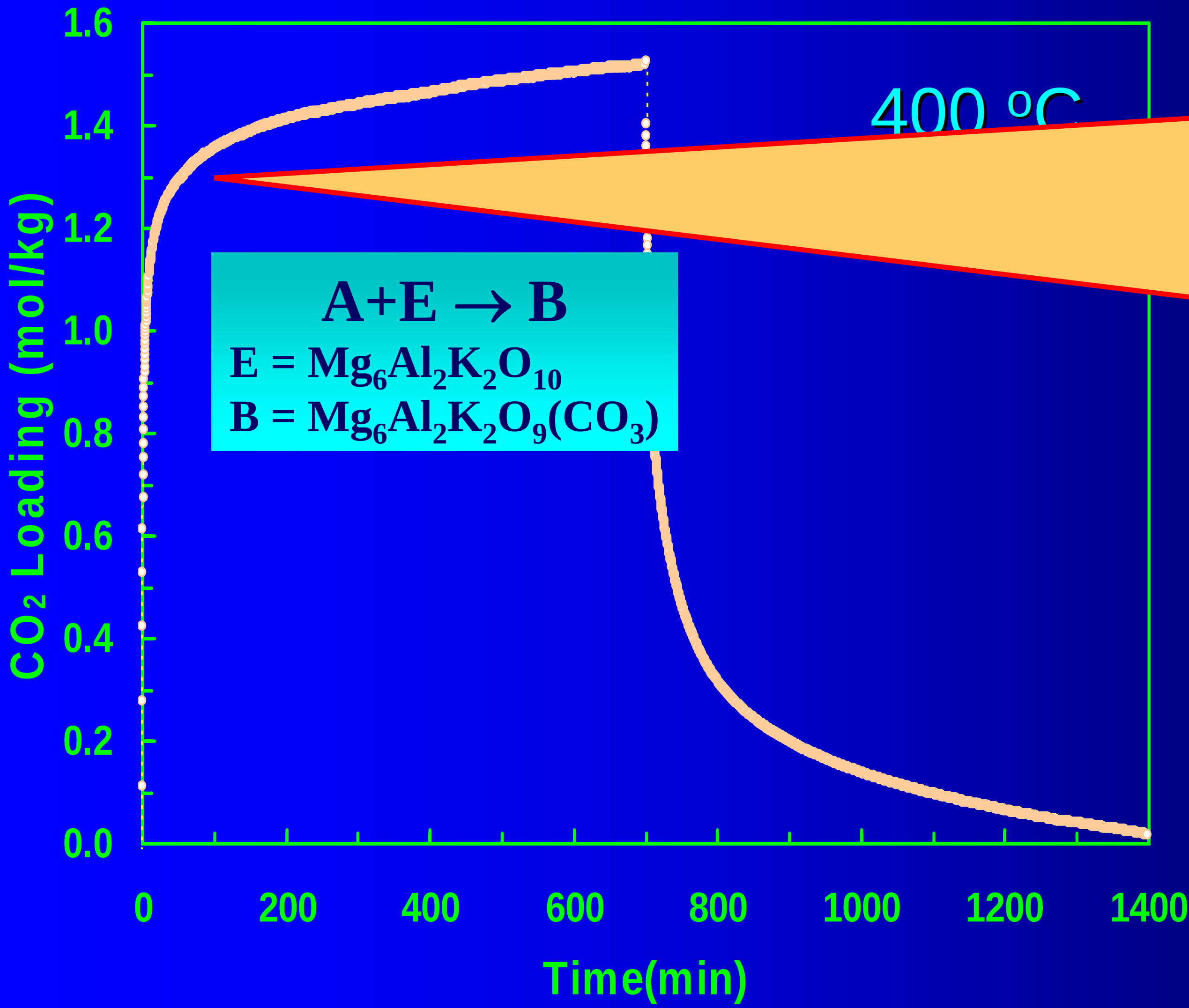
What we think is going on: adsorption.



ADSORPTION PATH:

- **After activation, CO_2 adsorption takes place through a fast MT limited process to form weakly sorbed phase A**

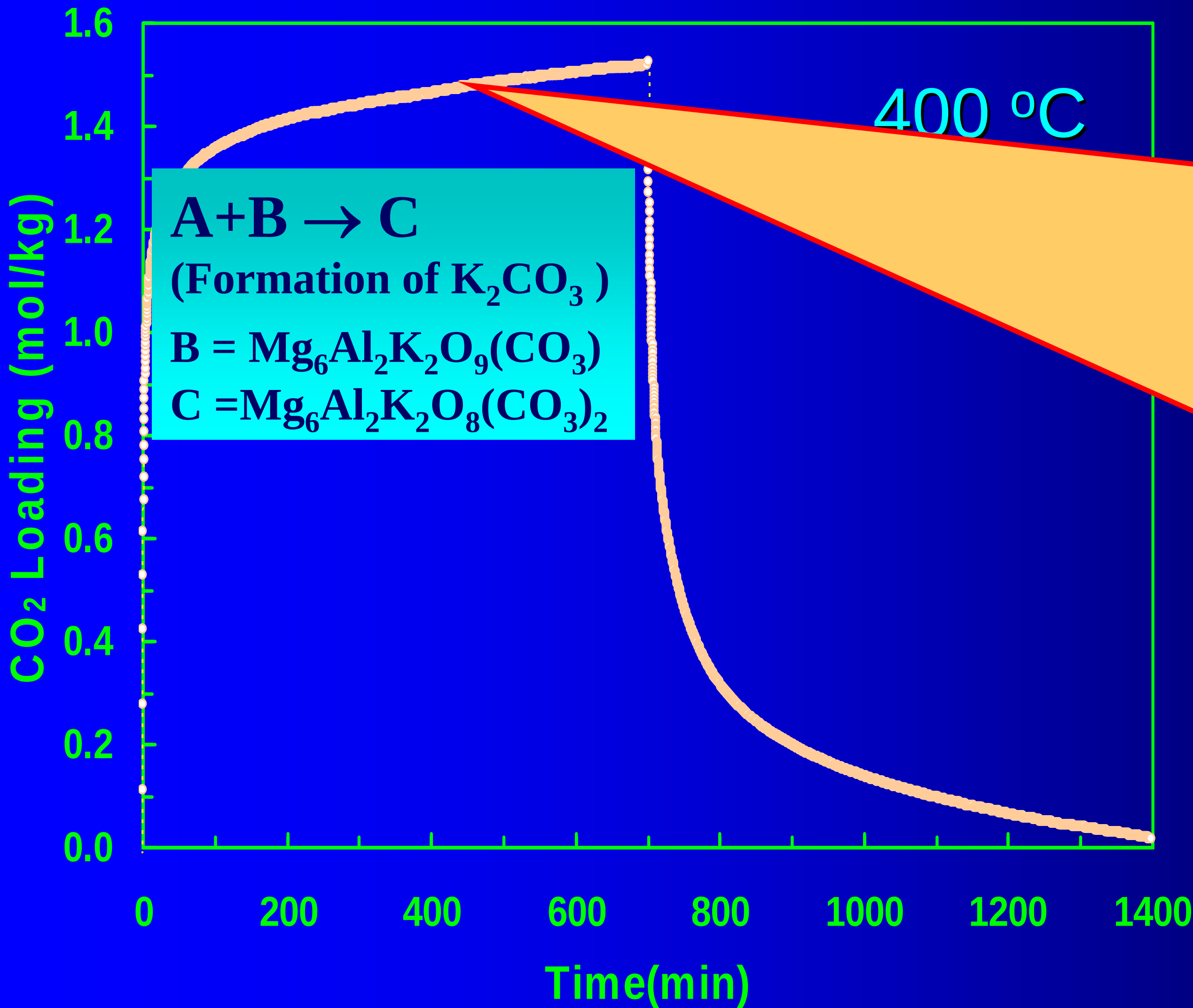
What we think is going on: adsorption.



ADSORPTION PATH:

- **After activation, CO_2 adsorption takes place through a fast MT limited process to form weakly sorbed phase A**
- **When adsorption slows down, process becomes controlled by reaction between diffusing phase A and empty crystal phase E to form intermediate phase B**

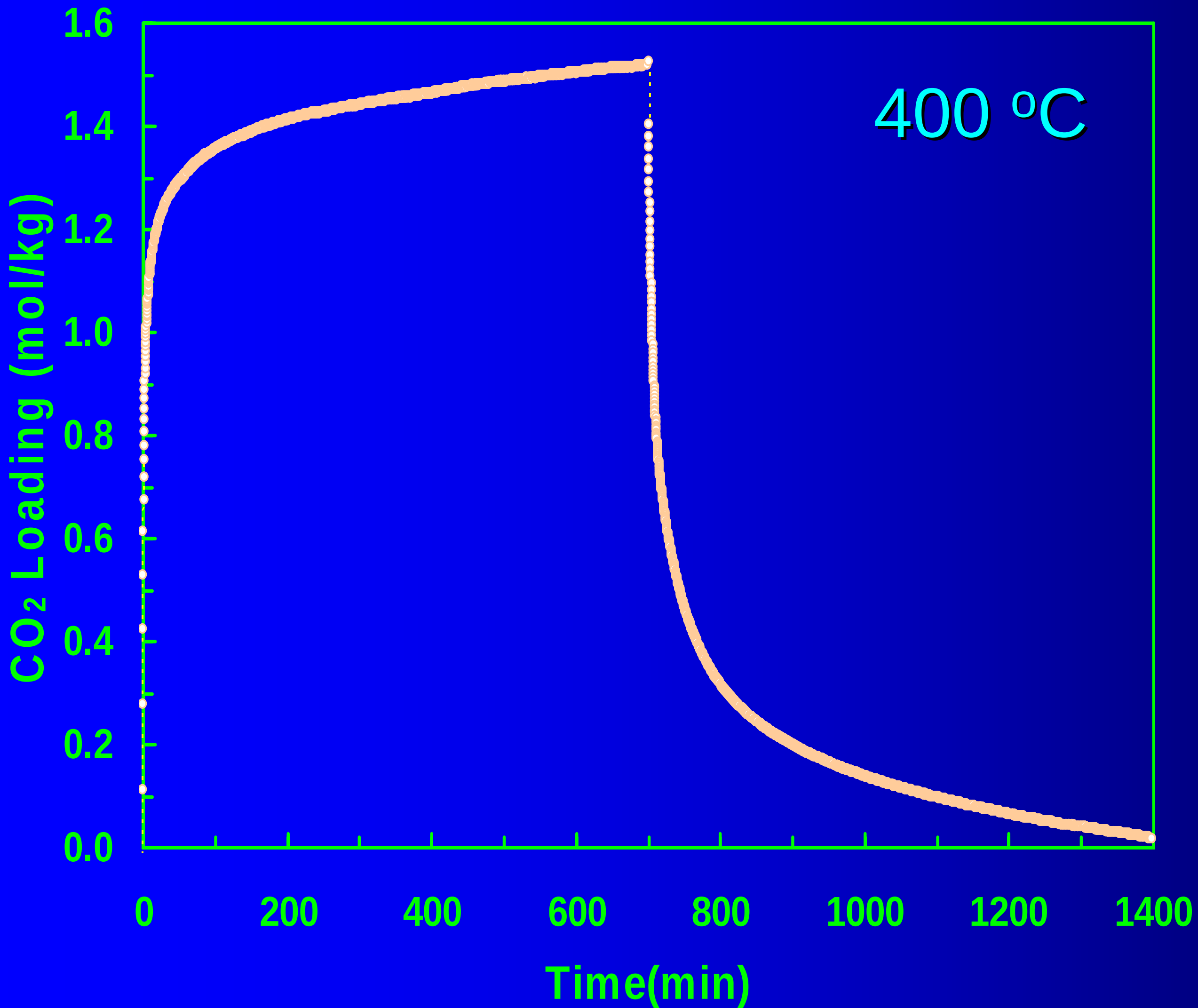
What we think is going on: adsorption.



ADSORPTION PATH:

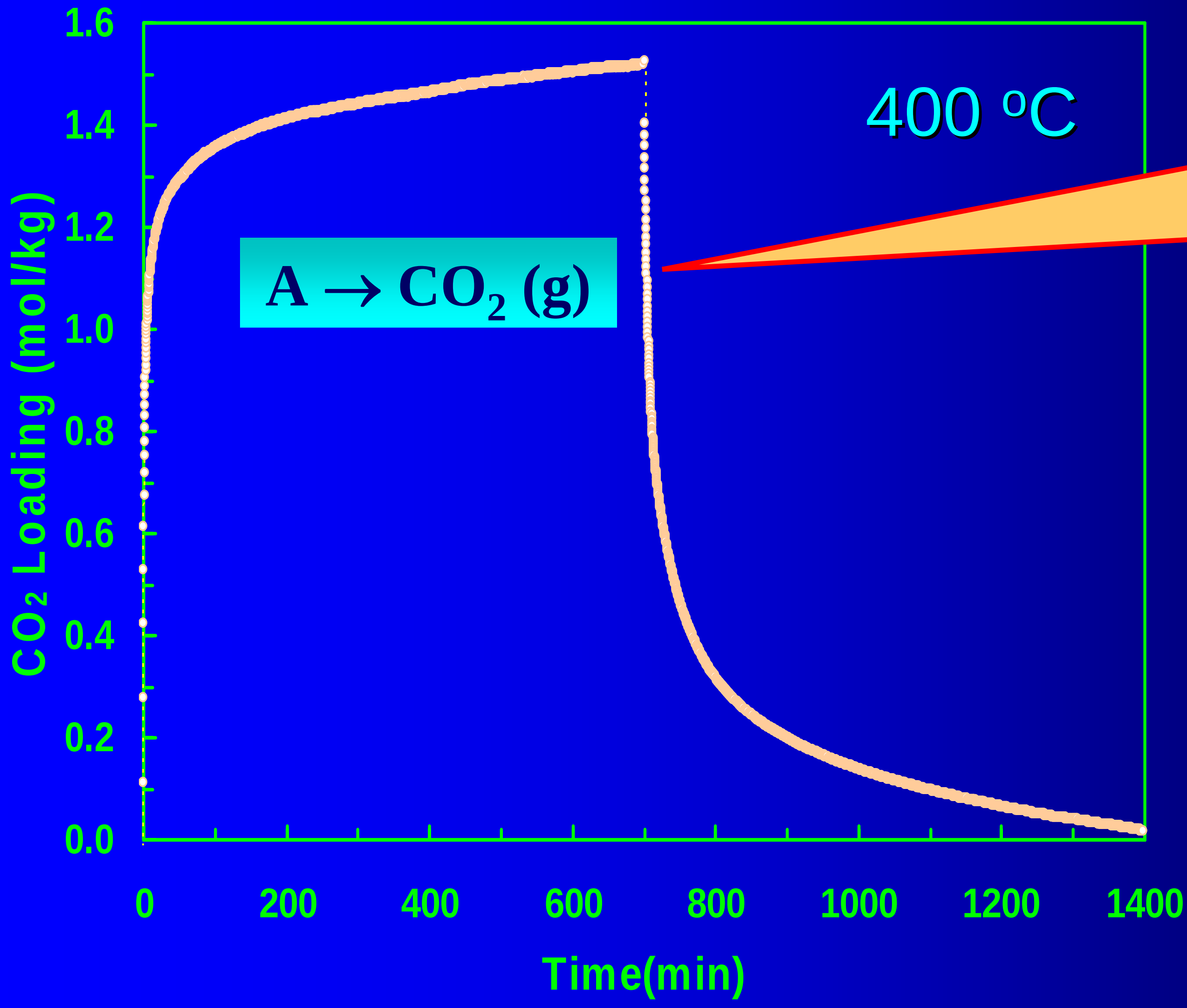
- **After activation, CO_2 adsorption takes place through a fast MT limited process to form weakly sorbed phase A**
- **When adsorption slows down, process becomes controlled by reaction between diffusing phase A and empty crystal phase E to form intermediate phase B**
- **Finally, the last reaction path is dominated by reaction of extra A with B to form CO_2 saturated phase C**

What we think is going on: adsorption.



