RTI INTERNATIONAL

# Pilot Testing of a Modular System for Oxygen Production

DOE Cooperative Agreement DE-FE-0031527
NETL Gasification Virtual Peer Review
September 2, 2020


Air Liquide
creative oxygen

Georgia Tech

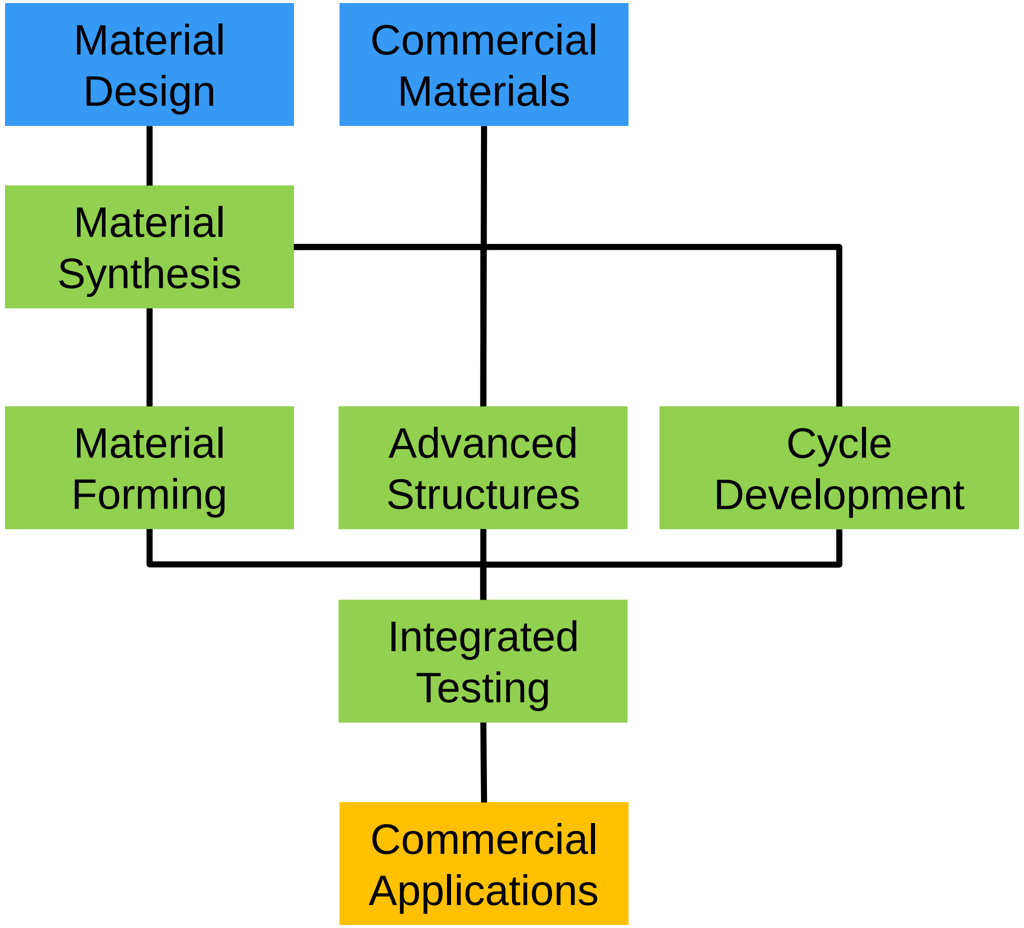
# Project objectives

***Objectives:*** The design, fabrication, and testing of a 10 to 20 kg/day modular oxygen ($O_2$) production system

- Be cost competitive with current state-of-art process
- Modular process for small scale oxygen production
- Sorbent bed-factor less than 600 lb-sorbent/TPD $O_2$ (tons/day $O_2$)
- $O_2$ purity greater than 95%

## *Specific Challenges*

- Rapid PSA cycle development
- Structured sorbent module development
- Rapid cycle modeling tool development and cycle optimization
- Material and module scale up and manufacturing
- Design and fabrication of pilot O2 production system
- Parametric and long-term testing
- Techno-economic analysis



# Success criteria

## Success Criteria

Determination of optimized $O_2$ sorbent formulation and engineered bed (module) structure for this sorbent to scale up to pilot production, as supported by Task 2 experimental results and Task 3.1 rapid-cycle process model projections

1. Structured sorbent mechanically robust and stable after >1,000 rapid sorption/desorption cycles
2. Either the $O_2$ binding sorbent or the conventional sorbent has sufficient working capacity for an $O_2$ production system with predicted BSF<600.

Process design package & final techno-economic analysis for full-scale, modular, rapid-cycle PSA $O_2$ production system using novel structured sorbent to produce 10-50 TPD of high-purity (≥95%) $O_2$ from air as the oxygen feed for DOE’s 1- to 5-MW oxygen-blown REMS gasifier skid for power generation

1. Target $O_2$ production cost below SOTA (target is < $45/ton)
   Target Bed Size Factor [BSF] ~ 600
   (smaller than benchmark BSF of 850 for commercial VPSA for $O_2$ production)

# Development Roadmap

| Previous Work | DE-FE0027995 | DE-FE0031527 | Future Development / Sustainment | |
|---|---|---|---|---|
| 2016 | 2017 – 2019 | 2018 – 2020 | 2021 – 2023 | 2023+ |
| Proof of Concept / Feasibility | | | | Commercial Roll-Out |

## Laboratory Validation

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- Synthesis and characterization of $O_2$ binding materials
- Formation into sorbents and membranes
- Assessment of materials for the air separation process
- Initial design of modular air separation unit
- Preliminary techno-economic assessment

## Pilot Testing

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- Development and scale-up of materials into commercially producible form factor (commercial scale sorbent or membrane module, sorbent quantities)
- Design, engineering and construction of a modular test system (~10 kg/d $O_2$)
- Pilot operation
- Development of a full process model
- Detailed TEA
- Development of process design package for full scale modular demonstration system (5-50 TPD $O_2$)
- Business arrangement with commercial partner, transfer in preparation of commercial offering

## Commercial Offering / Manufacturing 1st Adopter Demonstration

**Potential Technology Owners:**

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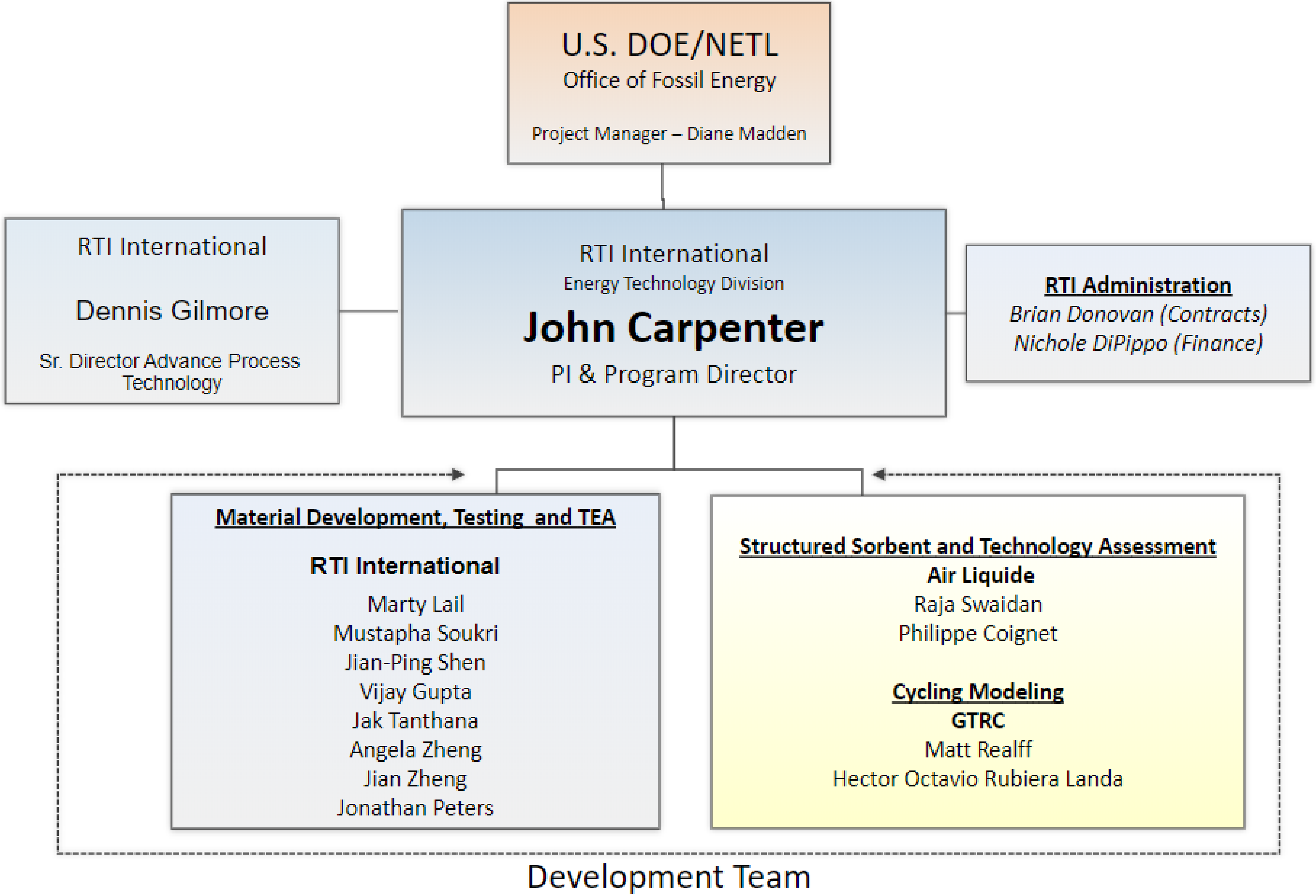
- Membrane module / sorbent manufacturing
- Design, engineering and construction of modular system (5-50 TPD $O_2$)
- Commercial scale demonstration at 1st adopter site

