University of Minnesota

Small Scale Ammonia Synthesis Using Stranded Wind Energy

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Featuring papers of Mahdi Malmali, Matt Kale, Deepak Ojha and Matt Palys

Small Scale Ammonia Synthesis Using Stranded Wind Energy

Outline:

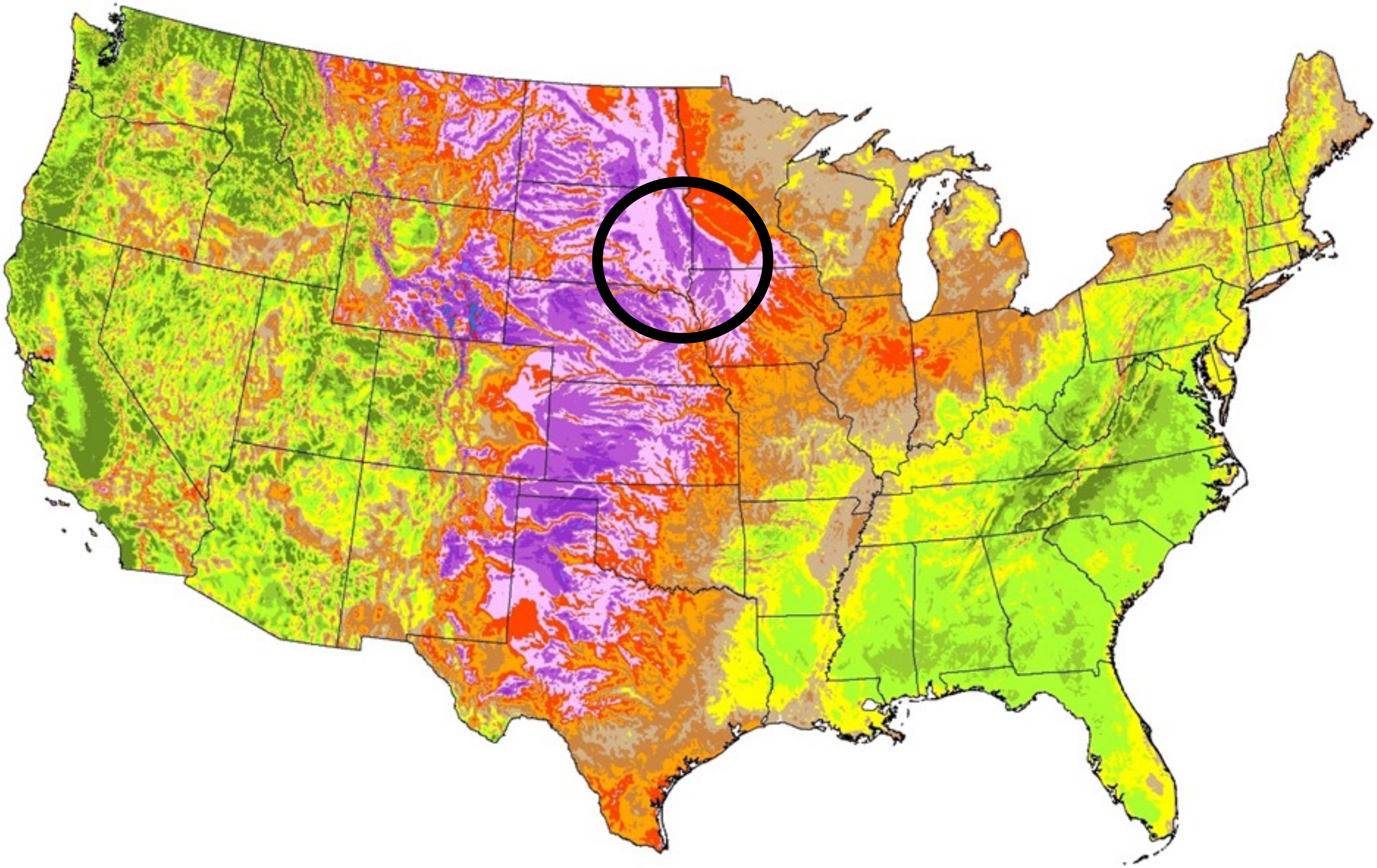
Reasons to make ammonia from stranded renewable energy in distributed, modular way

Lesson from first benchmark in Morris MN

Absorbents can help – but we have to help absorbents to help

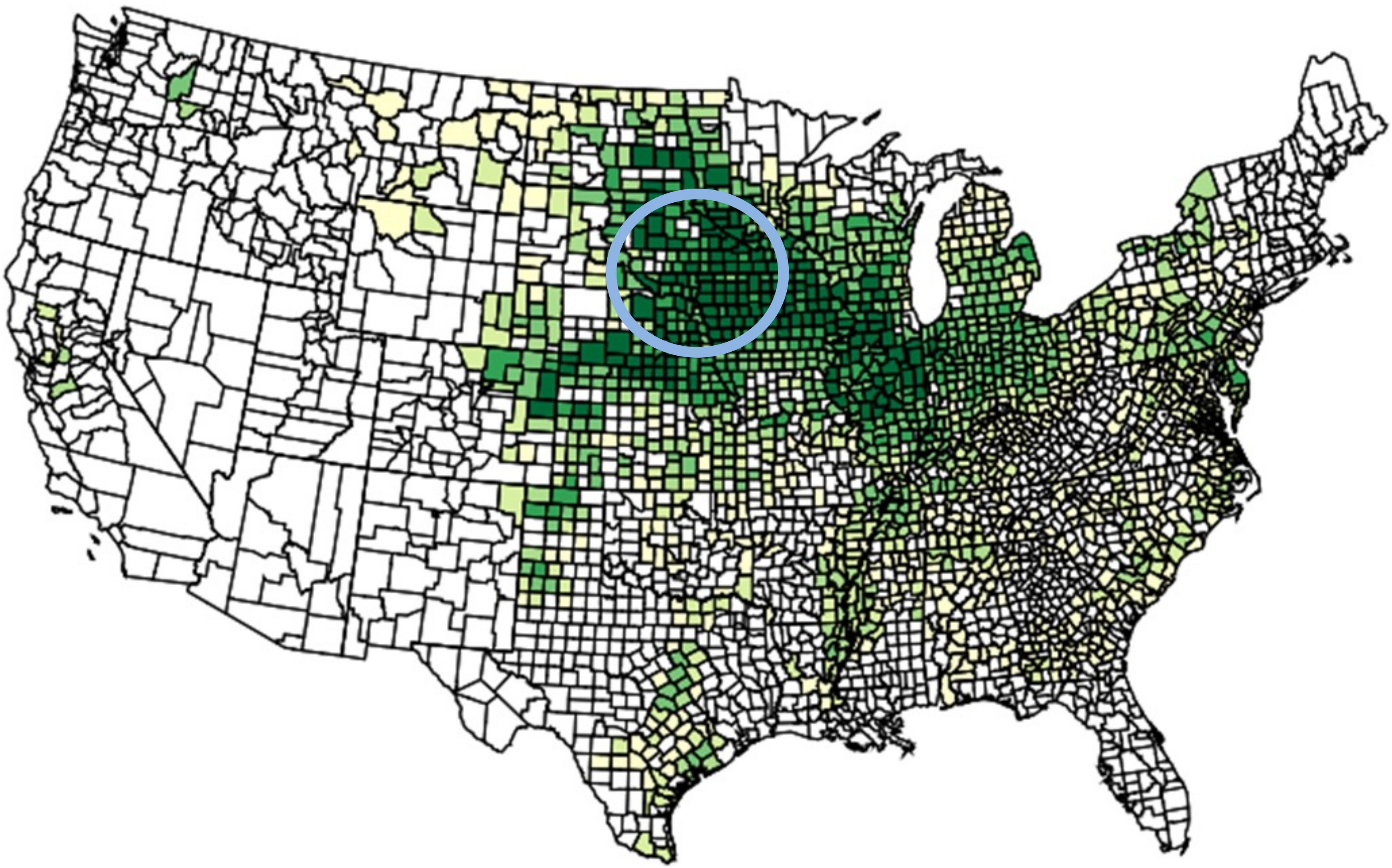
Way forward to feasible small-scale designs

Stranded Wind Resources



National Renewable Energy Laboratory, United States Department of Energy. Wind Resource Map (2014). http://www.nrel.gov/gis/wind.html

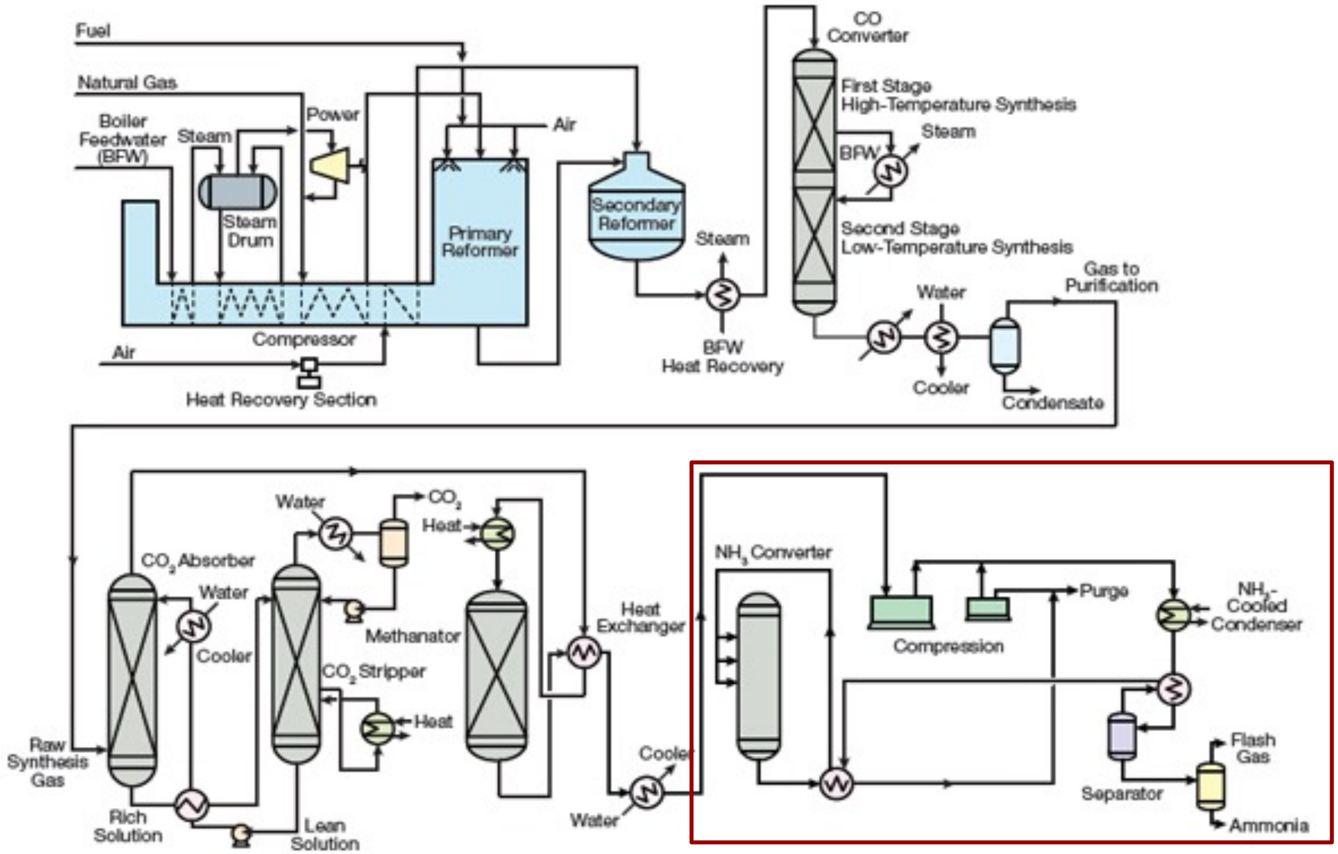
Ammonia Demand for Fertilizer



National Agricultural Statistics Service, United States Department of Agriculture. Planted Corn Acreage by County (2014). http://www.nass.usda.gov/Charts_and_Maps/Crops_County/#cr

