



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



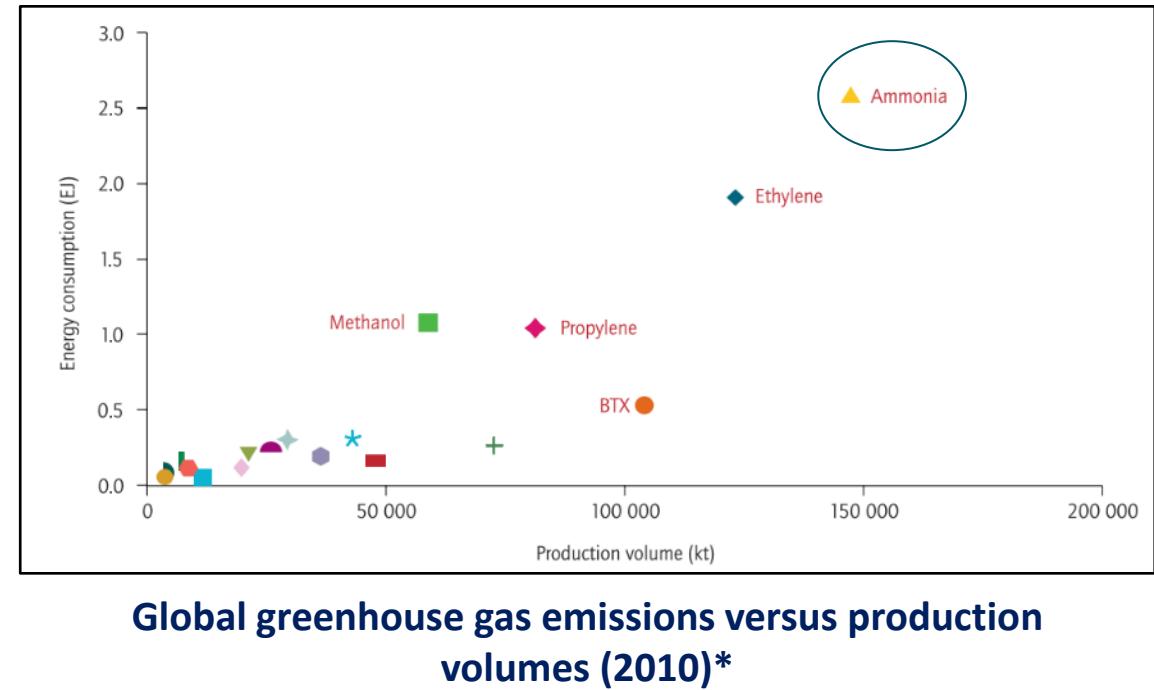
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Introduction



- Ammonia (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
- 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 H_2 production is responsible for ~1.8% of global CO_2 emissions¹
- Ammonia synthesis consumes > 1% of the total energy worldwide²

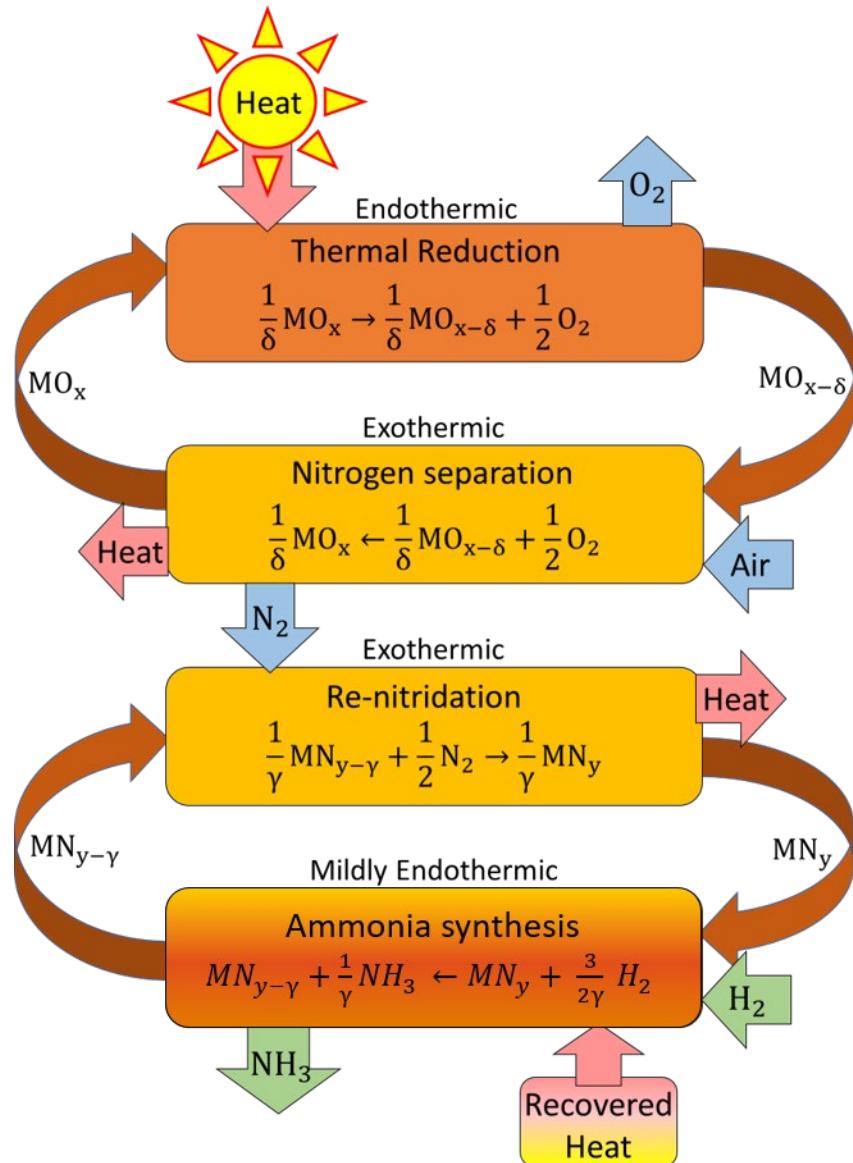


Production of NH_3 via a renewable, carbon-neutral technology powered by concentrating solar can mitigate climate and CO_2 impacts

¹*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>

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

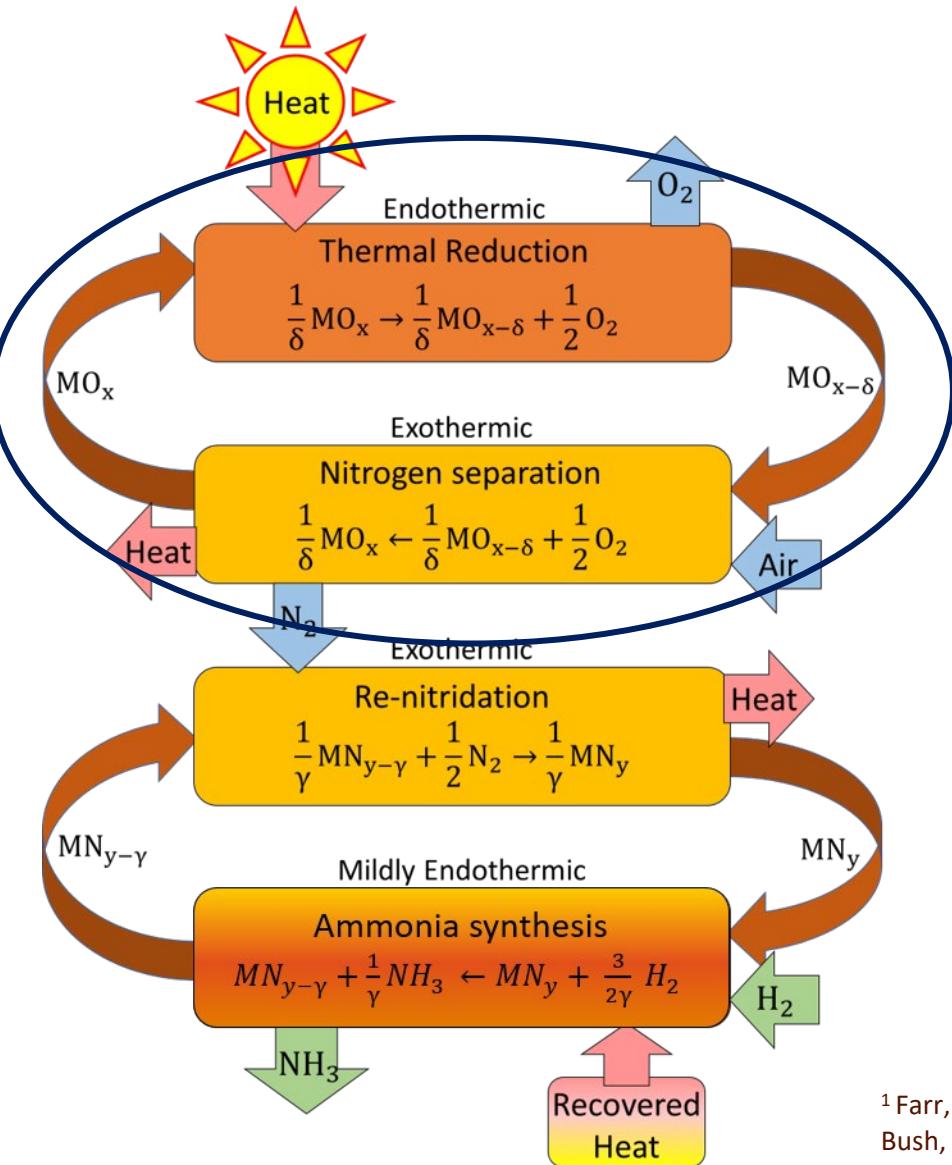
Solar Thermal Ammonia Production (STAP)