Phase A dependent only on P_{CO2} while phases E, B and C dependent on A, and E+B+C = constant.

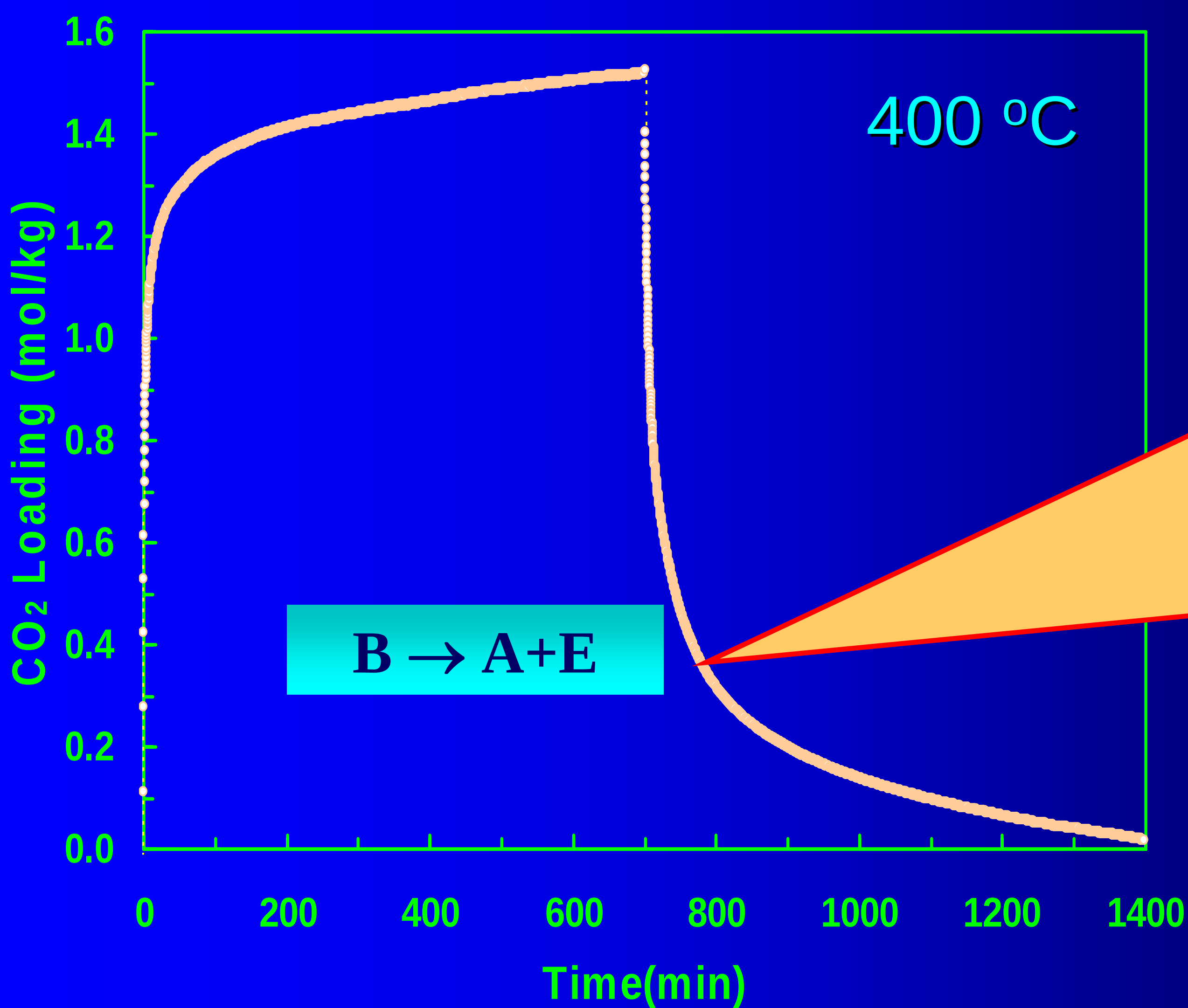
What we think is going on: desorption.



DESORPTION PATH:

- **After adsorption, CO_2 is desorbed through a fast MT limited process from weakly sorbed phase A**

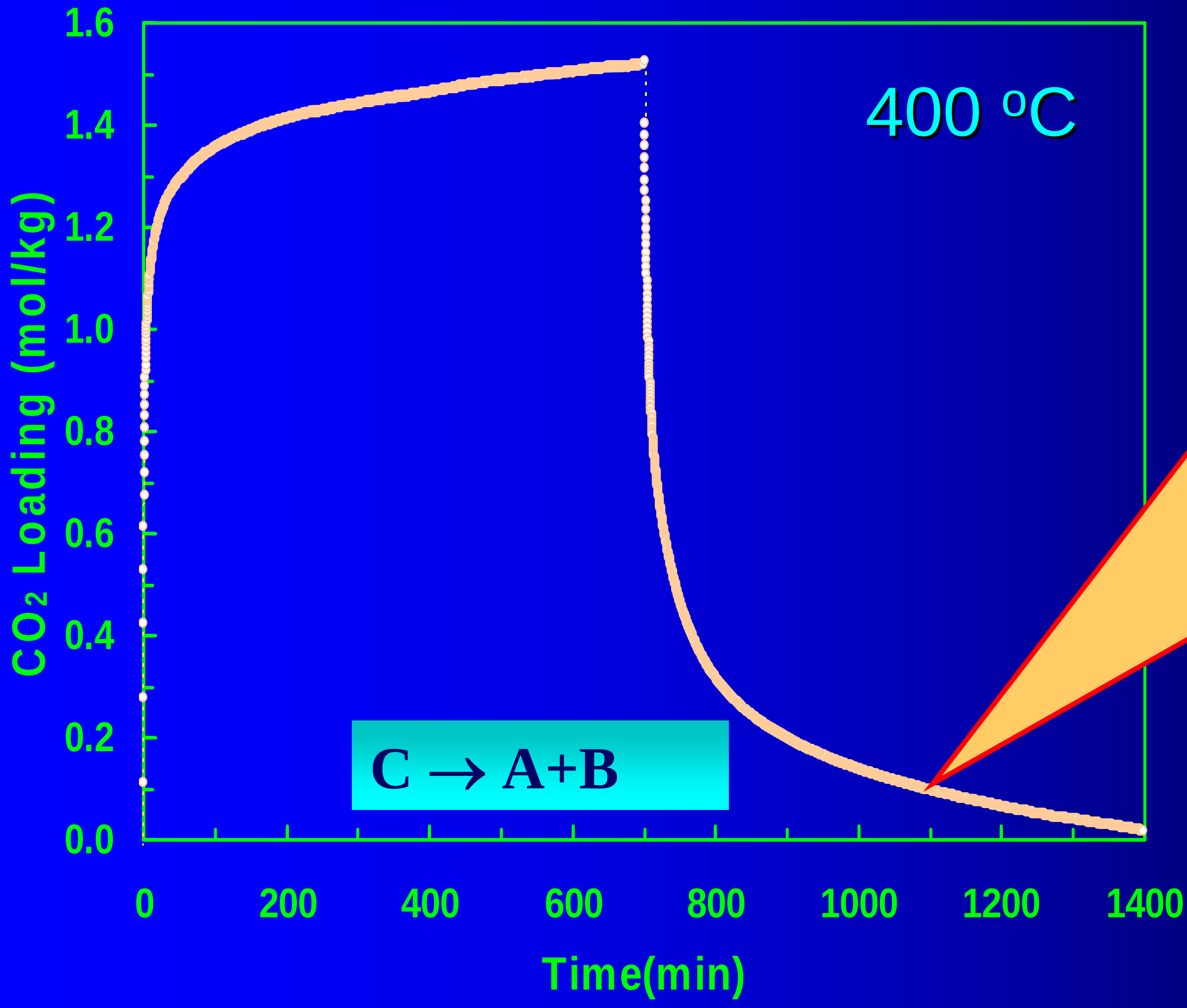
What we think is going on: desorption.



DESORPTION PATH:

- **After adsorption, CO_2 is desorbed through a fast MT limited process from weakly sorbed phase**
- **When desorption slows down, process becomes controlled by conversion of phase B into phases A and E**

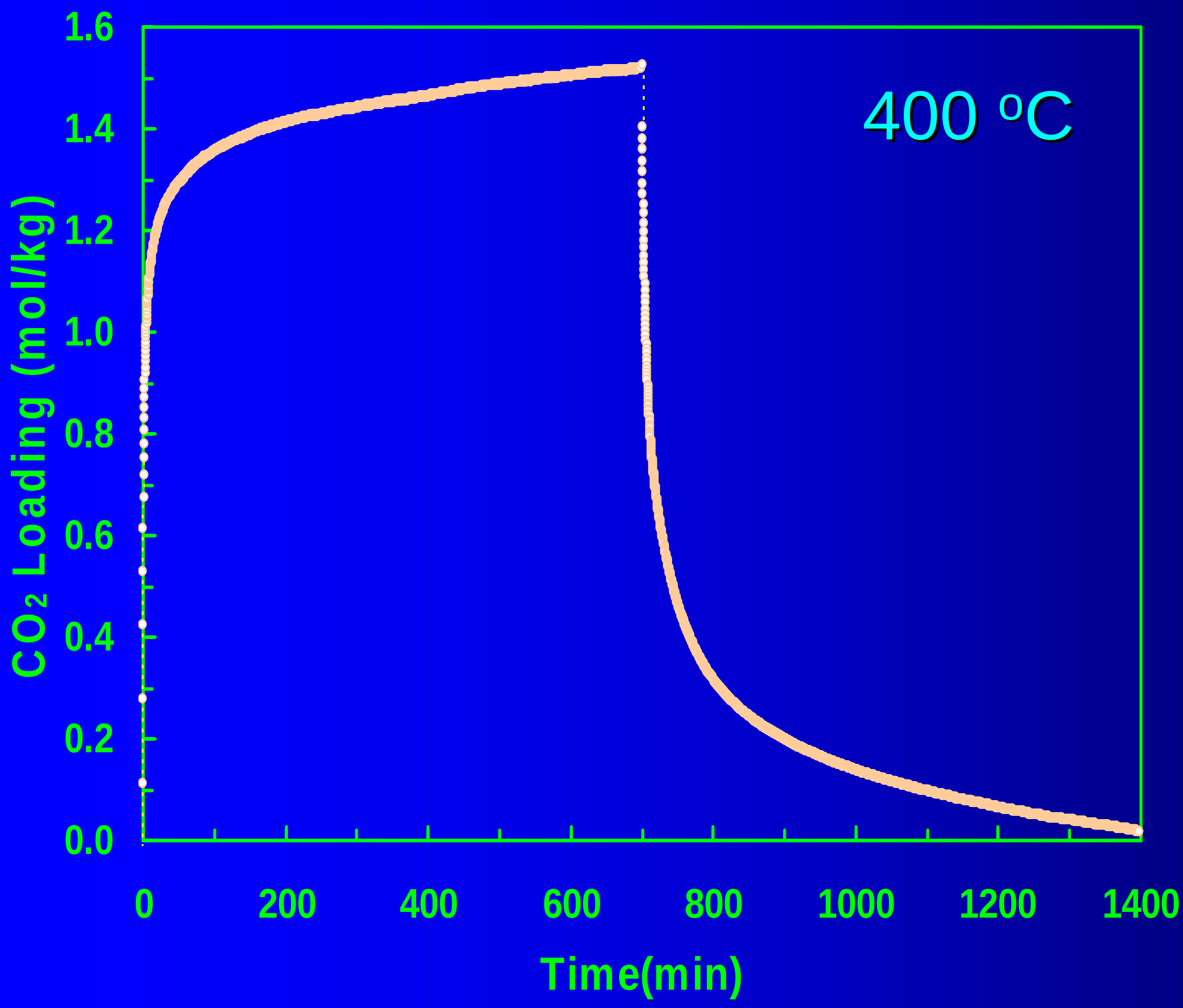
What we think is going on: desorption.



DESORPTION PATH:

- After adsorption, CO_2 is desorbed through a fast MT limited process from weakly sorbed phase
- When desorption slows down, process becomes controlled by conversion of phase B into phases A and E
- **Finally, the process is dominated by conversion of phase C into phases A and B**

What we think is going on: desorption.



Depending on the half cycle time, the sample may regenerate back to initial point

Non-Equilibrium Kinetic Model

Activation ↓ Desorption ↓ Adsorption ↑

$$I \rightarrow C + (n+8)H_2O$$

$$C \leftrightarrow B + A \quad (slow)$$

$$B \leftrightarrow A + E \quad (intermediate)$$

$$A \leftrightarrow CO_2(g) \quad (fast)$$

$$I \equiv [Mg_3Al(OH)_8]_2(CO_3) \cdot K_2CO_3 \cdot nH_2O$$

$$A \equiv CO_2(ad)$$

$$E \equiv Mg_6Al_2K_2O_{10}$$

$$B \equiv Mg_6Al_2K_2O_9(CO_3)$$

$$C \equiv Mg_6Al_2K_2O_8(CO_3)_2$$

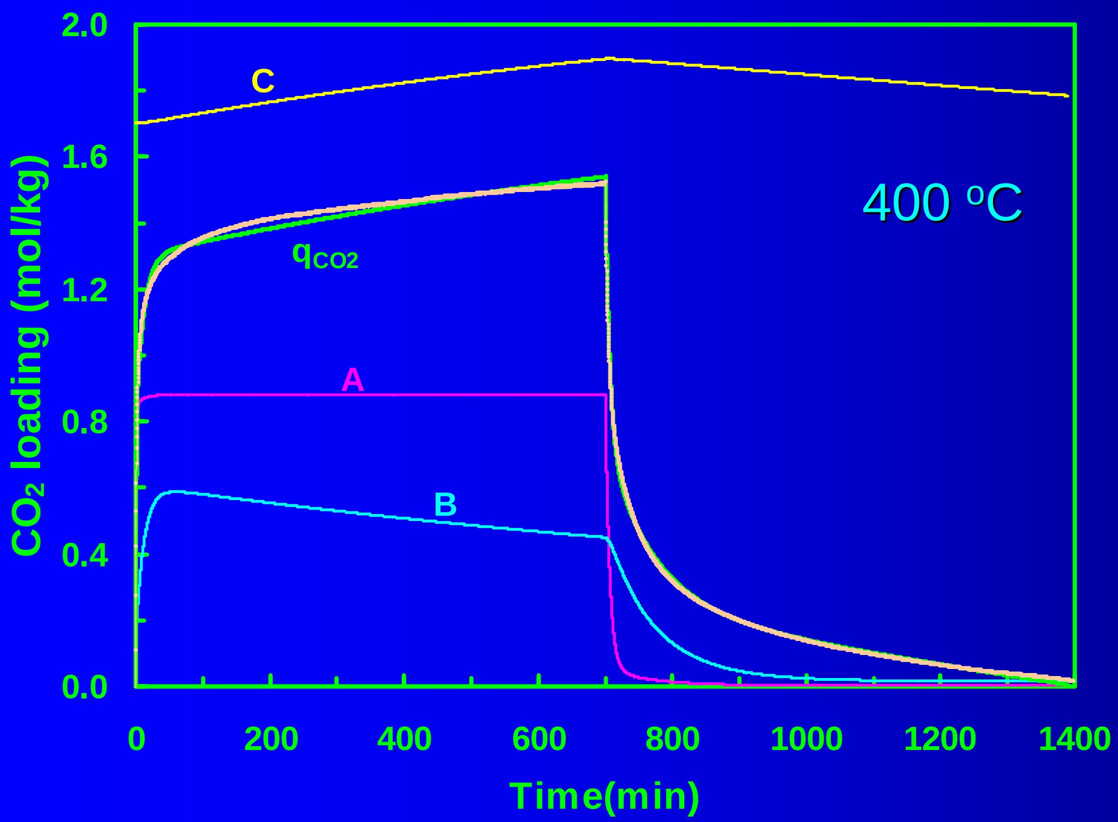
$$N_{total} = [E] + [B] + [C]$$

$$q = [A] + [B] + 2[C] - q_o$$

$$q_o = 2[C]_o$$

Non-Equilibrium Kinetic Model for CO_2 Uptake and Release from K-Promoted HTlc

- model fitted to 700 min half cycle time single cycle adsorption and desorption experiment
- 9 out of the 12 parameters needed to be fitted; 3 known

