2021 Virtual Annual UCFER Review Meeting

Crosslinked Microspherical Adsorbents from Lignite-derived Humic Acid for CO_2 Capture

Project No. 06-UND-Z1-13

Award No. DE-FE0026825/S001343-USDOE

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NETL collaborator: Dr. James Hoffman

Project Manager: Dr. Carl Laird

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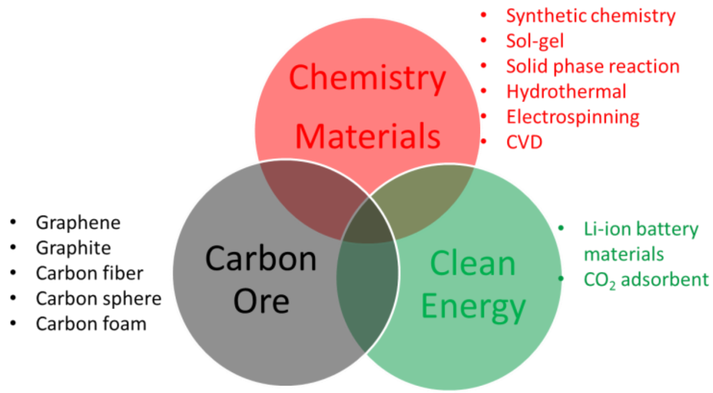
Outline

- IES Introduction
- Background
- Project overview
- Progress and Plan
- Q & A

Institute for Energy Studies (IES)

- Found in 2009
- One of eight units under CEM
- Mission: Energy Research-Education-Outreach
- Personnel (>25): Faculty, Engineers, and students
- Strong Industrial Collaboration
- Facilities
  - Materials Characterization Lab (MCL)
  - Bench and Pilot Facilities
  - Modeling and Simulation
- Degree Program
  - Energy Engineering Ph.D.
  - Energy Systems Engineering M.S. or M.Eng.



- **Use of fossil fuels in a carbon constrained environment / carbon management:**
  - Capture of CO_2 using sorbent materials
  - Novel combustion technologies
  - New products from coal
- **Recovery of valuable/critical materials:**
  - Recovery of **rare earth elements** from coal and coal by-products
  - Recovery of lithium, nickel and other valuable materials from oil field process waters
  - Rare earth value chain including recovering other critical materials
  - Co-producing graphene and rare earth elements from Leonardite and lignite
- **Building a renewable energy portfolio – moving beyond fossil fuel:**
  - Li-ion batteries (cathode/Anode material development, battery management systems)
  - Developing and integrating energy storage devices into the grid – chemical (battery); thermochemical (CLC), and others
  - Energy policy using system dynamic analysis
  - Geothermal energy development

Background-Post Combustion CO_2 Capture

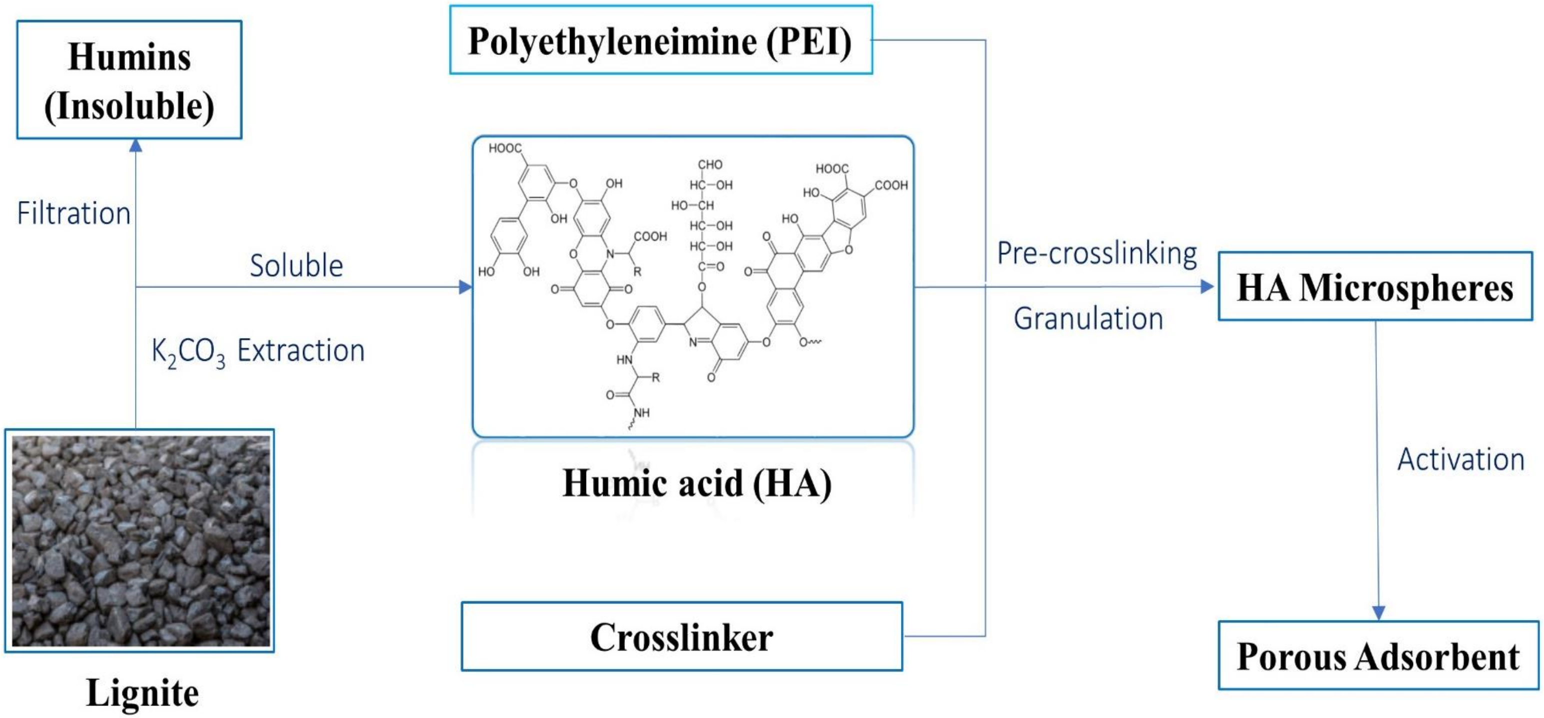
	Examples	TRL	Advantages	Disadvantages
Absorbent (chemical)	Monoethanolamine (MEA) K_2CO_3	9	The classic and most applicable approach in power plant	High regeneration energy and hazardous byproducts
Adsorbent (physical)	MOF, zeolites, activated carbon, carbon nanomaterials	7	Fit to power plant Cover wide T-P range Suitable for DAC Environmentally friendly	High regeneration energy
Membrane	Polymer, Dense inorganic	3-6	Cost-effective, flexible and reliable	maximize gas permeance & selectivity