An advanced solar thermochemical looping technology to produce and store nitrogen (N_2) from air for the subsequent production of ammonia (NH_3) via an advanced two-stage process

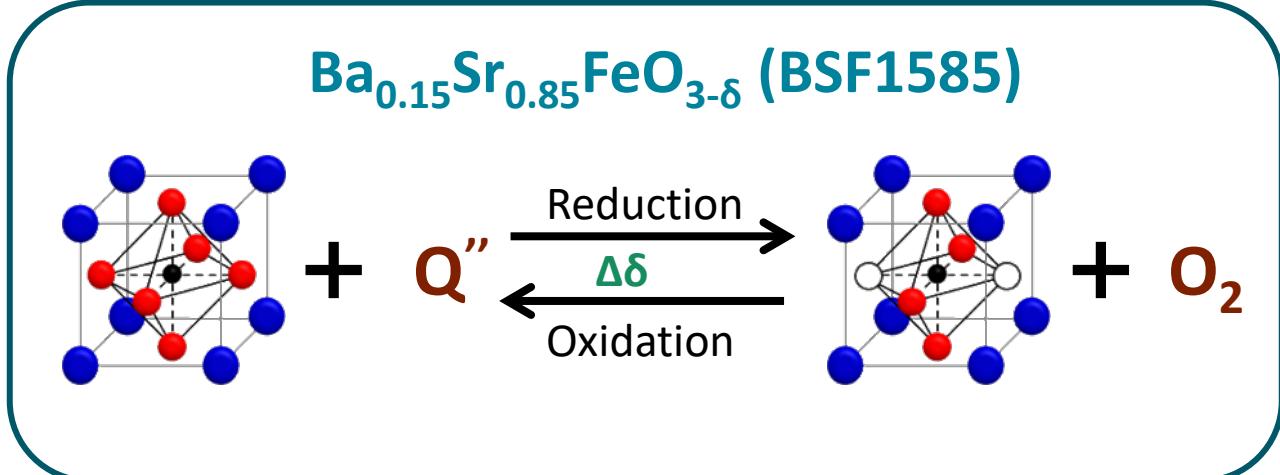
- Inputs are sunlight, air, and hydrogen; the output is ammonia
- Significantly lower pressures than Haber-Bosch
- Greatly decreases or eliminates carbon footprint
- The process consumes neither the oxide nor the nitride particles, which actively participate cyclically

Cycle I: Nitrogen Separation



Identify and optimize redox active metal oxide (MO_x) materials for N₂ recovery via air separation¹

- MO_x thermally reduced by concentrated solar heat to form oxygen-deficient compound, MO_{x-δ}
- MO_{x-δ} reacts with O₂ in air to re-oxidize, leaving behind purified N₂

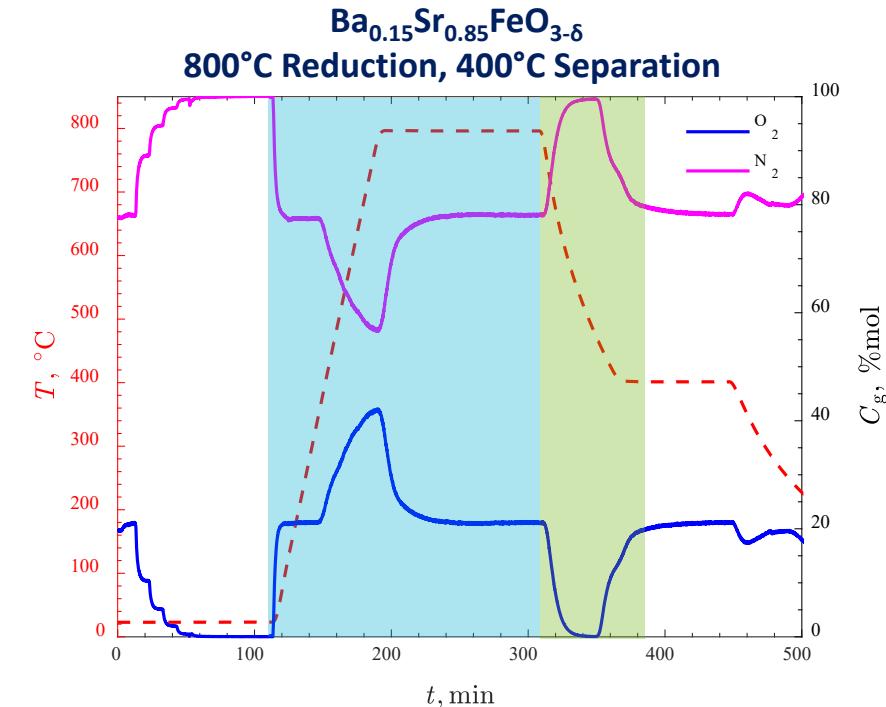
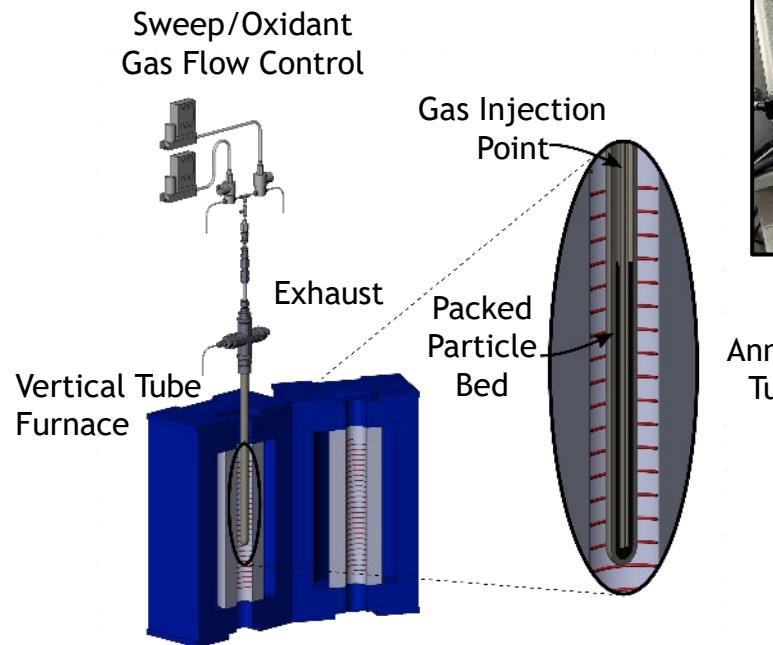