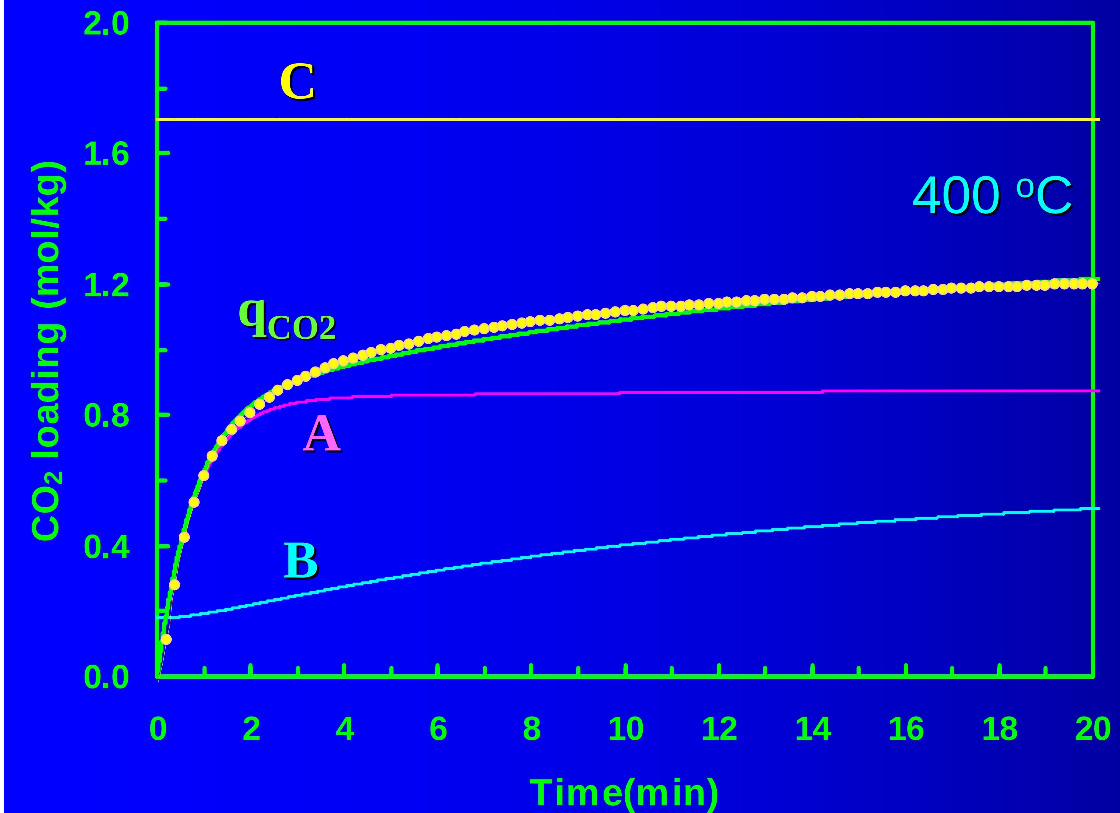


Parameter	Value	
$k_{m,a}$	1.218E 00	1/min
$k_{m,d}$	1.397E-01	1/min
$k_{1,f}$	1.600E-04	1/min
$k_{1,b}$	1.222E-03	kg/mol/min
$k_{2,f}$	2.192E-02	1/min
$k_{2,b}$	5.793E-02	kg/mol/min
$q_{A,e,a}$	0.932	mol/kg
$q_{A,e,d}$	0.000	mol/kg
q_T	2.283	mol/kg
$q_{A,o}$	0.000	mol/kg
$q_{B,o}$	0.000	mol/kg
$q_{C,o}$	1.587	mol/kg

Ebner et al, I&ECR (2007).

Non-Equilibrium Kinetic Model for CO_2 Uptake and Release from K-Promoted HTlc

Initial uptake and release kinetics provided new estimation of the LDF mass transfer coefficients for adsorption.



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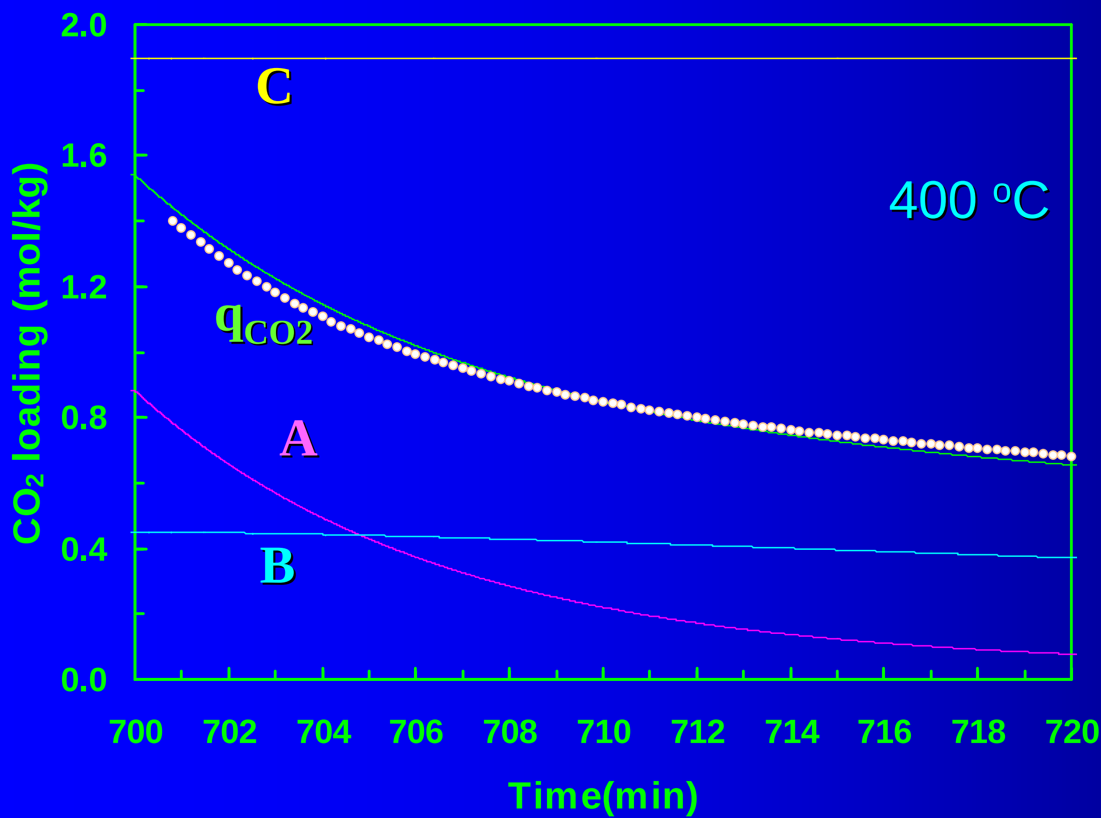
Non-Equilibrium Kinetic Model for CO_2 Uptake and Release from K-Promoted HTlc

Initial uptake and release kinetics provided new estimation of the LDF mass transfer coefficients for desorption.



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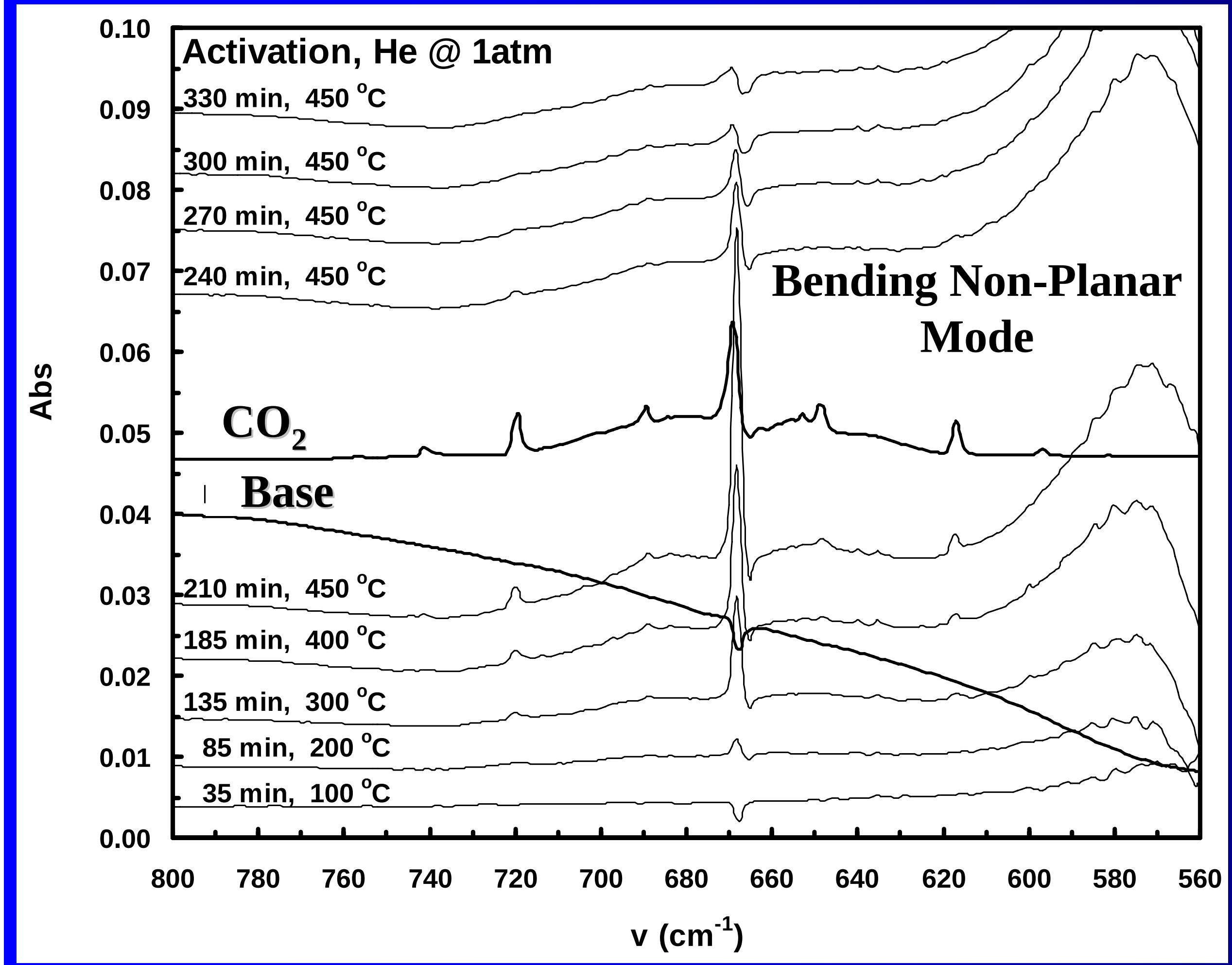
Ebner et al, I&ECR (2007).

FTIR Spectra of K-Promoted HTlc

Activation in He @ 1atm for 330 min

0 → 210 min, T ramping @ 2°C/min from 35 → 450 °C

210 → 330 min, T soaking @ 450 °C



Process characterized by development of peak @ 667 cm^{-1}.

A few other peaks @ 620, 650, 690 and 720 cm^{-1} also appeared, displaying a max @ 210 min.

Then, all peaks waned during soaking phase.

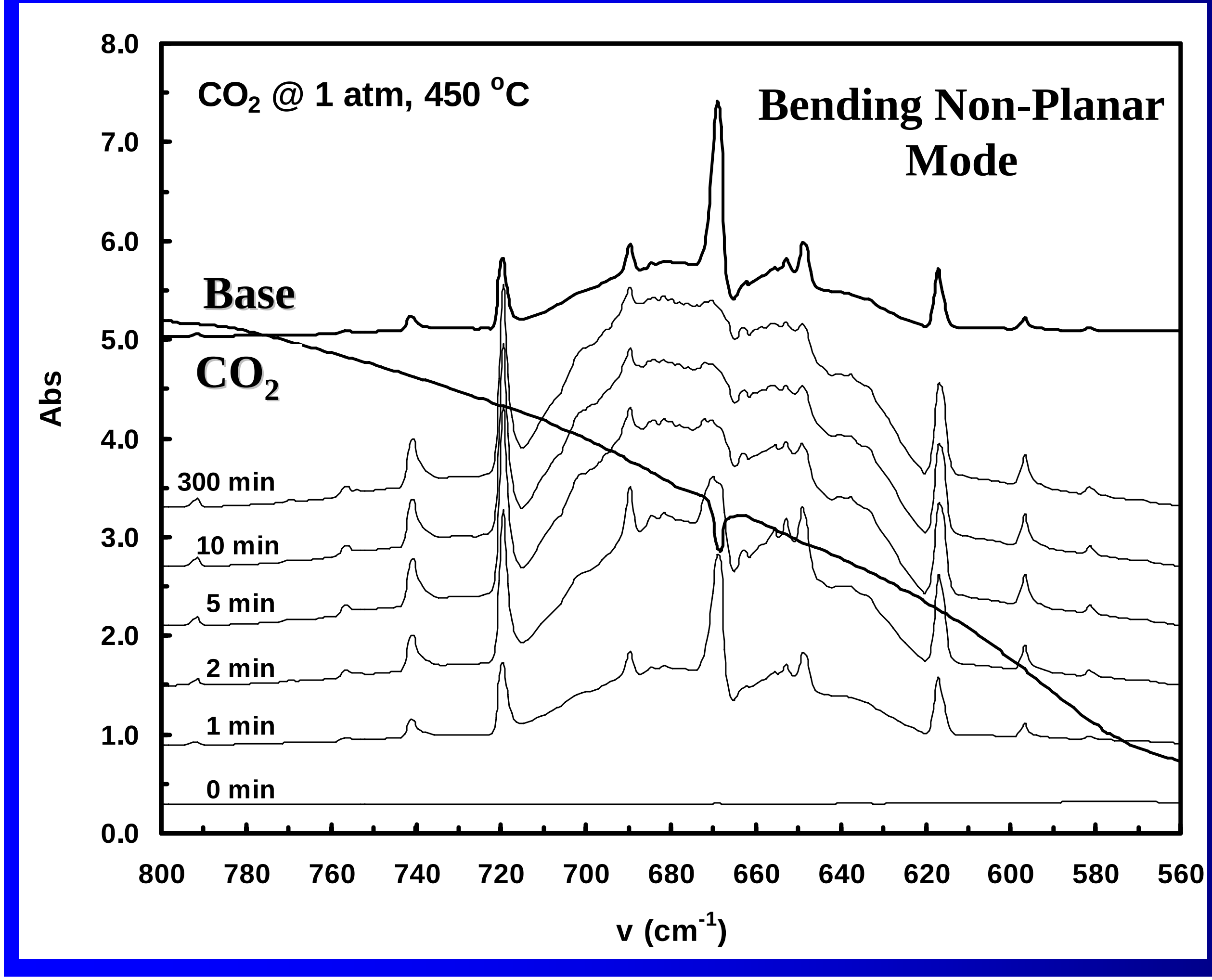
A "bump" encompassing all those peaks remained.