Goal & Objectives

Goal: develop a new low-cost, multi-functional and environmentally friendly sorbent for CO_2 capture

Attributes	Target
Adsorption capacity	>2mmol of CO_2/g
Half-time of sorption	<30min
Selectivity of CO_2/N_2	>50
Cyclic CO_2 capacity loss@100th cycle	<10%
Adsorbent mass loss@100th cycle	<5%
Adsorbent purchase cost	<$5/kg
Adsorbent OPEX	<$20/kg

Proposed Technology



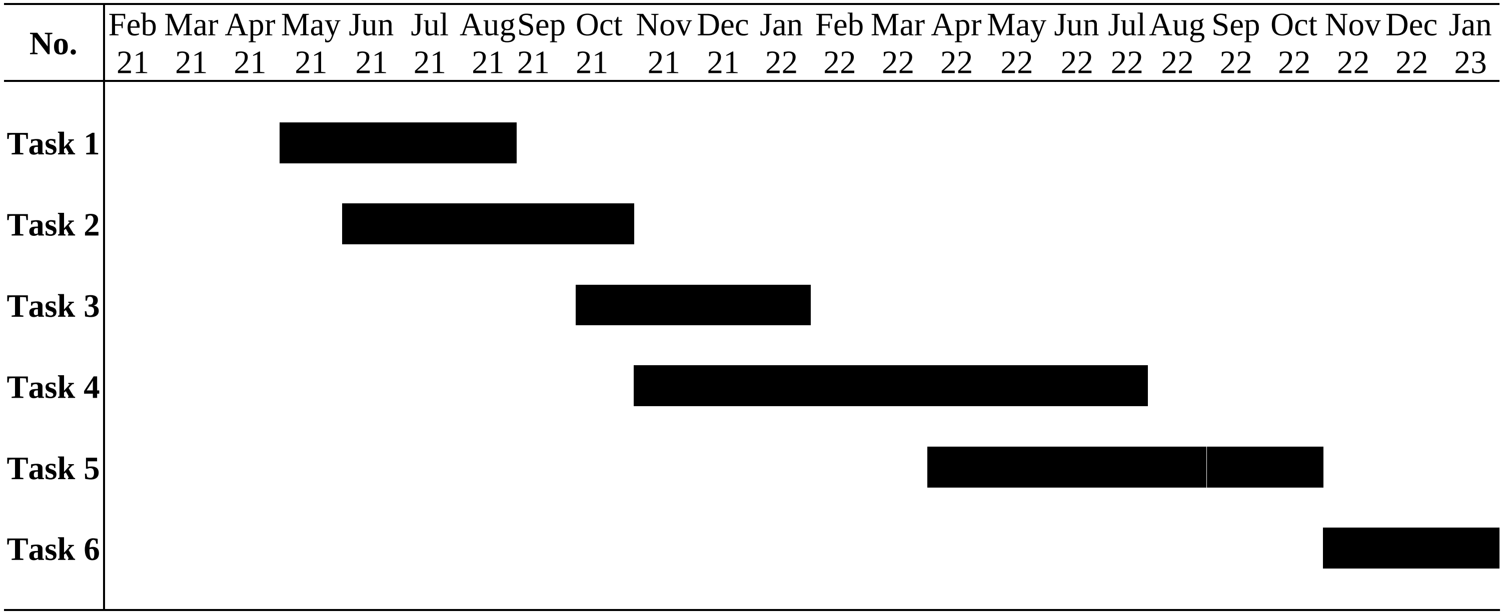
Scope of Work

- **Task 1. Extraction of HA from Lignite (Xiaodong)**
  - Established alkaline-based procedure
- **Task 2. Synthesis and characterization of HA microspheres (Xiaodong, NETL)**
  - Key performance metrics – diameter, specific surface area, K_2CO_3 and PEI loading
- **Task 3. Preparation of porous HA microspheres via activation (Xiaodong, NETL)**
  - Key performance metrics — PEI loading, specific surface area, and porosity, and pore size distribution will be evaluated as a function of temperature and pre-added K_2CO_3

Scope of Work

- **Task 4. Static test of CO_2 adsorption capacity (Junior, Hannes)**
  - Key performance metrics: adsorption capacity, amine efficiency, sorption half-time, and selectivity of CO_2, will be evaluated as a function of temperature and humidity /moisture
