Lab-Scale Development of a Solid Sorbent for CO_2 Capture Process for Coal-Fired Power Plants

Project Kick-off Meeting

DOE Project Manager: Steve Mascaro

DE-FE0026432

Mustapha Soukri, Ph.D.

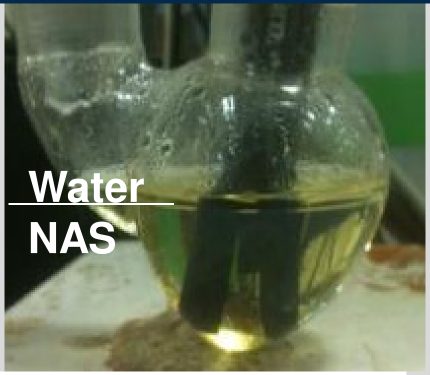
December 17, 2015

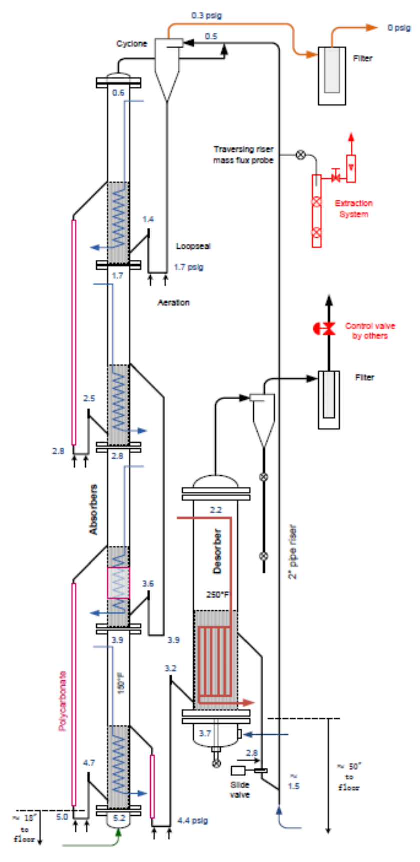
Presentation Outline

- RTI CO_2 Capture Program
- Solid Sorbent Based CO_2 Capture
- New Project
  - Project Scope and Objectives
  - Project Team & Organization
  - Project Structure
    - Budget Period 1
      - Task 1. Hybrid MOF-Based CO_2 Adsorbents
      - Task 1. Hybrid P-Dendrimer Based CO_2 Adsorbents
      - Task 1 & 2. Molecular Modeling
    - Budget Period 2
  - Project Milestones
  - Risk Management
  - Project Budget

RTI CO_2 Capture Program

Carbon Capture R&D Activities at RTI





- Over 15 years of continuous involvement in developing CO_2 capture technologies
- Broad technology portfolio with significant activity in all major areas
- Building key capabilities in materials and process development
- Growing IP portfolio
- Key industrial partnerships

Post-Combustion Capture Areas

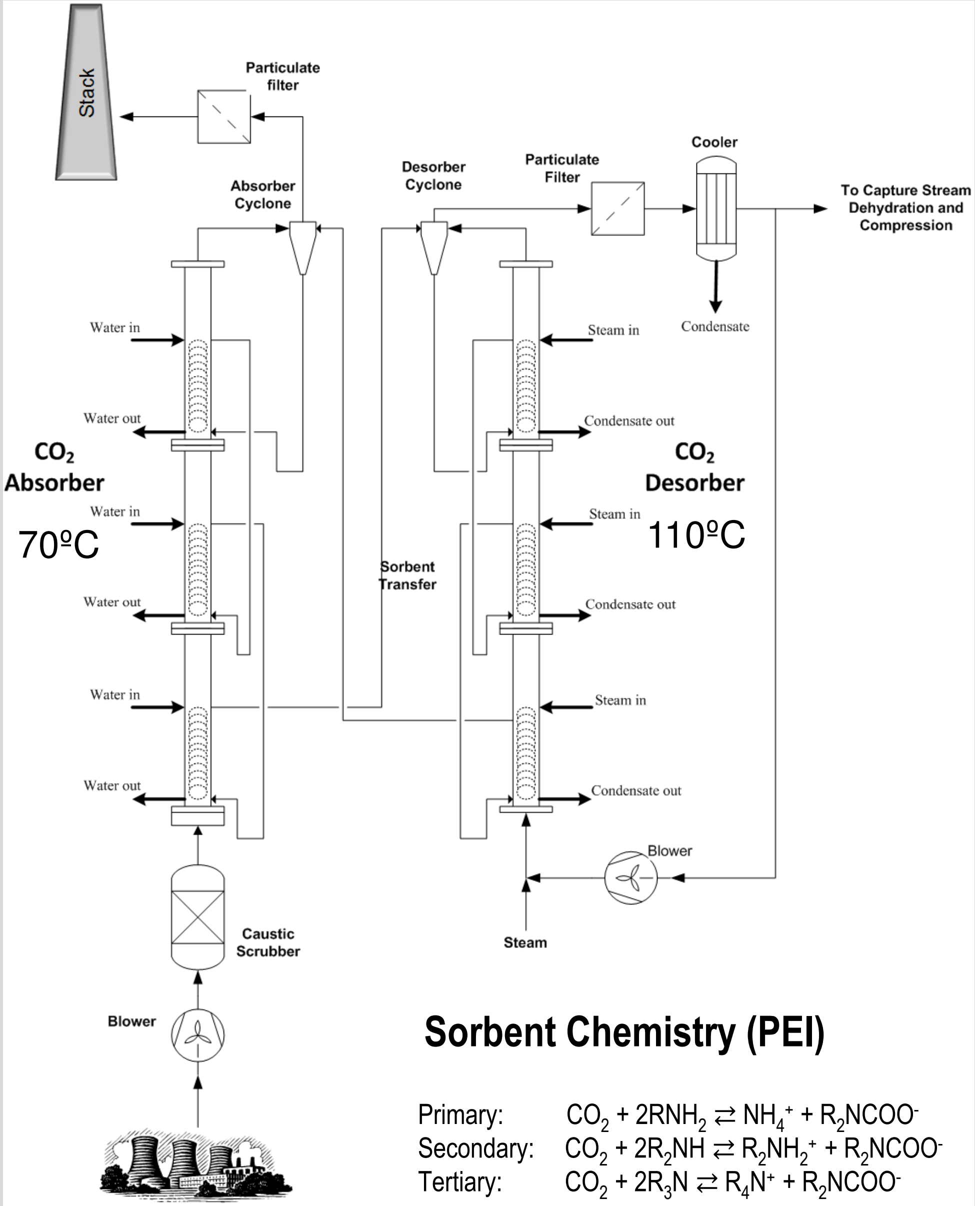
- Non-Aqueous Solvents
- Advanced Solid Sorbents
- Membrane Processes
- Hybrid Processes

Pre-Combustion Capture Areas

- Sorbents for warm CO_2 removal from syngas
- Integration of advanced CO_2 capture processes with RTI's Warm Desulfurization Process