***Ongoing membrane, module & process refinements to increase market relevance and economic competitiveness***

**Technology Readiness Level**

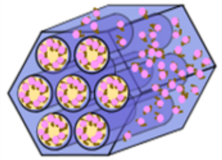
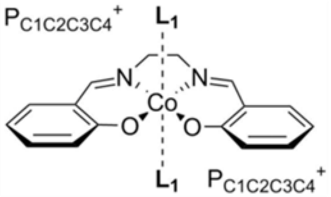
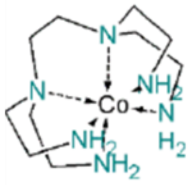
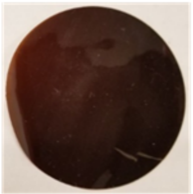
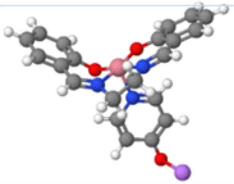
1 2 3 4 5 6 7 8 9

# Project team

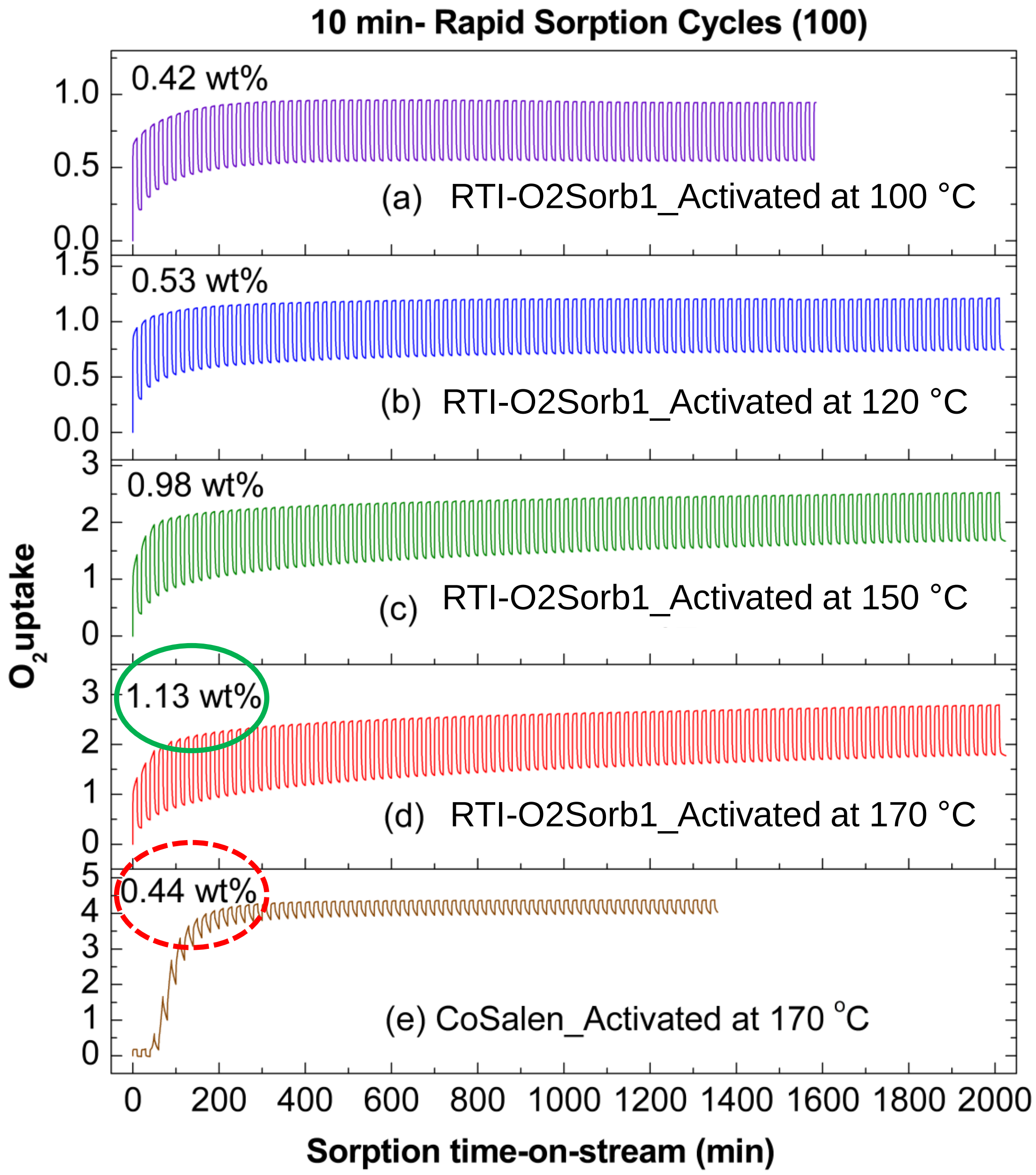


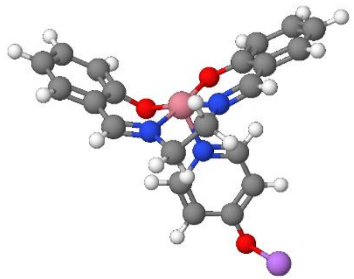
# Materials Scale-up

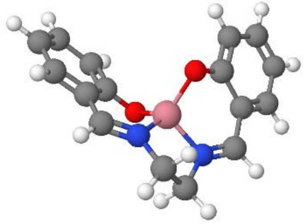
# Bio-Inspired $O_2$ Sorbent Material Development Summary

| Material type | Structure/ Illustration | Material form | Material performance |
|---|---|---|---|
| Co-organometallic complex/silica |  | Solid | • Moderate $O_2$ sorption capacity (as high as 1.2 wt%)<br>• Slow $O_2$ sorption/ desorption kinetics<br>• Low $O_2$/ $N_2$ selectivity |
| Co Complex – Ionic Liquid |  | Ionic liquid | • Moderate $O_2$ sorption capacity (as high as 1.1 wt%)<br>• Slow $O_2$ sorption/ desorption kinetics<br>• High $O_2$/ $N_2$ selectivity |
| Co Complex/ porous support | • Complex on Mesoporous silica or zeolites<br>• $O_2$ binding metal organic frameworks | Solid | • Low-moderate $O_2$ sorption capacity<br>• Slow $O_2$ sorption/desorption kinetics<br>• Low $O_2$/ $N_2$ selectivity |
| Co-PEI |  | Solid/ Solution | • High $O_2$ capacity, solid vs. liquid (3-6 wt% vs. 0.2 wt% in solution)<br>• Low $O_2$/ $N_2$ selectivity |
| Co Complex- $O_2$ membrane | <br>10 wt% Co Complex in Matrimid film | Solid membrane | • Low $O_2$/ $N_2$ selectivity |
| ★ RTI-O2Sorb |  | Solid | ✓ High $O_2$ sorption capacity (as high as 3.0 wt%)<br>✓ Fast $O_2$ sorption kinetics (rapid cycle <10 min)<br>✓ High $O_2$/ $N_2$ selectivity |

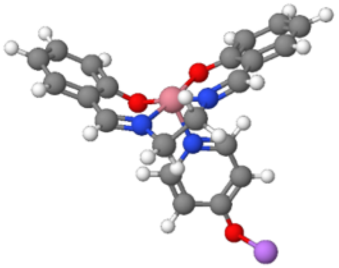
# TGA Cyclic $O_2$ Sorption of RTI's RTI-O2Sorb1 vs. Commercial Co-Salen

