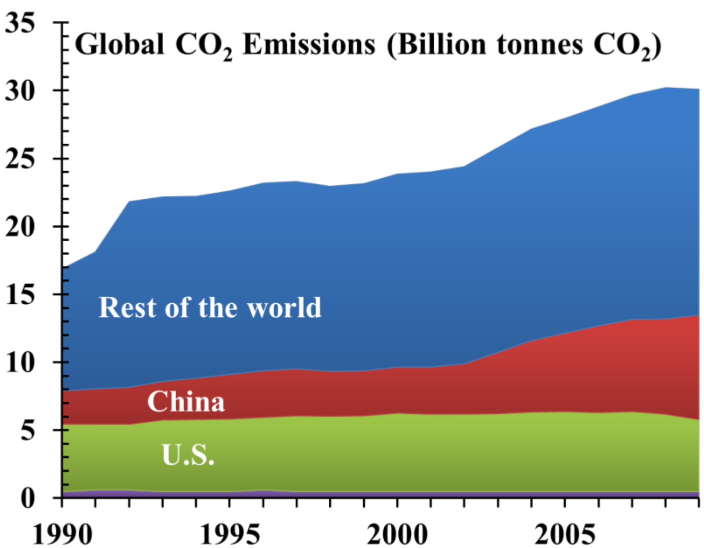
Rapid-Temperature Swing Adsorption Using Polymeric/Supported Amine Hollow Fiber Materials

Georgia Institute of Technology

DOE Award #: DE-FE0007804



International Energy Outlook 2013, US Energy Information Administration 2013, DOE/EIA-0484

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Key Idea:

***Combine*:**

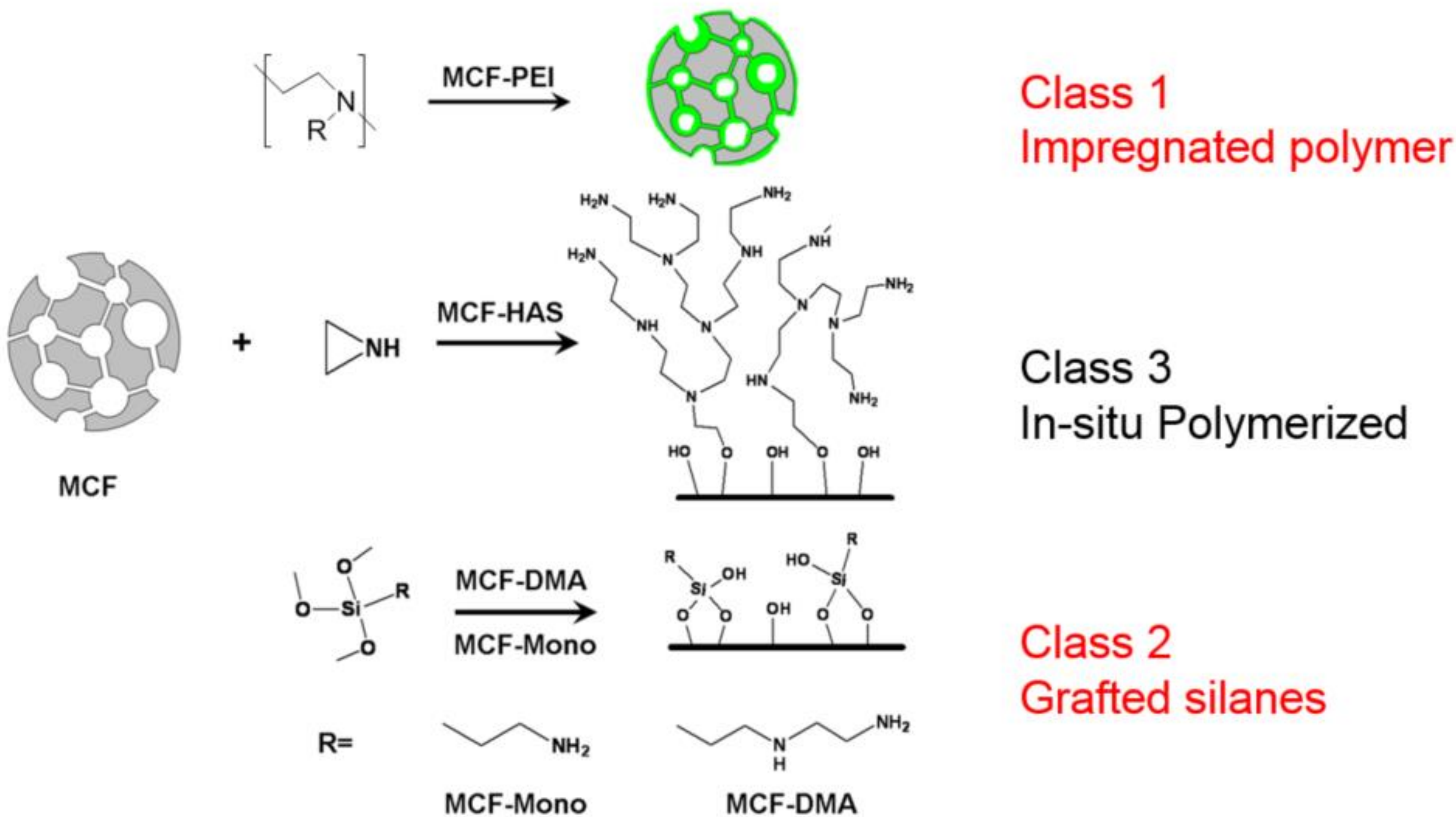
(i) state-of-the-art supported amine adsorbents, with

(ii) a new contactor tuned to address specific weaknesses of amine materials,

to yield a novel process strategy

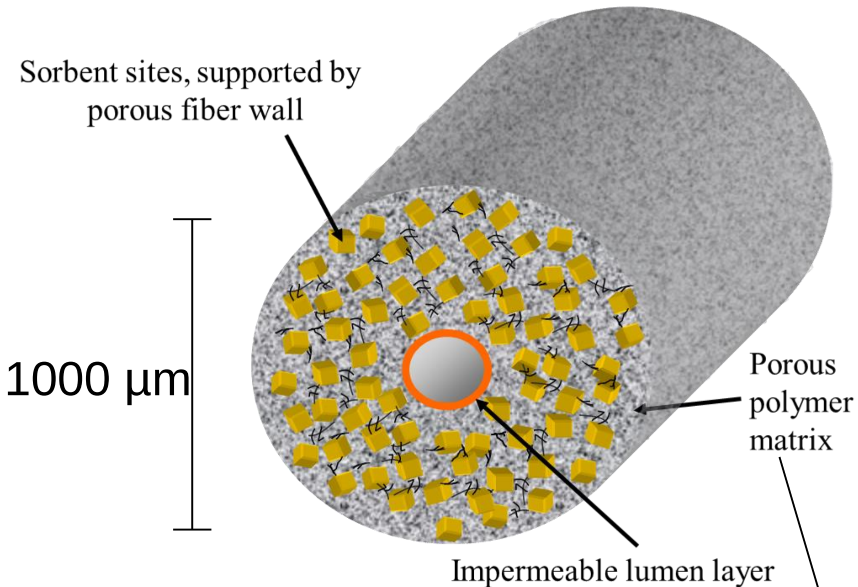
Silica-Supported Amine Sorbents

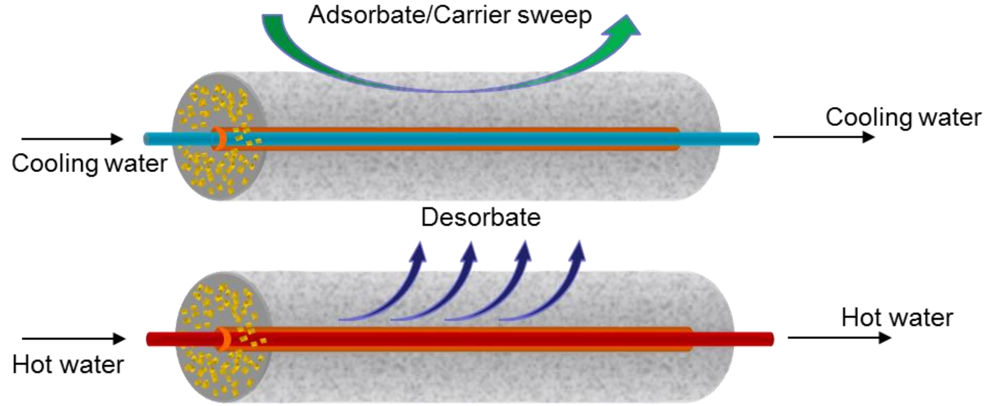
Amine sorbents widely studied in academia – but little work on scalable contactors



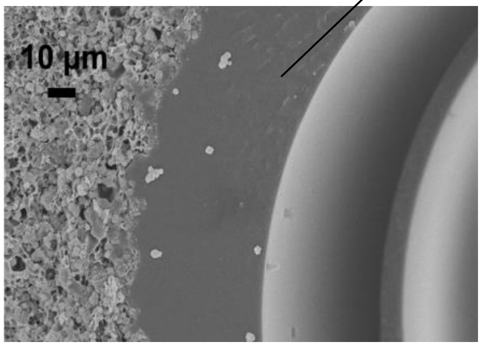
Supported amine sorbents require efficient heat management, $-\Delta H_S$ = 65-85 kJ/mol.

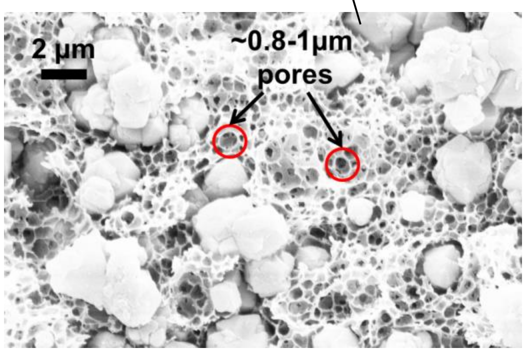
Hollow fiber sorbents: a mass producible structured sorbent inspired by hollow fiber membrane spinning