- **Task 5. System design and dynamic test (Junior, Hannes, NETL)**
  - The best formulation from Tasks 1 to 4 will be performed for testing in a lab-scale continuous system
  - The adsorption-desorption cycling performance (>100 cycles), including the CO_2 adsorption capacity retention and adsorbent mass loss will be evaluated
- **Task 6. Techno-economic analysis (TEA) of Process (Junior, Hannes)**
  - Include direct comparison with the benchmark technologies

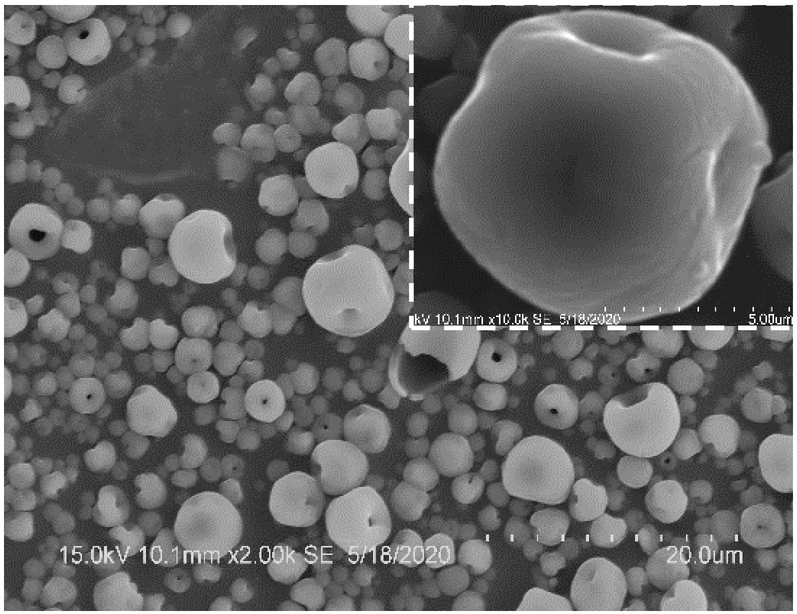
Timelines and Milestones



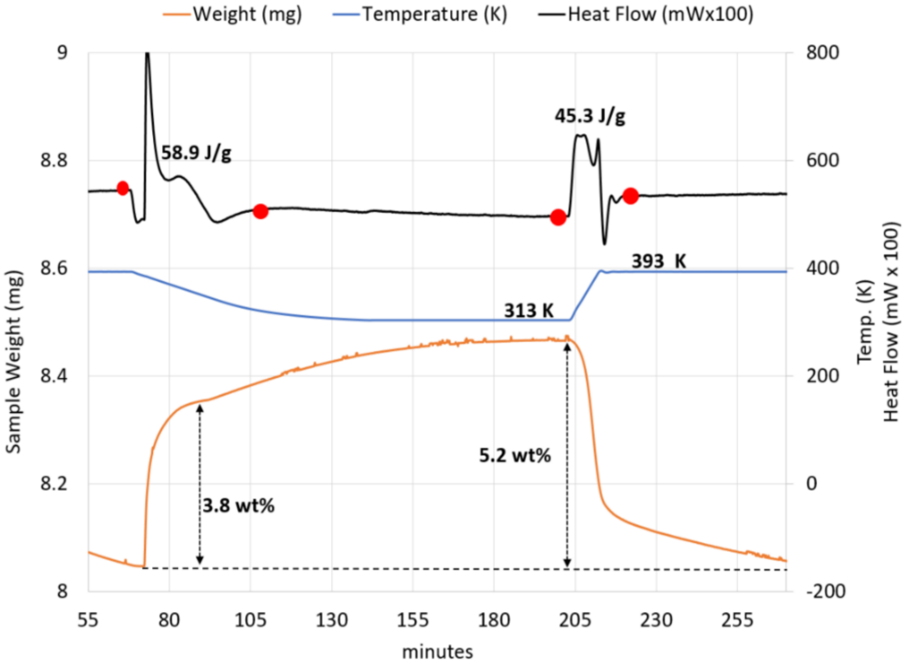
No.	Description	Planned Date
1	Completion of the refinement of HA extraction procedure	08/31/21
2	Determination of an optimized HA spray drying process	10/30/21
3	Completion of the optimization of microspheres activation process	01/30/22
4	Completion of the CO_2 adsorption capacity static tests and determination of the optimal porous HA microspheres synthetical procedure	06/30/22
5	Completion of the dynamic test on a lab-scale system and cyclic performance evaluation	10/30/22
6	Completion of the TEA and submission of the final project report	01/31/23