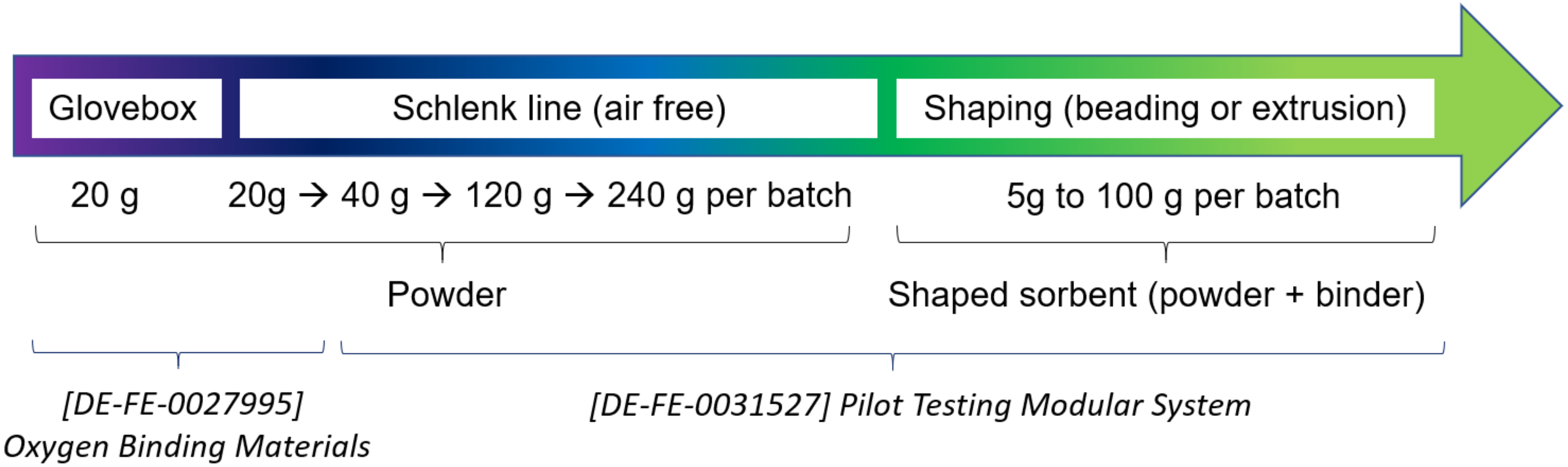




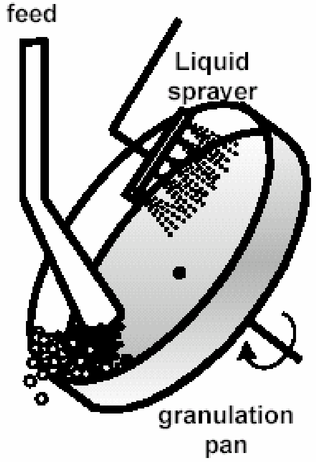
# Progress on Scale-up of RTI-O2Sorb

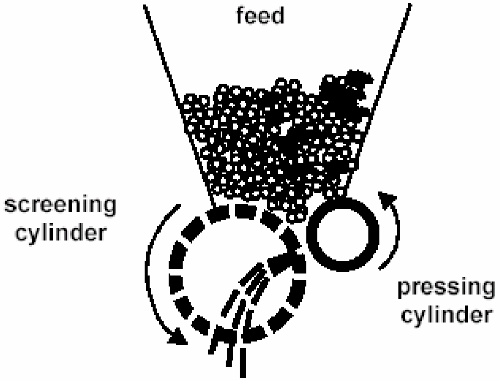


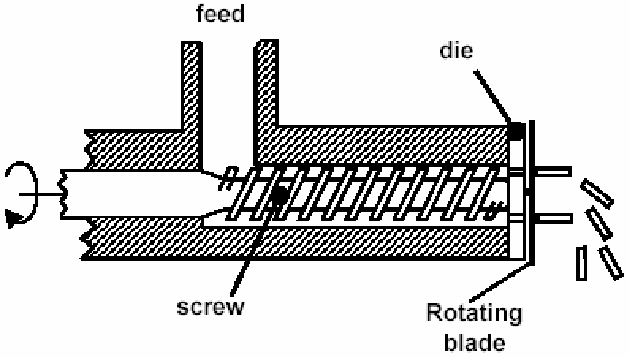



- ✓ **Successfully repeated batch synthesis for maximum $O_2$ sorption performance**
  (reversible $O_2$ uptake of 1~1.5 wt% with powder sample after activation at 170 $^{o}$C)
- ✓ **Successfully synthesized powder material with same performance using Schlenk line**
  (which allows large batch synthesis)
- ✓ **Successfully scaled up powder material synthesis with same sorption performance**
  (20g → 40 g → 120 g → 240 g per batch)

# Agglomeration of Powder into Structured Form



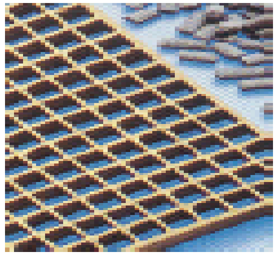









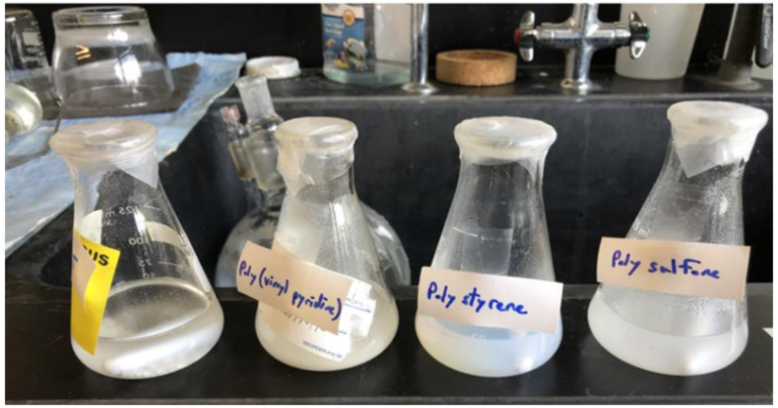


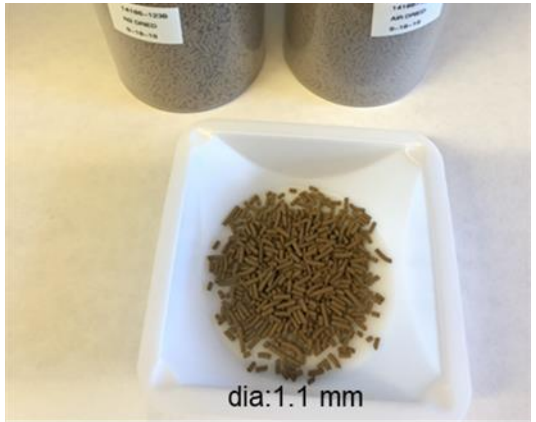
Granulation

Pelletization

**Extrusion**

# Optimization of Extrudate Formulation




After exposed in 100% $O_2$
@ 100ºC 0.5hr,
and continued for 100 $N_2$-$O_2$ cycles

