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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Caitlin Czernik, 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
April 3rd, 2024

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
- **Bola Odunaro** – PhD Student

Collaborators

- Forge Nano
  - **Andrew Broerman** – Principal Engineer
  - **Caitlin Czernik** – R&D Jr. Engineer
- National Ready Mixed Concrete Association (NRMCA)
  - **Colin Lobo** – VP

Overview: Year 4 of 4-Year Project (NCE)

Timeline

Project Start Date: 5/1/2020

Project End Date: 9/30/2024

% Complete: 80%

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

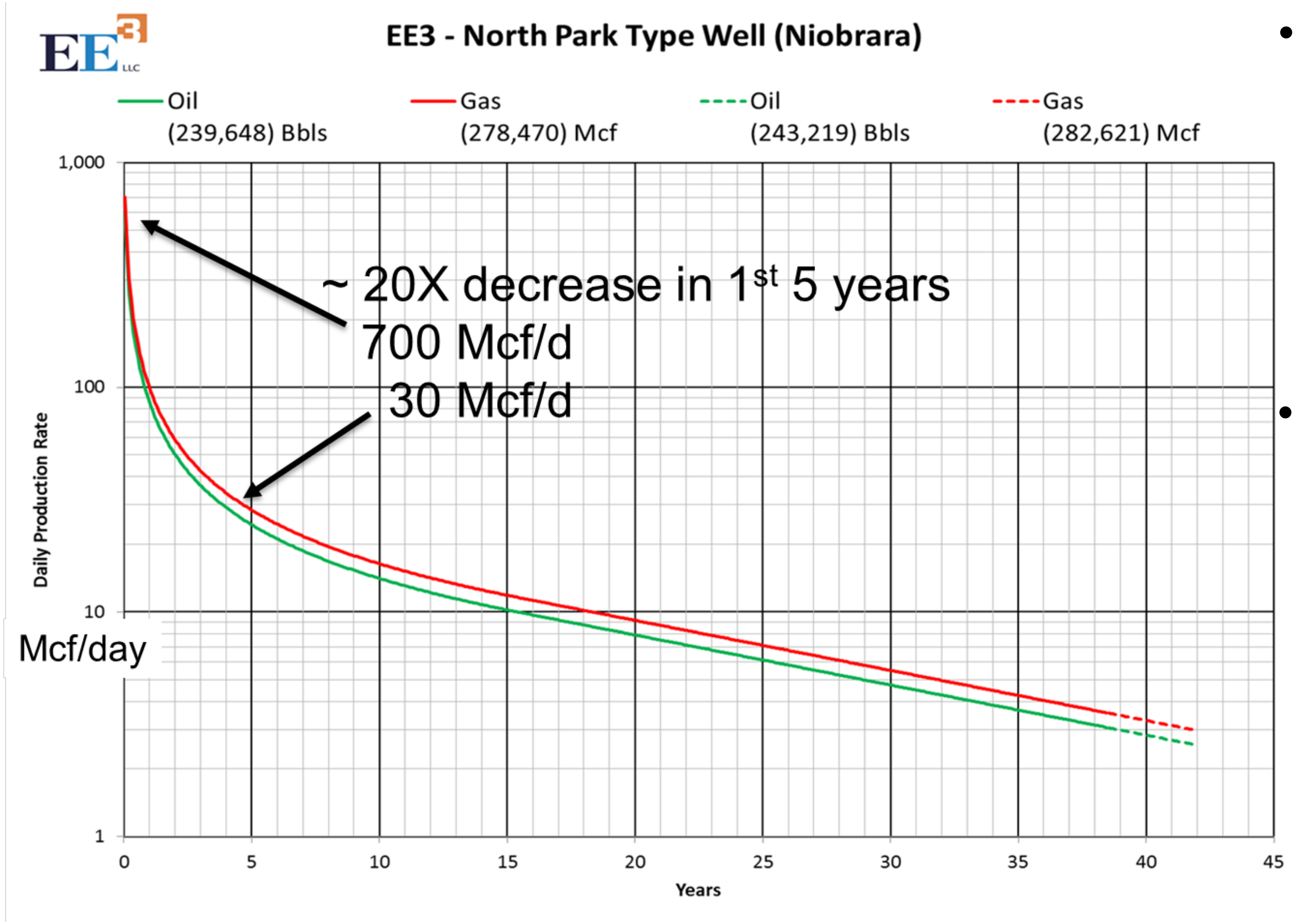
ForgeNano, Thornton, CO

- 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 **low-cost, scale-able, & distributed** process to **reduce carbon emissions** while **providing** for a valuable **carbon nano-product (CNP**)
- **Sequester CNP** in ultra-high performance concrete (UHPC) – **improving crack resistance/increasing lifetime**
  - **GHG reduction:**
    - sequestration
    - less concrete

Approach – CVD using "Sacrificial Catalyst"

Process Challenges				
Process	**Wall Deposition Challenges**	**Carbon Separation Challenges**	**Scalability Challenges**	**Typical Temperature Range (°C)**
Direct Thermal Cracking	Yes	No	Yes	> 1500°C
Plasma Assisted	Yes	No	Yes	> 2000°C
CVD	No	Yes	No	600 – 800°C
Laser Ablation	No	No	Yes	
Arc Discharge	No	No	Yes	
Molten Metal	No	Yes	Probably	> 1000°C
Molten Salt	No	Yes	Probably	600-800°C
This Research	**No**	**No**	**No**	**600-800°C**

Instead of separating CNPs from a catalyst support after synthesis:

- use **silica fume as the support**;
- highly dispersed **ALD nano-metal catalyst**
- **avoid separation** costs;
- **avoid** health and safety issues of **handling carbon nano fibers, etc.**;
- **use combined product as a crack-bridging additive in concrete**

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**

***Experimental study** is applied to **establish the cement design relationships to hydration, cracking, and ductility**.*

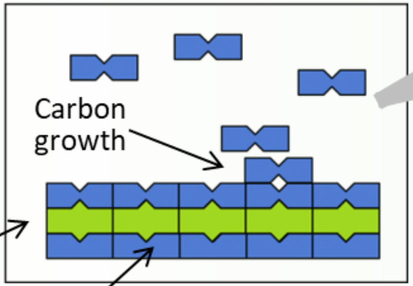
[1]W. Meng, K.H. Khayat (2016) "Mechanical properties of ultra-high-performance concrete enhanced with graphite nanoplatelets and carbon nanofibers". Composites Part B 107 113-12..

Technical Approach

Research

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

Low cost ALD



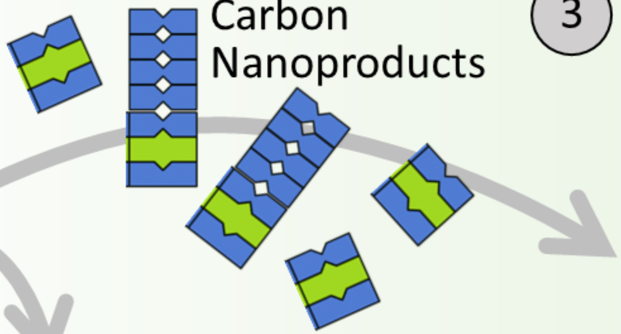
Addresses controlled carbon deposition with high conversion

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

Silica fume support

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

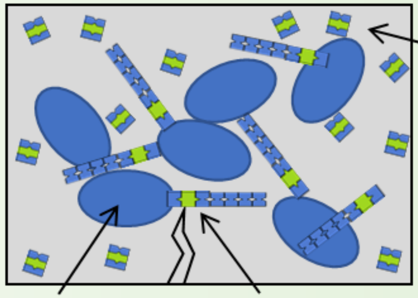
Carbon Nanoproducts



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

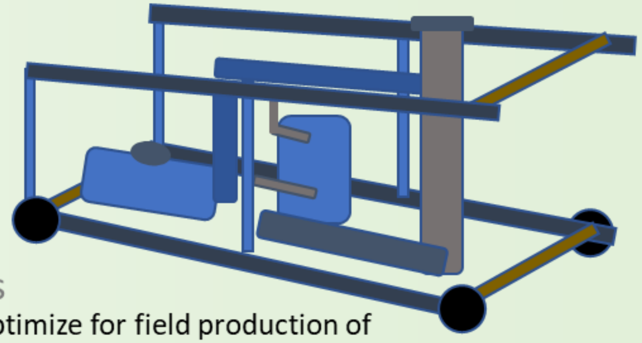
Dispersed Nanofibers
Arrest cracks to increase toughness