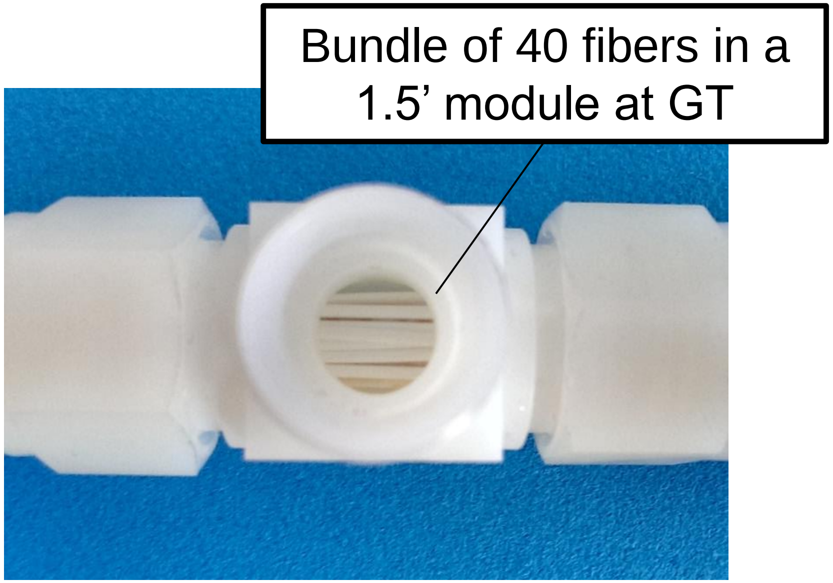




Ideal temperature swing adsorption

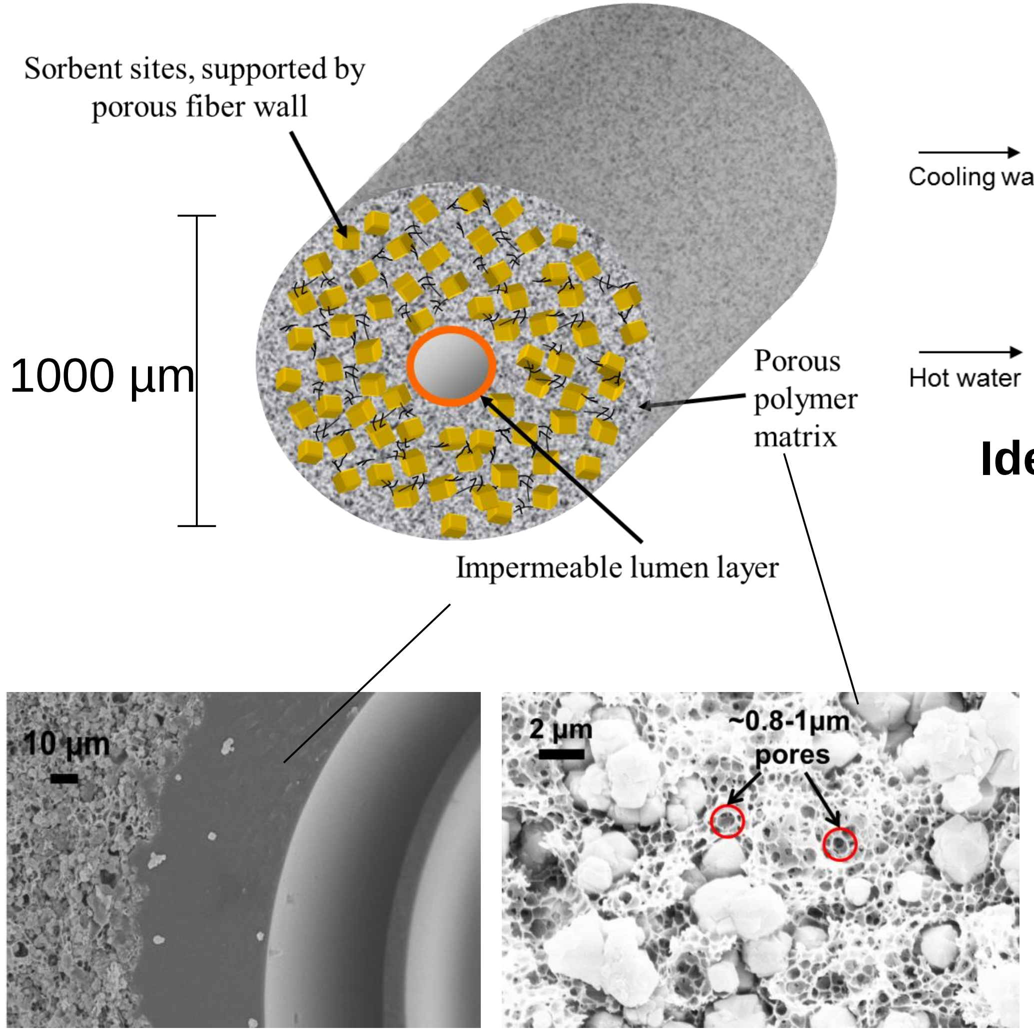


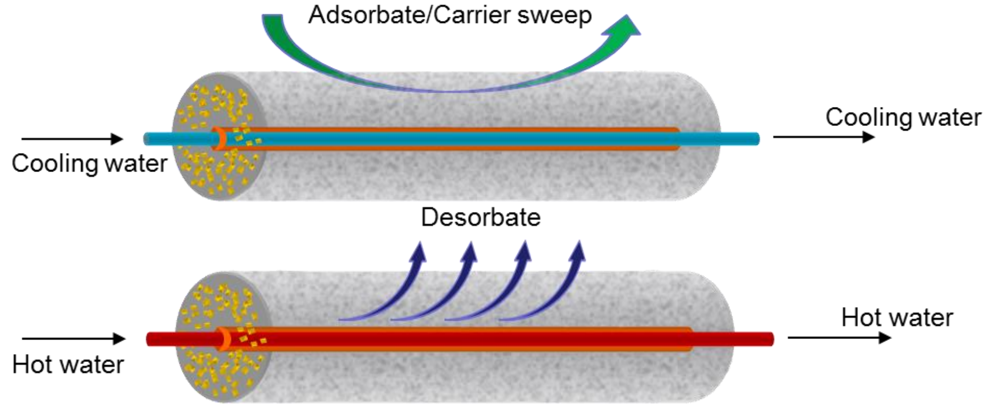




RP Lively et al., *Ind. Eng. Chem. Res.*, **2009**, 48, 7314-7324

Hollow fiber sorbents: a mass producible structured sorbent inspired by hollow fiber membrane spinning



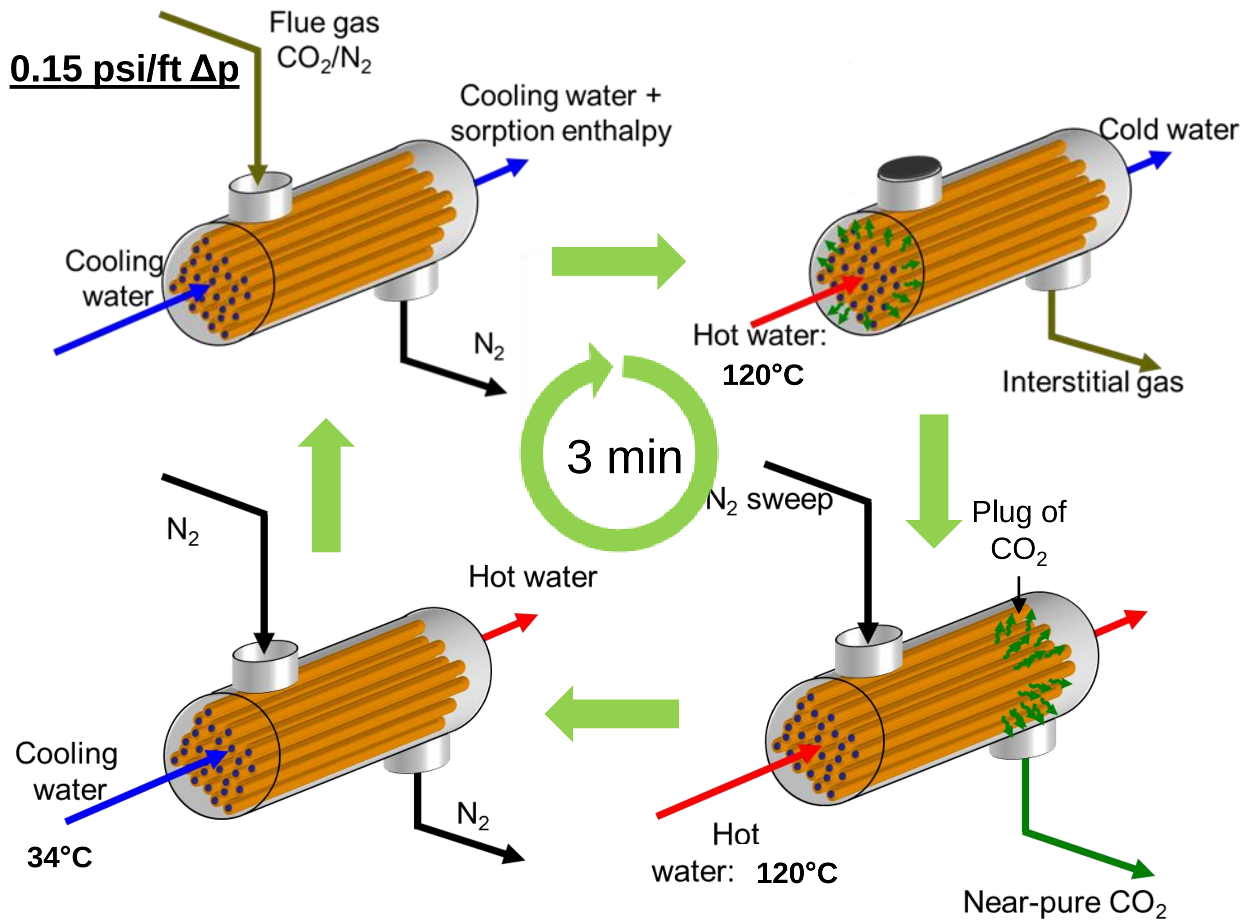


Ideal temperature swing adsorption

Large CO_2/CH_4 module
76 cm OD x 1.8 m
Used on 700 MMSCFD offshore platform
Courtesy, E. S. Sanders NAMS 2003 plenary

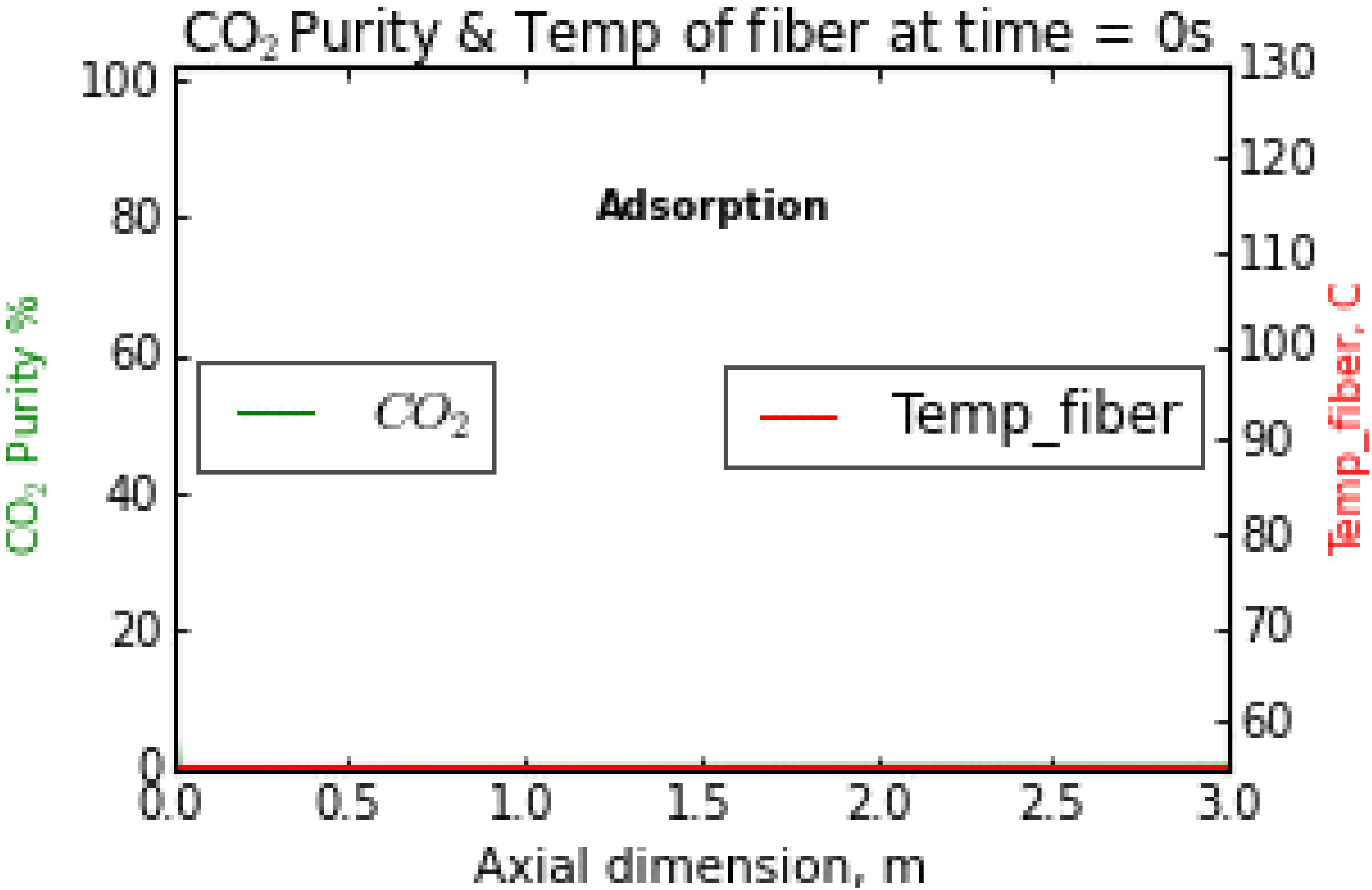
RP Lively et al., *Ind. Eng. Chem. Res.*, **2009**, 48, 7314-7324

Rapid temperature swing adsorption (RTSA)



Lively RP, et al., *Int. J. Greenhouse Gas Control* **2012**, 10, 285

Rapid temperature swing adsorption (RTSA)