Solid Sorbent Based CO_2 Capture (Post-Combustion)

Solid Sorbent CO_2 Capture



Sorbent Chemistry (PEI)

Primary: $CO_2 + 2RNH_2 \rightleftarrows NH_4^+ + R_2NCOO^-$
Secondary: $CO_2 + 2R_2NH \rightleftarrows R_2NH_2^+ + R_2NCOO^-$
Tertiary: $CO_2 + 2R_3N \rightleftarrows R_4N^+ + R_2NCOO^-$

Advantages

- Potential for reduced energy loads and lower capital and operating costs
- High CO_2 loading capacity; higher utilization of CO_2 capture sites
- Relatively low heat of absorption; no heat of vaporization penalty (as with aqueous amines)
- Avoidance of evaporative emissions
- Superior reactor design for optimized gas-solid heat and mass transfer and efficient operation

Challenges

- Heat management / temperature control
- Solids handling / solids circulation control
- Physically strong / attrition-resistant sorbent
- Stability of sorbent performance

Technology Development Approach

Previous Work	Current Project	Future Development		
< 2011	2011-15	2016 - 18	2018-22	> 2022
		Pilot	Demo	Commercial
		0.5 - 5 MW (eq)	~ 50 MW	

Proof-of-Concept / Feasibility

Laboratory Validation (2011 – 2013)

Economic analysis
- Favorable technology feasibility study

Sorbent development
- Successful scale-up of fluidized-bed sorbent

Process development
- Working multi-physics, CFD model of FMBR
- Fabrication-ready design and schedule for single-stage contactor

Prototype Testing (2015)

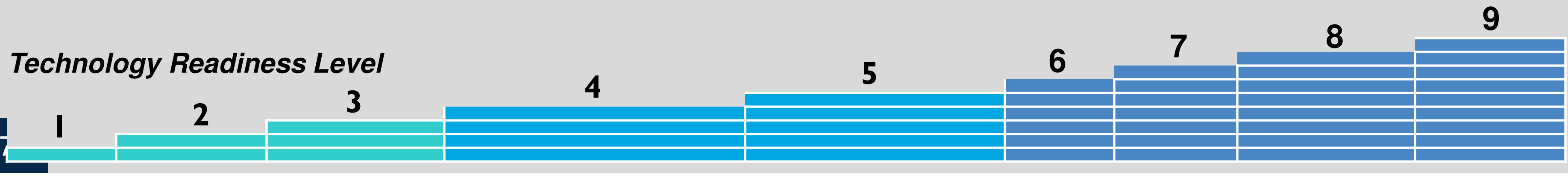
Prototype Testing
- Operational FMBR prototype capable of 90% CO_2 capture
- Parametric and long-term testing

Updated Economics
- Favorable technical, economic, environmental study (i.e. meets DOE targets)

Relevant Environment Validation (2013 – 2014)

Process development
- Fully operational bench-scale FMBR unit capable of absorption / desorption operation
- Fabrication-ready design and schedule for high-fidelity, bench-scale FMBR prototype

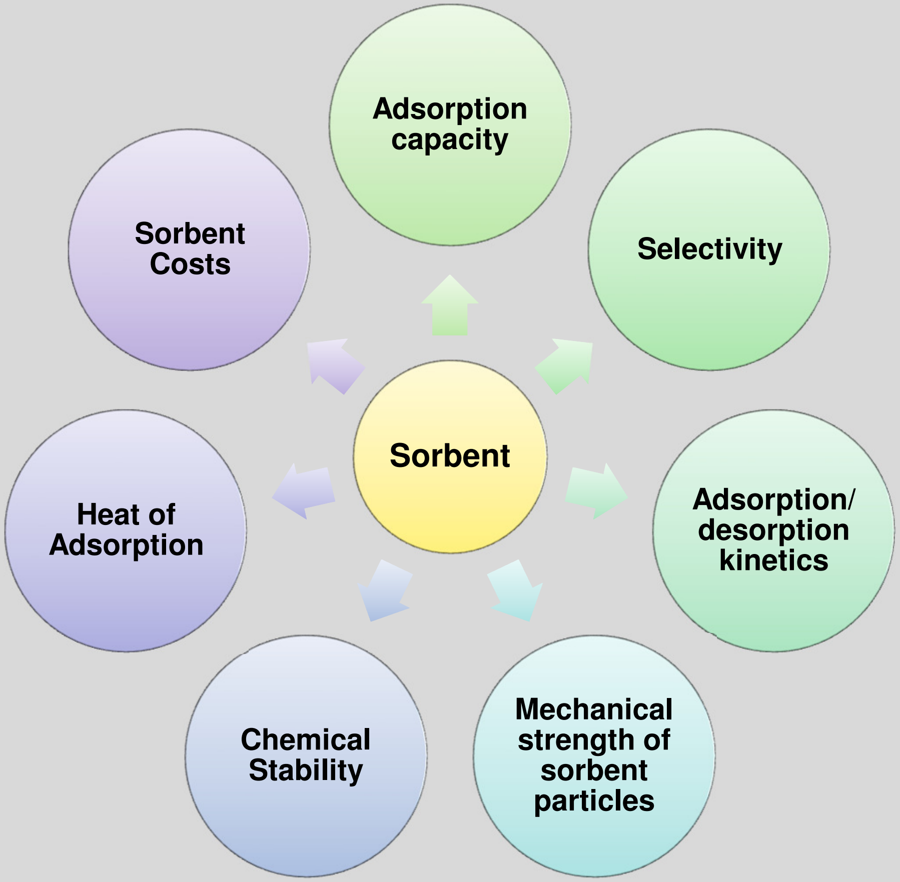
Sorbent development
- Scale-up of sorbent material with confirmation of maintained properties and performance


Technology Readiness Level

Selection Criteria for CO_2 Solid Sorbents

Develop and design CO_2 capture solid sorbent that is chemically, thermally, and physically stable over a multiple absorption/regeneration cycles and shows significant potential to meet the DOE program targets for CO_2 capture (*>90% CO_2 capture rate with 95% CO_2 purity and <30% increase in cost of electricity).*

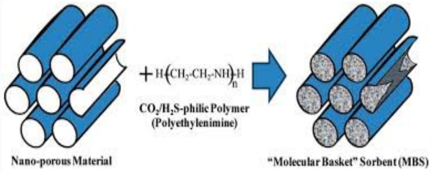
- Fluidizable material
- High CO_2 loadings, high selectivity for CO_2
  - ≥ 12 wt% CO_2 capture
- No PEI leaching or degradation
  - Thermal & oxidative stability
- Low heat of adsorption
- Acceptable density
  - Density ~ 0.6 to 1 g/cc
- Acceptable attrition resistance
  - Low makeup rate
- Economically practical
  - Low cost and easy scalability

