Modular Processing of Flare Gas for Carbon Nanoproducts

DOE Project Award Number: DE-FE0031870

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Theodore Champ, Andrew Broerman – Forge Nano (Thornton, CO)
Colin Lobo – NRMCA (Alexandria, VA)

U.S. Department of Energy

National Energy Technology Laboratory
2021 Carbon Management and Oil and Gas Research Project Review Meeting
August 2021

Presentation Outline

- Technical Status
  - Impact
  - Goals
  - Approach
  - Progress
- Accomplishments to Date
- Lessons Learned
- Synergy Opportunities
- Project Summary

Technical Status: Potential Impact

Sequestering of Flare Gas

- CH_4 is the main component of natural gas, an abundant energy resource
- In 2019, over 500,000 MMcf of natural gas was vented or flared in the US[1]
- Natural gas wells exhaust in <5 years, making pipelines a poor solution.
- A modular process to react methane to value-added CNF product 'sequesters' carbon from CH_4 as a solid and can be used for multiple well sites.

CNPs for high performance concrete

- CNPs: instead of separating CNPs from catalyst/silica fume, use combined product as a crack-bridging additive in concrete
- Silica is already added to concrete to improve its properties
- Cement production accounts for 8% of global CO_2 emissions[1]
- Increasing the service life of concrete structures using optimized mixtures using a more economical CNF product

[1]U. S. E. I. Natural Gas Gross Withdrawals and Production.

[2]Johanna Lehne, F. P. (2018). *Making Concrete Change Innovation in Low-carbon Cement and Concrete*.

Technical Status: Project Goal

Develop a modular unit that will utilize a one-step chemical vapor deposition (CVD) process to grow carbon nanoproducts (nanoparticles and nanofibers) (CNPs) during natural gas decarbonization. A low-cost and scalable process for producing CNPs will be demonstrated at a minimum 25% Investors Rate of Return (IRR).

Develop the introduction of the carbon nanoproduct into ultra-high performance concrete (UHPC), providing a value-added product for the construction industry. The experimental study is applied to establish the cement design relationships to hydration, cracking, and ductility.

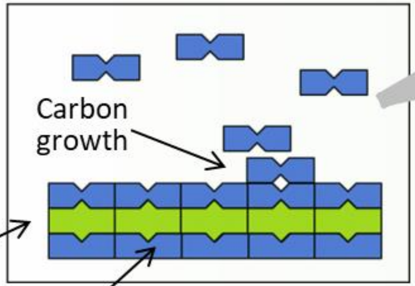
Technical Status: R&D Approach

Research

1 **Methane Decarbonization Development for Carbon Nanoproducts Production (CU, PI)**

Low cost ALD

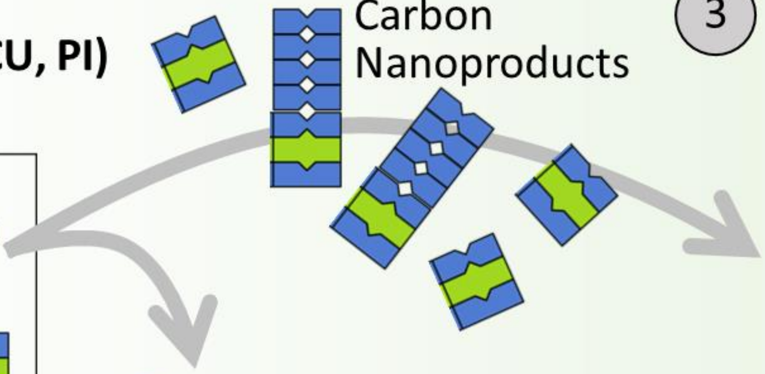
Addresses controlled carbon deposition with high conversion



Ad-atom Fe, Fe/Ni, Fe/Co metal nanocatalysts

Silica fume support

- T, P, GHSV, kinetics and growth
- Typical associated gas composition



H_2/NG

Indirect Heating for Decarbonization

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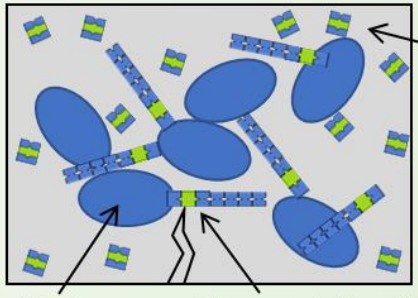


Dispersed Nanoparticles
- create a dense concrete
- increase flowability
- maximize concrete displacement with nanocarbon product

Concrete binder C-S-H grains

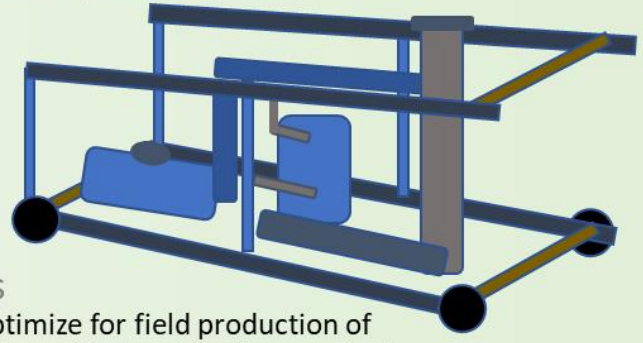
Dispersed Nanofibers Arrest cracks to increase toughness

2 **Engineering Design of Modular Unit (Forge Nano/CU)**

Development

- Target production scaling challenges & concrete utilization scaling
- Review technical developments with Forge Nano and NRMCA consultants

4 **Construction (CU) and Operation (Forge Nano) of Modular Unit**



Optimize for field production of value-added nanocarbon product

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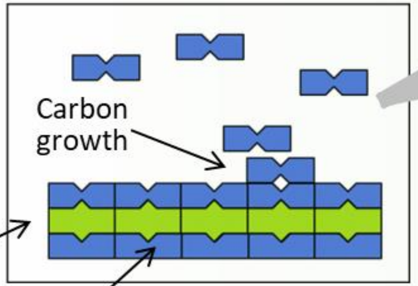

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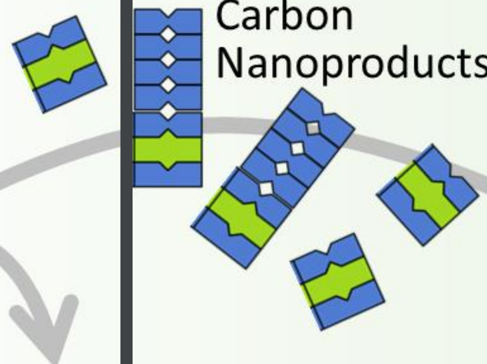

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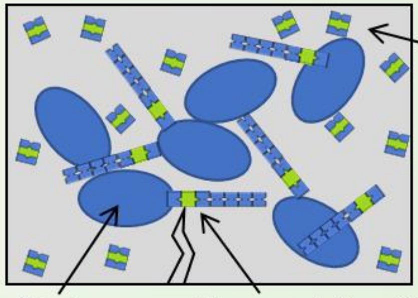

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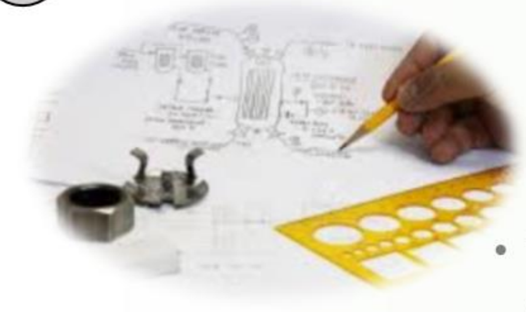

