Modular Processing of Flare Gas for Carbon Nanoproducts

DOE Project Award Number: DE-FE0031870

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Co-PI: Mija Hubler (Civil Engineering)

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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
Resource Sustainability Project Review Meeting
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Overview: Year 2 of 3-Year Project

Timeline

Project Start Date: 5/1/2021

Project End Date: 9/30/2023

% Complete: 65%

Technical Barriers Addressed

B. CVD is Carried Out.

D. Module Operation

F. Optimal cement mix design parameters will be identified

Budget

Total project funding: $3,750,000

Sub-contract: $750,000

Collaborators

ForgeNano, Thornton, CO

- Reactor/process design and technoeconomic analysis

National Ready Mixed Concrete Association (NRMCA), Alexandria, VA

- Concrete materials, mix design, and consulting

Project Overview: Overall Project Objectives

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.

Project Overview: Team

Alan Weimer (Chemical Engineering) PI
- **Kent Warren** – Postdoctoral Fellow
- **Jessica Hauck** – PhD Student
- **Robert Anderson** – Principal Engineering Scientist
- **Samantha Harshberger** – Undergraduate Student
- **Dragan Mejic** – Instrument Shop Supervisor

Mija Hubler (Civil Engineering) co-PI
- **Boning Wang** – PhD Student
- **Ethan Borenstein** – Master Student

Collaborators
- Forge Nano
  - **Andrew Broerman** – Principal Engineer
  - **Theodore Champ** – Application Engineer II
- National Ready Mixed Concrete Association (NRMCA)
  - **Colin Lobo** – VP

Repurposing of Wasted Methane in Natural Gas Flaring

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 as 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*.

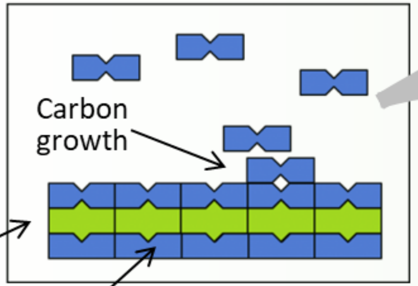
Technical Approach

Research

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

Low cost ALD

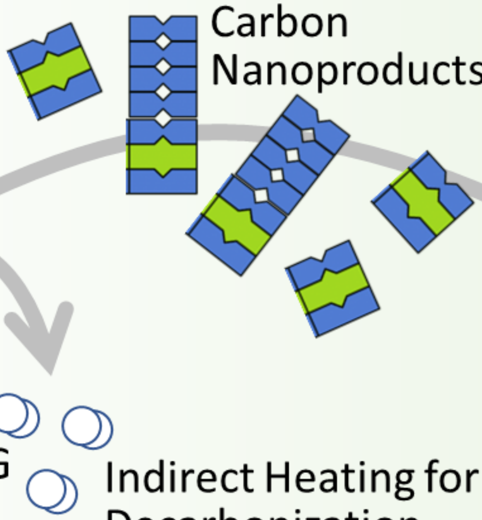
Addresses controlled carbon deposition with high conversion



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

Silica fume support

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

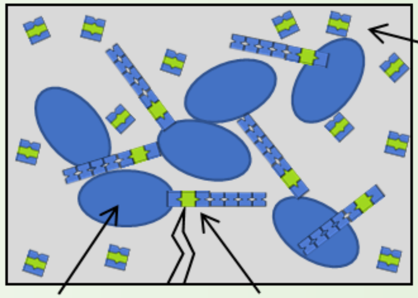


Carbon Nanoproducts

H_2/NG

Indirect Heating for Decarbonization

3 **Value-added Product: Concrete Design to meet Ultra High Performance Concrete Properties at a Low Cost (CU, Co-PI; NRMCA)**



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

Concrete binder C-S-H grains

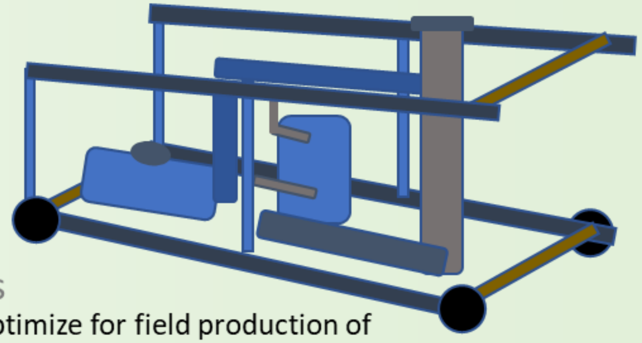
Dispersed Nanofibers
Arrest cracks to increase toughness