¹ Farr, T. P.; Nguyen, N. P.; Bush, H. E.; Ambrosini, A.; Loutzenhiser, P. G., *Materials* **2020**, *13* (22).
 Bush, H. E.; Nguyen, N. P.; Farr, T.; Loutzenhiser, P. G.; Ambrosini, A., *Solid State Ion.* **2021**, *368*, 115692.
 Nguyen, N. P.; Farr, T. P.; Bush, H. E.; Ambrosini, A.; Loutzenhiser, 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 pO₂ range
- Fully cyclic thermal reduction and air separation
- Multi-cycle testing
- Range of T, \dot{V} , pO₂



White = calibration

Blue = thermal reduction and purge

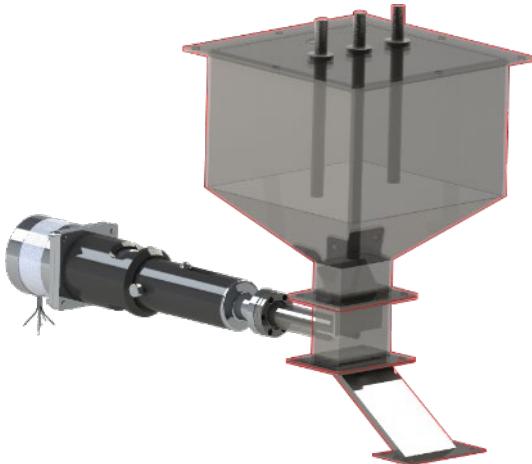
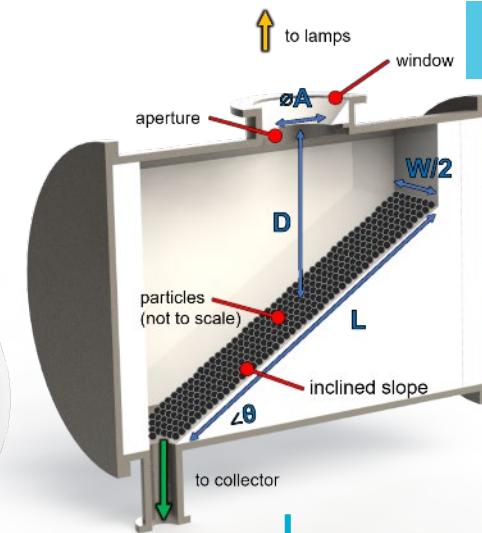
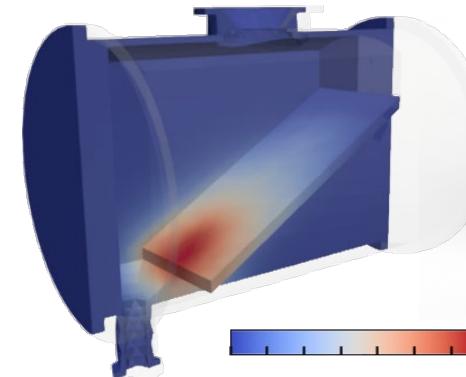
Green = air separation

- 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, O₂ gettered by material (BSF1585), leaving purified N₂

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 O₂
- Load cell to measure flow rate
- Thermocouples for particle and cavity measurements

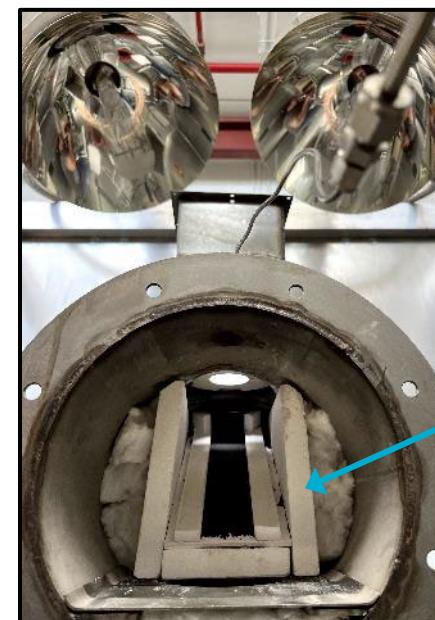
Heat Transfer Model



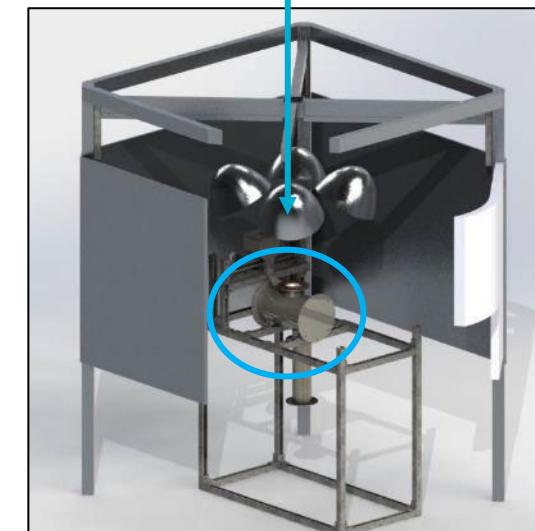
Pre-heated Hopper Design



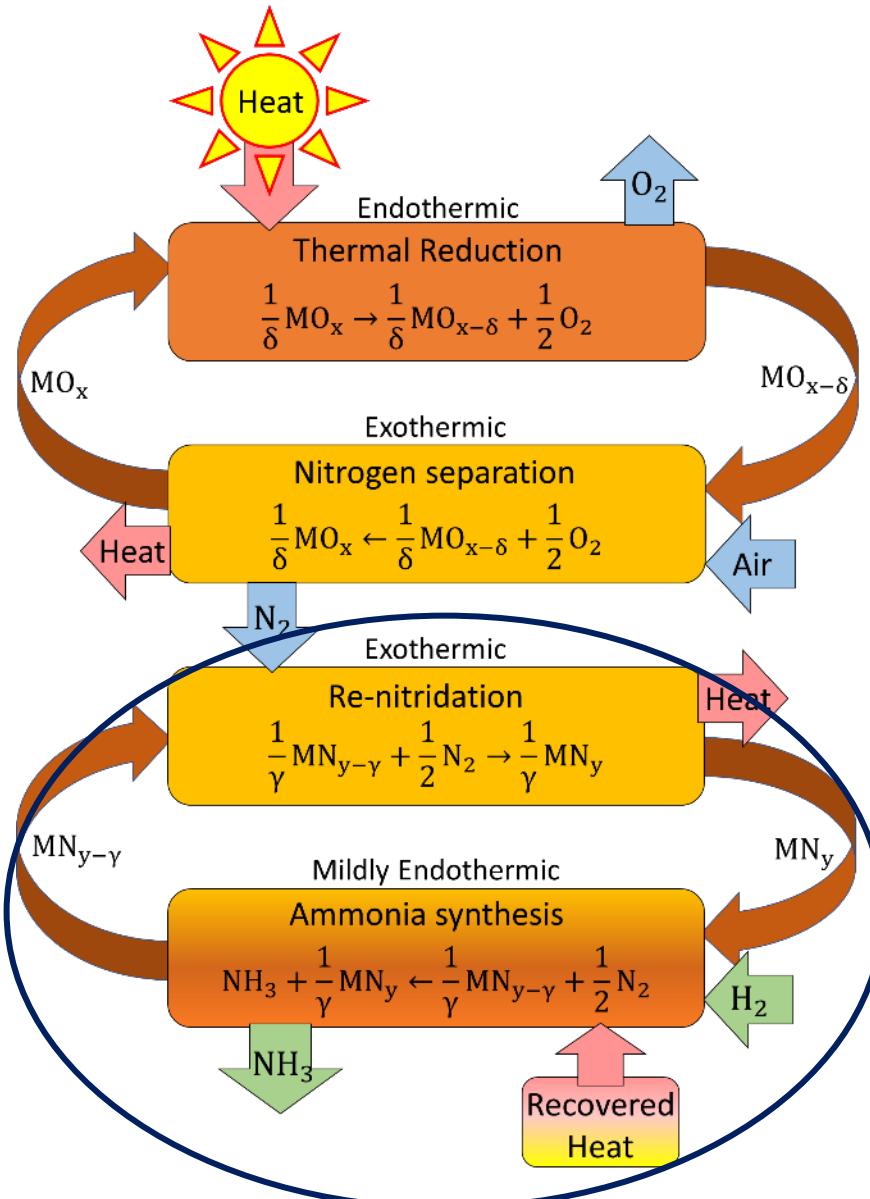
Flow Calibration



HFSS Lamps
Particle Flow



Cycle 2: NH₃ Production



Identify and optimize metal nitride material (MN_y) that can be reduced by H₂ to produce NH₃, then re-nitridized directly by N₂ to close the cycle