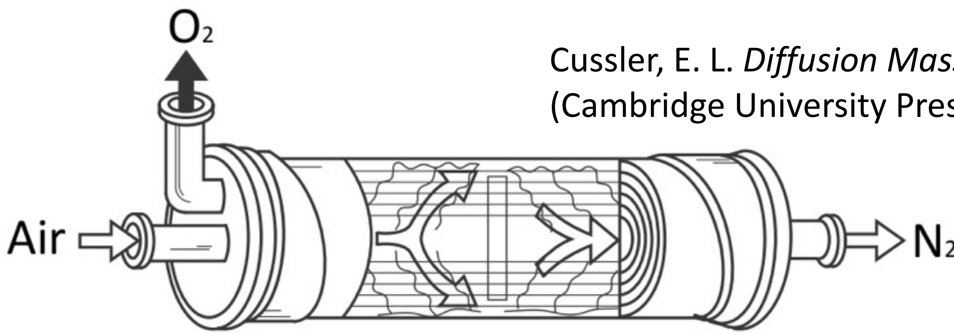
The Haber-Bosch Process

- ~1% global energy consumption, carbon emissions
- Centralized massive production - transportation

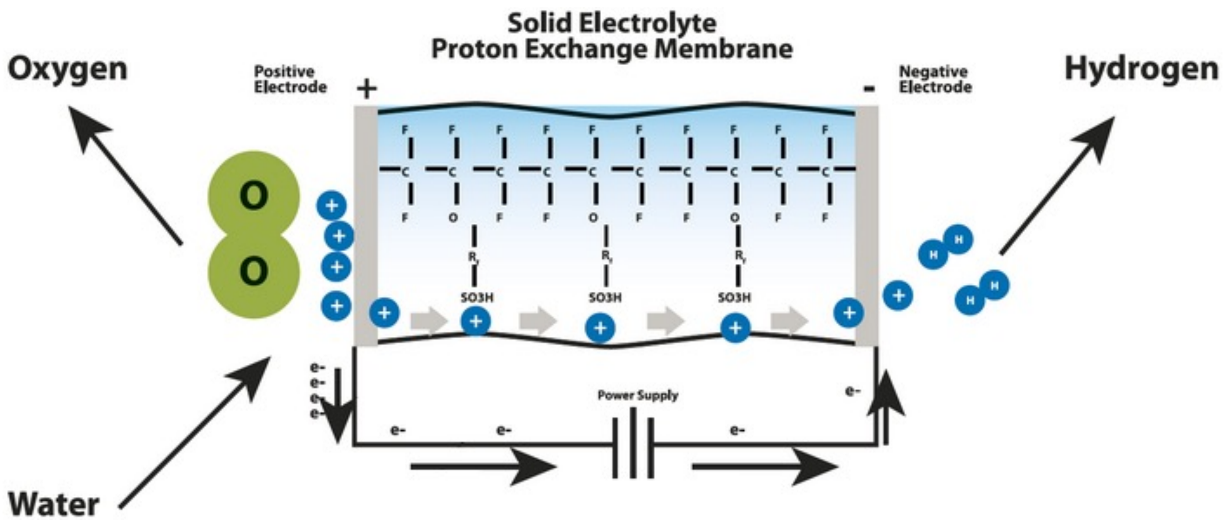


Source: Pattabathula & Richardson, *CEP*, September 2016, 69-75.

N_2 from Air, H_2 from Water



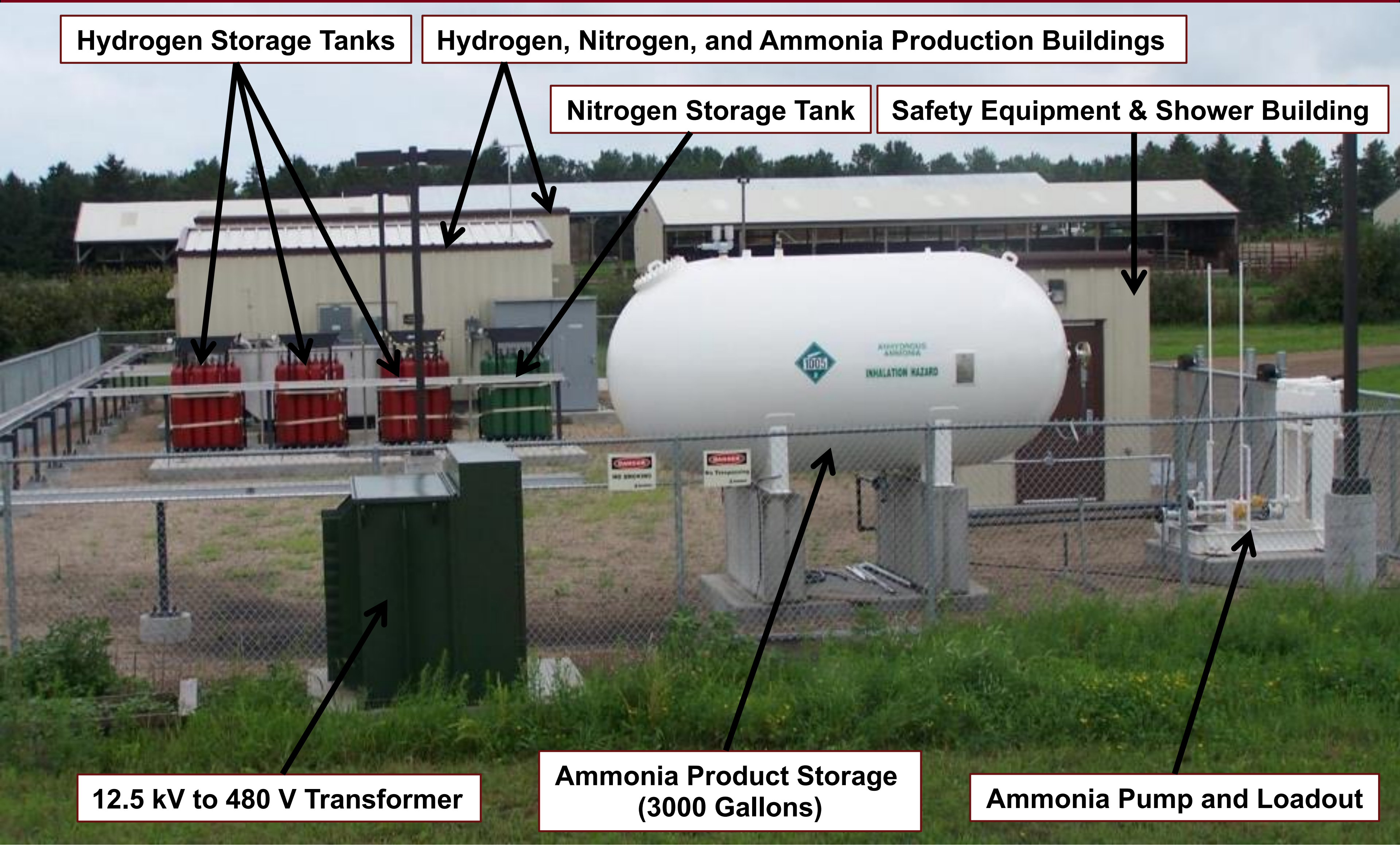
Cussler, E. L. *Diffusion Mass Transfer in Fluid Systems*. (Cambridge University Press).



Source: http://protononsite.com/products/hydrogen-generator/

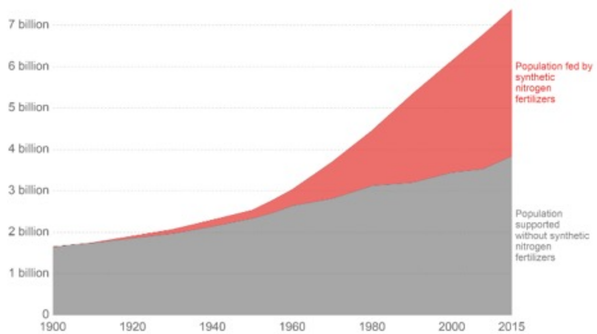
- Nitrogen via membrane or PSA separation
- Hydrogen via electrolysis of water

U of MN Renewable Hydrogen and Ammonia Pilot Plant

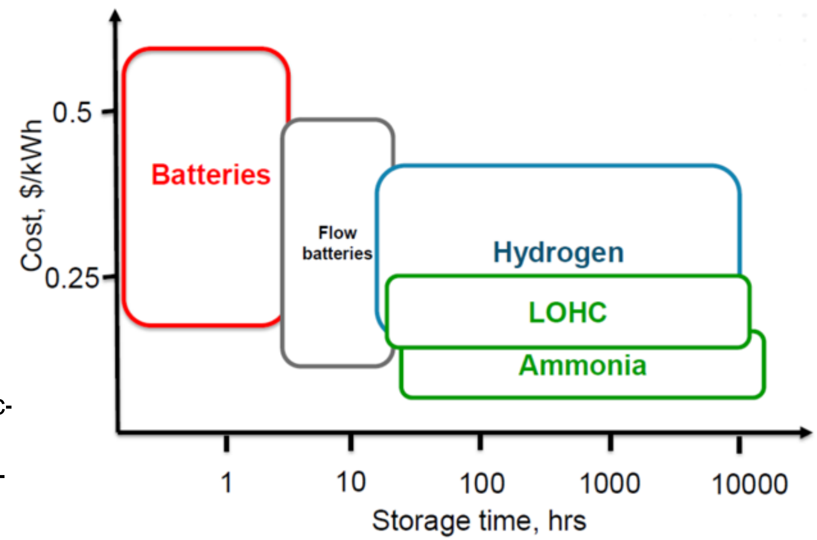


Ammonia: Feeding the World, New Fuel and H carrier

- Backbone of nitrogen fertilizer: Feeds half of the global population
- Energy-dense, inexpensive H carrier and fuel



Source: Ritchie, *Our World in Data*: https://ourworldindata.org/how-many-people-does-synthetic-fertilizer-feed#note-4; Erisman et al., 2008, Nat. Geoscience, 1 (10), 636-639.