Net effect: dehydration and CO_2 removal.

FTIR Spectra of K-Promoted HTlc

CO_2 Adsorption-Desorption Cycle for 600 min

Adsorption: 0 → 300 min, CO_2 @ 1 atm and 450 °C



A strong signal became readily apparent at short times (<2 min) into the adsorption step.

All Peaks previously identified along with a strong "bump" reappeared.

Bump associated with a loosely chemisorbed CO_2 phase-carbonate structure.

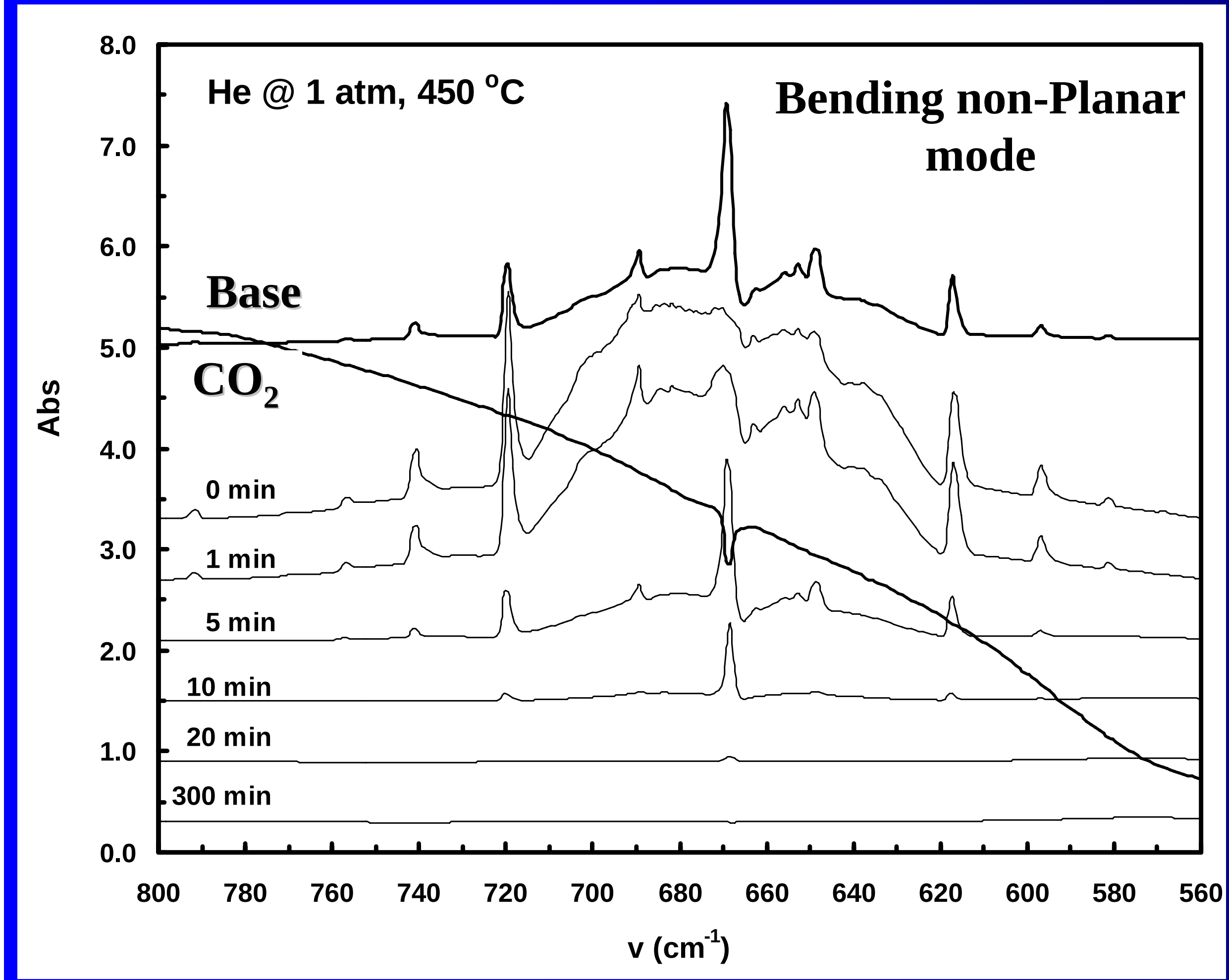
No further or apparent changes after 5 min into adsorption step.

Net effect: rapid CO_2 uptake as carbonate.

FTIR Spectra of K-Promoted HTlc

CO_2 Adsorption-Desorption Cycle for 600 min

Desorption: 300 min → 600 min, He @ 1 atm and 450 °C



Bump and all other signals disappeared after 5 min into desorption step.

This and previous results were quite consistent with rates of adsorption and desorption of TGA runs.

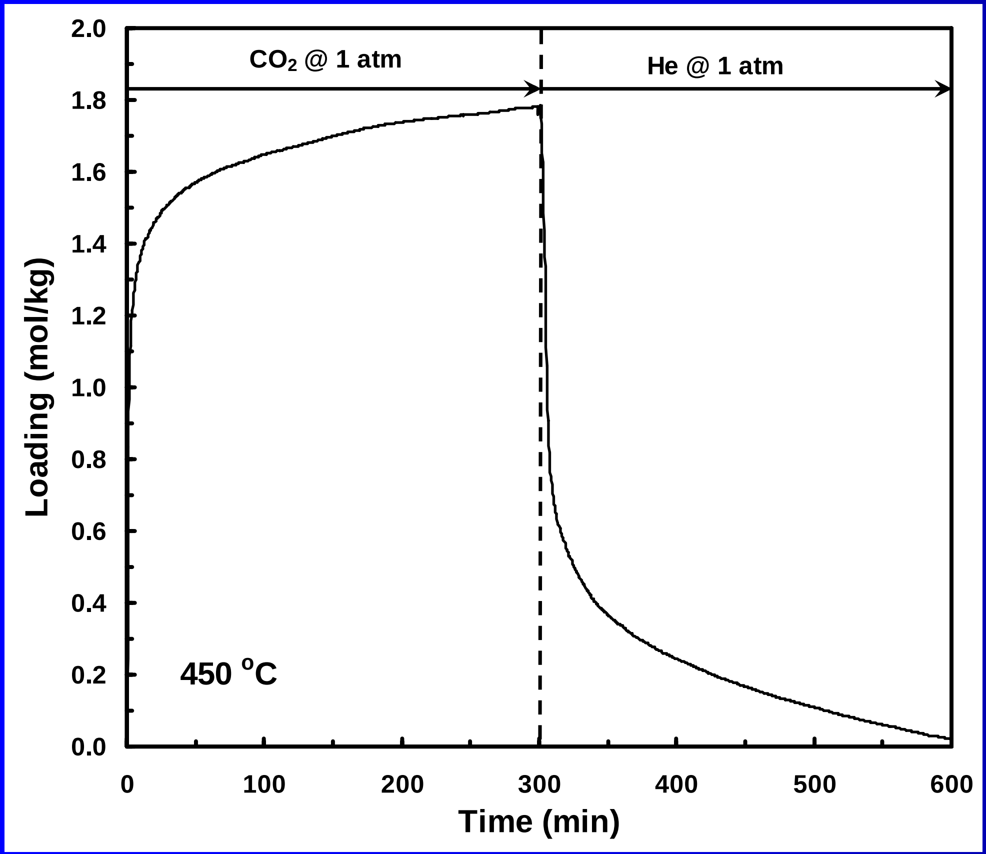
Net effect: rapid CO_2 release from carbonate.

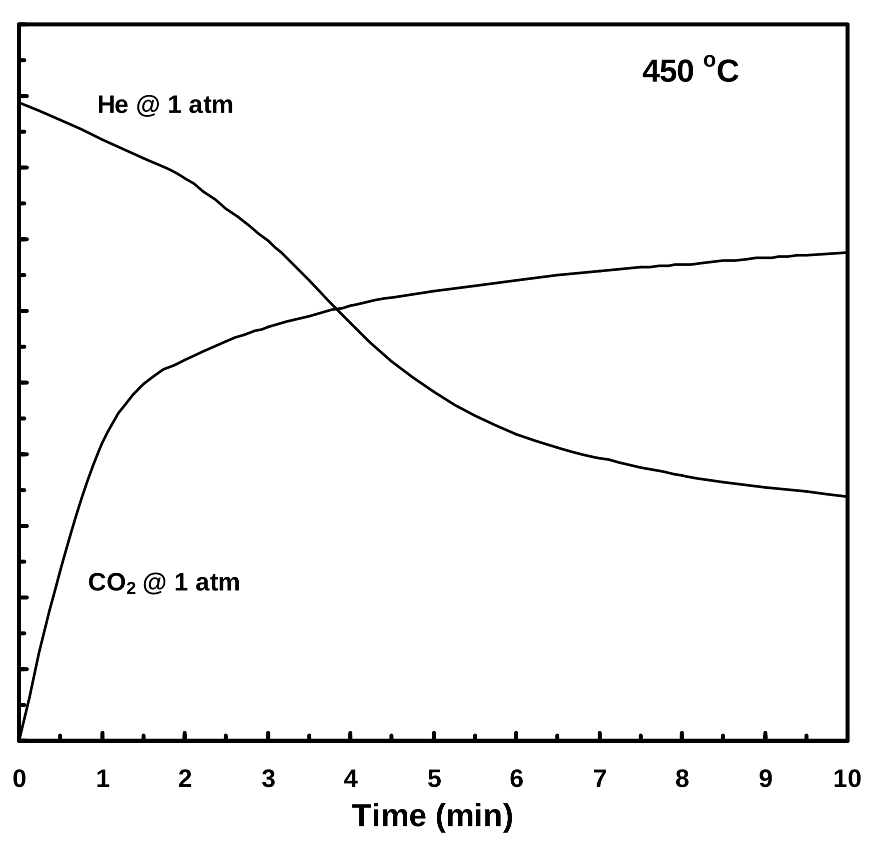
Adsorption and Desorption Rates

600 min, CO_2 Adsorption-Desorption Cycle

0 → 300 min, CO_2 @ 1 atm and 450 °C

300 min → 600 min, He @ 1 atm and 450 °C





HTlc Materials Conclusions

- TGA dynamic adsorption and desorption cycling experiments revealed reversible non-equilibrium kinetic mechanism for adsorption of CO_2 on K-promoted HTLc
- mechanism modeled in terms of three step mass transfer limited Langmuir-Hinshelwood model using long 700 min HCT cycle at 400 ^oC
- findings have important implications for development of high temperature PSA process for CO_2 capture from flue gas
- research ongoing to make the model temperature (300-500 ^oC) and pressure dependent for use in the PSA simulator

Presentation Overview

- results: adsorption cycle research

Novel Heavy Reflux Cycles in Pressure Swing Adsorption Processes

Objectives

…..Based on interpreting results and evaluating performance trends from literally thousands of simulations of nine different PSA cycle configurations so far:

- introduce the heavy reflux concept
- describe PSA cycles that include heavy reflux
- present simulation results revealing performance differences of seemingly similar cycles

Heavy Reflux PSA Concept

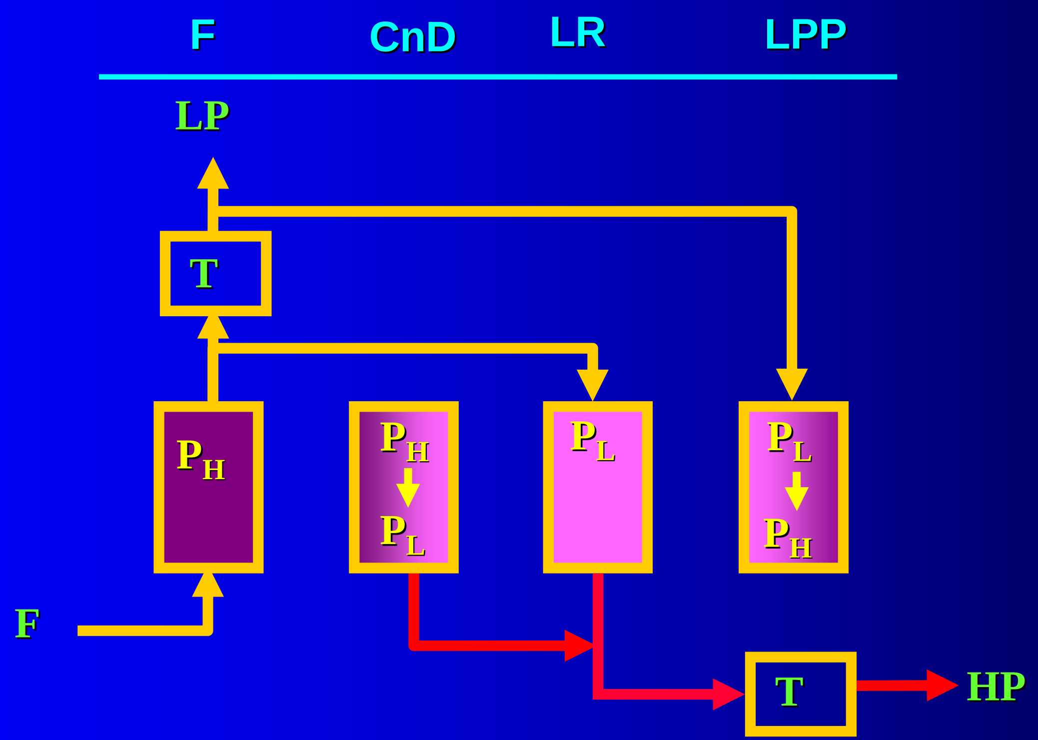
- heavy reflux or rinse step used to increase heavy component loading in the column, e.g., CO_2, to increase its concentration in the heavy product

  However….

- Which cycle step effluent should be used as heavy reflux?
  - countercurrent depressurization step (typical), or
  - light reflux purge step (if step part of cycle), or both
- What should be done with the light gas effluent coming from the column undergoing heavy reflux?
  - taken as light product
  - recycled back to the feed step
  - add a recovery step just after the feed step but prior to the HR step

Stripping PSA Cycle with LR

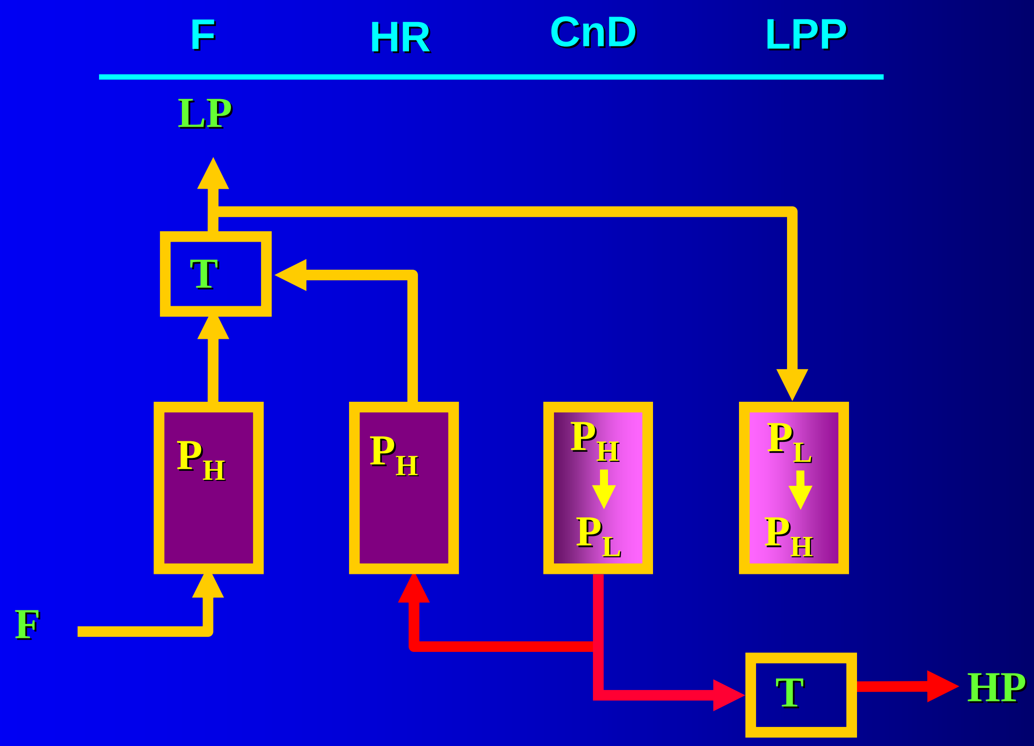
All CnD and LR Effluents Taken as Heavy Product



Basic 4-step Skarstrom-type cycle.