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

Technical Background: CNPs in Concrete

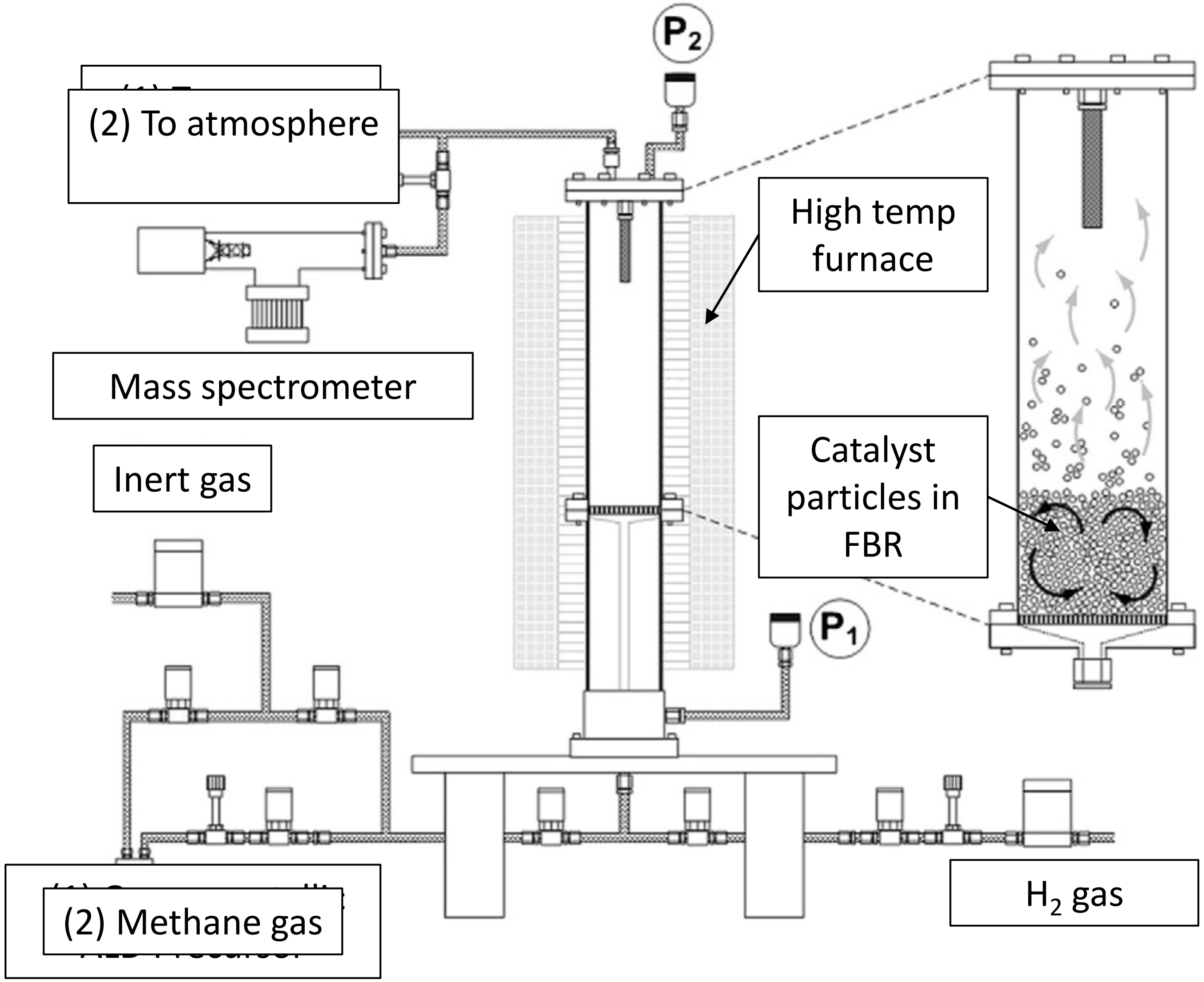
- The fracture process of concrete starts at the nano-scale. The addition of CNPs acts through a bridging effect after cracks appear.
- Previous research[1] has stated that as the content of CNF increased from 0 to 0.3 wt.% of binder, the tensile strength increased by 56%.
- Advantages: Potential improvement in crack resistance performance of UHPC
- Challenges: An efficient and economic dispersion of CNPs in the cement paste

[1]W. Meng, K.H. Khayat (2016) "Mechanical properties of ultra-high-performance concrete enhanced with graphite nanoplatelets and carbon nanofibers". Composites Part B 107 113-12..

Technical Approach: Fluidized Bed Reactor

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

Key Process Parameters	
Catalyst ALD fabrication	Ex-situ
Catalyst Support	Silica fume
Catalyst Metal	Transition metal (Ni, Fe)
Pressure Range Explored	0 – 500 psig
Temperature Range	500 – 800°C
Scale-up	Modular process
Carbon Nanoproduct Application	Ultra-high performance concrete