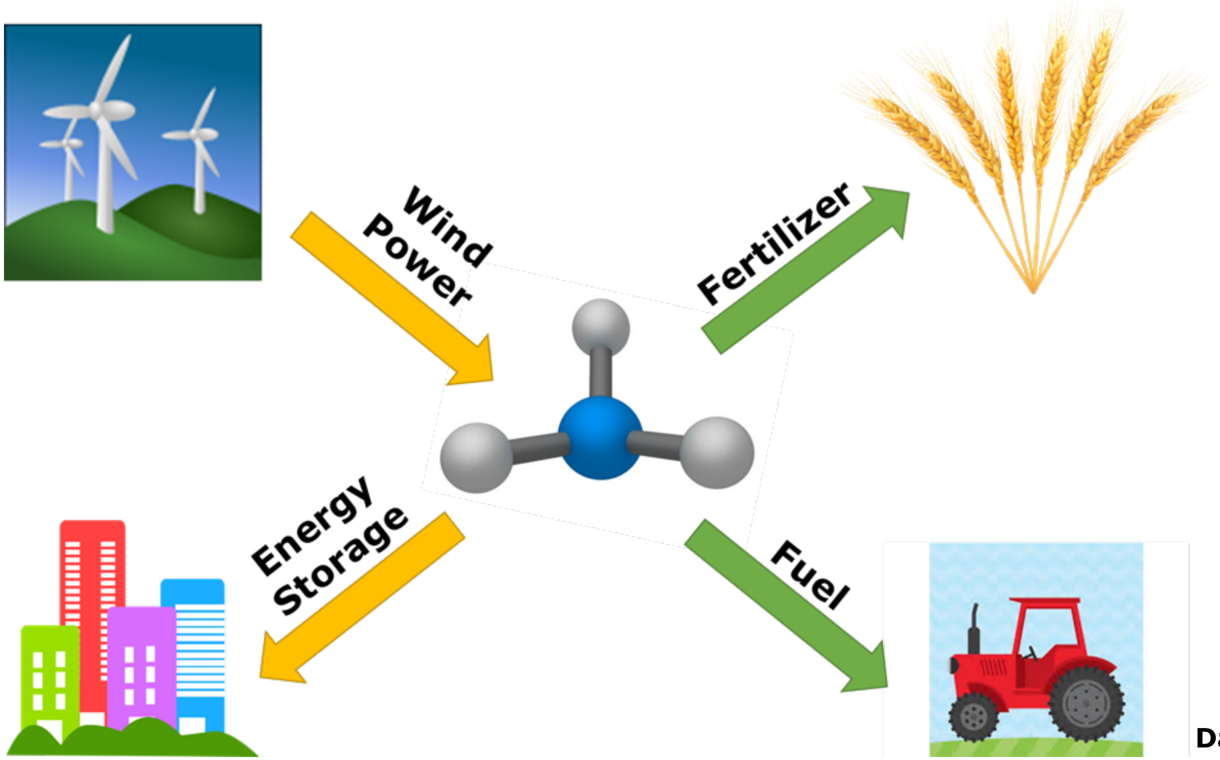


G. Soloveichik, US Dept. of Energy, 2016

Ammonia-Based Sustainable Energy and Agriculture

At a farm or co-op scale, use renewable energy to:

1. Make ammonia as fertilizer *and* fuel (*grain drying*, tractors, …)
2. Meet local electrical power demands
3. Export power to grid



Daoutidis, 2019

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Way forward to feasible small-scale designs

Early analysis (Cussler, Reese, Tiffany) Small-scale NH_3 Costs At Least 2X Conventional at Distributed Scale

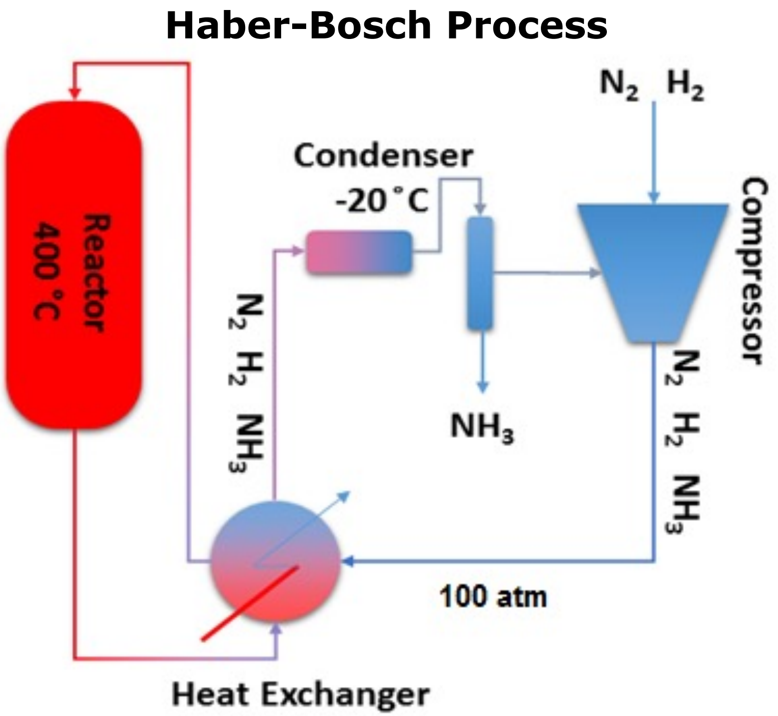
Benchmark learning - Need Cheaper Small-Scale Ammonia Synthesis

Catalysis

- High temperature/pressure
- Many efforts globally in academia and industry

Separation

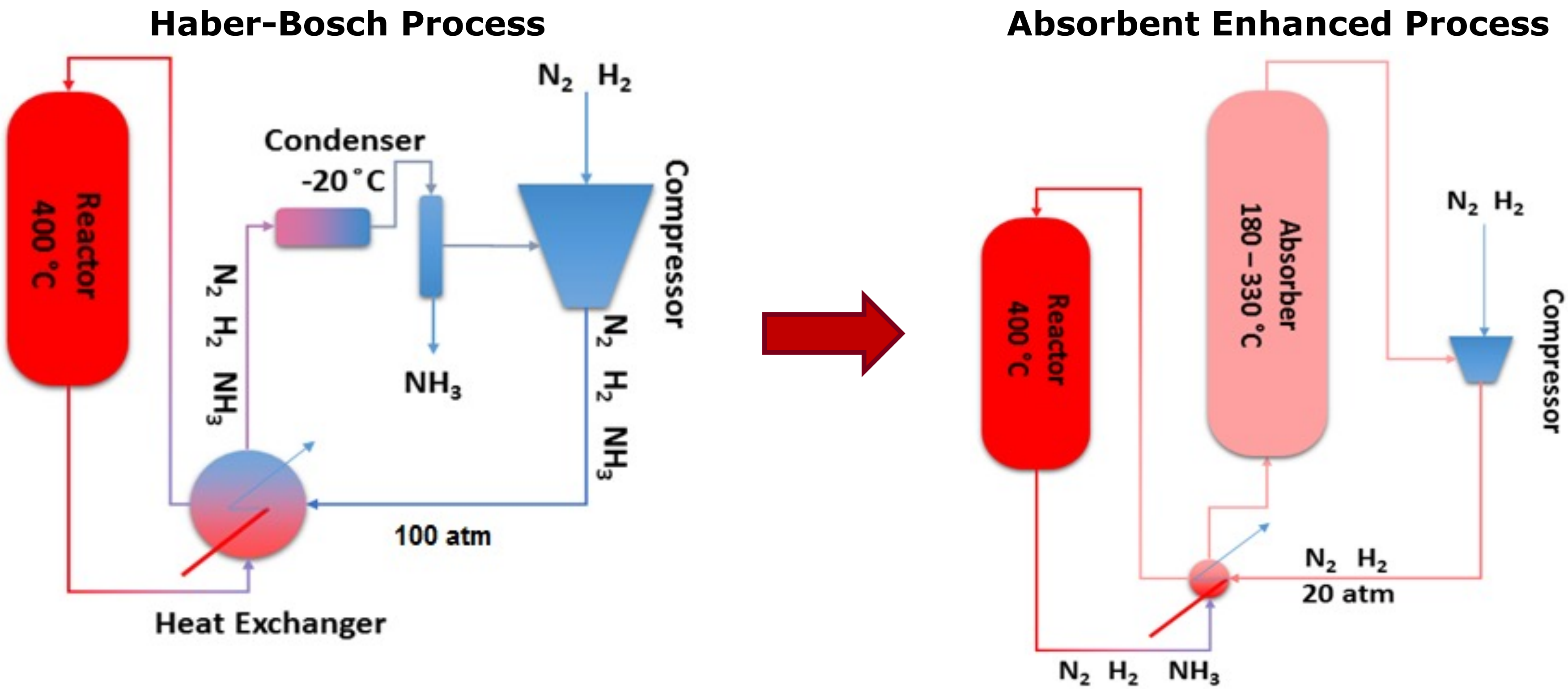
- Low temperature
- ~2-5mol% ammonia returned to reactor
- Opportunity?



Source: Malmali et al., 2018, *ACS Sustainable Chem. Eng.*, 6, 6536-6546.