- Nitride is reduced by H₂ to form Mn_{y-y} + NH₃, then regenerated by N₂ from 1st cycle
- Bulk reaction, not exclusively surface-catalyzed
- Nitride materials more challenging than oxide development
 - Pool of candidates much smaller
 - Thermodynamics are challenging; NH₃ dissociates at high temperature
 - Nitrogen diffusion in metal nitrides is slower and less common
 - Synthesis more complex – usually reacting under flowing NH₃ at high temperature in ammonolysis reaction

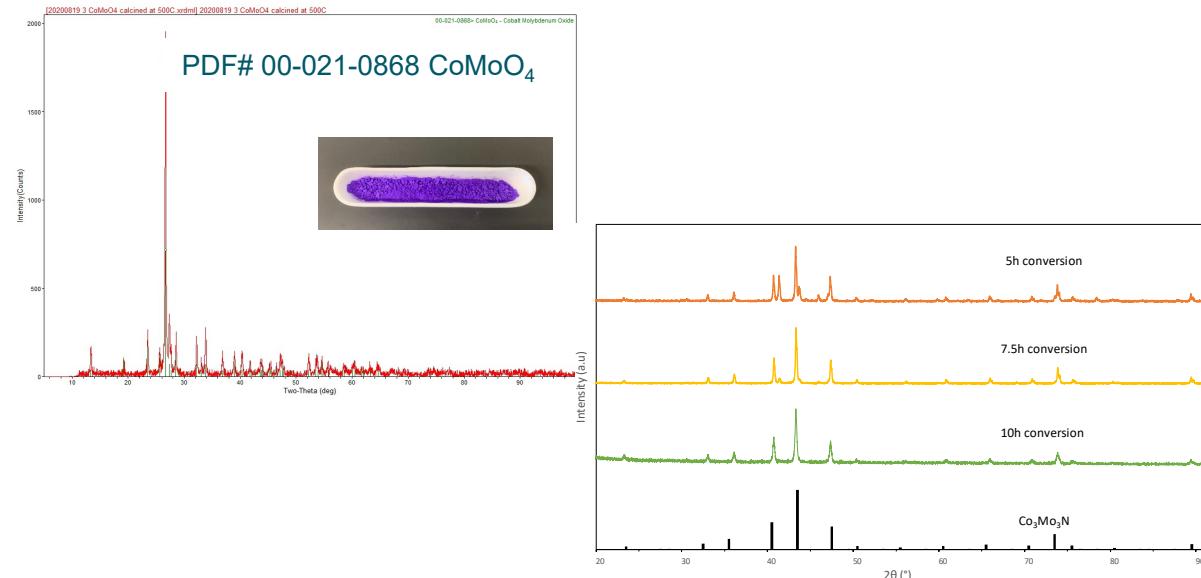
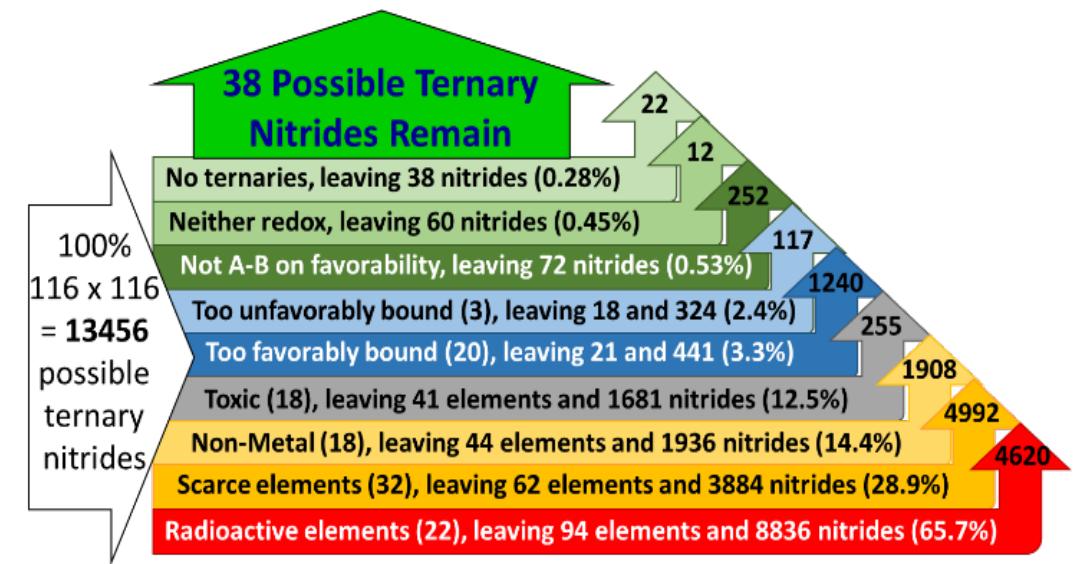
Candidate Identification



- 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:



- Both phases crystallize in same space group (Fd-3m) – facilitate kinetics?
- Reports that material can be regenerated directly by N_2
- Synthesized via oxide precursor method
- Expanded candidate pool to a family of single-phase $\text{A}_3\text{B}_x\text{N}$ ($\text{A}=\text{Co, Ni, Fe}$; $\text{B}=\text{Mo, W}$; $x = 2, 3$) 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.

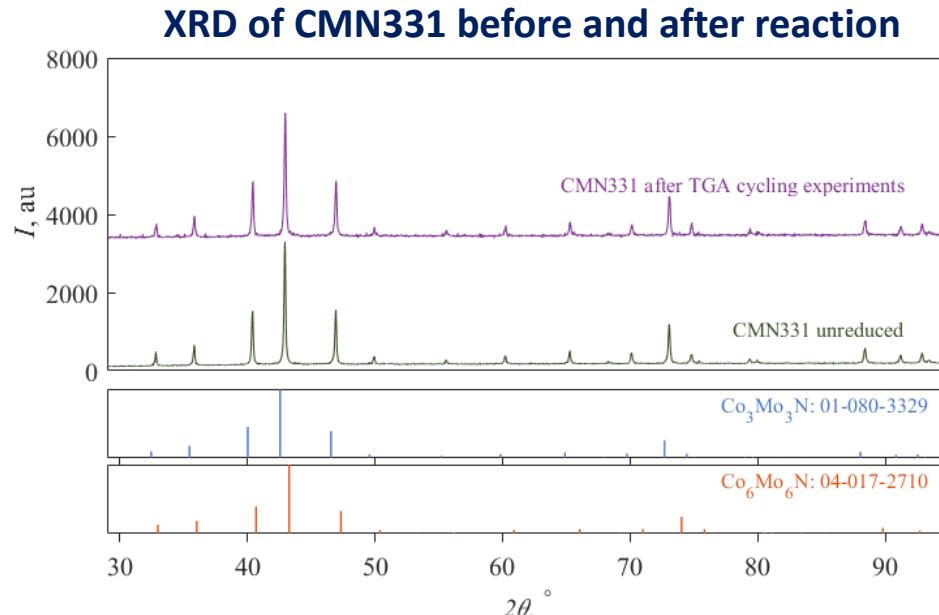
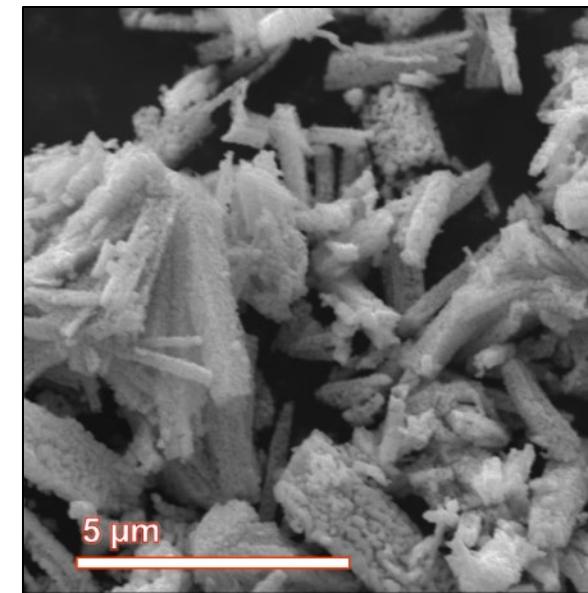
Gregory, D.H., Hargreaves, J.S.J., Hunter, S.M., Catalysis Letters, 2011, 141(1), pp. 22-26.