Stripping PSA Cycle with HR

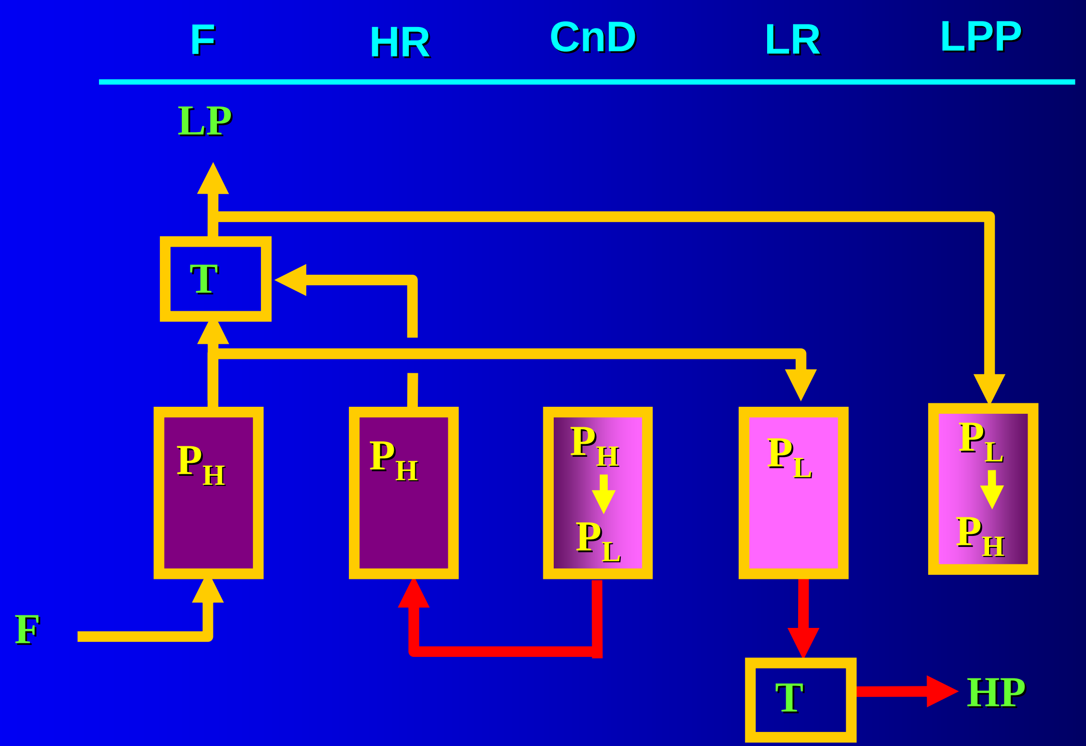
Fraction of CnD Effluent Used as HR with Remaining CnD Effluent Taken as Heavy Product



Basic 4-step HR cycle, with the HR step replacing the LR step.

Stripping PSA Cycle with LR and HR

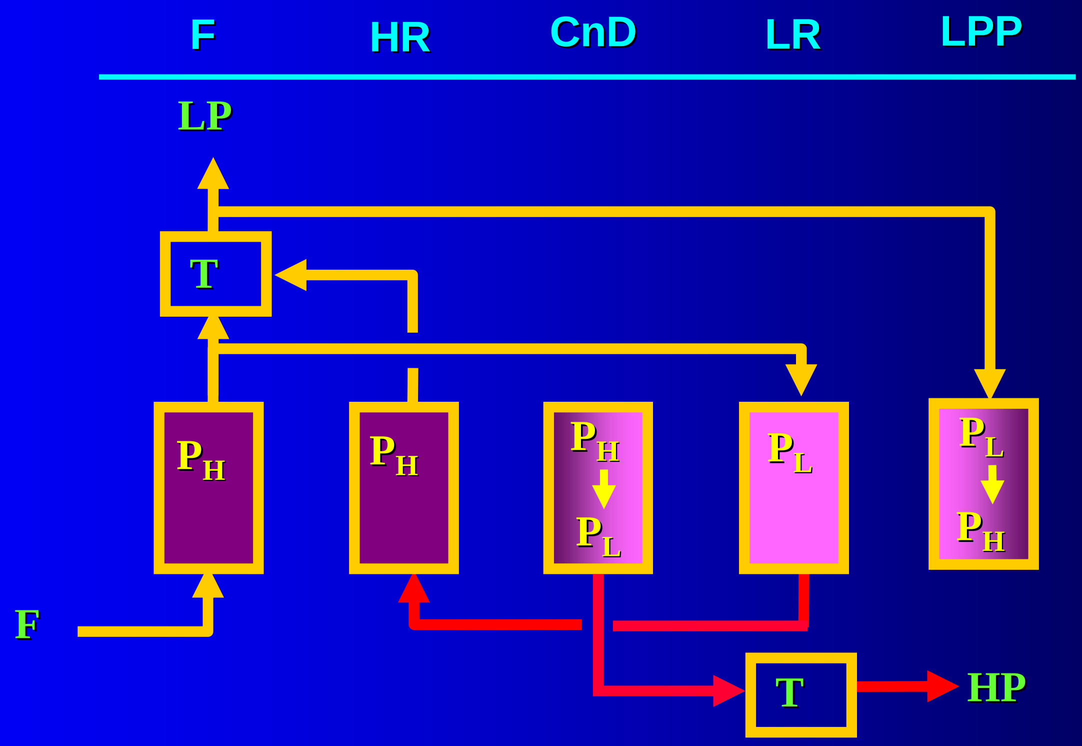
All CnD Effluent Used as HR with All LR Effluent Taken as Heavy Product



Simplest dual reflux (DR) cycle, with both, LR and HR steps.

Stripping PSA Cycle with LR and HR

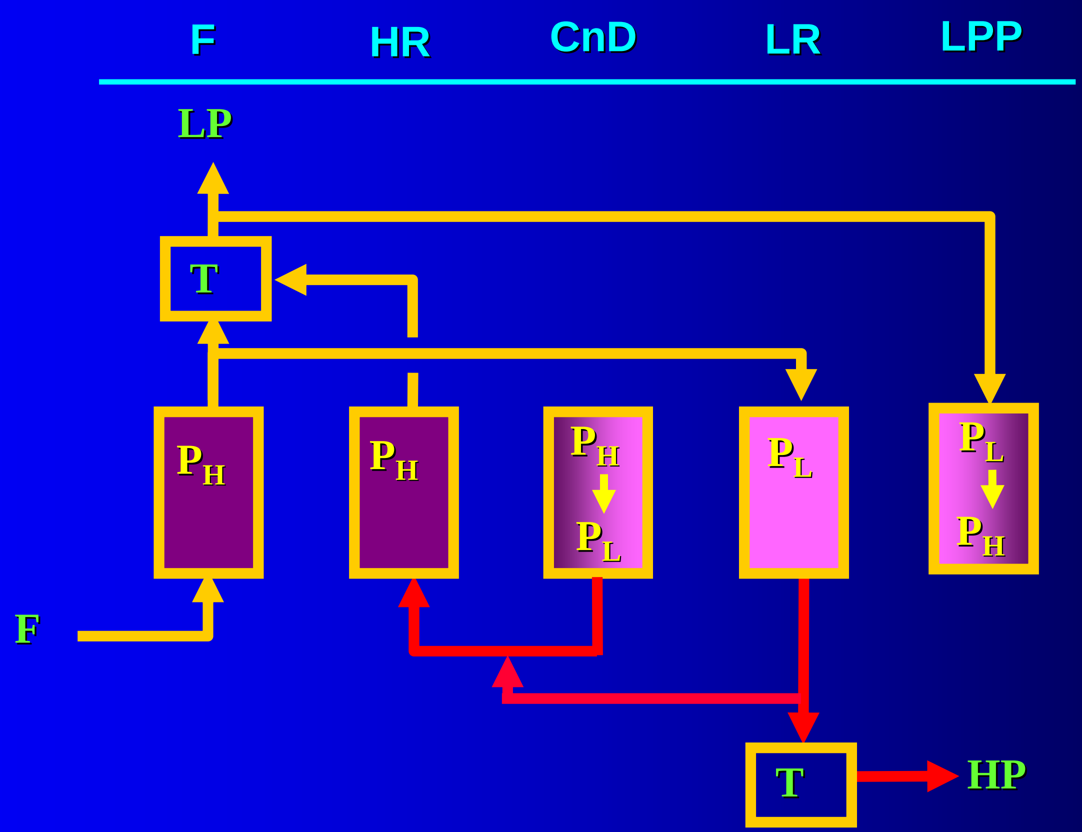
All LR Effluent Used as HR with All CnD Effluent Taken as Heavy Product



Simplest dual reflux (DR) cycle, with origin of HR gas switched.

Stripping PSA Cycle with LR and HR

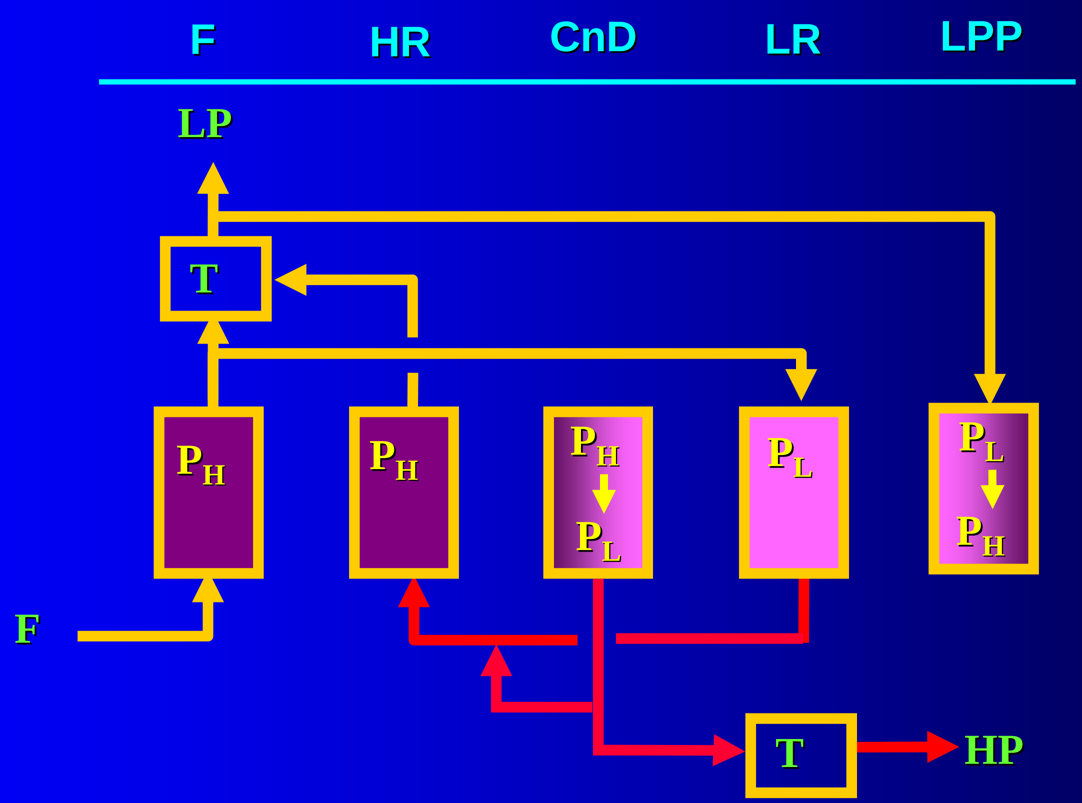
All CnD and Fraction of LR Effluents Used as HR with Remaining LR Effluent Taken as Heavy Product



DR cycle, with blended HR from CnD and LR steps.

Stripping PSA Cycle with LR and HR

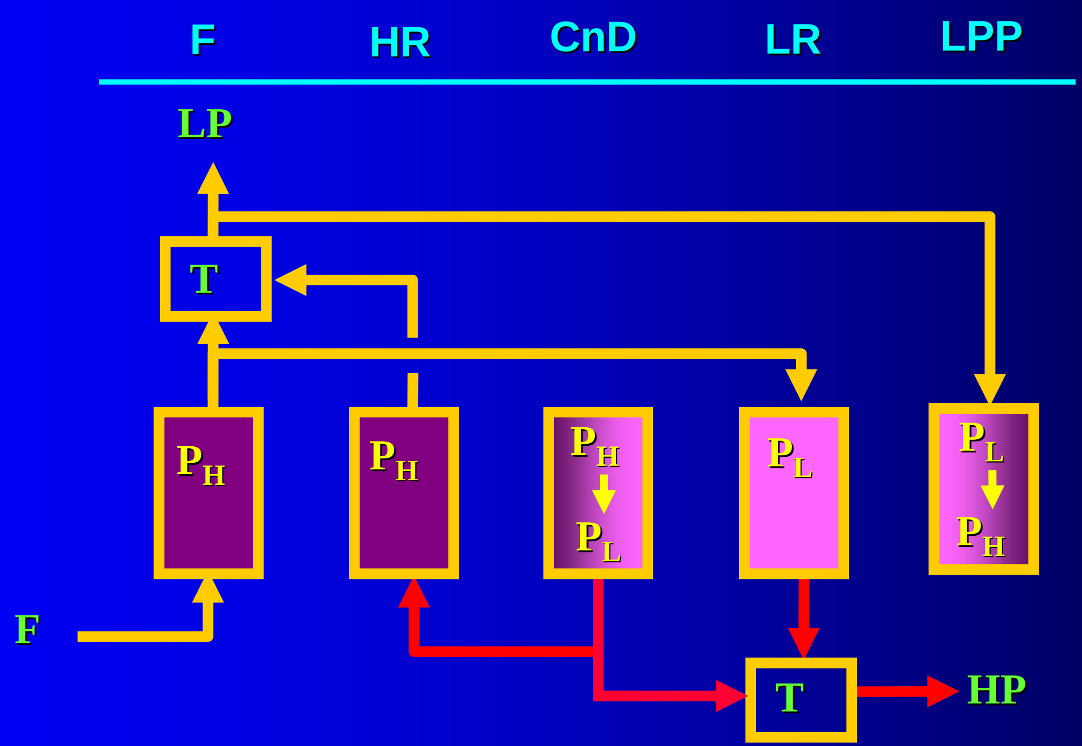
All LR and Fraction of CnD Effluents Used as HR with Remaining CnD Effluent Taken as Heavy Product



DR cycle, with blended HR from CnD and LR steps.