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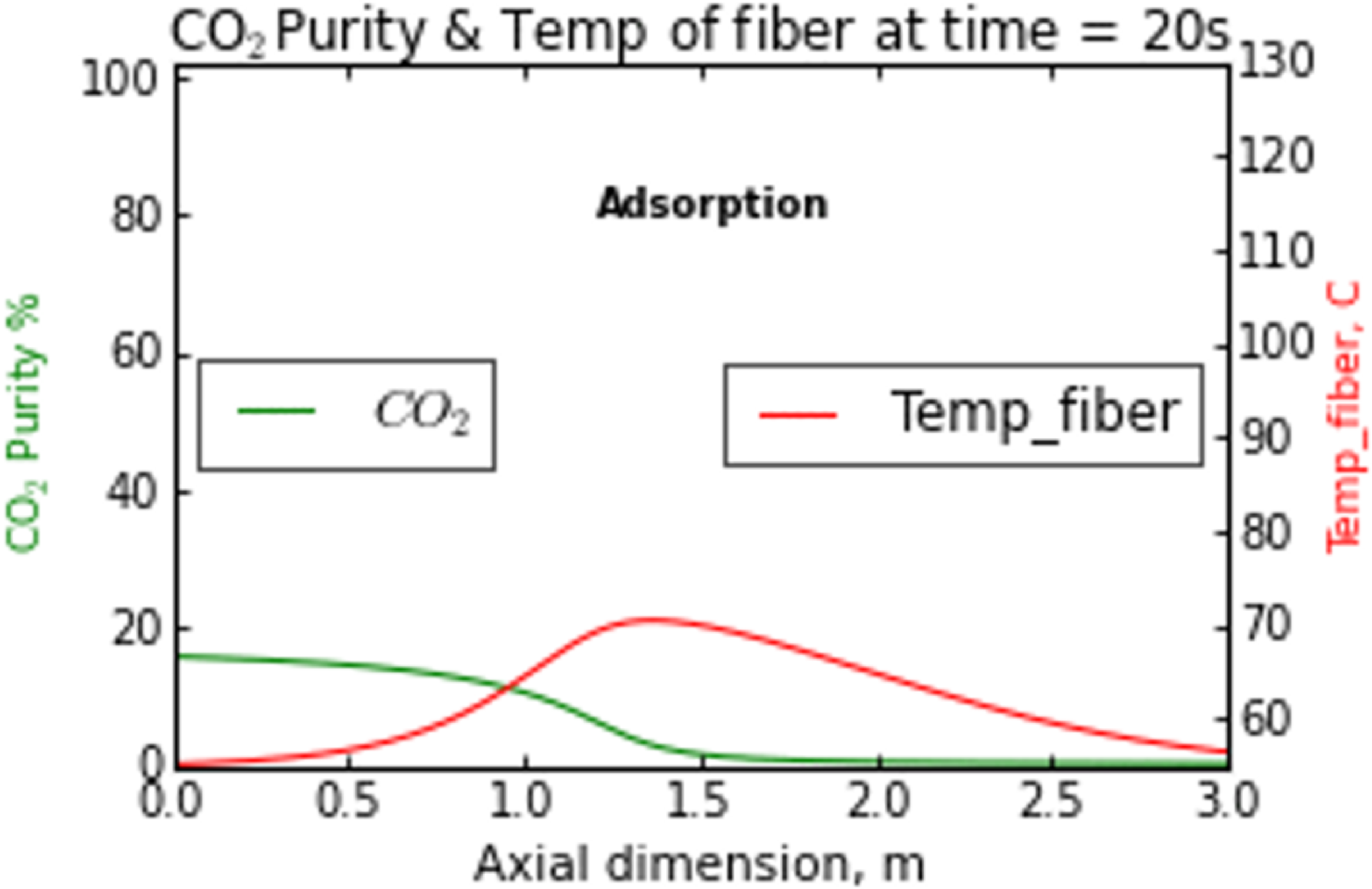

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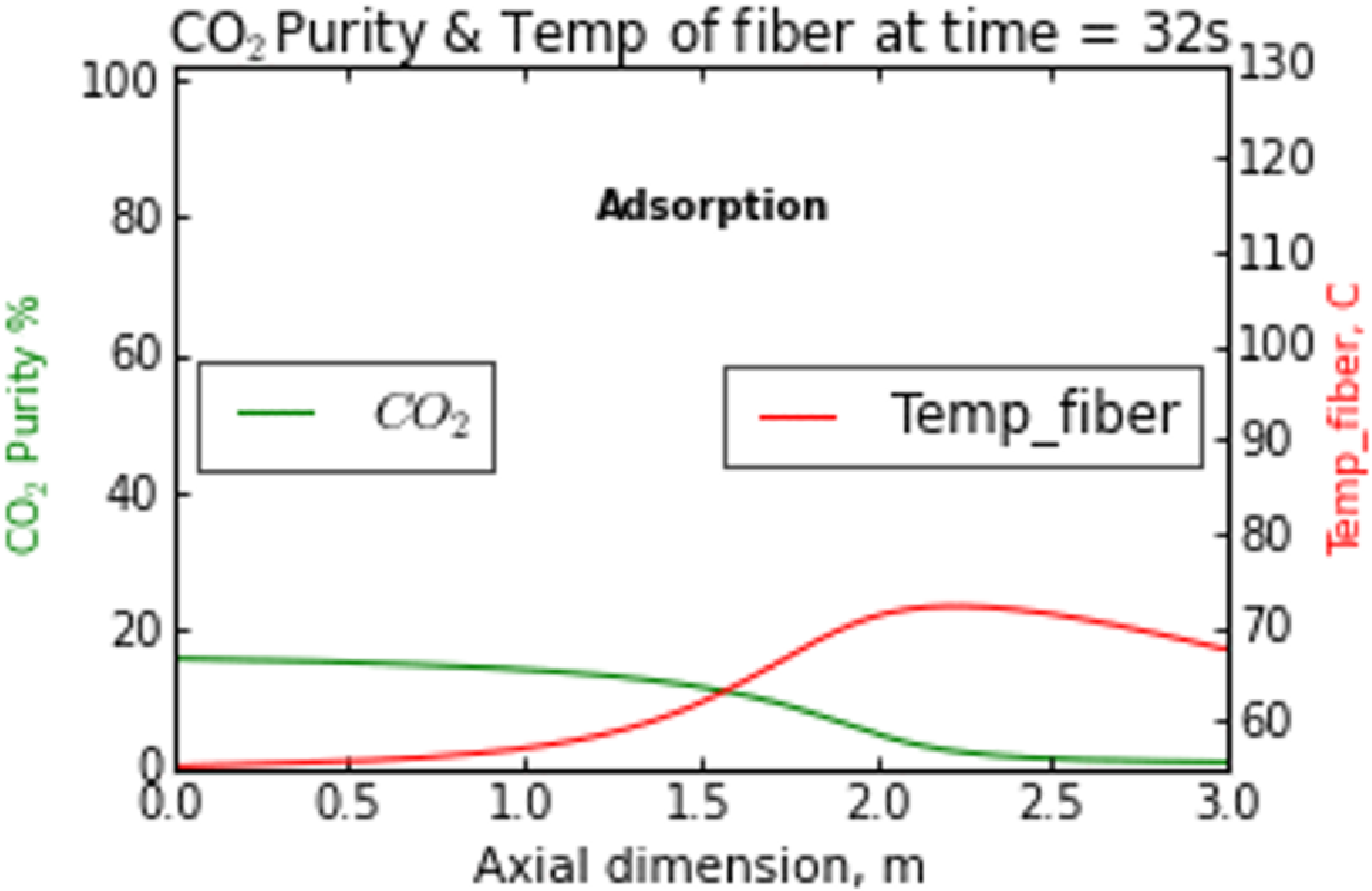

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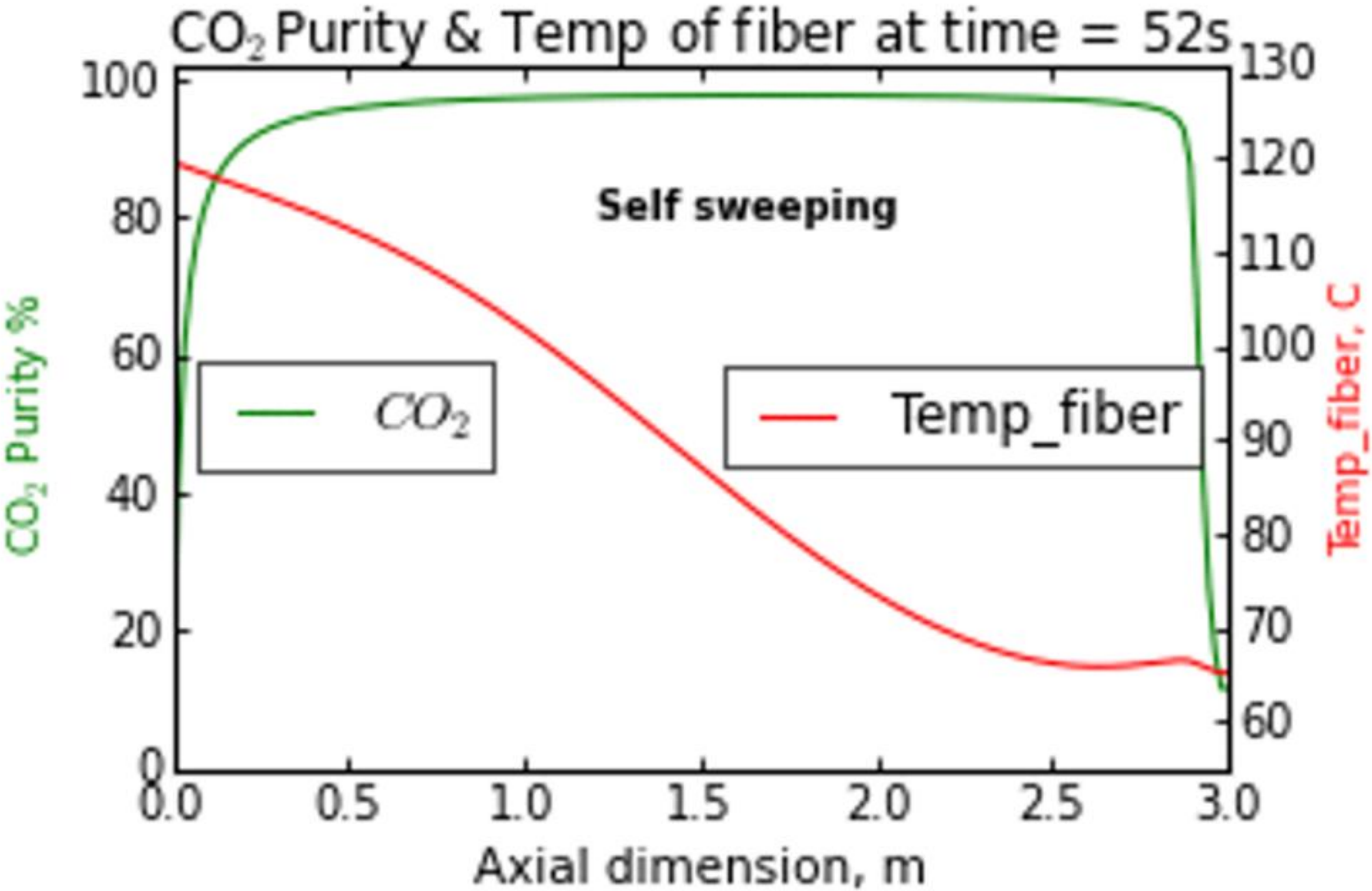

