

28 September, 2022

Talk #30208

# Solar-Thermal Ammonia Production: A Renewable, Carbon-Neutral Route to Ammonia via Concentrating Solar Thermochemistry

**Andrea Ambrosini**

**Sandia National Laboratories**

**aambros@sandia.gov**

**H. Evan Bush, Ivan Ermanoski, Xiang Gao, Nhu (Ty) Nguyen, Alberto de la Calle, Ivan Ermanoski, Tyler Farr, Kevin Albrecht, Matthew W. Kury, James E. Miller, Peter Loutzenhiser, Ellen B. Stechel**



**Sandia National Laboratories**

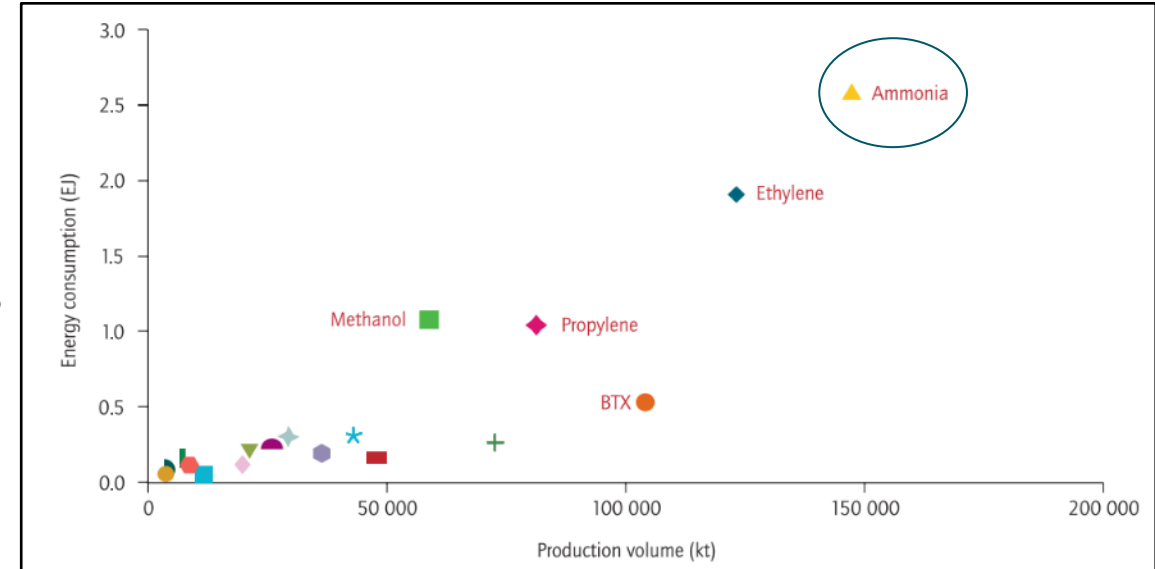
Sandia National Laboratories is a multimission laboratory managed and operated by National Technology & Engineering Solutions of Sandia, LLC, a wholly owned subsidiary of Honeywell International Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525.

Sandia National Laboratories is a multimission laboratory managed and operated by National Technology & Engineering Solutions of Sandia, LLC, a wholly owned subsidiary of Honeywell International Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525.

# Introduction



- Ammonia ( $\text{NH}_3$ ) is an energy-dense chemical and a vital component of fertilizer
  - Also finds use as potential fuel and in CSP thermochemical energy storage
- $\text{NH}_3$  synthesized via the Haber-Bosch process
  - Requires high pressures (15-25 MPa) and temperatures (400-500 °C)
    - Capital-intensive and only practical with large facilities
    - Process including  $\text{H}_2$  production is responsible for ~1.8% of global  $\text{CO}_2$  emissions<sup>1</sup>
- Ammonia synthesis consumes > 1% of the total energy worldwide<sup>2</sup>



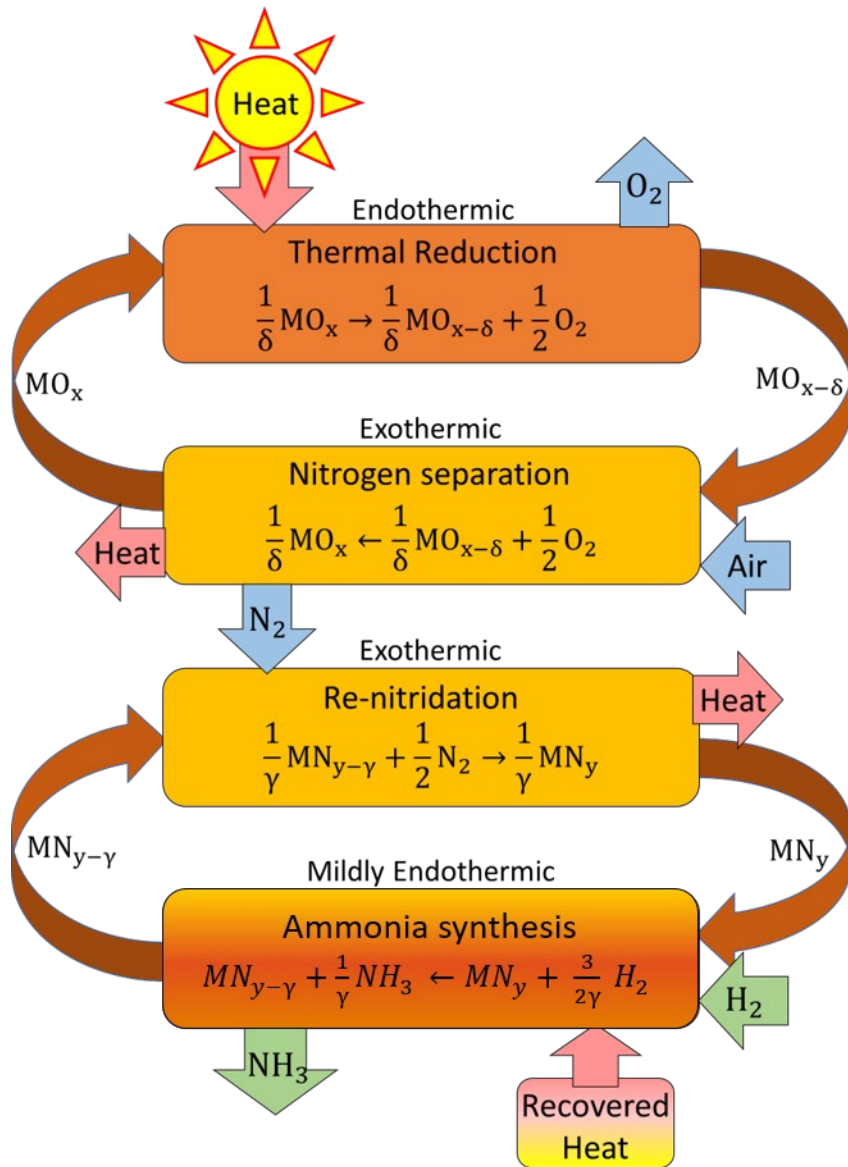
**Global greenhouse gas emissions versus production volumes (2010)\***

Production of  $\text{NH}_3$  via a renewable, carbon-neutral technology powered by concentrating solar can mitigate climate and  $\text{CO}_2$  impacts

<sup>1</sup>IEA (2013), Technology Roadmap - Energy and GHG Reductions in the Chemical Industry via Catalytic Processes, IEA, Paris <https://www.iea.org/reports/technology-roadmap-energy-and-ghg-reductions-in-the-chemical-industry-via-catalytic-processes>

<sup>2</sup>Institute for Industrial Productivity. Industrial Efficiency Technology Database <http://ietd.iipnetwork.org/content/ammonia>.

