Pilot Testing of a Modular System for Oxygen Production

DOE Cooperative Agreement DE-FE-0031527
2021 DOE/FE Spring R&D Project Review Meeting
May 4, 2021


Air Liquide
creative oxygen

Georgia Tech

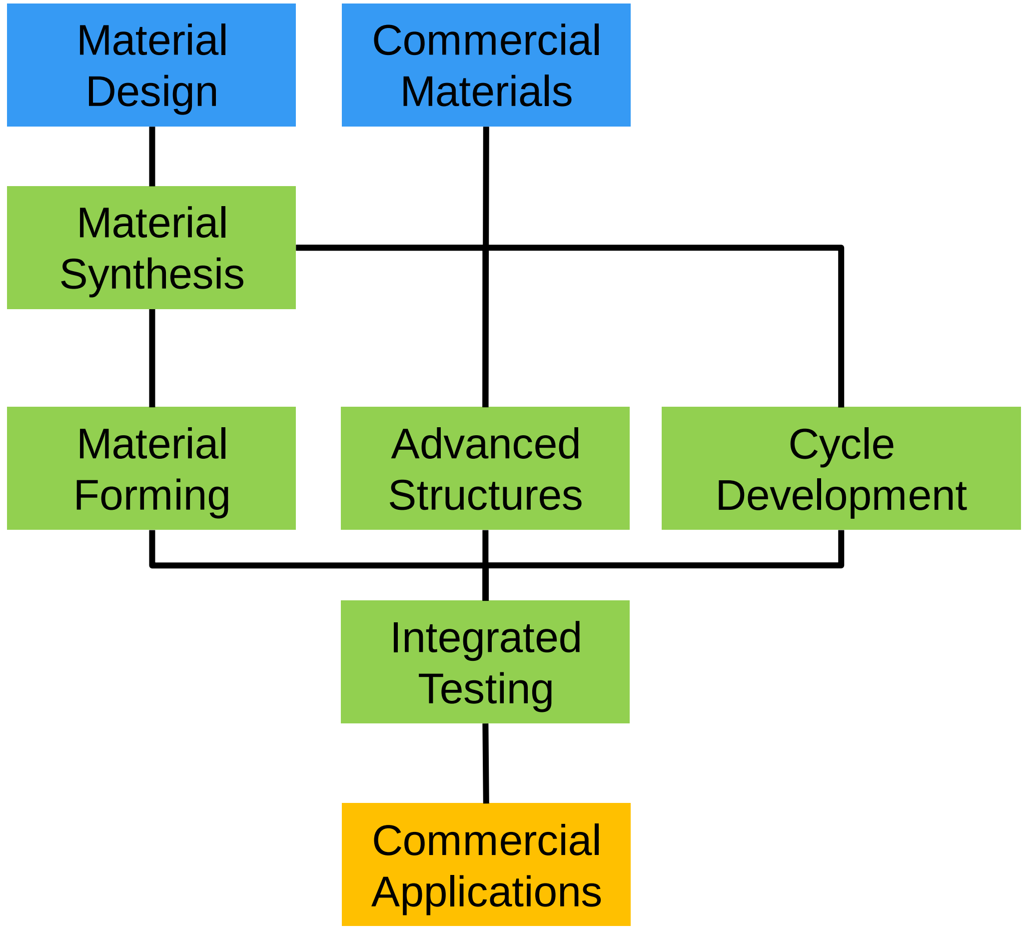
Project objectives

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
- Target lowering sorbent bed-factor

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



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

- 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

- 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:

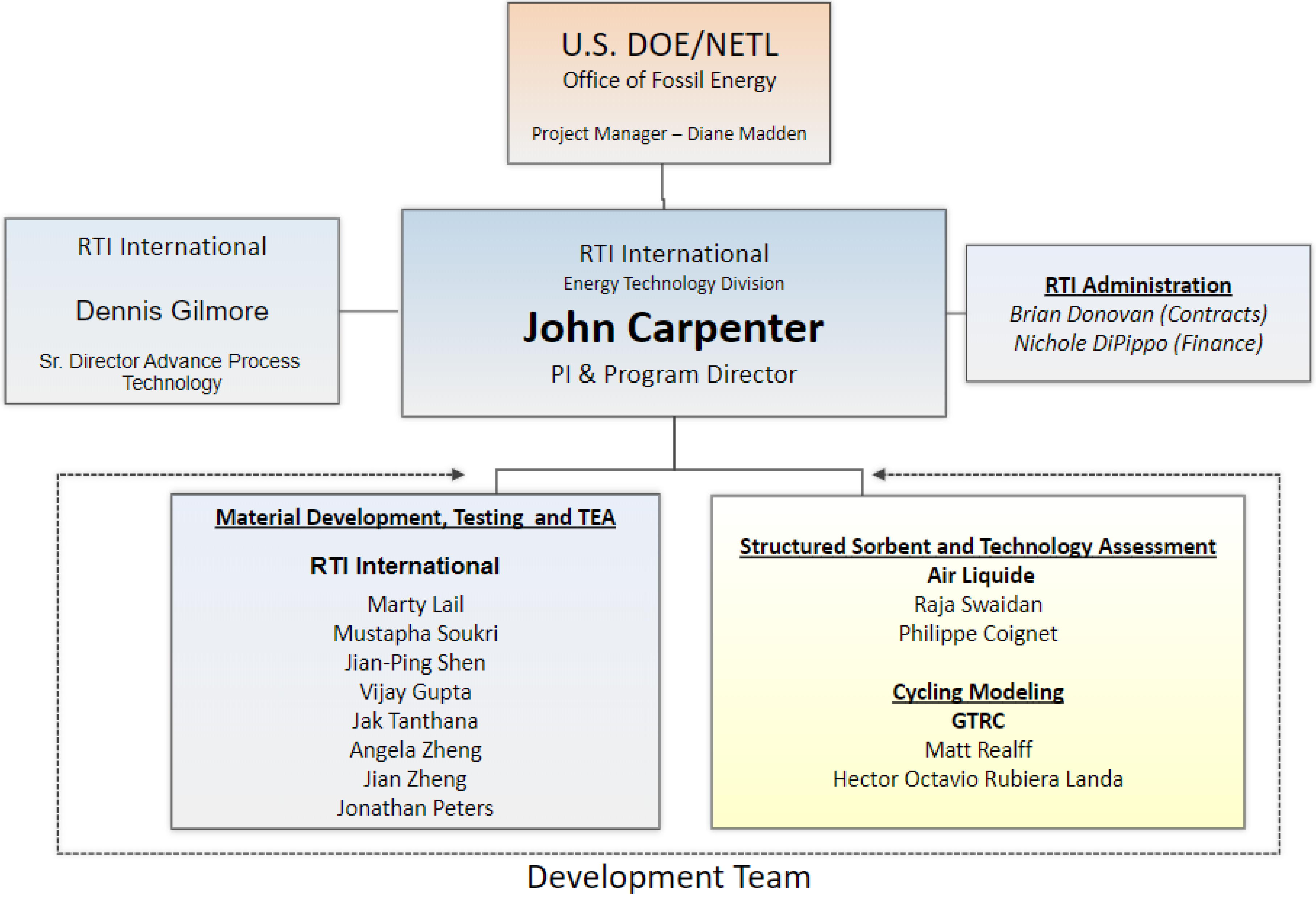
- Membrane module / sorbent manufacturing
- Design, engineering and construction of modular system (5-50 TPD O_2)
- Commercial scale demonstration at 1st adopter site

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

Technology Readiness Level

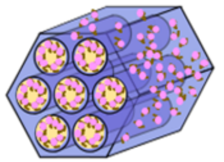
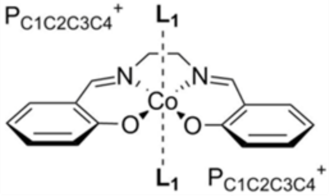
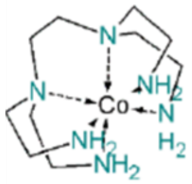
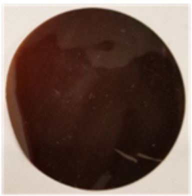
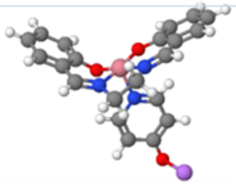
1 2 3 4 5 6 7 8 9