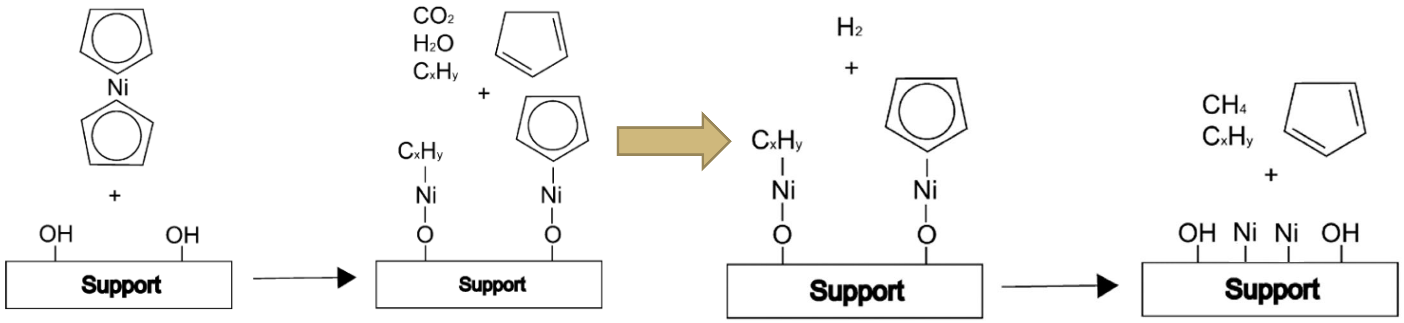


Progress and Current Status of Project

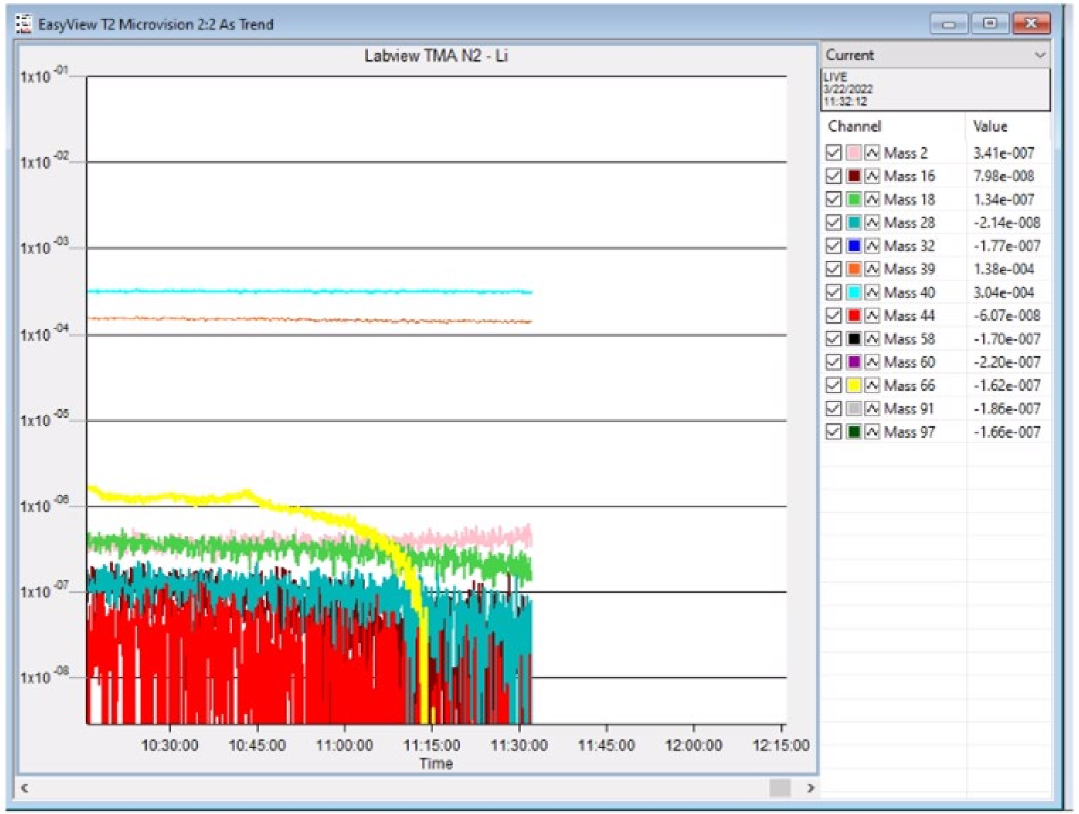
Milestone Title/Description		Actual Completion Date	Status
Task 2.0 ALD & CVD			
Subtask 2.2 Milestone B	CVD will be carried out.	6/30/2022	Carbon content >25wt% achieved. CVD studies ongoing to further understand how to manipulate carbon yield while minimizing metal content.
Task 3.0 Module Operation			
Subtask 3.2 Milestone D	Module operation	On track for 12/30/2022	On track for complete module installed at Forge Nano and operational.
Task 4.0 Cement			
Subtask 4.2 Milestone F	Optimal cement mix design parameters will be identified	9/30/2021	Met UHPC performance metrics using commercially available carbon nanoparticles and CNFs

Progress: CVD is Carried Out

Catalyst Synthesis



Sample ID #	Ni Loading (wt%)
FN0403_4_3	5.1
FN0403_4_4	4.7
FN0403_4_5	5.0
FN0403_4_6	9.2



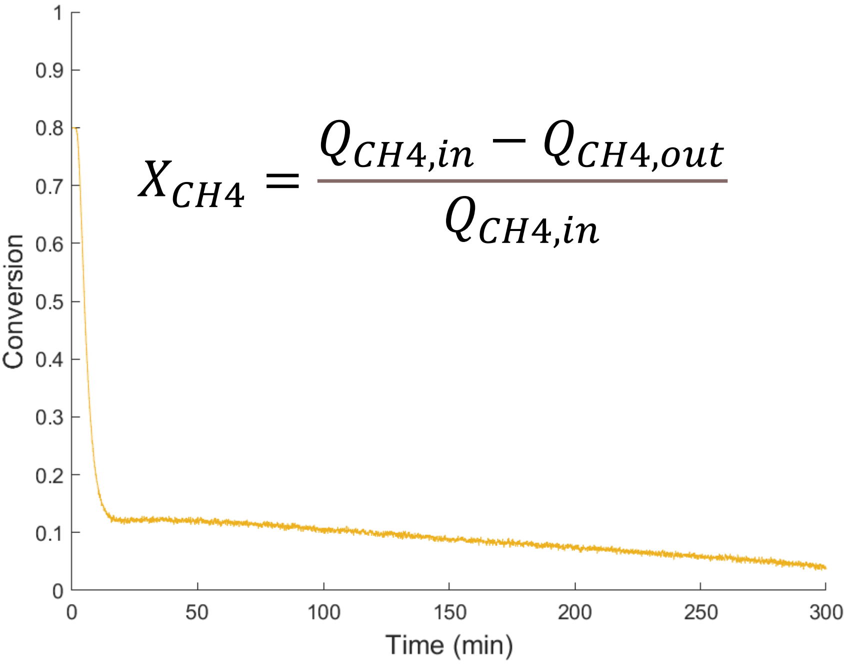
Mass spectrometer trace during synthesis. The signal on M/Z=66 (yellow, likely cyclopentadiene) dropping to ~0 torr was used to determine when all nickelocene had been consumed