After normal $N_2$-$O_2$ 100 cycles

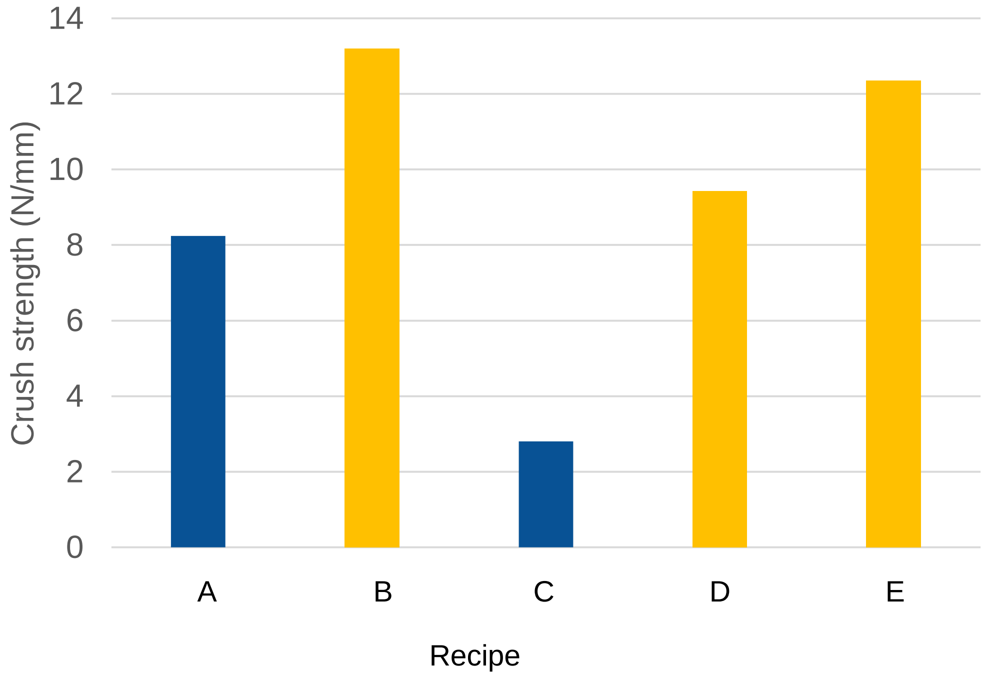
# Extrudate Formation Characteristics

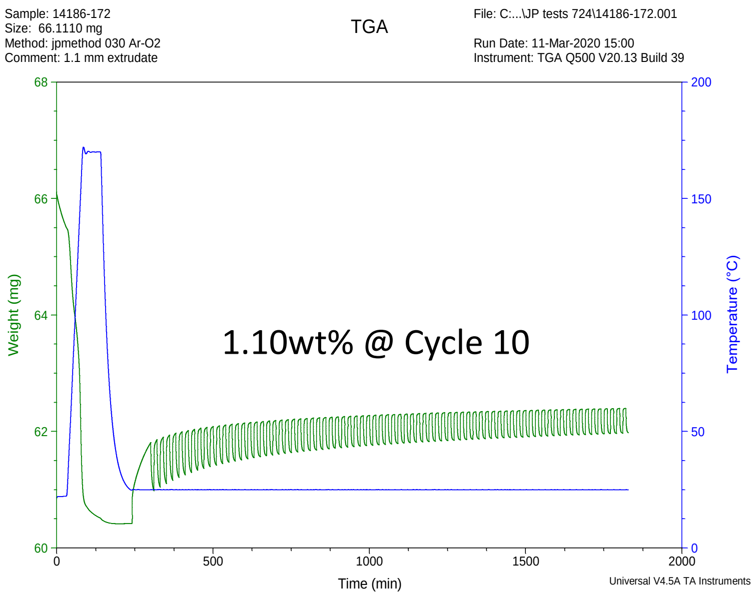
*Key characteristics of Forming Extrudate:*

- $O_2$ capacity, mechanical strength, size

*Key variables of Forming Extrudate:*

- binder ratios and solvent
- extrusion pressure and temperature, drying temperature

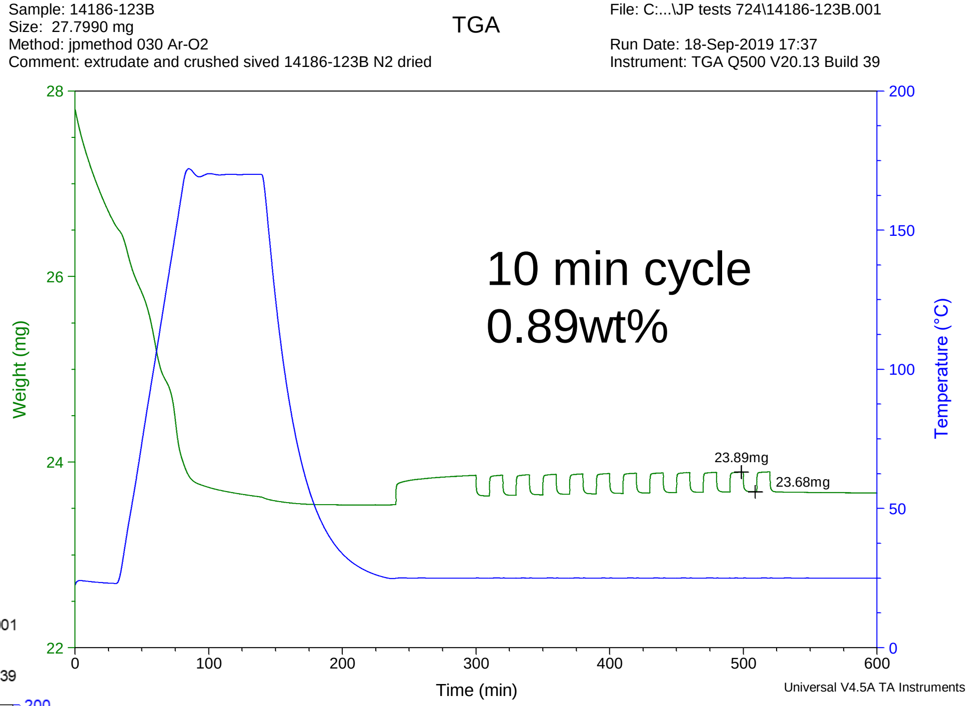


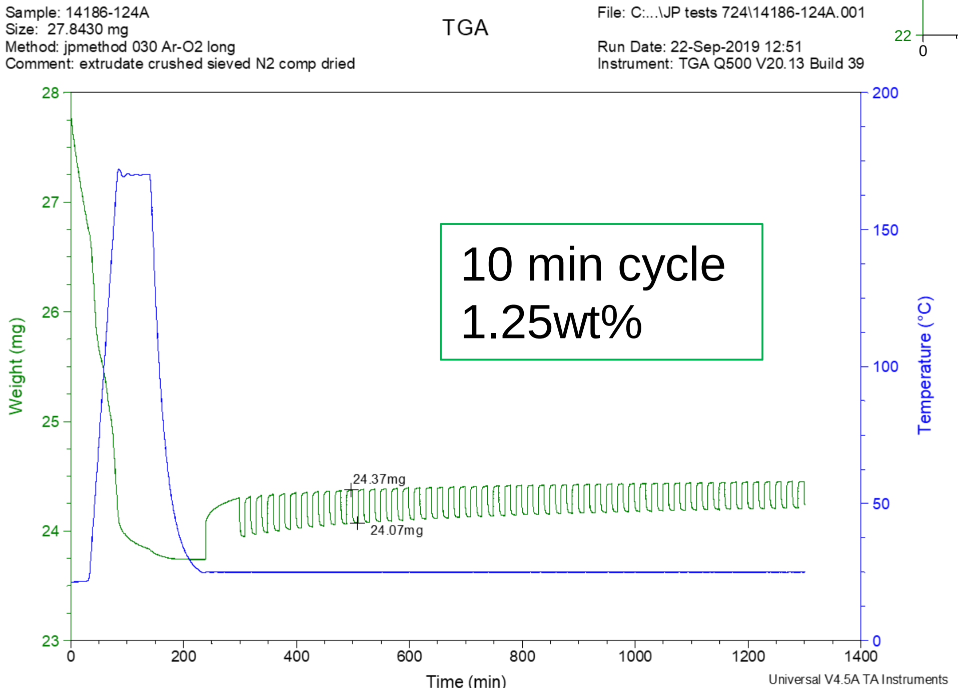




| Dia (in) | Dia (mm) | N | N/mm |
|---|---|---|---|
| 0.054 | 1.3716 | 13.6 | 9.915427 |
| 0.053 | 1.3462 | 21.4 | 15.8966 |
| 0.055 | 1.397 | 12.9 | 9.234073 |
| 0.052 | 1.3208 | 15.4 | 11.6596 |
| 0.052 | 1.3208 | 15.4 | 11.6596 |
| 0.054 | 1.3716 | 17.6 | 12.83173 |
| 0.052 | 1.3208 | 11.9 | 9.009691 |
| 0.053 | 1.3462 | 16.8 | 12.47957 |
| 0.052 | 1.3208 | 12.1 | 9.161114 |
| 0.055 | 1.397 | 11.8 | 8.446671 |
| | | | |
| | | Avg | 11.02941 |

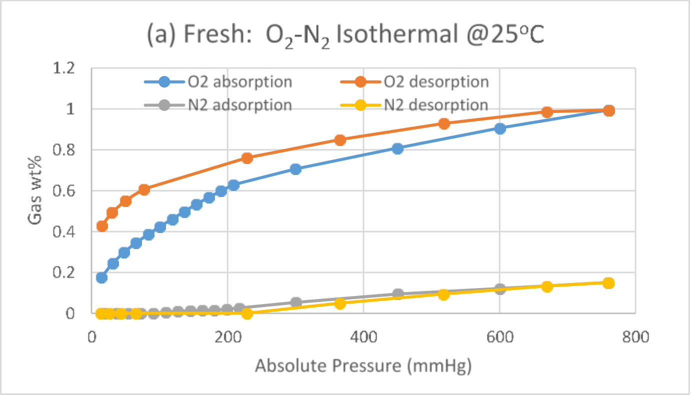
| Binder (wt%) | Density (g/cc) | Dia. (mm) | Length (mm) | Crush strength (N/mm) | Dynamic oxygen capacity (wt%) |
|---|---|---|---|---|---|
| 16.7 | 0.55-0.62 | 1.2-1.5 | 2.0-10.0 | 8.0-12.0 | 0.8-1.2 |

