SAND2022-13089C

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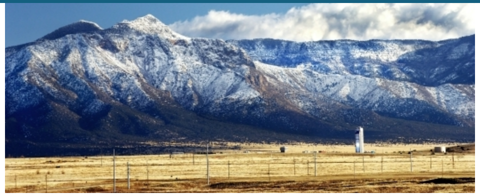
Demonstration of a Solar Air Separation Process to Produce High-Purity N_2 via $Ba_{0.15}Sr_{0.85}FeO_{3-\delta}$ Redox Cycles



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Solar Thermal Ammonia Production

Motivation

- NH_3 production accounts for 1.8%† global CO_2 emissions
- Concentrated solar has many advantages for industrial process heating, chemical reaction engineering

Solution

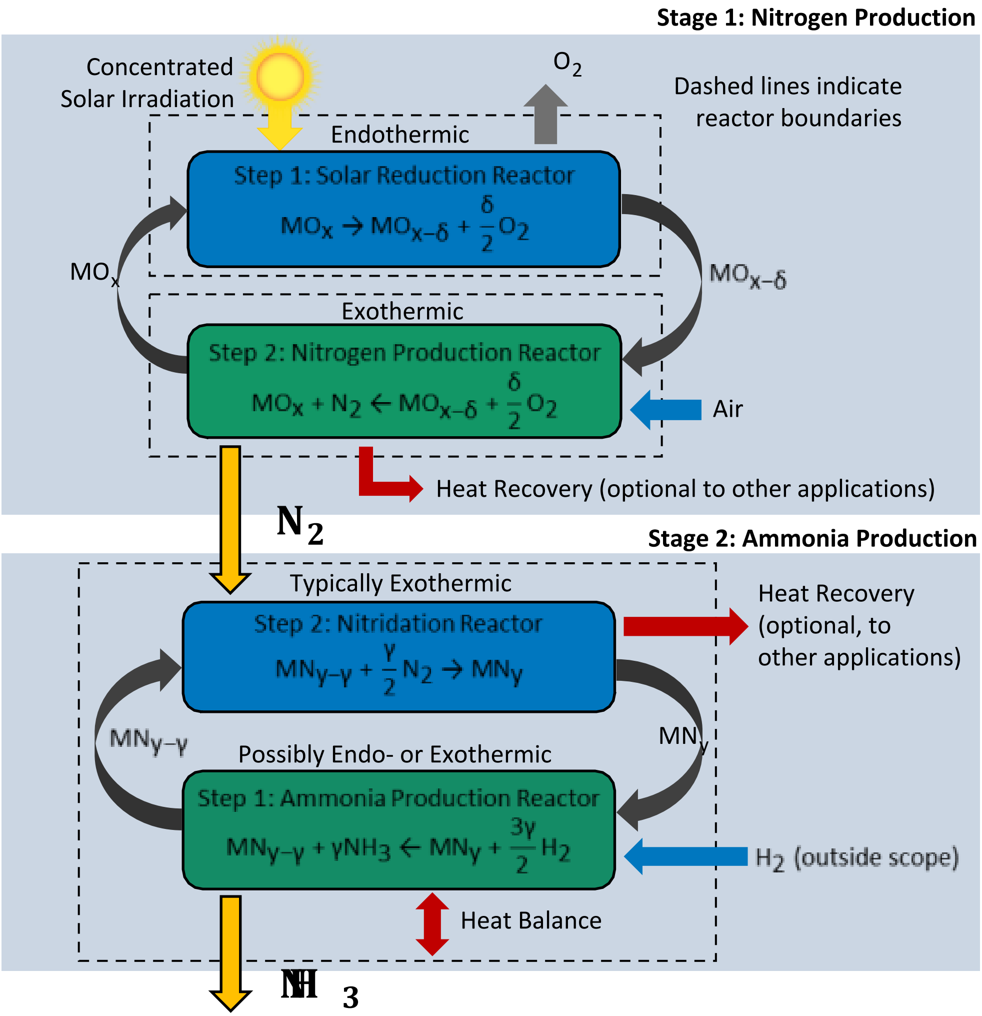
Two-stage, two step process

Stage 1: N_2 production

- Step 1: Thermal reduction
- Step 2: Air separation

Stage 2: NH_3 production

- Step 1: Ammonia synthesis
- Step 2: Re-nitridation (regeneration)