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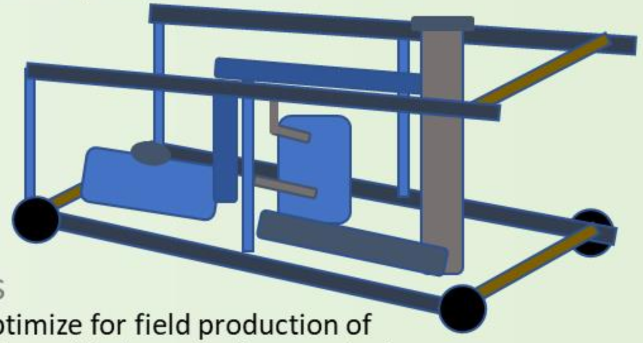
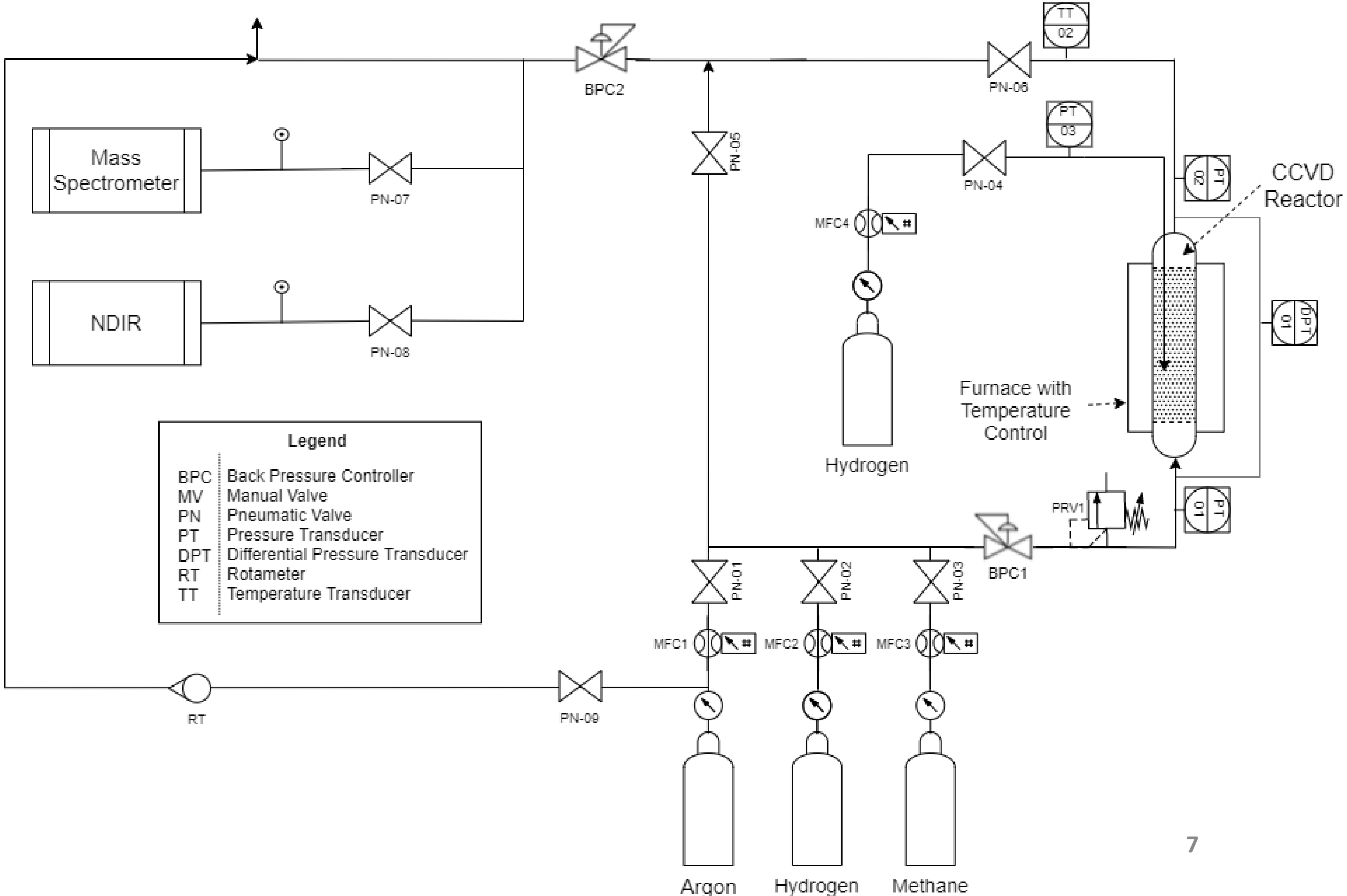


Optimize for field production of value-added nanocarbon product

Technical Status: Fluidized Bed Reactor Modification

$$CH_4 \rightarrow C + 2H_2 \qquad \Delta H = 74.85\ \text{kJ/mol}$$

Key Process Parameters	
Catalyst ALD fabrication	Ex-situ
Catalyst Support	Silica fume
Catalyst Metal	Bimetallic (e.g, Fe/Co, Ni/Co, Fe/Ni etc…)
Pressure Range	400 – 500 psig
Temperature Range	500 – 800°C
Scale-up	Modular process
Carbon Nanoproduct Application	Ultra-high performance concrete