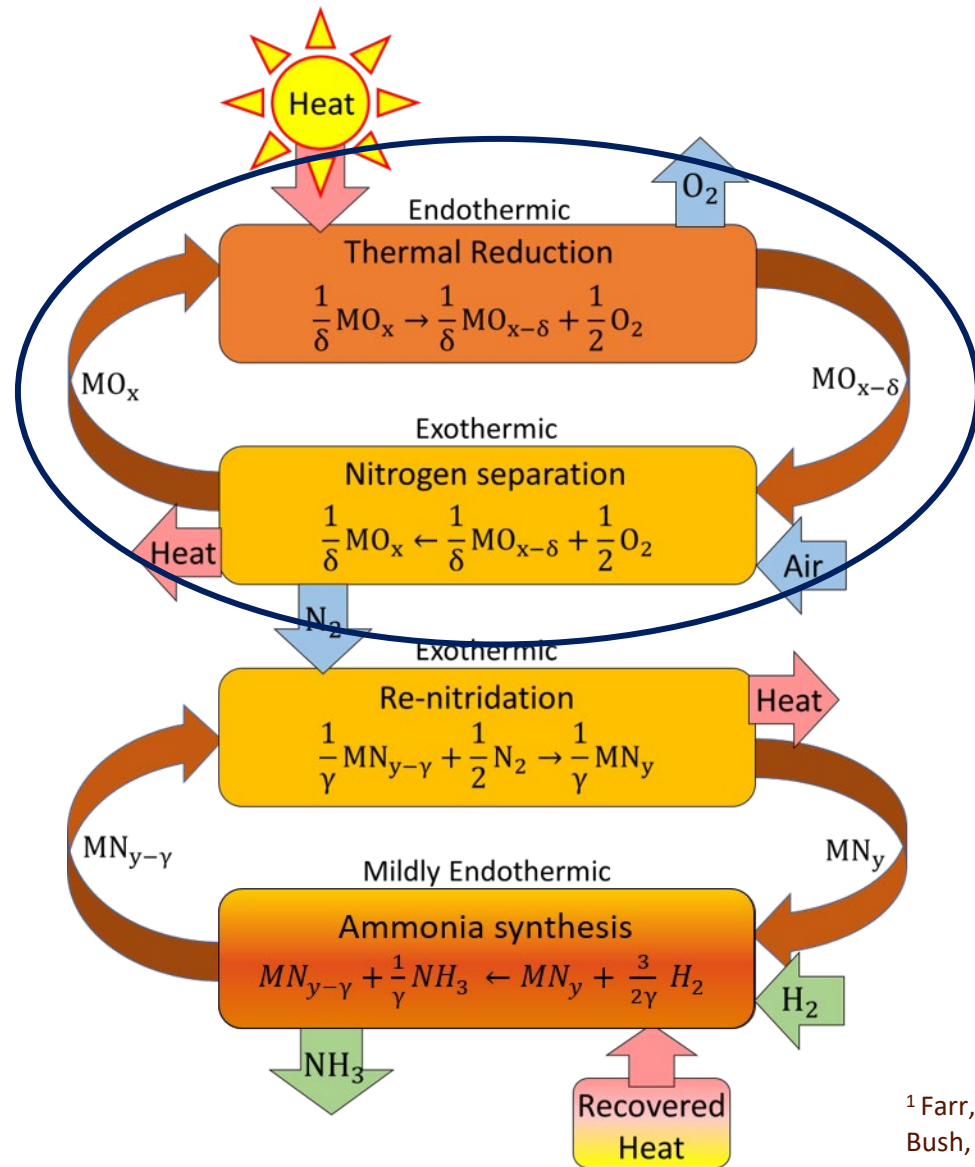
# Solar Thermal Ammonia Production (STAP)



An advanced solar thermochemical looping technology to produce and store nitrogen ( $\text{N}_2$ ) from air for the subsequent production of ammonia ( $\text{NH}_3$ ) via an advanced two-stage process

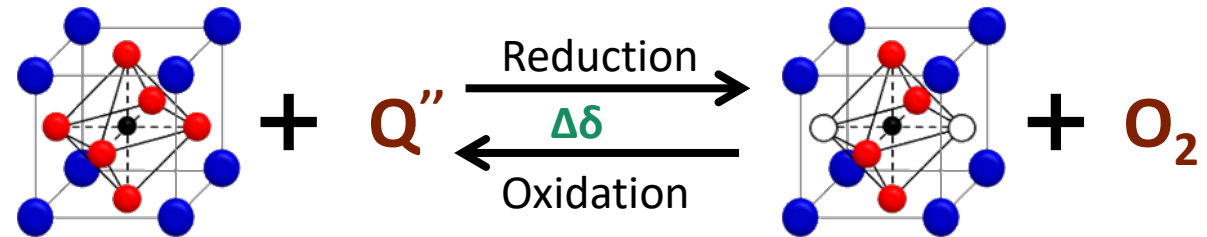
- Inputs are sunlight, air, and hydrogen; the output is ammonia
- Significantly lower pressures than Haber-Bosch
- Greatly decreases or eliminates carbon footprint
- The process consumes neither the oxide nor the nitride particles, which actively participate cyclically

# Cycle I: Nitrogen Separation



Identify and optimize redox active metal oxide (MO<sub>x</sub>) materials for N<sub>2</sub> recovery via air separation<sup>1</sup>

- MO<sub>x</sub> thermally reduced by concentrated solar heat to form oxygen-deficient compound, MO<sub>x-δ</sub>
- MO<sub>x-δ</sub> reacts with O<sub>2</sub> in air to re-oxidize, leaving behind purified N<sub>2</sub>



<sup>1</sup> Farr, T. P.; Nguyen, N. P.; Bush, H. E.; Ambrosini, A.; Loutzenhiser, P. G., *Materials* **2020**, 13 (22).

Bush, H. E.; Nguyen, N. P.; Farr, T.; Loutzenhiser, P. G.; Ambrosini, A., *Solid State Ion.* **2021**, 368, 115692.

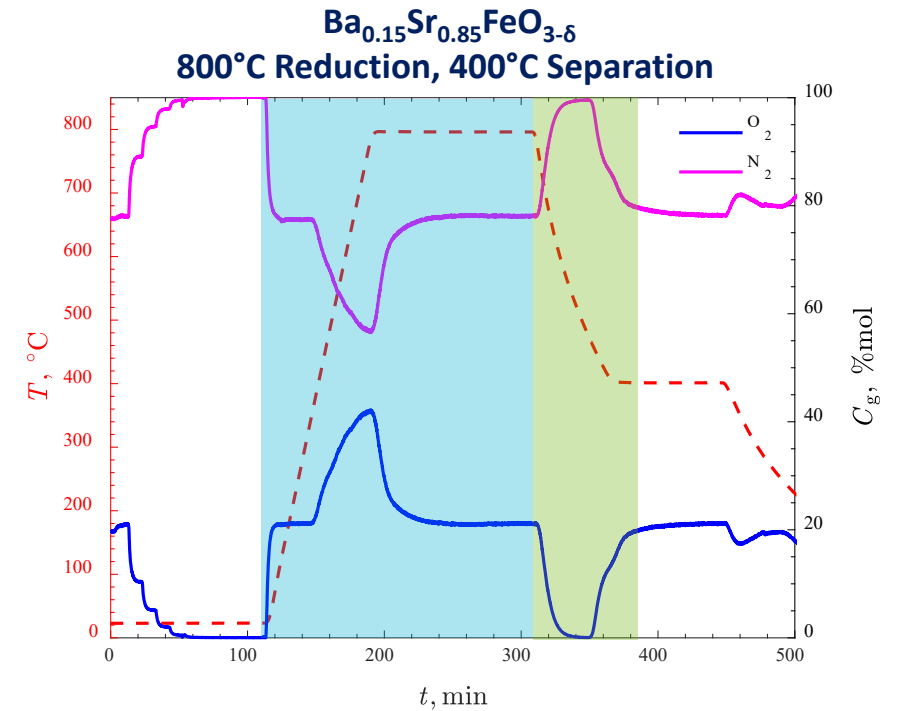
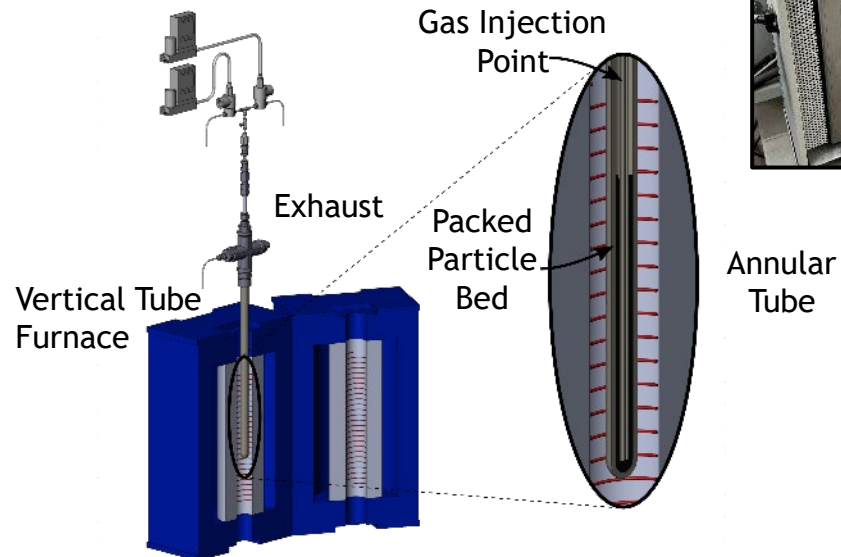
Nguyen, N. P.; Farr, T. P.; Bush, H. E.; Ambrosini, A.; Loutzenhiser, P. G., *Phys Chem Chem Phys* **2021**, 23 (35), 19280-19288.