† - https://royalsociety.org/-/media/policy/projects/green-ammonia/green-ammonia-policy-briefing.pdf

Solar Thermochemical Air Separation

N_2 Separation Material

Undergoes thermal reduction, air separation (oxidation)

Recyclable metal oxide (MO_x) oxygen getter/carrier

- Perovskite oxide
- Oxygen vacancies (V_O) cyclically created and filled
- Rapid oxygen diffusion
- Continuous reduction/oxidation with T, p_{O2}
- Materials studies:

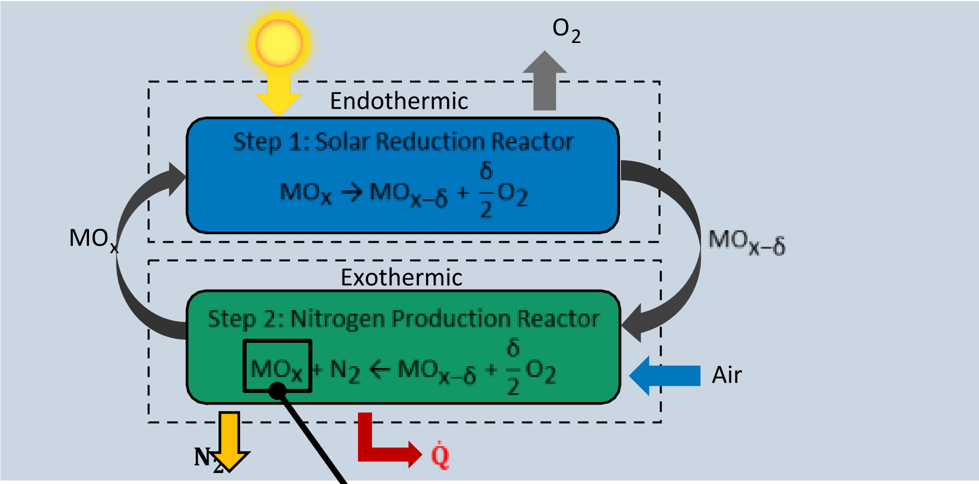
$SrFeO_{3-\delta} \rightarrow (Ba,La)_xSr_{1-x}FeO_{3-\delta} \rightarrow Ba_xSr_{1-x}FeO_{3-\delta} \rightarrow Ba_{0.15}Sr_{0.85}FeO_{3-\delta}$ **BSF1585**

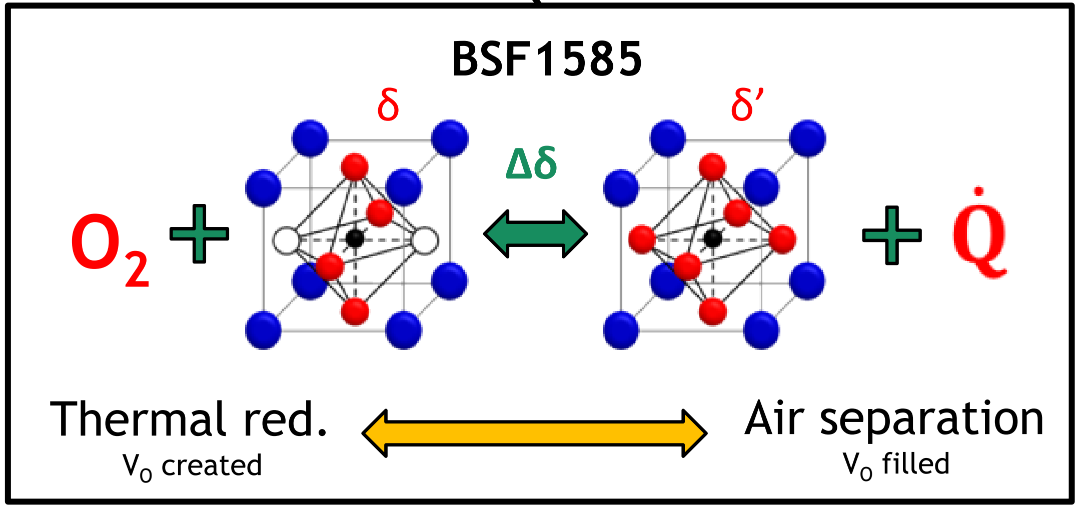
Reactor Demonstrations

Two reactors:

- Stationary vertical packed bed: air separation, cycling
- On-sun inclined flow: thermal reduction

Stage 1: Nitrogen Production





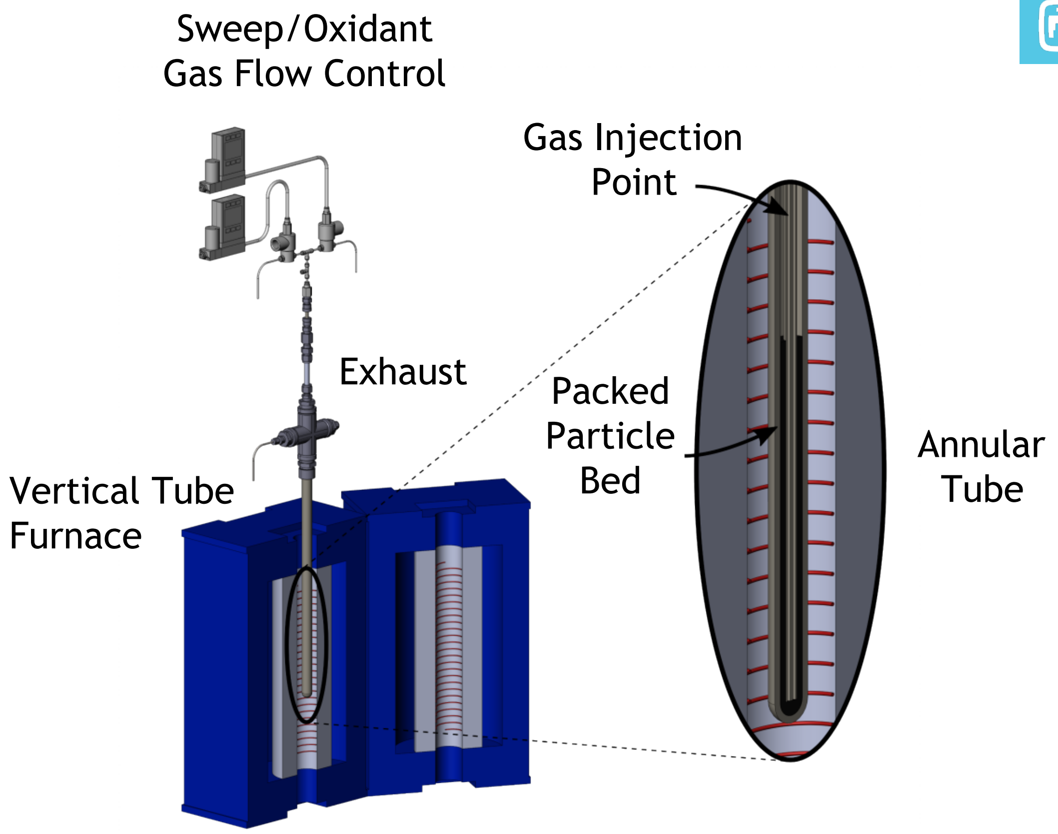
Packed Bed Reactor

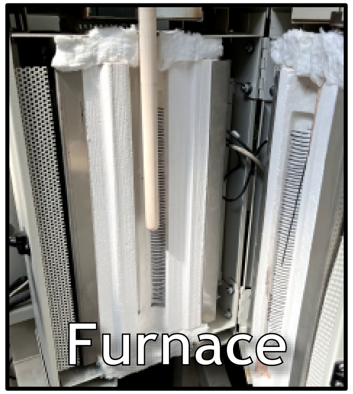
Characteristics

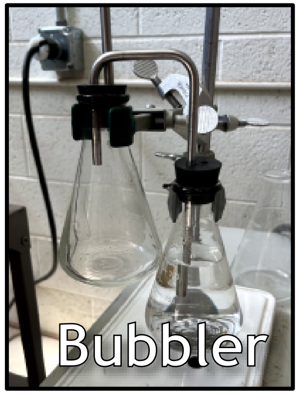
- Demonstrates air separation reaction
- Stationary bed (35-40 g BSF1585) with sweep airflow
- Mounted in tube furnace to control reaction T
- Gas measurement via RGA calibrated for p_{O2} range
- Thermocouples embedded in bed, gas domain, and furnace heated zone
- Water bubbler to maintain gas environment
- LabView control and measurement of T, p, $\dot{V}$

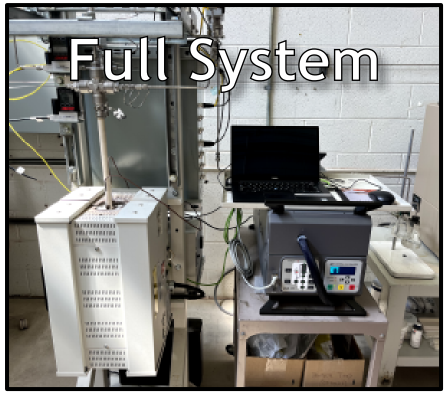
Capabilities

- Fully cyclic thermal reduction and air separation
- Multi-cycle testing
- Range of T, $\dot{V}$, p_{O2}









Dispersion Characterization