Preliminary Results (Pre-Award)

Adsorbent composition:
52% HA
26% K_2CO_3
23% branched PEI(Mw1200)



SEM image of synthesized sorbent



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Current Progress

- **Task 1. Extraction of HA from Lignite**

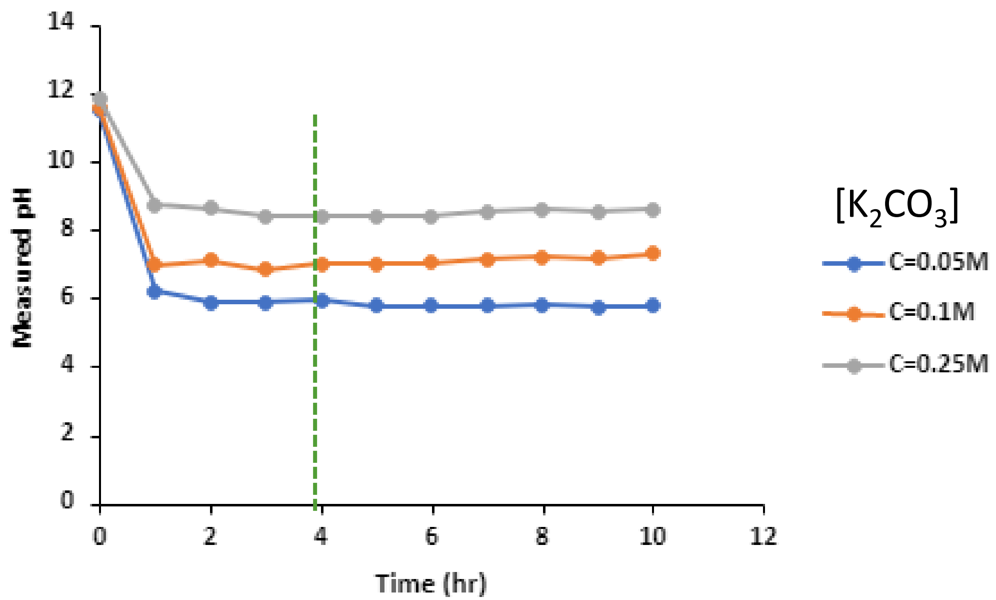
Optimize the major factors of the previous extraction procedure from Leonardite

Temperature: 47°C

Time: < 4h

[K_2CO_3]: Final pH >9.0

balanced yield and operation efficiency/cost



Current Progress

- **Task 1. Extraction of HA from Lignite**

  Run Total 18 tests to refine the secondary factors aimed for high yield

  1) Reduce particles size (not significant)

  2) Liquid: solid ratio (not significant)

  3) stirring rate (not significant)

  4) Adding KOH/NaOH (gelatinization)

  5) Different lignite Coal sources !

Test	Results
Leonardite	Yield =47%
KOH/NaOH	Gelatinized
Lignite (high ash >50%)	Yield <10%
Lignite (low ash <20%)	Yield= 38.6%

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Current Progress

- **Task 2. Synthesis and characterization of HA microspheres**

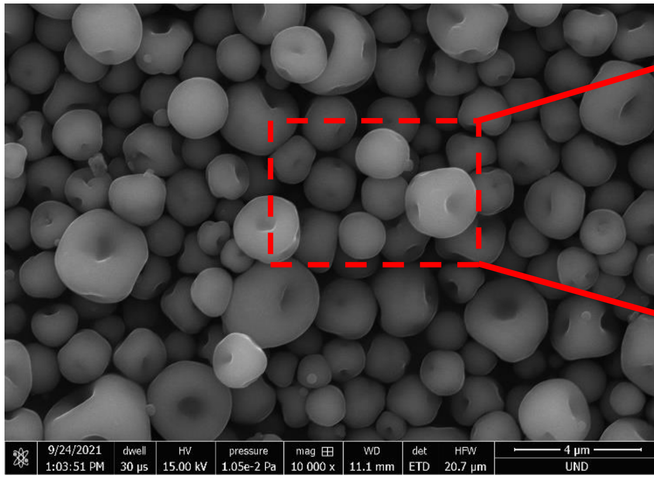
We completed 16 experiments on the synthesis, the characterization is ongoing