Stripping PSA Cycle with LR and HR

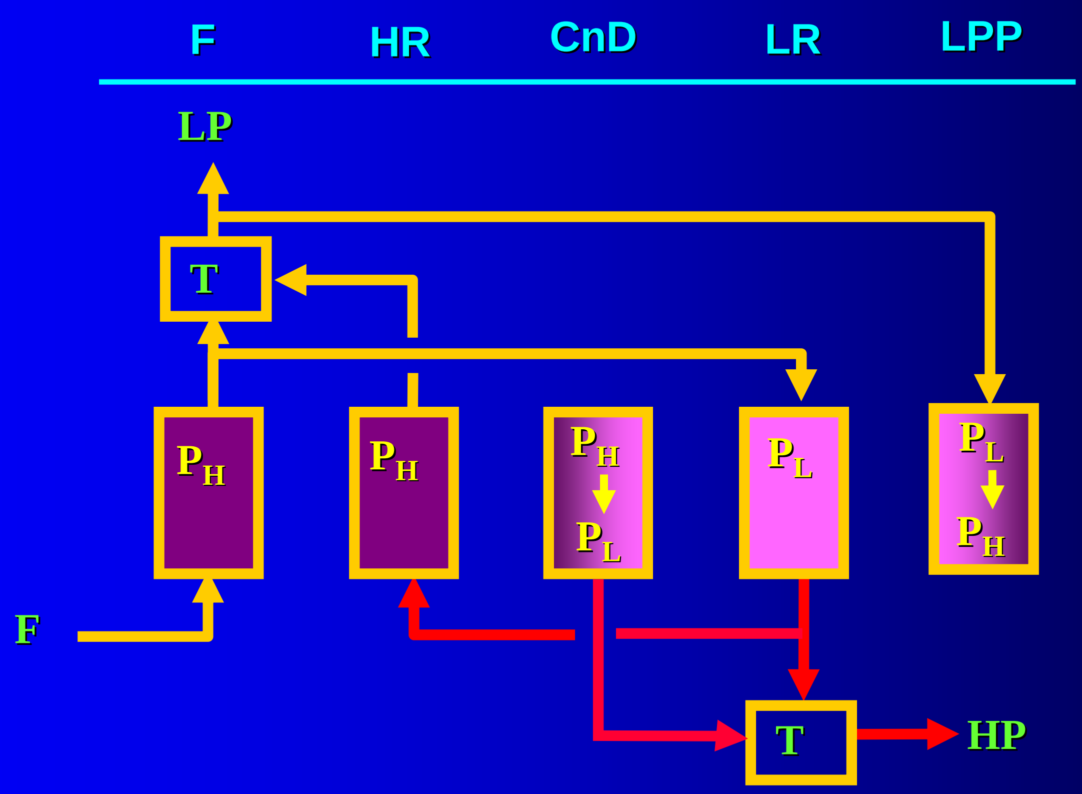
Fraction of CnD Effluent Used as HR with Remaining CnD and All LR Effluents Taken as Heavy Product



DR cycle, with blended heavy product (HP) from CnD and LR steps.

Stripping PSA Cycle with LR and HR

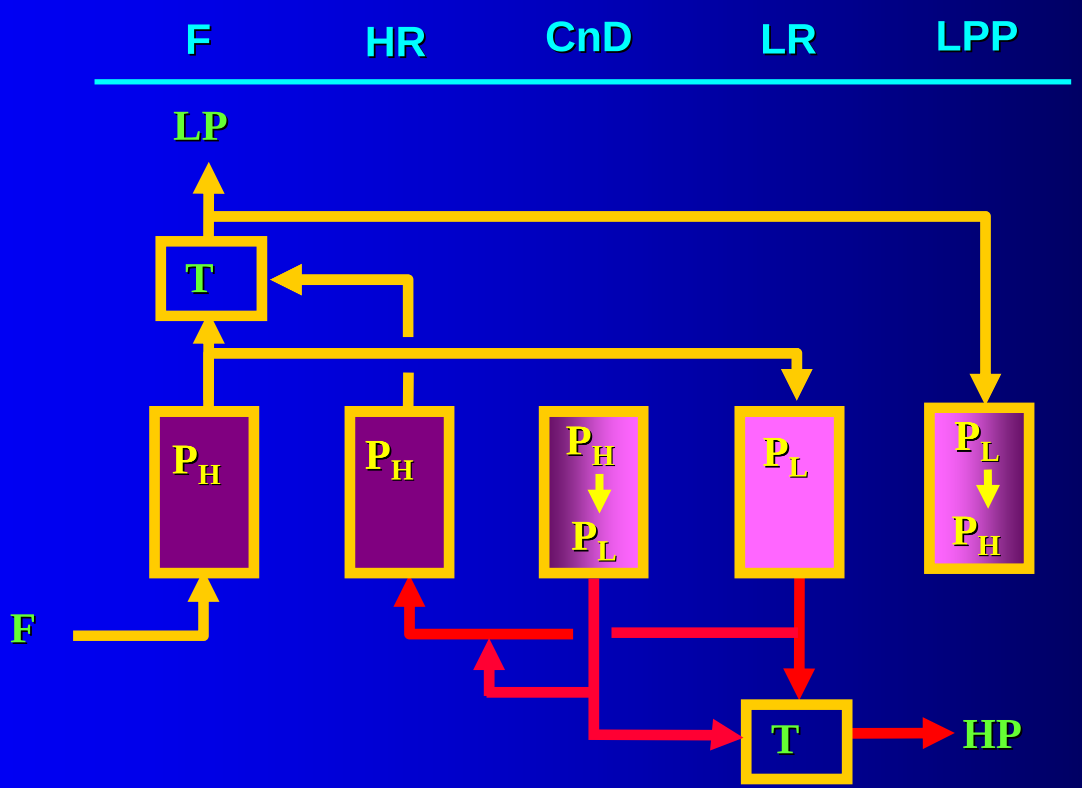
Fraction of LR Effluent Used as HR with Remaining LR and All CnD Effluents Taken as Heavy Product



DR cycle, with blended heavy product (HP) from CnD and LR steps.

Stripping PSA Cycle with LR and HR

Fractions of CnD and LR Effluents Used as HR with Remaining CnD and LR Effluents Taken as Heavy Product

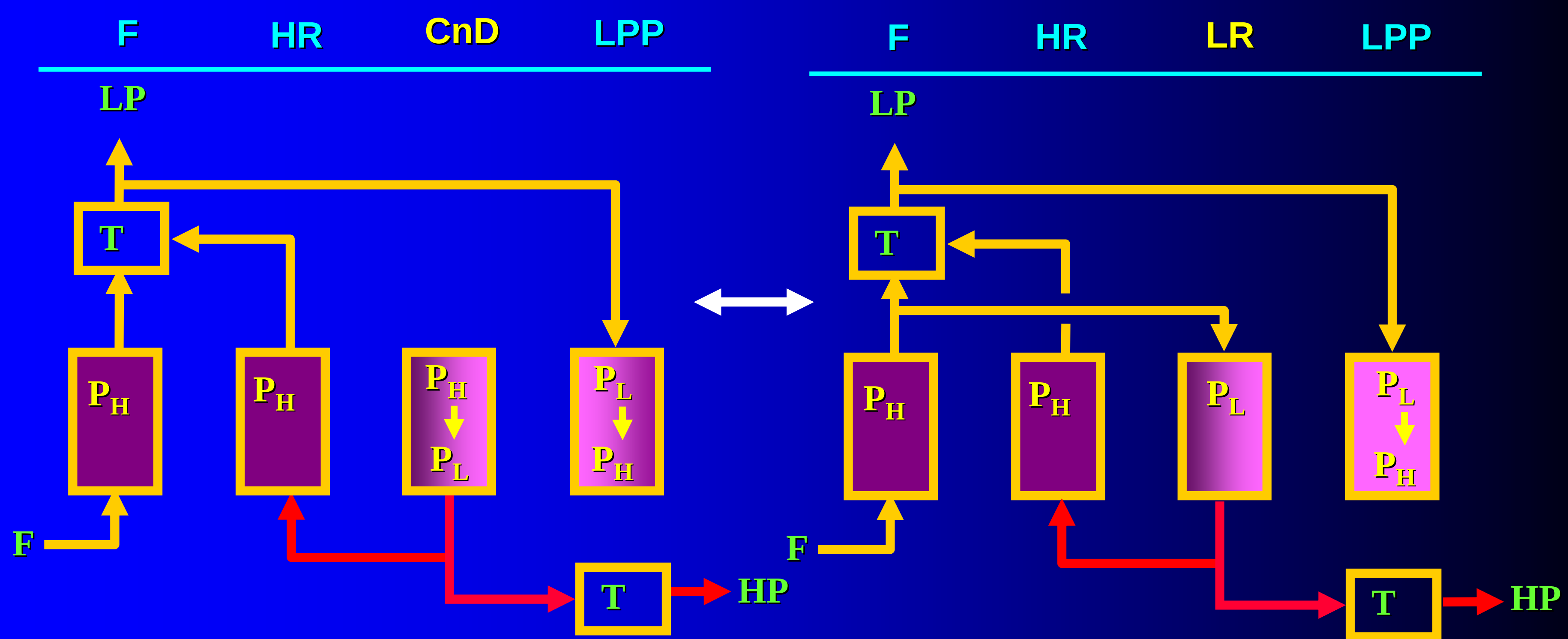


DR cycle, with blended HR and HP from CnD and LR steps.

This can be done simultaneously. Or, …..

Stripping PSA Cycle with LR and HR

Fractions of CnD and LR Effluents Used as HR with Remaining CnD and LR Effluents Taken as Heavy Product

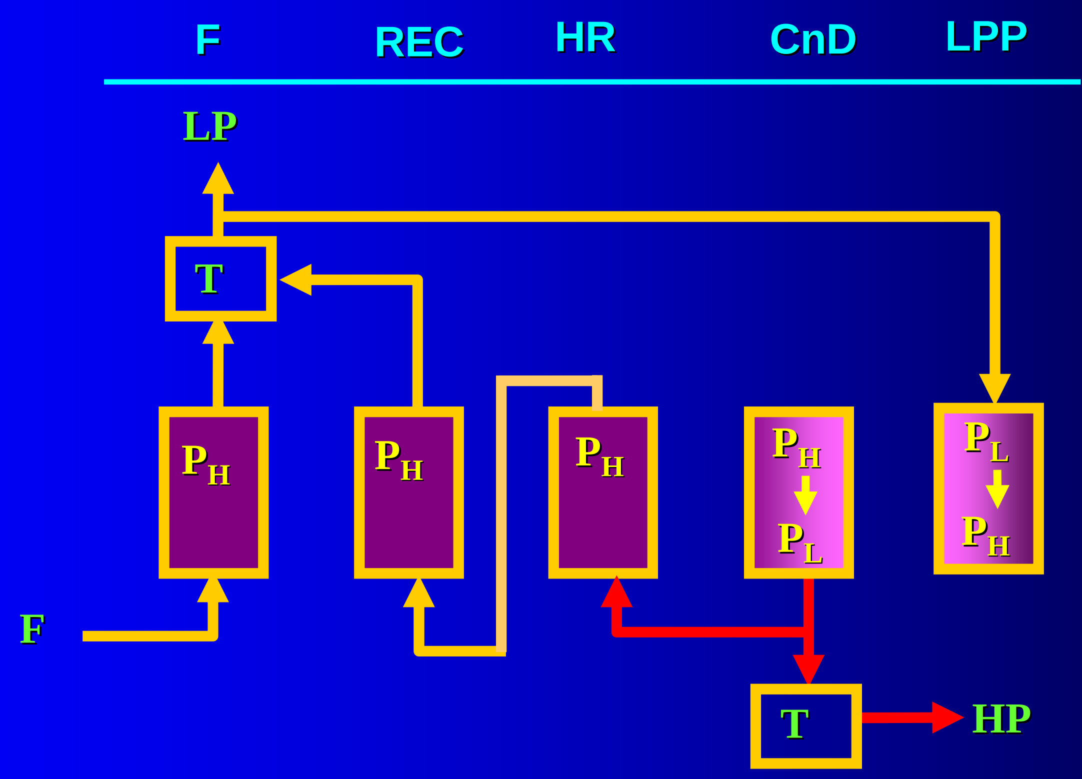


DR cycle, with blended HR and HP from CnD and LR steps.

this can be done sequentially, but now with unequal step times.

Stripping PSA Cycle with HR and REC

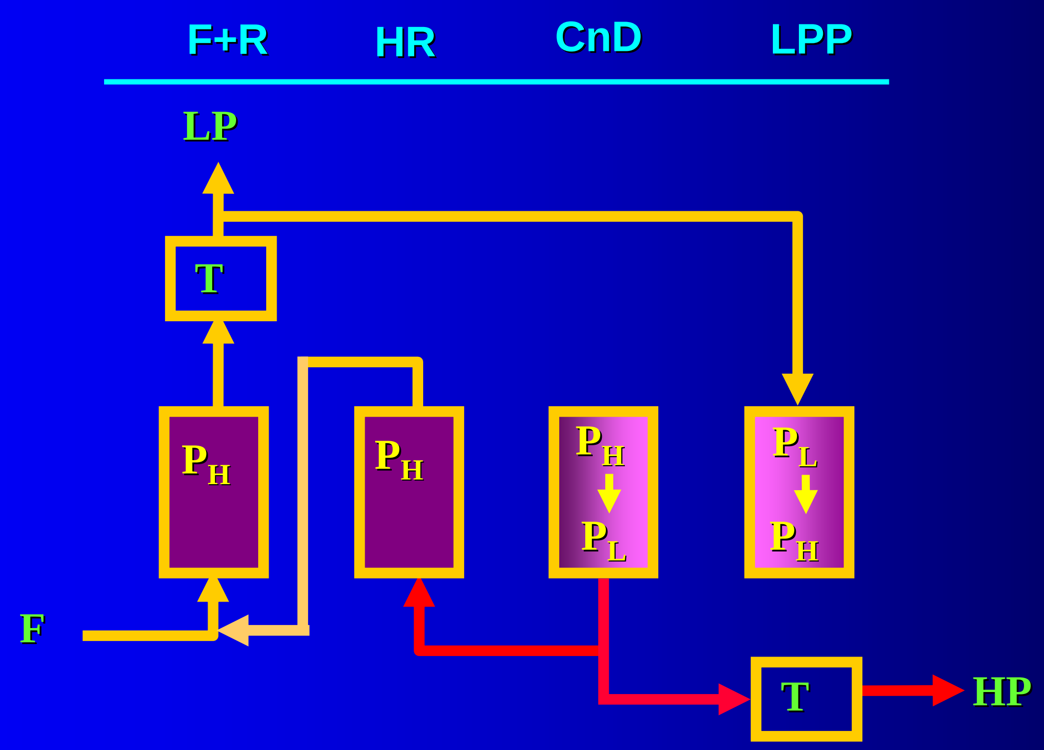
Fraction of CnD Effluent Used as HR with Remaining CnD Effluent Taken as Heavy Product



Basic HR cycle, with recovery (REC) step added.

Stripping PSA Cycle with HR and F+R

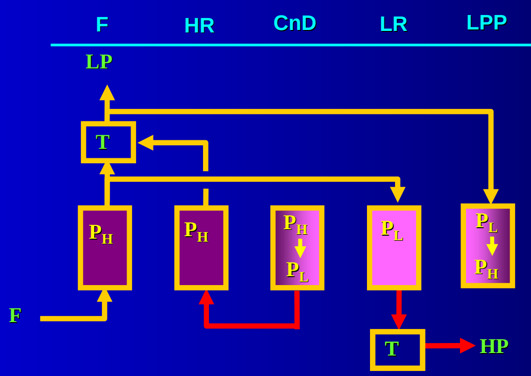
Fraction of CnD Effluent Used as HR with Remaining CnD Effluent Taken as Heavy Product



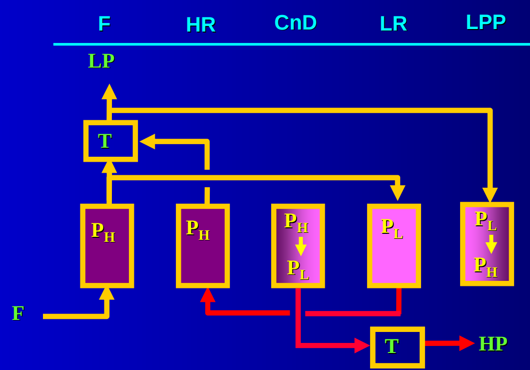
Basic HR cycle, with feed plus recycle (F+R) step added.