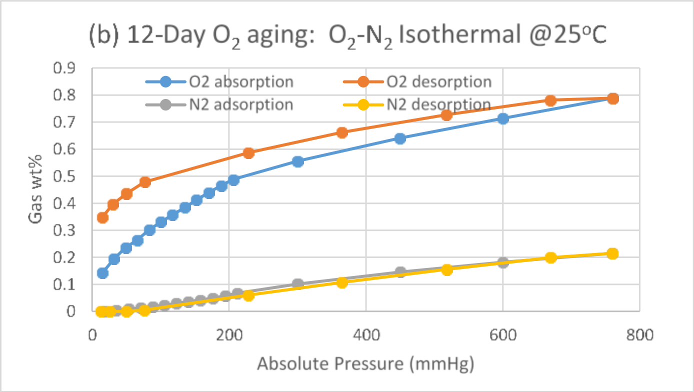
# TGA Profile of Extrusion Shaped RTI-O2Sorb (crushed to 300~425 µm)

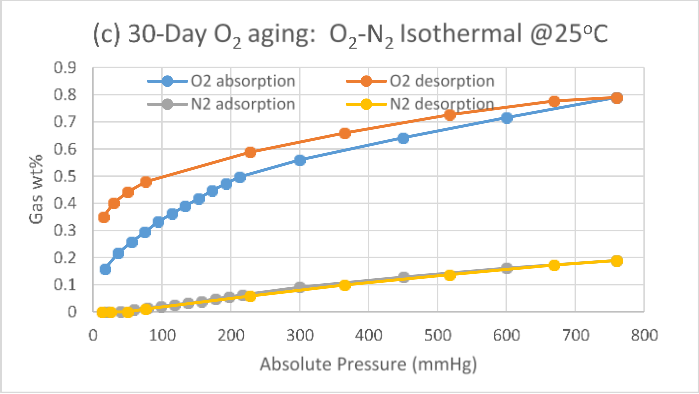



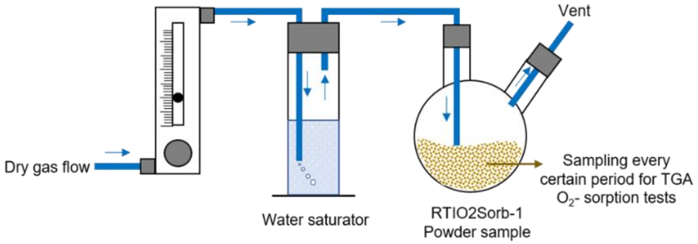

# Exposure/Aging Testing

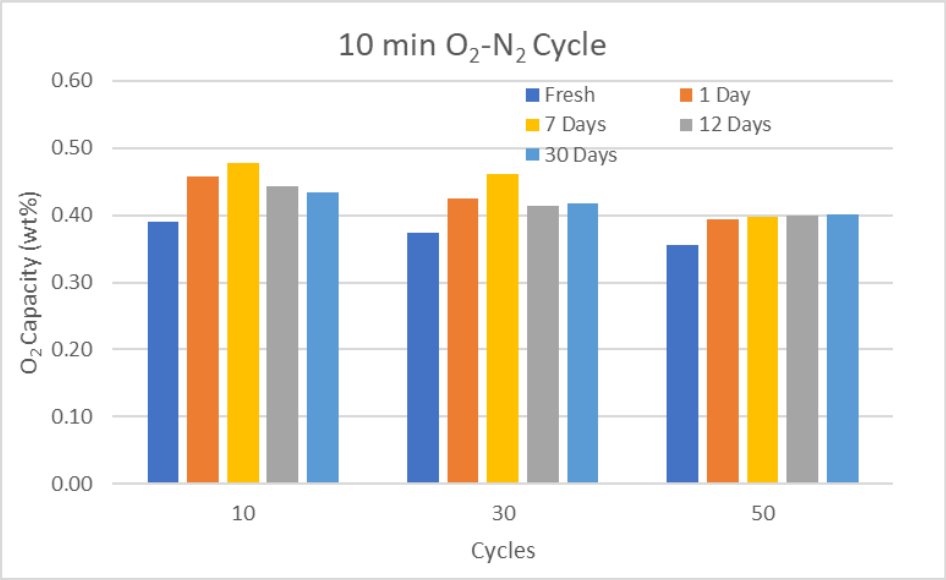



- 2.62 vol% $H_2O$ (g), balance $N_2$
  - 45d exposed, similar to long term cycling
- 1.5% $O_2$,19.5 $CO_2$, balance $N_2$
  - Exposed 36d – no degradation
- 2.62 vol% $H_2O$ (g), 20.40% $O_2$, balance $N_2$
  - Similar to long term cycling in TGA
- 99% vol% O2, , balance $N_2$
  - Some degradation through day 12,
  - day 30 similar to day 12 ( See graphic to left)



# Forming of Structured Sorbents


## *Air Liquide Objectives:*

- Develop novel structured adsorbents production techniques using conventional sorbent materials
- Apply and adapt the techniques developed on conventional adsorbents to the novel oxygen-binding adsorbent materials
- Manufacture and ship 2 to 4 structured adsorbers for pilot testing based on novel oxygen-binding adsorbent
- Support activities (e.g. Pilot design, Techno-Economic Analysis)

# Sorbent and Structured Sorbent Module Development and Characterization

## *Highlights of BP1*

- Air Liquide BP1 objectives successfully met on time *(by June 30$^{th}$, 2019)*
- Formulations were developed and characterized for (1) air dehumidification and (2) for conventional nitrogen ($N_2$)-binding adsorbent
- Activation protocols for each adsorbent formulation were developed
- Forming techniques to produce structured beds were developed

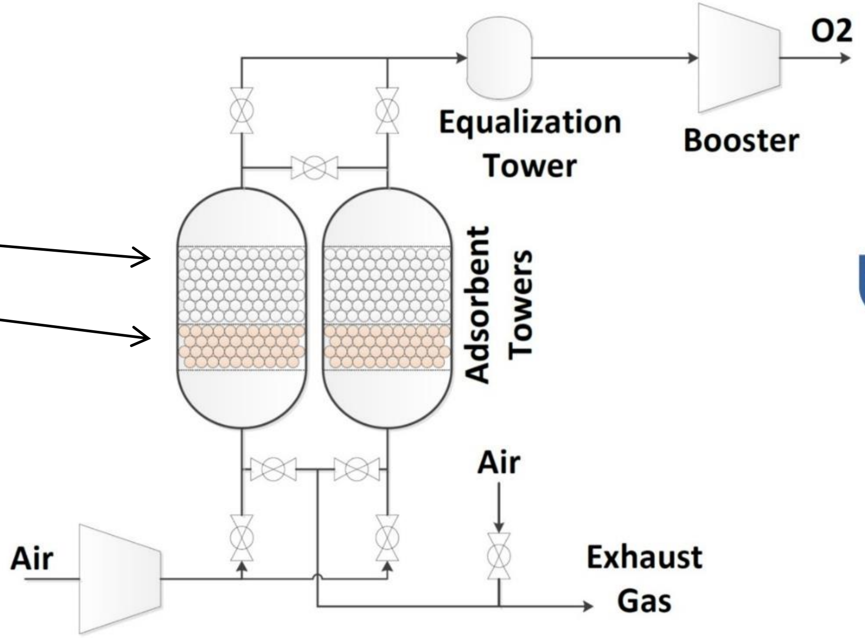
## *Highlights of BP2 so far*

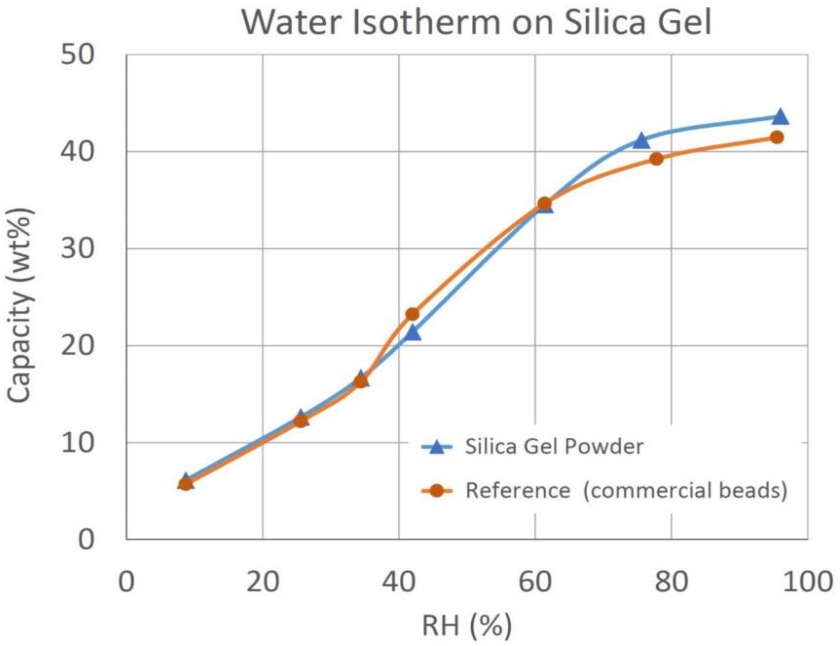
- Forming techniques and activation tool were scaled up for beds of up to 1 kilogram
- Reviewed and provided feedback on the pilot design
- Ongoing work on adapting formulation and forming techniques to novel oxygen-binding adsorbent. Multiple samples were received from RTI, characterized and used to support adaptation-work on formulation and forming