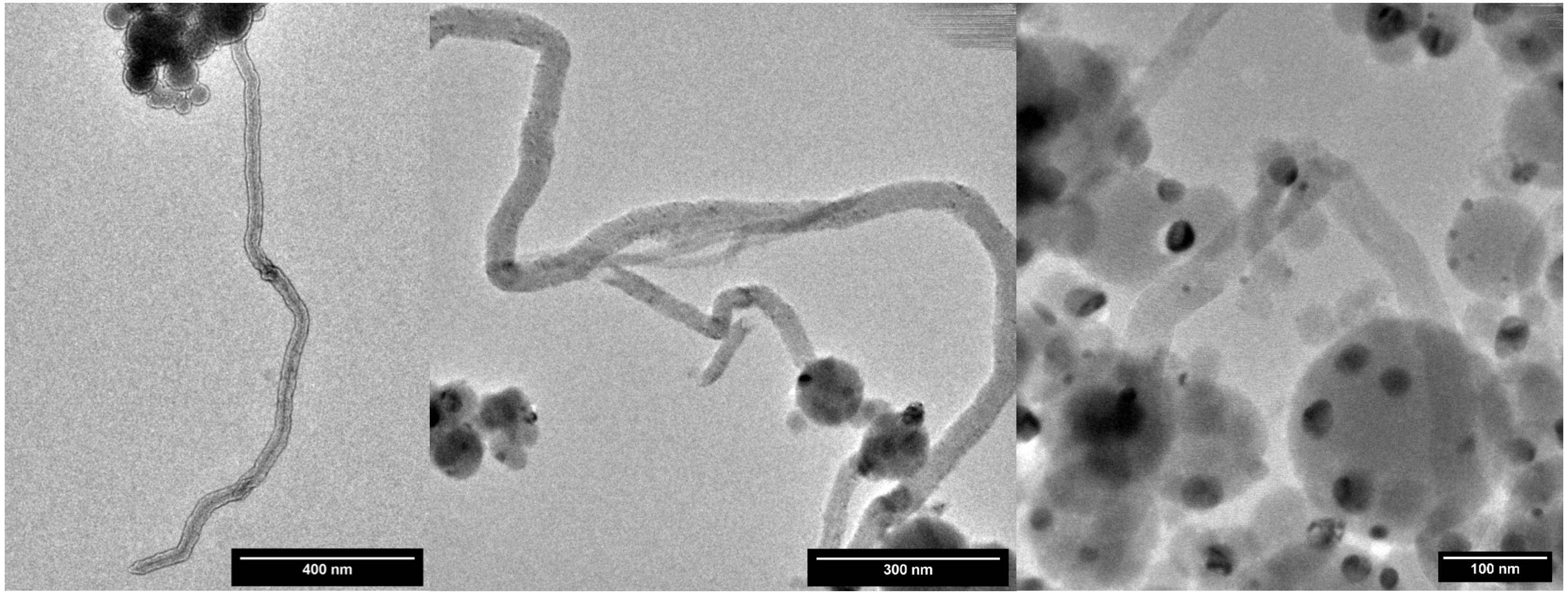
Progress: CVD is Carried Out

Constants
• Weight hourly space velocity: 18 $L_n/g_{cat} \cdot h$ • Reaction Time: 5 hr • $P_{CH4}:P_{H2}$ 2:1 • CVD Temp: 550°C • Ni loading: 9.3wt%

Factor	Value
Reduction Step	500°C 1 hour 50% H2, 50% Ar
Methane Concentration (Vol%)	16.7%
Carbon content (wt%)	**31.8wt%**

$$X_{CH4} = \frac{Q_{CH4,in} - Q_{CH4,out}}{Q_{CH4,in}}$$

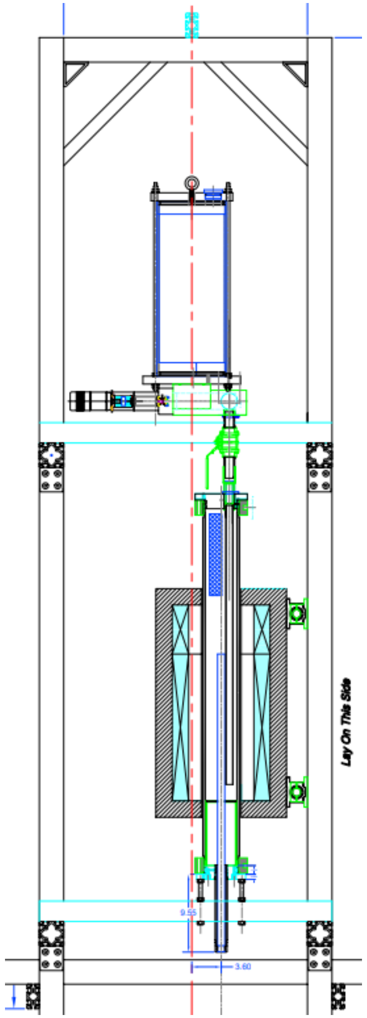




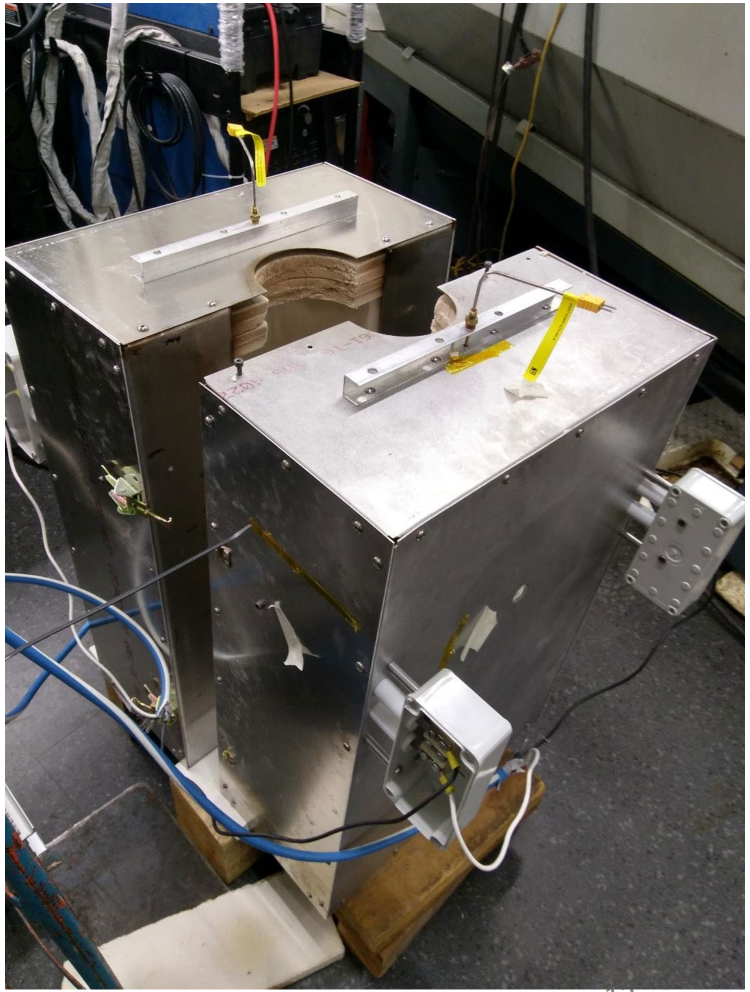
Carbon filaments contain L:D >10

Progress: Module Operation

Level 1 Integration



Module Construction Update



Progress: Module Operation

Modular Skid Facility of Operation

Forge Nano, located in Thornton, CO, has multiple lab facilities and over 80 employees.