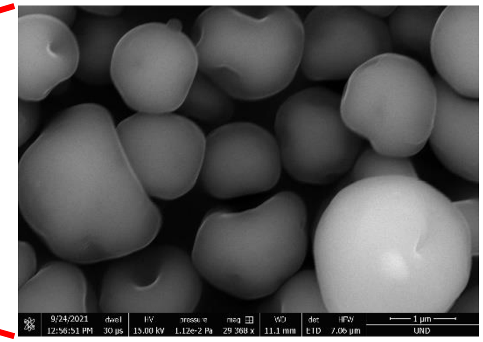
[K2CO3]	PEI percent	SD pump speed	SD temperature	CO_2 uptake %	Yield	BET	Cost
0.1	0	15	175				
0.1	20	25	195				
0.1	30	35	215				
0.1	50	45	235				
0.2	0	25	215				
0.2	20	15	235				
0.2	30	45	175				
0.2	50	35	195				
0.3	0	35	235				
0.3	20	45	215				
0.3	30	15	195				
0.3	50	25	175				
0.4	0	45	195				
0.4	20	35	175				
0.4	30	25	235				
0.4	50	15	215				

Current Progress

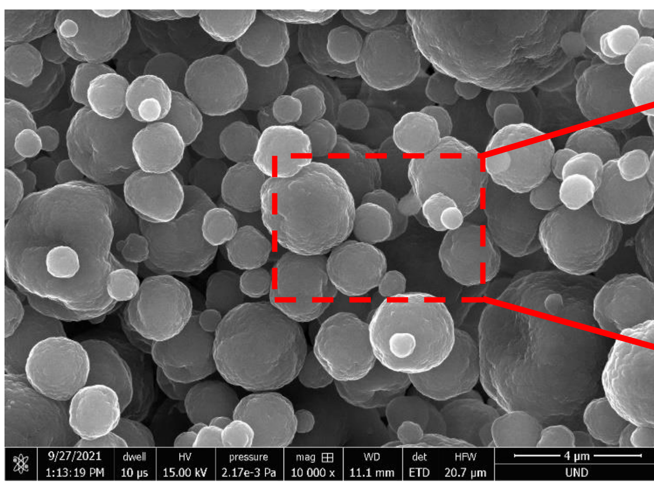
- **Task 2. Synthesis and characterization of HA microspheres**