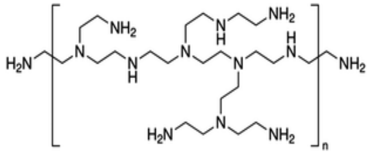


RTI’s CO_2 Solid Sorbents Development Chronology

RTI 1st Generation: Mesoporous Silica Supported Polyethylenimine (PEI)

- Good CO_2 Capture
- Good Selectivity
- Fluidizable
- Good Heat of Adsorption





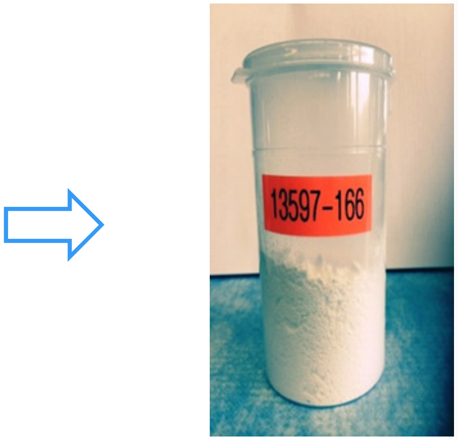
PEI

Wet Impregnation

RTI 2nd Generation: Water-Stable Sorbent (TEOS/PEI Co-Precipitation)

- Excellent CO_2 Capture
- Good Selectivity
- Water Stable
- Good Heat of Adsorption

Sol-gel method



Cement Application – Ongoing Demo in Norway

NORCEM
HEIDELBERGCEMENT Group

Objective: Demonstrate RTI's advanced, solid sorbent CO_2 capture process in an operating cement plant and evaluate economic feasibility

Norcem's Cement Plant – Brevik, Norway

Photo Source: Norcem

RTI's Lab-scale Sorbent Test Unit

Photo Source: Norcem

Phase I – *Complete*

- Performed sorbent exposure testing with real cement flue gas using lab-scale test unit
- Performed techno-economic study

Phase II – *Ongoing* (July '14 to Dec '16)

- Pilot field testing of RTI's technology at Norcem's Brevik cement plant

Lab-Scale Development of a Solid Sorbent for CO_2 Capture Process for Coal-Fired Power Plants (RTI 3rd Generation)

DOE Project Manager: Steve Mascaro

Project Details - DE-FE0026432

Funding: $1,989,415M ($1,591,532M DOE)
Period: October 2015 – September 2017

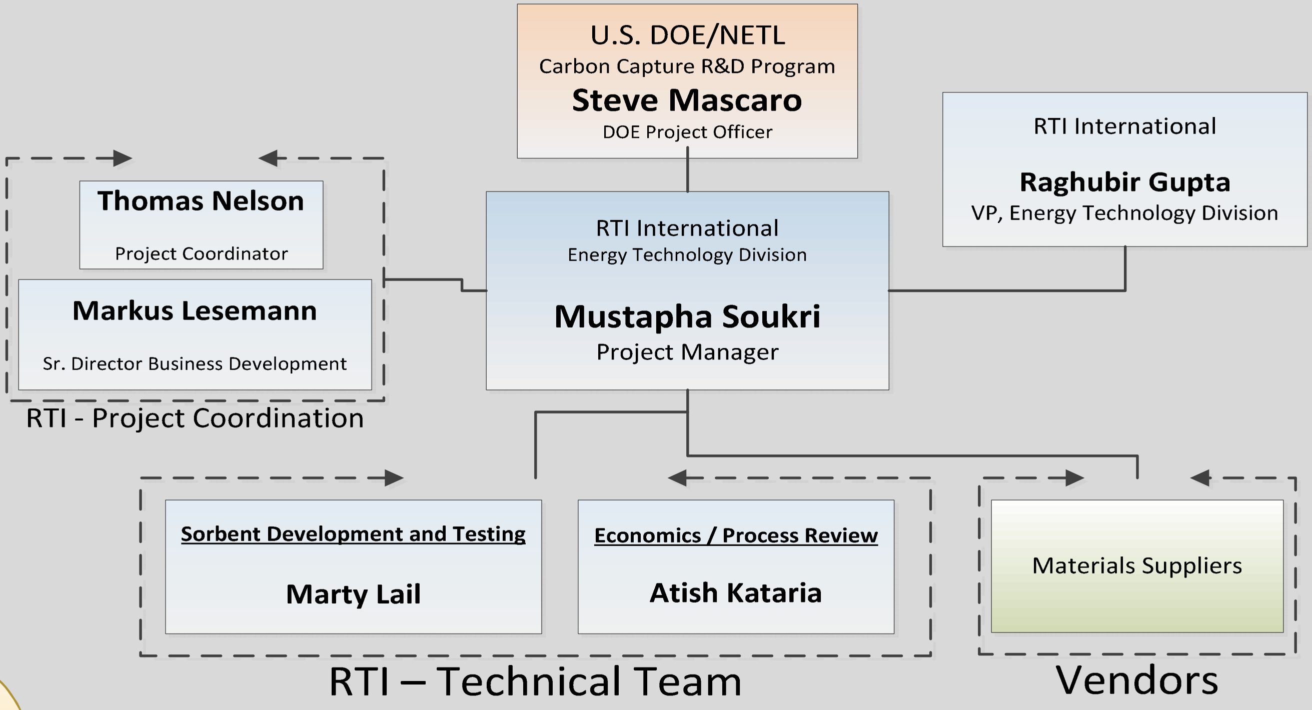
Goals/Objective:

- Develop novel 3rd generation fluidizable solid sorbents for RTI's sorbent-based CO_2 capture process:
  - Fluidizable, hybrid-metal organic frameworks (MOFs)
  - Fluidizable hybrid-phosphorus dendrimers

Proposed Project Outline:

- Design and synthesize two novel types of fluidizable CO_2 adsorbents
- Demonstrate the superior performance of these advanced CO_2 solid sorbents at the lab scale
- Evaluate the impact of flue gas contaminants such as SOx, NOx, O_2 , and H_2O on these advanced solids sorbents
- Conduct a high level techno-economic analysis

Project Team & Organization


U.S. DOE/NETL
Carbon Capture R&D Program
Steve Mascaro
DOE Project Officer

RTI International
Raghubir Gupta
VP, Energy Technology Division

Thomas Nelson
Project Coordinator

Markus Lesemann
Sr. Director Business Development

RTI - Project Coordination

RTI International
Energy Technology Division
Mustapha Soukri
Project Manager

Sorbent Development and Testing
Marty Lail

Economics / Process Review
Atish Kataria

RTI – Technical Team

Materials Suppliers

Vendors

Dr. Mustapha Soukri: Project Manager & Lead Chemist

- Strong experience in R&D in an industrial environment.
- Co-inventor of novel water stable solid sorbent (US 62/024,705)
- Leading the synthesis effort of *P*-dendrimers hybrid solid sorbent.