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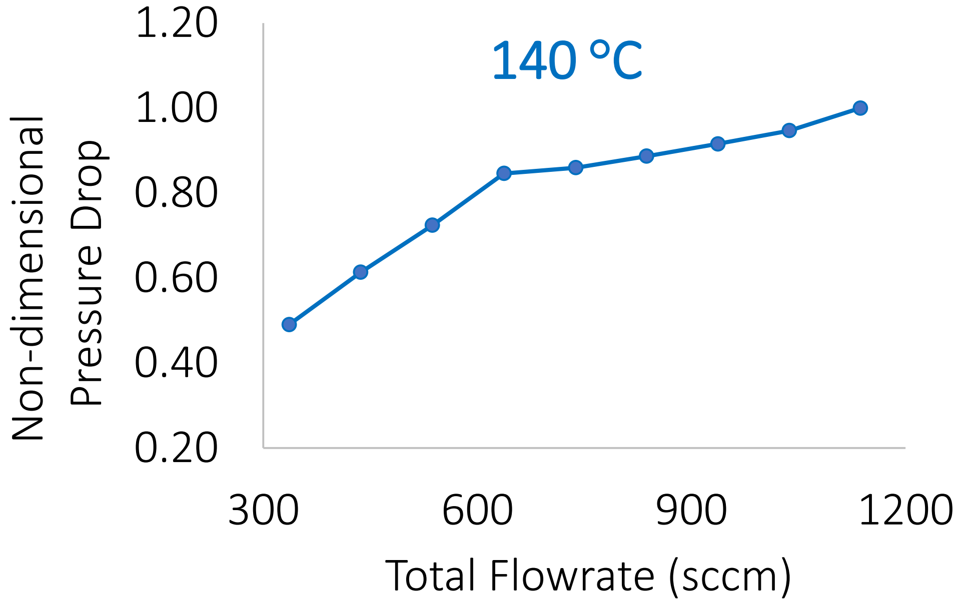
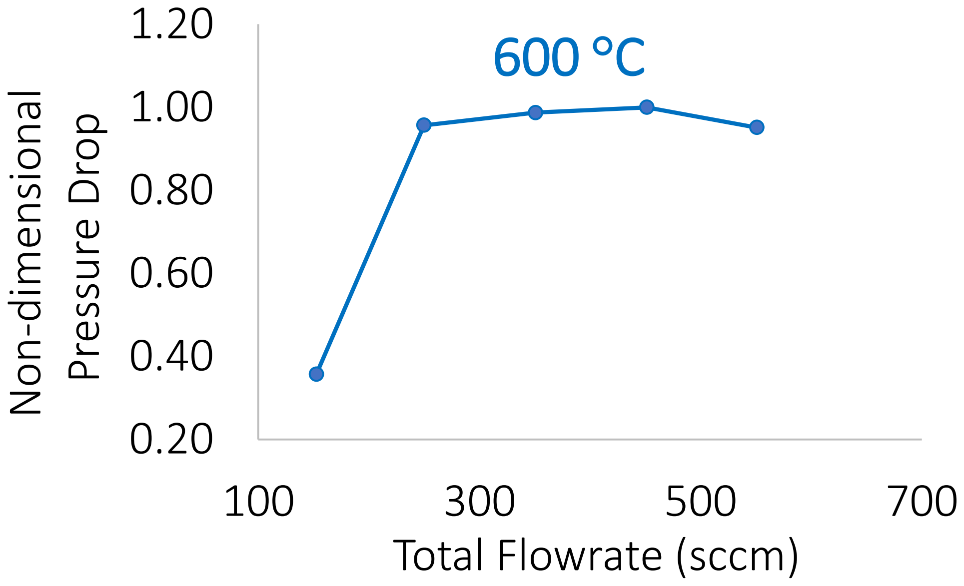
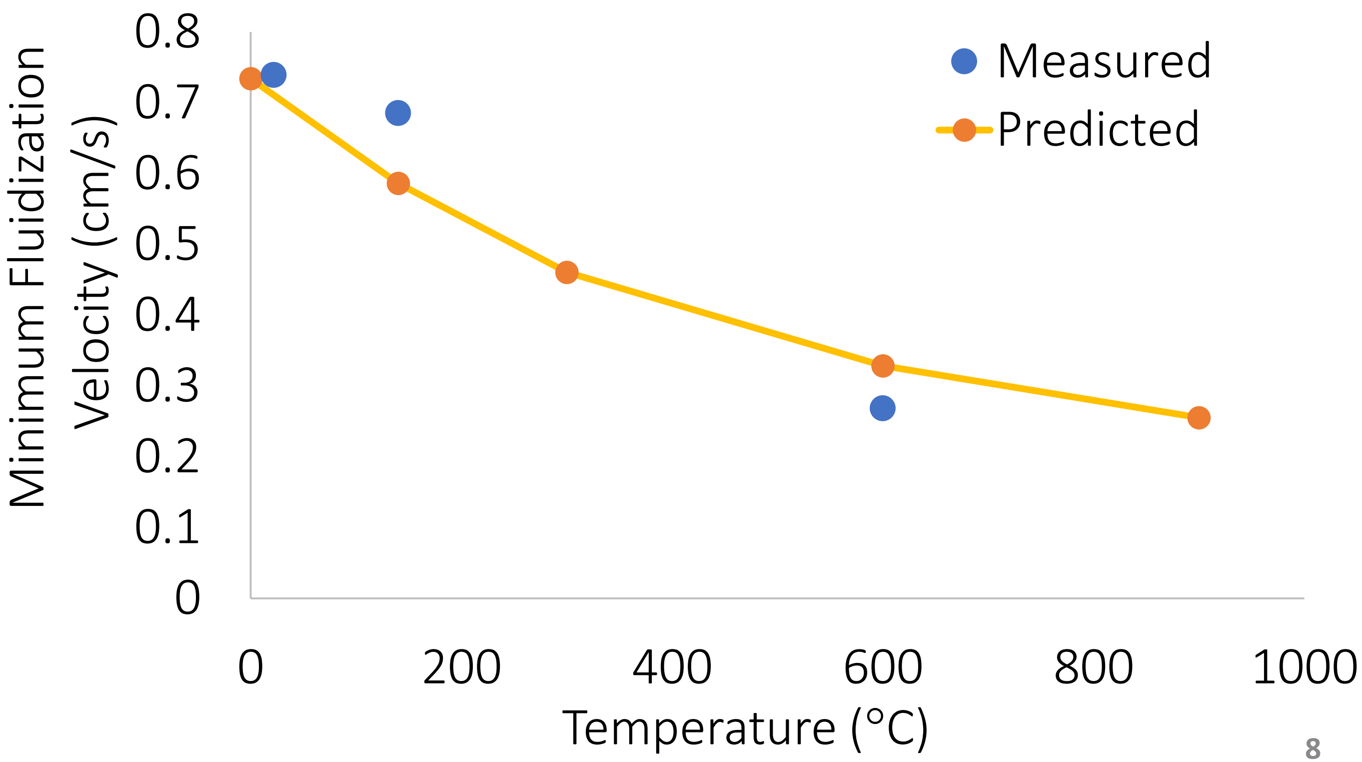




- Reactor modification verified via measured minimum fluidization velocity of silica fume
- Wen & Yu correlation compared to measured values



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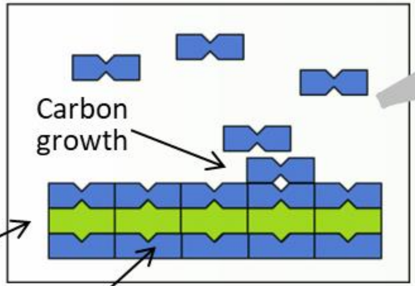

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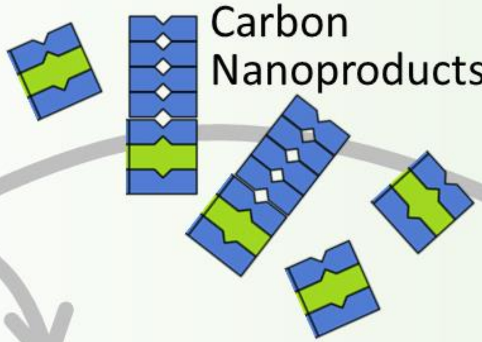

H_2/NG

Indirect Heating for Decarbonization

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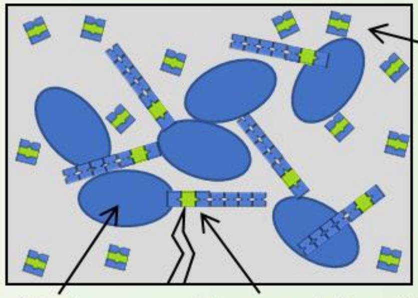

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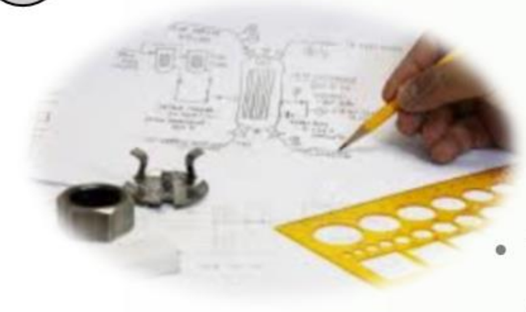

Development

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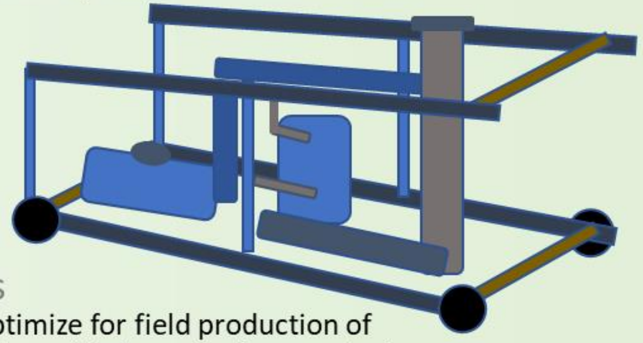