Location of modular skid system post-construction.

Progress: Mix design and dispersion of CNFs

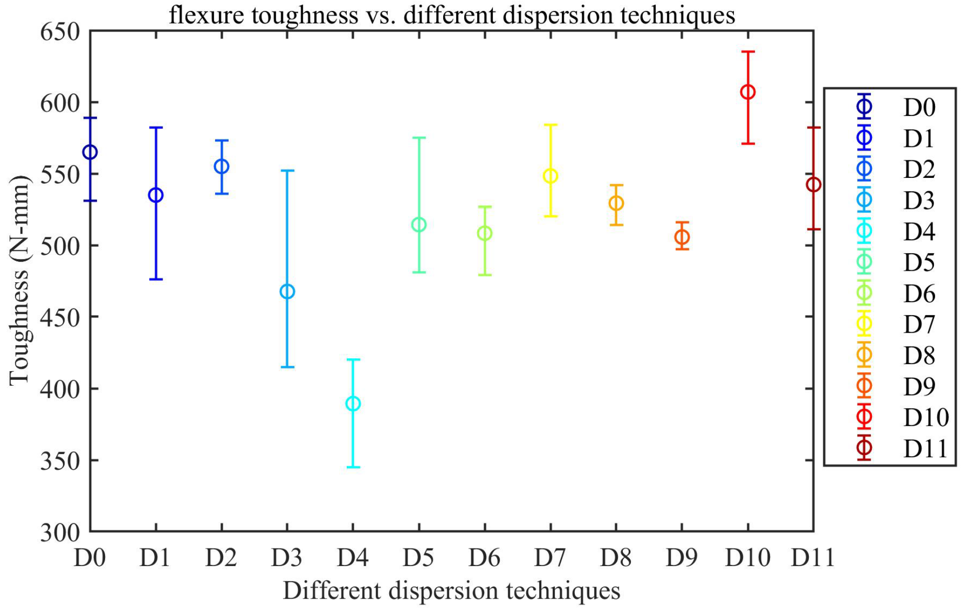
Optimized UHPC-CNFs mix design (wt.%)

w/c	Cement	Water	Sand	SF	HRWR	CNFs
0.18	35.83	6.45	49.50	6.63	1.55	0.04

Commerical CNFs used: PR-19-XT-PS ($174/lb)

Various CNF dispersion methods considered (methods D0 –D11):

Premixing wet ingredients, premixing dry ingredients, Methylcellulose addition, low speed stirring, high speed stirring, ultrasonic dispersion, polyacrylic acid addition and combinations.

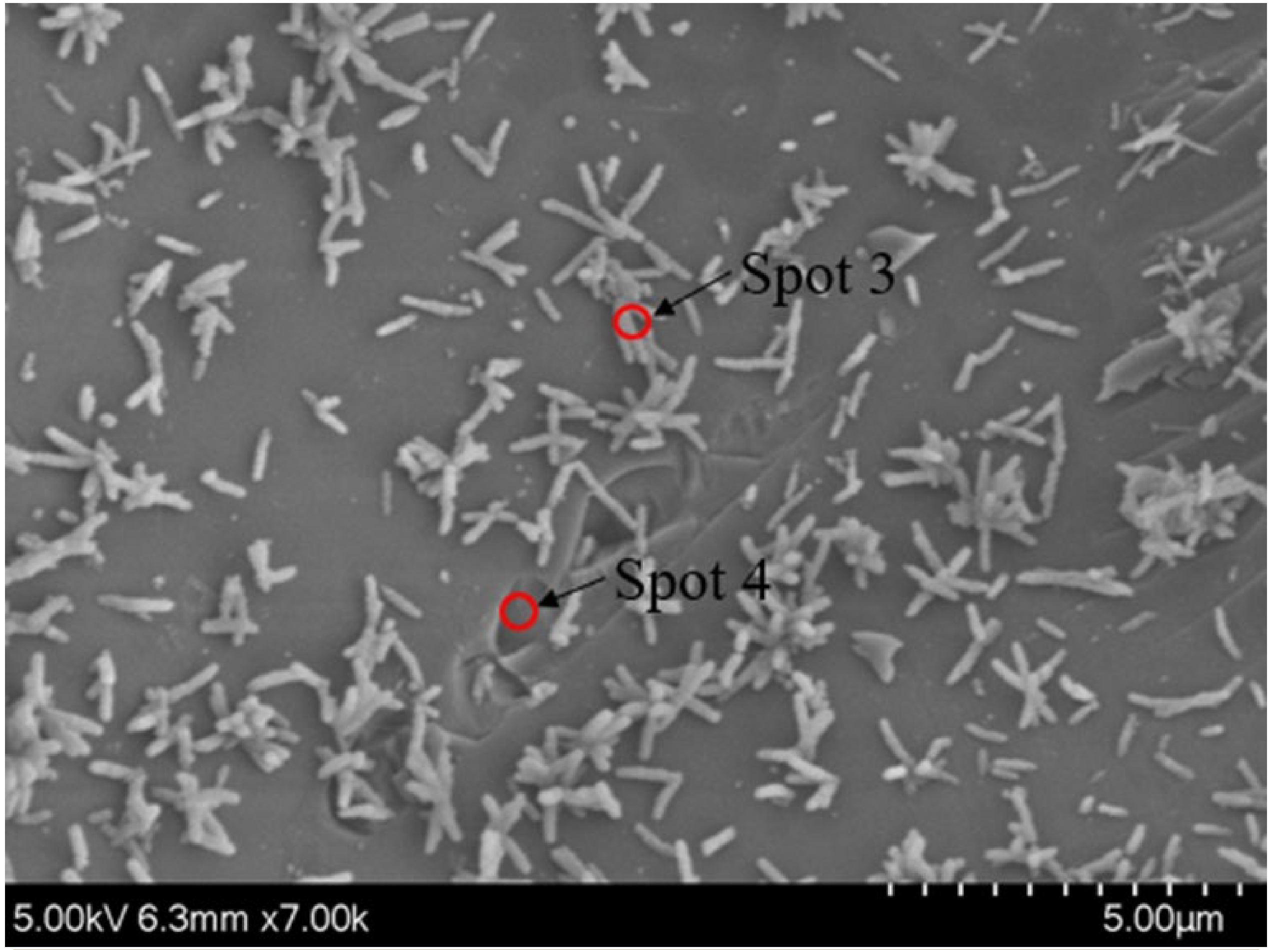


Premixing

Ultrasound dispersion

- Dispersion method D10 showed the best performance in terms of toughness improvement.
- This method involves premixing CNFs with water and part of the liquid admixtures, using a highspeed magnetic stirrer for 10 min, then running ultrasound dispersion for 10 mins.