Dr. Marty Lail: Lead – Solid Sorbents

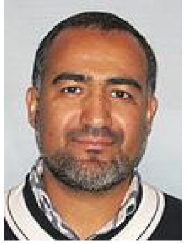
- Co-inventor of novel water stable solid sorbents as well as NASs
- Strong background and experience in the MOF synthesis and development

Dr. Atish Kataria: Lead – Process Economics

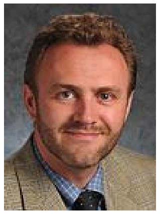
- Has lead several design and TEA evaluations
- Proficient in ASPEN Plus, Process Economic Analyzer
- Key member of RTI's 50MW syngas cleanup technology team

RTI Team


J. Zhou

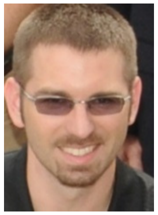

M. Soukri


R. Gupta


M. Lesemann


T. Nelson

T. Bellamy


J. Farmer


L. Perry


J. Tanthana


A. Kataria


M. Lail


P. Himanshu

TBH

Project Structure – Budget Period 1

Objective: Develop several novel hybrid solids sorbents as well as packed-bed reactor testing.

Timeframe: 10/1/15 to 9/30/16 (12 months)

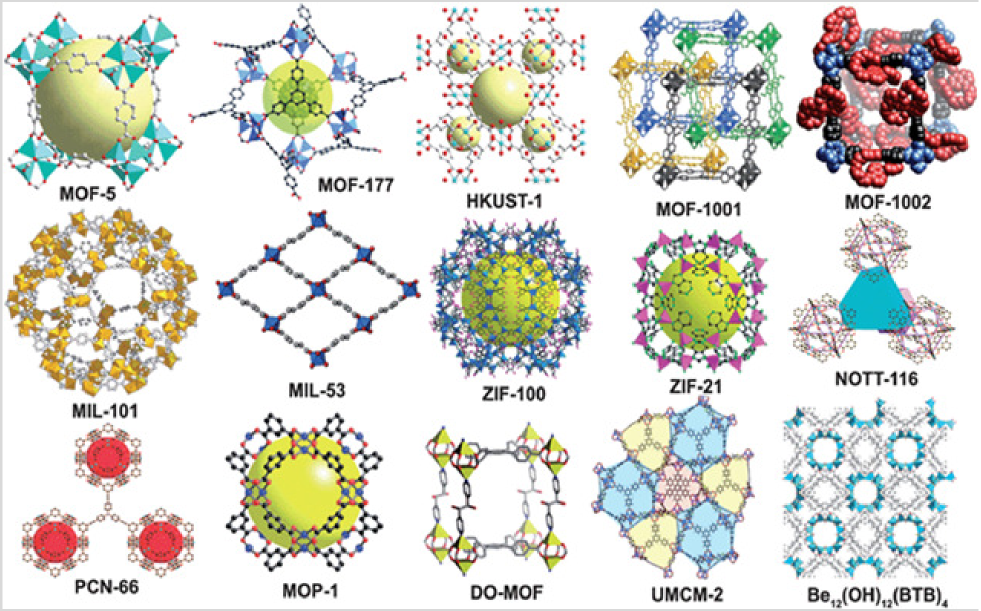
Cost: $1,104,416 M

Task	Description	Objectives / Activities
1	**Project Management and Planning**	Coordinate, manage and plan project activities that will include, monitoring and controlling of project scope, technical, budgetary and scheduling activities, project and task planning, asset management, cost tracking, progress reporting and updating Project Management Plan document appropriately
2	**Hybrid MOF-based CO_2 adsorbents**	2.1 – Hybrid MOF-based sorbents synthesis and characterization 2.2 – Hybrid MOF-based sorbents evaluation and characterization 2.3 – Molecular modeling of Hybrid MOF-based sorbents
3	**Hybrid *P*-Dendrimer-based sorbents**	3.1 – hybrid *P*-Dendrimer-based sorbents synthesis and characterization 3.2 – Hybrid *P*-Dendrimer-based sorbents evaluation and characterization 3.3 – Molecular Modeling of Hybrid *P*-Dendrimer-based sorbents
4	**Multi-cycle Performance Testing and Technical Merit Comparison**	4.1 – Multi-cycle performance testing of most promising *P*-Dendrimer-based and MOF-doped sorbents 4.2 – Preliminary sorbent production cost review

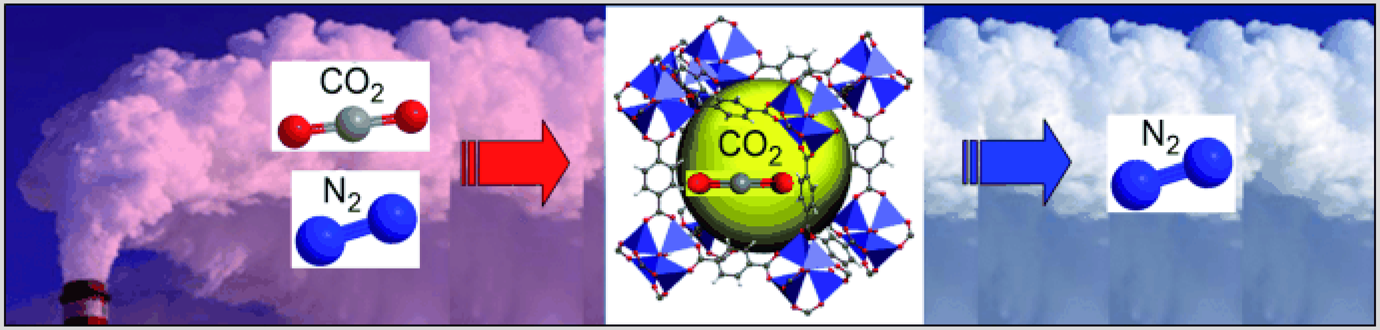
Task 1. Hybrid MOF-Based CO_2 Adsorbents

Metal-Organic Frameworks

- BET surface areas up to 6000 m^2/g
- Density around 0.4 g/cm^3
- Tunable pore sizes up to 5 nm
- Channels connected in 1-, 2-, or 3-D
- Internal surface can be functionalized
- RTI scaled up MOFs to kilogram quantities