Optimize for field production of value-added nanocarbon product

Technical Status: Concrete Mix Design

- Optimized UHPC mix design (wt%)

w/c	Cement	Water	All-purpose sand	SF	HRWR
0.18	35.84	6.45	49.52	6.63	1.55

CNFs applied: length of 50-200 um; diameter of 100-200 nm

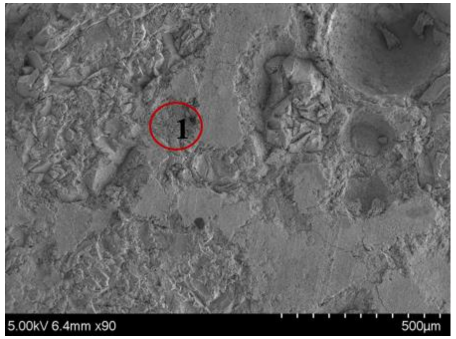
Selected from the compression test and slump test => **137 MPa compressive strength at 28 days and 24 cm slump**

- CNFs dispersion technique

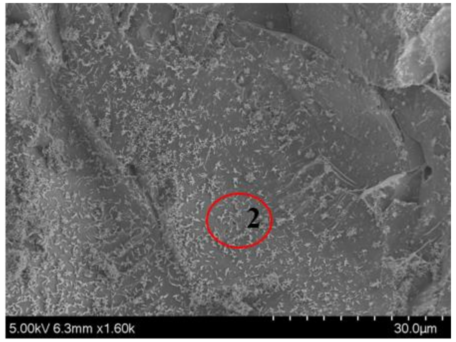
Dispersion method	Dispersion time (mins)	HRWR:CNFs	Dosage of CNFs (cwt%)	Sand type	Antifoam
High speed premix+ultrasonic dispersion	10+10	5 (flexural stress)/10 (flexural strain)	0.1	Fine	No

Selected from the flexure test results

- Images of dispersed sample (a) large scale image (b) spot 1 zoom-in (c) spot 2 zoom-in



(a)



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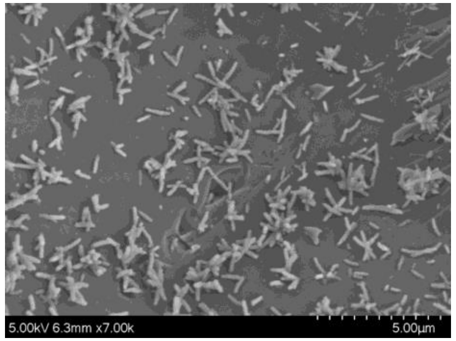


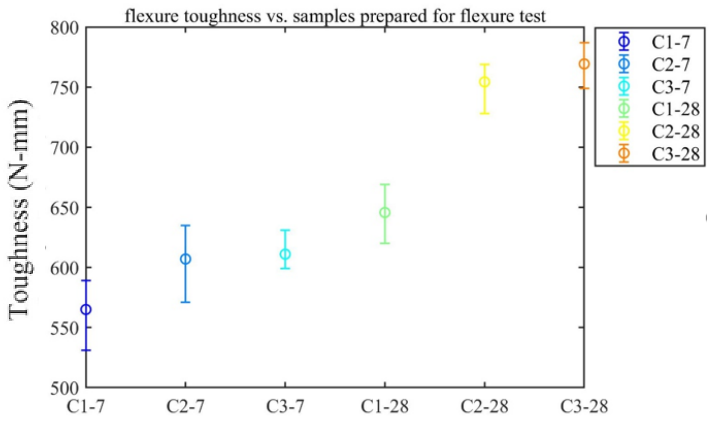
(c)

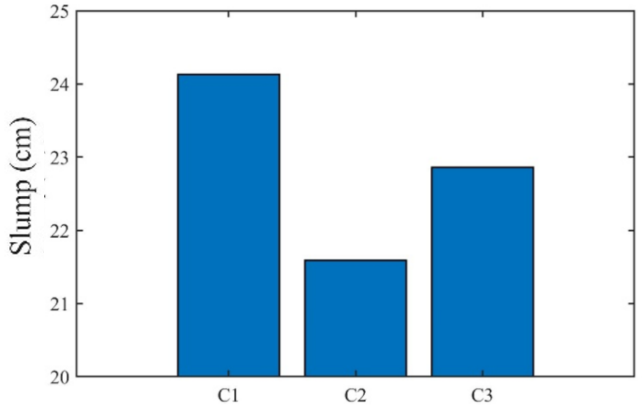
With dispersion, the CNFs are uniformly distributed in the cement hydrate.

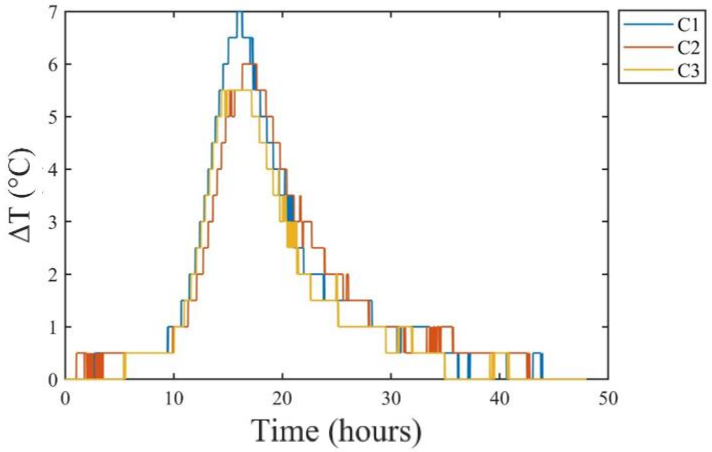
Technical Status: Concrete Mix Design

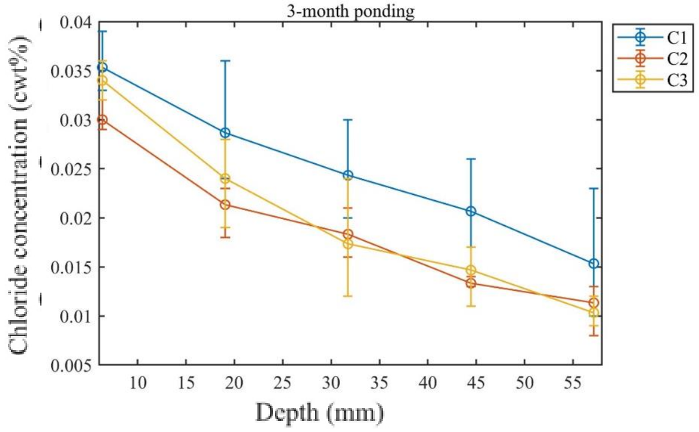
- Samples prepared for tests

Specimen	Description
C1-7/28	Reference: UHPC only; cured for 7/28 days.
C2-7/28	UHPC-CNFs; HRWR:CNFs=5:1 for dispersion; cured for 7/28 days.
C3-7/28	UHPC-CNFs; HRWR:CNFs=10:1 for dispersion; cured for 7/28 days.









Key findings:

(1) **24%** (28 days) flexural toughness improvement can be achieved.

(2) the slump dropped around **10.5%**.

(3) The peak temperature during the hydration process was decreased about **14.3-22.4%** with around **10-30 mins** retardation.

(4) A 3-months chloride ponding test shows the chloride resistance of UHPC with CNFs is increased up to **32%**.