Progress: CNF Dispersion Confirmation in UHPC-CNF



SEM Image of a well-dispersed UHPC-CNFs sample

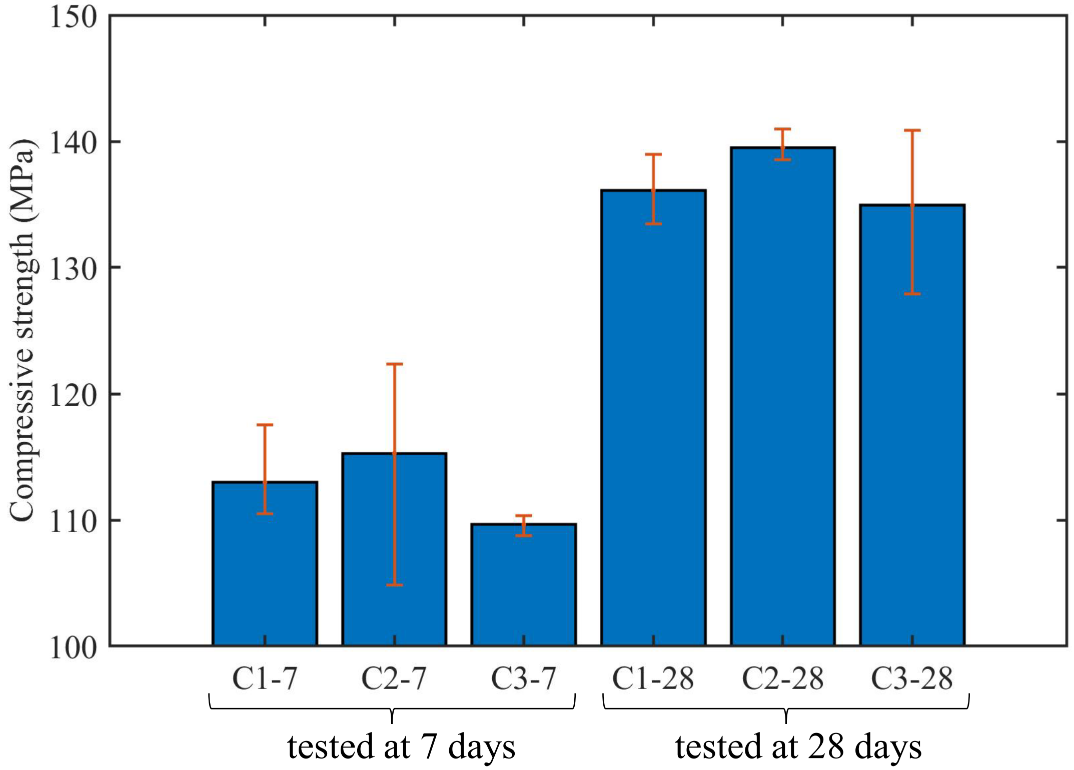
Visual confirmation of successful dispersion with SEM

- SEM shows fibers are well-dispersed with dispersion method D10.
- Images of poorly-dispersed CNFs show large-scale bundles of fibers.
- FIB-FESEM and EDS of Spot 3 and Spot 4 were used to confirm white features are single CNFs.

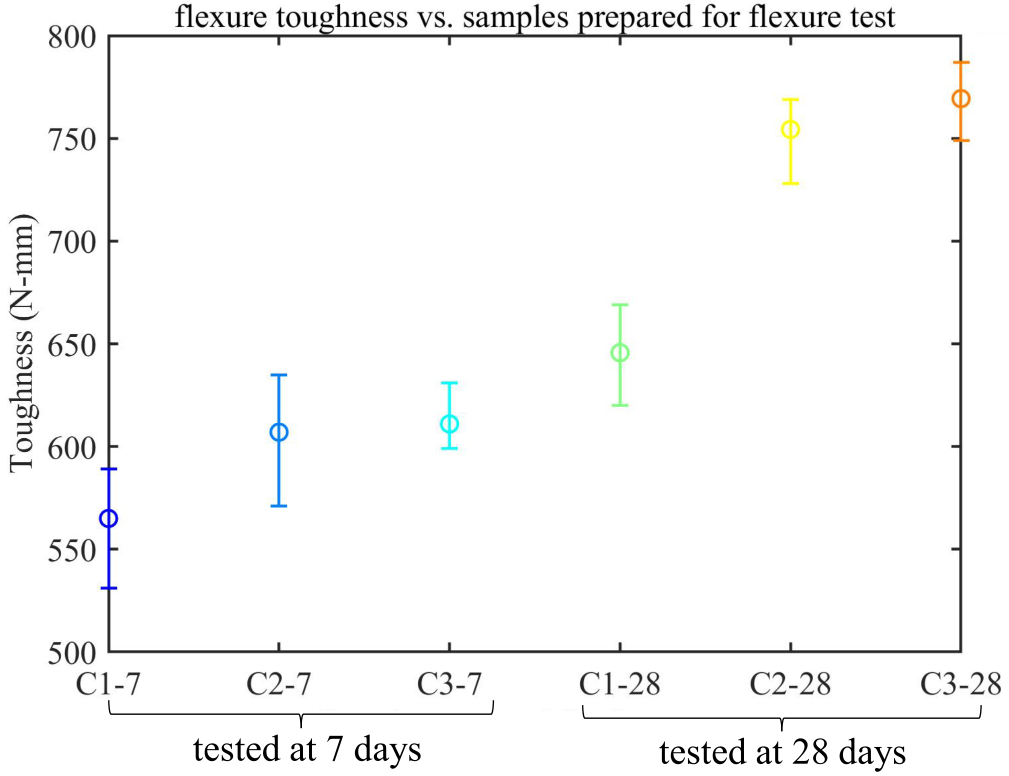
Progress: Optimize CNF addition amount

Specimen	Description
C1-7/28	**Control Sample**: 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.