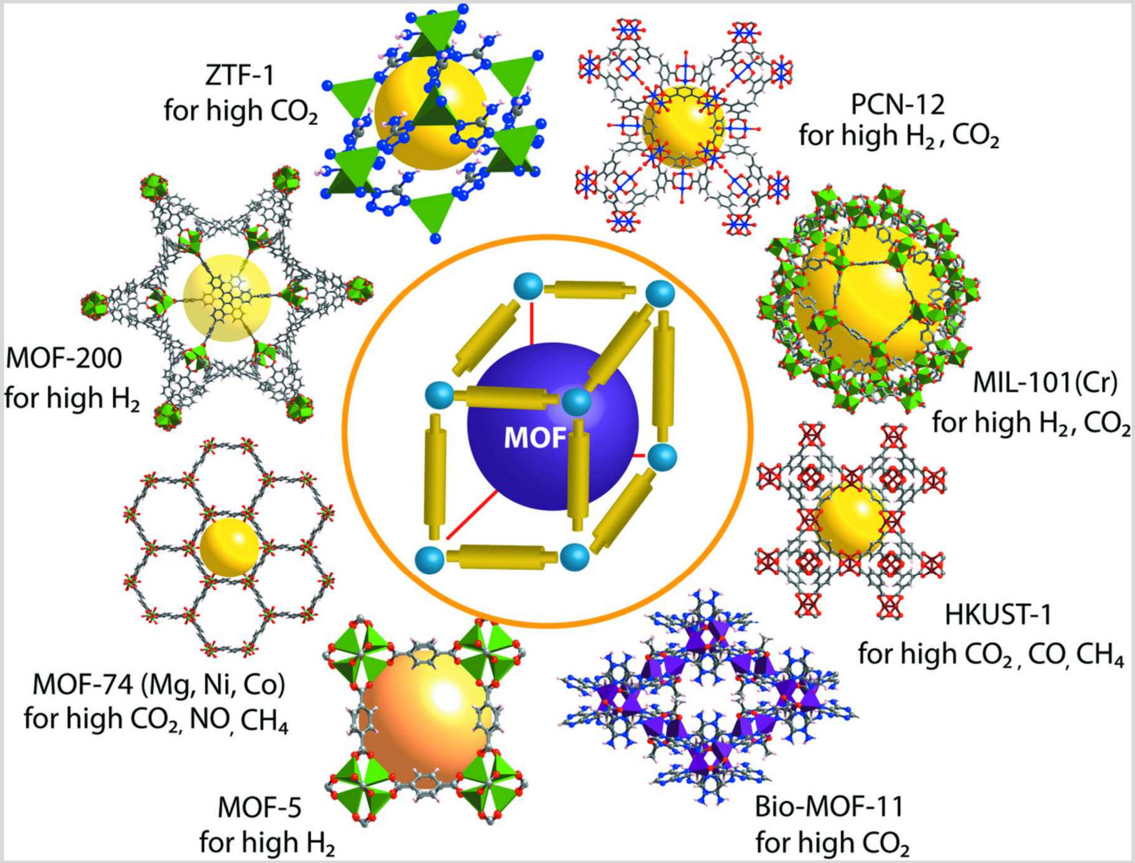
Can these high-surface area materials be used for CO_2 capture?



MOFs Designed and Engineered for CO_2 Capture

The viability of the MOFs under realistic flue stream conditions requires:

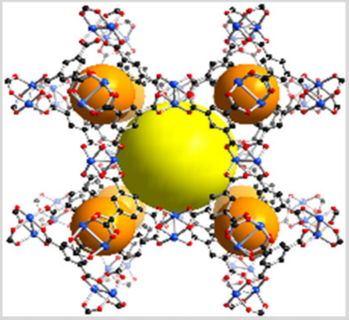
- ➢O_2 and water stability
- ➢Material of construction
- ➢High thermal stability
- ➢High selectivity for CO_2 over other components in flue gas (N_2 and O_2)



Task 1. Hybrid MOF-Based CO_2 Adsorbents

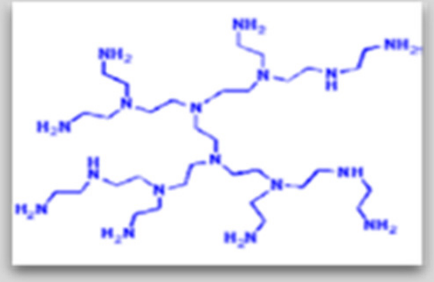
Silica

- Attrition resistance
- Fluidizable
- Low cost
- Acceptable density



MOF (HKUST-1)

- Exceptionally high surface areas
- Tunable pore sizes
- Commercially available linker



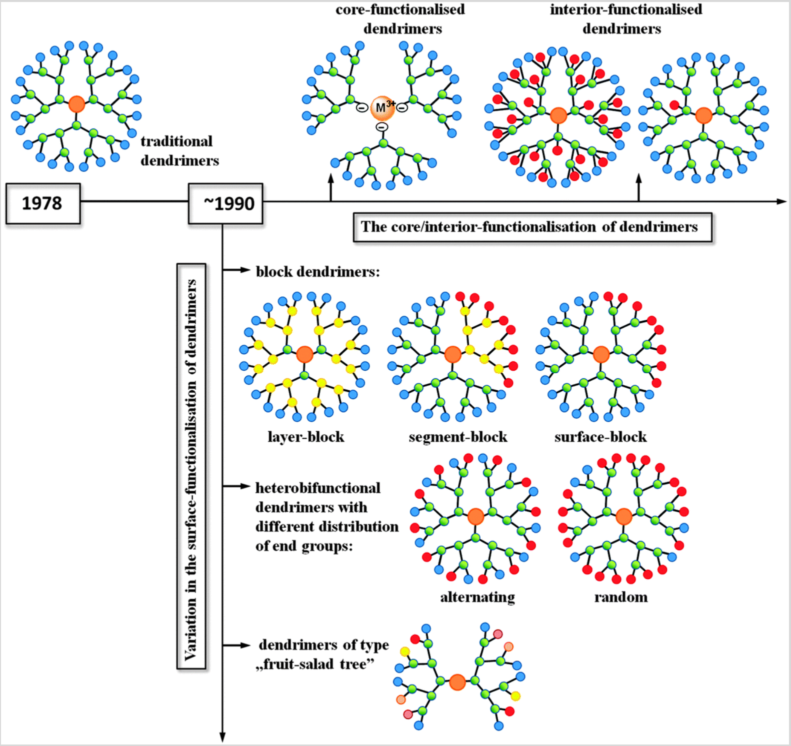
PEI

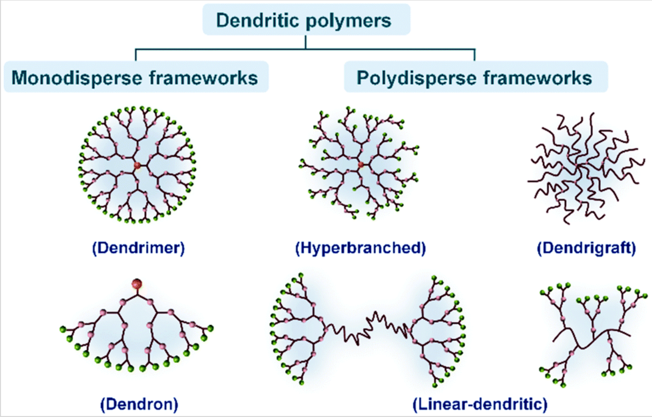
- High amine content
- High CO_2 affinity
- Relatively low cost materials

Task 2. Hybrid Phosphorus-Dendrimer-based Sorbents

Dendrimers

- Dendrimers are repeatedly branched, roughly spherical large molecules. The name comes from the Greek word, which translates to "tree”
- Vogtle laboratory in 1978 reported the first concept of branching by repetitive growth (originally named “cascade” molecules)
- In 2008 there were over 10000 scientific reports and 1000 patents dealing with dendritic structures
- They can be used in applications such as:
  - Catalysis, Sensors, Surface engineering
  - Targeted drug-delivery
  - Biomimetic material
  - Macromolecular carriers