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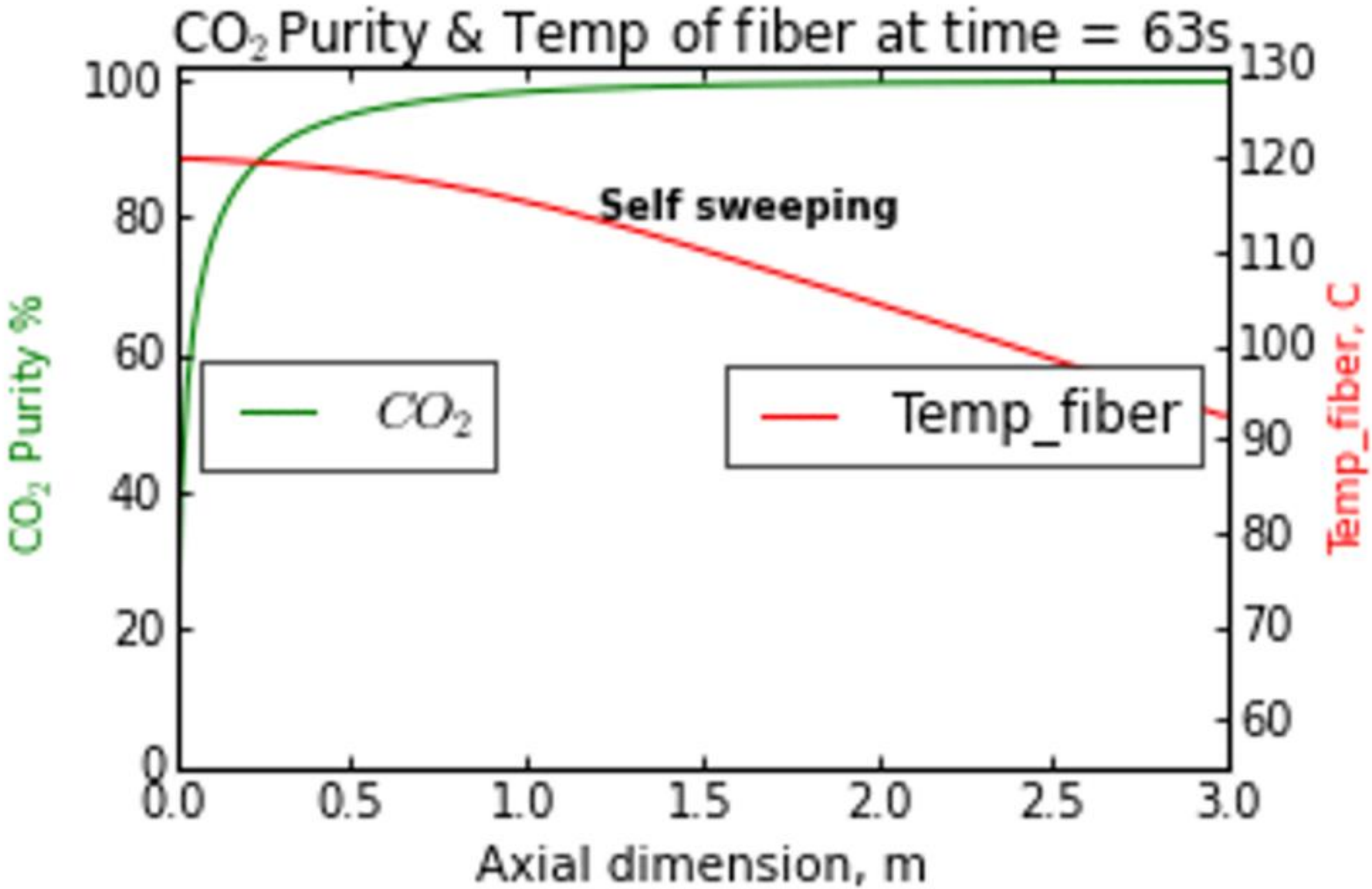

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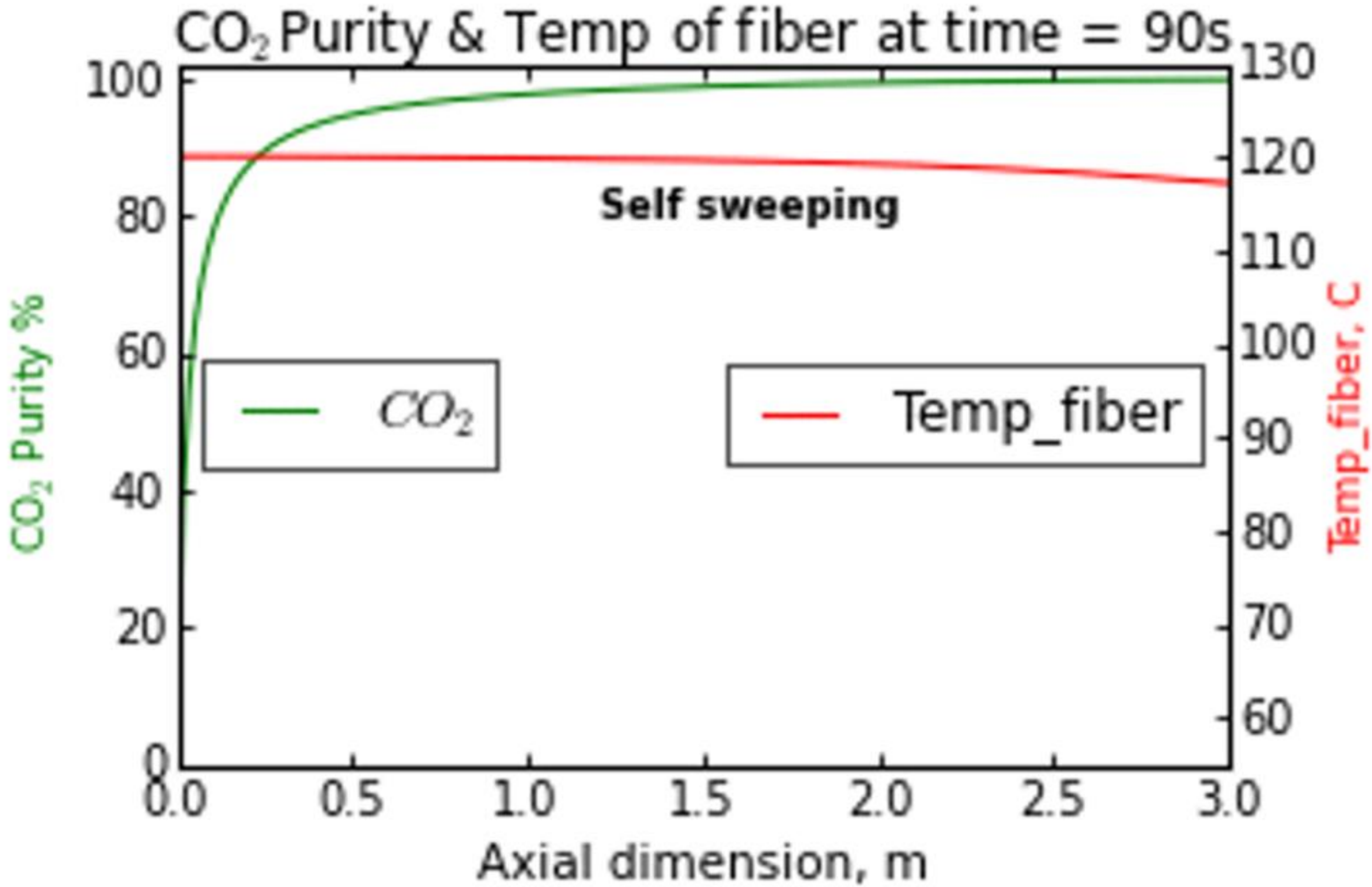

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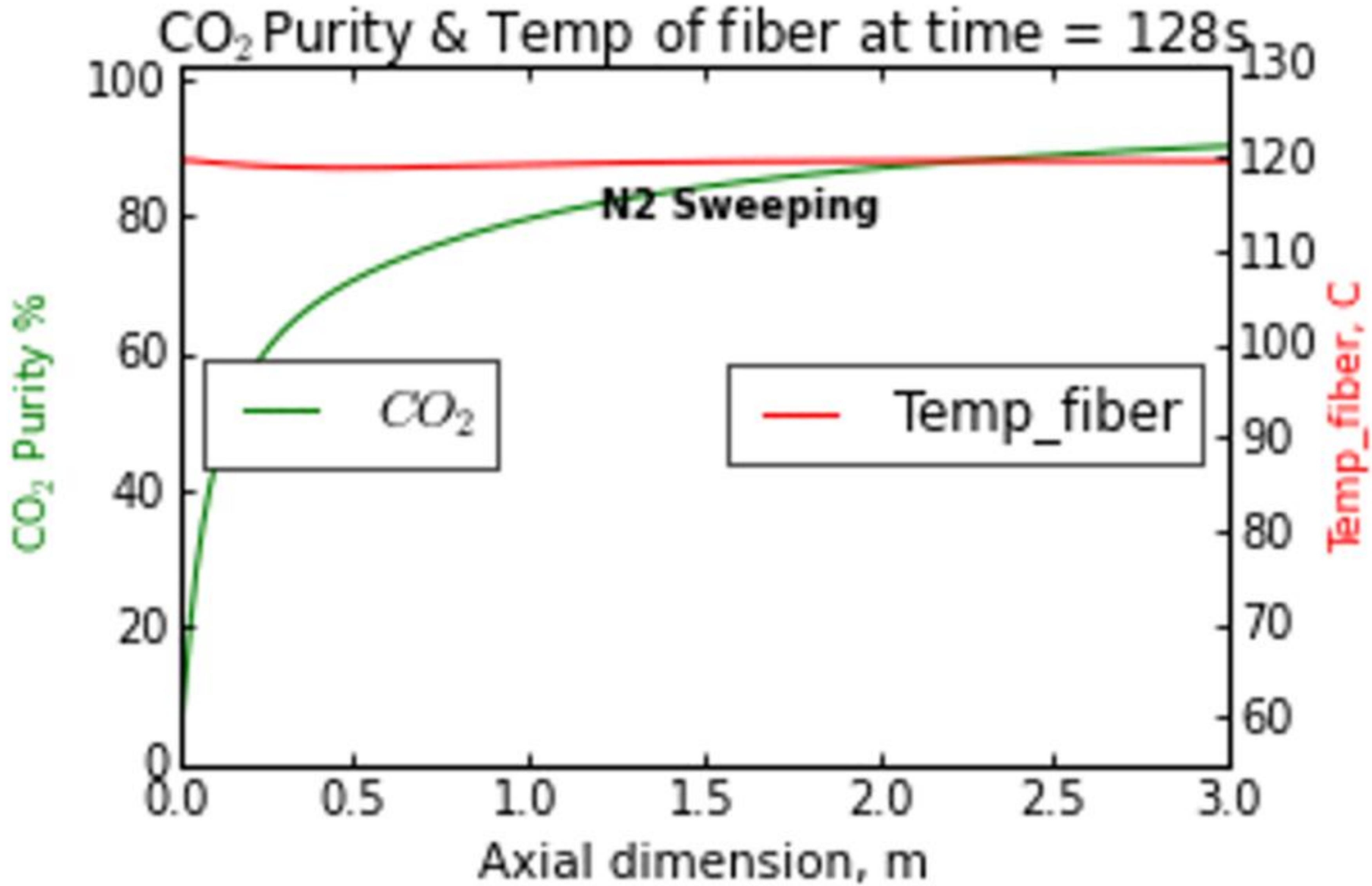

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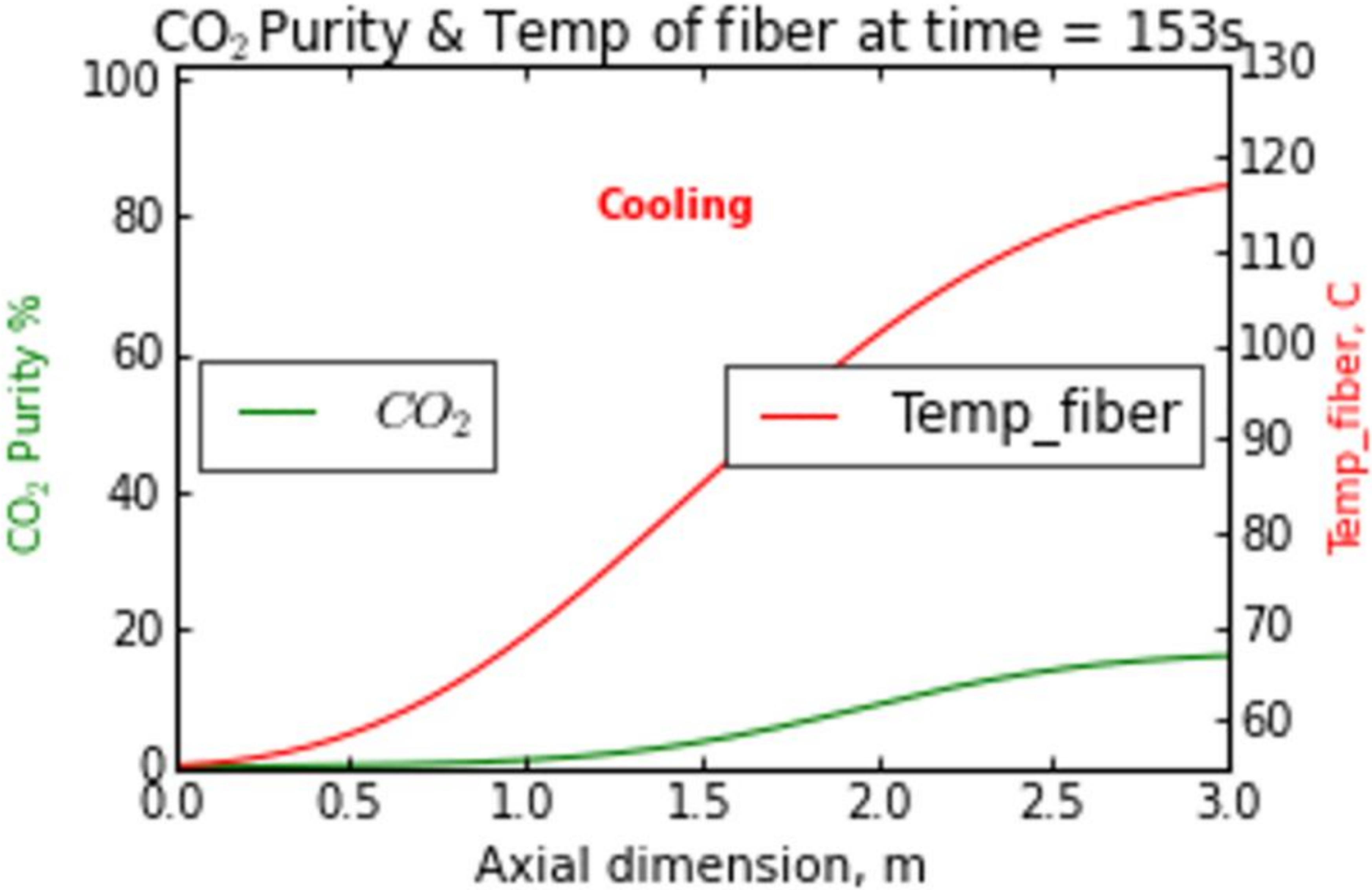