Technical Status: R&D Approach

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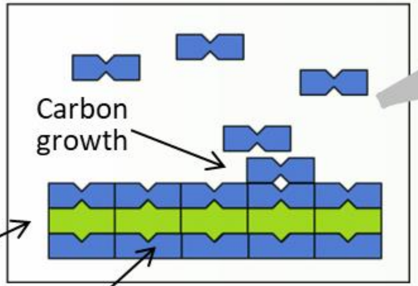

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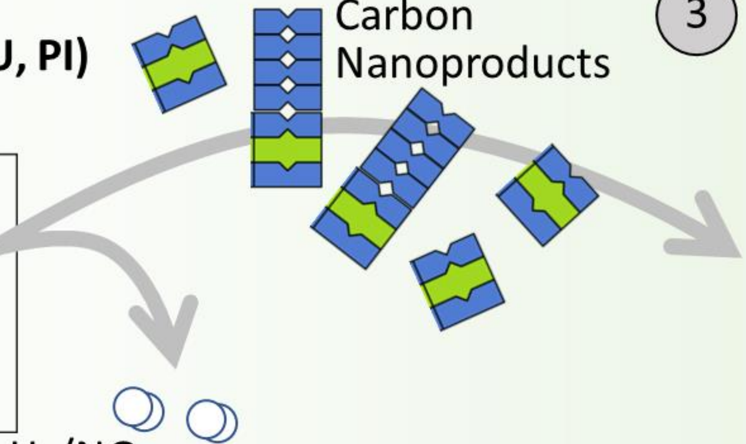

Carbon Nanoproducts

H_2/NG

Indirect Heating for Decarbonization

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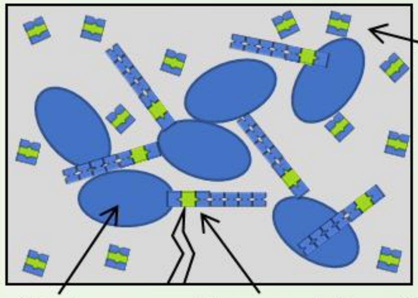

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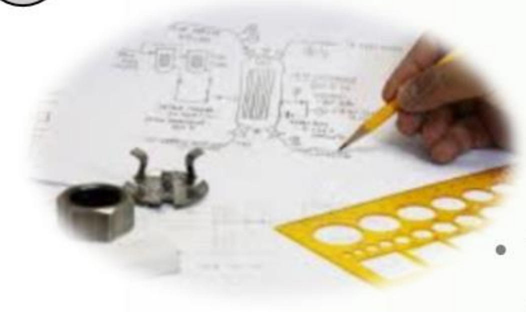

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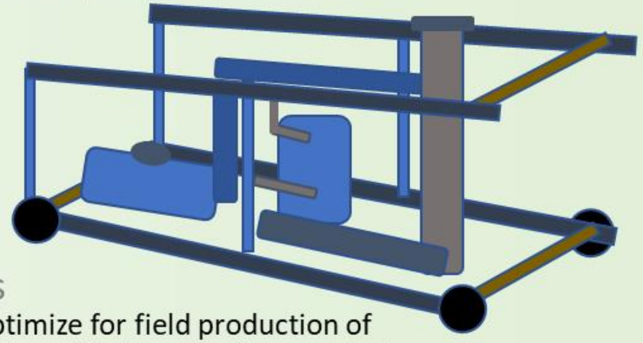
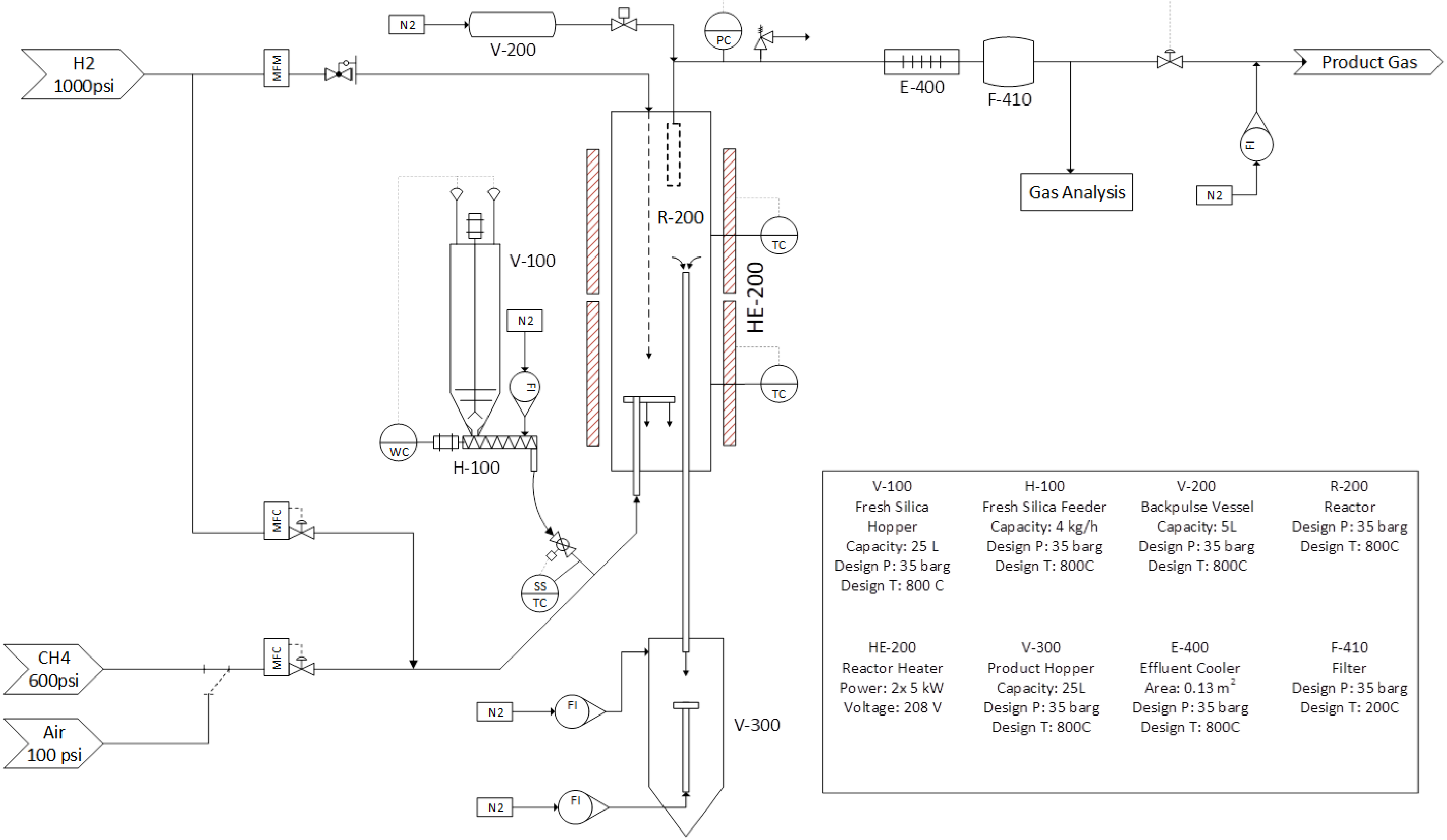