Comparison of Three Basic HR Cycles

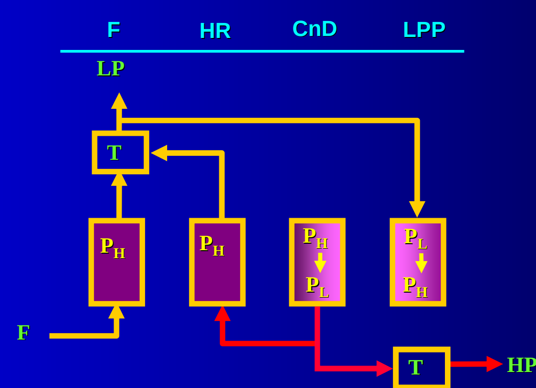
5-Bed 5-Step with LR and HR from CnD



5-Bed 5-Step with LR and HR from LR Purge

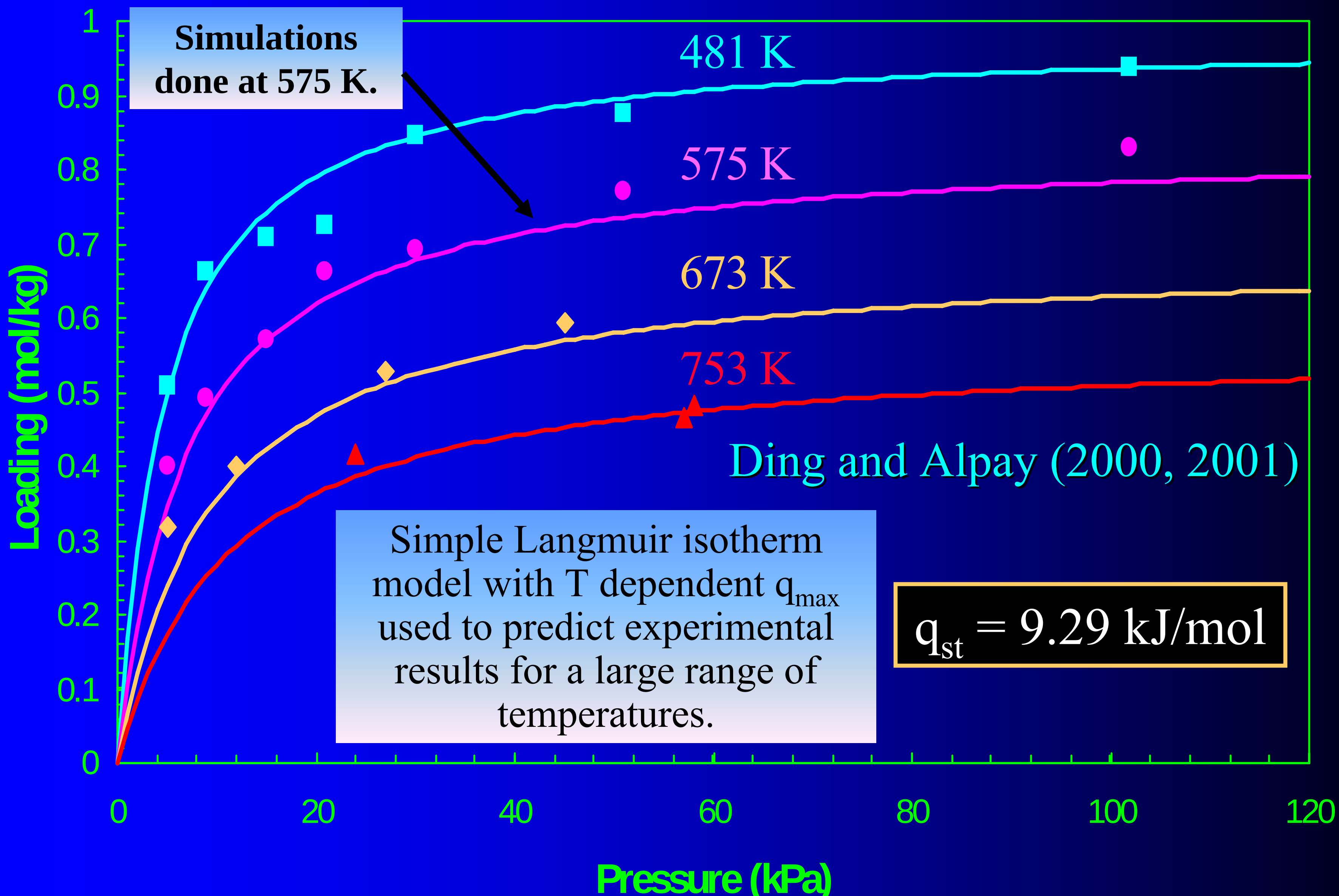


4-Bed 4-Step with HR from CnD



CO_2 Adsorption Isotherms on K-Promoted HTlc

$Mg_6Al_2K_2O_{10}(CO_3)_2 \cdot MH_2O$



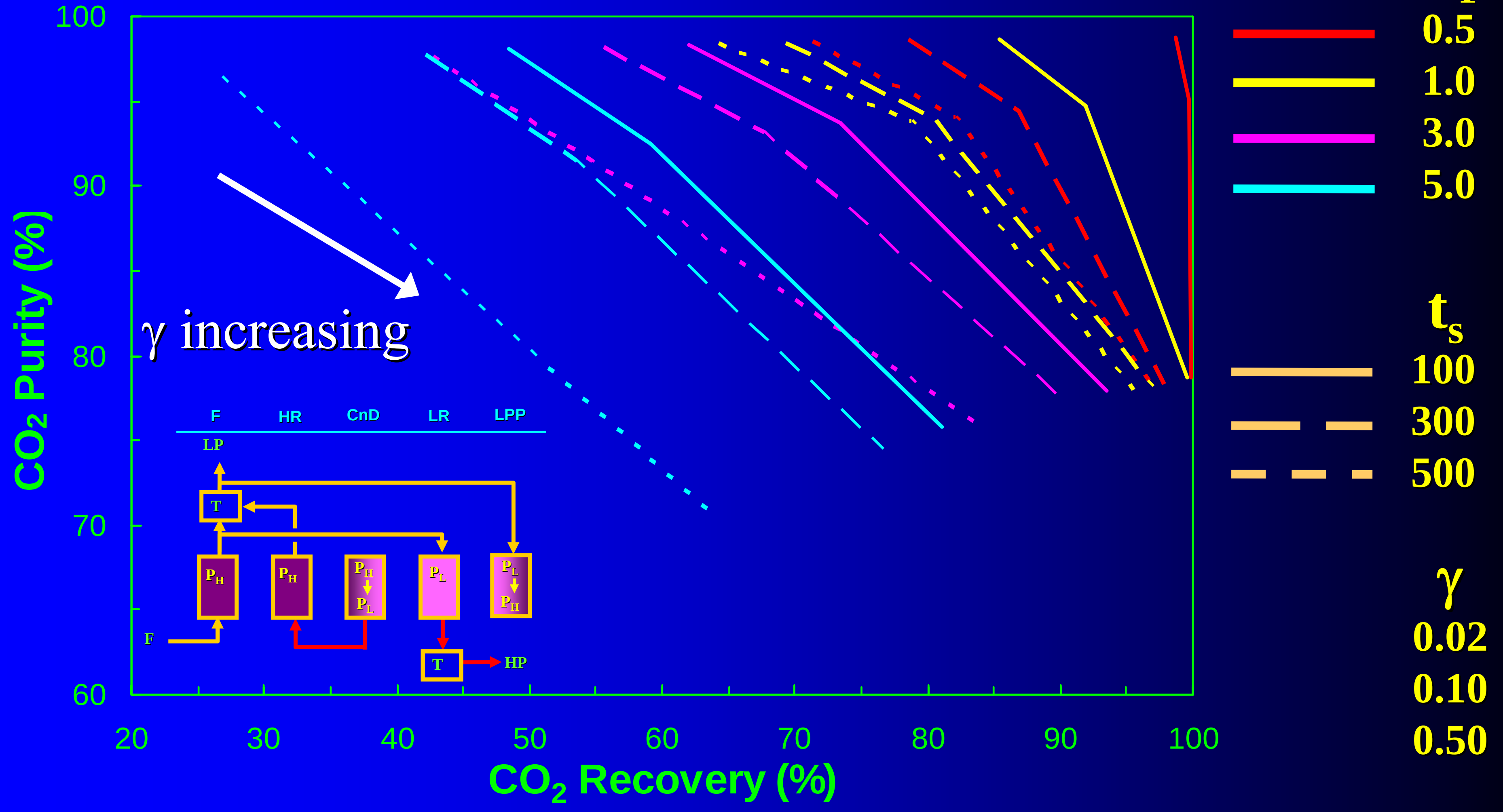
Base Case Bed Characteristics, Adsorbent Properties, and Transport Properties

Ebner et al (2007); Liu et al. (1998)

Bed Dimensions and Operating Conditions	L_b (m)	0.2724
	r_b (m)	0.0387
	Q_F (SLPM)	1.0 – 5.0
	T_F, T_o (K)	575
Adsorbent Properties	ε_b	0. 48
	ρ_p (kg/m^3)	1563
	r_p (m)	1.375×10^{-3}
	$C_{p,s}$ (kJ/kg/K)	0.850
Heat and Mass Transfer Coefficients	h_b (kW/m^2/K)	0.00067
	$k_{CO2,ad}$ (s^{-1})	0.029
	$k_{CO2,de}$ (s^{-1})	0.003

Different Mass Transfer Rate Constants for Adsorption and Desorption ($k_{CO2,ad}$, $k_{CO2,de}$)

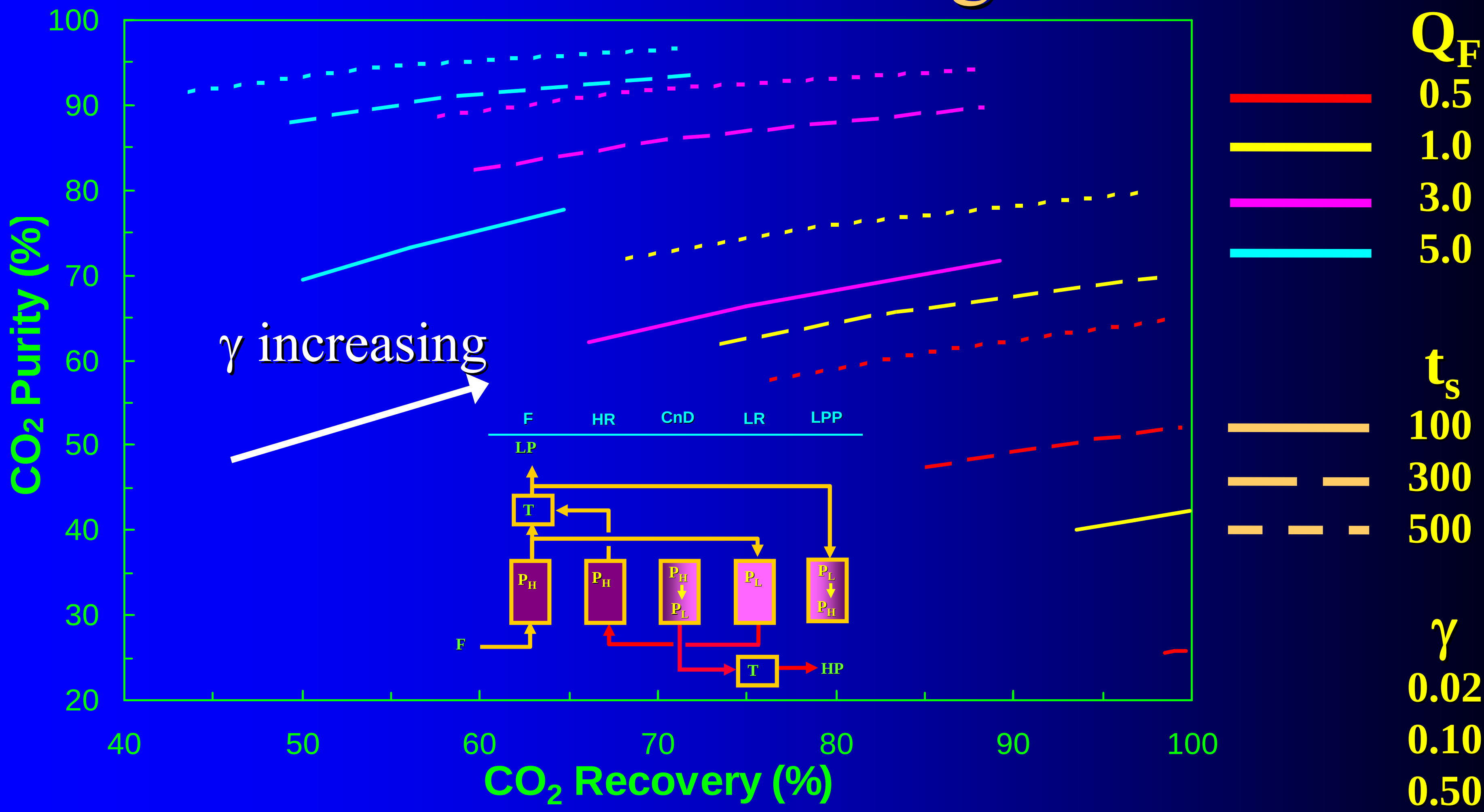
5-Bed 5-Step Cycle with LR and HR from CnD