Nitride Characterization

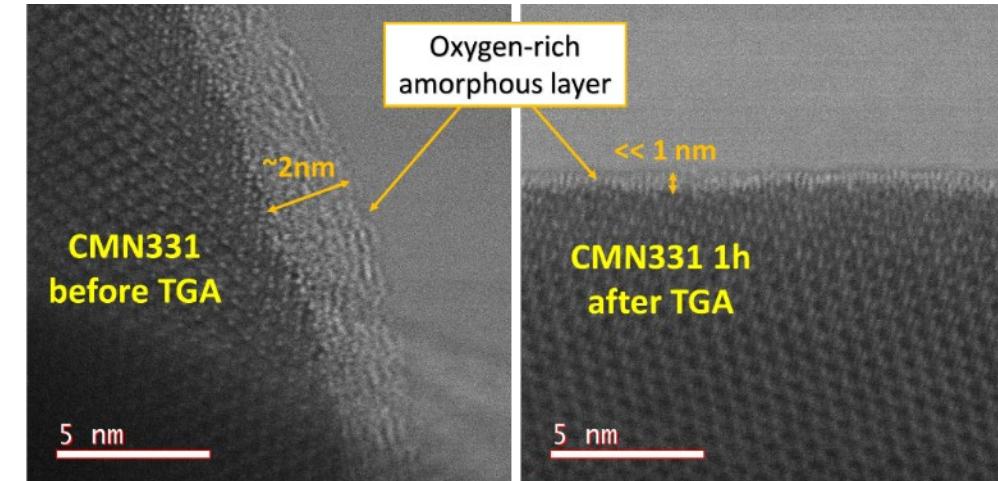


- XRD before/after cycling for phase identification
- Elemental analysis performed using ICP-OES and CHN to identify $\text{Co}_3\text{Mo}_3.1\text{N}1.13$
- Particle surface composition investigated with XPS, SEM/EDS, and TEM identified oxide surface layer
- Oxygen detected on particles surface using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

CMN331 particle morphology



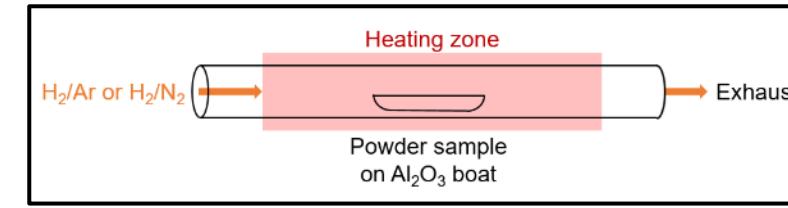
TEM images of CMN331 particle



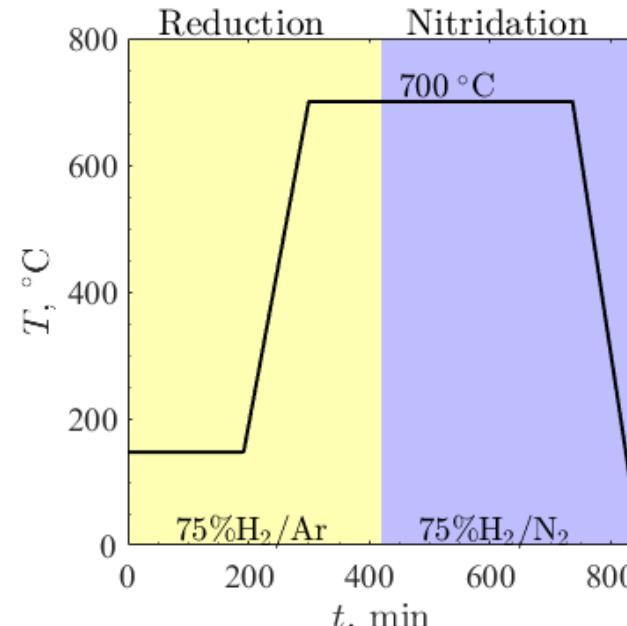
Nitride Reactivity at Ambient Pressure



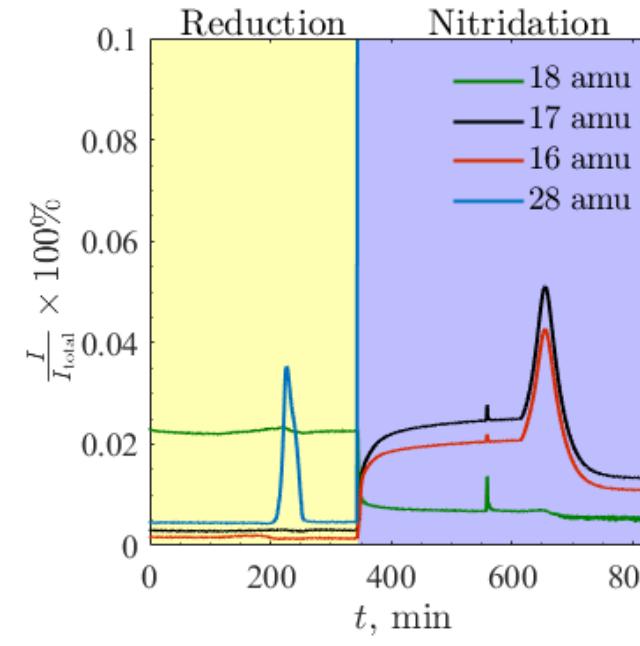
- Series of reductions/re-nitridations performed at varying T and P_{H_2}
- Performed in TGA (low P_{H_2}) and tube furnace (high P_{H_2} , below)
- NH_3 detected under both reduction and re-nitridation, *under certain conditions*
 - Catalytic + bulk behavior?
- Does nitride activity differ under pressure?