Necessary to separate **chemical reaction behavior** from **reactor behavior**

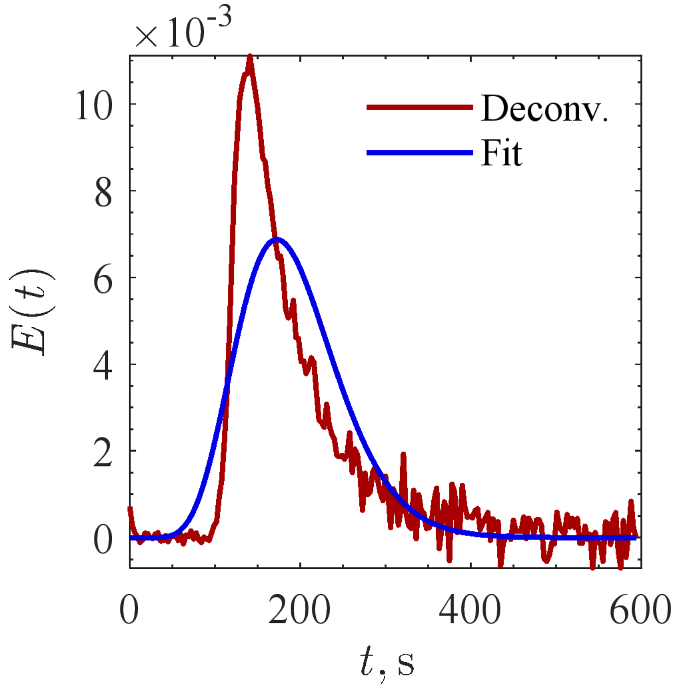
Dispersion: diffusion of gas along flow direction

Dispersion correction needed for 1:1 model to experiment comparison

Reactor found to have significant lag, minimal dispersion

Correction Method:

1. Introduce tracer gas (with known time profile) through system
2. Measure outlet concentration of tracer over time
3. Compare input and output profiles to calculate residence time distribution (RTD)
4. Use RTD to correct all experimental measurements to remove dispersion effects



Parameter	Value
Number of Tanks	8.0
Space Time (s)	179
Lag (s)	~90

Air Separation Experiments

Experimental Work:

Air separation studied via parametric analysis of reduction, air separation temperatures, multi-cycling

Error propagation analysis performed to obtain 95% CI on O_2 percentage measurements