# Packed Bed Reactor

- Demonstrates air separation reaction
- Stationary bed (35-40 g BSF1585) with sweep airflow
- Gas measurement via RGA calibrated for pO<sub>2</sub> range
- Fully cyclic thermal reduction and air separation
- Multi-cycle testing
- Range of  $T$ ,  $\dot{V}$ , pO<sub>2</sub>

Sweep/Oxidant  
Gas Flow Control



**White = calibration**

**Blue = thermal reduction and purge**

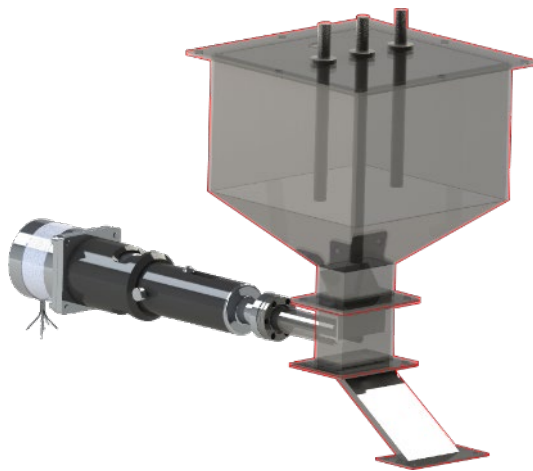
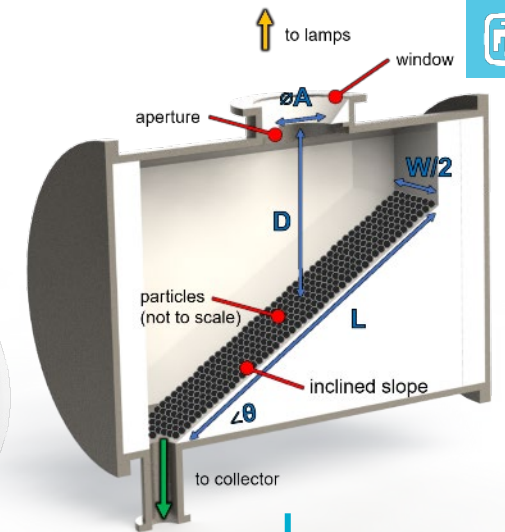
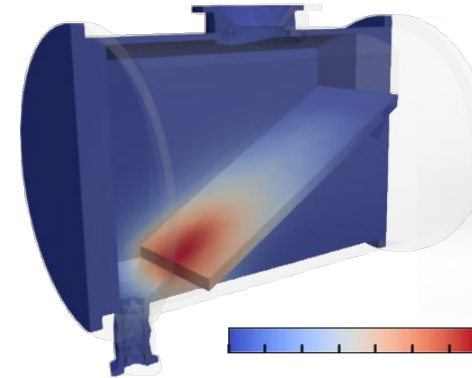
**Green = air separation**

- Air separation studied via parametric analysis of reduction, air separation temperatures, multi-cycling
- Validation of heat and mass transfer flow models
- All reactions (reduction/reoxidation) performed in air
- During reoxidation step, O<sub>2</sub> gettered by material (BSF1585), leaving purified N<sub>2</sub>

# Directly Irradiated Incline Flow Reactor

- Directly irradiated cavity receiver, water cooled quartz window
- Thermal input from high flux solar simulator (HFSS)
- Flowing inclined bed of BSF1585
- Heated 5 kg hopper with linear actuator-controlled valve
- Collection and measurement of product  $O_2$
- Load cell to measure flow rate
- Thermocouples for particle and cavity measurements