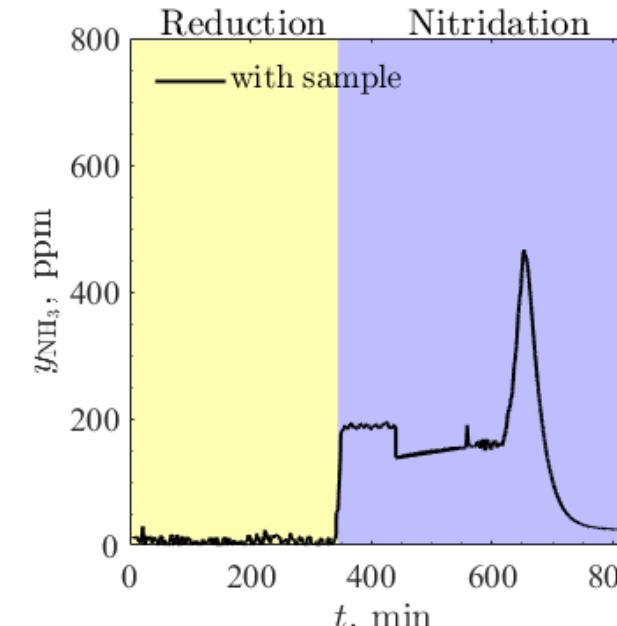
Experimental conditions



RGA



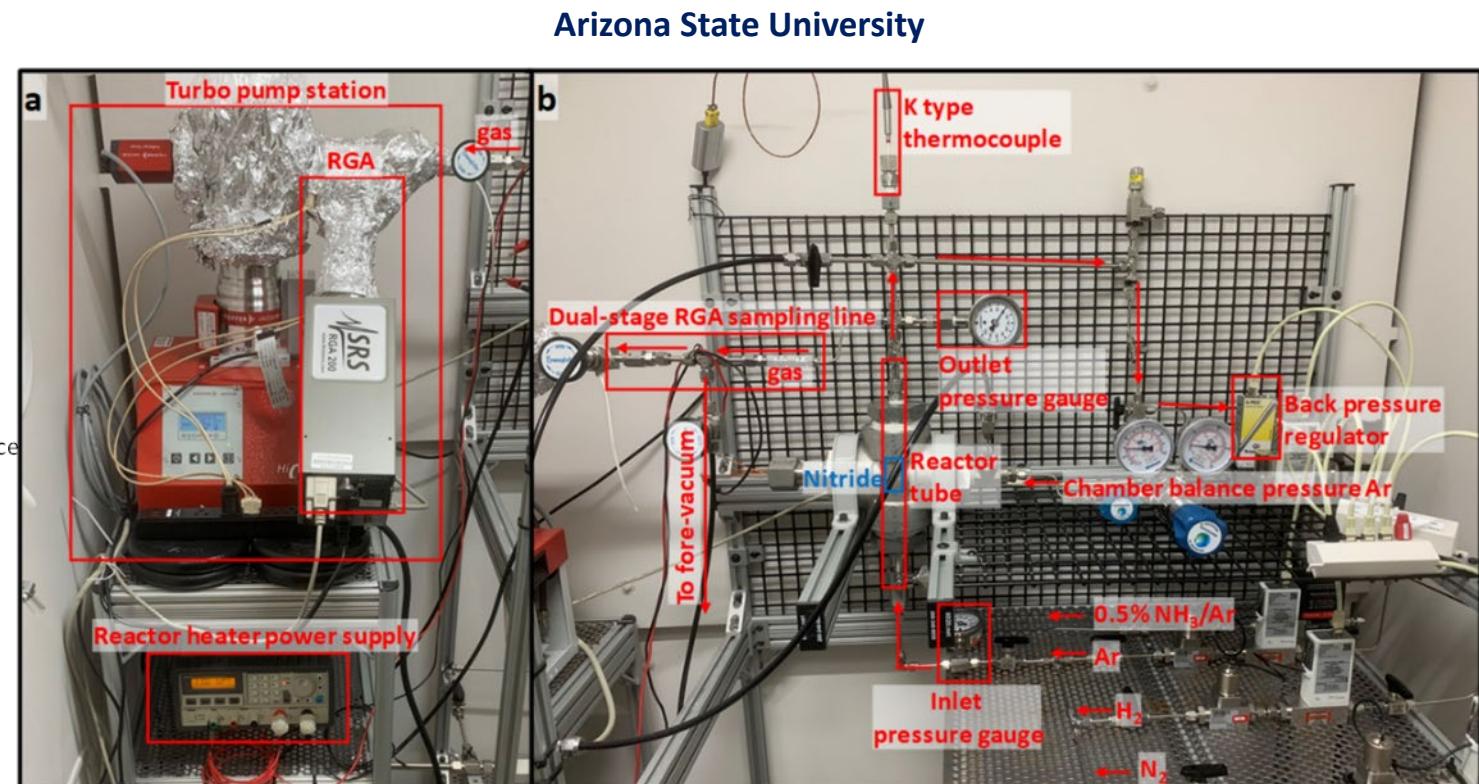
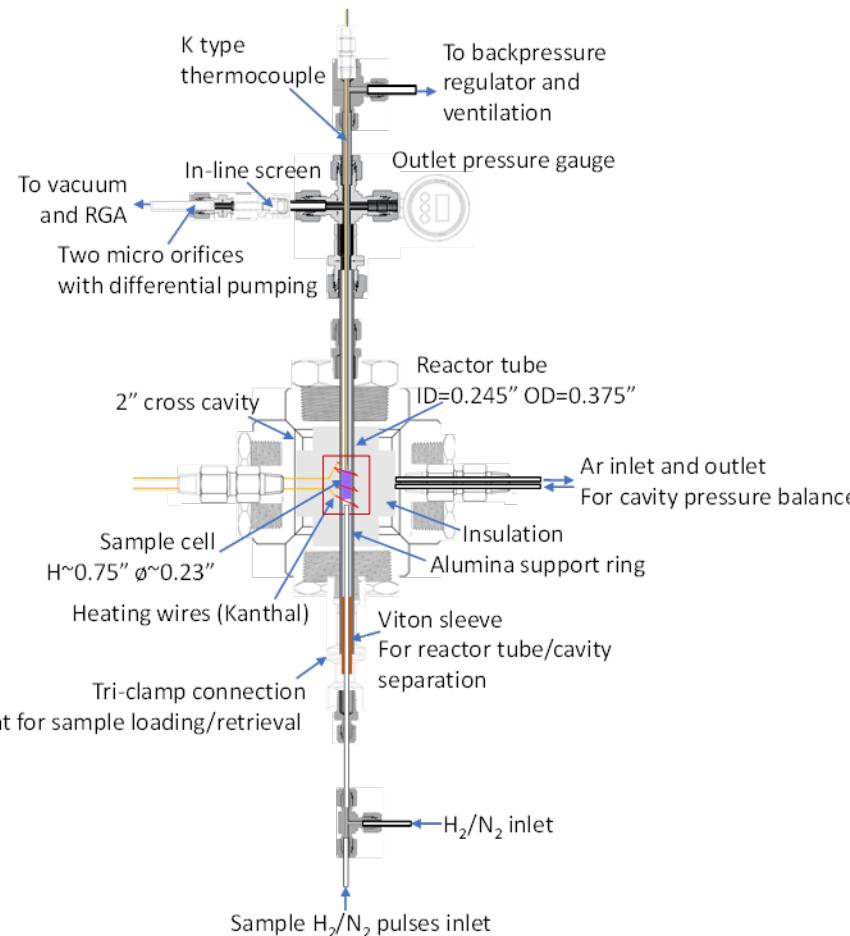
Detected NH_3



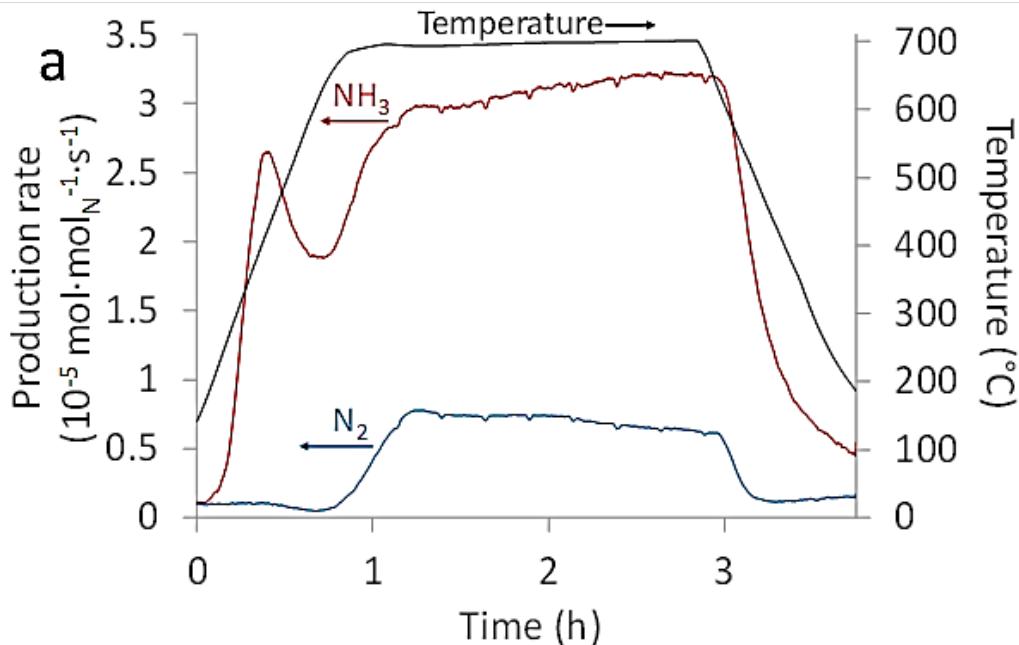
Ammonia Synthesis Reactor (ASR)