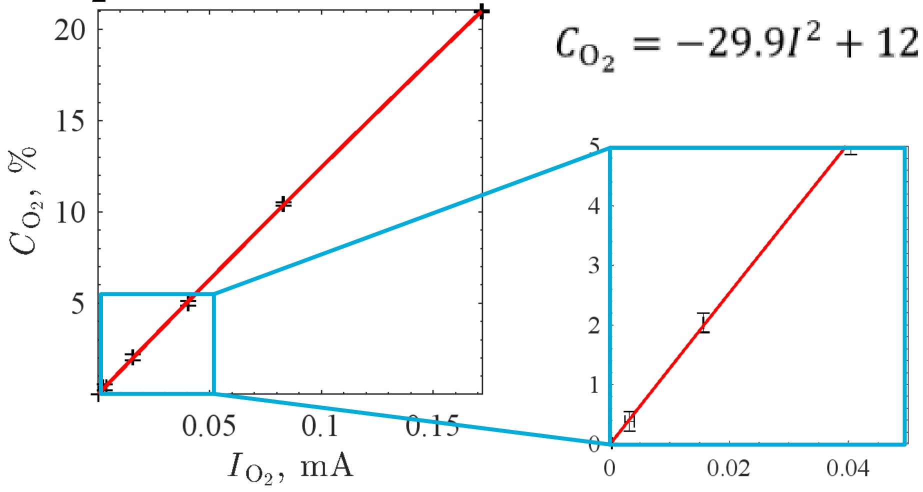
Model validations currently being performed

Procedure:

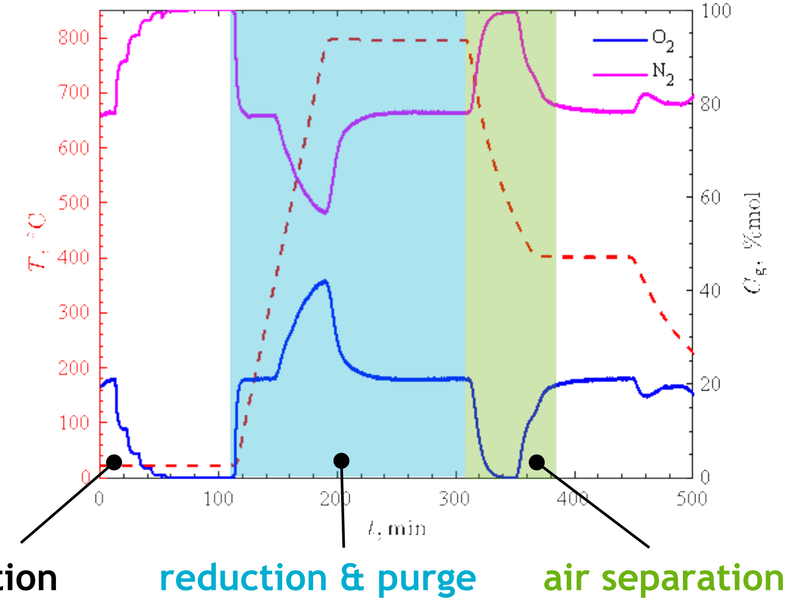
- Multi-point calibration with 100 ppm O_2 in N_2 and air
- Sample heated and thermally reduced under air
- Air purge of excess O_2
- Sample cooled to perform air separation
- Purged under air until O_2 removal ceases (fully reoxidized)

O_2 Calibration Example

$$C_{O_2} = -29.9I^2 + 127.4I$$



800 °C Reduction, 400 °C Separation



Air Separation Experiments

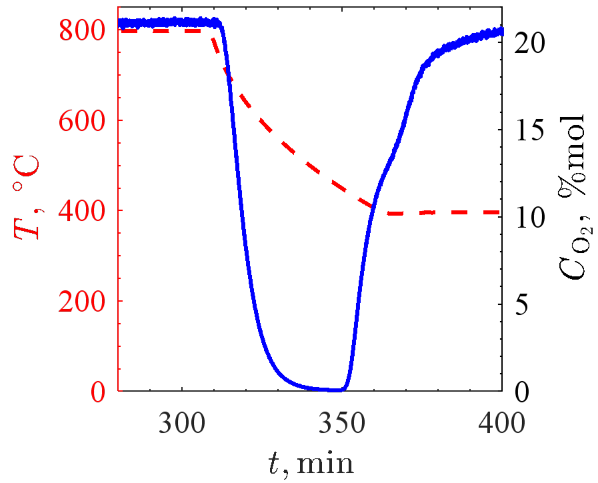
Results

Cyclic thermal reduction followed by separation, all under air
- Sharp front in O_2 profile suggests thermodynamic limit