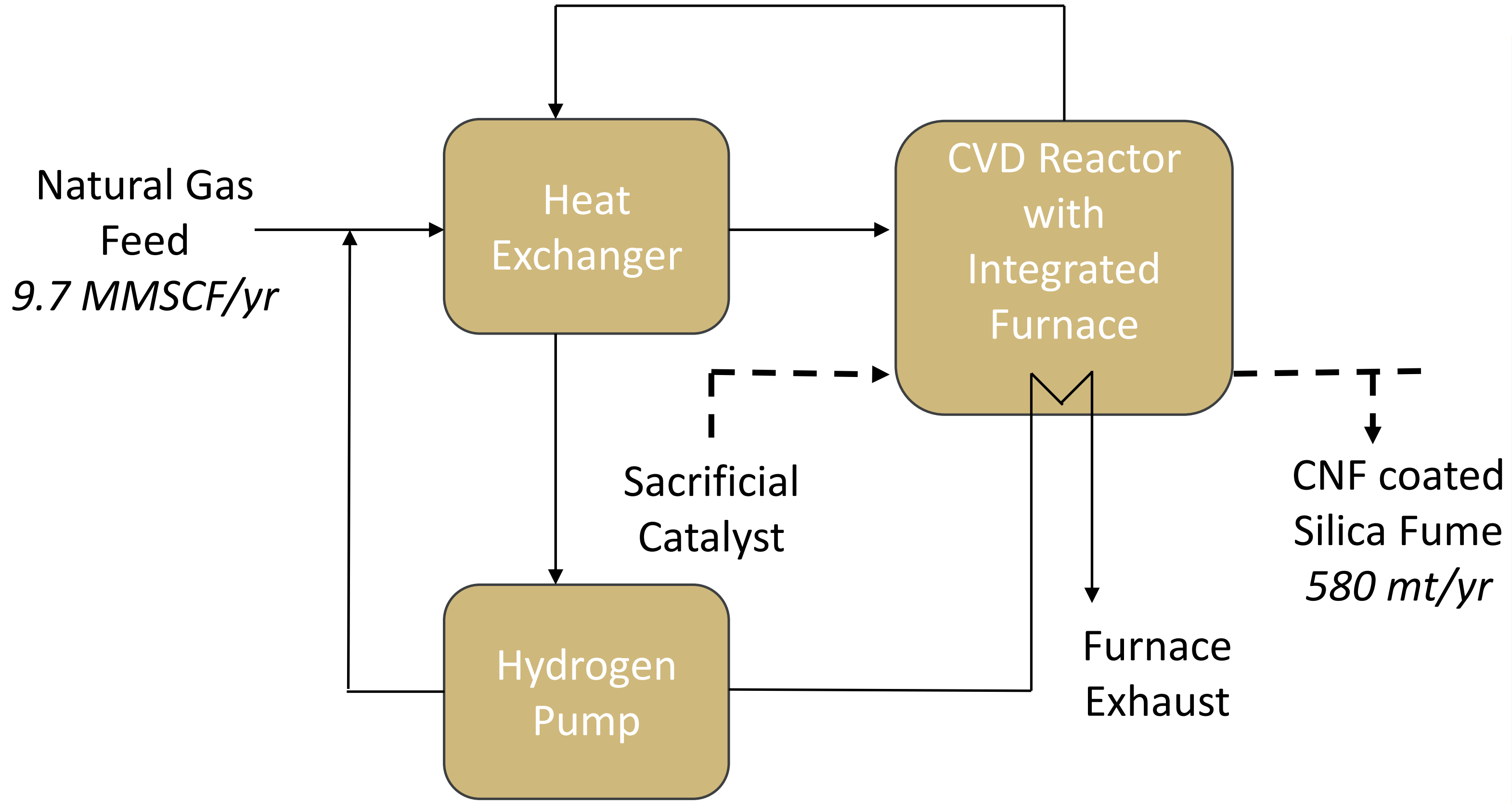
Optimize for field production of value-added nanocarbon product

Technical Status: Modular Unit Design



V-100 Fresh Silica Hopper Capacity: 25 L Design P: 35 barg Design T: 800 C	H-100 Fresh Silica Feeder Capacity: 4 kg/h Design P: 35 barg Design T: 800C	V-200 Backpulse Vessel Capacity: 5L Design P: 35 barg Design T: 800C	R-200 Reactor Design P: 35 barg Design T: 800C
HE-200 Reactor Heater Power: 2x 5 kW Voltage: 208 V	V-300 Product Hopper Capacity: 25L Design P: 35 barg Design T: 800C	E-400 Effluent Cooler Area: 0.13 m^2 Design P: 35 barg Design T: 800C	F-410 Filter Design P: 35 barg Design T: 200C

Technical Status: Technoeconomic Analysis



Parameters

NG cost: Free

IRR: 25%

Lifetime: 15 years

Estimated TDC: $1M-2M

Cost of Capital: 8.5%

Results

CNF/CNP coated silica, price range:

$2 - $4 per kg

Pure CNF, price range:

$10 - $20 per kg

Pure CNF, current technology:

$287 per kg (quote from Pyrograf)

Experimental Data to Inform Future TEA

- Catalyst Loading [g Fe/g catalyst]
- Carbon Loading [g CNP/g Fe]
- Reactor Conversion