Reactor designed to perform NH_3 synthesis and nitride re-nitridation reaction under variable pressure and temperature, up to 30 bar and 800 °C, respectively



Ammonia Production and Re-nitridation of CMN331



NH_3 , N_2 production rates and temperature profile of representative reduction step under 100% H_2 (Cycle 6)

- Initial NH_3 peak assumed to be hydrogenation of surface adsorbed N_2
- At $T > 600 \text{ }^{\circ}\text{C}$, consistent co-production of NH_3 and N_2 in 100% H_2 (no external N_2 feed)
- Sample can be re-nitridized under 100% N_2 with no side-reactions observed
 - $P = 20 \text{ bar}$, $T = 700 \text{ }^{\circ}\text{C}$ for both reactions

Results imply that lattice nitrogen participates in NH_3 production in reversible $\text{CCM331} \rightarrow \text{CCM661}$ bulk reaction

Co₃Mo₃N 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 NH₃ yield and two times of N₂ yield (theoretical max CMN331 → CMN661 = 0.5)

Selectivity to NH₃ was calculated by percentage of NH₃ yield in the reacted solid-state nitrogen

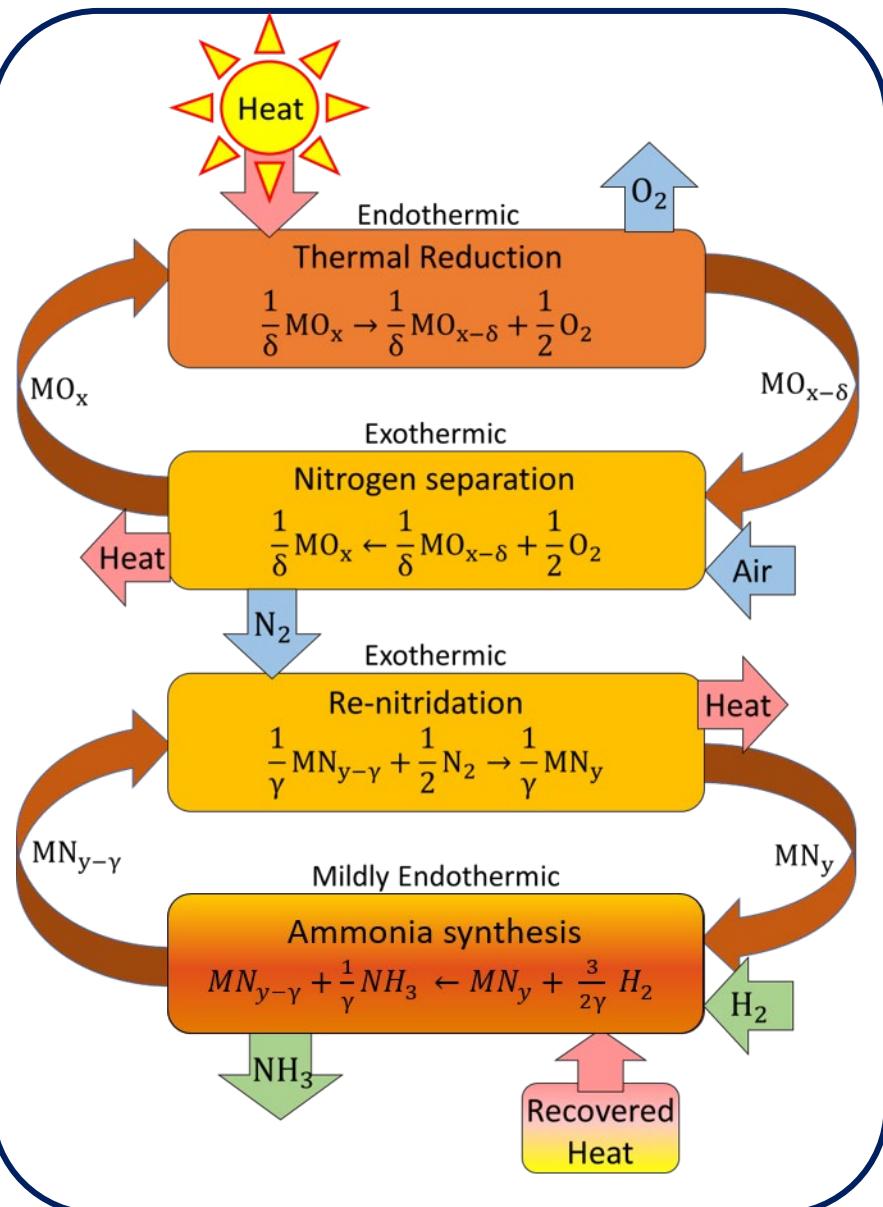
| Reduction step | P(H ₂) bar | T _{hold} °C | t _{hold} h | Steady r(NH ₃) 10 ⁻⁵ mol mol _N ⁻¹ s ⁻¹ | Steady r(N ₂) 10 ⁻⁵ mol mol _N ⁻¹ s ⁻¹ | NH ₃ yield mol/mol _N | N ₂ yield mol/mol _N | Reacted solid-state nitrogen mol mol _N ⁻¹ | Selectivity to NH ₃ |
|----------------|------------------------|----------------------|---------------------|--|---|--|---|---|--------------------------------|
| 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, pH₂, t)

- All re-nitridation steps were performed with 20 bar of 10% H₂/N₂ at 700 °C
- Sample held at 5 sccm H₂ / 15 sccm Ar overnight, 1.2 atm, 120 °C

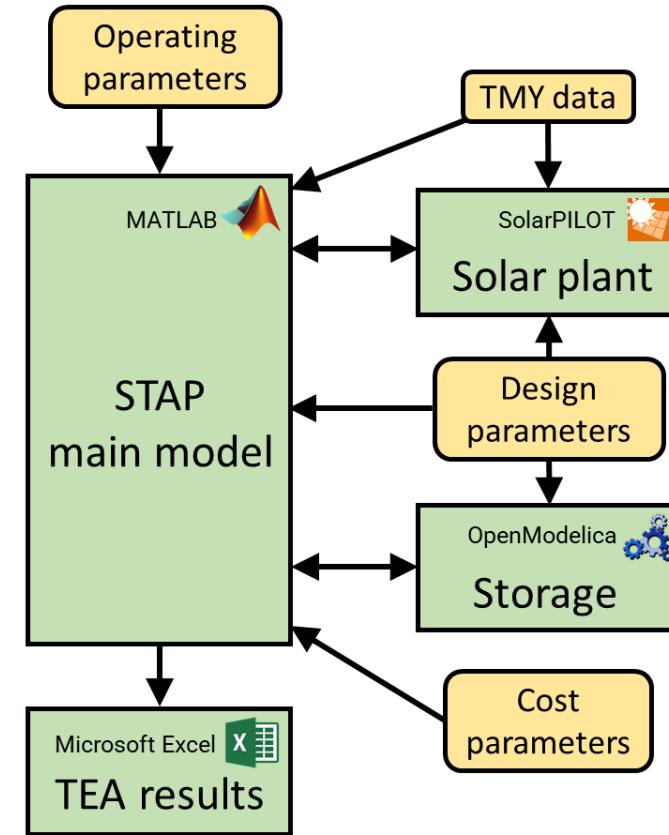
All cycles on same Co₃Mo₃N sample – **Reaction is cyclic**