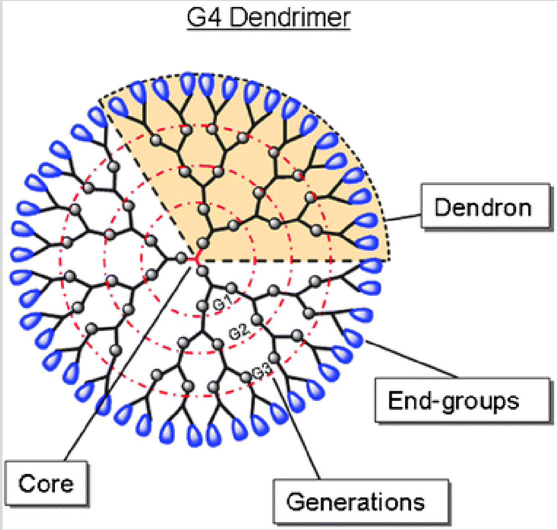


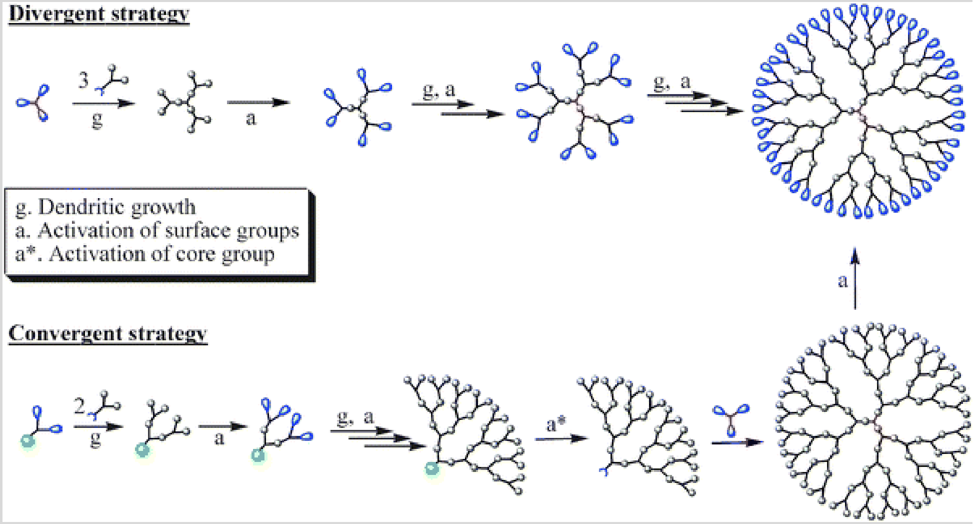
Phosphorus Dendrimers

Specificity of the *P*-dendrimers:

- Rigid scaffold due to the multiple double bond and aromatic rings forming the backbone
- Hydrophobic interior with well defined cavity as well as Well-defined spatial location of functional groups.
- Highly versatile surface function
- High thermal stability
- Low immunogenicity and toxicity