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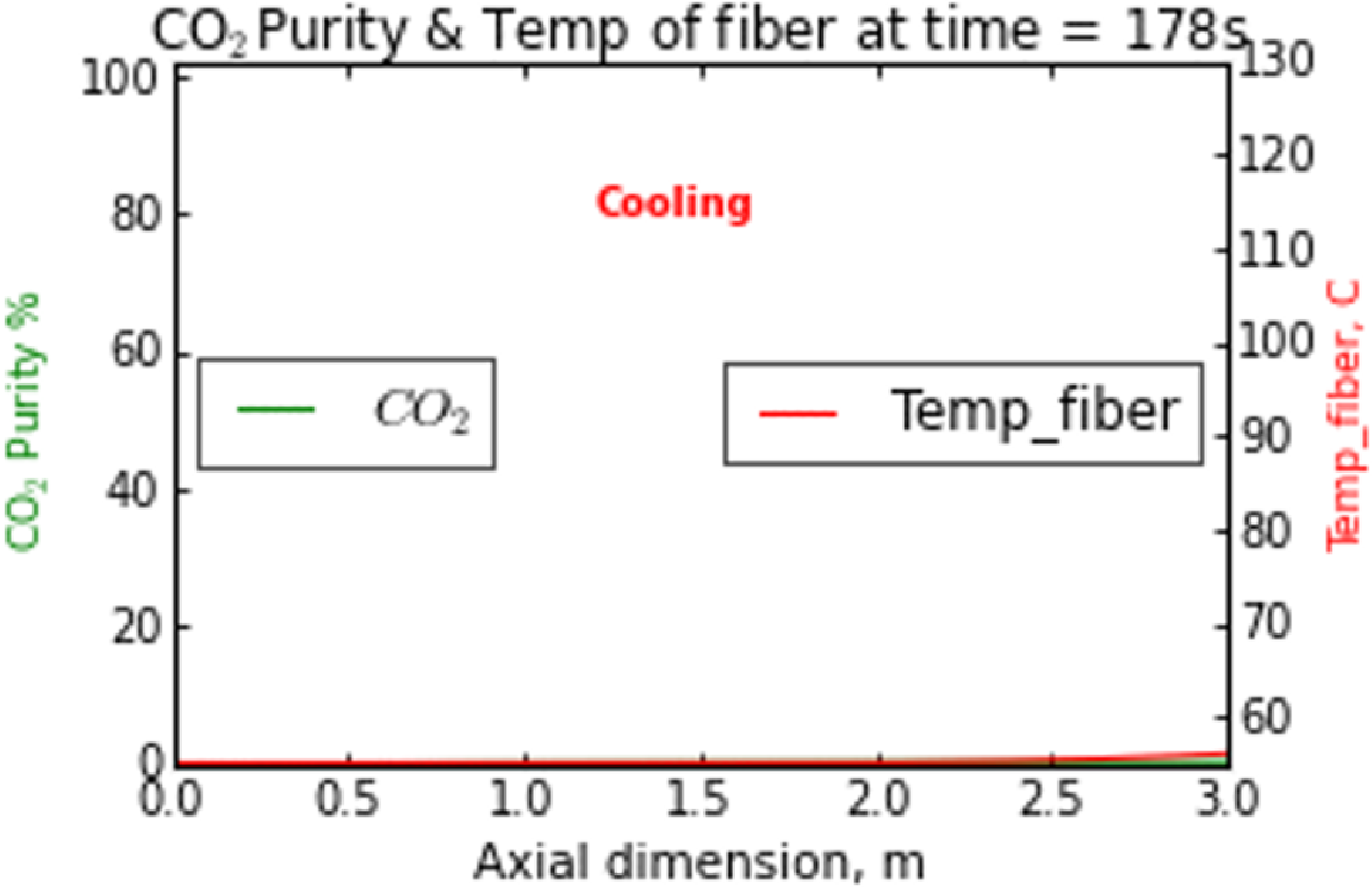
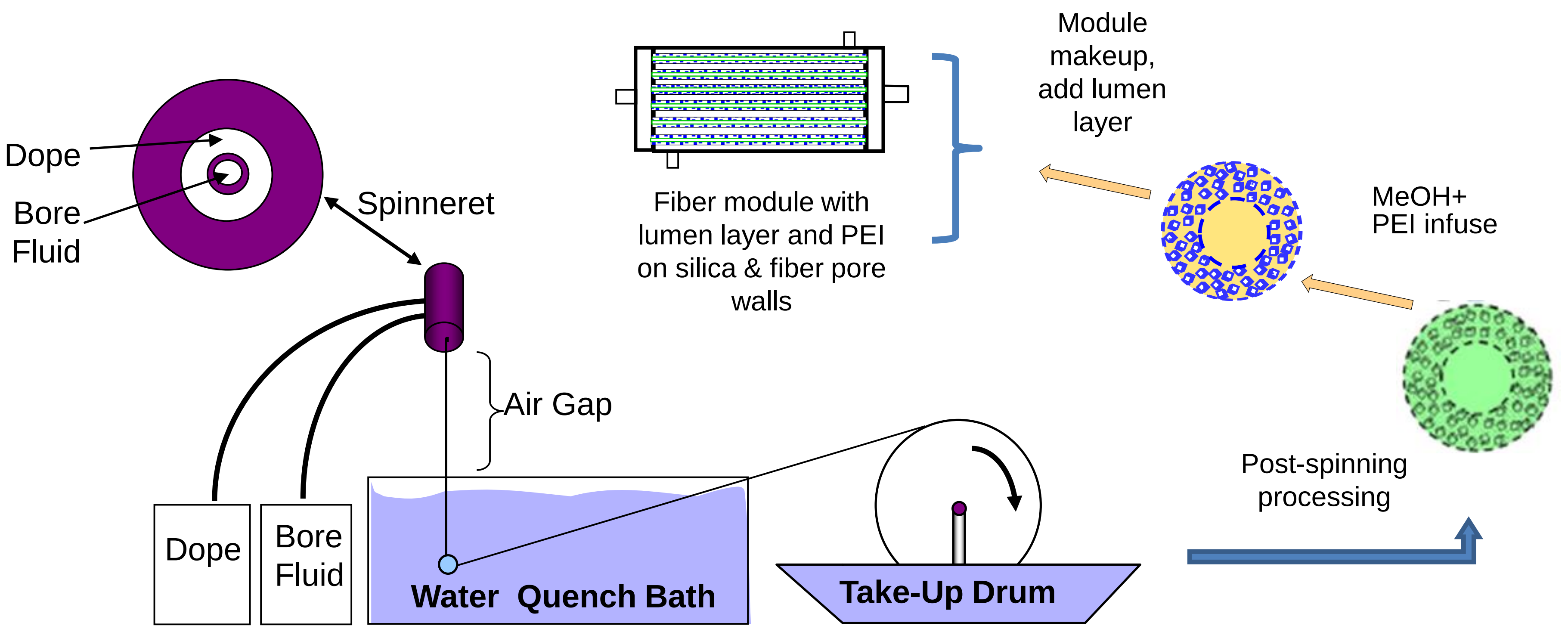


Creating the hollow fiber sorbents: Post-spinning amine infusion

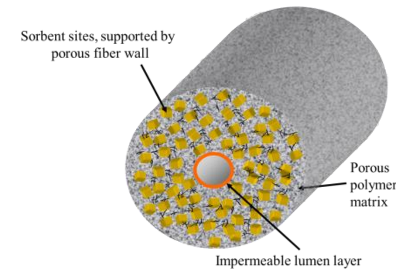
New method for amine-containing fiber sorbent synthesis



- **First successful spinning of polymer/silica/PEI hollow fiber sorbent**
- **Simple, scalable procedure—does not appreciably change current solvent exchange procedure**
- **Proved the concept with cellulose acetate (CA) - CA/silica/PEI**

Labreche et al., *Chem. Eng. J.*, **2013**, 221, 166-175.

Hollow Fiber Contactor as Heat Exchanger



Constructing a barrier lumen layer in the fiber bore allows the fibers to act as an adsorbing shell-in-tube heat exchanger.

Two approaches:

(i) Post-treatment: Flow of a polymeric, Neoprene ® latex and cross-linker through fibers

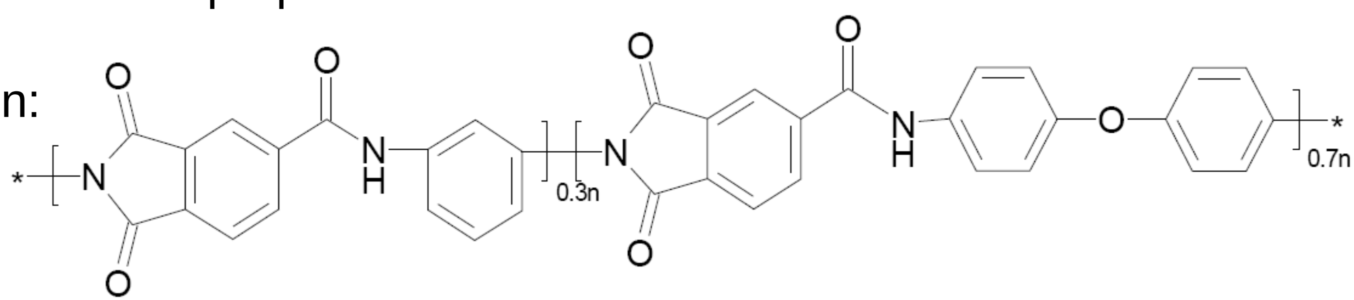
- Disadvantage – fibers can become clogged by latex, requires careful handling of latex

(ii) Dual layer fiber spinning – spin the lumen layer when initial fiber formed

- Advantage – highly scalable synthesis when poly(amide-imide) like Torlon® employed

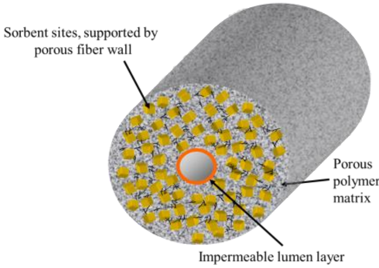
- Main fiber: porous Torlon® containing 50-60 wt% silica;
  Lumen layer: dense Torlon®; post-treatment with PDMS gives excellent barrier properties

Torlon:



Labreche et al., *J. Appl. Polym. Sci.*, **2015**, 132, 4185.