II. Absorbent Enhanced Ammonia Production: Replace Condensation with Absorption

- Lower exit ammonia partial pressure
- Higher temperature (less heat exchange, no chilling)
- More complete separation might permit lower pressure synthesis loop – safety mitigation savings



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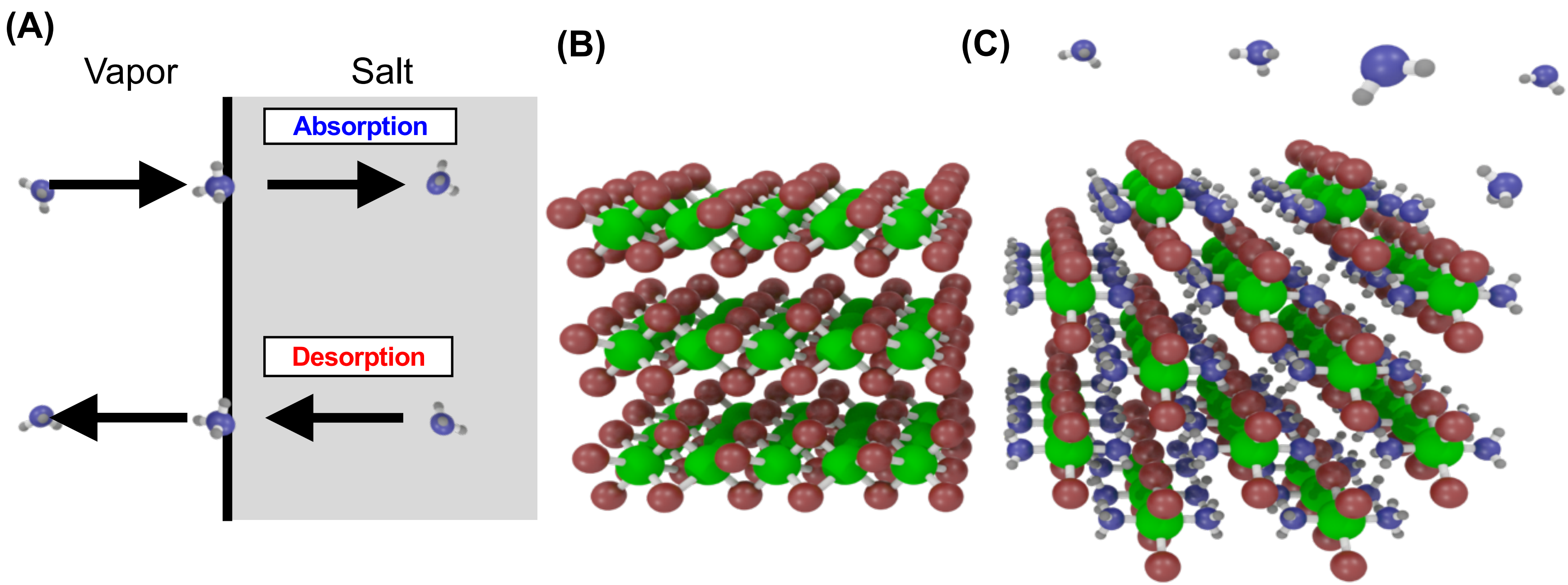
Absorption Uptake/Release via Solid/Gas Reaction



Kale Ojha Biswas Militti McCormick Schott Dauenhauer Cussler,
ACS Applied Energy Materials 2020 3 (3), 2576-2584. 10.1021/acsaem.9b02278

$MgCl_2$ Application	Researchers	Institute	Description	Year	Reference
Chemical Heat Pump	Saito et al.	University of Tokyo	Absorption of ammonia into alkaline earth metal halides	1994	Jpn. Kokai Tokkyo Koho JP 06136357
Low pressure ammonia synthesis & storage	Aika et al.	Tokyo Institute of Technology	Absorption isotherms of halide mixtures and phases	2002	Chem. Let. 31, 798-799
				2004	Procedure. Bull. Chem. Soc. Jpn. 77, 123-131.
				2004	Ind. Eng. Chem. Res. 43, 7484-7491
Ammonia Storage	Aristov et al.	Boreskov Institute of Catalysis	Alkaline earth metal confined in alumina	2005	React. Kinet. Catal. Lett. 1, 183-188
Hydrogen Storage as Ammonia	Christensen, Vegge, Norskov, Johannessen et al.	Technical University of Denmark	Opportunities for hydrogen storage	2005	J. Mater. Chem 15, 4106-4108
			Absorption/desorption difficulties	2006	J Am. Chem. Soc. 128, 16-17
			DFT studies for crystal structure	2010	Energy Environ. Sci. 3, 448-456
Desorption and characterization	Owen-Jones, Royce, David, et al	Oxford	Frontiers in characterization and understanding	2013-14	Chem Phys, 427, 38-43 2014 NH3FC
Distributed/facilitated Ammonia production	Cussler, McCormick et al.	University of Minnesota	Absorption of ammonia at Haber process conditions	2012	AIChEJ 58, 3526-3552
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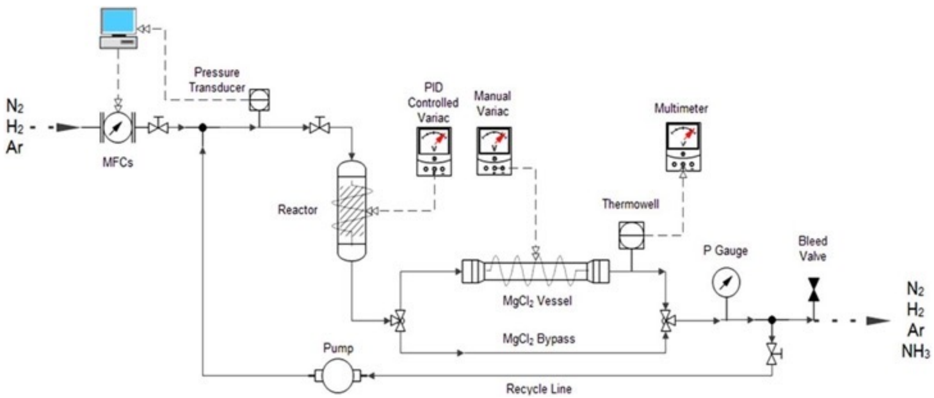
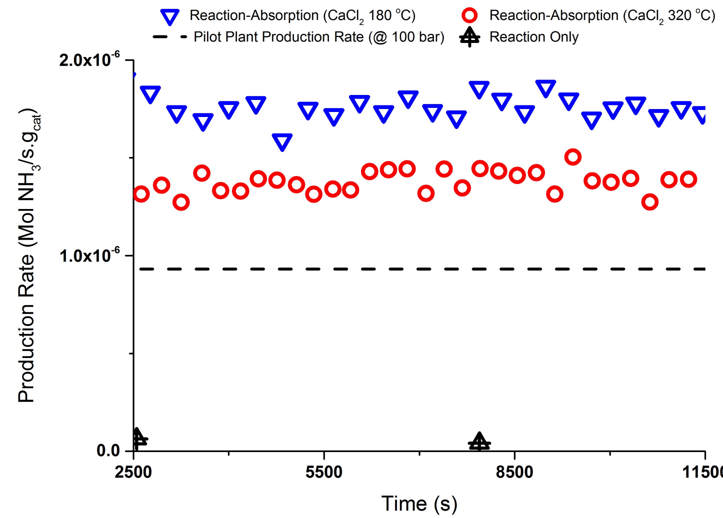
Ammonia Storage Fuel Cell	Van Hassel et al.	United Technologies	Alkaline earth metal confined in activated carbon	2015	Sep. Purif. Technol. 142, 215-226

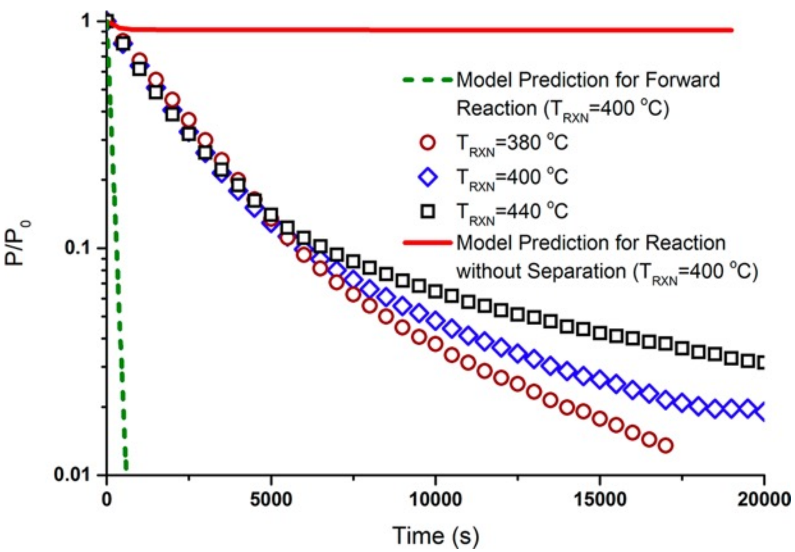
Absorption Design Can Increase Overall Productivity cf. Condensation, Even with Lower Pressure Reactor

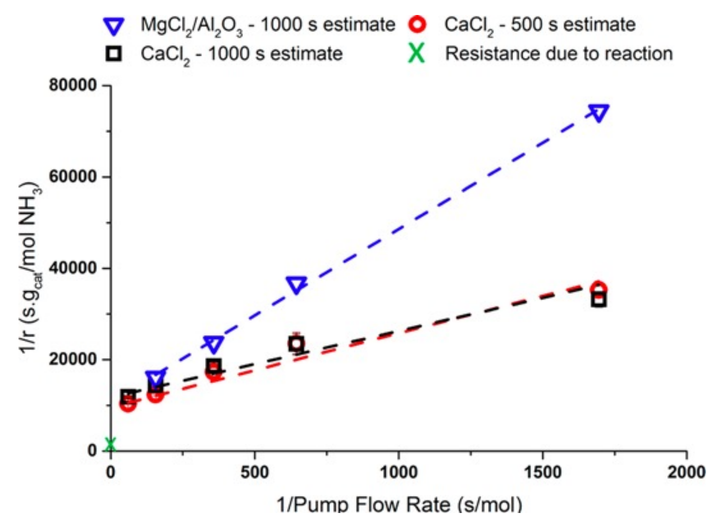


FED CIRCULATING BATCH



CIRCULATING BATCH

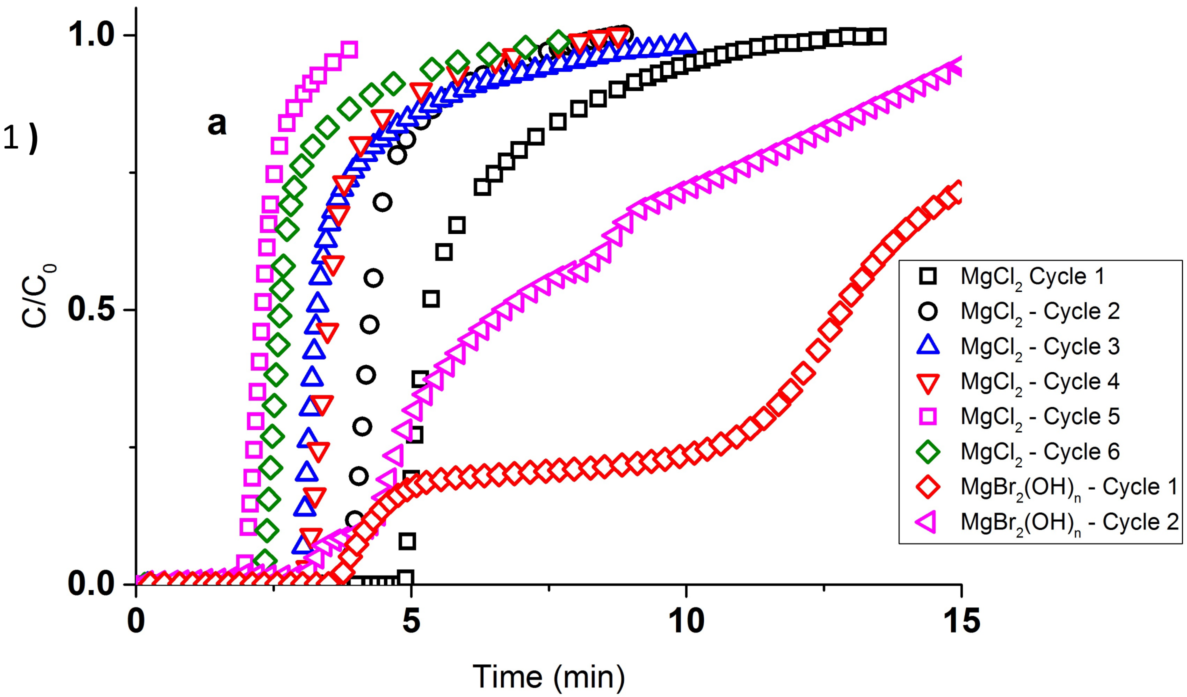




Malmali et al., *ACS Sustainable Chem. Eng. 2018, 6, 827−834*

Challenge: Stable Absorbents?