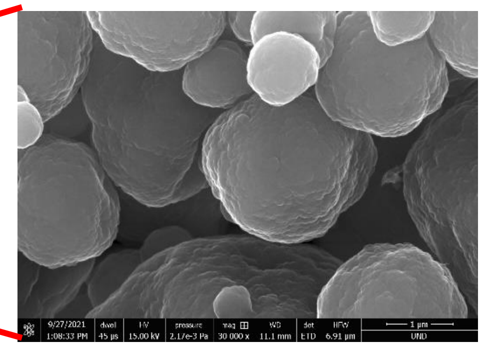
<u>DoE test 1</u>
0%PEI





<u>DoE test 2</u>
20% PEI

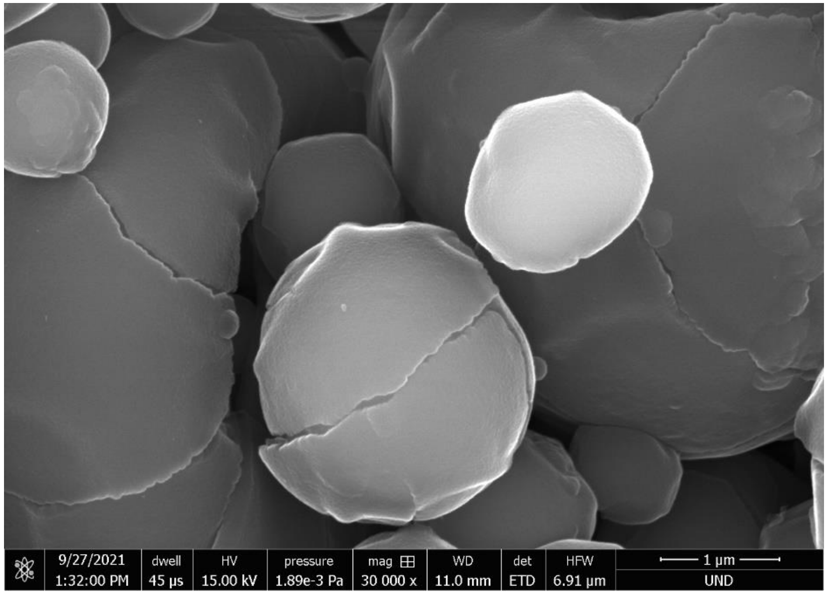




Current Progress

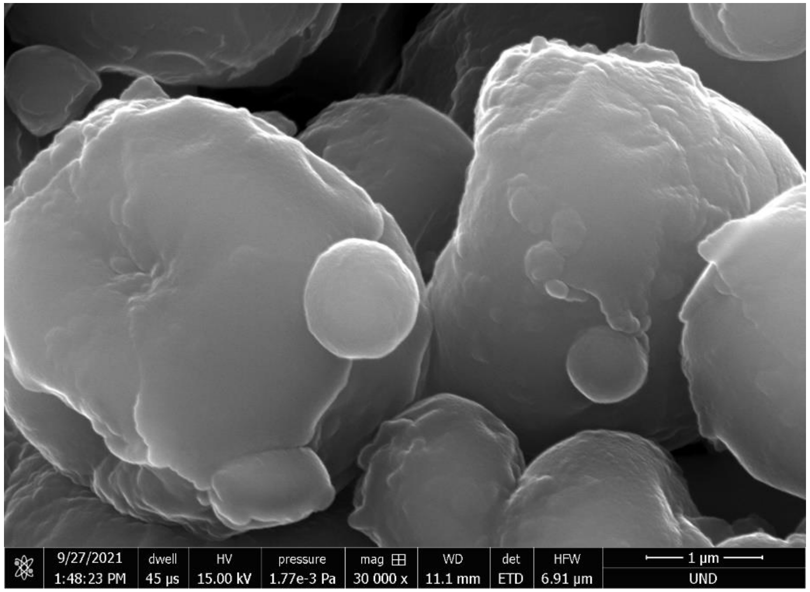
- **Task 2. Synthesis and characterization of HA microspheres**

T=215°C



DoE test 5: [K2CO3]=0.2M

T=235°C

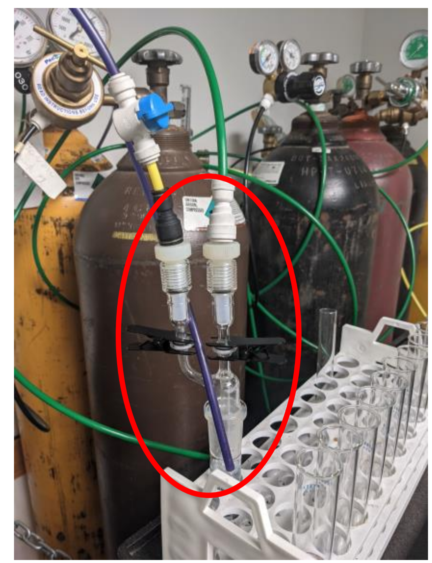


DoE test 9: [K2CO3]=0.3M

Current Progress

- **Task 4. Static test of CO_2 adsorption capacity**
  - Linseis TGA: moisture generator but requires major maintenance to correct the baseline measurement issue.

  - We switched to repaired SDT Q 600 TA instrument and ran couple of tests using a house-made humidifier



<u>CO_2 humidifier</u>

Current Progress

- **Task 4. Static test of CO_2 adsorption capacity**

Selectivity ?