Development

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

- 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

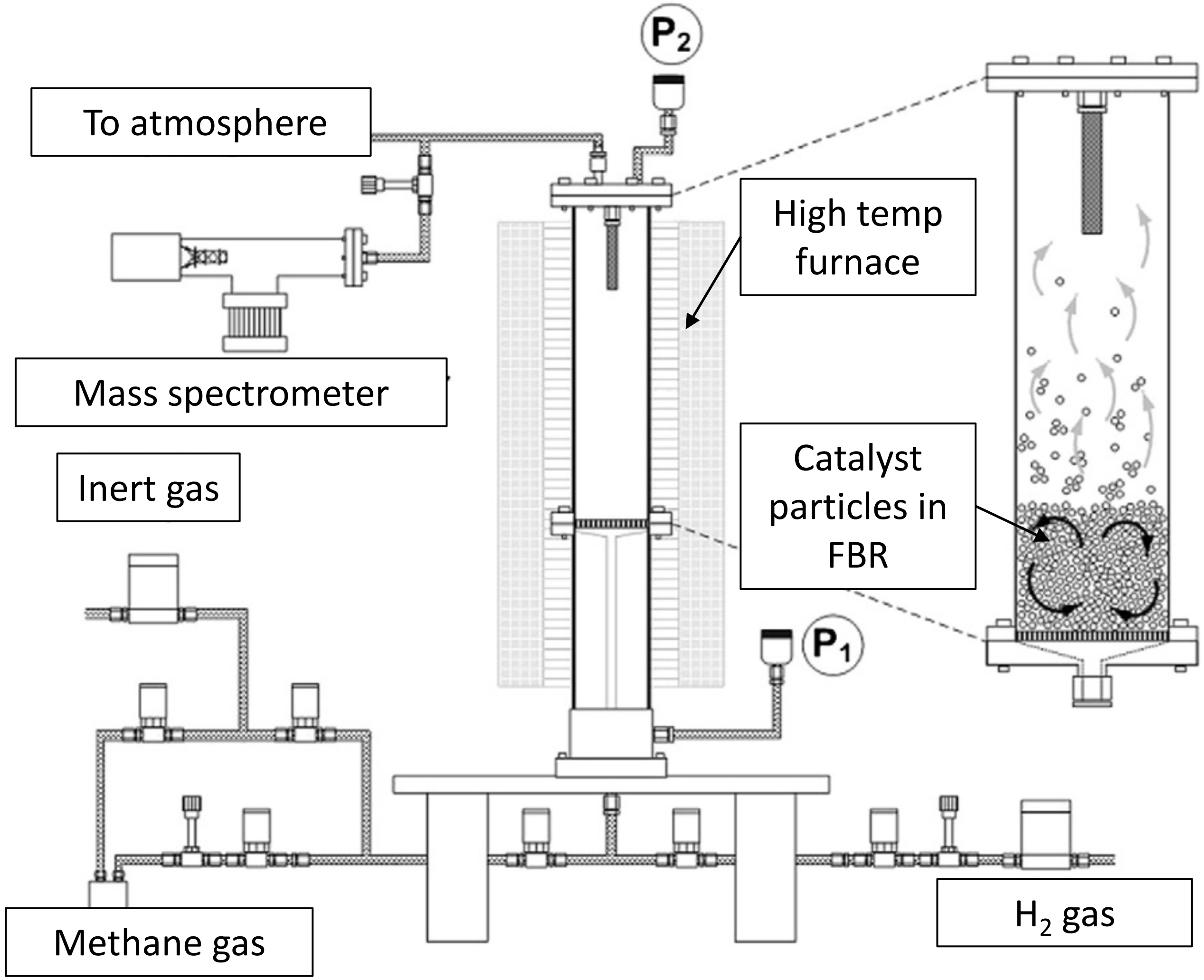


Optimize for field production of value-added nanocarbon product

Technical Approach: Fluidized Bed Reactor

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

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

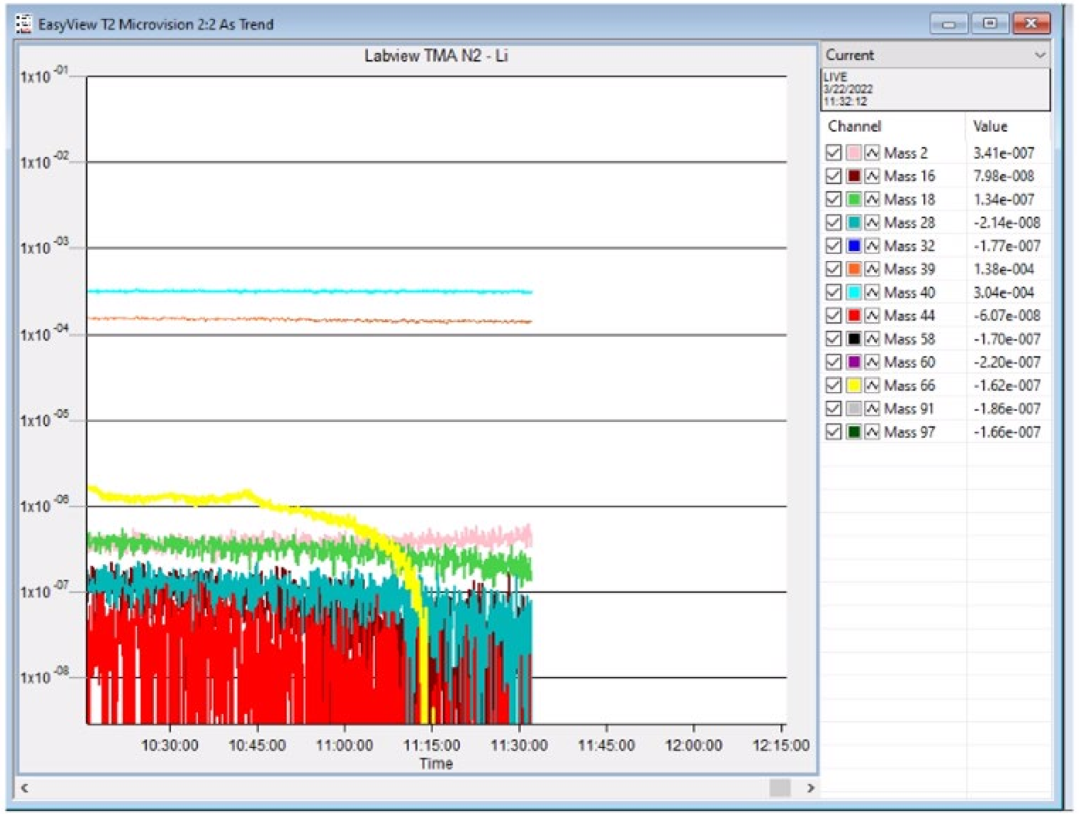


Progress: CVD is Carried Out

Catalyst Synthesis

- 750g of catalyst (mass substrate + nickel) have been synthesized and delivered to CU Boulder
- Another 6kg have been synthesized for CVD module operation
- **Construction of large-scale catalyst synthesis module is completed**