$y_{CO2,F} = 0.15$; $P_H = 137.9$ kPa; $P_H/P_L = 12$; $T = 575$ K

S. P. Reynolds et al, *Adsorption*, submitted *(2007)*.

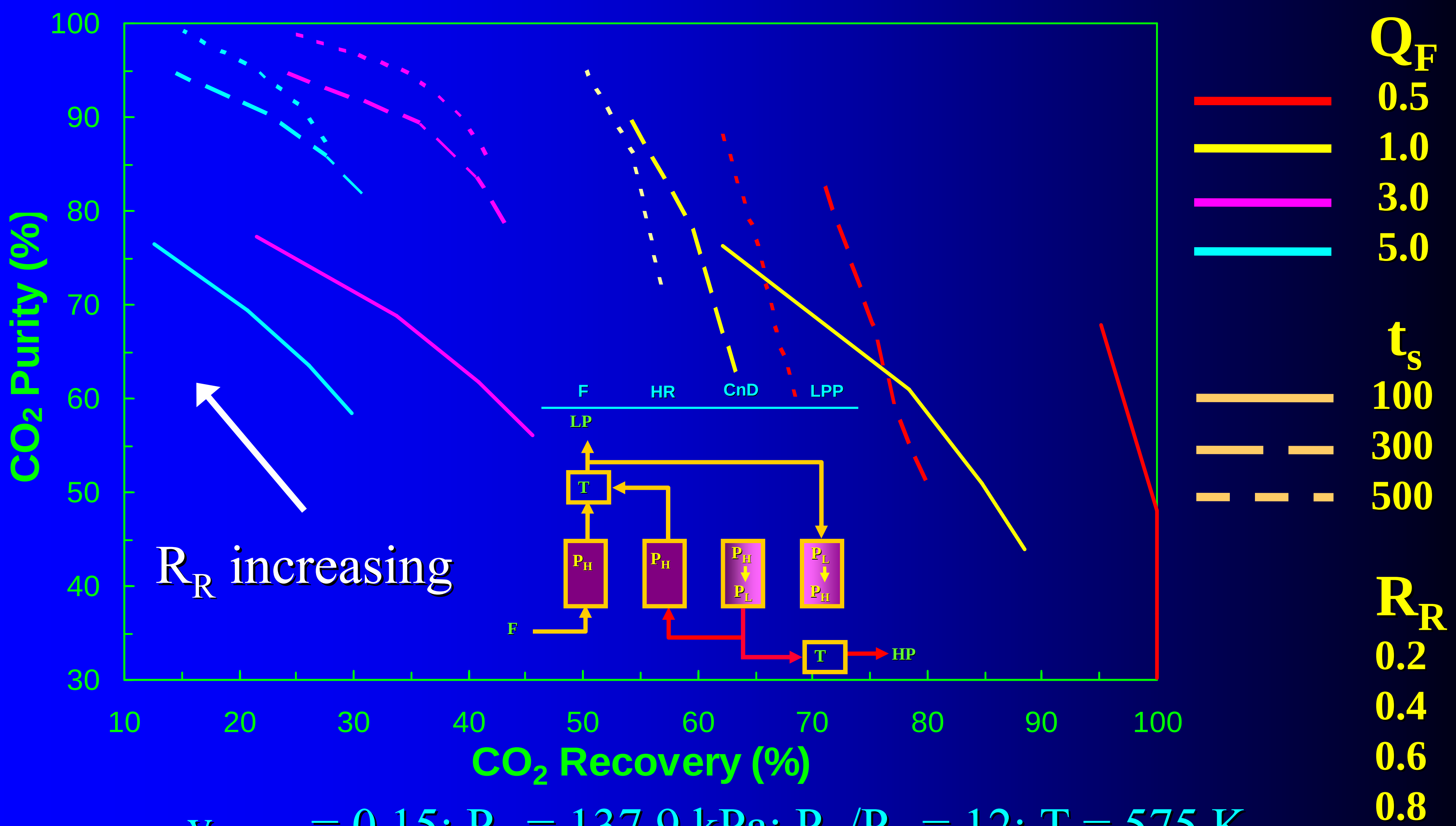
5-Bed 5-Step Cycle with LR and HR from LR Purge



$y_{CO2,F} = 0.15$; $P_H = 137.9$ kPa; $P_H/P_L = 12$; $T = 575$ K

S. P. Reynolds et al, *Adsorption*, submitted *(2007)*.

4-Bed 4-Step Cycle with HR from CnD

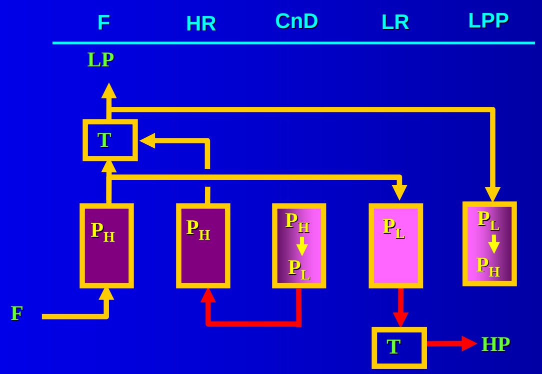


$y_{CO2,F} = 0.15$; $P_H = 137.9$ kPa; $P_H/P_L = 12$; $T = 575$ K

S. P. Reynolds et al, *Adsorption*, submitted *(2007)*.

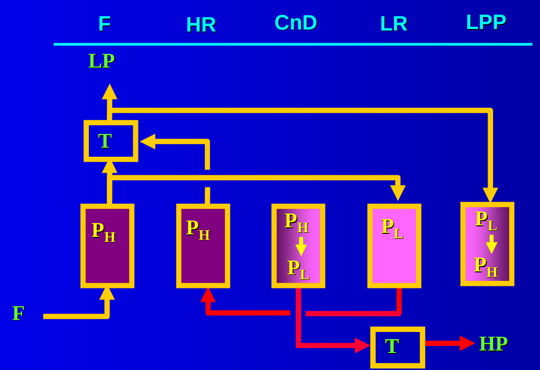
Maximum Performance Based on CO_2 Purity

5-Bed 5-Step with LR and HR from CnD



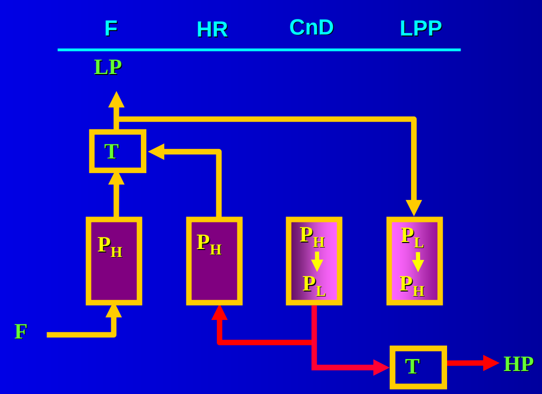
Maximum
$y_{CO2,HP}$ = 98.7 vol%
R_{CO2} = 98.7 %
(θ = 5.8 L STP/hr/kg)

5-Bed 5-Step with LR and HR from LR Purge



Maximum
$y_{CO2,HP}$ = 96.6 vol%
R_{CO2} = 71.1 %
(θ = 57.6 L STP/hr/kg)

4-Bed 4-Step with HR from CnD

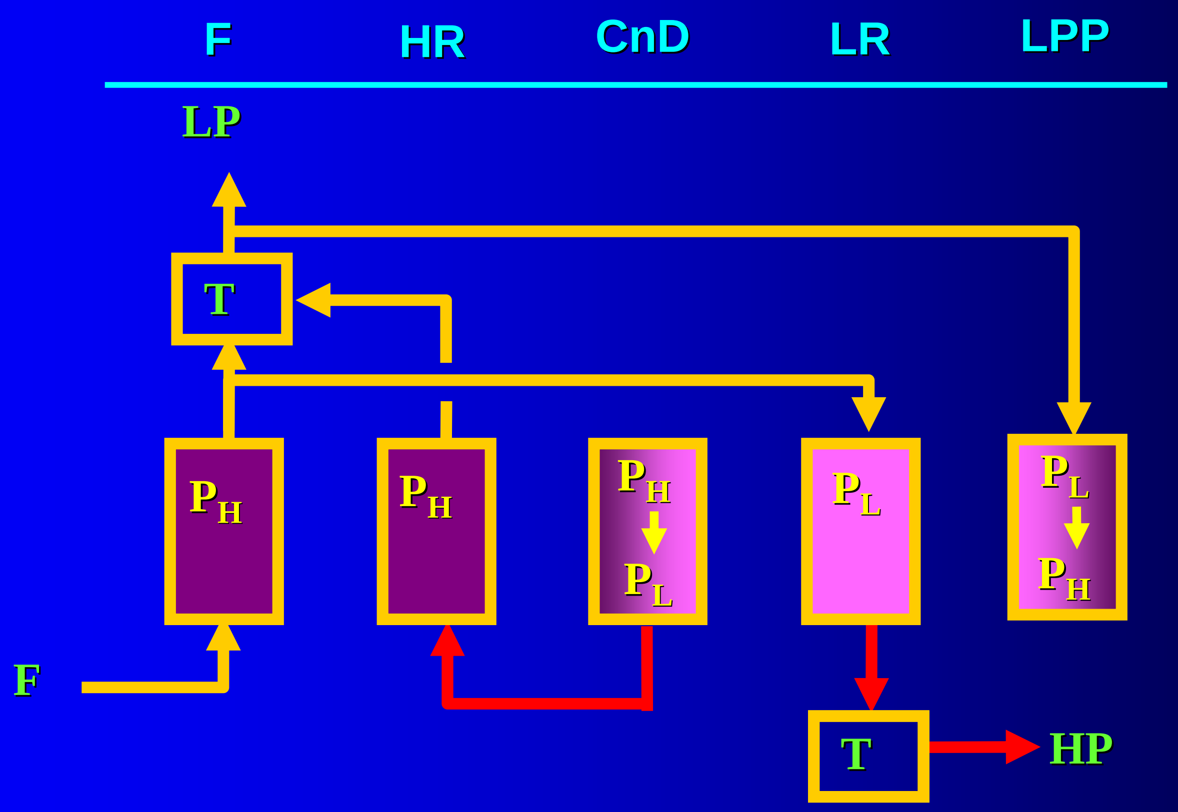


Maximum
$y_{CO2,HP}$ = 99.2 vol%
R_{CO2} = 15.2 %
(θ = 57.6 L STP/hr/kg)

Summary

5-bed 5-step stripping PSA cycle with LR and HR from CnD

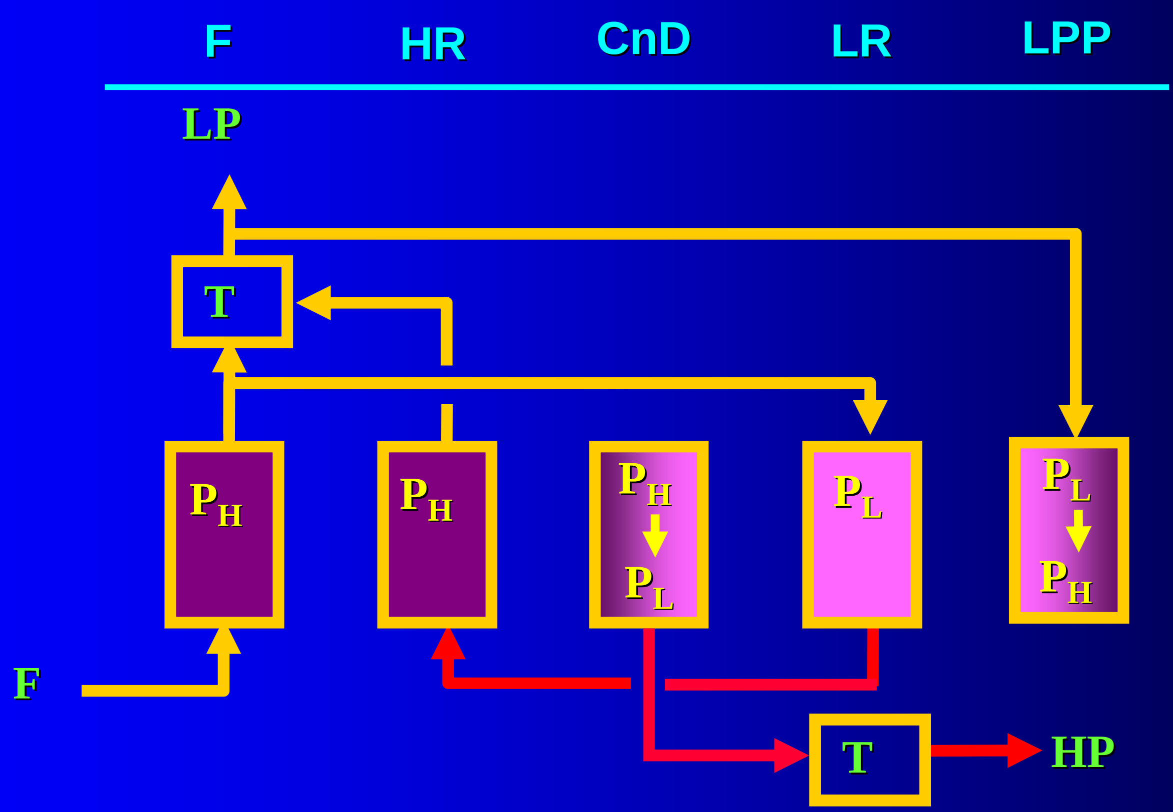
- good configuration for processes that need high purity and high recovery no matter the throughput
- trace light reflux important; lower γ tends to improve the performance considerably



Summary

5-bed 5-step stripping PSA cycle with LR and HR from LR Purge

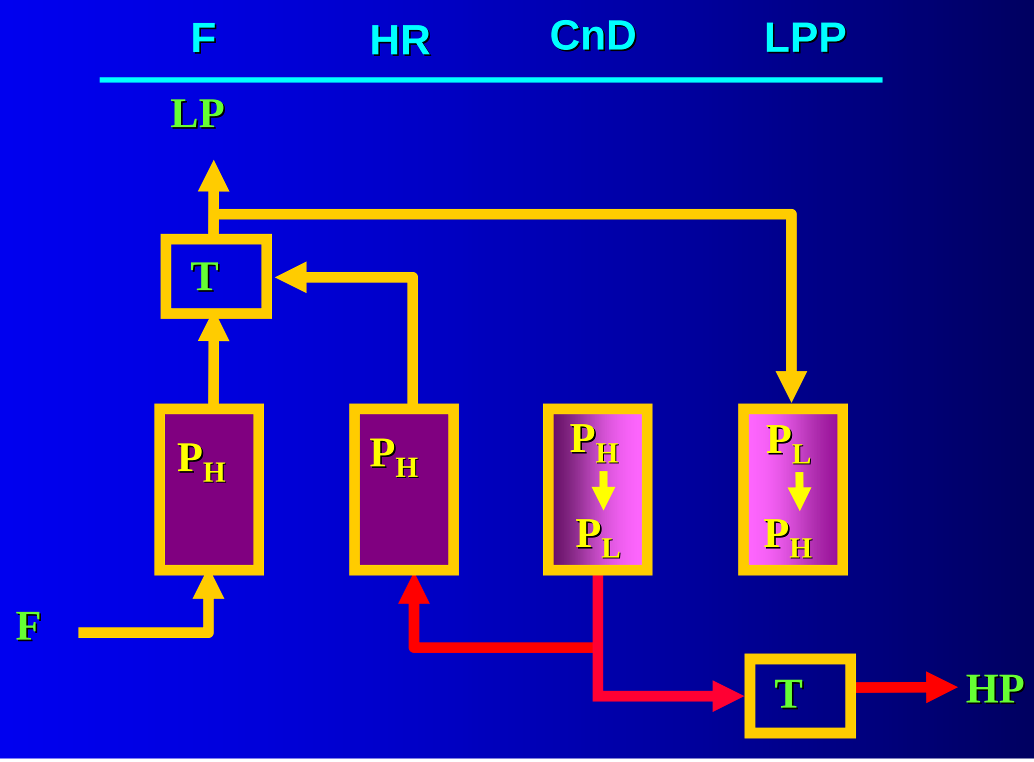
- good configuration for processes that need high purity and high throughputs with intermediate recovery
- light reflux important; higher γ tends to improve the performance considerably



Summary

4-bed 4-step stripping PSA cycle with HR from CnD

- good configuration for processes that need high purity and high throughputs no matter the recovery
- showed that what mattered was where the HR gas came from, not so much where the HP gas came from
- revealed how important the LR step was to the overall performance as it regenerates the adsorbent



HR PSA Cycle Conclusions

- many cycle permutations exist when adding a HR step to a cycle, especially with a LR step
- both surprising and counterintuitive effects were found when changing the source of the HR and HP gases
- study not exhaustive; more cycle permutations yet to be evaluated (REC, F+R, EQ, $t_{s,unequal}$,…)
- economic evaluation of best PSA cycles forthcoming (Air Products and Chemicals, Inc.)

Presentation Overview

- remaining work to be done in 3rd year

Future Work

- PSA cycle research continuing to gain better understanding of the HR PSA cycle configuration on process performance
- with high CO_2 purities and CO_2 recoveries now achievable, focus will be to
  - further evaluate effects of thermodynamics (heats)
  - increase feed throughput by learning how to configure unequal step time cycles
  - decrease power costs by incorporating one or more equalization steps in cycle configuration
- HTlc materials research and modeling is continuing
  - gain mechanistic understanding
  - better estimation of capacity and uptake and release rates of CO_2 in K-promoted HTlc
- commercial K-promoted HTLC finally obtained
  - fixed bed testing will be under way soon

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Thank You!

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