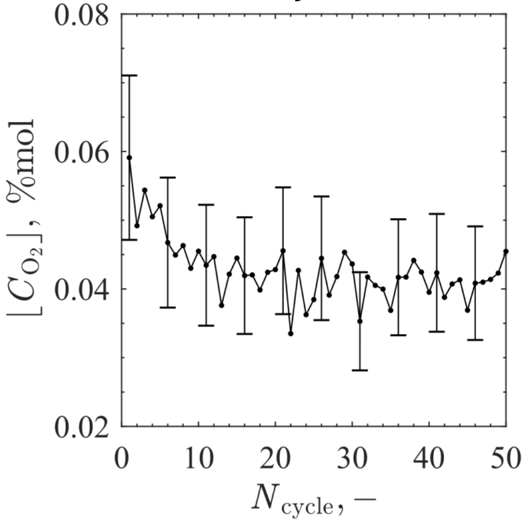
Parametric analysis for thermal reduction, separation T
- Higher T, Larger ΔT produces purer N_2

Multi-cycle experiments show repeatable separation
- Break-in due to higher initial oxidation state (O_2 release)

Thermal Reduction



50 Cycles



Minimum O_2 % Attained

T (°C)		Thermal Reduction		
		600	700	800
Air Separation	400			0.05 ± 0.01
	500	7.45 ± 0.15	0.50 ± 0.02	0.08 ± 0.03
	600			0.28 ± 0.02

Duration of Air Separation

Time (min)		Thermal Reduction		
		600	700	800
Air Separation	400			37.8
	500	11.6	24.6	34.1
	600			29.9

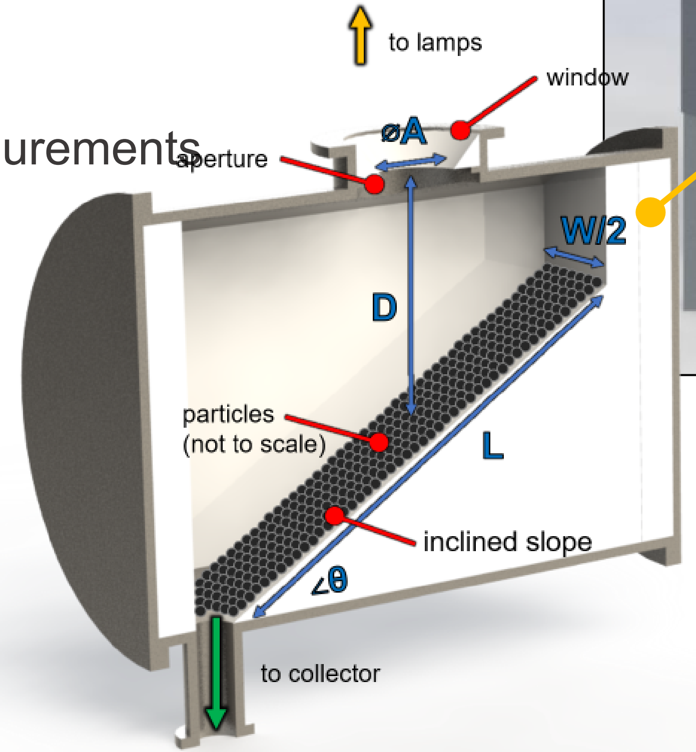
Directly Irradiated Incline Flow Reactor