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

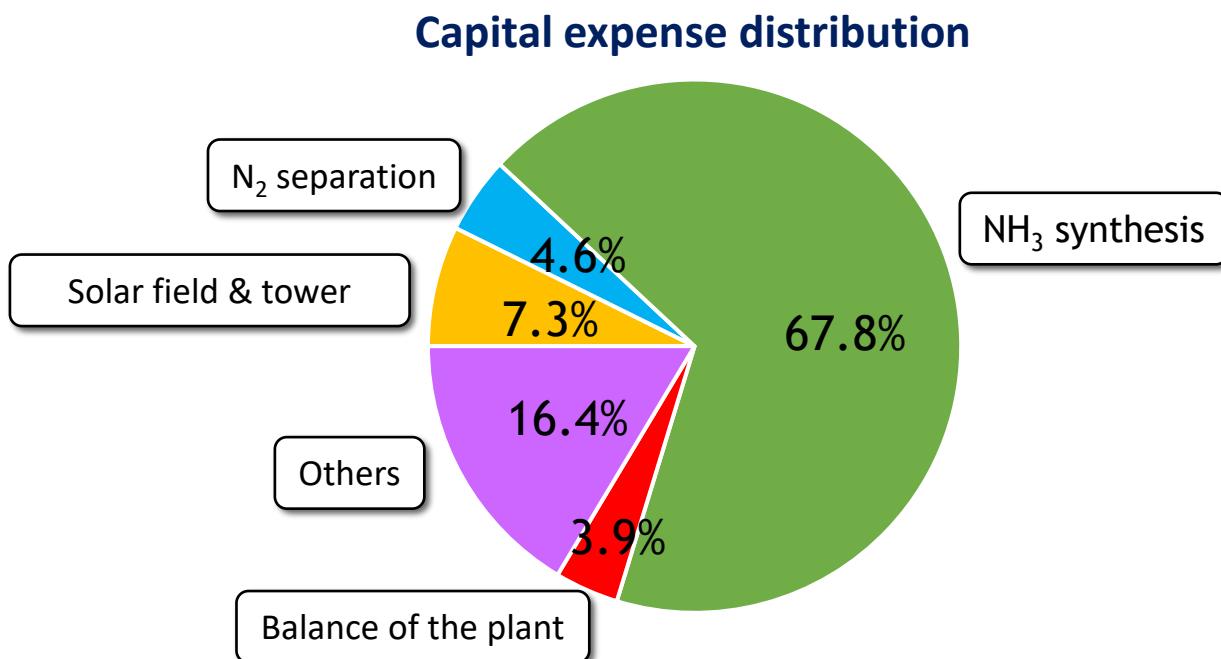
Integration completed in a single MATLAB script that communicates with other support software to perform the simulation



Techno-economic analysis

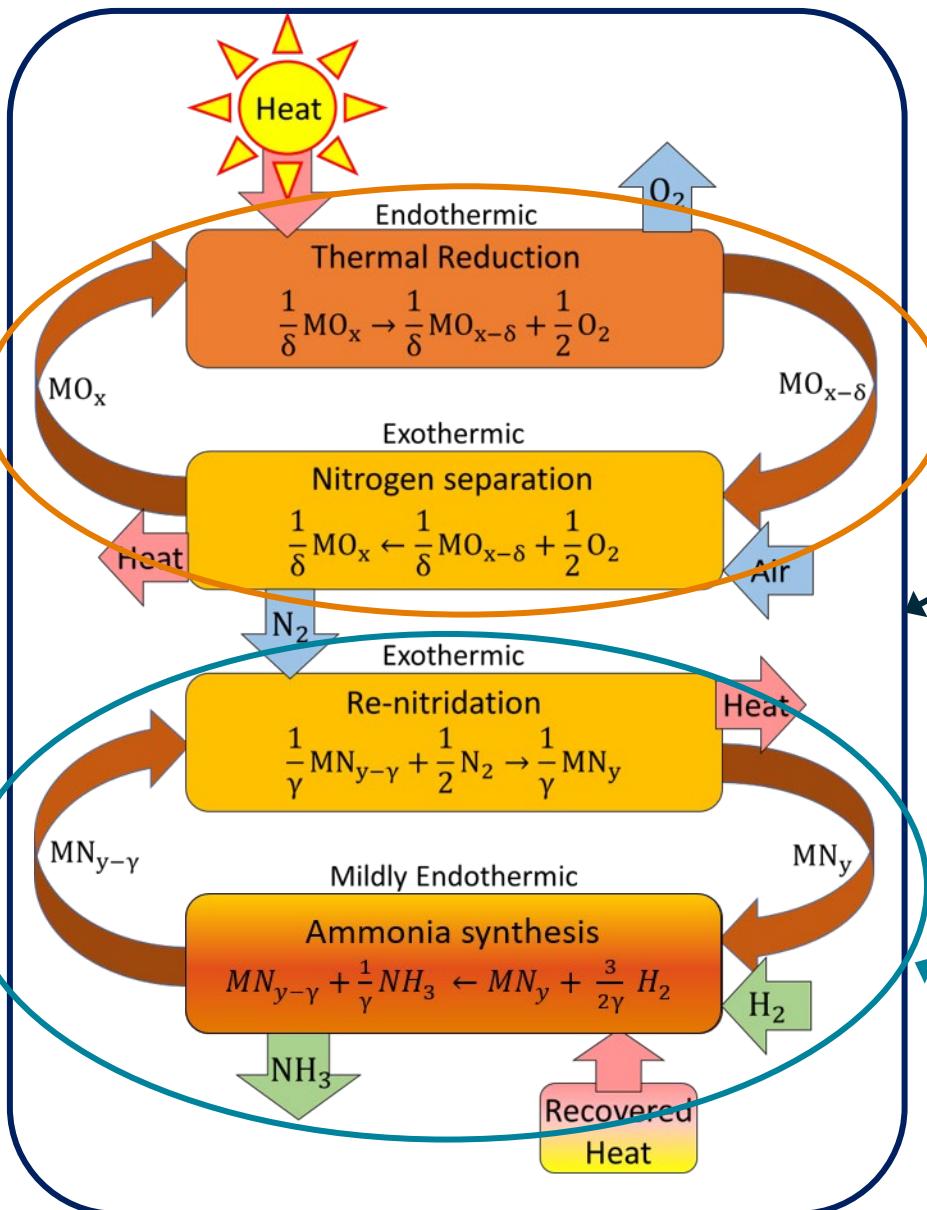


- NH₃ yield and cycle time have a high impact on the total cost of the plant
- The nitride cost is the most significant system expense, accounting for more than the 50% of the total CapEx, but it is also the most uncertain variable



| Costs Calculation | Units | Value |
|---|----------|-----------------------|
| Heliosstat 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 N ₂ /H ₂ | \$ | - |
| AS & RN Reactors | \$ | 3,326,583.31 |
| MN particles | \$ | 91,336,698.62 |
| Subtotal direct cost | \$ | 116,926,973.02 |
| Contingency | \$ | 8,184,888.11 |
| Total direct cost | \$ | 125,111,861.14 |
| Land cost | \$ | 1,007,571.02 |
| EPC and owner cost | \$ | 13,762,304.72 |
| Total indirect cost | \$ | 14,769,875.74 |
| Total CapEx | \$ | 139,881,736.88 |
| OpEx (fixed) | \$/y | 2,797,634.74 |
| Particle loss | \$/y | 355,128.85 |
| Additional heat | \$/y | - |
| OpEx (variable) | \$/y | 355,128.85 |
| Total OpEx | \$/y | 3,507,892.45 |
| Total revenue | \$/y | 474,058.12 |
| LCOA w/o H₂ | \$/tonne | 213.11 |

Upcoming STAP SolarPACES Talks



Evan Bush: "Demonstration of a Solar Air Separation Process to Produce High-Purity N₂ via Ba_{0.15}Sr_{0.85}FeO_{3-δ} 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 Co₃Mo₃N Reduction/Re-nitridation Extents as a Function of Temperature and N₂ Partial Pressure for Solar Thermochemical NH₃ Production," Friday, 9:10

James Miller: "Solar Ammonia Production via Novel Two-step Thermochemical Looping of a Co₃Mo₃N/Co₆Mo₆N 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



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



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THANK YOU FOR YOUR ATTENTION