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



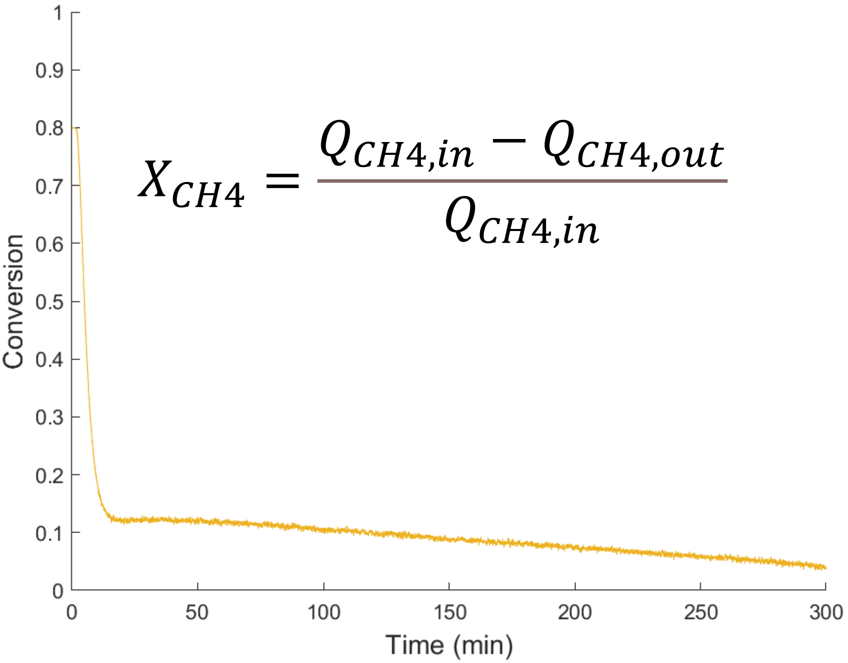
Mass spectrometer trace during synthesis. The signal on M/Z=66 (yellow, likely cyclopentadiene) dropping to ~0 torr was used to determine when all nickelocene had been consumed

1-cycle Particle ALD

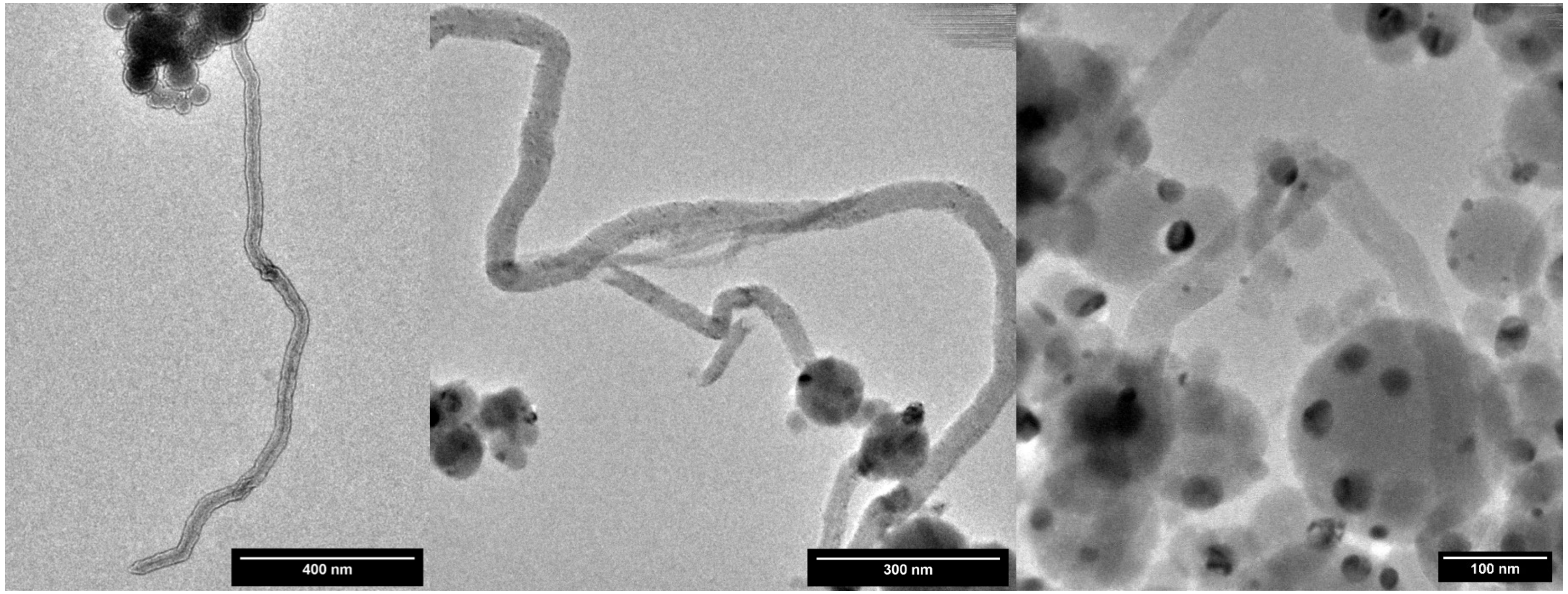
Progress: CVD is Carried Out

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

Factor	High Value (+1)
Reduction Step	500°C 1 hour 50% H2, 50% Ar
Methane Concentration (P_{CH4})	16.7%
Carbon content (wt%)	**31.8wt%**