# Sorbent and Structured Sorbent Module Development and Characterization

## *BP1 – Overall Approach*

- Conventional $O_2$ VSA ➔ uses 2 adsorbents
- Top adsorbent used to capture $N_2$
- Bottom adsorbent used for air drying
- Structured beds made of elementary shapes
- Elementary shapes produced by combining adsorbent powder and binder



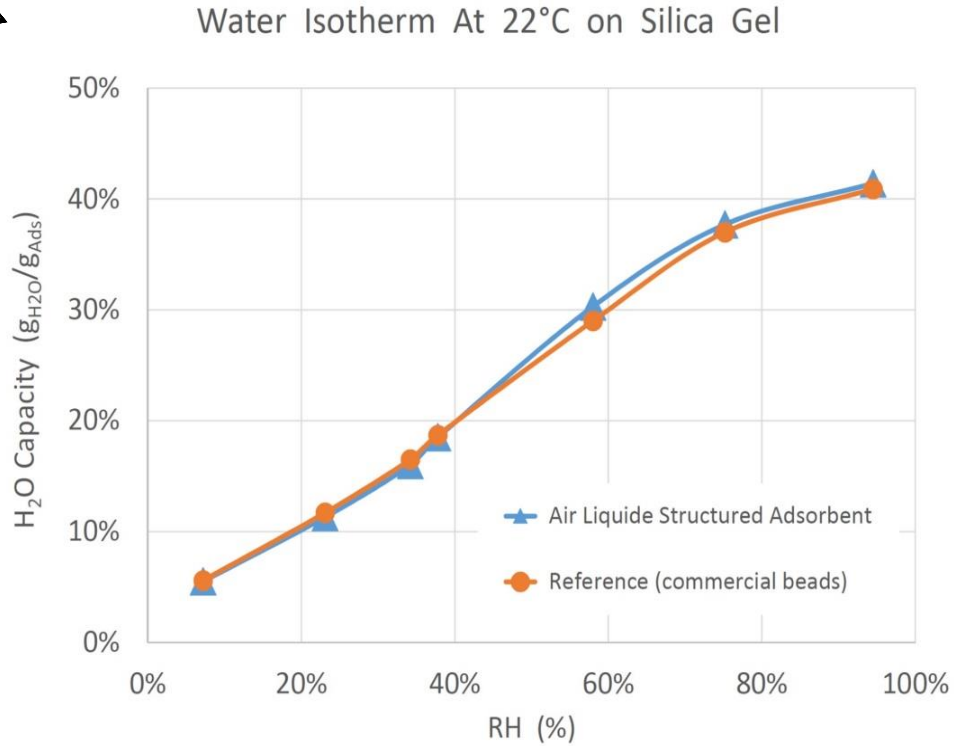

## *BP1 – Air Drying / Multi-Steps Approach*

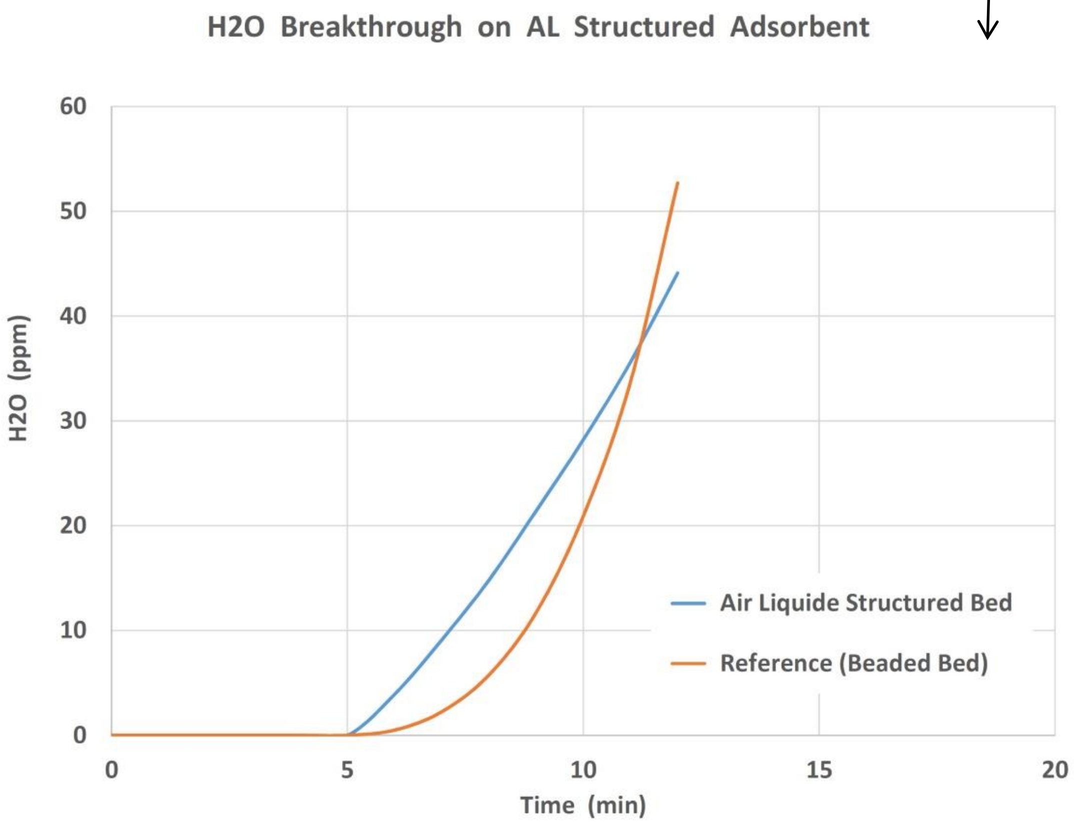
- 2 options: activated alumina (AA) or silica gel (SG)
- SG powder selected based on its highest water capacity
- SG powder formed with a binder into elementary shapes

# Sorbent and Structured Sorbent Module Development and Characterization

## *BP1 – Air Drying / Multi-Steps Approach*

- $H_2O$ capacity of SG elementary shapes meets expectations
- Small scale structured SG-bed formed and characterized
  - $H_2O$ breakthough curve comparable to conventional beaded bed
  - Pressure drop comparable to conventional beaded bed

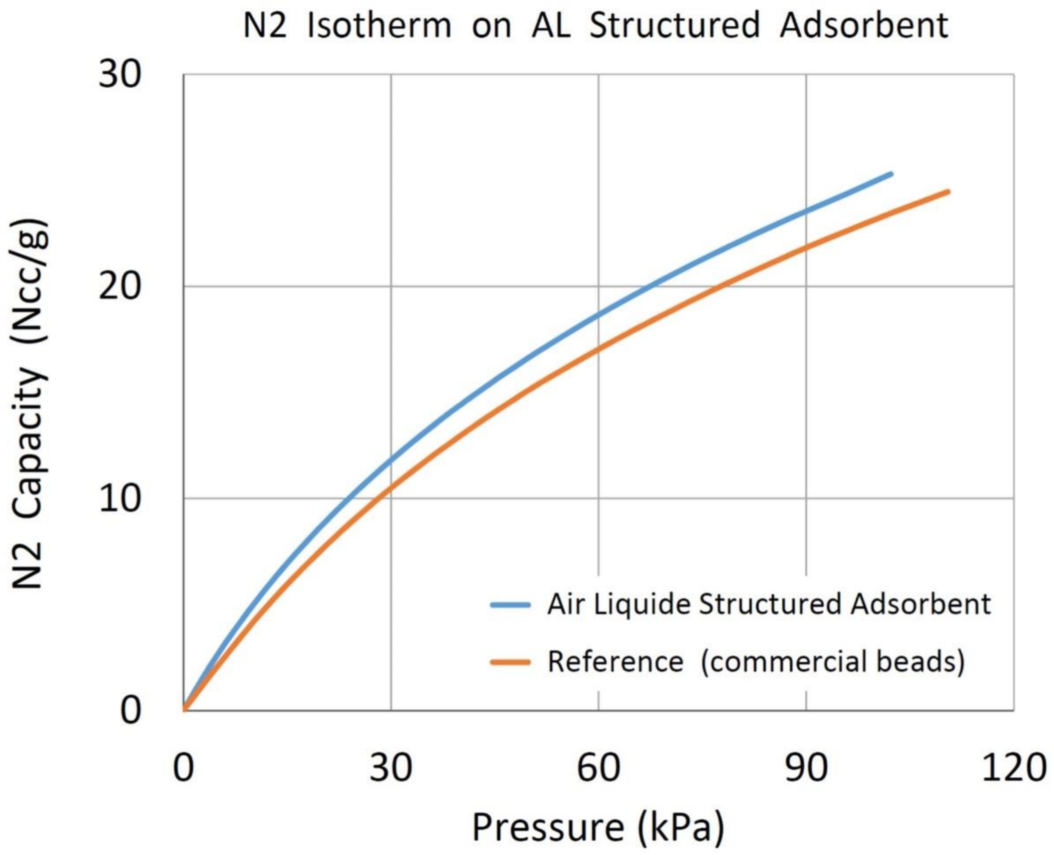


# Sorbent and Structured Sorbent Module Development and Characterization

### *BP1 – N2 Adsorbent / Multi-Steps Approach*

- Various zeolites typically used as $N_2$ binding adsorbents
- Selection of zeolite powder
- Forming with binder
- High temperature activation
- Similar $N_2$ capacity & selectivity compared to commercial adsorbents
- Faster kinetics