N_2/CO_2

H_2O/CO_2

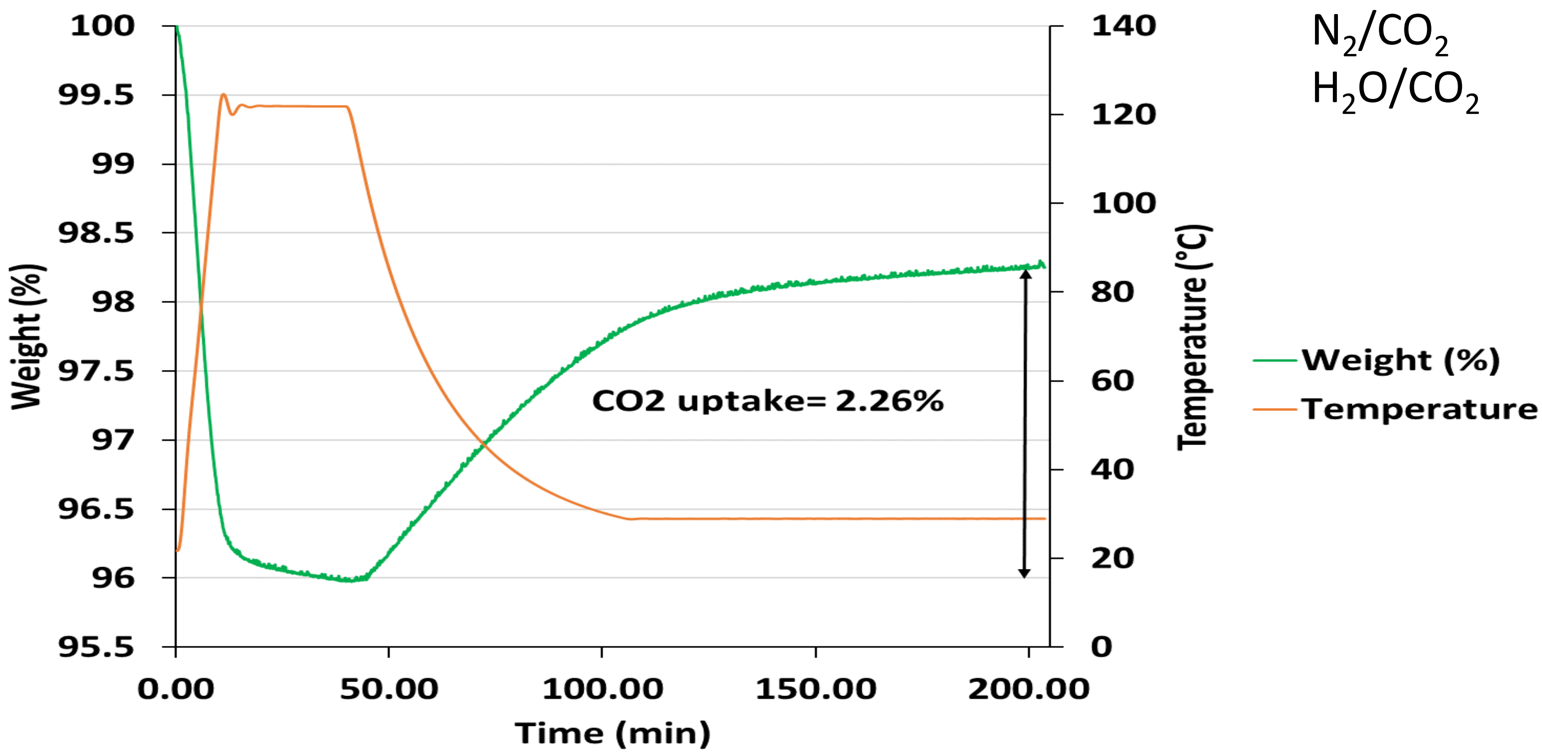


Figure 1: Adsorption process of humid CO2, DoE test 1 preparation conditions: $[K_2CO_3]$=0.1M, PEI=0%, spray dry conditions (DoE table).