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



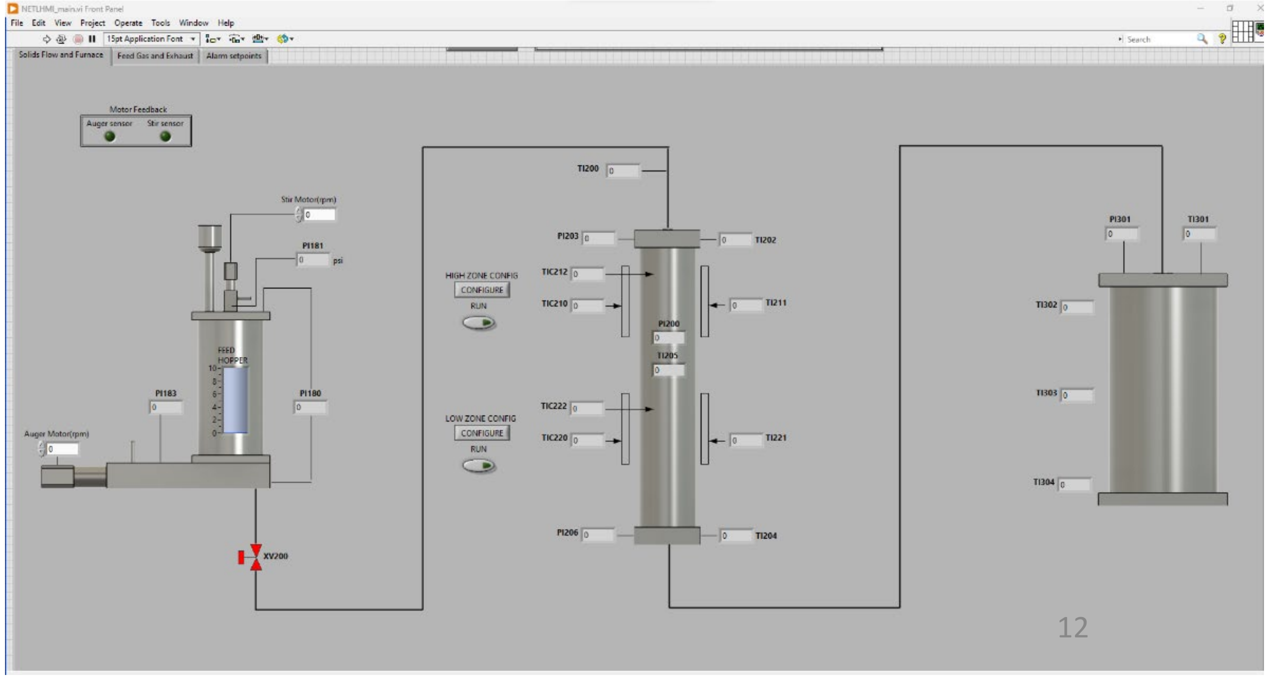
Carbon filaments contain L:D >10

Progress: Module Operation

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

Progress: Module Operation

*Modular skid has been constructed and installed at Forge Nano. **Commissioning and startup underway.***



Progress: Mix design and dispersion of CNFs

Optimized UHPC-CNFs mix design (wt.%)

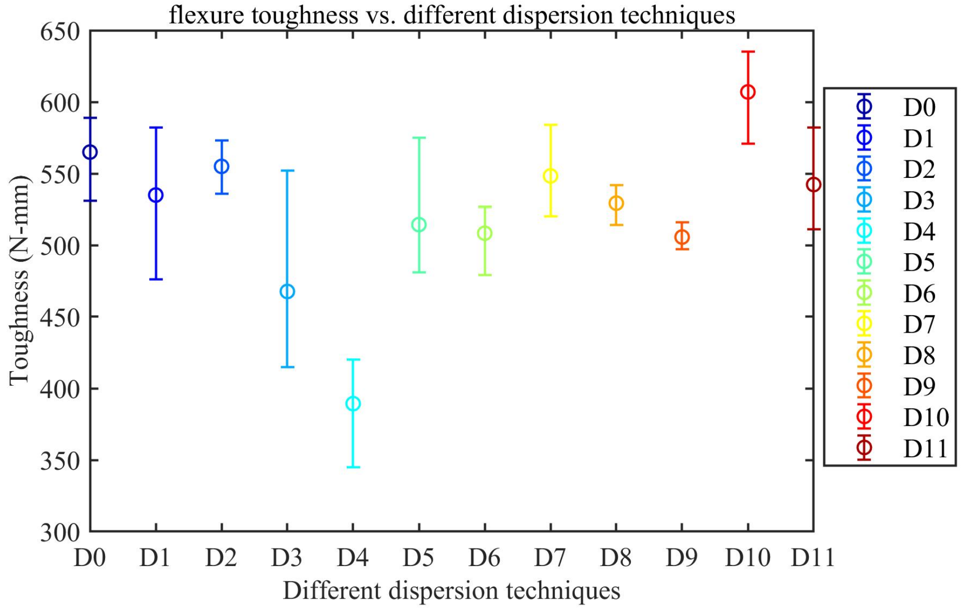
w/c	Cement	Water	Sand	SF	HRWR	CNFs
0.18	35.83	6.45	49.50	6.63	1.55	0.04

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

Premixing

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.