# Sorbent and Structured Sorbent Module Development and Characterization

Air Liquide creative oxygen

## *BP2 – Ongoing Adaptation Work on Novel $O_2$ Binding Adsorbent*

- Goal: form structured bed with novel adsorbent by adapting techniques developed over BP1
- First powdery samples of novel adsorbent received from RTI early Q2 2020
- Current focus is on producing an advantageous elementary shape while managing specific limitations of novel adsorbent
- An advantageous elementary shape is fast to produce and can yield low pressure drop once formed into a structured bed
- Performance of the formed adsorbent is checked by running N2/O2 isotherms on elementary shapes
- Next Steps
  - Finalize definition of elementary shapes based on lab trials
  - Performance check of elementary shapes based on N2/O2 isotherms
  - If formed-adsorbent performance meets expectations, then structured beds will be formed and shipped for pilot testing

*Novel powder of O2 binding adsorbent*

# Cycle Modeling

# Development of a vacuum pressure-swing adsorption (VPSA) full-order solver

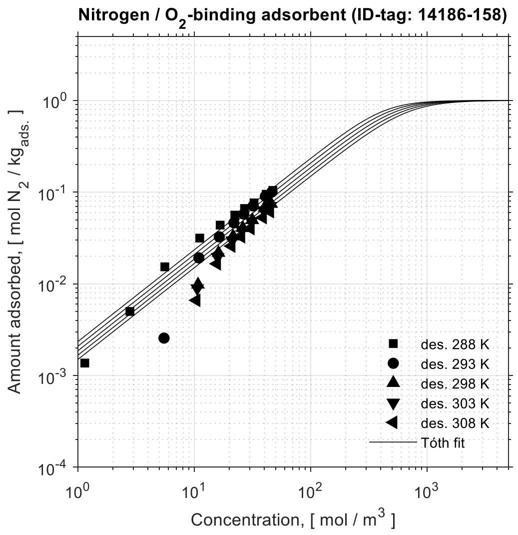
## Process modeling

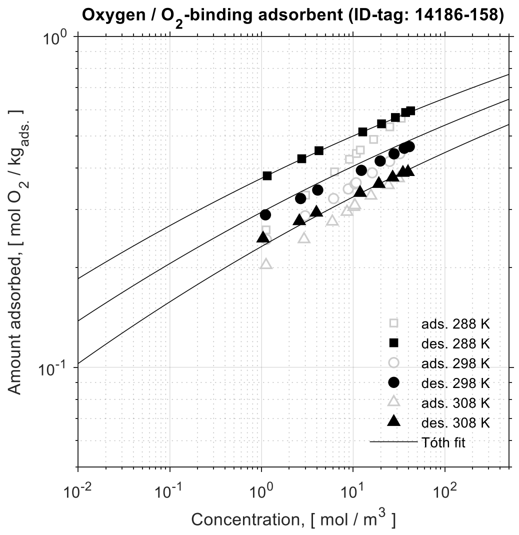
- 1D PDE system describing transient fixed-bed adsorber equations for 7 state variables: gas-phase compositions, adsorbed-phase concentrations, pressure, bed & casing temperatures
- Competitive **adsorption equilibria** modeled w/ IAST
- Linear driving-force (LDF) approximation for mass transfer
- First-principles heat transfer modeling considered
- Solved numerically w/ Finite Volume Method (FVM)
- Coded in MATLAB

## Optimization

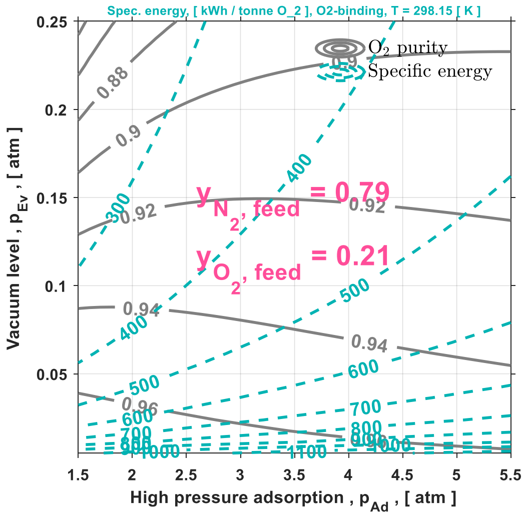
- Multi-objective optimization of relevant VPSA performance variables using genetic & surrogate-based algorithms

## Adsorption equilibria



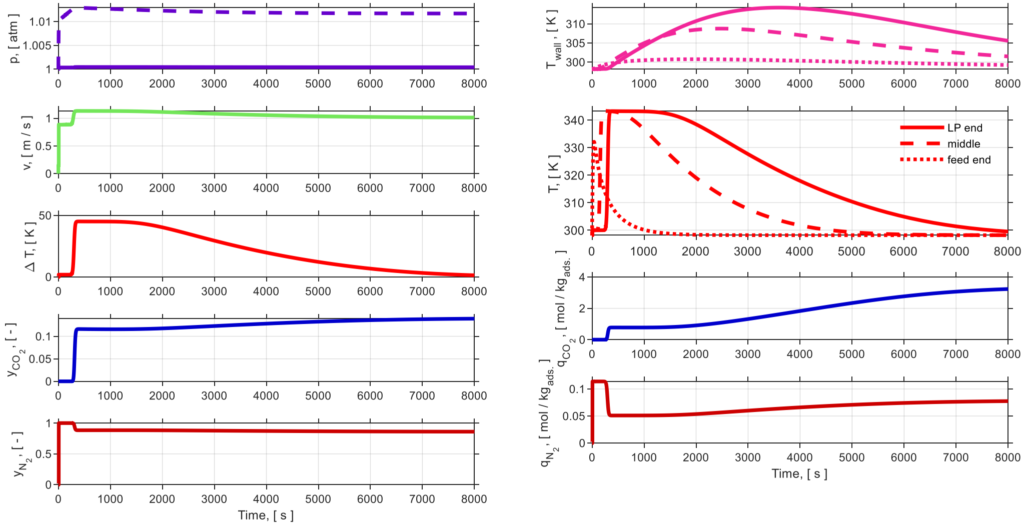

- Applied a short-cut method to test IAST implementation and obtain preliminary assessment for the oxygen-binding adsorbent



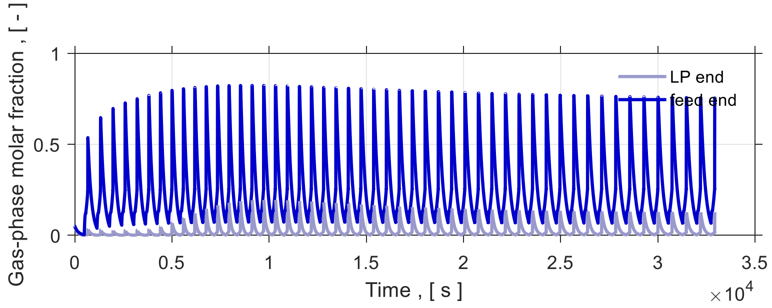
# Process modeling results

## Flue-gas separation results for model validation

- Dynamic column breakthrough (DCB)