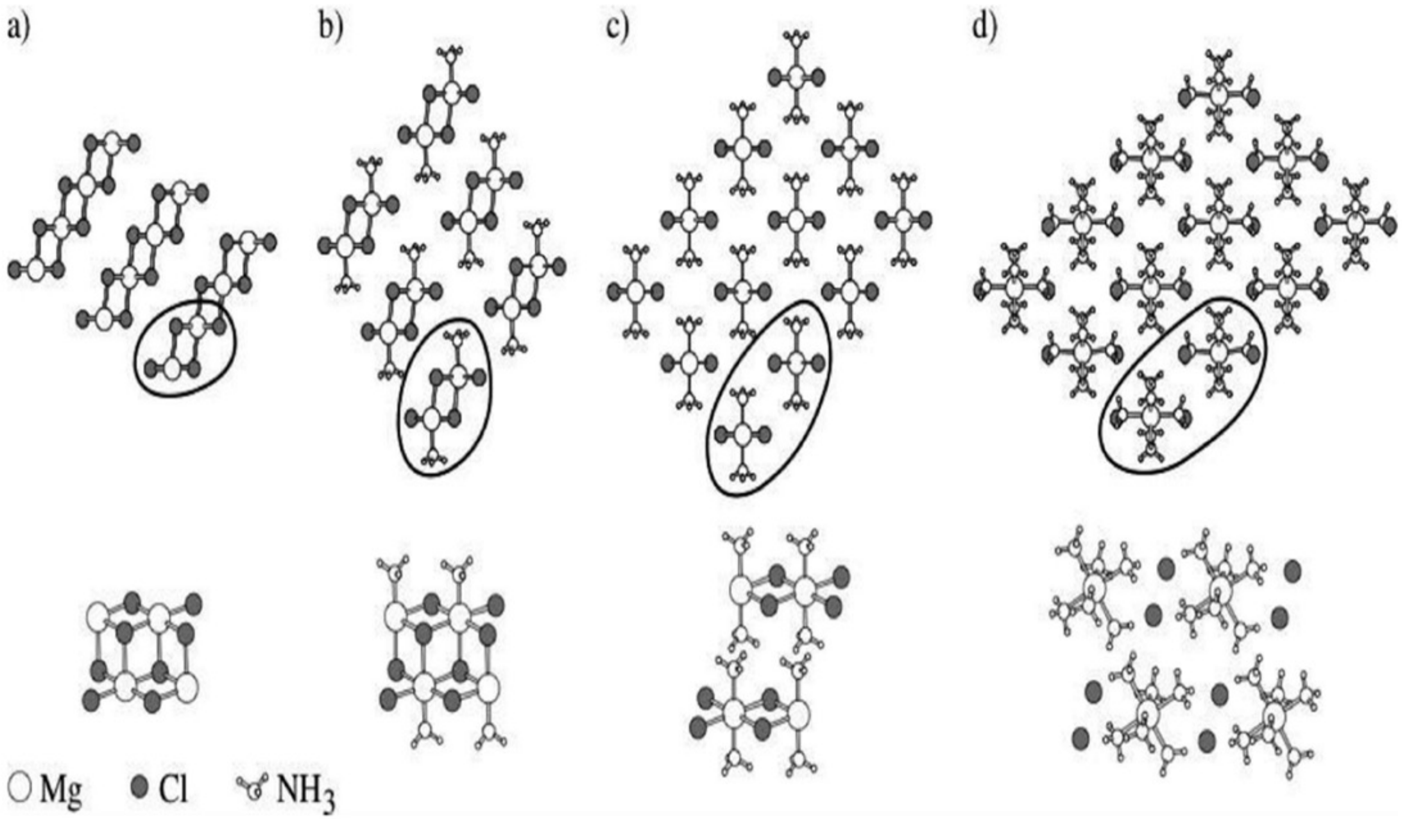
10 g $MgCl_2$
T=150 C
P=1 bar (N_2:NH_3 = 5:1)



Wagner, K., **Malmali, M.,** Smith, C., McCormick, A., Cussler, E. L., Zhu, M.Seaton, N. C. A. (2017) *AIChE J.*, *63* (7), 3058–3068.
Malmali, M., Reese, M., McCormick, A., & Cussler, E. L. (2017) *ACS Sustainable Chemistry & Engineering*, Accepted.

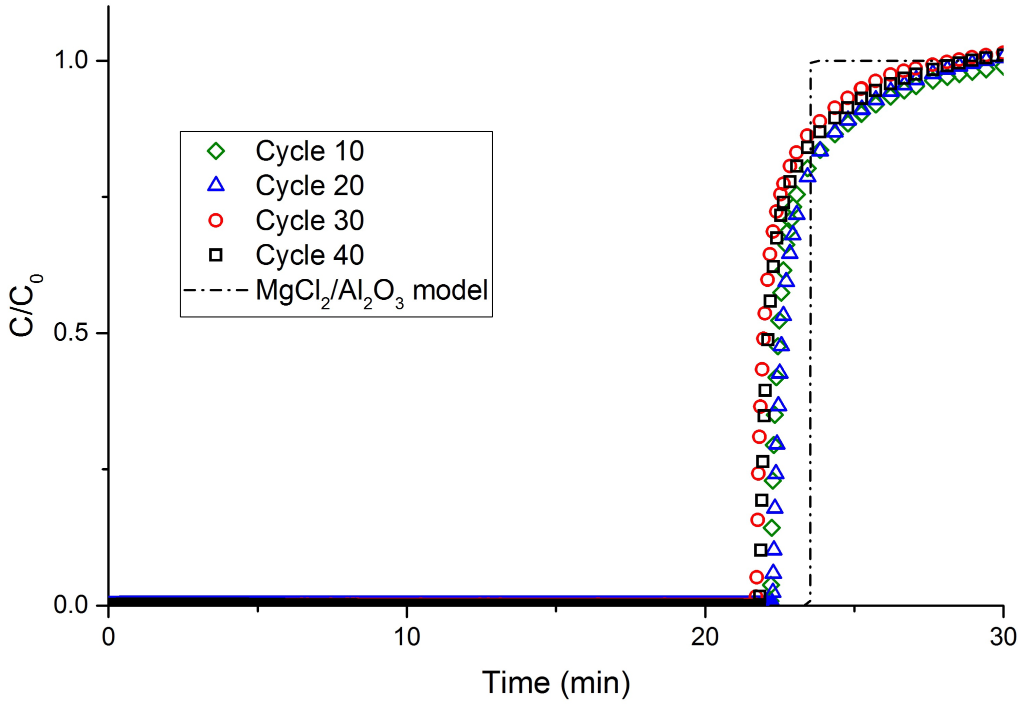
Absorbent Structure Changes as Ammonia is Absorbed

Christensen et al. *J. Am. Chem. Soc.*, 2008, **130**, 8660.

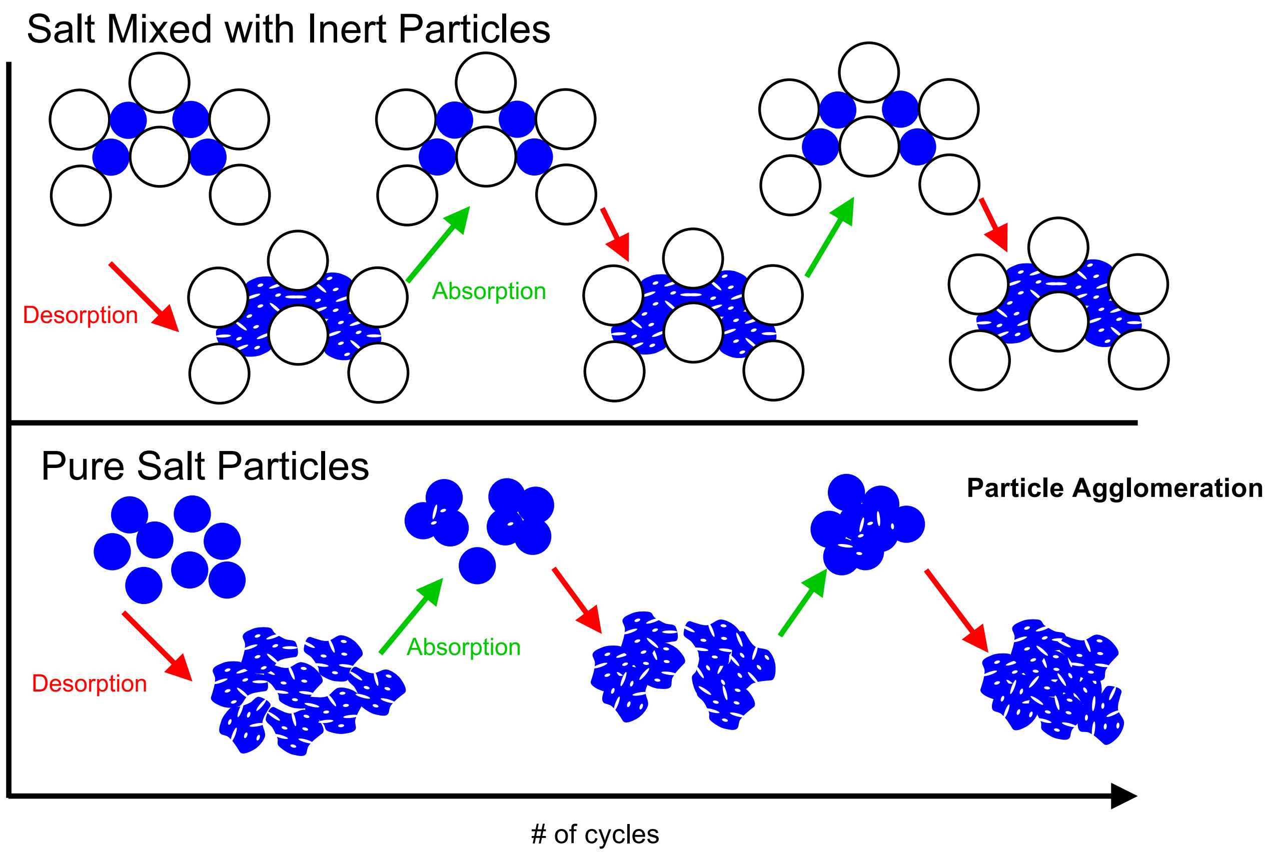


Calculated structures for $MgCl_2(NH_3)_x$ found by Technical University of Denmark group