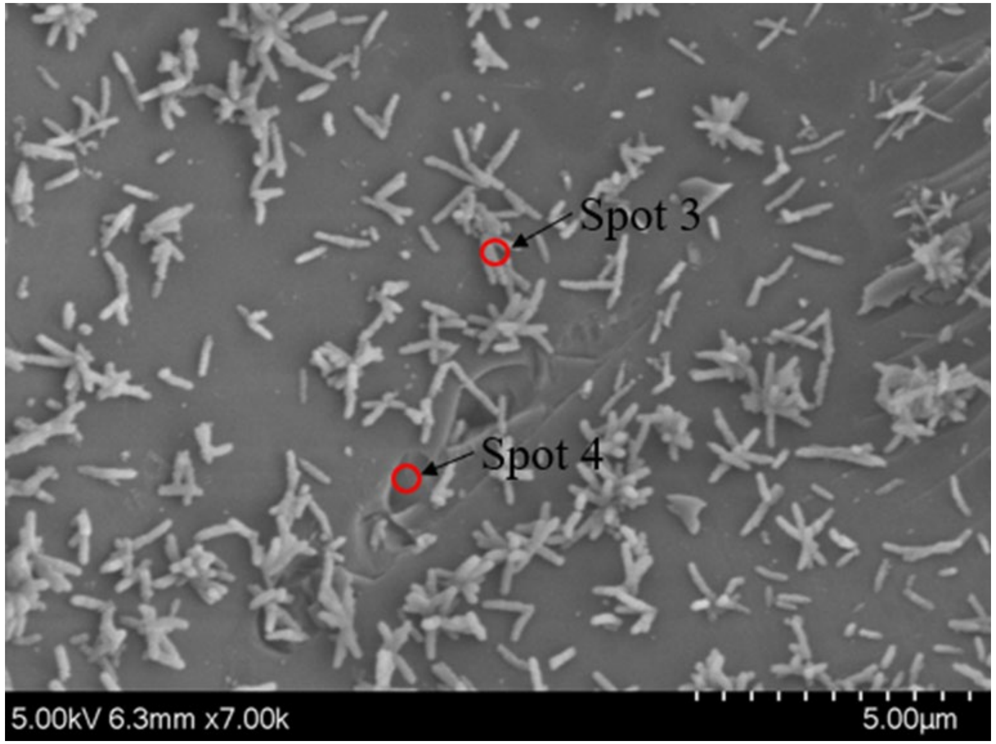


Ultrasound dispersion

- 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

Visual confirmation of successful dispersion with SEM



SEM Image of a well-dispersed UHPC-CNFs sample

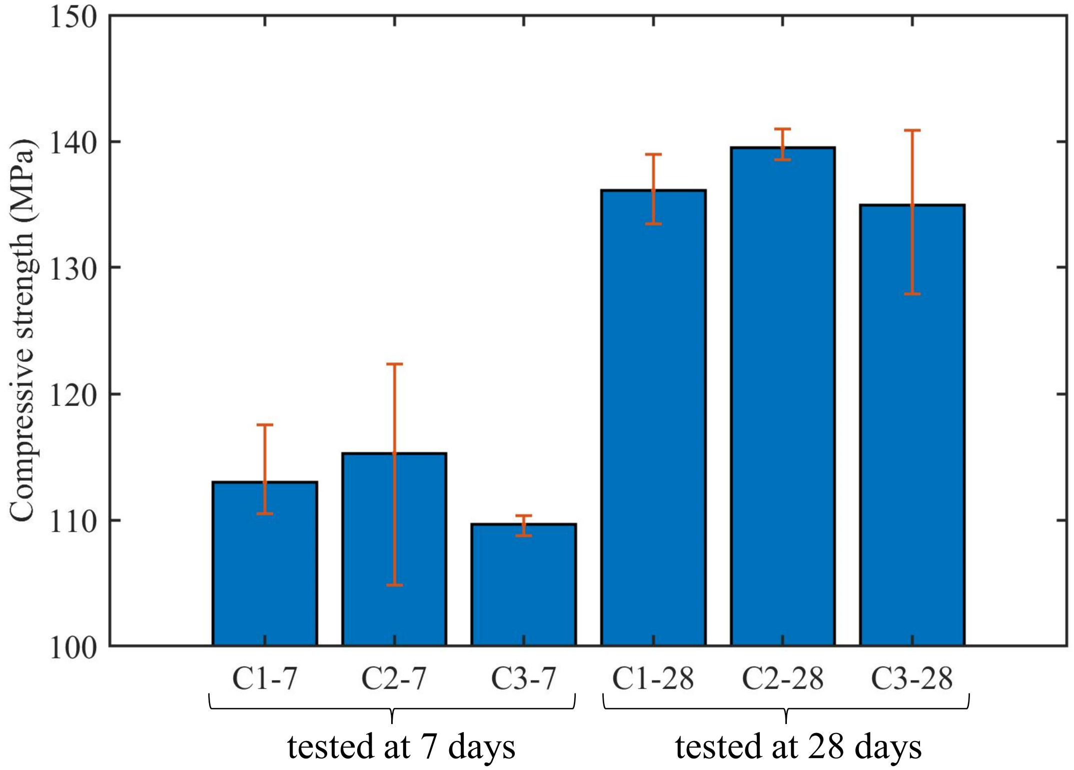
- SEM shows **fibers are well-dispersed** with dispersion method D10.
- Images of poorly-dispersed CNFs show large-scale bundles of fibers.
- FIB-FESEM and EDS of Spot 3 and Spot 4 were used to confirm **white features are single CNFs**.

Progress: Optimize CNF addition amount

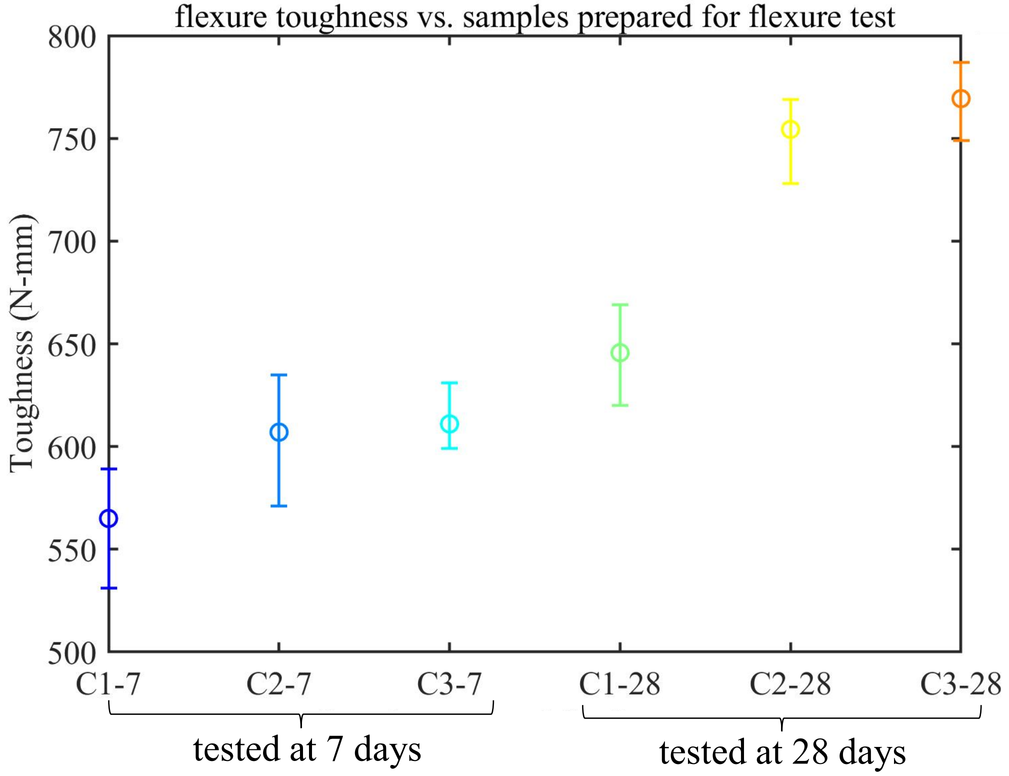
Samples with different CNF ratios tested at 7 days and 28 days