***P*-Dendrimers growth by divergent and convergent methods**

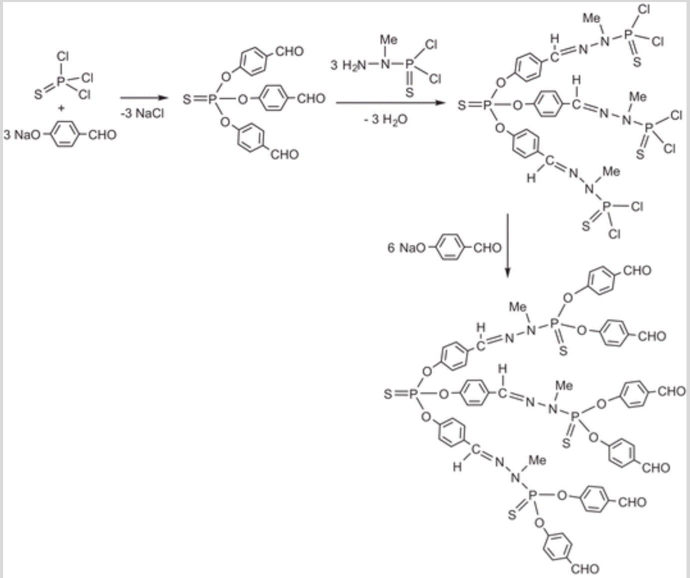


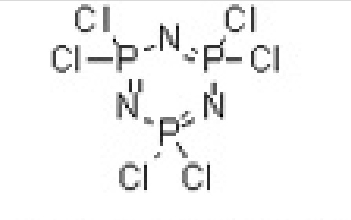


g. Dendritic growth
a. Activation of surface groups
a*. Activation of core group

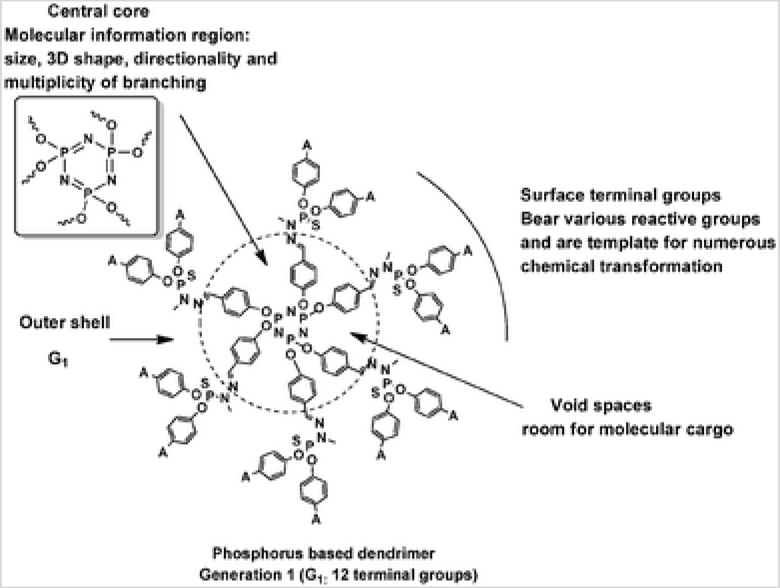
P-Dendrimers Synthesis

Thiophosphoryol trichloride





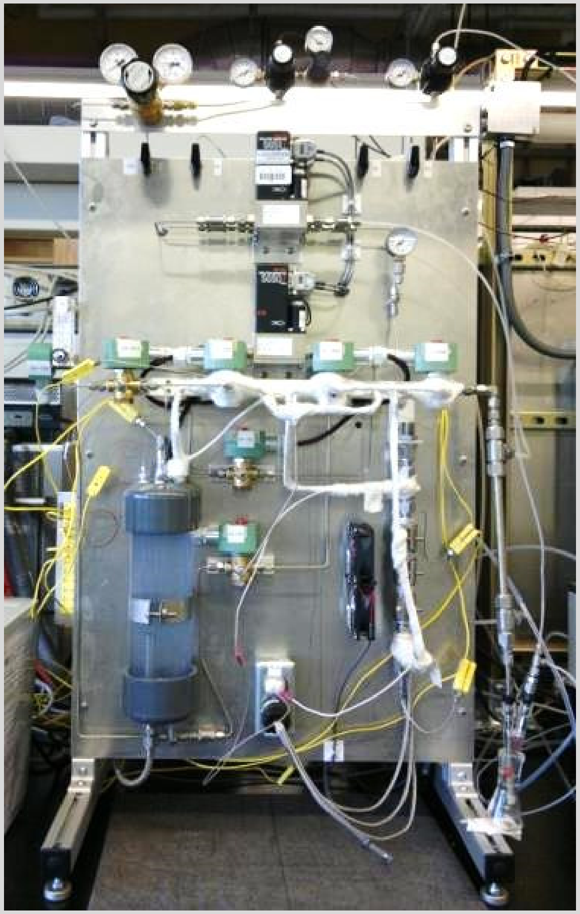
Hexachloro cyclotriphosphazine

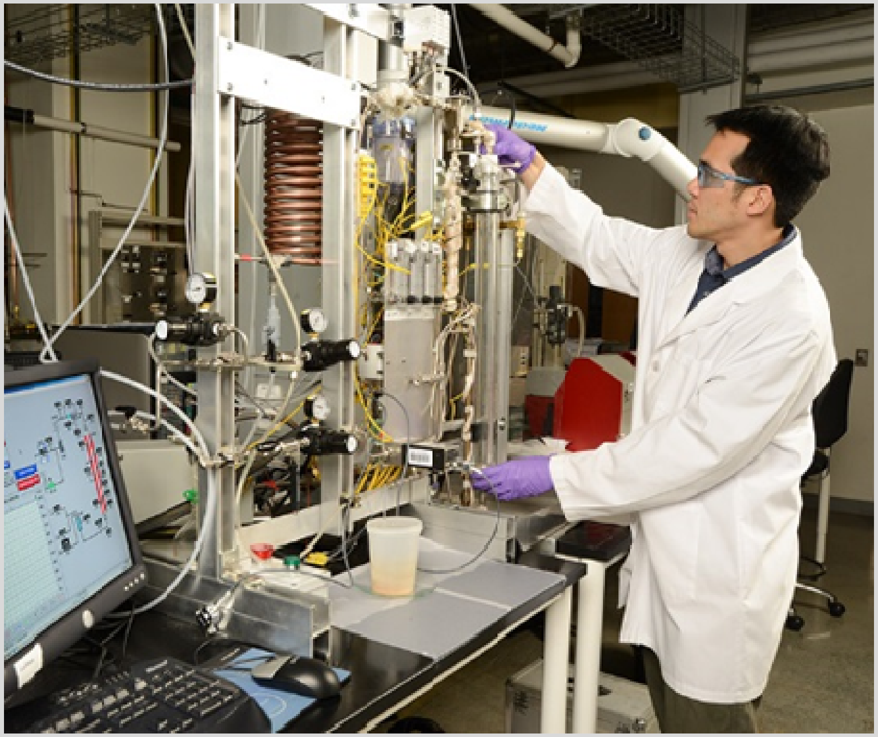


Test Equipment

Packed-bed Reactor

- Fully-automated operation and data analysis; multi-cycle absorption-regeneration
- Rapid sorbent screening experiments
- Measure dynamic CO_2 loading & rate
- Test long-term effect of contaminants





"Visual" Fluidized-bed Reactor

- Verify (visually) the fluidizability of PEI-supported CO_2 capture sorbents
- Operate with realistic process conditions
- Measure △P and temperature gradients
- Test optimal fluidization conditions

Molecular Modeling of Hybrid Sorbents

Molecular Modeling / Molecular Simulation

❑ Molecular simulation is a modeling technique which can provide information on CO_2 absorption at a molecular level.

❑ Molecular simulation of Metal Organic Framework (MOF) compounds, as they recently gained much attention for their potential in gas adsorption

❑ Molecular simulations can be used to choose a specific structure for individual applications by evaluating its uptake properties (e.g. separation, hydrogen storage, CO_2 uptake).

❑ A useful tool for:
- Quantitative predictions
- Additional molecular-level insights
- Screening

Molecular Modeling / Molecular Simulation

❑ Structures of hybrid-MOF and hybrid *P*-dendrimer sorbents

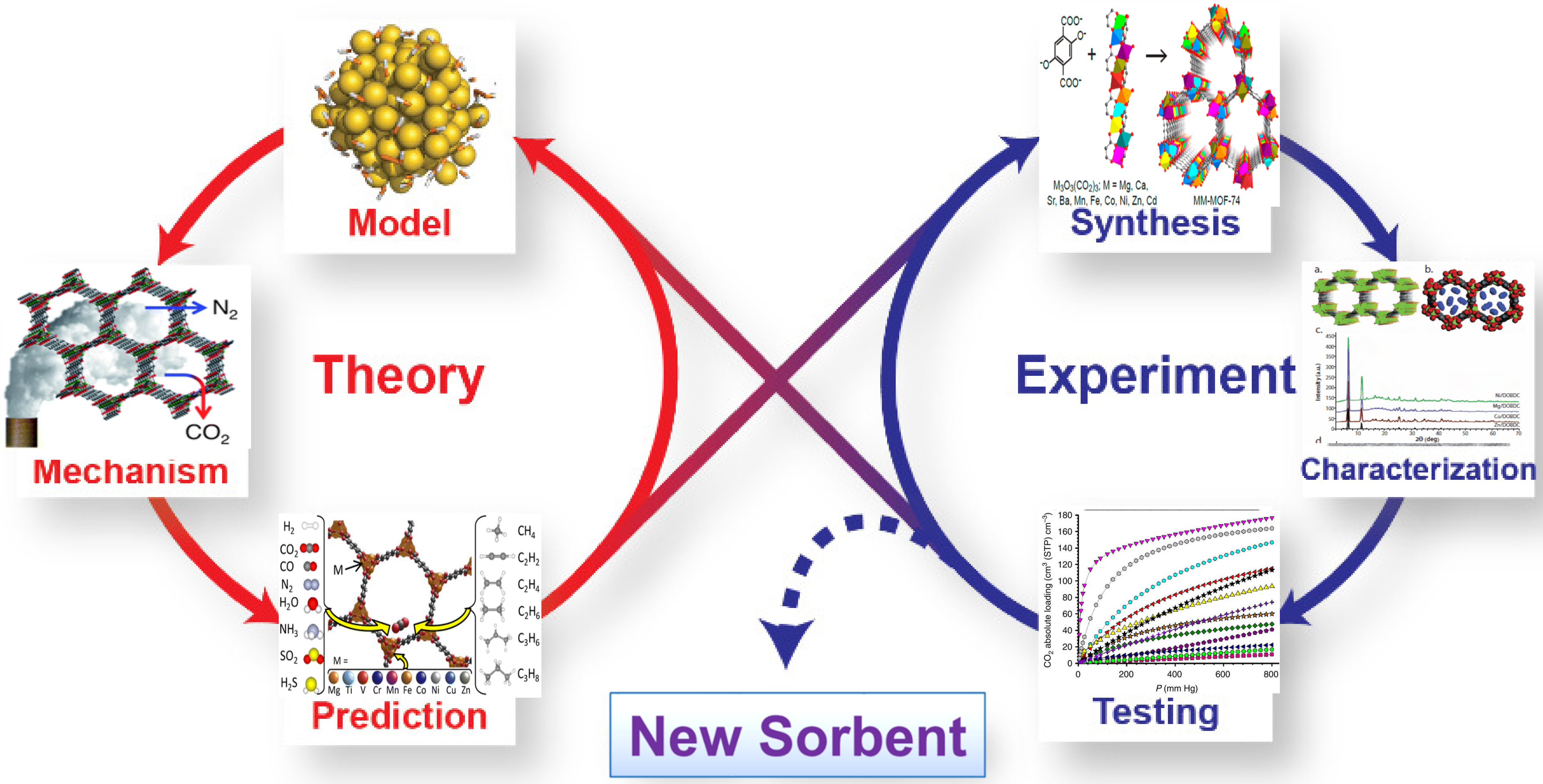
- Changes with sorption
- Changes with temperature