Project team

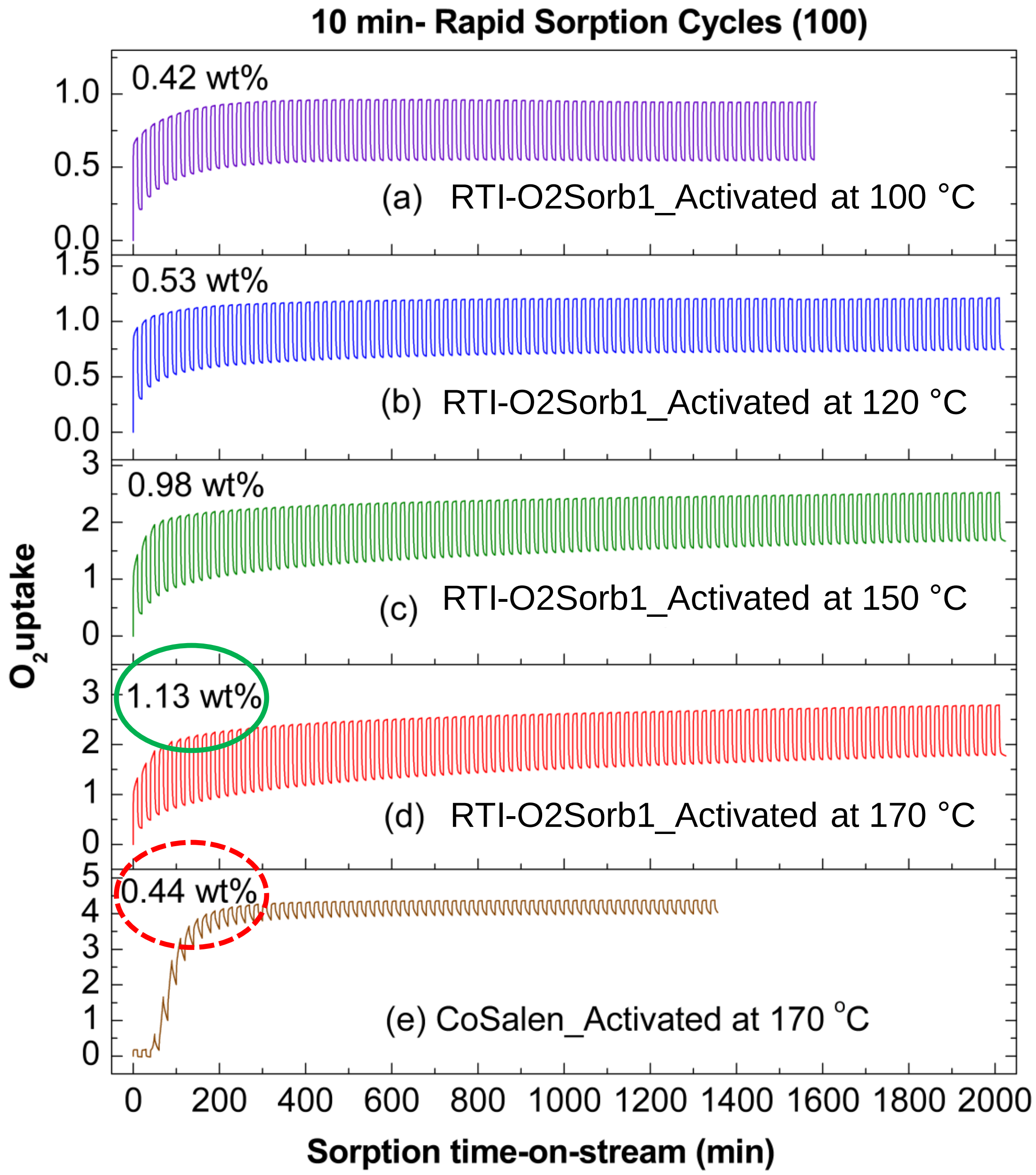


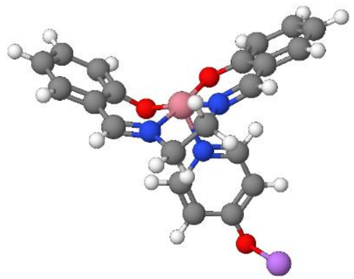
Materials Scale-up

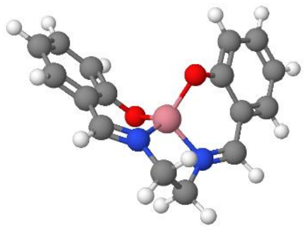
Bio-Inspired O_2 Sorbent Material Development Summary

Material type	Structure/ Illustration	Material form	Material performance
Co-organometallic complex/silica		Solid	• Moderate O_2 sorption capacity (as high as 1.2 wt%) • Slow O_2 sorption/ desorption kinetics • Low O_2/ N_2 selectivity
Co Complex – Ionic Liquid		Ionic liquid	• Moderate O_2 sorption capacity (as high as 1.1 wt%) • Slow O_2 sorption/ desorption kinetics • High O_2/ N_2 selectivity
Co Complex/ porous support	• Complex on Mesoporous silica or zeolites • O_2 binding metal organic frameworks	Solid	• Low-moderate O_2 sorption capacity • Slow O_2 sorption/desorption kinetics • 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) • Low O_2/ N_2 selectivity
Co Complex- O_2 membrane	 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%) ✓ Fast O_2 sorption kinetics (rapid cycle <10 min) ✓ High O_2/ N_2 selectivity

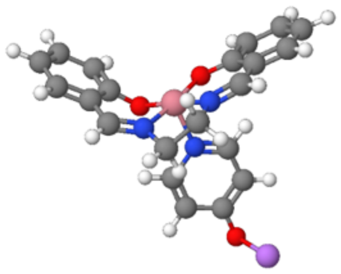
TGA Cyclic O_2 Sorption of RTI's RTI-O2Sorb1 vs. Commercial Co-Salen







Progress on Scale-up of RTI-O2Sorb



Glovebox | Schlenk line (air free) | Shaping (beading or extrusion)

20 g | 20g → 40 g → 120 g → 240 g per batch | 5g to 100 g per batch

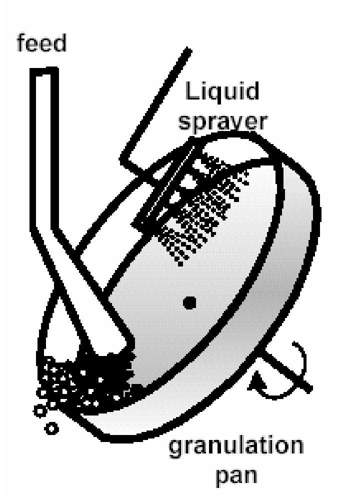
Powder | Shaped sorbent (powder + binder)

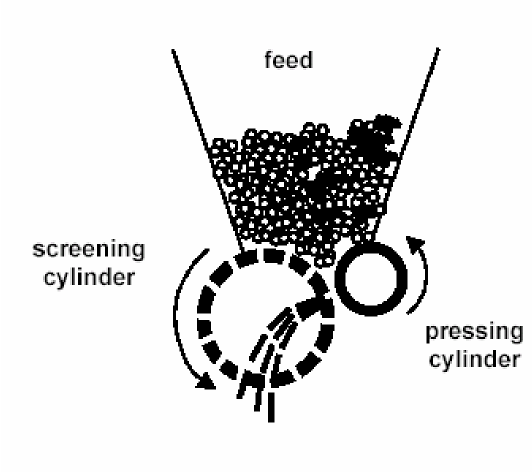
[DE-FE-0027995] Oxygen Binding Materials

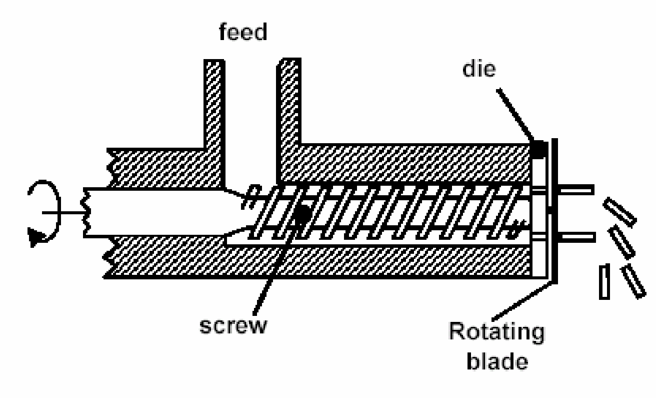
[DE-FE-0031527] Pilot Testing Modular System

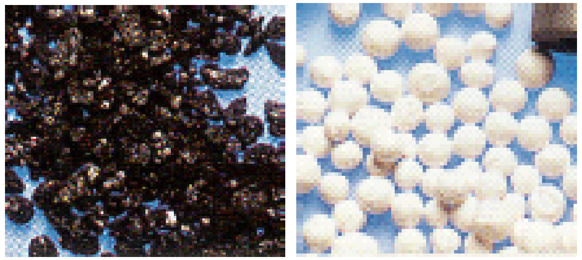
- ✓ **Successfully repeated batch synthesis for maximum O_2 sorption performance**
  (reversible O_2 uptake of 1~1.5 wt% with powder sample after activation at 170 ^{o}C)
- ✓ **Successfully synthesized powder material with same performance using Schlenk line**
  (which allows large batch synthesis)
-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







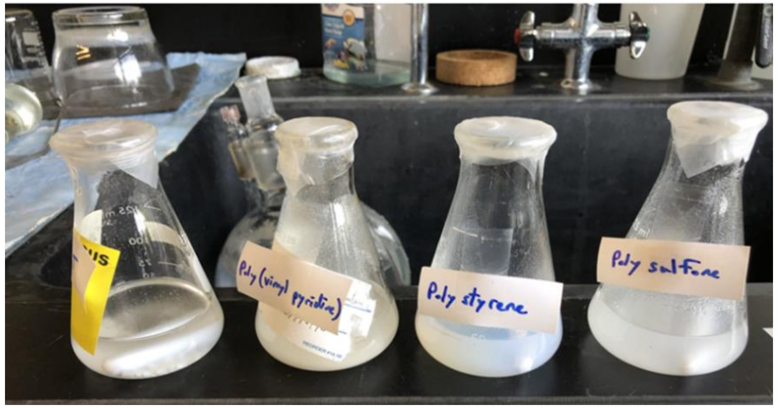


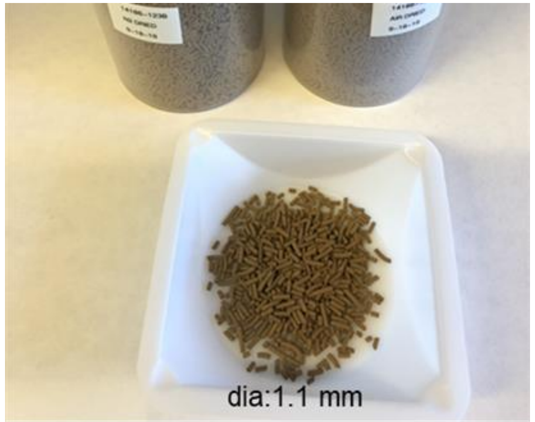
Granulation

Pelletization

Extrusion

Optimization of Extrudate Formulation





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

After normal N_2-O_2 100 cycles

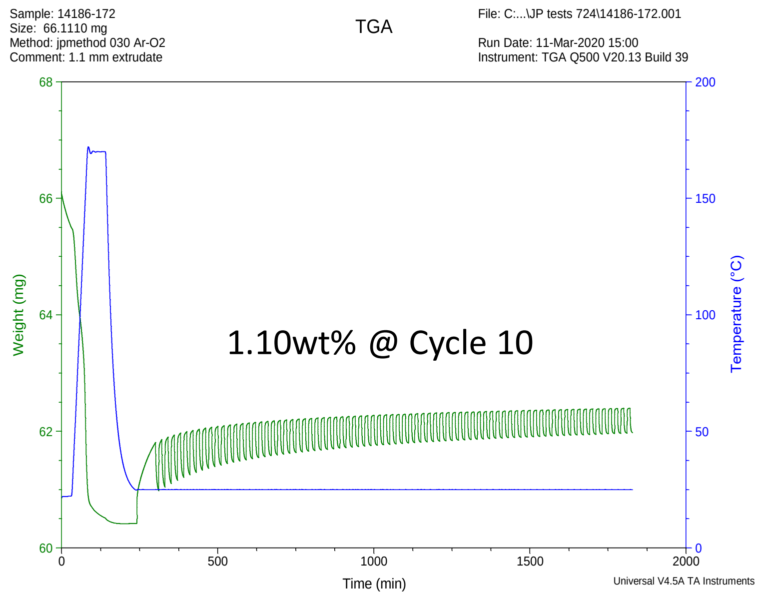
Extrudate Formation Characteristics

Key characteristics of Forming Extrudate:

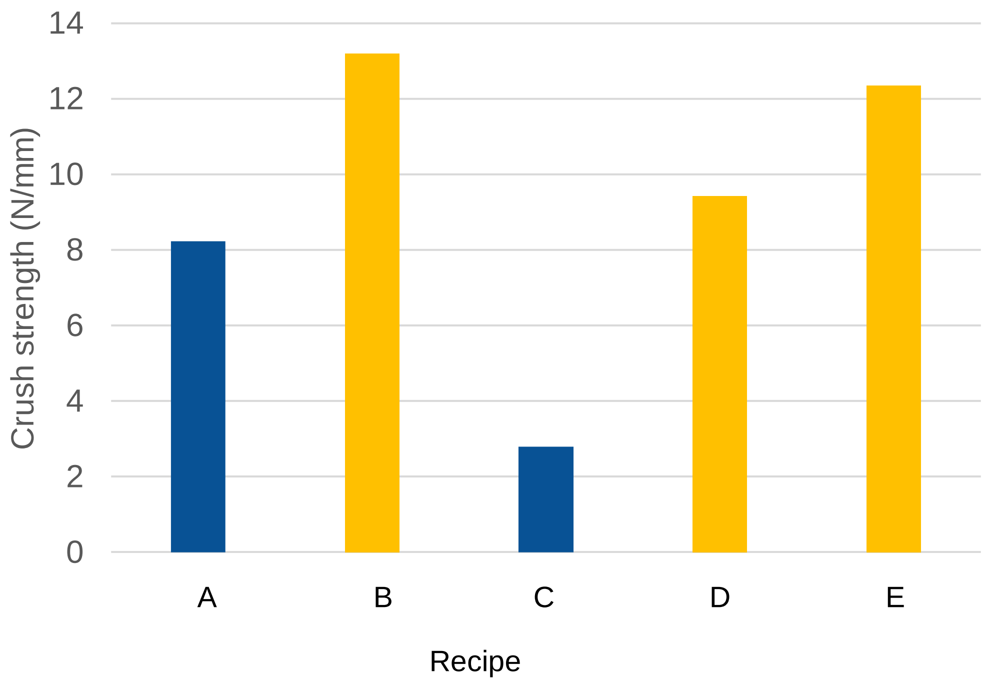
- O_2 capacity, mechanical strength, size

Key variables of Forming Extrudate:

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

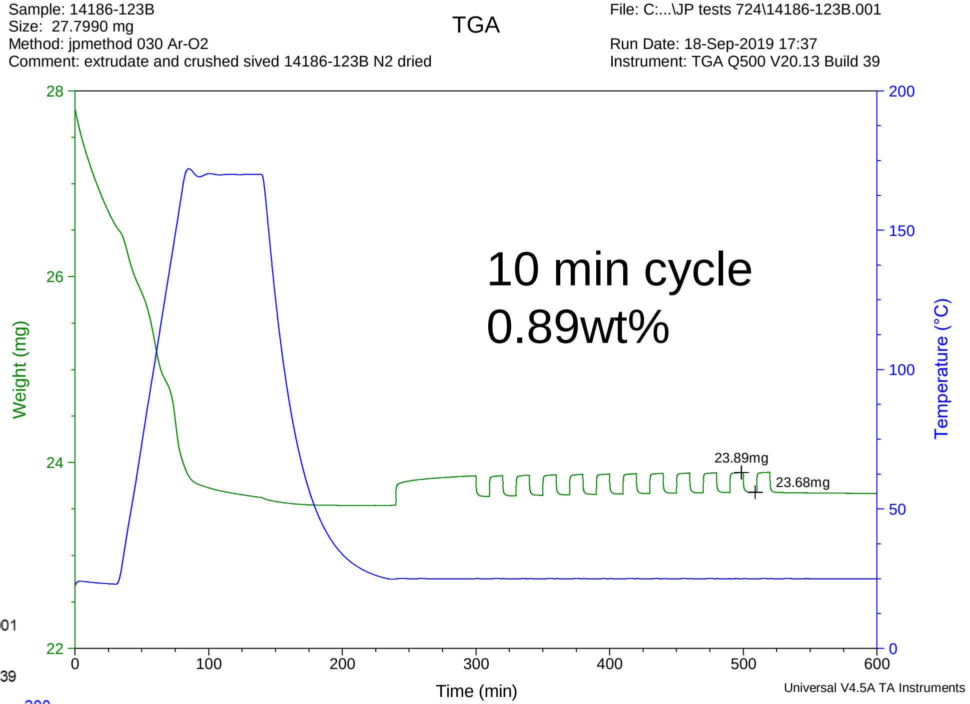


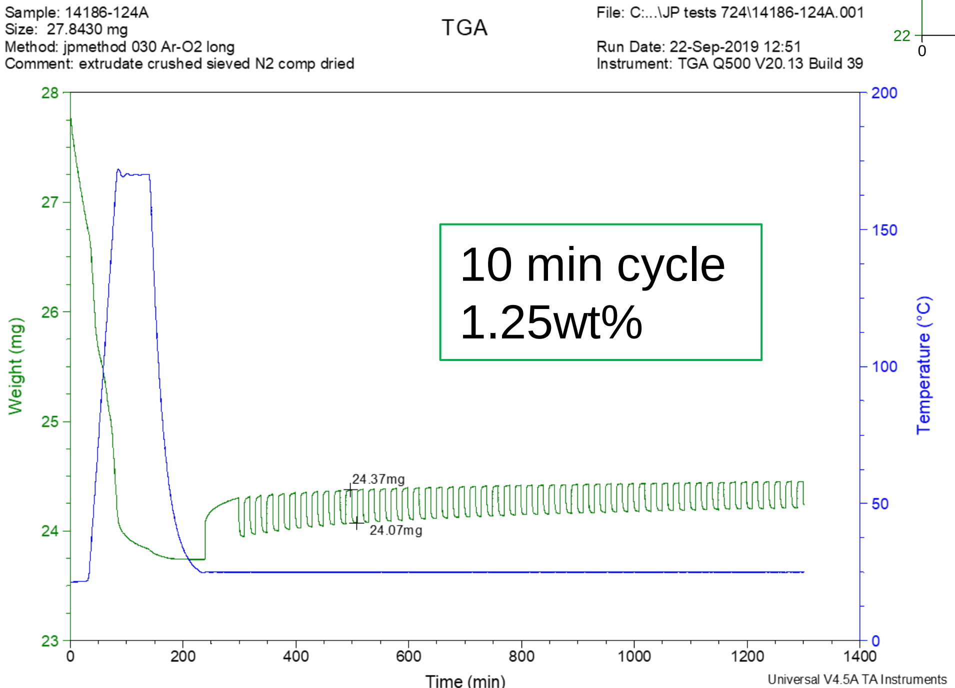
Dia (in)	Dia (mm)	N	N/mm
0.054	1.3716	13.6	9.915427
0.053	1.3462	21.4	15.8966
0.055	1.397	12.9	9.234073
0.052	1.3208	15.4	11.6596
0.052	1.3208	15.4	11.6596
0.054	1.3716	17.6	12.83173
0.052	1.3208	11.9	9.009691
0.053	1.3462	16.8	12.47957
0.052	1.3208	12.1	9.161114
0.055	1.397	11.8	8.446671
		Avg	11.02941



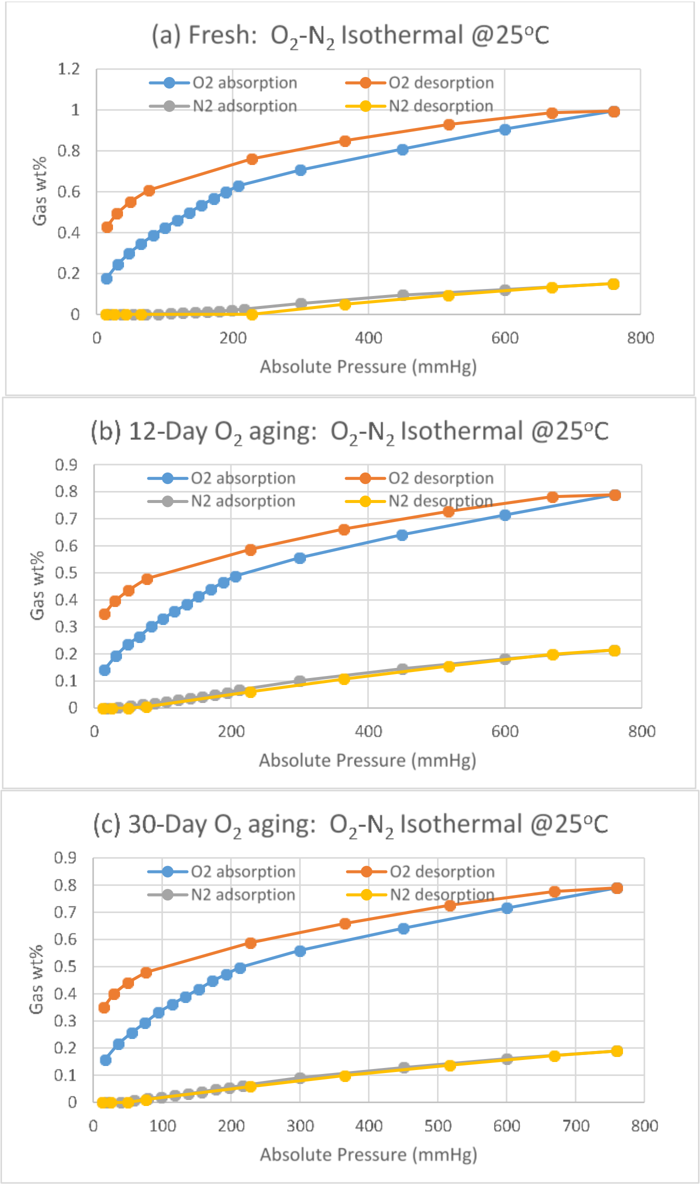
Binder (wt%)	Density (g/cc)	Dia. (mm)	Length (mm)	Crush strength (N/mm)	Dynamic oxygen capacity (wt%)
16.7	0.55-0.62	1.2-1.5	2.0-10.0	8.0-12.0	0.8-1.2