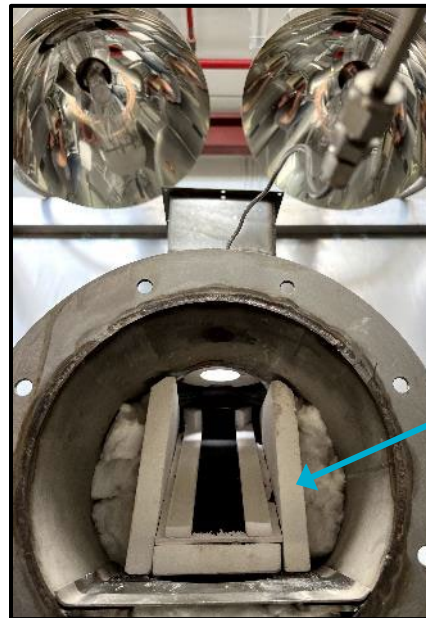
**Heat Transfer Model**



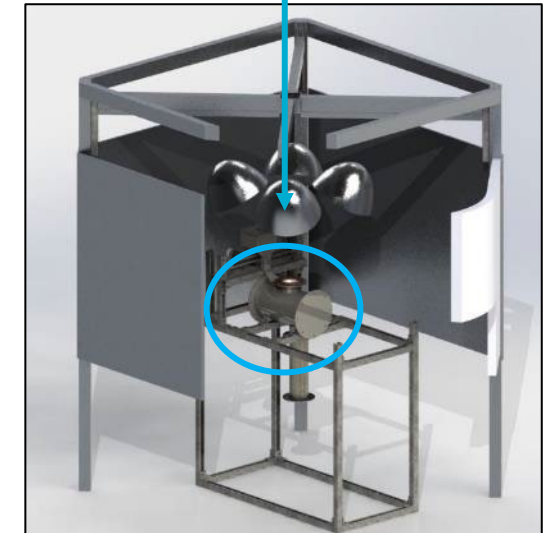
**Pre-heated Hopper Design**



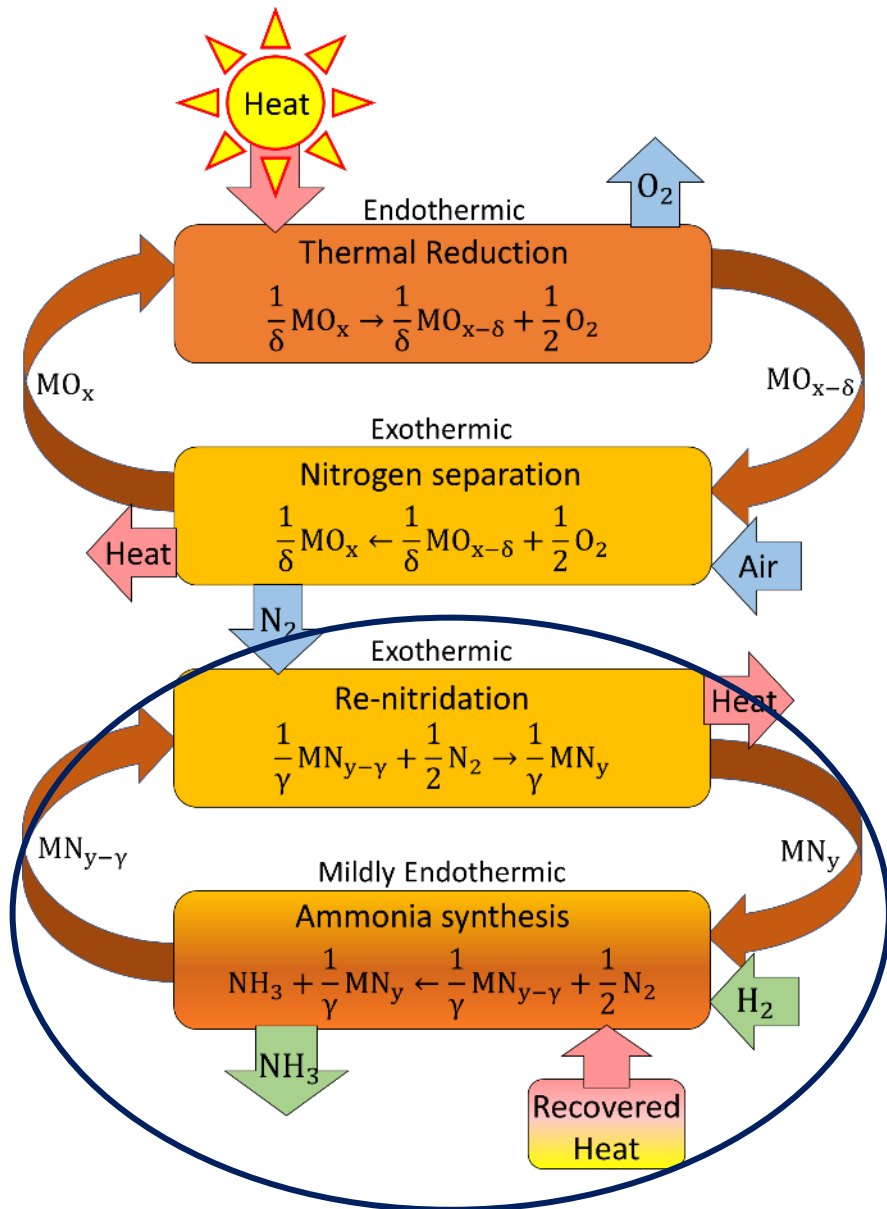
**Flow Calibration**



**HFSS Lamps  
Particle Flow**



# Cycle 2: NH<sub>3</sub> Production



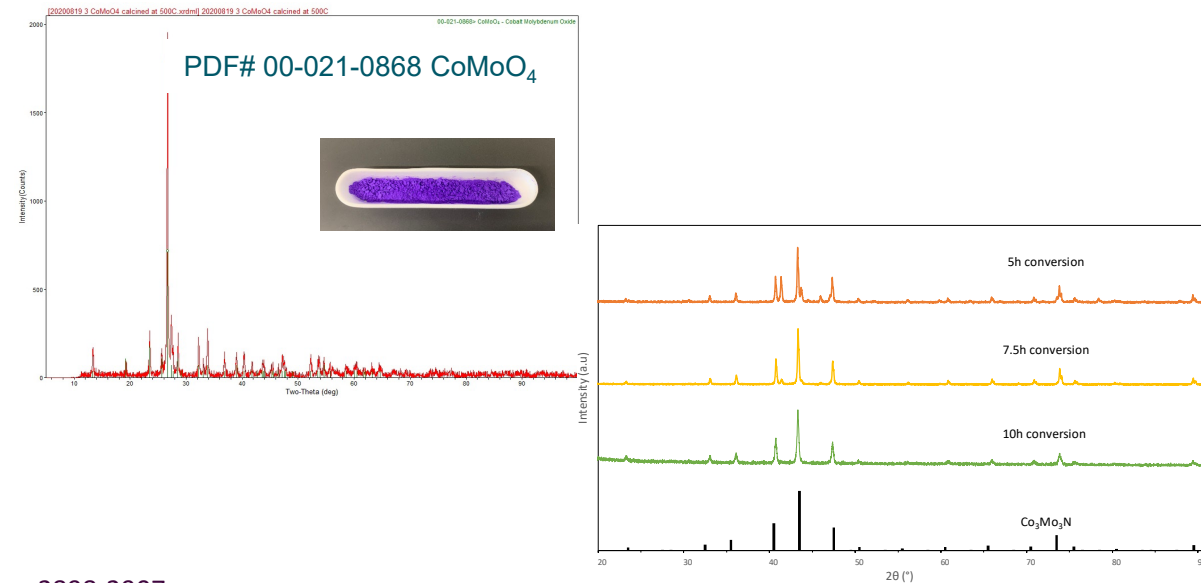
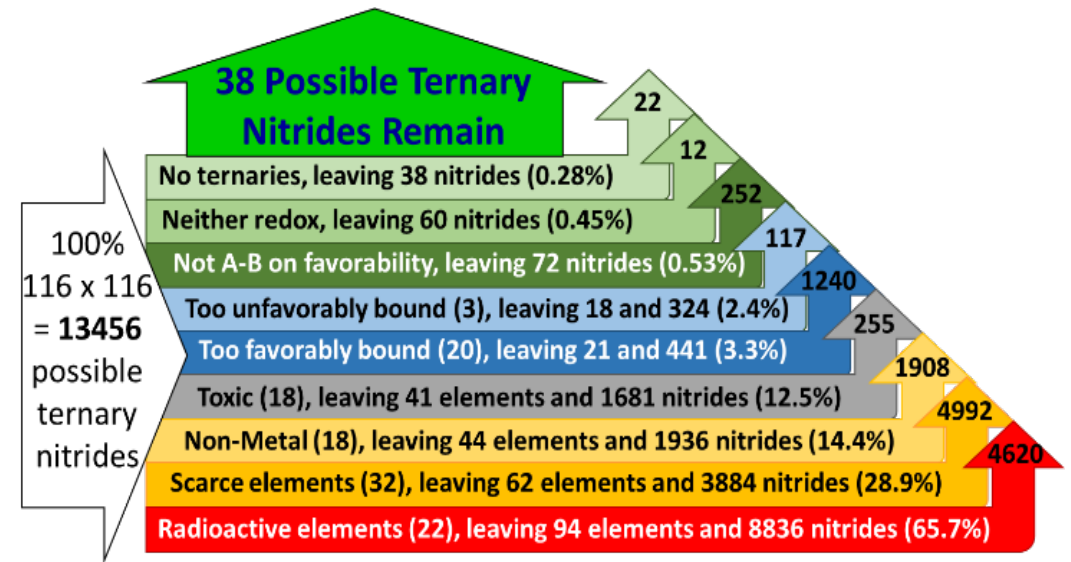
Identify and optimize metal nitride material (MN<sub>y</sub>) that can be reduced by H<sub>2</sub> to produce NH<sub>3</sub>, then re-nitridized directly by N<sub>2</sub> to close the cycle

- Nitride is reduced by H<sub>2</sub> to form Mn<sub>y-γ</sub> + NH<sub>3</sub>, then regenerated by N<sub>2</sub> from 1<sup>st</sup> cycle
- Bulk reaction, not exclusively surface-catalyzed
- Nitride materials more challenging than oxide development
  - Pool of candidates much smaller
  - Thermodynamics are challenging; NH<sub>3</sub> dissociates at high temperature
  - Nitrogen diffusion in metal nitrides is slower and less common
  - Synthesis more complex – usually reacting under flowing NH<sub>3</sub> at high temperature in ammonolysis reaction

# Candidate Identification

- Initial thermodynamic calculations determined that material should be at least a ternary nitride (MM'N)
- Down-selected to 38 possible ternary compounds
- Preliminary candidate:  $\text{Co}_3\text{Mo}_3\text{N}$  (CMN331)
  - Can undergo reversible phase change to CMN661, losing 50 mol% of nitrogen:
 
$$2\text{Co}_3\text{Mo}_3\text{N} + 3/2\text{H}_2 \rightarrow 2\text{Co}_6\text{Mo}_6\text{N} + \text{NH}_3$$

$$\text{Co}_6\text{Mo}_6\text{N} + 1/2\text{N}_2 \rightarrow 2\text{Co}_3\text{Mo}_3\text{N}$$
  - Both phases crystallize in same space group (Fd-3m) – facilitate kinetics?
  - Reports that material can be regenerated directly by  $\text{N}_2$
  - Synthesized via oxide precursor method
- Expanded candidate pool to a family of single-phase  $\text{A}_3\text{B}_x\text{N}$  (A=Co, Ni, Fe; B=Mo, W; x = 2, 3) ternary and quaternary nitride solid solutions



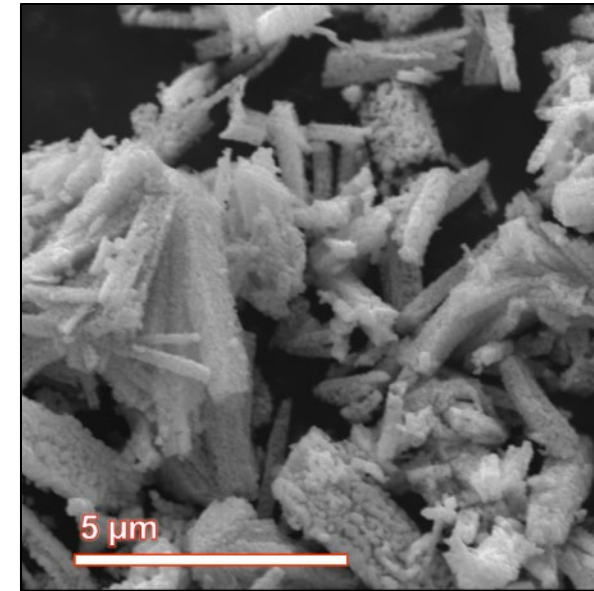
\*Hunter, S.M., McKay, D., Smith, R.J., Hargreaves, J.S.J., Gregory, D.H., 2010, Chemistry of Materials, 22(9), pp. 2898-2907.  
 Gregory, D.H., Hargreaves, J.S.J., Hunter, S.M., Catalysis Letters, 2011, 141(1), pp. 22-26.