Hollow Fiber Contactor as Heat Exchanger



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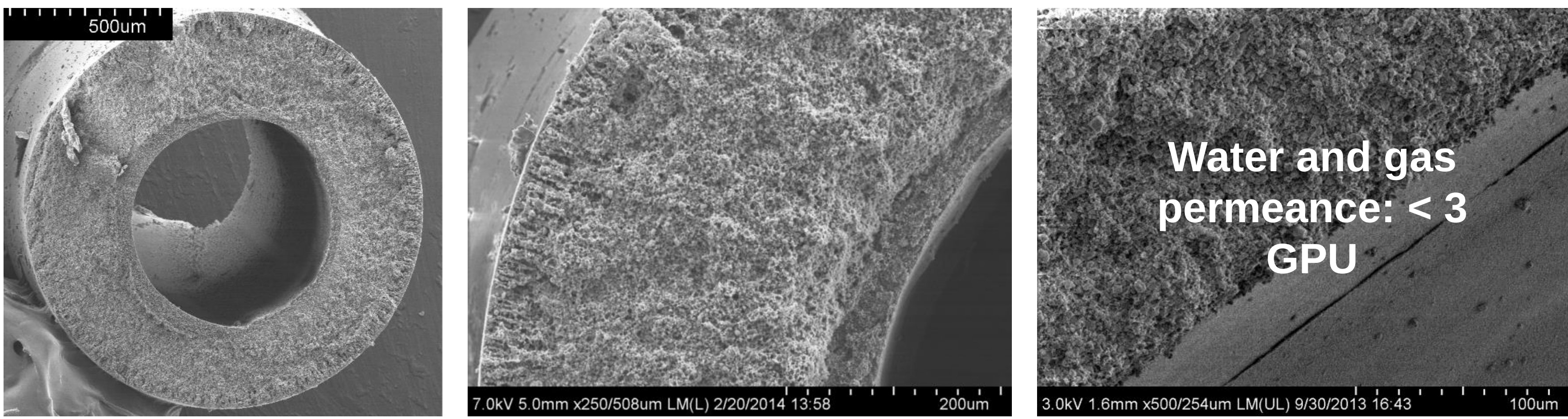
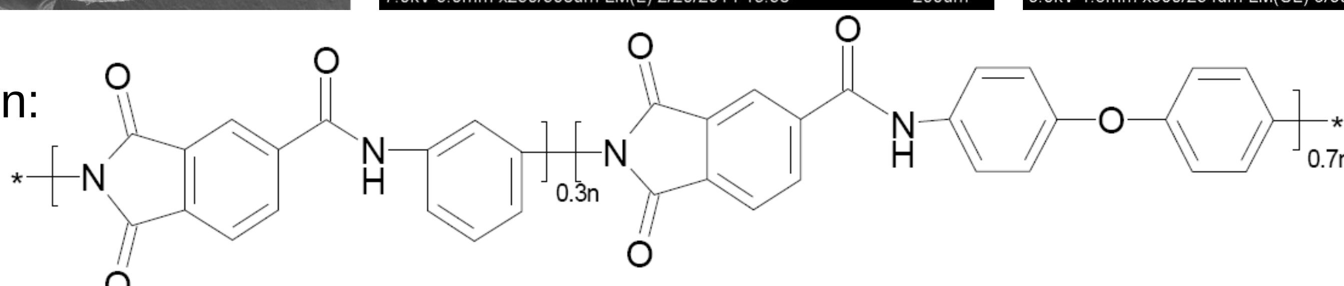
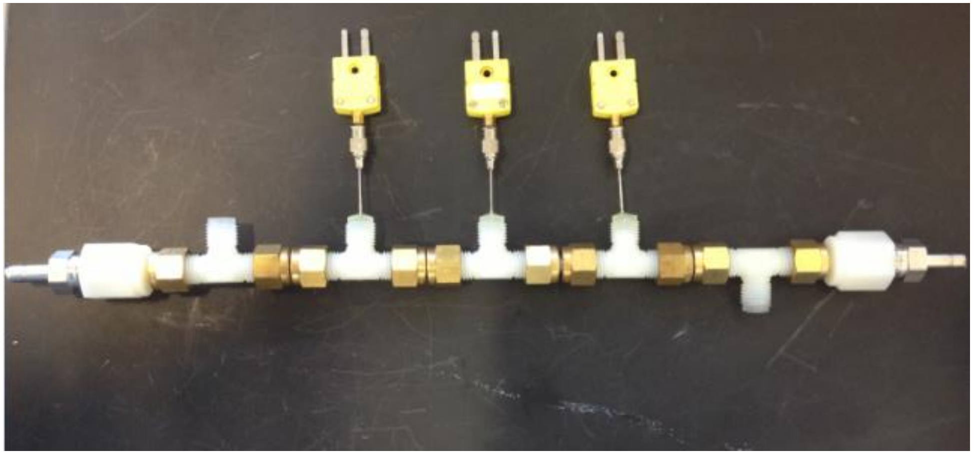


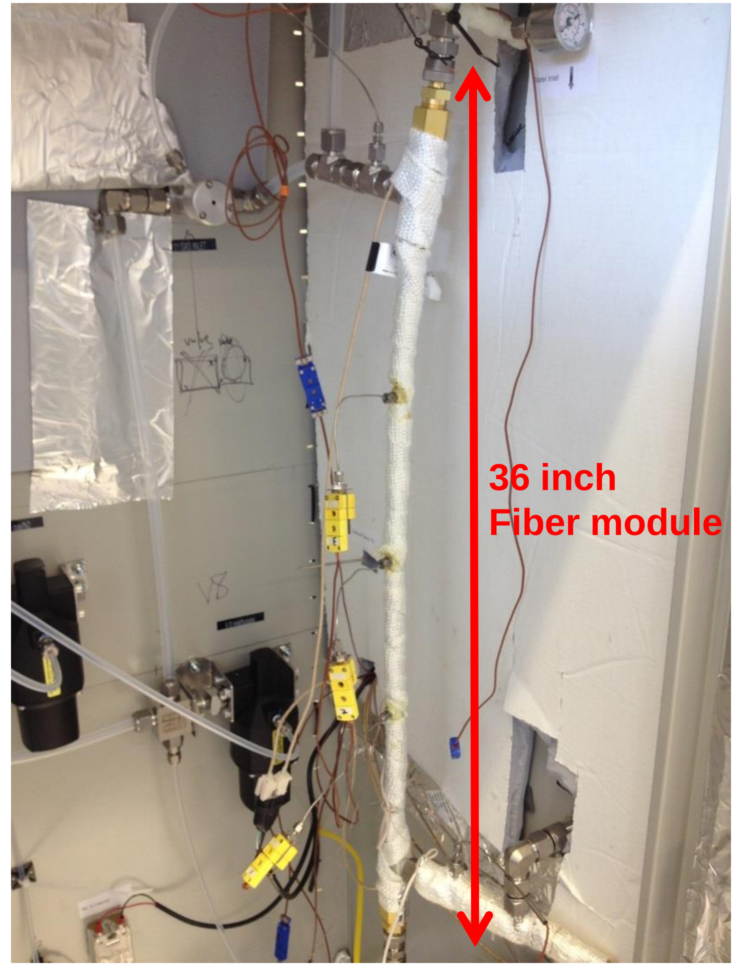
Torlon:

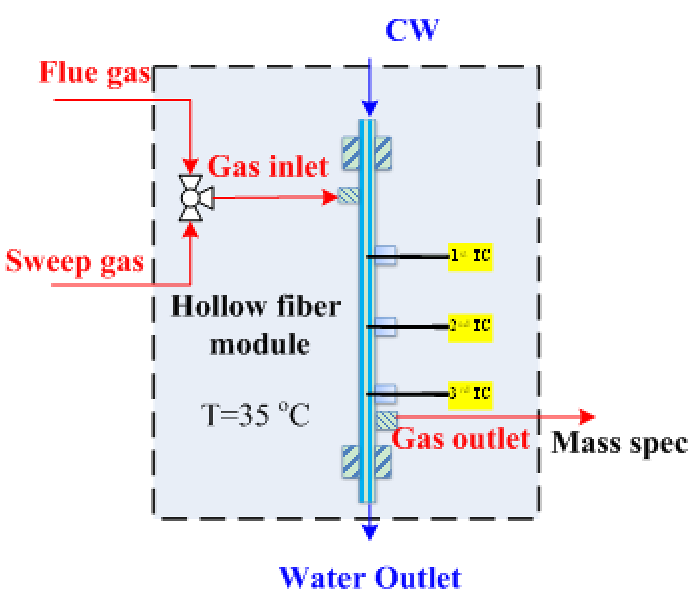


Labreche et al., *J. Appl. Polym. Sci.*, **2015**, 132, 4185.

Lab-scale RTSA design and operation





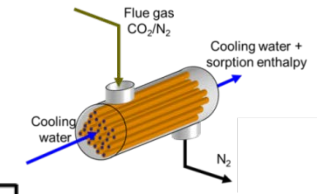


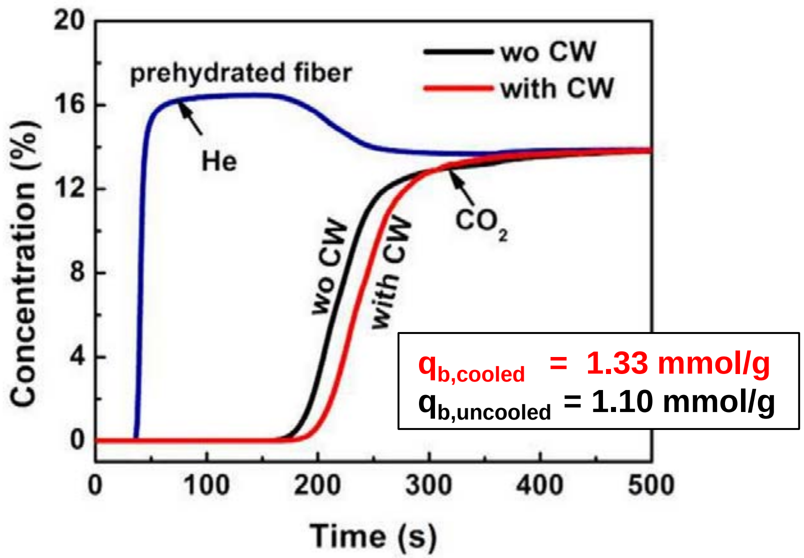
Flue gas composition: 35 °C, 1 atm

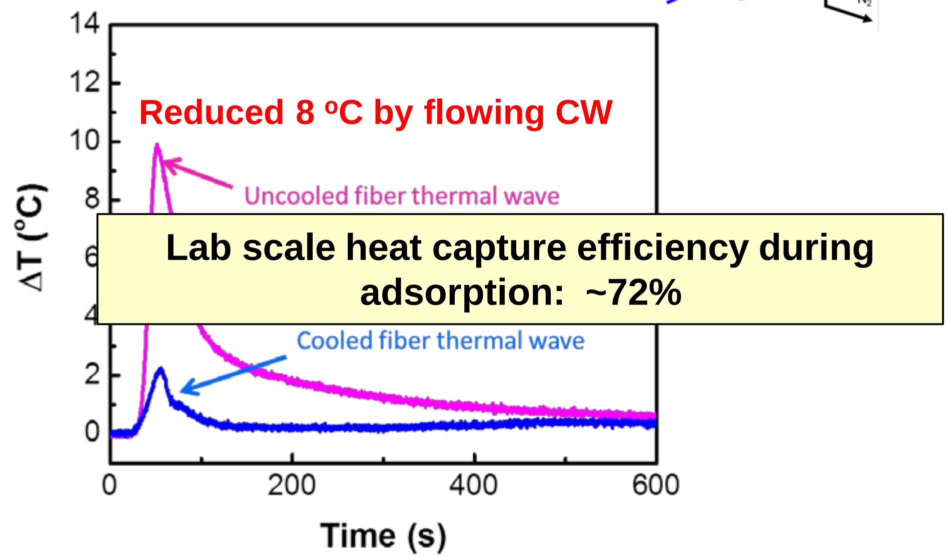
~ 13% CO_2, ~13% He (Inert tracer), 6% H_2O, balance gas N_2