Compression test



Flexure test

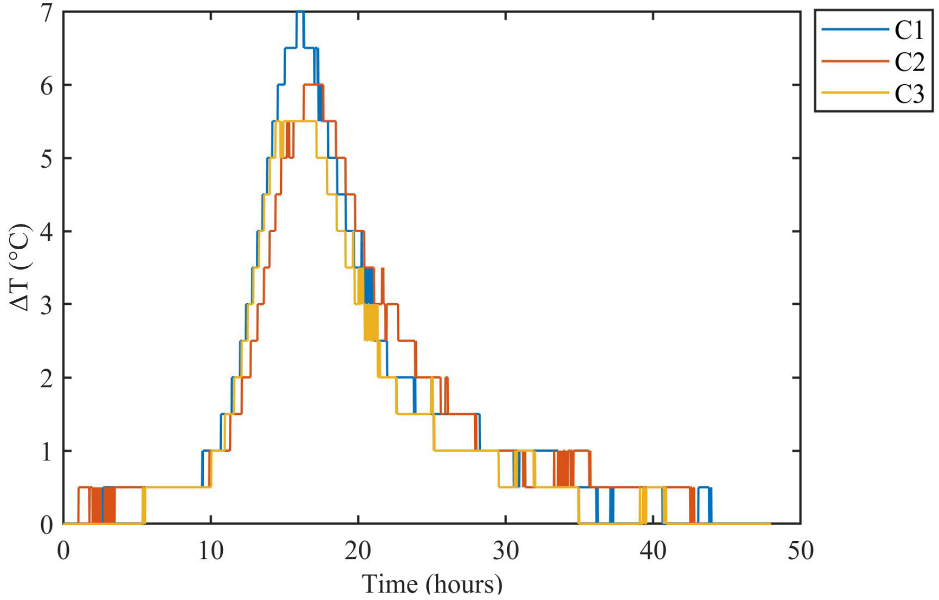


- A High Range Water Reducer (HRWR):CNF ratio of 10:1 showed the highest Flexure Toughness

Progress: Hydration rate and slump

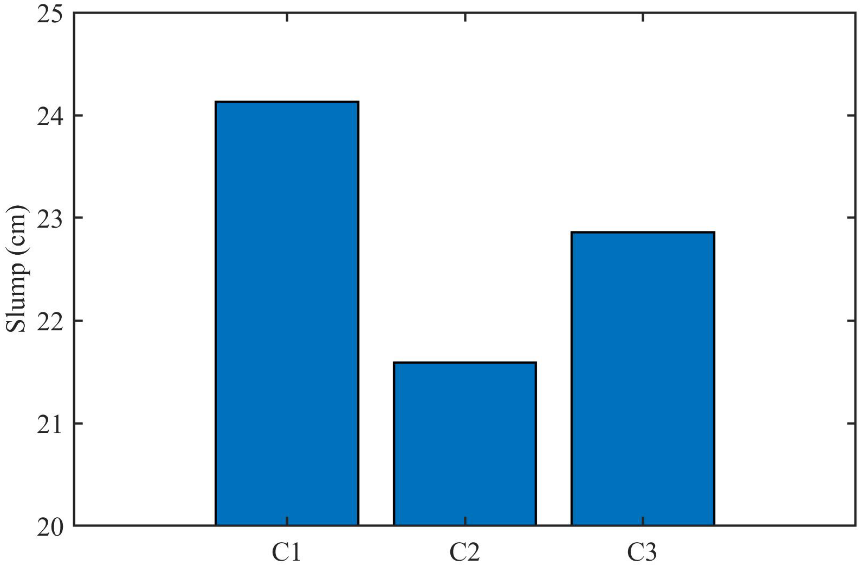
CNF impact on Hardening assessed by Heat Evolution