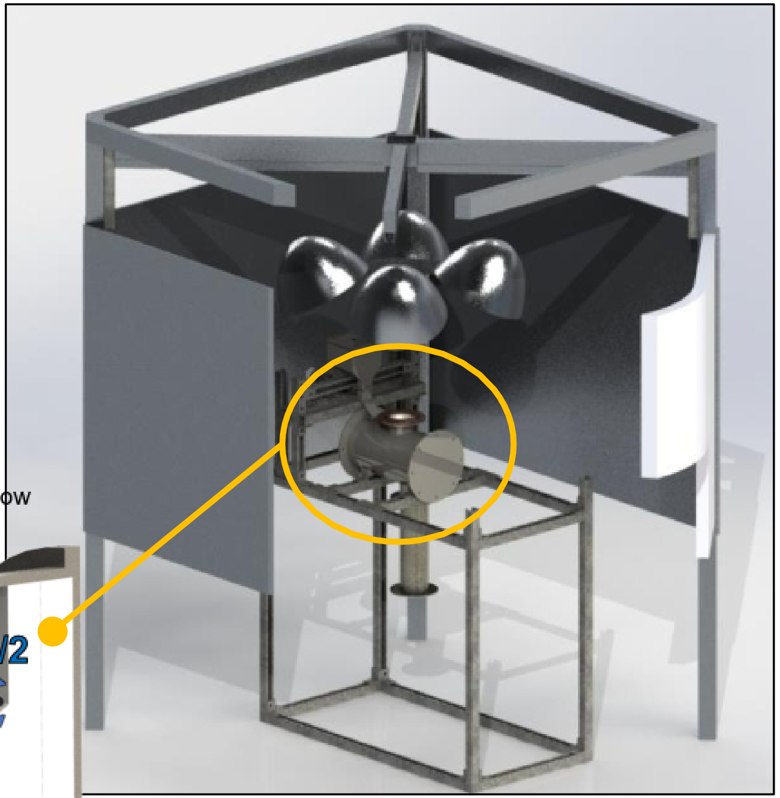
Characteristics

- 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

HFSS

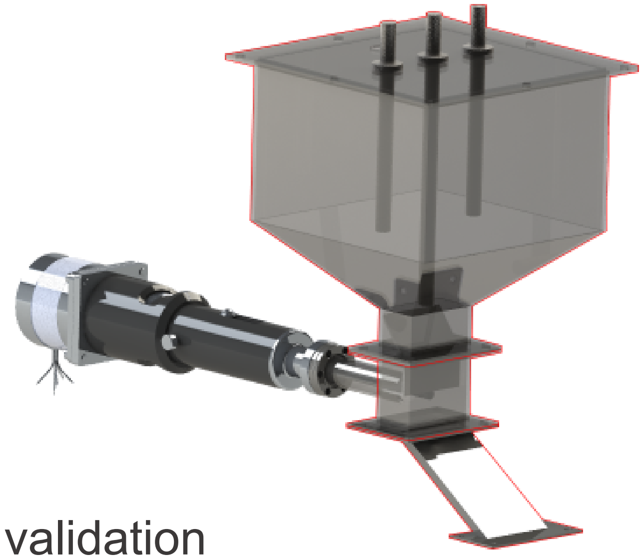
- Vertical axis
- Four lamps
- Metal Halide
- 1.8 kW_e
- Ellipsoidal reflectors
- Common focus

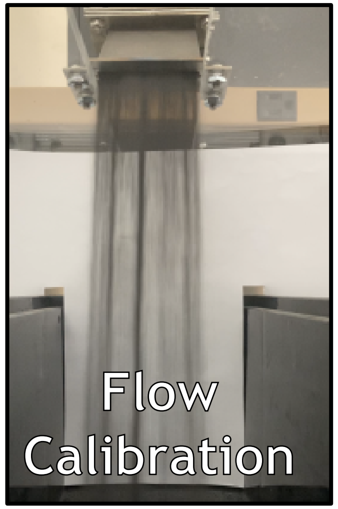




Reactor Development

Pre-heated Hopper Design





Work to Date:

- Design, modeling, and fabrication
- Particle flow calibration and cold tests
- Measurement and controls implementation

Next Steps

- Operate on-sun reactor with inert media for validation
- Perform thermal reduction experiments with BSF1585