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

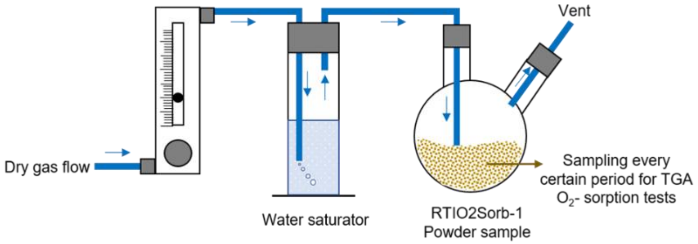


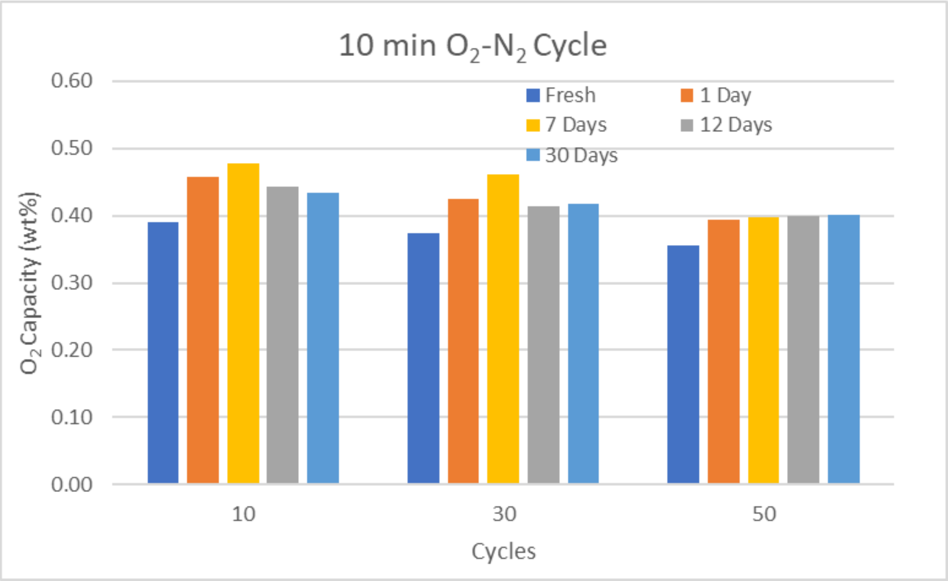


Exposure/Aging Testing



- 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

Air Liquide creative oxygen

Focus on Traditional Materials

- Air Liquide BP1 objectives successfully met on time *(by June 30th, 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

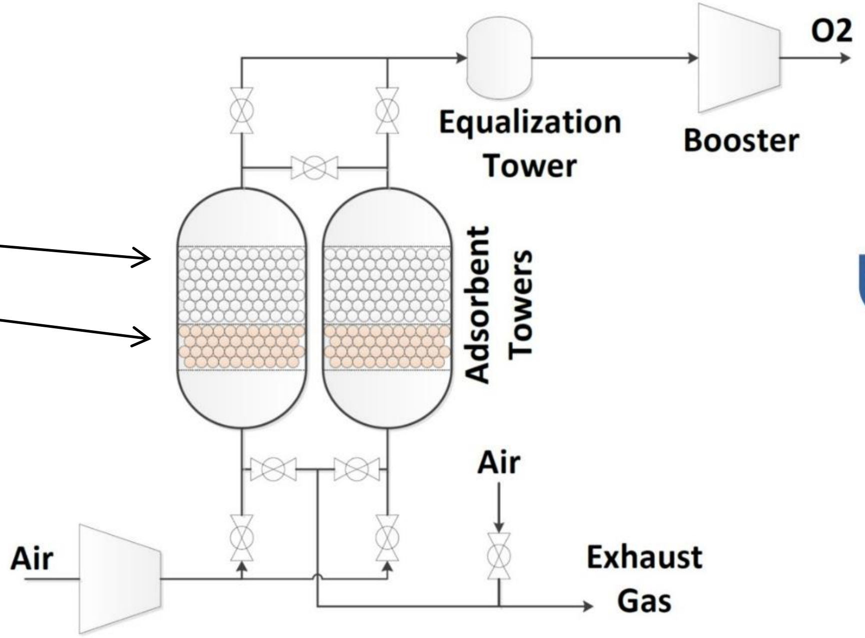
Adapting Method to RTI Sorbent

- Forming techniques and activation tool were scaled up for beds of up to 1 kilogram
- Reviewed and provided feedback on the pilot design
- Explored 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

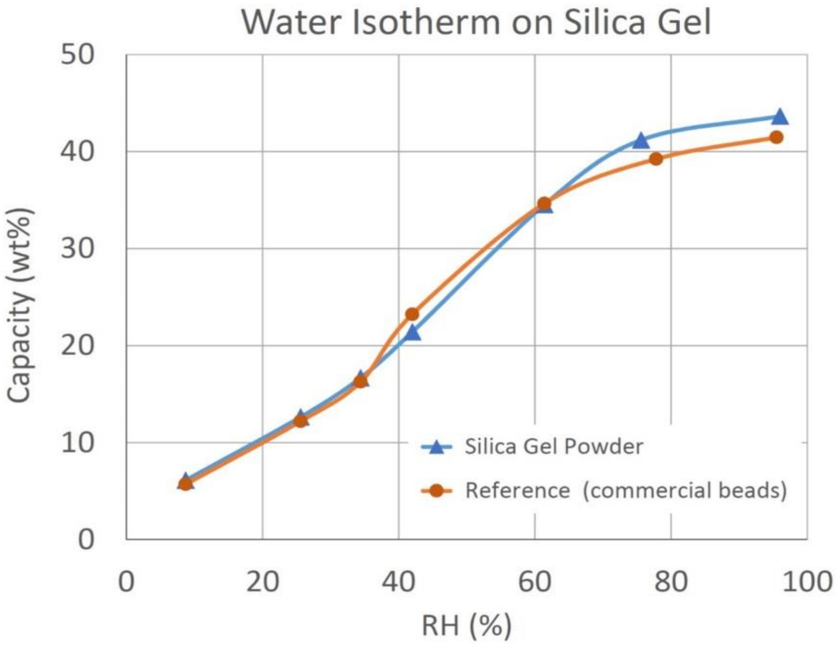
Sorbent and Structured Sorbent Module Development and Characterization