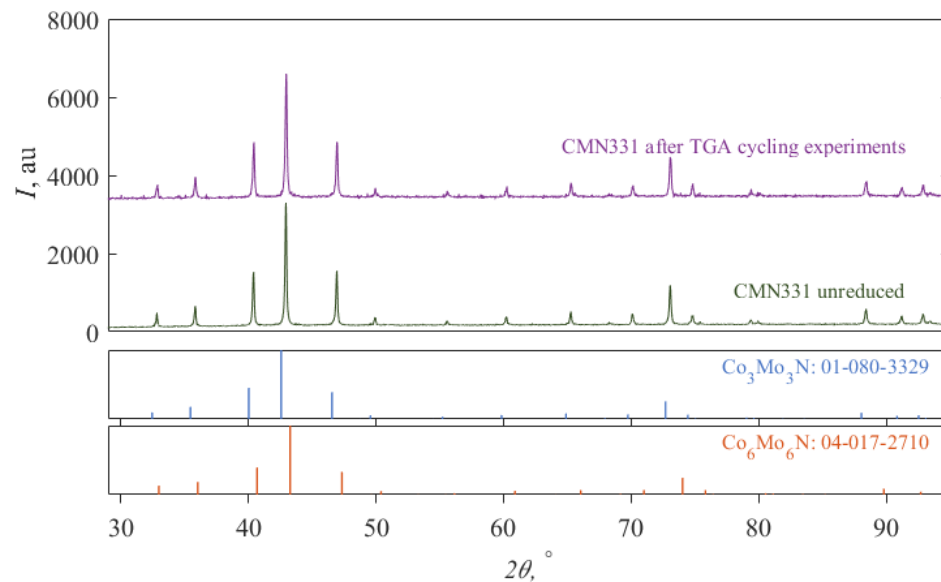
# Nitride Characterization

- XRD before/after cycling for phase identification
- Elemental analysis performed using ICP-OES and CHN to identify  $\text{Co}_3\text{Mo}_3.1\text{N}_{1.13}$
- Particle surface composition investigated with XPS, SEM/EDS, and TEM identified oxide surface layer
- Oxygen detected on particles surface using XPS and EDS
  - Surface oxygen-rich layer observed

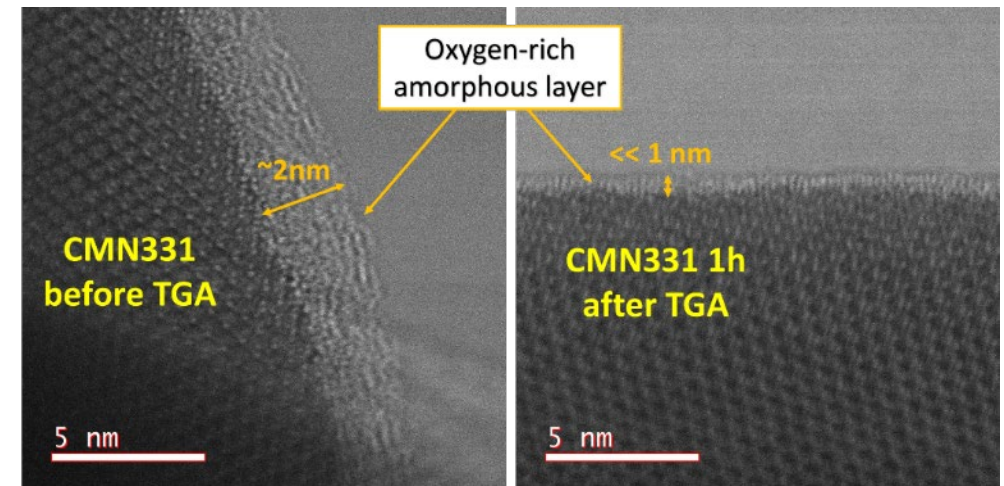
CMN331 particle morphology



XRD of CMN331 before and after reaction



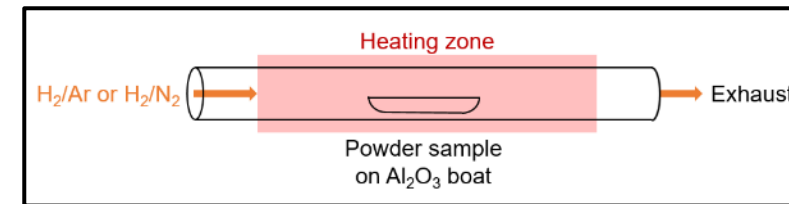
TEM images of CMN331 particle



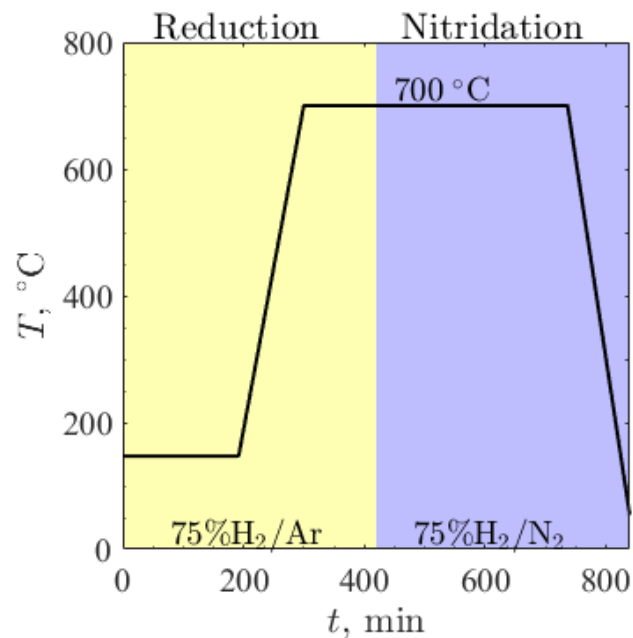
# Nitride Reactivity at Ambient Pressure



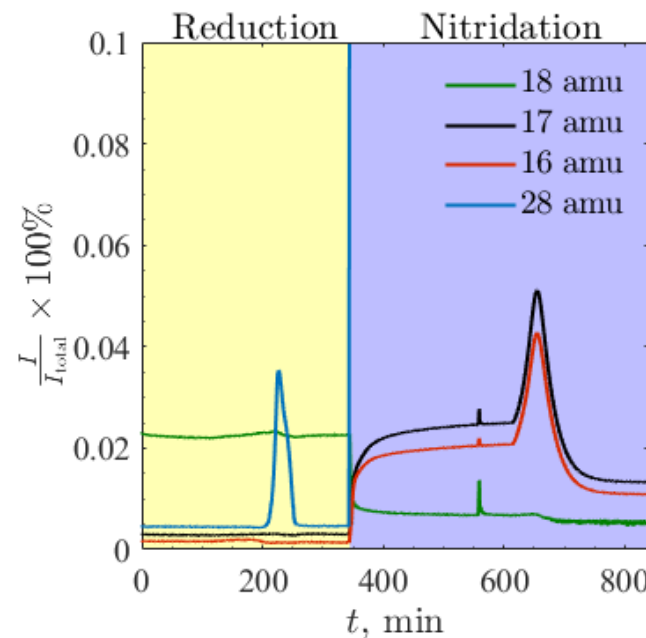
- Series of reductions/re-nitrations performed at varying  $T$  and  $P_{H_2}$
- Performed in TGA (low  $P_{H_2}$ ) and tube furnace (high  $P_{H_2}$ , below)
- $NH_3$  detected under both reduction and re-nitridation, *under certain conditions*
  - Catalytic + bulk behavior?
- Does nitride activity differ under pressure?