Maturity test



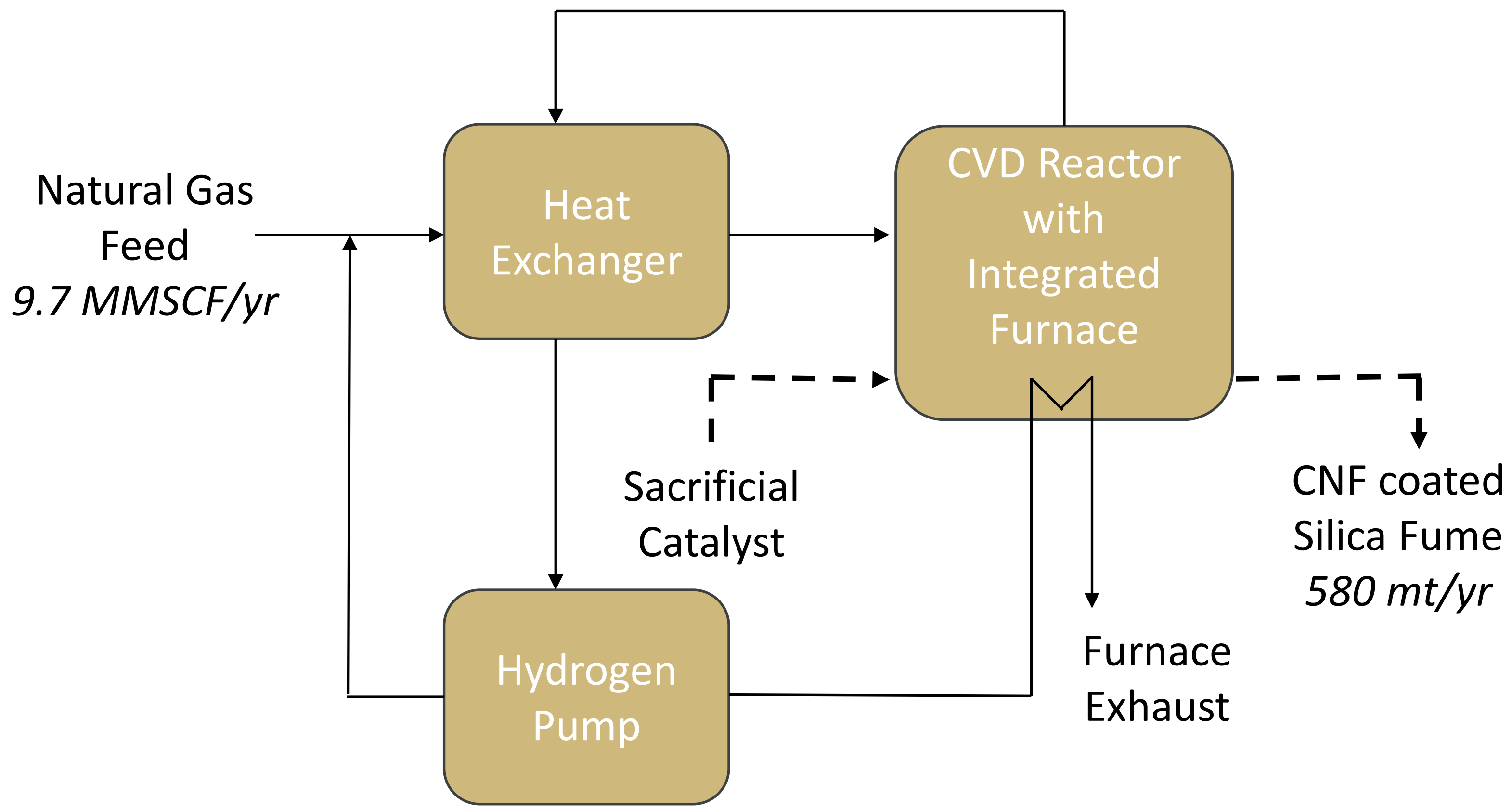
CNF impact on Concrete Flow by Slump

Slump test



- Samples C1-C3 as defined in previous slide.
- Minimal change in set time and slump can be addressed with commercial admixtures.

Progress: Preliminary TEA



Parameters

NG cost: Free

IRR: 25%

Lifetime: 15 years

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:
$300 per kg (bulk)

Future Work

Lab-Scale CVD

- The lab-scale CVD studies performed in BP2 will be used to inform the modular operation in BP3.
- Catalyst focus will switch to Fe.
- CVD focus will switch to minimized metal content.

Modular Skid System

- CVD will be carried out to produce carbon nanoproduct (CNP) at both lab scale and modular scale, with the modular system producing 1kg product/hr.
- Modular system performance and continued lab scale studies will inform the final commercial path assessment of this technology.

Concrete Mix Designs

- Tests introducing the CNP synthesized from the skid system in UHPC will commence.

Potential **Technical** Work Beyond Current Project

CVD solid carbon production	Concrete	Additional Markets for Carbon

• Catalyst optimization
  • Natural gas feed
• Correlate process conditions to carbon product form
• Design of deployable skid
• Alternative catalyst substrates
	• Mix optimization in conjunction with catalyst optimization
	• Increase carbon fraction in concrete
		• Develop understanding of Carbon Fiber properties
		  • Conductivity (H & E)
		  • Strength
		  • Corrosion resistance
		  • Optical
		• Other carbon structures
		  • Amorphous
		  • Graphitic

Potential **Commercialization** Work Beyond Current Project

CVD solid carbon production	Concrete Market	Additional Markets for Carbon

• Identify customers for wellhead skid implementation
• Refine TEA, GHG, Energy efficiency analyses
• Collaborate with well head owner
	• Collaborate with concrete producer
	• Improve market understanding
	    • Coated silica Product specs
	    • Concrete specs
	• Identify customers
	    • Product spec optimization
		• Market Assessment
		    • Battery raw materials
		    • Carbon black
		    • Additive manufacturing
		    • Polymer Reinforcement
		    • Others?

Outreach and Workforce Development Efforts

- **Outreach**
  - *Undergraduate Research Opportunities Program (UROP)* – Undergraduate Mentoring
  - *Discovery Learning Apprenticeship (DLA)* – Undergraduate Mentoring
  - *Social Justice in Science (SJS)* – Graduate Student Led Discussion/Book Group
  - *Elementary Arts Lab* – workshops for elementary school students and resources for teachers to explore scientific concepts through art, dance and music
  - *Arrupe Jesuit High School Corporate Work-study Program* – internship program for underserved high school students in Denver to gain STEM job experience
- **Workforce Development**
  - Training graduate students, including Jessica Hauck (Chemical Engineering), Boning Wang (Civil Engineering), Ethan Borenstein (Civil Engineering)
  - Training undergraduate students, including Samantha Harshberger (Chemical Engineering)
  - Training Postdoctoral Associates, including Kent Warren (Chemical Engineering) and Linfei Li (Civil Engineering)

Project Summary

CVD Lab Scale & Modular Operation	Concrete mix design using commercial CNFs	Technoeconomic analysis
• CVD was carried out in lab-scale system on ALD catalyst – target carbon yields achieved. • All major modular skid parts have been constructed • All major pieces of equipment have been ordered. • Expected operation 12/2022 due to supply chain issues	• The optimal dispersion of CNFs and mix design of UHPC-CNFs were delivered with an improvement of tensile ductility (8% flexure toughness) • With 0.1 cwt% CNFs added, the slump decreased up to 10% • No obvious compressive strength or setting time change of UHPC by adding CNFs	• Preliminary TEA and H2A analysis complete • Aspen plus simulation and PFD for modular flare gas scale process developed • CNP product selling price estimated at \$2-\$4/kg for 25% IRR

Acknowledgements

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

NATIONAL ENERGY TECHNOLOGY LABORATORY

University of Colorado Boulder

Thank you for listening!

Any questions?

University of Colorado
Boulder

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]
  - Ethan Borenstein, Masters 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 Status: end of BP2

Completed Tasks

1.1 Project Mgt. Plan
1.2 Project Maturation Plan
1.3 TEA
2.1 Lab CVD Construction
2.2 Lab CVD Operation
3.1 Skid Design
4.1 & 4.2 Concrete Mix Design

Current Tasks

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