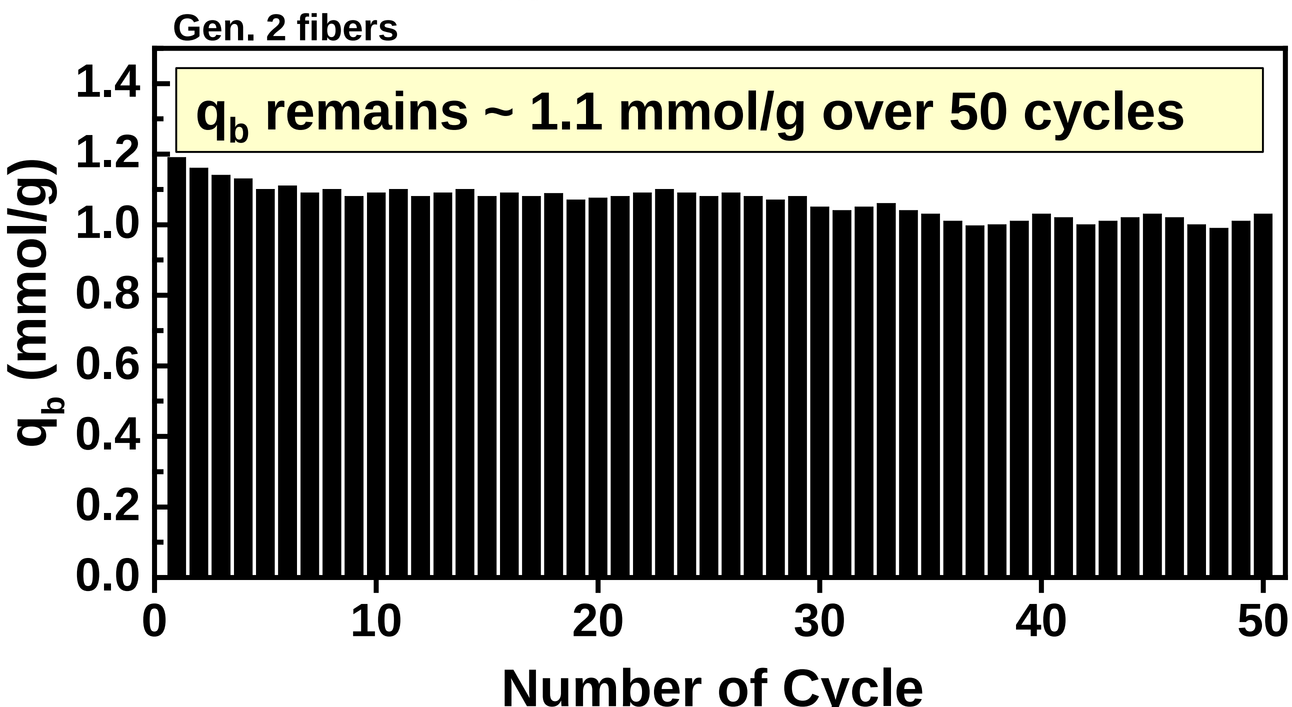
q_b: breakthrough capacity

Cooled Torlon-C803-PEI Fiber Sorbent Generation 3 Fibers





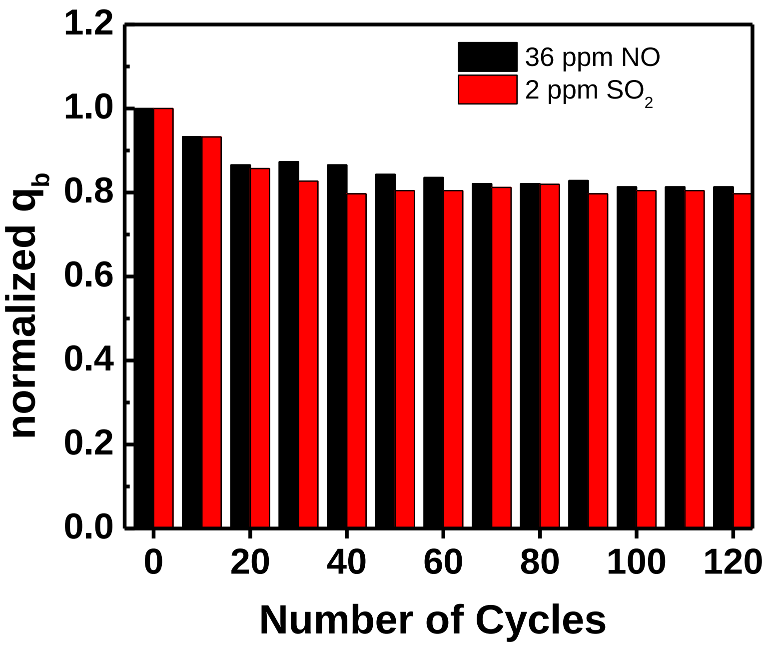


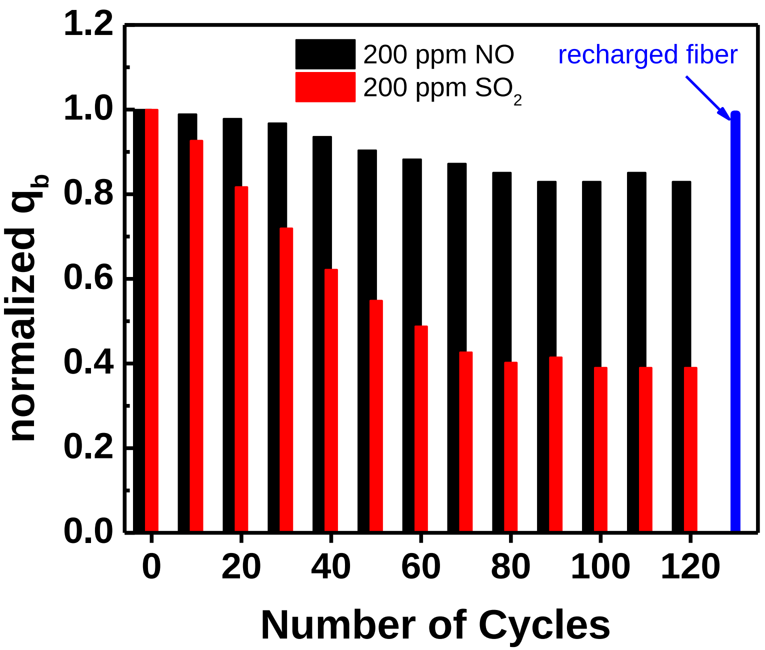


Gen. 3 fibers:
q_b~1.4 mmol/g
q_{swing}~0.85 mmol/g

Target q_S ~1 mmol/g

Impact of SO_x/NO_x on Fiber Module Operation





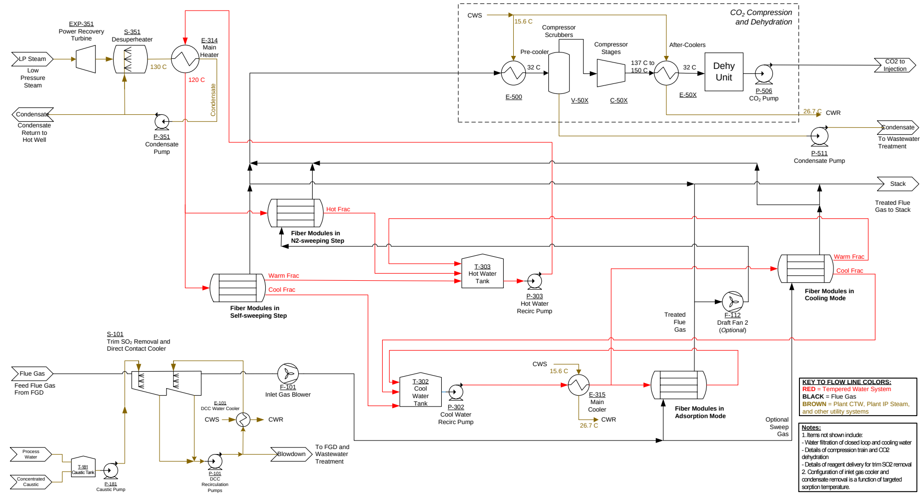
- **NO_2, SO_2** adsorb strongly, but have modest impact at low concentration
- Saturation capacity loss observed
- High concentration of gases (200 ppm) cause significant capacity loss, but a plateau was observed. Low concentration NO_2 had no measurable impact on capacity for class 1 fibers.
- Deactivated fibers can be <u>stripped of amine and recharged in the field</u> for **<u>full capacity regeneration.</u>**

Fan et al., *AIChE J.*, **2014**, 60, 3878-3887.

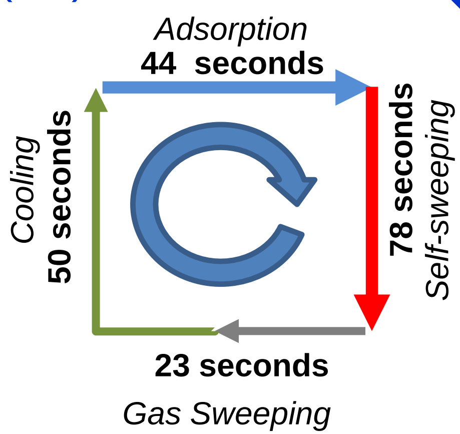
Overall approach

Trimeric Corp.

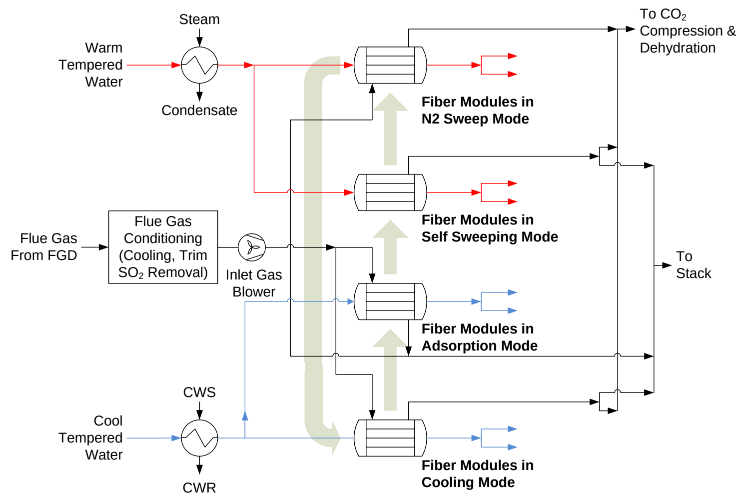
DOE Metric Calculation. Feedback to single fiber design and optimization



Cycle Design on Single Fiber (GT)



Cycle Model Validation and Scale Up to Module Level (GT and Trimeric)



Water Looping for Heat Integration

Integration with Plant Design and Escalation for TEA (Trimeric)

Performance Evolution during Project and Future Directions

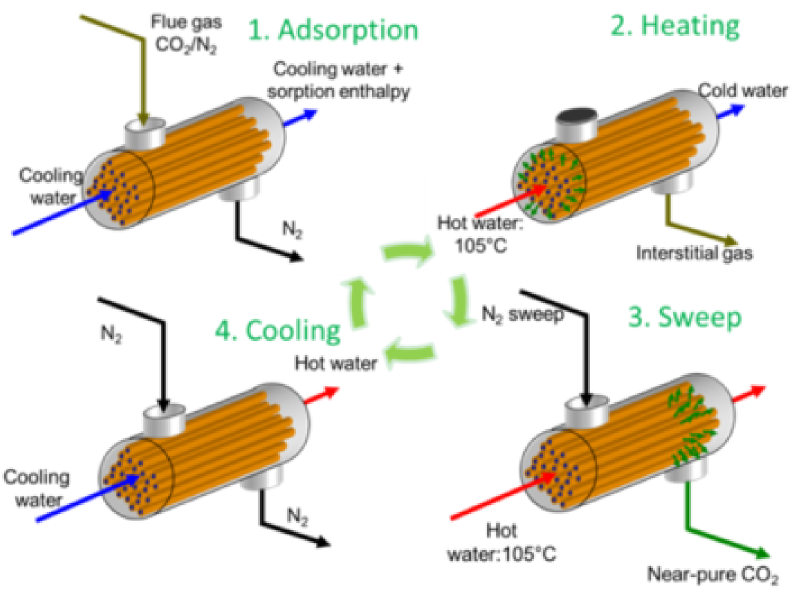
Description	Units	Year 2 Q4 (Sept 2013)	Year 3 (July 2014)	Year 3 (Jan 2015)
		RTSA	RTSA	RVTSA – 0.2 bar
Escalation Factor		**1.67**	**1.53**	**1.40**
Levelized Costs of Electricity and Steam				
Levelized cost of electricity	mills/kWh	178	154	126
Levelized cost of steam	$/1,000 lb	16.2	14.0	11.5
Cost of CO_2 Capture				
Total Annual Cost of CO_2 Capture	MM$/year	277	302	237
Impact of CO_2 Capture on Plant Efficiency				
Net Plant Efficiency without CO_2 Capture (HHV)	%	39.3	39.3	39.3
Net Plant Efficiency with CO_2 Capture (HHV)	%	22.0	25.6	28.8
Change in Net Plant Efficiency	%	-17.3	-13.7	-10.5