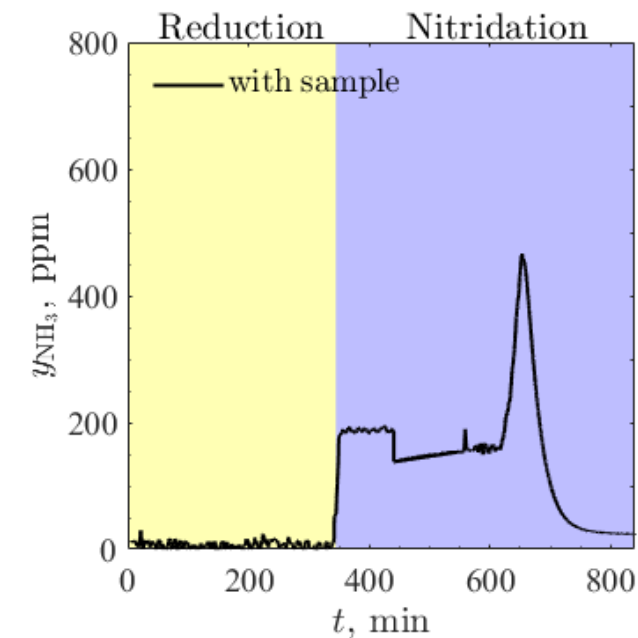
## Experimental conditions



## RGA



## Detected $NH_3$

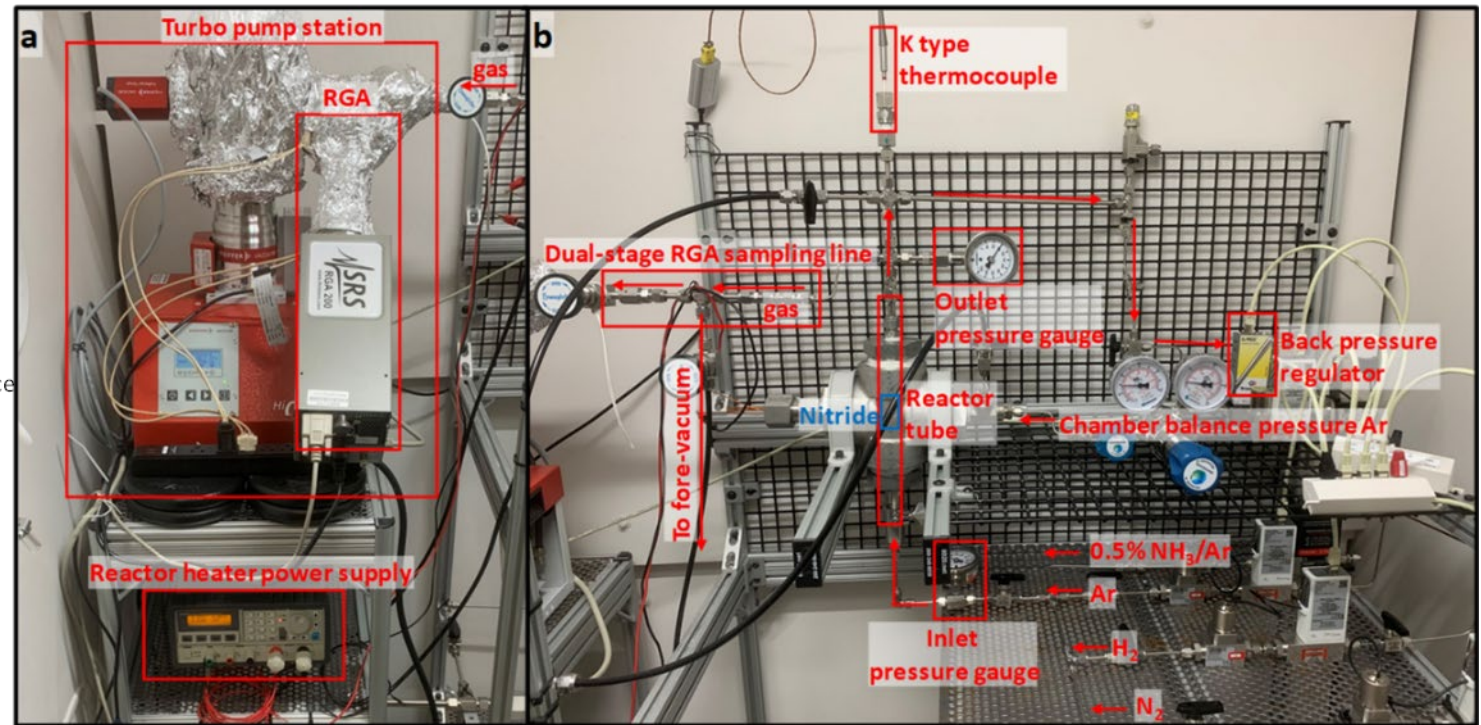
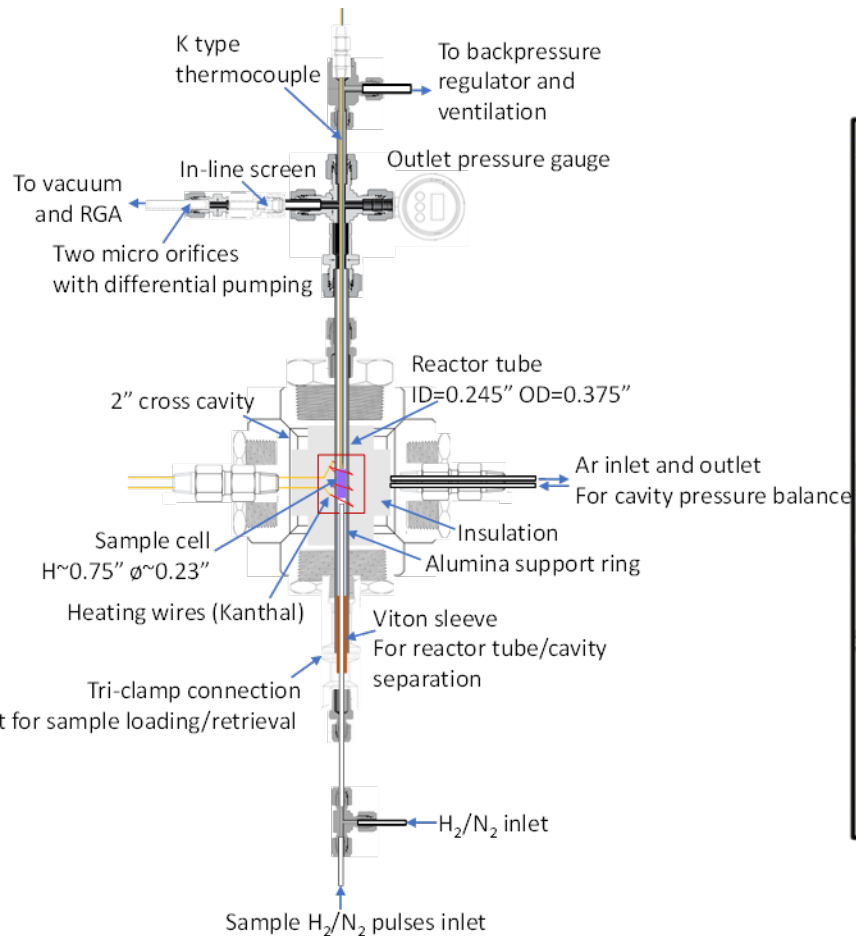


# Ammonia Synthesis Reactor (ASR)

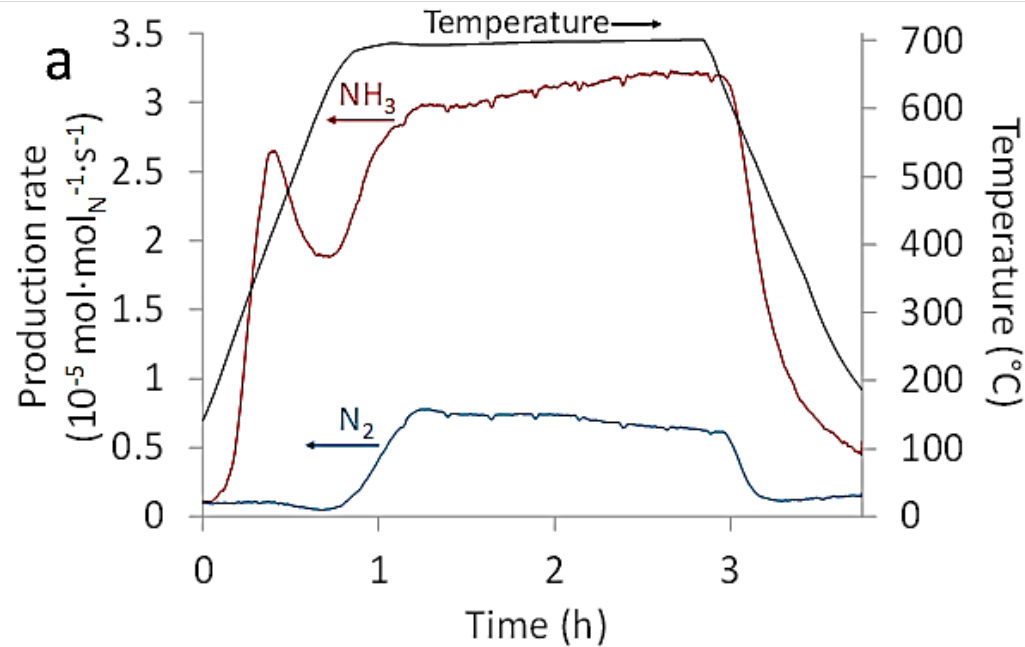


Reactor designed to perform  $\text{NH}_3$  synthesis and nitride re-nitridation reaction under variable pressure and temperature, up to 30 bar and 800 °C, respectively

Arizona State University



# Ammonia Production and Re-nitridation of CMN33 I



**$\text{NH}_3$ ,  $\text{N}_2$  production rates and temperature profile of representative reduction step under 100%  $\text{H}_2$  (Cycle 6)**

- Initial  $\text{NH}_3$  peak assumed to be hydrogenation of surface adsorbed  $\text{N}_2$
- At  $T > 600^{\circ}\text{C}$ , consistent co-production of  $\text{NH}_3$  and  $\text{N}_2$  in 100%  $\text{H}_2$  (no external  $\text{N}_2$  feed)
- Sample can be re-nitridized under 100%  $\text{N}_2$  with no side-reactions observed
  - $P = 20 \text{ bar}$ ,  $T = 700^{\circ}\text{C}$  for both reactions

Results imply that lattice nitrogen participates in  $\text{NH}_3$  production in reversible  $\text{CCM331} \rightarrow \text{CCM661}$  bulk reaction



# Co<sub>3</sub>Mo<sub>3</sub>N ASR Cycle Results



Steady production rates were calculated using averages of the last 10 min of stabilized rate data before cool-down

Reacted solid-state nitrogen was calculated by adding NH<sub>3</sub> yield and two times of N<sub>2</sub> yield (theoretical max CMN331 → CMN661 = 0.5)

Selectivity to NH<sub>3</sub> was calculated by percentage of NH<sub>3</sub> yield in the reacted solid-state nitrogen