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



Air Liquide creative oxygen

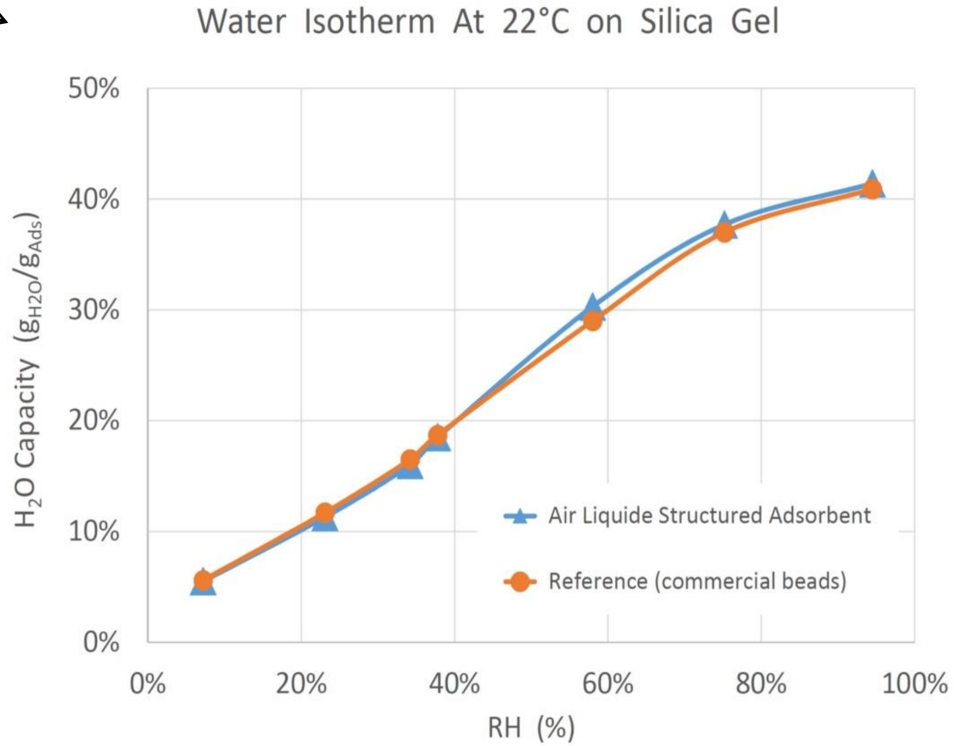


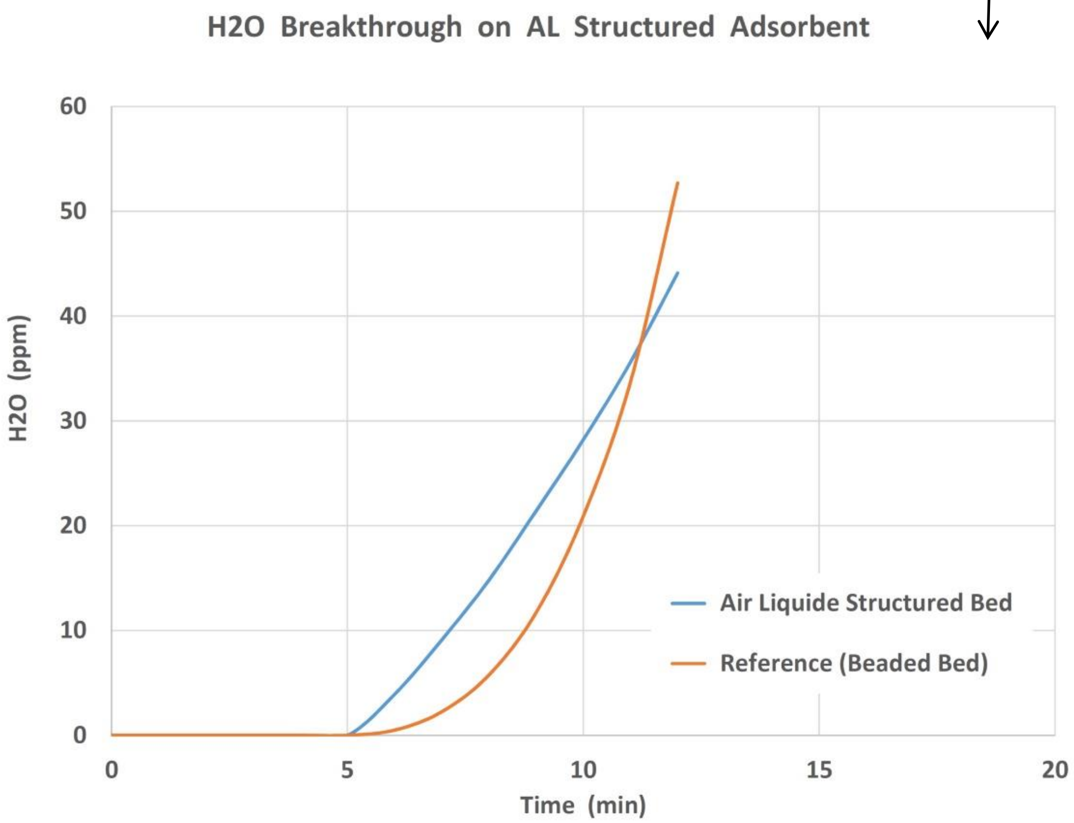
Air Drying / Multi-Steps Approach

- <u>2 options</u>: 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

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

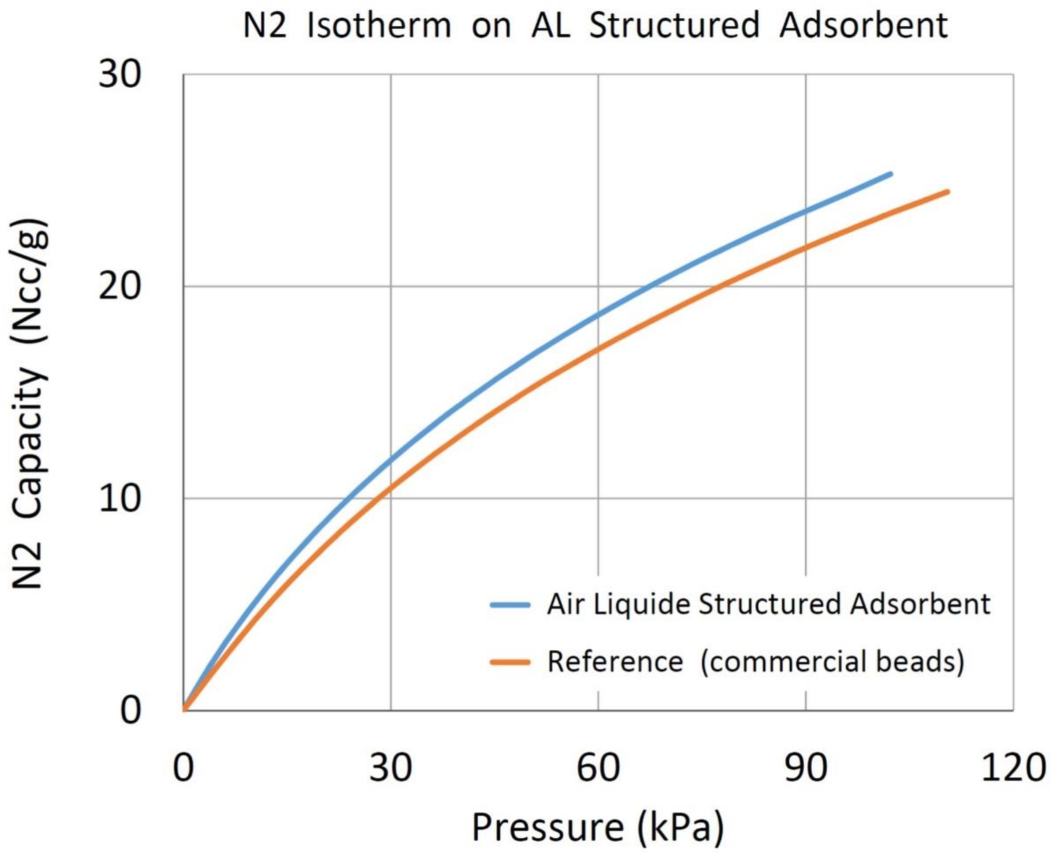




Sorbent and Structured Sorbent Module Development and Characterization

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

Adaptation Work on Novel O_2 Binding Adsorbent

- Goal: form structured bed with novel adsorbent by adapting techniques developed with traditional sorbents
- Focused 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
- Forming of the novel O2 binding adsorbent was unable to achieve mechanical strength for full module forming
- Focused on extrudate formations

Novel powder of O2 binding adsorbent

Cycle Modeling

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

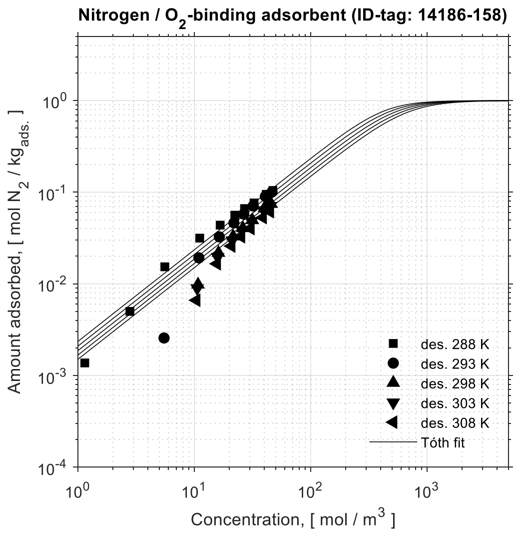
Process modeling

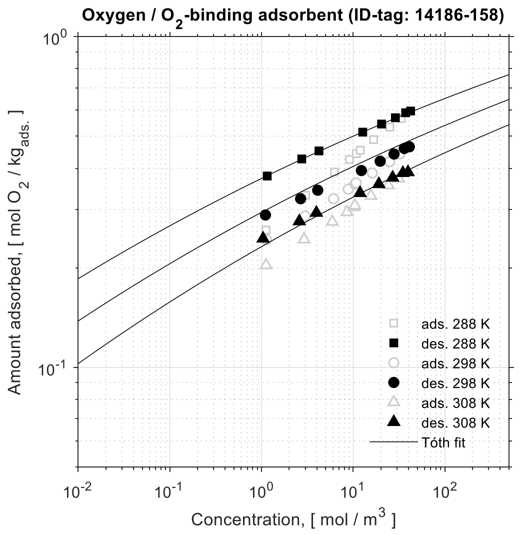
- 1D PDE system describing transient fixed-bed adsorber equations for 7 state variables: gas-phase compositions, adsorbed-phase concentrations, pressure, bed & casing temperatures
- Competitive **adsorption equilibria** modeled w/ IAST
- Linear driving-force (LDF) approximation for mass transfer
- First-principles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

Optimization

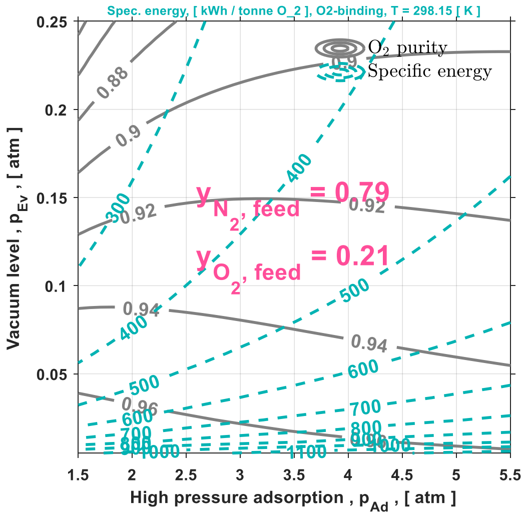
- Multi-objective optimization of relevant VPSA performance variables using genetic & surrogate-based algorithms

Adsorption equilibria





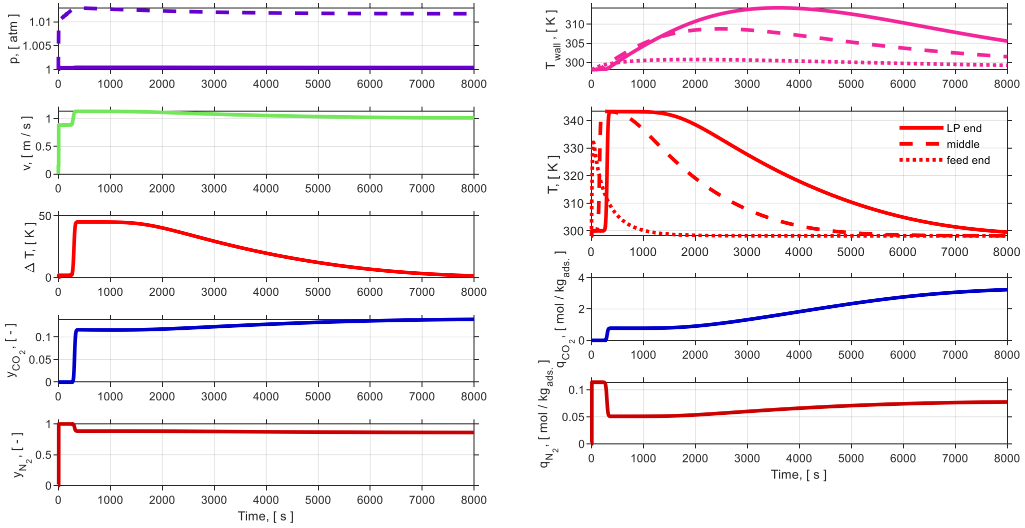
- Applied a short-cut method to test IAST implementation and obtain preliminary assessment for the oxygen-binding adsorbent