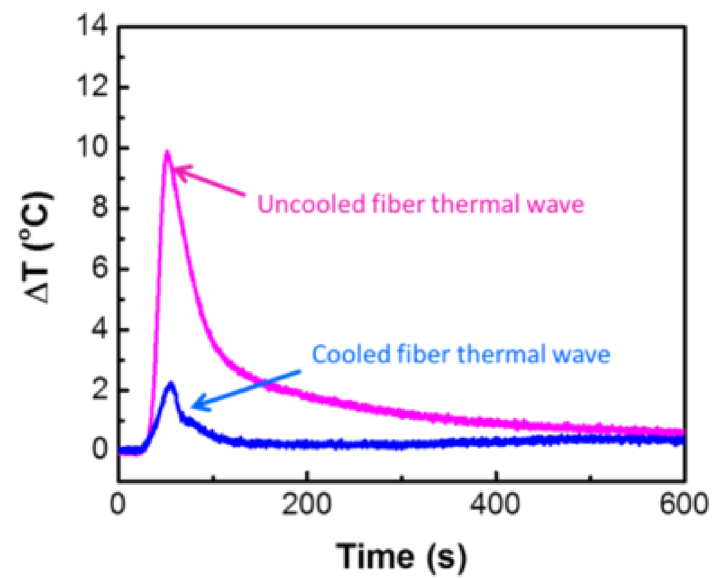
Future directions:

Process configuration	RVTSA adsorption heat recovery	RVTSA CA polymer and 1 μm silica sorbent	RVTSA New polymer and 4 μm silica sorbent	RVTSA New polymer and 500 nm silica
Swing capacity [mmol/gfiber]	0.48	0.65	0.76	0.93
Number of modules	2002	1278	1096	894
Annual cost of CO_2 capture [MM$/year]	182	201	181	159
CO_2recovery [%]	75	90	90	90
CO_2purity [%]	95	96	96	95
Escalation factor	**1.35**	**1.35**	**1.33**	**1.31**

Summary, Major Advances, and Remaining Challenges

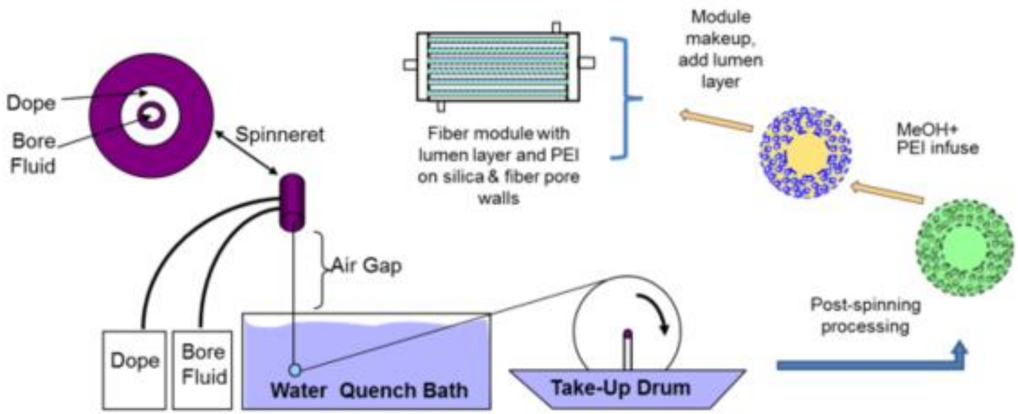
- **Rapid Temperature Swing Adsorption (RTSA) enabled by a new contactor** combined with solid amine sorbents.
  - Cycle allows **quasi-isothermal adsorption with significant latent heat recovery** due to nanoscopic shell-tube heat exchanger design.
- We are developing a fundamentally new contactor with modern sorbents – significant advances in first three years.
- Technoeconomic analysis suggests targets for improvement.

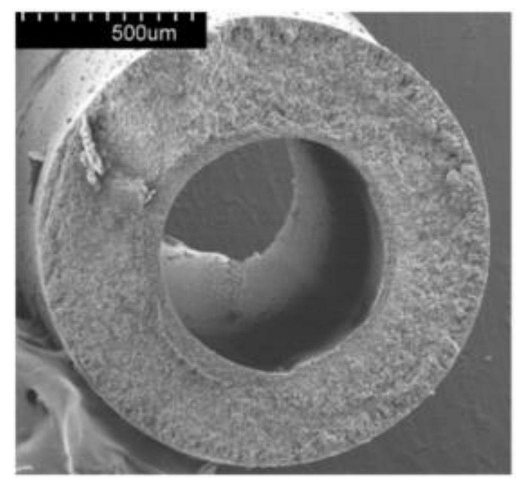




Summary, **Major Advances,** and Remaining Challenges

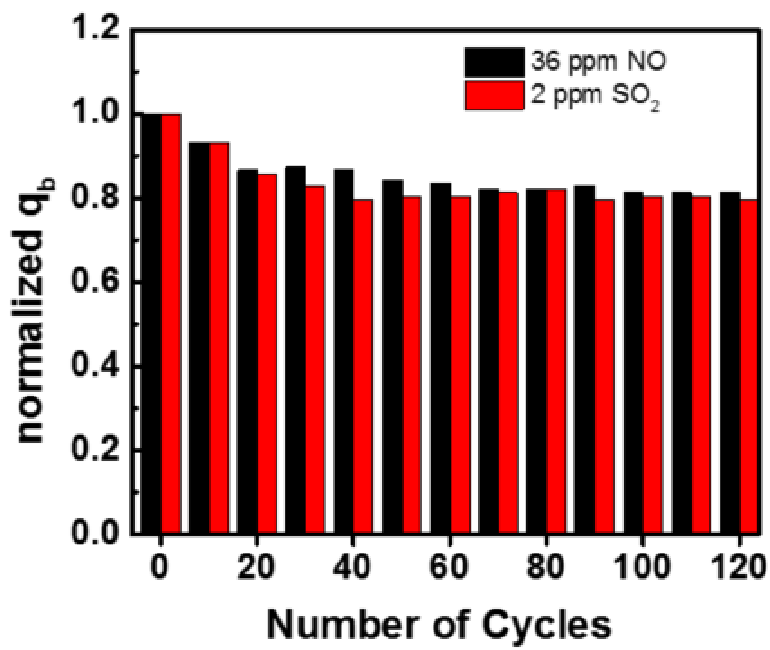
- Invention of post-spinning amine infusion method of creating and recharging sorbents
- Development of dual layer spinning method for scalable lumen layer formation
- Up to 70% recovery of the heat of adsorption via heat integration
- Detailed single fiber model validated with experiments
- Reduction of RTSA cycle times to 3 minutes
- Development of multi-scale model spanning the nanoscale to the plant scale, with rapid data transfer across scales





Summary, Major Advances, and Remaining Challenges

- Large scale, low cost process control (for practical operation, not for lab scale)
- Understanding dynamics by long term operation of complete cycles with bore-side heating/cooling
  - -- conducted >100 consecutive cycles with external heating/cooling
  - -- conducted <10 consecutive cycles with bore-side heating/cooling
- Complexities associated with water (humidity)
  - -- model results based on dry feeds
  - -- experimental tests with humidity conducted, humidity helps capacity and kinetics
- Incremental increases in breakthrough capacity
- Manufacturing cost estimates of fibers have significant uncertainty



Publication and Inventions

Publications

1. Labreche, Ying., Lively, Ryan ; Rezaei, Fateme; Chen, Grace; Jones, Christopher W; Koros, William J., *Post-spinning infusion of poly(ethyleneimine) into polymer/silica hollow fiber sorbents for carbon dioxide capture.* Chemical Engineering Journal, 2013, 221, 166-175.
2. Rezaei, Fateme; Lively, Ryan; Labreche, Ying; Chen, Grace; Fan,Yanfang; Koros, William; Jones, Christopher, *Aminosilane-grafted polymer/silica hollow fiber adsorbents for CO_2 capture from flue gas.* ACS Applied Materials & Interfaces, 2013, 5, 3921-3931.
3. Rezaei, Fateme; Jones, Christopher, *Stability of Supported Amine Adsorbents to SO_2 and NO_x in Post-Combustion CO_2 Capture Process-1. Single Component Adsorption*.. Industrial & Engineering Chemistry Research, 2013, 52, 12192-12201.
4. Fan,Yanfang; Lively, Ryan; Labreche, Ying; Rezaei, Fateme; Koros, William; Jones, Christopher, *Evaluating CO_2 dynamic adsorption performance of polymer/silica supported poly(ethylenimine) hollow fiber sorbents in rapid temperature swing adsorption.* International Journal of Greenhouse Gas Control, 2014, 21, 61-71**.**
5. Labreche, , Ying; Fan, Yanfang; Rezaei, Fateme; Lively, Ryan; Jones, Christopher; Koros, William, *Poly (amide-imide)/Silica Supported PEI Hollow Fiber Sorbents for Postcombustion CO_2 Capture by RTSA.* ACS. Appl. Mater. Interfaces, 2014, 6, 19336-19346.
6. Rezaei, Fateme; Jones, Christopher, *Stability of Supported Amine Adsorbents to SO_2 and NO_x in Post-Combustion CO_2 Capture Process-2. Multicomponent Adsorption*.. Industrial & Engineering Chemistry Research, 2014, 53, 12103-12110.
7. Fan,Yanfang; Labreche, Ying; Lively, Ryan; Koros, William; Jones, Christopher, *Dynamic CO_2 Adsorption Performance of Internally Cooled Silica Supported Poly(ethylenimine) Hollow Fiber Sorbents.* AIChE J., 2014, 60, 3878-3887**.**
8. Rezaei, Fateme; Swernath, Subramanian; Kalyanaraman, Jayashree; Lively, Ryan; Kawajiri, Yoshiaki; Realff, Matthew, *Modelling of Rapid Temperature Swing Adsorption Using Hollow Fiber Sorbents.* Chem. Eng. Sci., 2014, 113, 62-67.
9. Kalyanaraman, Jayashree; Fan, Yanfang; Lively, Ryan; Koros, William; Jones, Christopher; Realff, Matthew; Kawajiri, Yoshiaki, *Modelling and Experimental Validation of Carbon Dioxide Sorption on Hollow Fibers Loaded with Silica-Supported Poly(ethylenimine).* Chem. Eng. J., 2015, 259, 737-751.
10. Labreche, Ying; Fan, Yanfang; Lively, Ryan; Jones, Christopher; Koros, William, *Direct Dual Layer Spinning of Aminosilica/Torlon® Hollow Fiber Sorbents with a Lumen Layer for CO_2 Separation by Rapid Temperature Swing Adsorption.* J. Appl. Polym. Sci., 2015, 132, 4185.
11. Fan,Yanfang; Kalyanaraman, Jayashree; Labreche, Ying; Rezaei, Fateme; Lively, Ryan; Realff, Matthew; Koros, William; Jones, Christopher; Kawajiri, Yoshiaki, *CO_2 Sorption Performance of Composite Polymer/Aminosilica Hollow Fiber Sorbents.* Ind. Eng. Chem. Res., 2015, 54, 1783-1795**.**
12. Swernath, Subramanian; Searcy, Kathine; Rezaei, Fateme; Labreche, Ying; Lively, Ryan; Realff, Matthew; Kawajiri, Yoshiaki, *Optimization and Techno-Economic Analaysis of Rapid Temperature Swing Adsorption (RTSA) Process for Carbon Capture from Coal-Fired Power Plant.* Comput. Aided Chem. Eng., 2015, in press.
13. Add Jayashree’s paper that is submitted.
14. Fan, Yanfang; Rezaei, Fateme; Labreche, Ying; Lively, Ryan P.; Koros, William J.; Jones, Christopher W. *Stability of Amine-based Hollow Fiber CO2 Adsorbents to NO and SO_2*. Fuel, to be submitted 04/15.

Inventions

1. " Dual Layer Spinning with Lumen Layer PAI Polymer/Silica/PEI Hollow Fiber Sorbent for RTSA" submitted on 11/25/ 2013, The internal reference number is GTRC ID 6560. The invention is sponsored by GE and US DOE. Y. Labreche, W.J. Koros, R. P. Lively
2. “Novel Amine Post-Spinning Infused Polymer/Silica Composite Hollow Fiber Sorbents” submitted on 07/18/2012. The internal reference number is GTRC ID 6142. The invention is supported by GE and US DOE. Y. Labreche, W.J. Koros, R. P. Lively, F. Rezaei, G. Chen, C. W. Jones, D. S. Sholl