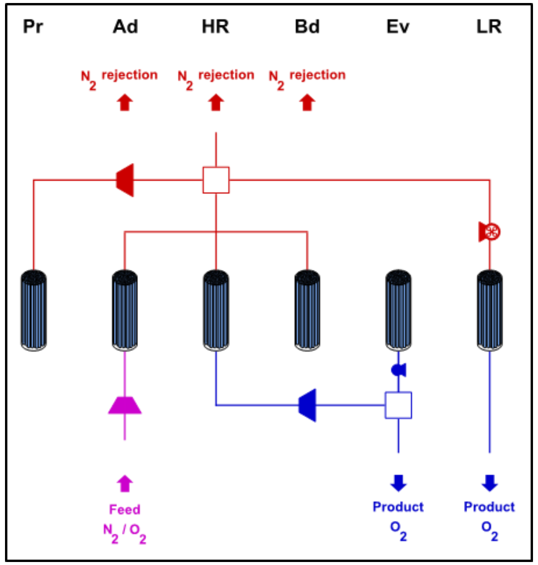



- 4-step VPSA w/ LPP for heavy-product recovery




## On-going sub-tasks

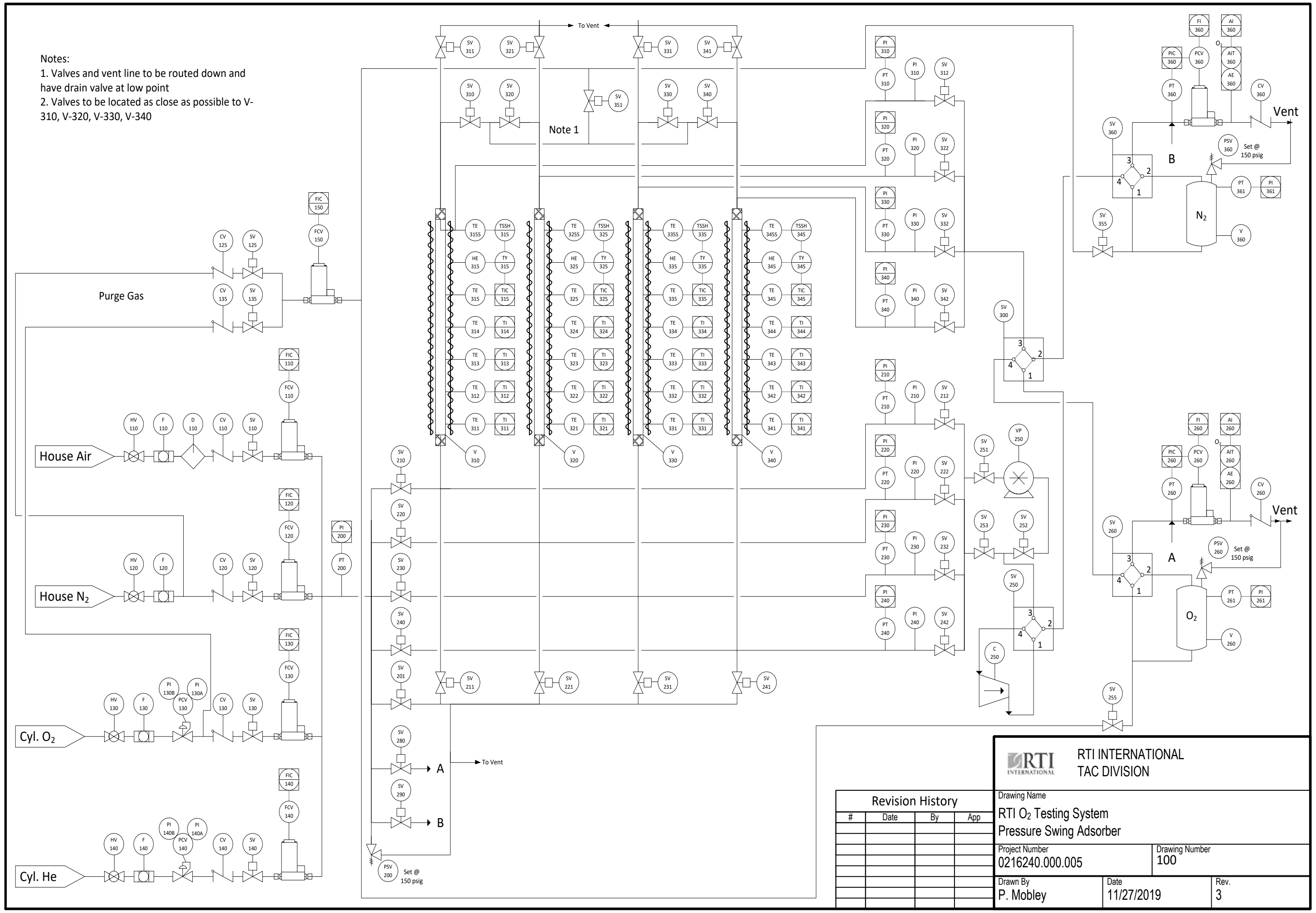
- Implementation of 6-step cycle to simulate the operation of the air separation skid under construction




- Efficiency improvements of IAST calculations to speed-up optimization runs
- Implementation & execution of multi-objective optimization runs for 4-step and 6-step cycles to identify suitable operating conditions

# Integrated Test Skid

# 10 kg Pilot Modular System Process Flow Diagram




- $O_2$ production rate
- $O_2$ purity
- Cycle optimization
- Bed size factor
- Unit power consumption
- Material stability

- Techno-economic analysis for $O_2$ cost projection

## Steps

- HMB - completed
- Sizing – completed
- Safety Review Internal – completed
- AL feedback – completed
- Order Key Instruments - completed
- Fabrication\Controls - Ongoing
- Commissioning
- Testing

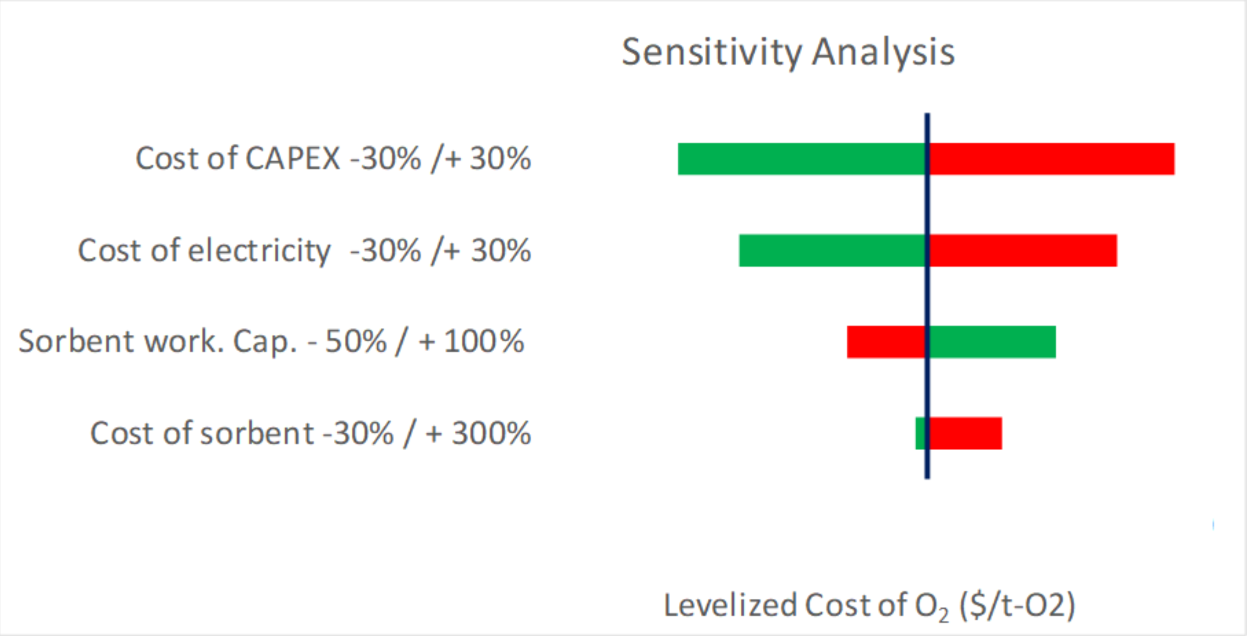
# TEA Refinement

For DOE Internal Use Only

- Data from the 10 kg/d test bed will provide key data for sorption/desorption kinetics at relevant conditions
  - O2-binding sorbent data will be used for cycle modeling and optimization by GTRC
  - N2-binding, if tested, will be modeled by Air Liquide

- Air Liquide will provide input module costs

- System design will be updated from DE-FE0027995 (10 TPD design) to incorporate
  - Refined sizing and utilities
  - Update utilities and equipment cost
  - Update modular construction costs
  - Determine overall $O_2$ production cost



# Outcomes

## *Results*

- Converted RTIO2Sorb synthesis from glove box to scalable protocol
- Developed structured sorbent modules with N2 sorbents
- Developed O2 sorbent VPSA cycle model
- Design of 10 kg/d testing system

## *Next step*

- Integrated 10 kg/d system testing
- Incorporate RTIO2Sorb into structured sorbent modules
- Refining process modeling for large scale design and cost

## *Future*

- Catalyst manufacturing development
- Large pilot-scale testing or 1 TPD prototype

*Enable small-scale applications of oxygen such as 10-30MW gasifiers or 1 to 10 TPD systems by providing air separation at small-scale matching air separation cost of larger cryogenic separation systems.*

# Acknowledgements

DOE/NETL Cooperative Agreements
DE-FE0031527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Dr. Jian Zheng
Dr. Vijay Gupta
Dr. Mustapha Soukri
Jonathan Peters

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