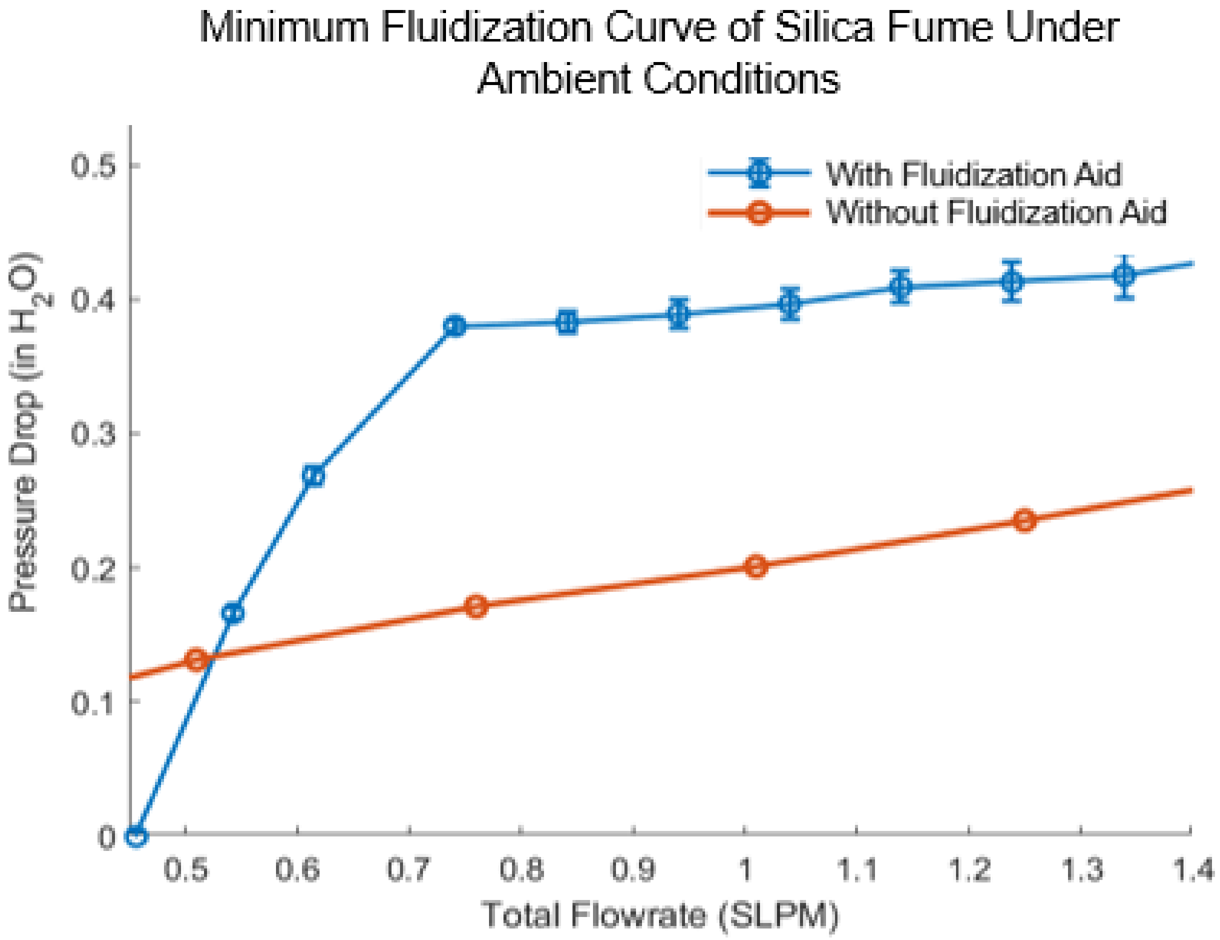
Accomplishments to Date

1 Methane Decarbonization at Lab-Scale	2 Engineering Design of Modular Unit	3 Value Added Product UHP Concrete Mix Design
✓ Minimum fluidization velocity determined for silica fume at temperatures of 140°C and 600°C. ✓ Reactor safely operated at 900°C. ✓ Fluidization enabled with proprietary aid	✓ The process and mechanical conceptual designs have been developed into a feasible system design. ✓ Process flow diagram, material and energy balances, major equipment sizing, mechanical general arrangement, and critical mechanical component details have all been completed. ✓ Cold flow designs to initiate testing have been completed.	✓ The UHPC mix design was optimized based on compressive strength and fluidity. ✓ Met UHPC performance metrics using commercially available CNFs. ✓ The improvement of mechanical property and permeability was achieved by adding well dispersed CNFs.

Preliminary techno-economic analysis meets goal of 25% IRR with a carbon nanoproduct coated silica selling price of $2 - $4 per kg.

Lessons Learned

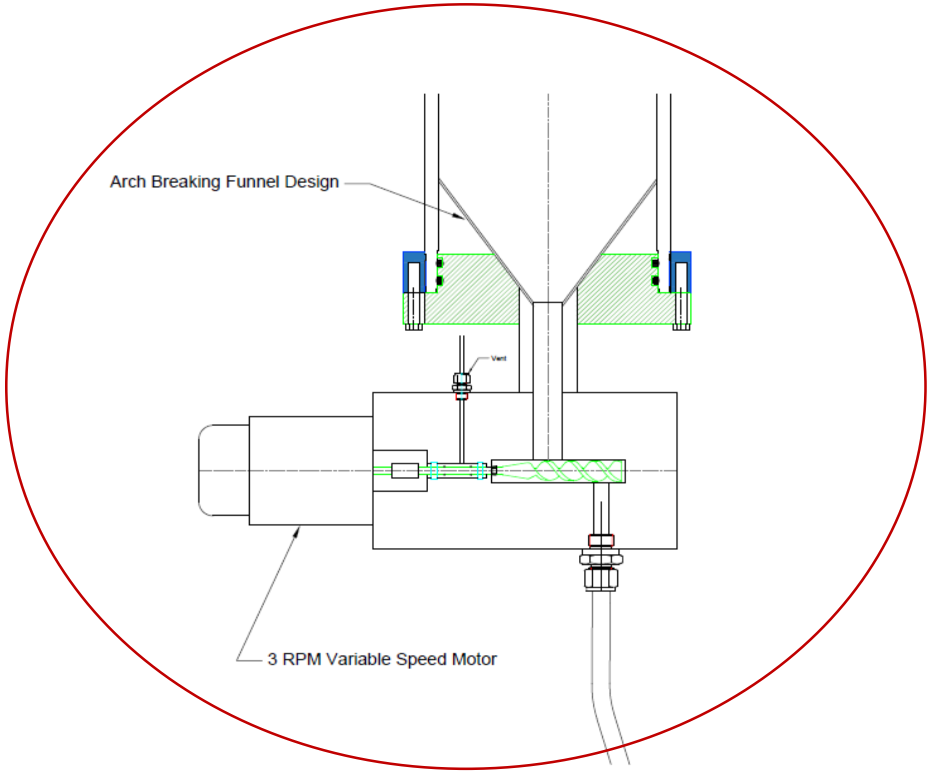
Silica fume is a Geldart C powder that requires extreme velocities or a fluidization aid to achieve desired fluidization behavior

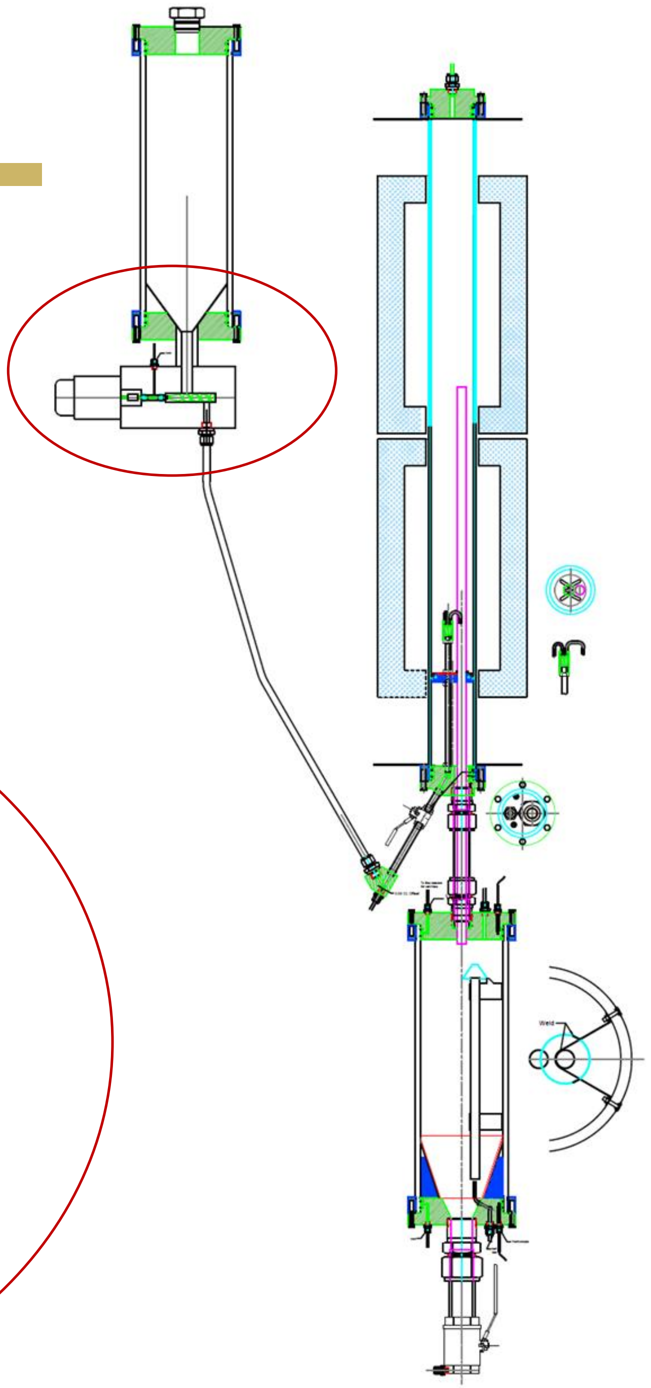


A *proprietary fluidization aid* was incorporated to enhance fluidization

Lessons Learned

Cold flow modeling of the silica fume powder is required to effectively design a continuous process





Synergy Opportunities: Department & Industry Collaboration

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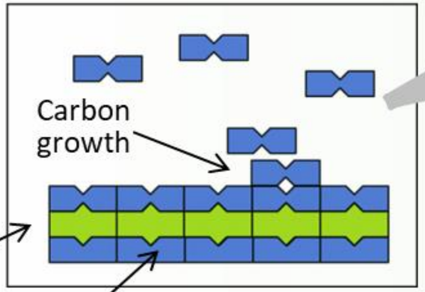