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



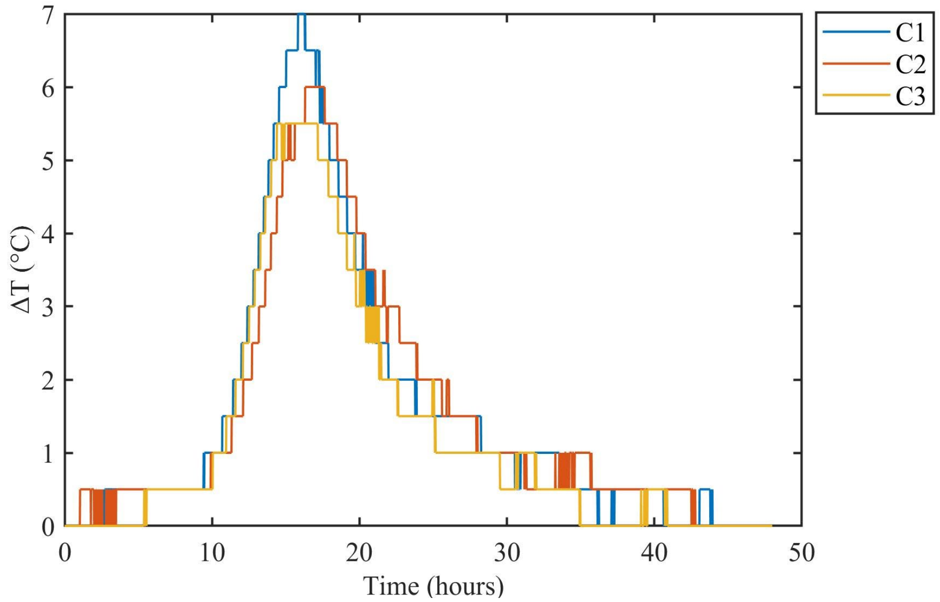
- A High Range Water Reducer (HRWR):CNF ratio of 10:1 showed the highest Flexure Toughness