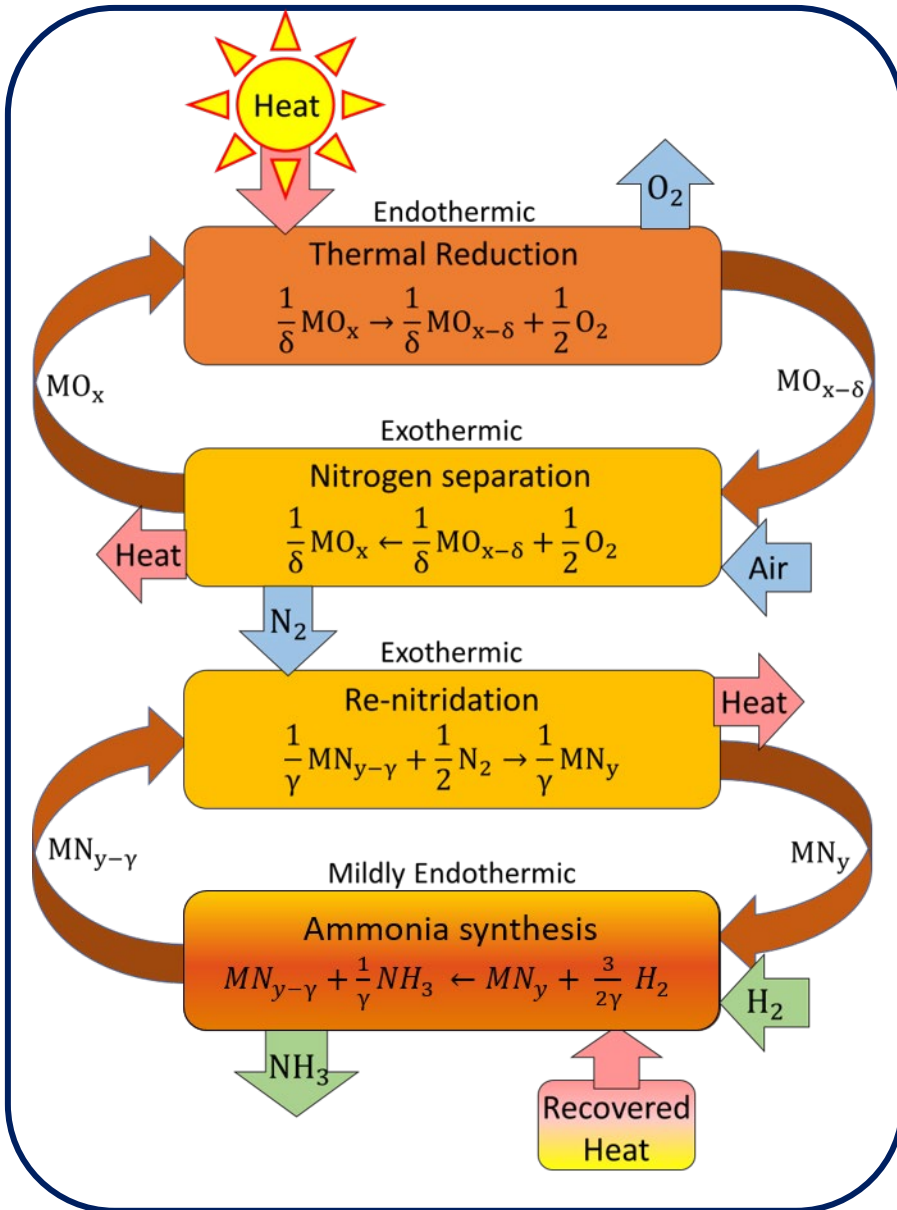
Reduction step	P(H <sub>2</sub> ) bar	T <sub>hold</sub> °C	t <sub>hold</sub> h	Steady r(NH <sub>3</sub> ) 10 <sup>-5</sup> mol mol <sub>N</sub> <sup>-1</sup> s <sup>-1</sup>	Steady r(N <sub>2</sub> ) 10 <sup>-5</sup> mol mol <sub>N</sub> <sup>-1</sup> s <sup>-1</sup>	NH <sub>3</sub> yield mol/mol <sub>N</sub>	N <sub>2</sub> yield mol/mol <sub>N</sub>	Reacted solid-state nitrogen mol mol <sub>N</sub> <sup>-1</sup>	Selectivity to NH <sub>3</sub>
2	20	700	2	2.32	0.455	0.121	0.0610	0.243	49.8%
3	20	700	2	2.93	0.923	0.151	0.111	0.372	40.5%
4	20	700	2	4.27	0.985	0.271	0.113	0.498	54.5%
5	20	700	2	2.86	0.413	0.154	0.0496	0.253	60.8%
6	20	700	2	3.20	0.643	0.183	0.0742	0.331	55.2%
7	20	700	2	3.29	0.792	0.225	0.0842	0.393	57.2%
8	20	600-720	0.5×5	--	--	0.180	0.0641	0.308	58.4%
9	15	600-720	0.5×5	--	--	0.148	0.0510	0.250	59.1%
10	10	600-720	0.5×5	--	--	0.0995	0.0506	0.201	49.6%
11	5	600-720	0.5×5	--	--	0.0428	0.0382	0.119	35.9%

Cycling runs (constant T, pH<sub>2</sub>, t)

- All re-nitridation steps were performed with 20 bar of 10% H<sub>2</sub>/N<sub>2</sub> at 700 °C
- Sample held at 5 sccm H<sub>2</sub> / 15 sccm Ar overnight, 1.2 atm, 120 °C

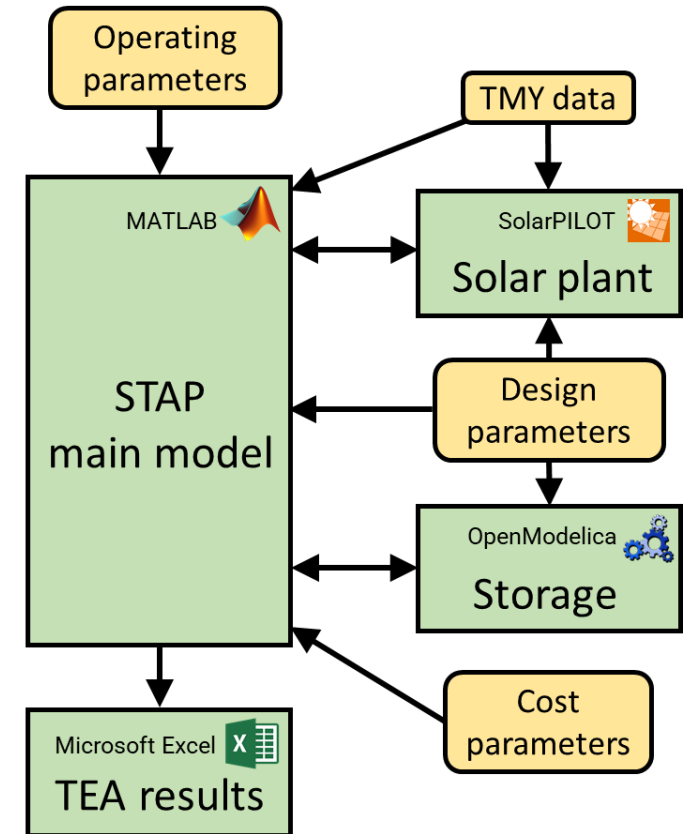
All cycles on same Co<sub>3</sub>Mo<sub>3</sub>N sample – *Reaction is cyclic*

# System and Technoeconomic Analyses



Develop and refine systems and technoeconomic models to guide materials choices, reactor design, and determine projected cost for a scaled-up system

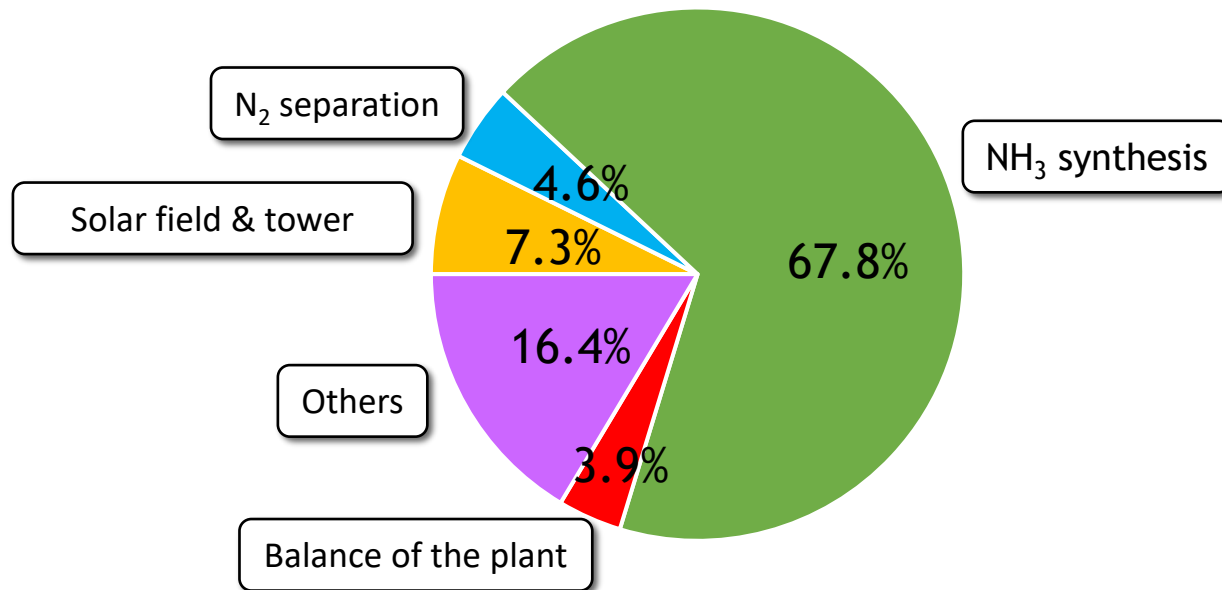
Integration completed in a single MATLAB script that communicates with other support software to perform the simulation