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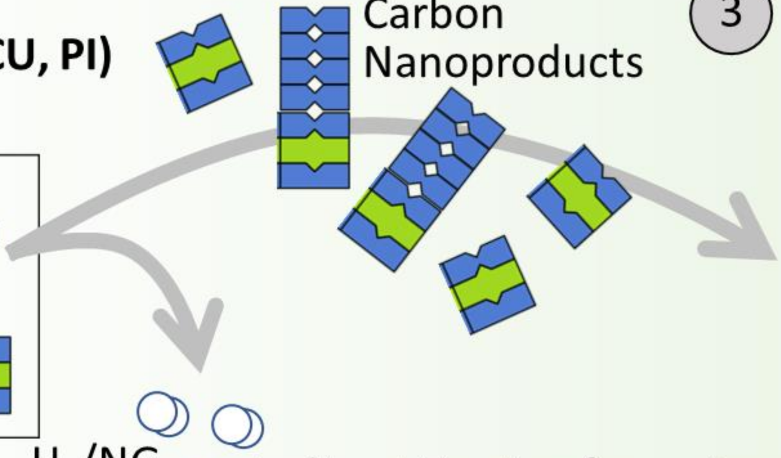

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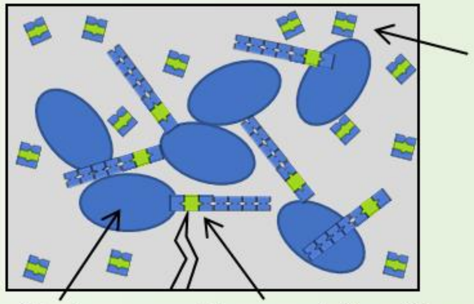

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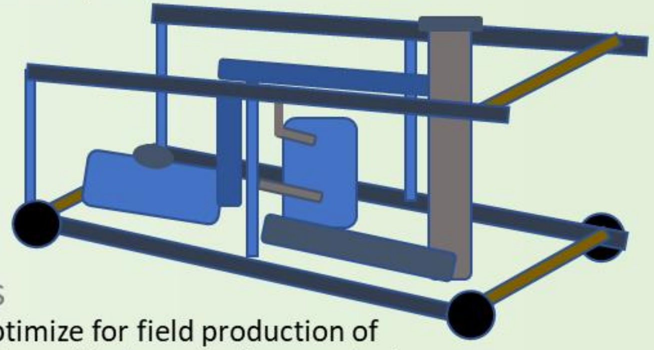

Optimize for field production of value-added nanocarbon product

FORGE NANO

NRMCA NATIONAL READY MIXED CONCRETE ASSOCIATION

Project Summary

	1 Methane Decarbonization at Lab-Scale	2 Engineering Design of Modular Unit	3 UHP Concrete Mix Design
Key Findings	✓ Minimum fluidization velocity determined for silica fume at elevated temperatures to verify FBR modification	✓ The process and mechanical conceptual designs have been developed into a feasible system design.	✓ The UHPC mix design has been optimized with adding commercial well dispersed CNFs.
Next Steps	❑ Deposition of metallic catalyst via particle ALD will be demonstrated. ❑ Reaction rate studies will be carried out for an ALD catalyst with temperature, CH_4 concentration, and residence time varying.	❑ Construction of modular skid will be completed in collaboration with Forge Nano. ❑ Operation of modular process will occur with production of carbon nanoproduct at the prescribed scale.	❑ Introduce carbon nanoparticles (CNPs) in UHPC mix design. ❑ Increase the amount of CNFs/CNPs involved in UHPC.

Technoeconomic Analysis will be updated with product results from lab and modular scale.

Acknowledgements

- Weimer Research Group – Department of Chemical & Biological Engineering
- Hubler Research Group – Department of Civil, Environmental, and Architectural Engineering
- Andrew Broerman, Theodore Champ – Forge Nano
- Colin Lobo – National Ready Mixed Concrete Association

NATIONAL ENERGY TECHNOLOGY LABORATORY

University of Colorado Boulder

Thank you for listening!

Any questions?

University of Colorado
Boulder

Benefit to the Program

Program Goal

The program goal being addressed is the up-cycling of flare gas into transportable value-added carbon nanoproducts (CNPs) for infrastructure applications.

Project Benefits Statement

This project potentially benefits the improved lifetime of concrete while reducing GHG production via the sequestration of carbon.

Project Overview – Budget Period 1

Milestone Title/Description		Planned Completion Date	Actual Completion Date	Verification Method
Task 1.0 - PM&P				
Subtask 1.1	Project Management Plan	5/1/2020	6/5/2020	Report
Subtask 1.2	Technology Maturation Plan	6/1/2020	9/27/2020	Report
Subtask 1.3	Techno-economic Analysis	10/31/2020	10/31/2020	Report
Task 2.0 ALD & CVD				
Subtask 2.1	The particle ALD FBR system is modified	End of Q6. 9/30/2021	9/30/2021	Minimum fluidization velocity determined for silica fume at up to 900°C
Milestone A	*Go/NoGo*			
Task 3.0 Module Design				
Subtask 3.1 **Milestone C**	Complete plans for module construction	End of Q6. 9/30/2021	9/30/2021	Review by engineer leading construction
Task 4.0 Cement				
Subtask 4.1 **Milestone E**	Mix design including carbon products	End of Q4. 3/31/2021	2/25/2021	Minimal (< 3 min) reduction in set time and an improved ductility compared to the baseline mix.
Subtask 4.2 **Milestone F**	Optimal cement mix design parameters will be identified	End of Q6. 9/30/2021	9/30/2021	Meet UHPC performance metrics using commercially available carbon nanoparticles and CNFs.

Project Overview – Budget Period 2

- CVD will be carried out to produce carbon nanoproducts, with the solid product comprising at least 25 wt% carbon. Knowledge from the lab-scale experiments will inform the construction and operation of the larger-scale modular process in BP2. By the end of BP2, the modular system will be operated and meet the production target of ~1 kg C/hr.

- Commercial carbon nanoparticles (CNPs) will be introduced in the cement research. A new composite of UHPC-CNFs-CNPs will be developed starting from the mix design and dispersion technique.

Milestone Title/Description		Planned Completion Date	Verification Method
Task 2.0 ALD & CVD			
Subtask 2.2 **Milestone B**	CVD will be carried out	End of Q8. 3/31/2022	The solid product will comprise at least 25 wt% as measured using LECO light element analysis
Task 3.0 Module Design			
Subtask 3.2	Module Operation	End of Q10. 9/30/2022	Production of carbon nanoproduct from associated gas at the prescribed scale
Milestone D	Go/NoGo		

Team Organization

- **Alan Weimer (Chemical Engineering) PI** ① ② ④
  - Kent Warren, Postdoctoral Fellow ① ④
  - Jessica Hauck, PhD Student ① ④
  - Robert Anderson, Principal Engineering Scientist ②
- **Mija Hubler (Civil Engineering) co-PI** ③
  - Linfei Li, Postdoctoral Fellow ③
  - Boning Wang, PhD Student ③
- **Collaborators**
  - Forge Nano ① ② ④
    - Andrew Broerman, Principal Engineer
    - Theodore Champ, Jr R&D Engineer
  - National Ready Mixed Concrete Association (NRMCA) ③
    - Colin Lobo, VP

1. Methane Decarbonization at Lab-Scale
2. Engineering Design of Modular Unit
3. UHPC Mix Design
4. Technoeconomic Analysis

Gantt Chart

<u>Completed Tasks</u>

1.1 Project Mgt. Plan
1.2 Project Maturation Plan
1.3 TEA

<u>Current Tasks</u>

2.1 Lab CVD Construction
3.1 Skid Design
4.1 & 4.2 Concrete Mix Design

<u>Next Tasks</u>

2.2 Lab CVD Operation
3.2 Module Construction & Operation
5.1 Concrete Mix Design with Lab Product