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Current Progress

- **Task 4. Static test of CO_2 adsorption capacity**

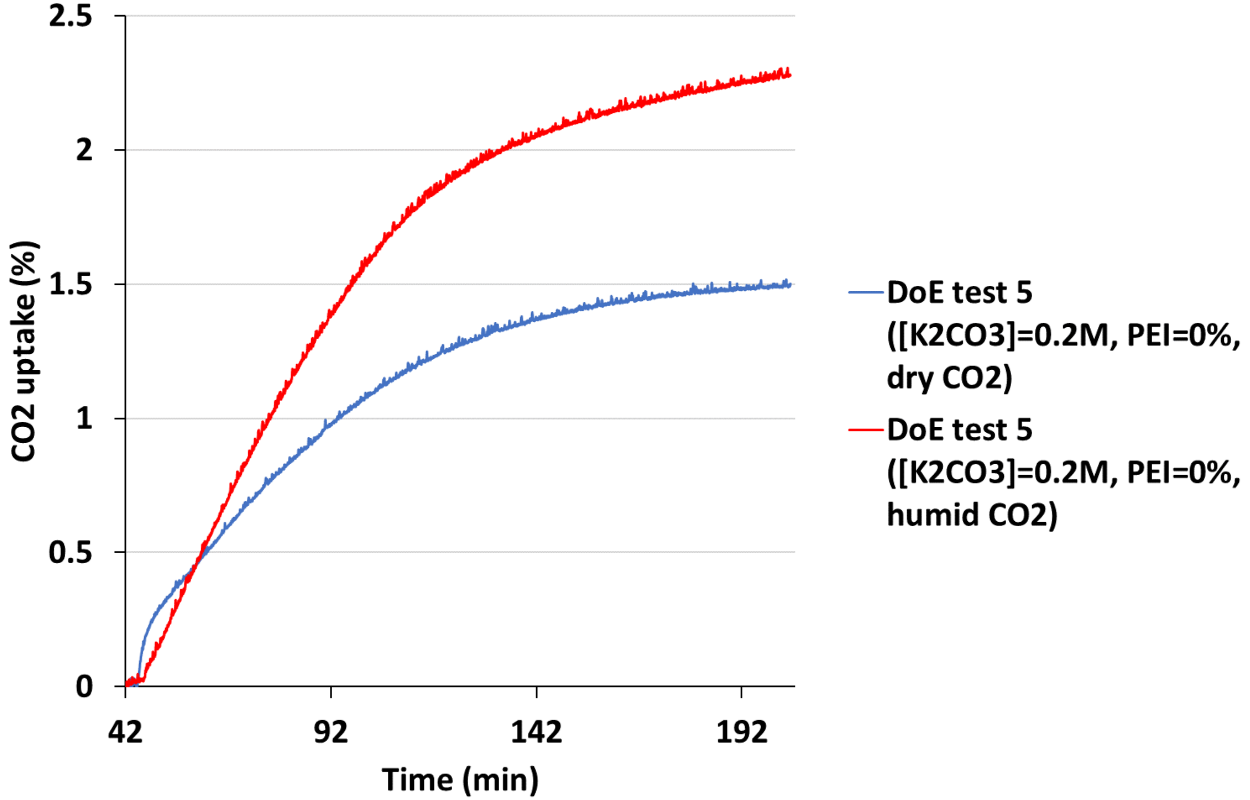

Figure 3: Effect of moisture on CO_2 uptake

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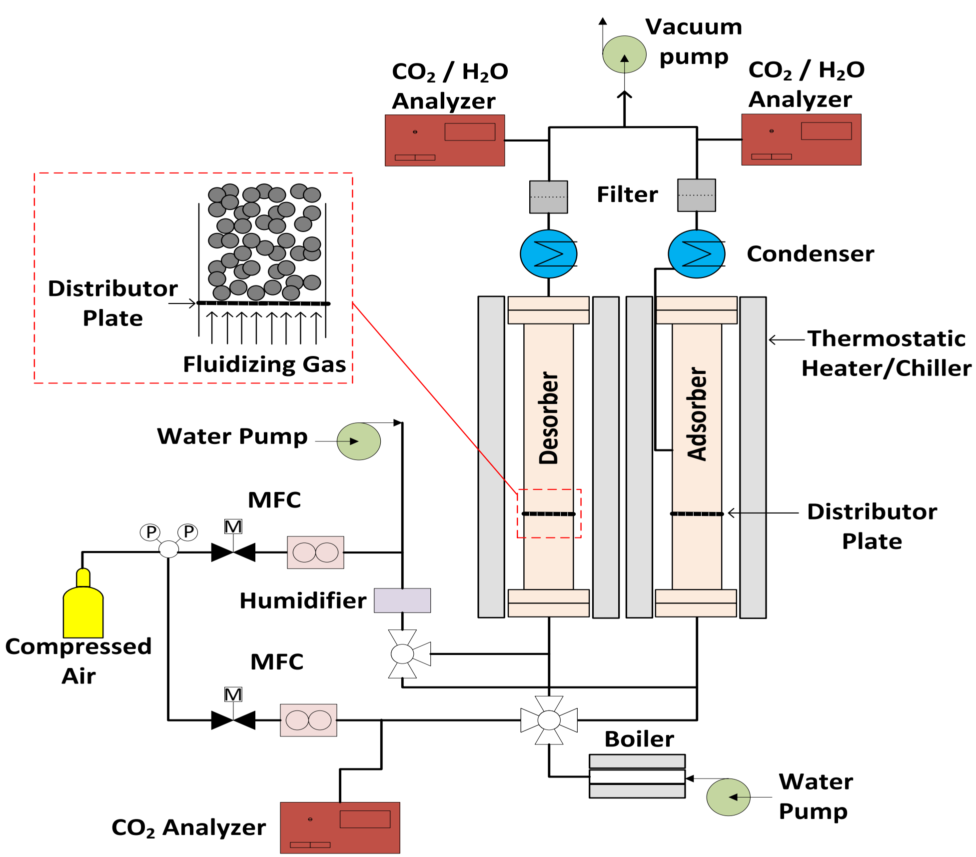
Bench-Scale CO_2 Test System



Schematic (left) and picture (right) of existing bubbling bed test system at UND

Collaboration with NETL via Dr. James Hoffman (MEM/ECE)

- Regular meetings: kick-off, monthly, annual UCFER review meeting
- Possibility materials characterization support
- Possibility of advising students

University of North Dakota (06-UND-Z1-13)

NETL RIC POC: James Hoffman
TDIC Task Monitor: Carl Laird
CRADA: TBD
Relevant NETL Core Competency: MEM/ECE

NETL Resources to Support Collaboration:

- Consultation/meetings/advisory role up to 0.05 FTE. Possibility of materials characterization support at the discretion of NETL which will be determined during the execution phase of the project. Possibility of co-advising students and/or student exchange which will be determined during the execution phase.

Summary and Next Plan

- In Task 1, the optimization of the HA extraction procedure is completed. A good yield (38.6%) was achieved with the optimal procedure.
- In Task 2, a total of sixteen HA microsphere samples were prepared. The characterization and testing are ongoing. We may further optimize the adsorbent properties such as morphology, size and size distribution, and porosity.
- In Task 3, we will start preparing the porous HA microspheres adsorbent via activation.
- In Task 4, we will continue to optimize the CO_2 adsorption-desorption testing procedure and complete the testing of the sixteen samples, and samples produced in Task 3.
- Task 5 System design and dynamic test
- Task 6 Techno-economic analysis of process

Acknowledgement

- **Sponsors**
  - DOE UCFER program
  - NACoal

- **Collaborators**
  - Dr. James Hoffman (NETL)
  - Dr. Carl Laird (NETL)
  - Dr. Gerard Goven (NACoal)

- **Students**
  - Bellal Abdelmalek
  - Xi Zhang

Questions?