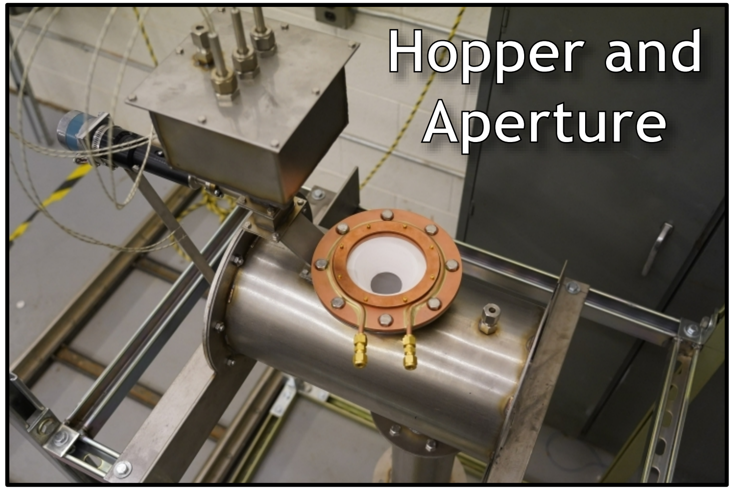
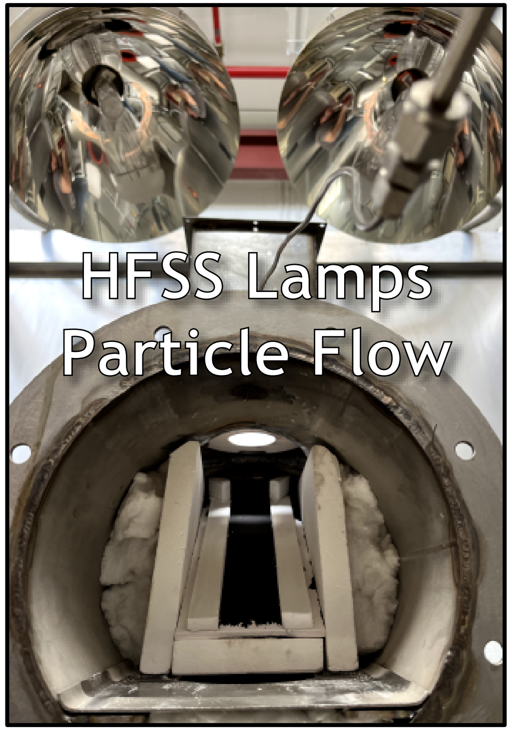


Photo Credit: Craig Victor, SNL



Conclusions

- Two reactors designed, constructed, and tested for solar thermochemical air separation with BSF1585
- Dispersion characterization and cyclic air separation demonstrated with packed bed tube furnace
- N_2 purity enhanced for high temperatures and temperature swings
- Rapid kinetics, thermodynamic limits in air separation apparent
- High repeatability observed over 50 cycles
- Construction and particle flow testing performed for on-sun thermal reduction reactor for use with solar simulator

Publications

Farr, T. P., et al. (2020). "An A-and B-Site substitutional study of $SrFeO_{3-\delta}$ perovskites for solar thermochemical air separation." Materials **13**(22): 5123.

Bush, H. E., et al. (2020). "Pairing directional solar inputs from ray tracing to solar receiver/reactor heat transfer models on unstructured meshes: Development and case studies." Journal of Solar Energy Engineering **143**(3).

Bush, H. E., et al. (2021). "Air separation via a two-step solar thermochemical cycle based on $(Ba,La)_xSr_{1-x}FeO_{3-\delta}$: Thermodynamic analysis." Solid State Ionics **368**: 115692.

Nguyen, N. P., et al. (2021). “Air separation via two-step solar thermochemical cycles based on $SrFeO_{3-\delta}$ and $(Ba,La)_{0.15}Sr_{0.85}FeO_{3-\delta}$ perovskite reduction/oxidation reactions to produce N_2: rate limiting mechanism(s) determination.“ Physical Chemistry Chemical Physics **23**:19280

Acknowledgements

Student Interns: Zachary Berquist, Tania Rivas, Madeline Finale

U.S. Department of Energy Solar Energy Technologies Office (SETO), Award No. DE-EE0001529

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Thank You!