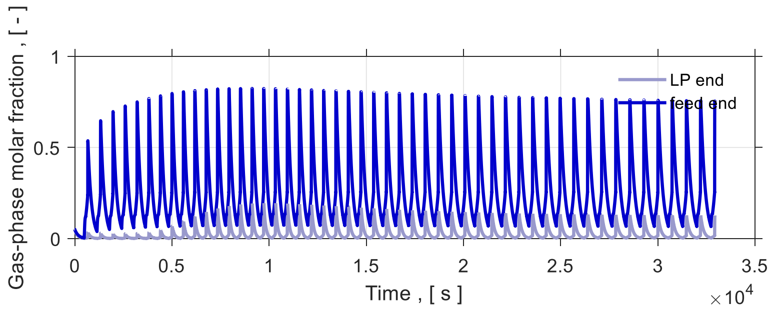
Process modeling results

Flue-gas separation results for model validation

- Dynamic column breakthrough (DCB)

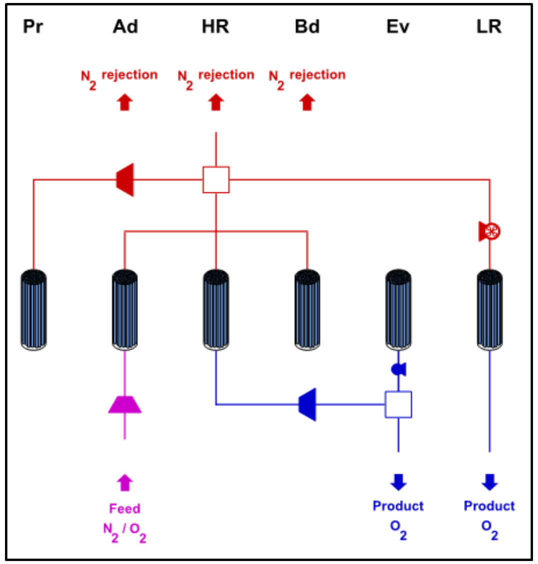


- 4-step VPSA w/ LPP for heavy-product recovery



On-going sub-tasks

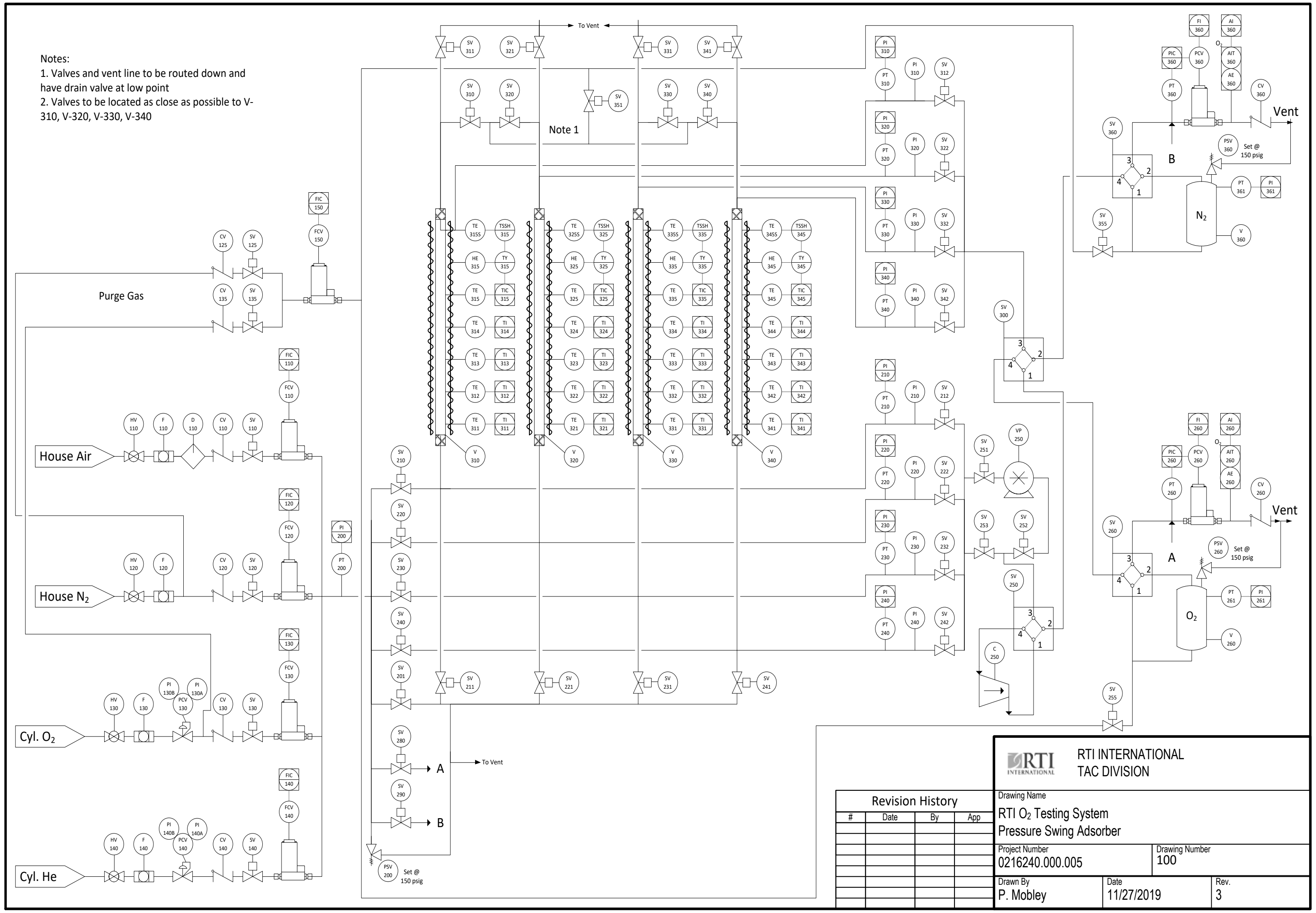
- Implementation of 6-step cycle to simulate the operation of the air separation skid under construction



- 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
- Sizing
- Safety Review Internal
- AL feedback
- Order Key Instruments
- Fabrication\Controls Commissioning
- Testing

Kg Extrudate Production

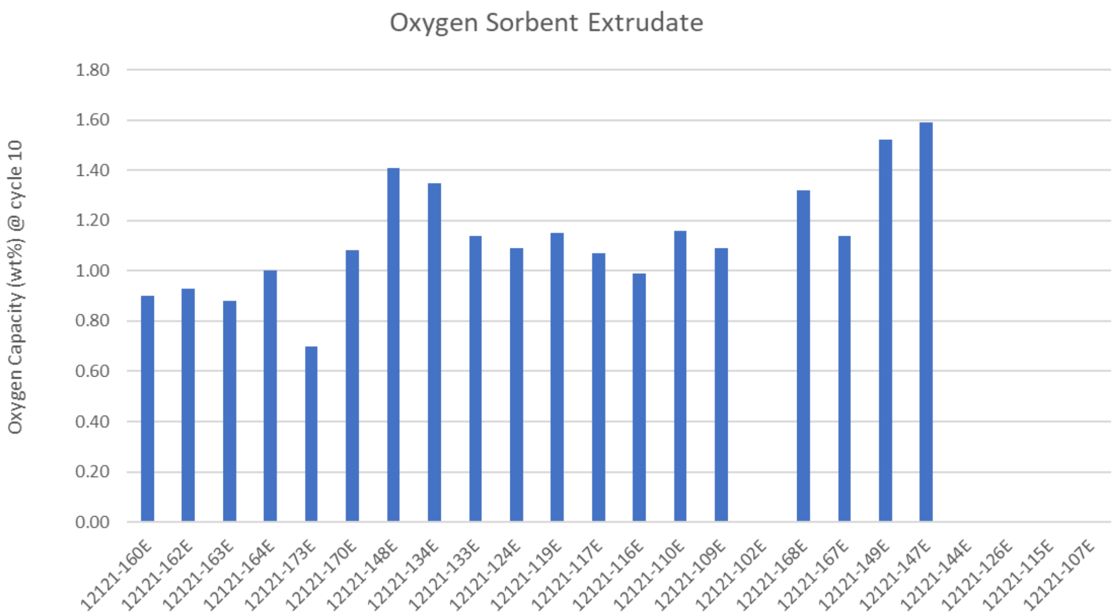
Produced 2.4 kg of O2 Sorb in extrudate form
- Due to size limitations of equipment this was performed in 150-250 gm batches

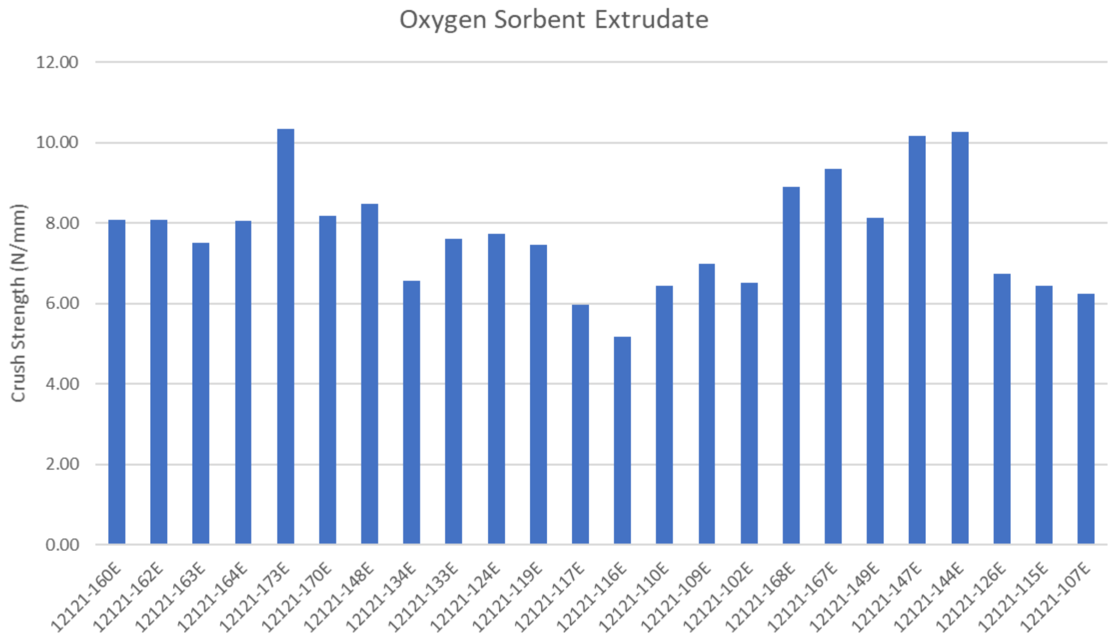


Forming → Drying → Sizing

Kg Extrudate Characterization

Key characterizations were O2 capacity under standard TGA test and crush strength
- Some variation from batch to batch