❑ Modeling CO_2 capture and regeneration in hybrid-sorbents

❑ Molecular level mechanism of CO_2 adsorption by identify binding sites:

- Primary and stronger binding sites
- Secondary and weaker site centers
- Specificity of CO_2 over N_2 as well as mechanism for CO_2/N_2 selectivity
- Adsorption isotherms, diffusion coefficients, detailed picture at molecular level

Molecular Modeling to Identify New Sorbent



Theory

Experiment

New Sorbent

Project Structure – Budget Period 2

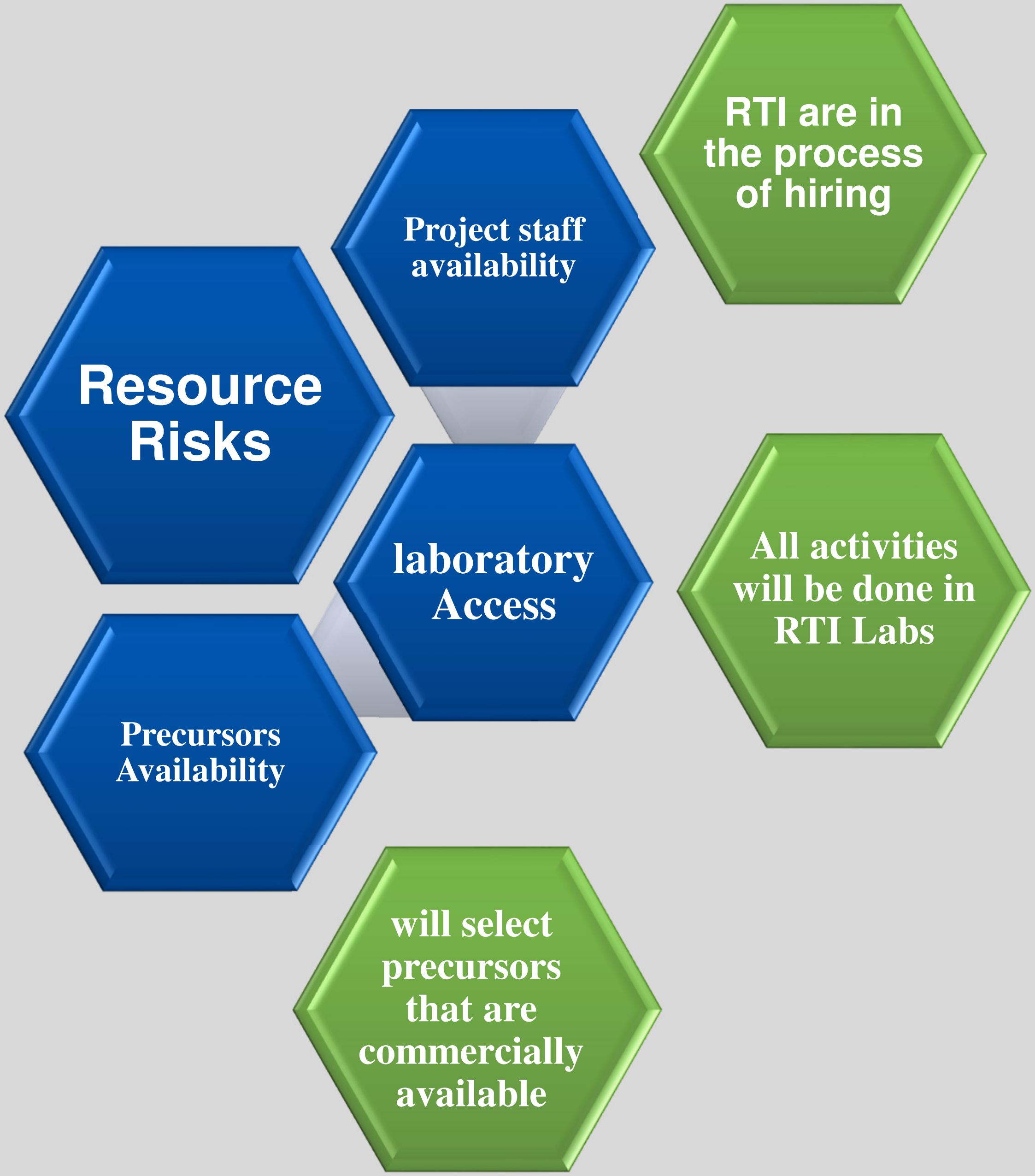
Objective: Lab-scale evaluation of the hybrid solid sorbents for CO_2 Capture

Timeframe: 10/1/16 to 9/30/17 (12 months)

Cost: $ 884,999

Task	Description	Objectives / Activities
1	**Project Management and Planning**	Continuation of BP1 project management and planning
5	**Scale-up and Testing of Selected Candidate**	5.1 – Scale up production of selected sorbent in fluidizable form 5.2 – Performance testing in lab-scale fluidized-bed reactor system 5.3 – Contaminant impact testing in packed-bed reactor 5.4 – Preliminary review of process requirements relative to conventional equipment 5.5 – Optimization of selected candidate and kilogram-scale production
6	**Preliminary Techno-Economic Analysis**	6.1 – Preliminary process design 6.2 – Preliminary economic evaluation

Risk Management – Resource Risks



Resource Risks

Project staff availability

RTI are in the process of hiring

laboratory Access

All activities will be done in RTI Labs

Precursors Availability

will select precursors that are commercially available

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