SUCCESS with Supported Sorbents:
First try: Metal Halide Supported on Alumina



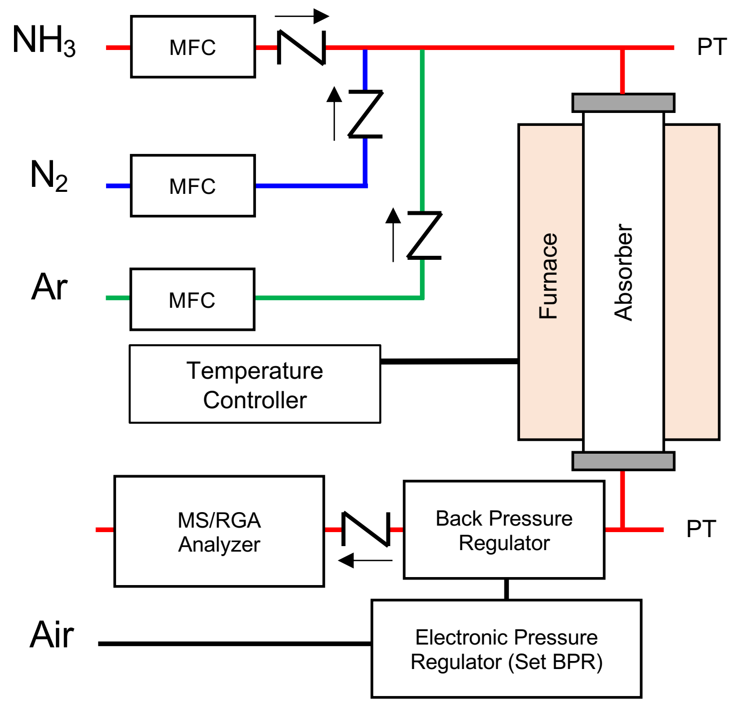
Absorbent Cycling Stabilized by Inerts



Kale 2020

What do we need to learn for optimal operation?

Cycling a small automated column in the lab

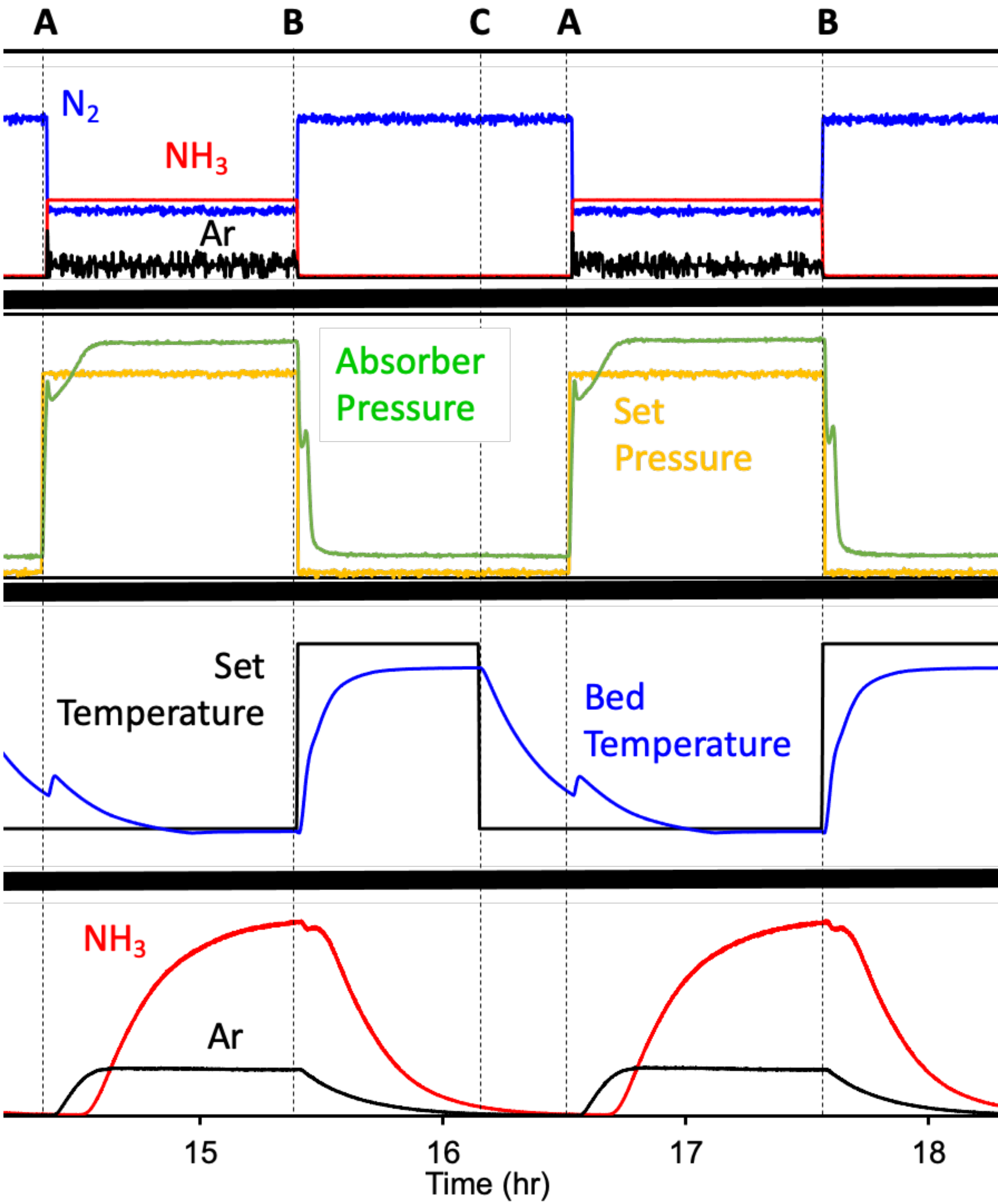


Kale Ojha Biswas Militti McCormick Schott Dauenhauer Cussler, ACS Applied Energy Materials 2020 3 (3), 2576-2584. 10.1021/acsaem.9b02278

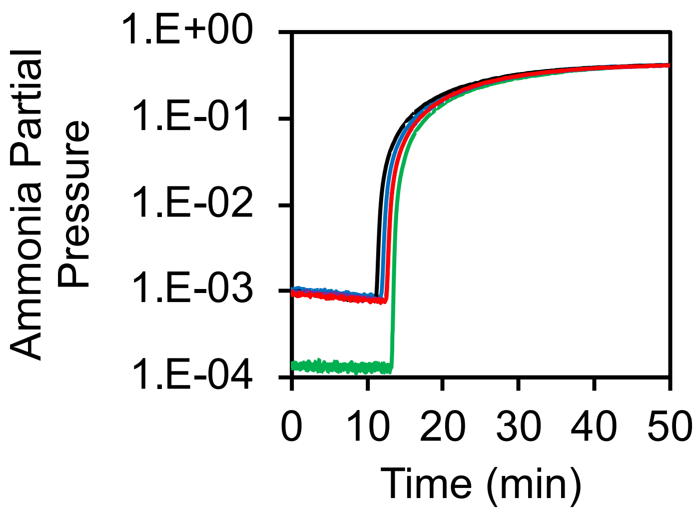
Effective working capacity depends on operating conditions