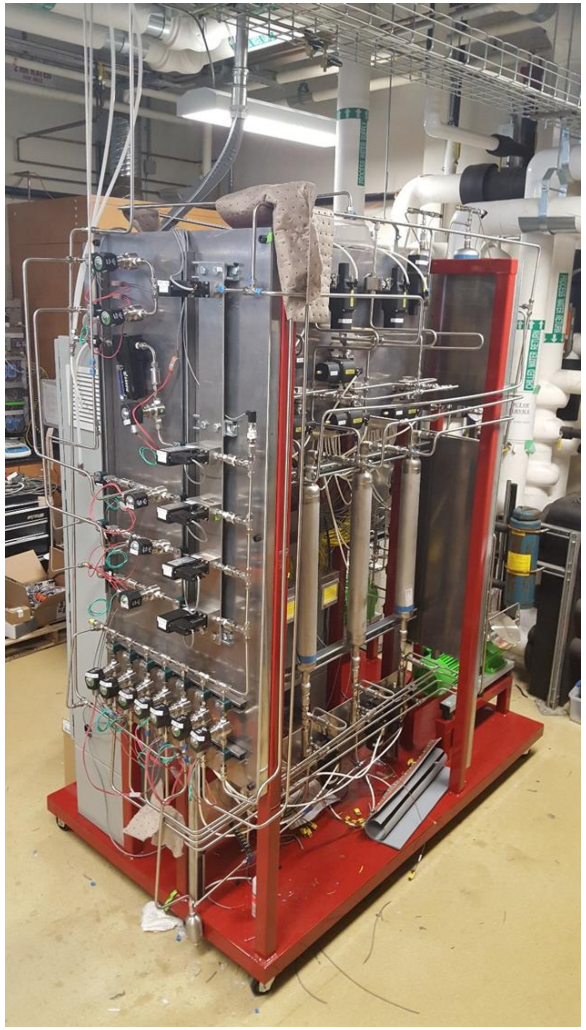




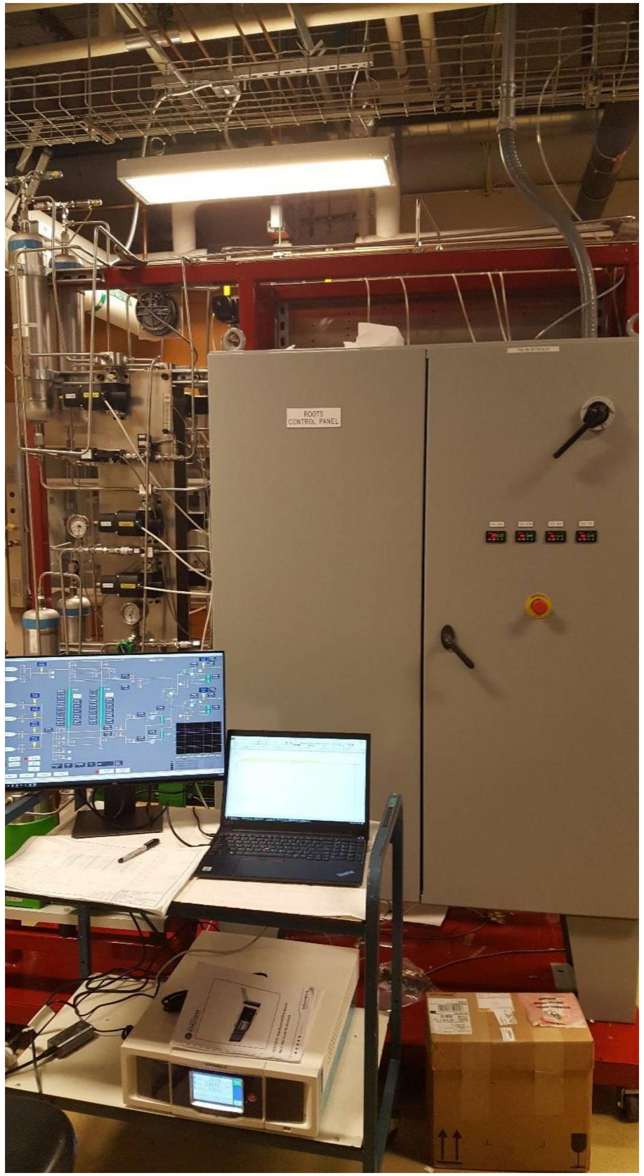
Target was> 1.0 wt% in TGA testing for goal of achieving > 0.5 wt% working capacity

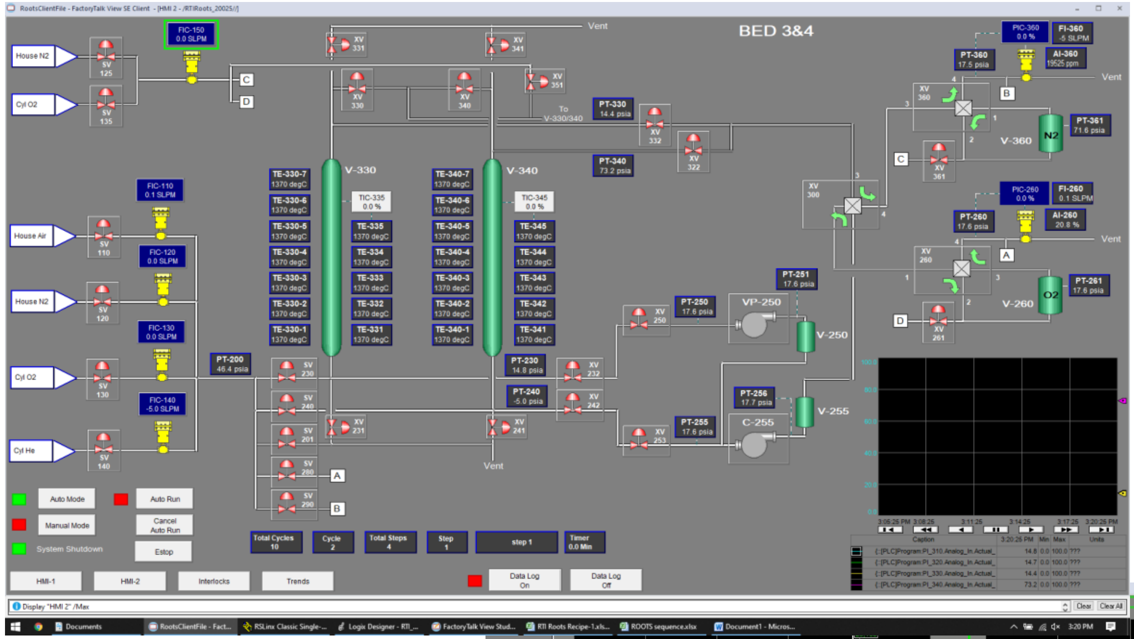
Target was > 5 N/mm in axial crush strength similar to commercial materials of similar structure