Progress: CNF not detrimental to Hydration rate and slump

CNF impact on Hardening Rate assessed by Heat Evolution

- **All samples reached the peak in hydration in similar time after mixing**

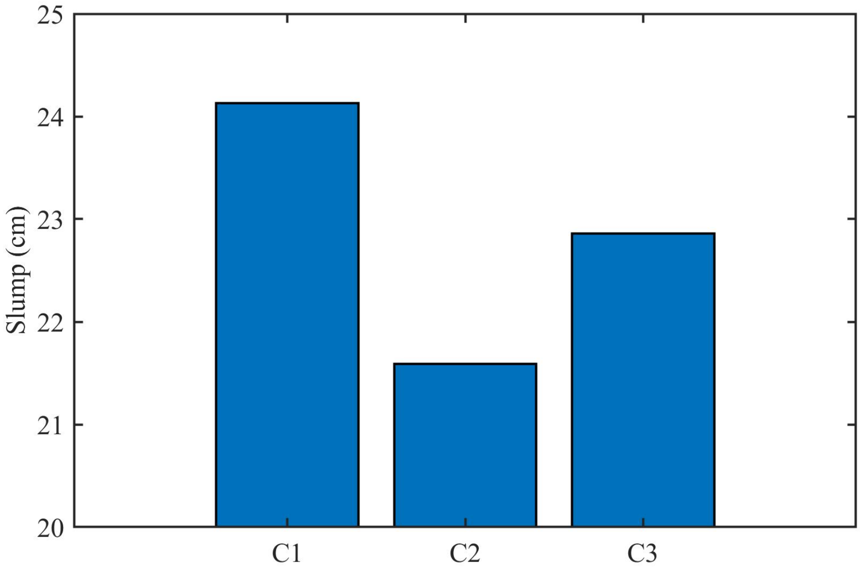
Maturity test



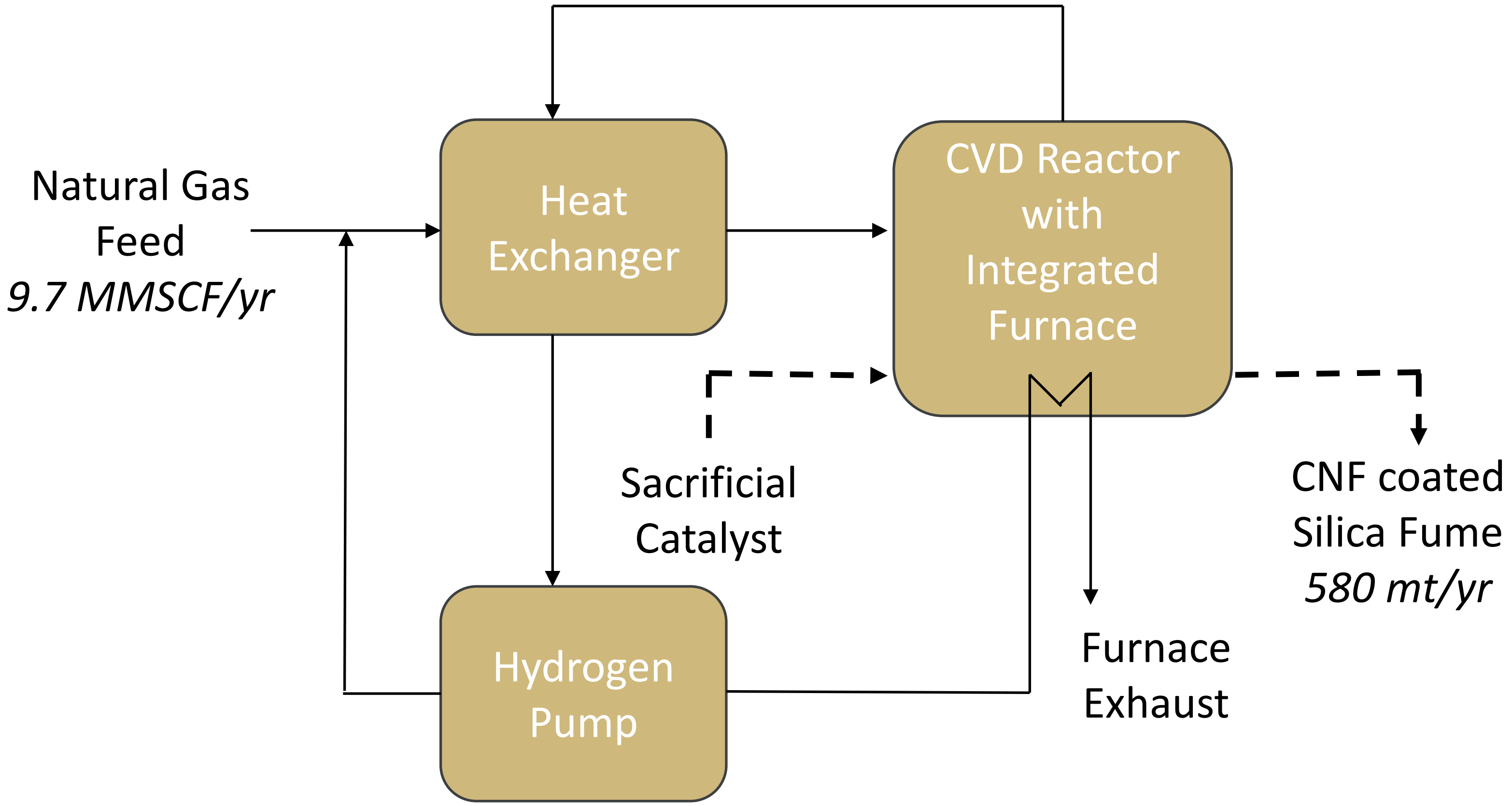
CNF impact on Concrete Flow by Slump

- **Minimal change** in **set time** and **slump** can be **addressed with commercial admixtures**. Research in progress

Slump test



Progress: TEA



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:

< $4 per kg

Pure CNF, price range:

< $20 per kg

Pure CNF, current technology:

***~$280 per kg* (bulk quote)**

Future Work

Lab-Scale CVD

- Additional lab-scale CVD studies to **inform modular operation**.
- Continue to investigate **impact of catalyst metal loading & CVD processing conditions** on ultimate CNP **performance in concrete**

Modular Skid System

- **CVD** will be carried out to produce carbon nanoproduct (CNP) at **1kg /hr**.
- **Modular system** performance will inform the final commercial path assessment of this technology & **supply larger scale product for concrete testing.**

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**
  • M loading/type
  • Natural gas feed
• **Design of deployable skid**
• **Catalyst manufacturing scale up (1-cycle spatial ALD)**
• 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
		  • Tubes (single/multi)

Potential Commercialization Work Beyond Current Project

CVD solid carbon production	Concrete Market	Additional Markets for Carbon

• **Identify** customers for wellhead located skid
• Logistics
• 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), Bola Odunaro (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

Particle ALD & CVD

Lab Scale and Modular Operation

- CVD was carried out in lab-scale system on ALD catalyst – target carbon yields achieved.
- **Modular skid has been constructed and installed at Forge Nano**
- **Commissioning and startup underway**.

Concrete mix design using commercial CNFs

- 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**

Technoeconomic analysis

- TEA and H2A analysis complete
- Aspen plus simulation and PFD for modular flare gas scale process developed
- **CNP product selling price estimated at < $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)
  - (1) Kent Warren (4) – Postdoctoral Fellow
  - (1) Jessica Hauck (4) – PhD Student
  - Robert Anderson (2) – Principal Engineering Scientist
- Mija Hubler (Civil Engineering) co-PI (3)
  - Linfei Li (3) – Postdoctoral Fellow
  - Bola Odunaro (3) – PhD Student
- 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: in BP3

<u>Completed Tasks</u>

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

<u>Current Tasks</u>

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