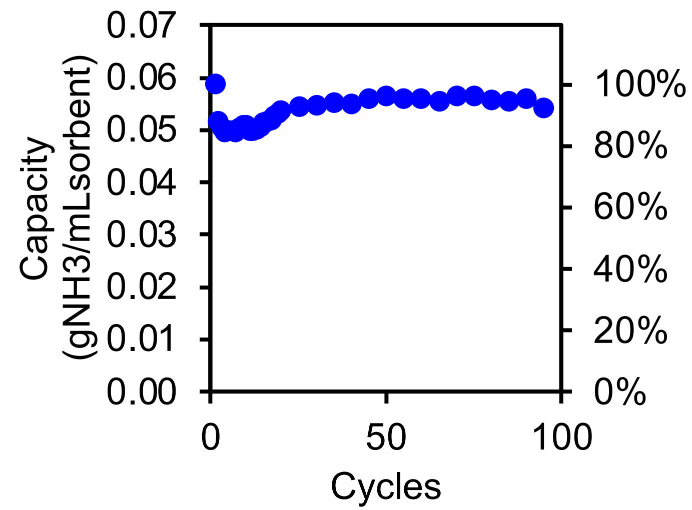
Kale 2020

Cyclic steady state conditions



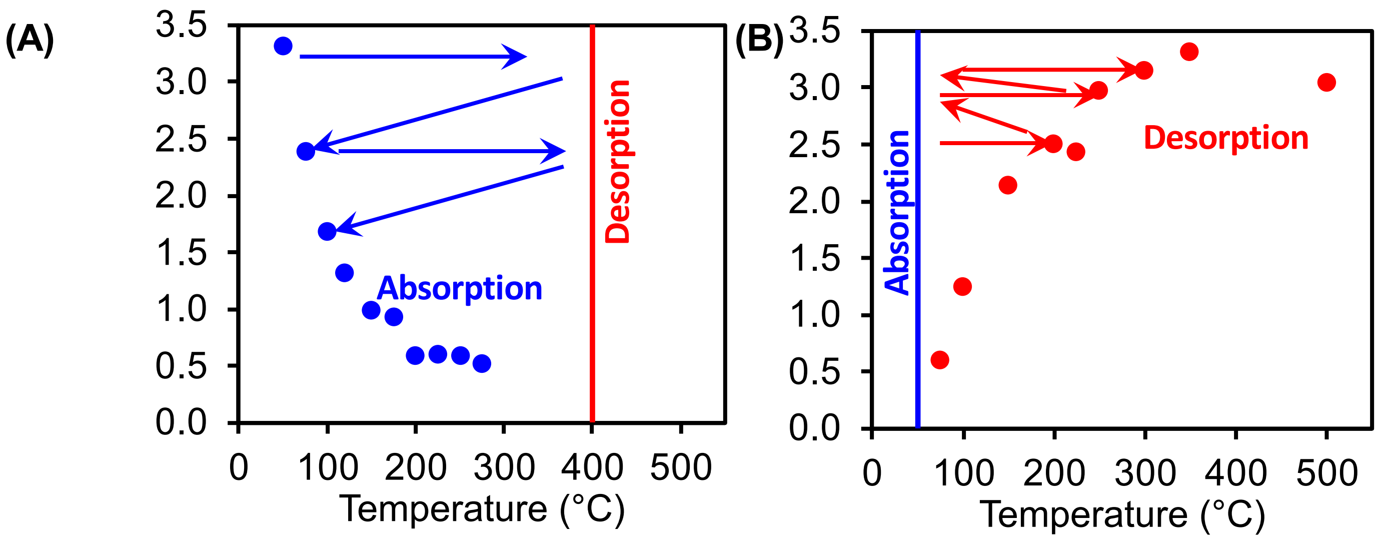
Absorbent is Stable





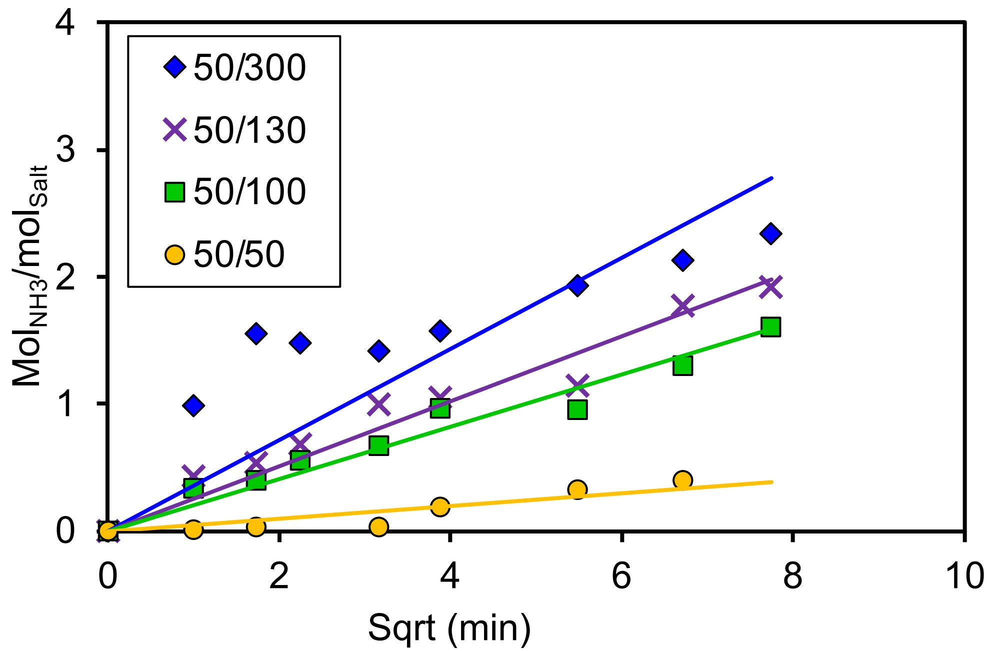
After "breaking in" runs, fast scans can reveal "working capacity" at varying uptake and release conditions

Working Capacity (mol_{NH3}/mol_{Salt})



Max ammonia partial pressure ca. 1.5 bar

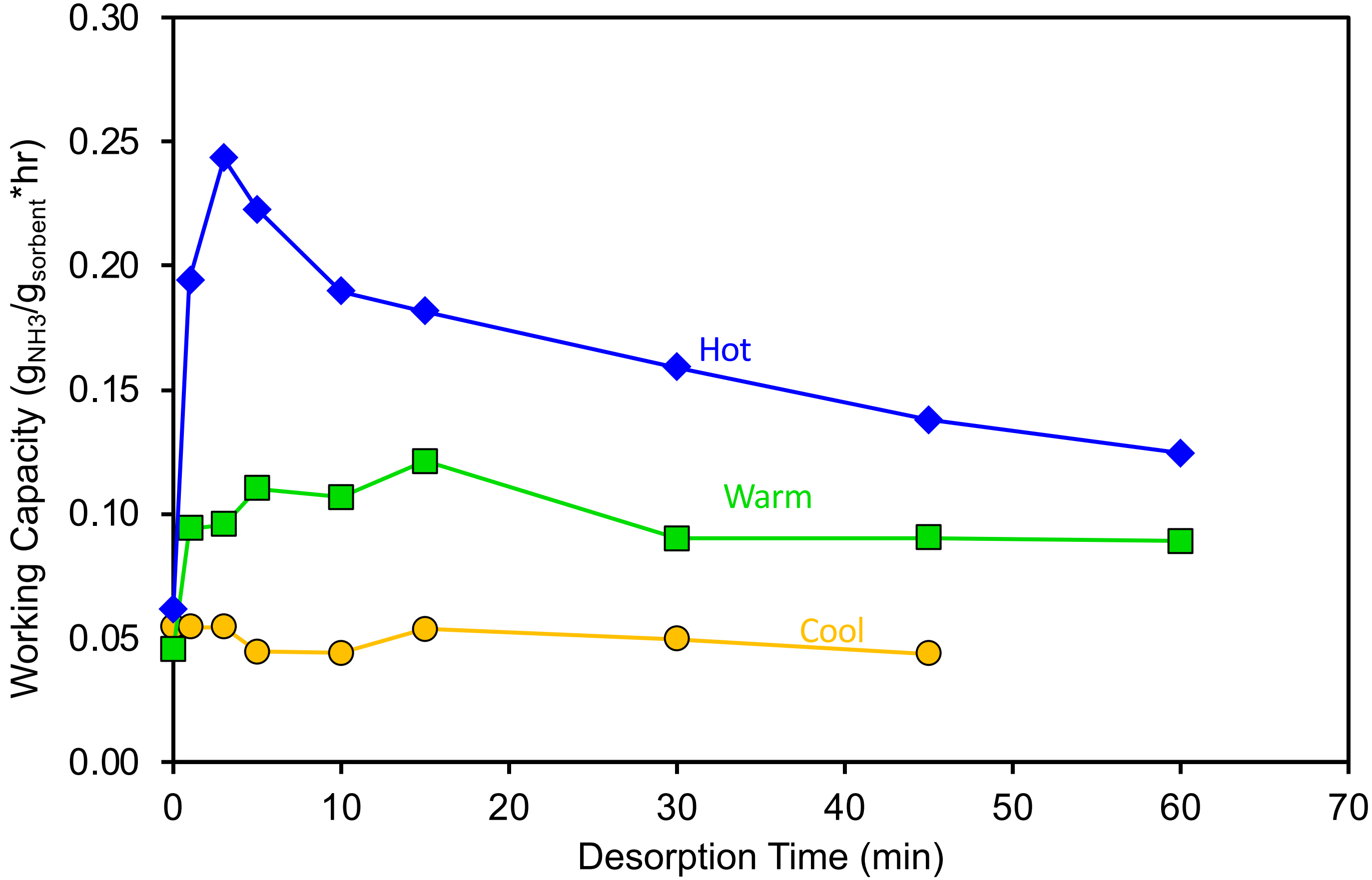
Desorption Controlled by Diffusion; Release Time Matters



Desorption in Ammonia Manufacture from Stranded Wind Energy, Ojha Kale Dauenhauer McCormick Cussler, 2020. 10.1021/acssuschemeng.0c03154

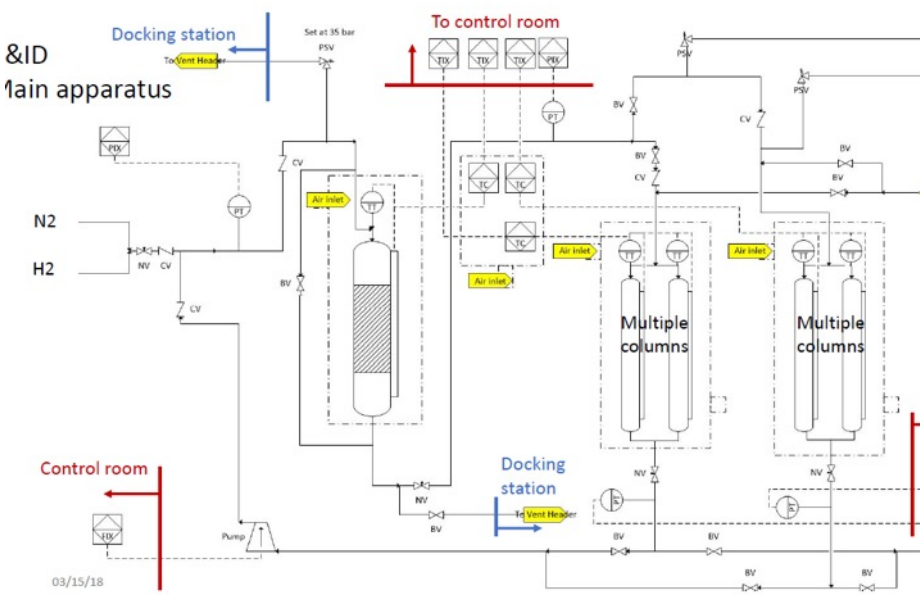
Production capacity depends on operating (cycling) parameters – example varying regeneration temperature

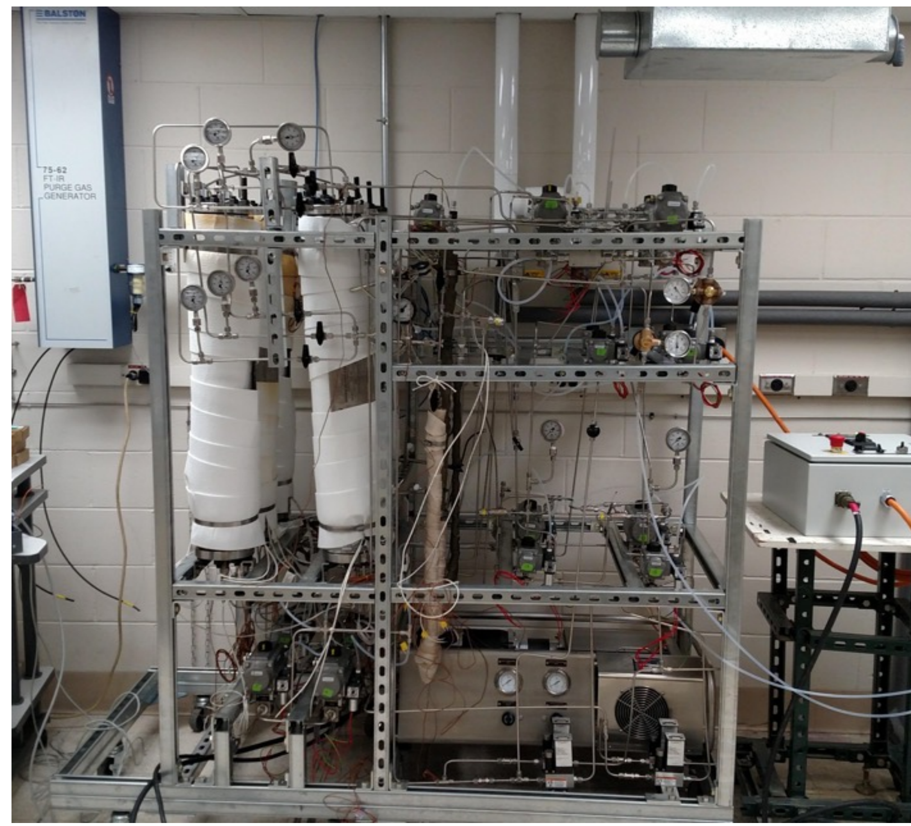
(details in Kale et al 2020)