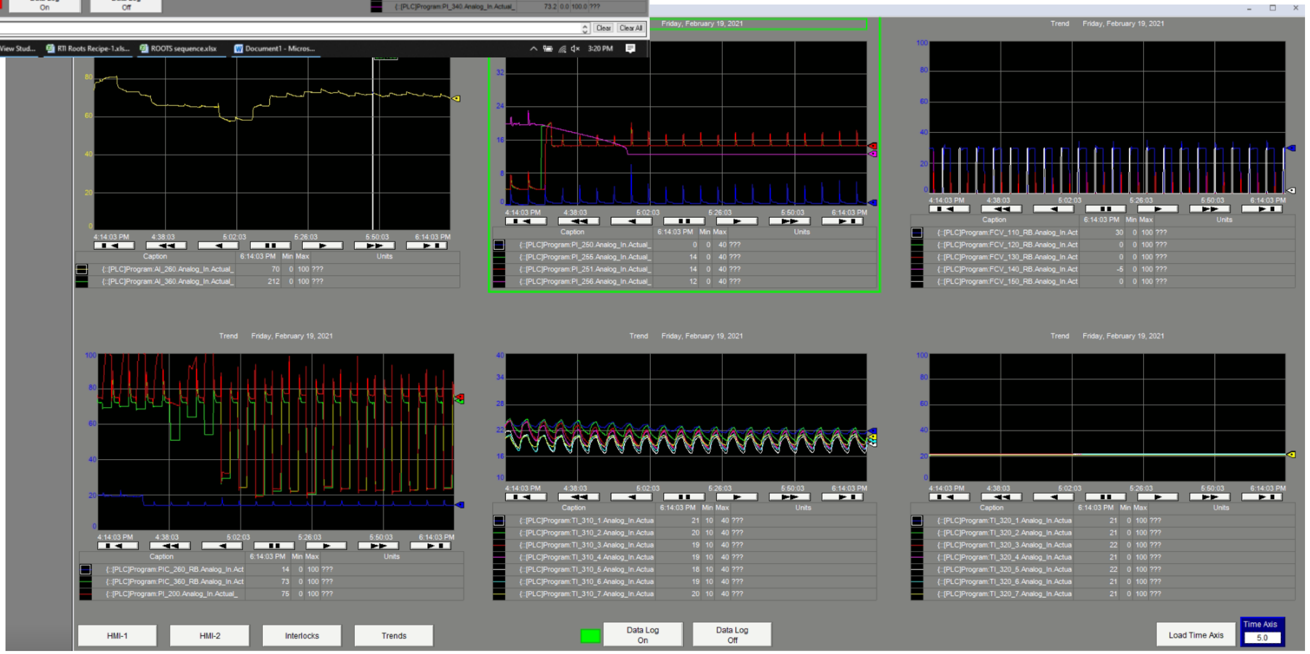
10 kg Pilot Modular System Build



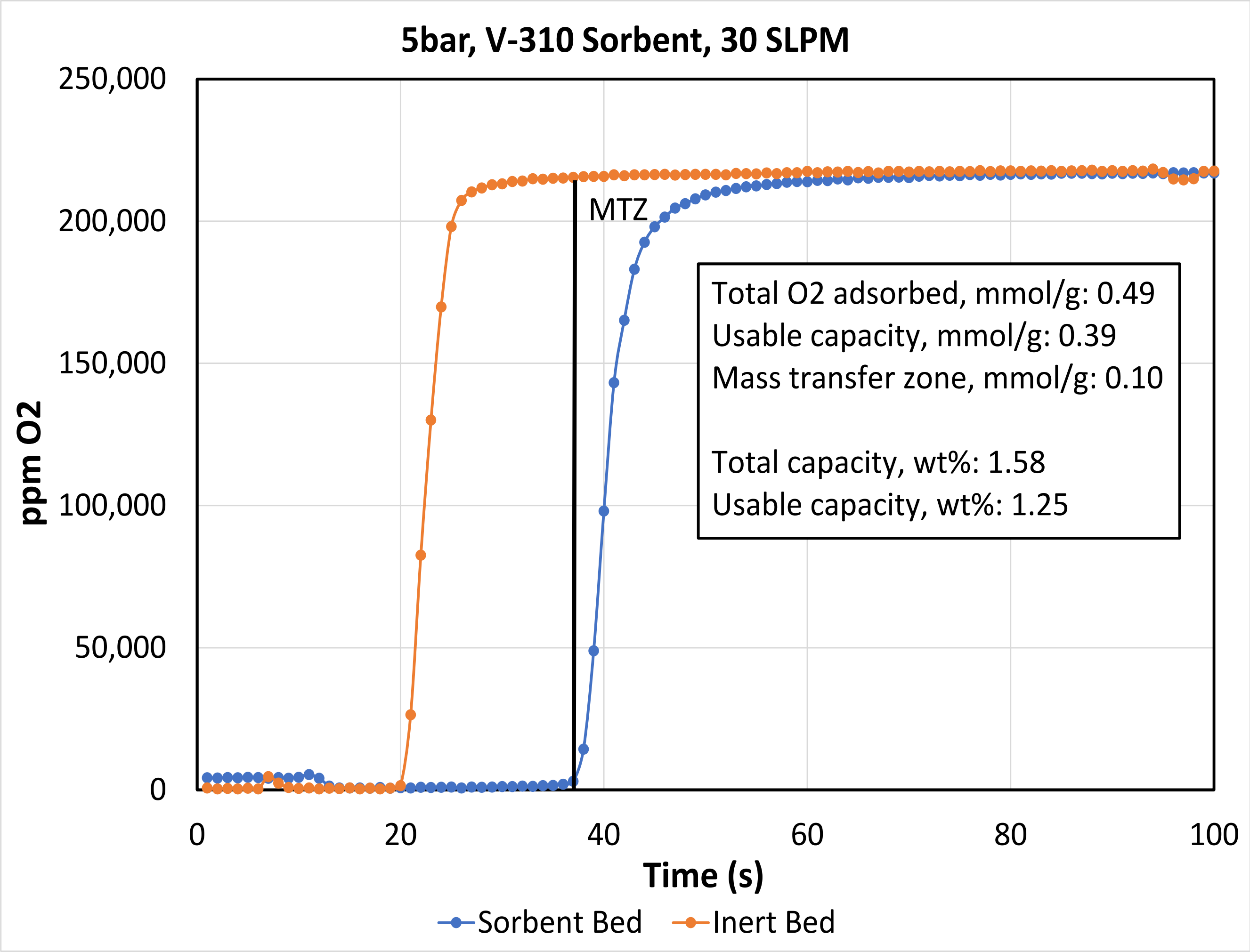
10 kg Pilot Modular System Controls





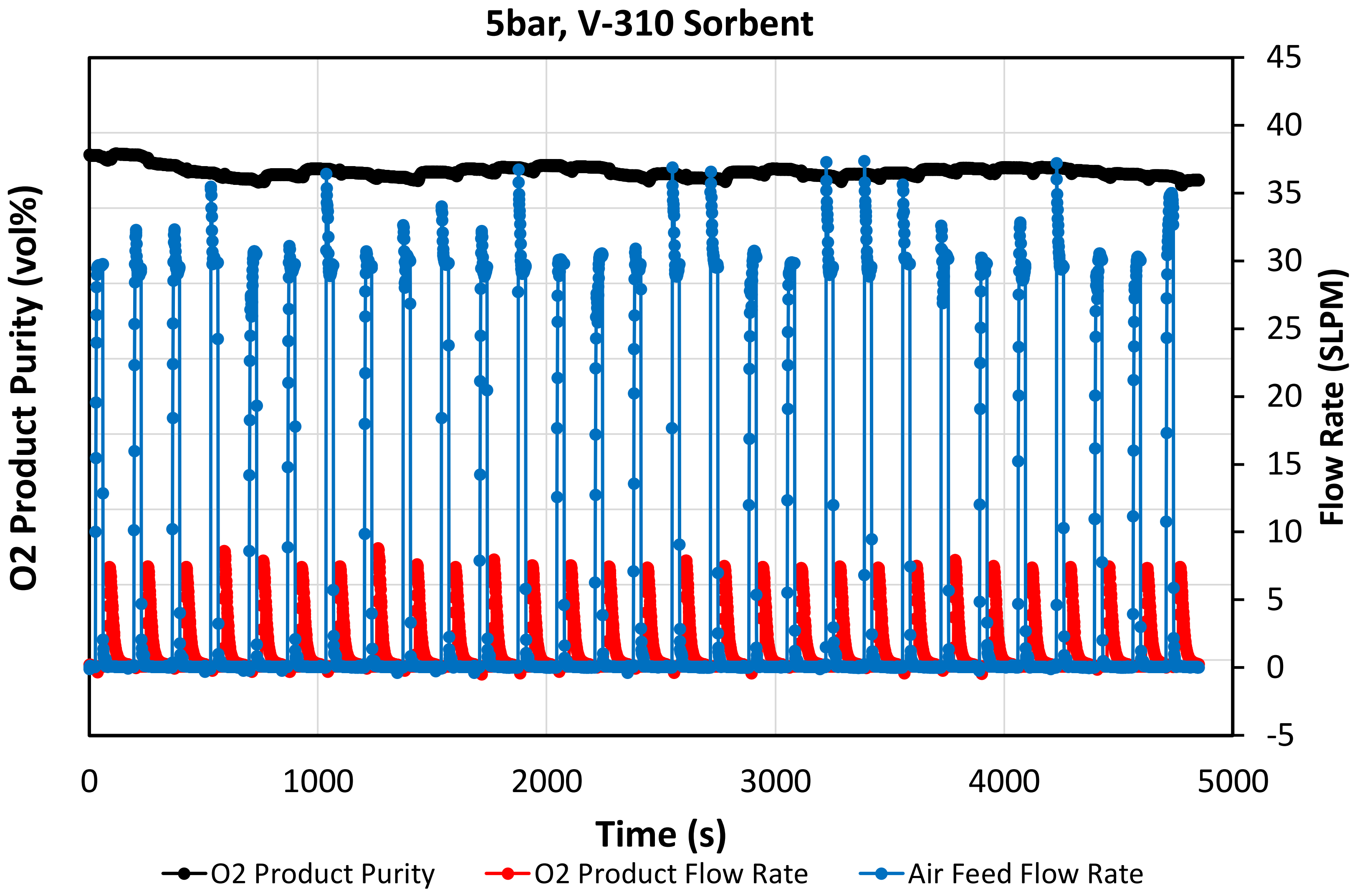


System Characterization – Breakthrought Testing



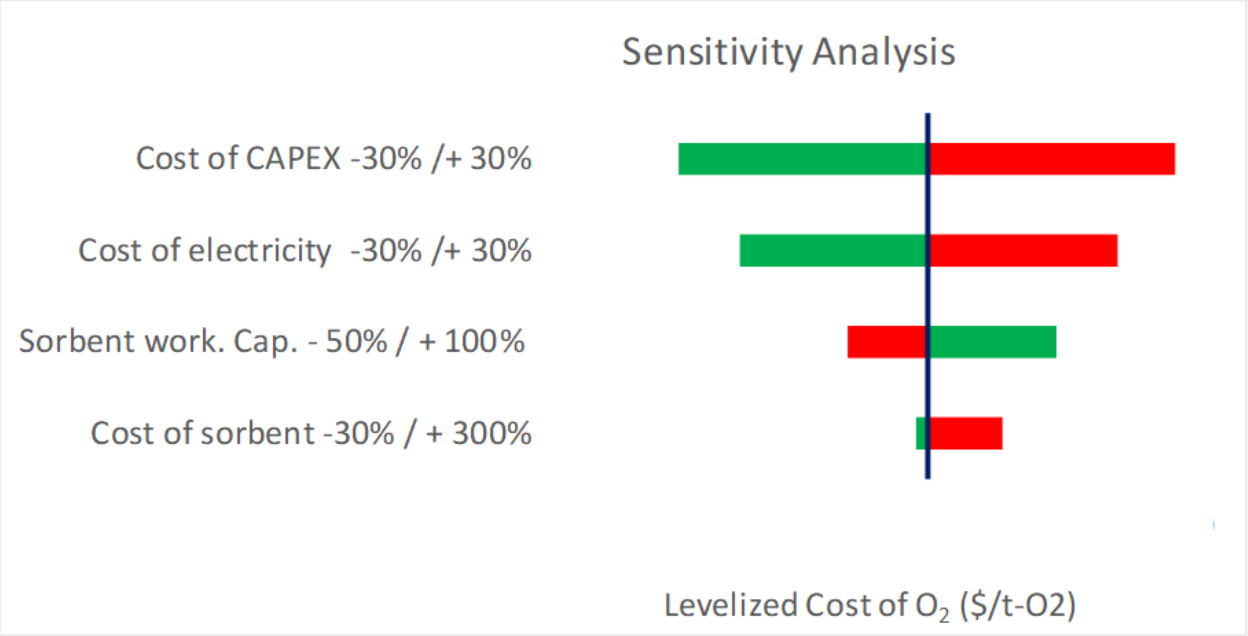
Example Parameter Set Test

Valve Sequence
1-Pressurization
2-Adsorption
3-Blowdown
4-Product Reflux
5-Evacutation



TEA Refinement

- 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 and fabricated of 10 kg/d testing system

Next step

- Integrated 10 kg/d system testing
- Refining process modeling for large scale design and cost

Future

- Focus on improving performance qualities of extrudate
- Sorbent powder properties improvement for structure formation
- 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.

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