# Techno-economic analysis

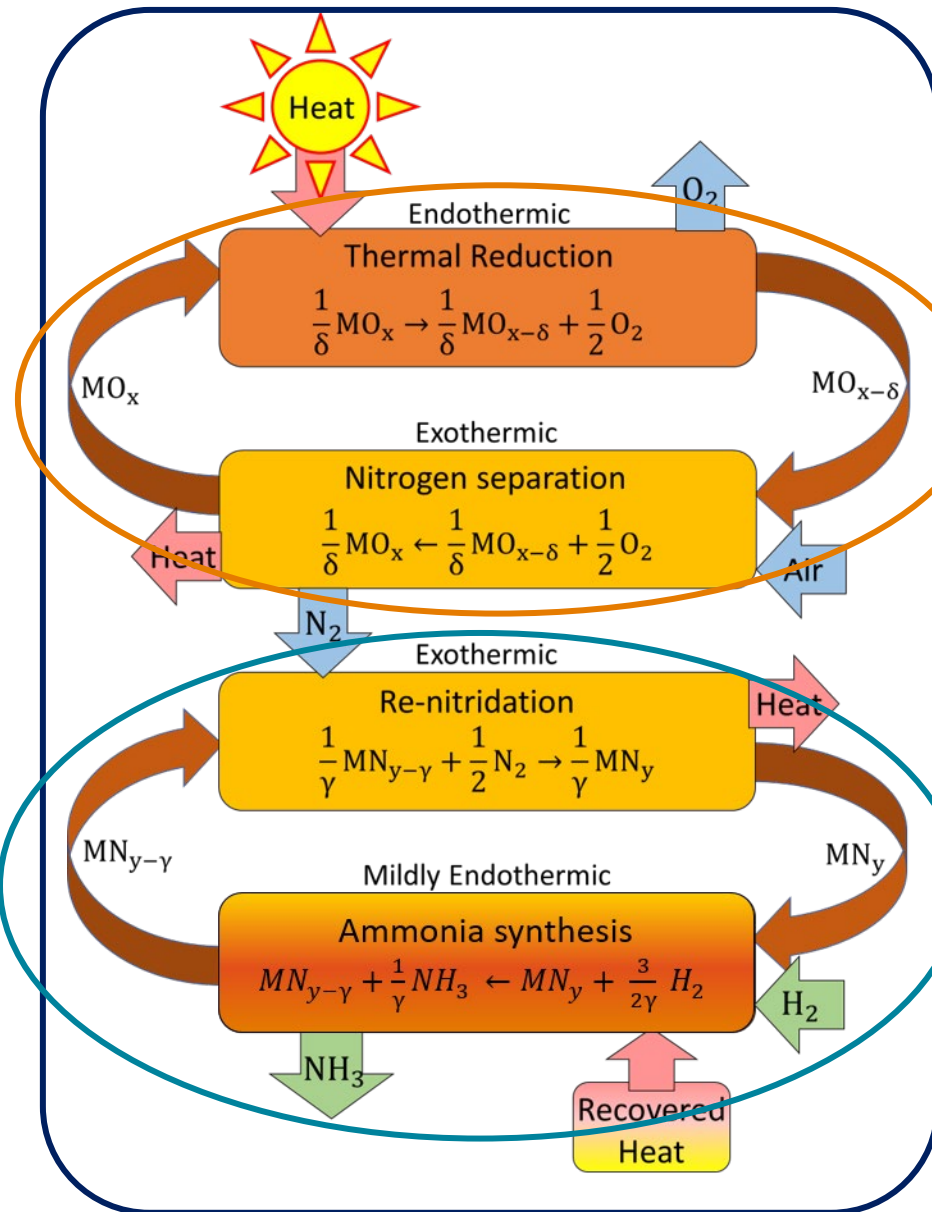
- $\text{NH}_3$  yield and cycle time have a high impact on the total cost of the plant
- The nitride cost is the most significant system expense, accounting for more than the 50% of the total CapEx, but it is also the most uncertain variable

Capital expense distribution



Costs Calculation	Units	Value
Heliostat field	\$	3,975,900.50
Tower	\$	6,251,716.68
Receiver	\$	1,009,800.00
OX reactor	\$	336,600.00
Lift	\$	259,740.16
Storage tanks ST1 & ST2	\$	1,344,389.90
MO particles	\$	3,551,288.54
Storage tank ST3 and material	\$	834,750.51
Heat Exchangers	\$	1,550,681.99
Turboexpander	\$	283,220.00
Power Block	\$	2,758,295.81
Separation NH3	\$	107,307.00
Separation N2/H2	\$	-
AS & RN Reactors	\$	3,326,583.31
MN particles	\$	91,336,698.62
<b>Subtotal direct cost</b>	<b>\$</b>	<b>116,926,973.02</b>
Contingency	\$	8,184,888.11
<b>Total direct cost</b>	<b>\$</b>	<b>125,111,861.14</b>
Land cost	\$	1,007,571.02
EPC and owner cost	\$	13,762,304.72
<b>Total indirect cost</b>	<b>\$</b>	<b>14,769,875.74</b>
<b>Total CapEx</b>	<b>\$</b>	<b>139,881,736.88</b>
OpEx (fixed)	\$/y	2,797,634.74
Particle loss	\$/y	355,128.85
Additional heat	\$/y	-
OpEx (variable)	\$/y	355,128.85
<b>Total OpEx</b>	<b>\$/y</b>	<b>3,507,892.45</b>
<b>Total revenue</b>	<b>\$/y</b>	<b>474,058.12</b>
<b>LCOA w/o H<sub>2</sub></b>	<b>\$/tonne</b>	<b>213.11</b>

# Upcoming STAP SolarPACES Talks



**Evan Bush:** “Demonstration of a Solar Air Separation Process to Produce High-Purity  $N_2$  via  $Ba_{0.15}Sr_{0.85}FeO_{3-\delta}$  Reduction/Oxidation Cycles,” Wednesday, 17:40 (Today!)

**Alberto de la Calle:** “Techno-Economic Analysis of Solar-Thermal Ammonia Production,” Friday, 8:30

**Ty Nguyen:** “Investigation of  $Co_3Mo_3N$  Reduction/Re-nitridation Extents as a Function of Temperature and  $N_2$  Partial Pressure for Solar Thermochemical  $NH_3$  Production,” Friday, 9:10

**James Miller:** “Solar Ammonia Production via Novel Two-step Thermochemical Looping of a  $Co_3Mo_3N/Co_6Mo_6N$  pair,” Friday, 9:50





- Solar Thermal Ammonia Production has potential to produce green ammonia using CSP, air, and water
- Air separation to purify  $N_2$  was successfully demonstrated with BSF1585 in packed bed reactor; on-sun reduction reactor under construction
- Metal nitrides ( $MN_y$ ) were successfully synthesized and characterized under both ambient and pressurized conditions
  - $Co_3Mo_3N$  shown to successfully produce  $NH_3$  when exposed to pure  $H_2$  at pressures between 5 – 20 bar 600 – 750 °C
    - Reaction with pure  $H_2$  ensures nitrogen source is bulk  $Mn_y$
    - Performance is cyclic
  - Ambient reaction experiments imply there may be a catalytic aspect as well
- Technoeconomic and systems analyses show a path towards scale-up

# Acknowledgements



Kevin Albrecht, H. Evan Bush, Matthew W. Kury, Tania Rivas, Madeline Finale, Luis Garcia Maldonado



Ellen B. Stechel (PI, ASU), James E. Miller, Ivan Ermanoski, Xiang Michael Gao, Alberto de la Calle, Alicia Bayon Sandoval, Nathaniel Anbar, Syed Shakeel and Jarett Prince



Peter Loutzenhiser (PI, GIT), Nhu “Ty” Nguyen, Tyler Farr, Shaspreet Singh



This work is supported by the U.S. Department of Energy’s Office of Energy Efficiency and Renewable Energy (EERE) under the Solar Energy Technologies Office (SETO) Award Number DE-EE0034250.





*THANK YOU FOR YOUR ATTENTION*