Kale 2020

Scale up issues:
Insights from the lab need to be tested on the ARPA-E prototype (ca. 1 kg/day)





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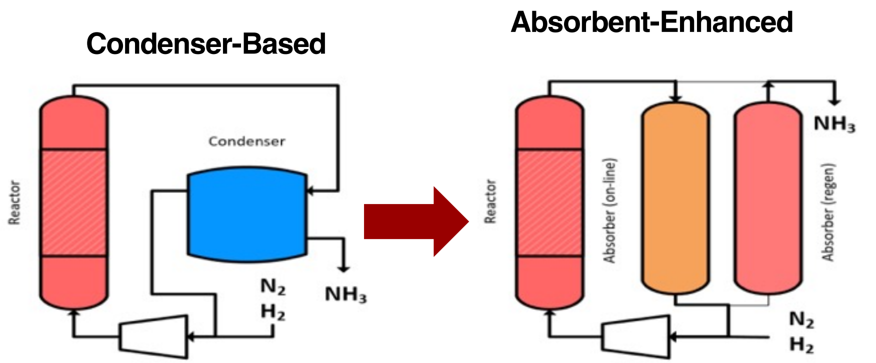
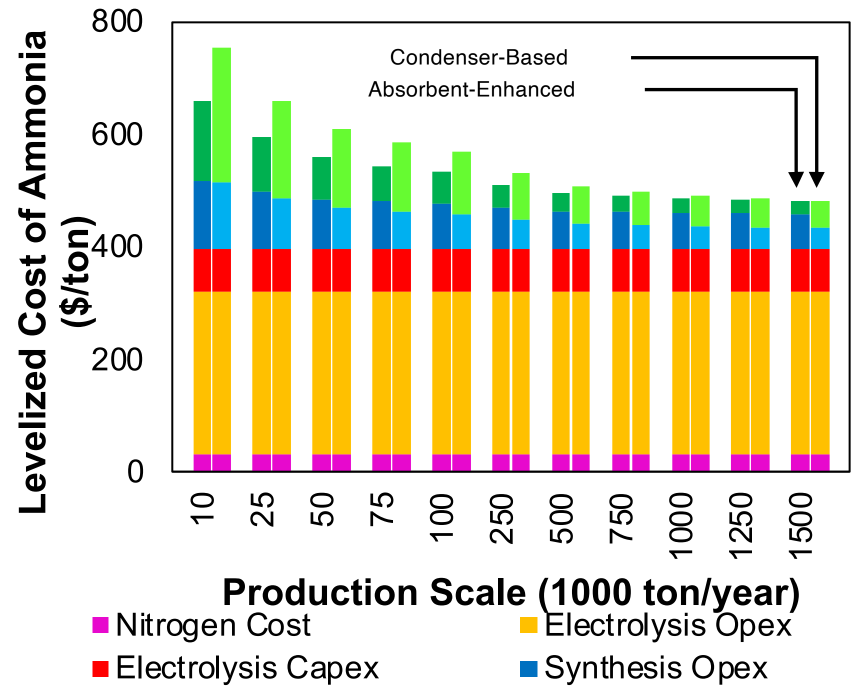
Comparison of Absorbent-Enhanced and Condenser-Based Processes Palys et al. (2019).

AIChE Annual Meeting 2019, Orlando, FL.





- Lower pressure
- Hotter separation

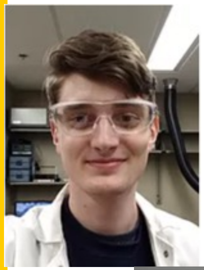
Absorbent-enhanced process:

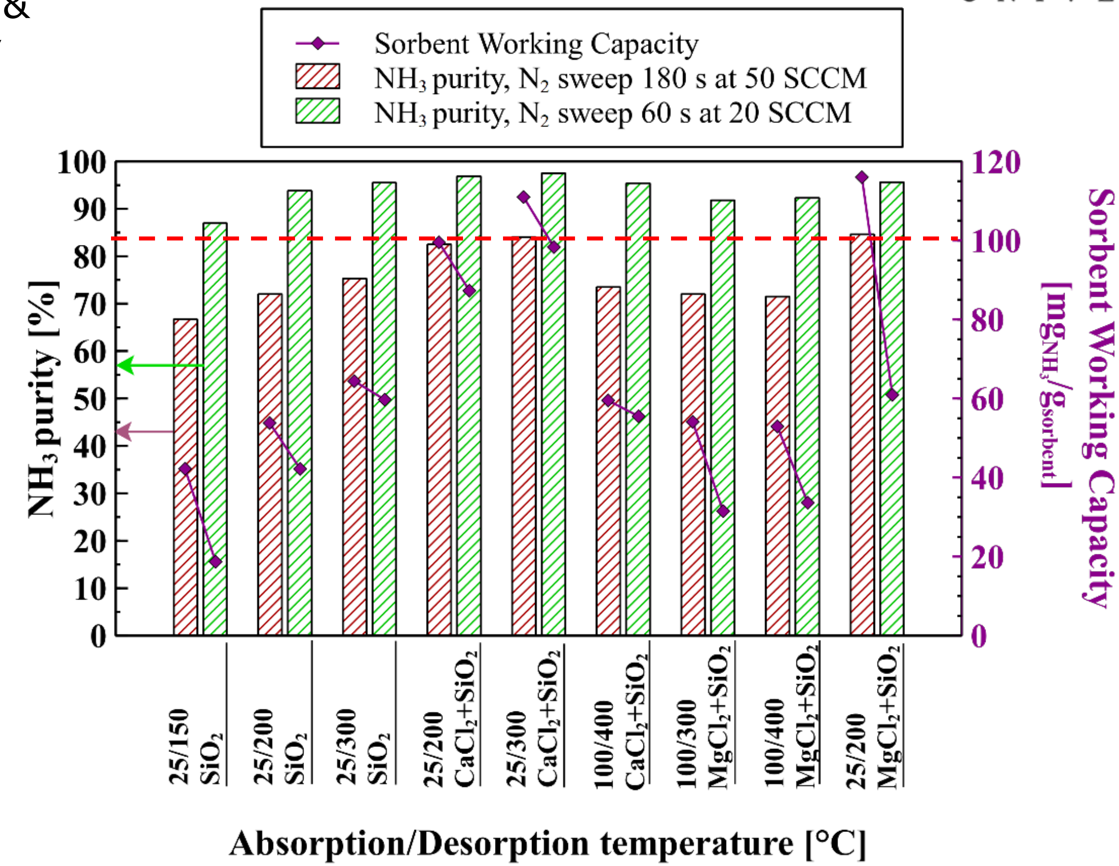
- Lower capital investment (~40%)
- Higher energy consumption due to heat needed for desorption (no integration)
- **Less expensive (~ 25%) synthesis at small production scales!**

Upcoming developments from Malmali (Texas Tech)

Ammonia purity with cyclic absorption/desorption

Hrtus, Nowrin, Malmali
ACS Sustainable Chemistry & Engineering *Under Review*





- For each absorbent chemistry, ammonia absorption and release should be optimized.
- Ammonia purity above 90% can be achieved with optimized absorption temperature and sweep flow.

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Collaborating, coauthoring graduate students, research engineers, postdocs, faculty

Heath Himstedt (now Johns Manville, CO), Mark Huberty,
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Deepak Ojha (now IIT Roorkee), Matt Kale (now Honeywell), Matt Palys, Emmanuel Onuoha

Co-PI's:

Lanny Schmidt, Ed Cussler, Prodromos Daoutidis, Paul Dauenhauer, Mike Reese,
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DOE Advanced Manufacturing Office (AMO) 2020 RAPID Institute Subtask 5.9

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Absorbents UMN

Huberty Wagner McCormick Cussler (2012) Ammonia absorption at Haber process conditions. AIChE J., 58: 3526–3532. doi: 10.1002/aic.13744

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Wagner Malmali Smith McCormick Cussler Zhu Seaton (2017) Column absorption for reproducible cyclic separation in small scale ammonia synthesis. AIChE J., 63: 3058–3068. doi:10.1002/aic.15685

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Malmali Reese McCormick Cussler, Converting Wind Energy to Ammonia at Lower Pressure, ACS Sustainable Chemistry & Engineering, DOI: 10.1021/acssuschemeng.7b03159. (2018) 6 (1), 827-834.

Smith Malmali Liu McCormick Cussler, Rates of Ammonia Absorption and Release in Calcium Chloride. ACS Sustainable Chem. Eng.2018,6 (9), 11827-11835. DOI: 10.1021/acssuschemeng.8b02108.

Optimizing the Conditions for Ammonia Production Using Absorption. Smith McCormick Cussler. ACS Sustainable Chem. Eng., 2019, 7(4):4019-4029. 10.1021/acssuschemeng.8b05395..

Optimizing Ammonia Separation via Reactive Absorption for Sustainable Ammonia Synthesis, Kale Ojha Biswas Militti McCormick Schott Dauenhauer Cussler, ACS Applied Energy Materials 2020 3 (3), 2576-2584. 10.1021/acsaem.9b02278

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TEA UMN

Allman Daoutidis, Optimal scheduling for wind-powered ammonia generation: Effects of key design parameters, Chem. Eng. Res. Des. (2017). 10.1016/j.cherd.2017.10.010

Palys McCormick Cussler Daoutidis, Modeling and Optimal Design of Absorbent Enhanced Ammonia Synthesis. Processes 2018, 6 (7). 10.3390/pr6070091.

Palys Allman Kuznetsov Daoutidis Concept and Design Optimization of a Novel Ammonia-Based System for Food-Energy- Water Sustainability, Computer Aided Chemical Engineering 47, 2019, 65-70. 10.1016/B978-0-12-818597-1.50011-4

Allman Palys Daoutidis, Scheduling-informed optimal design of systems with time-varying operation: A wind-powered ammonia case study, AIChE Journal 65 (7) 2019. https://doi.org/10.1002/aic.16434

Exploring the Benefits of Modular Renewable-Powered Ammonia Production: A Supply Chain Optimization Study, Palys Allman Daoutidis, Industrial & Engineering Chemistry Research 2019 58 (15), 5898-5908. 10.1021/acs.iecr.8b04189

Using hydrogen and ammonia for renewable energy storage: A geographically comprehensive techno-economic study, Computers & Chemical Engineering, 136,106785, 2020., Palys Daoutidis. 10.1016/j.compchemeng.2020.106785