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Extremely Durable Concrete using Methane Decarbonization Nanofiber Co-products with Hydrogen

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University of Colorado **Boulder**

DOE Hydrogen Program
2024 Annual Merit Review and Peer Evaluation Meeting

Project Goal

Develop a scalable low-cost chemical vapor deposition (CVD) process to produce carbon nanofibers (CNFs) and H_2 from CH_4 using a sacrificial ALD catalyst deposited on a fumed silica substrate. A minimum 10% Investors Rate of Return (IRR) for a process selling CNFs at an acceptable identified cost while selling H_2 for < \$2/kg.

Develop extremely durable concrete (High performance concrete) by adding the co-product carbon nanofibers (CNFs). The 28-day compressive strength should be at least 8000 psi. Comparing with the mix design which has no CNFs, the ductility should be improved at least 25%, and the chloride permeability should be 25% lower.

Overview: Year 3 of 3-Year Project

Timeline

Project Start Date: 5/1/2020

Project End Date: 10/31/2024

% Complete: 90%

Budget

Total project funding: $1,250,000

Sub-contract: $125,000

Total recipient cost share: $250,000

Total DOE funds received to date: $1,000,000

Collaborators

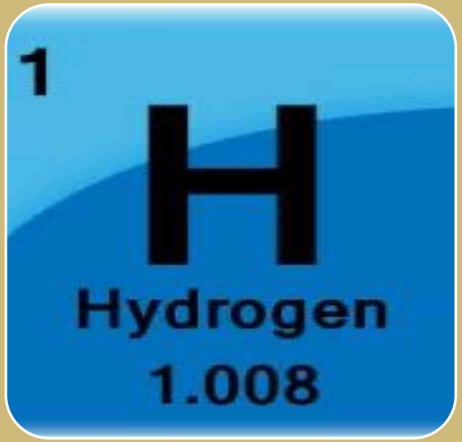
ForgeNano

- Thornton, CO
- Reactor/process design and technoeconomic analysis

National Ready Mixed Concrete Association (NRMCA),

- Alexandria, VA
- Concrete materials, mix design, and consulting

Potential impact: Hydrogen generation from decarbonization of methane



Large-scale H_2 production

- Potential to displace U.S. H_2 production by steam methane reforming (SMR) with a low-cost and scalable CVD process
- Unlike SMR, no CO_2 is produced directly from CVD of CH_4
- CH_4 is the main component of natural gas, an abundant energy resource
- The value-added CNF product 'sequesters' carbon from CH_4 as a solid

CNFs for high performance concrete

- CNFs: instead of separating CNFs from catalyst/fumed silica, 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

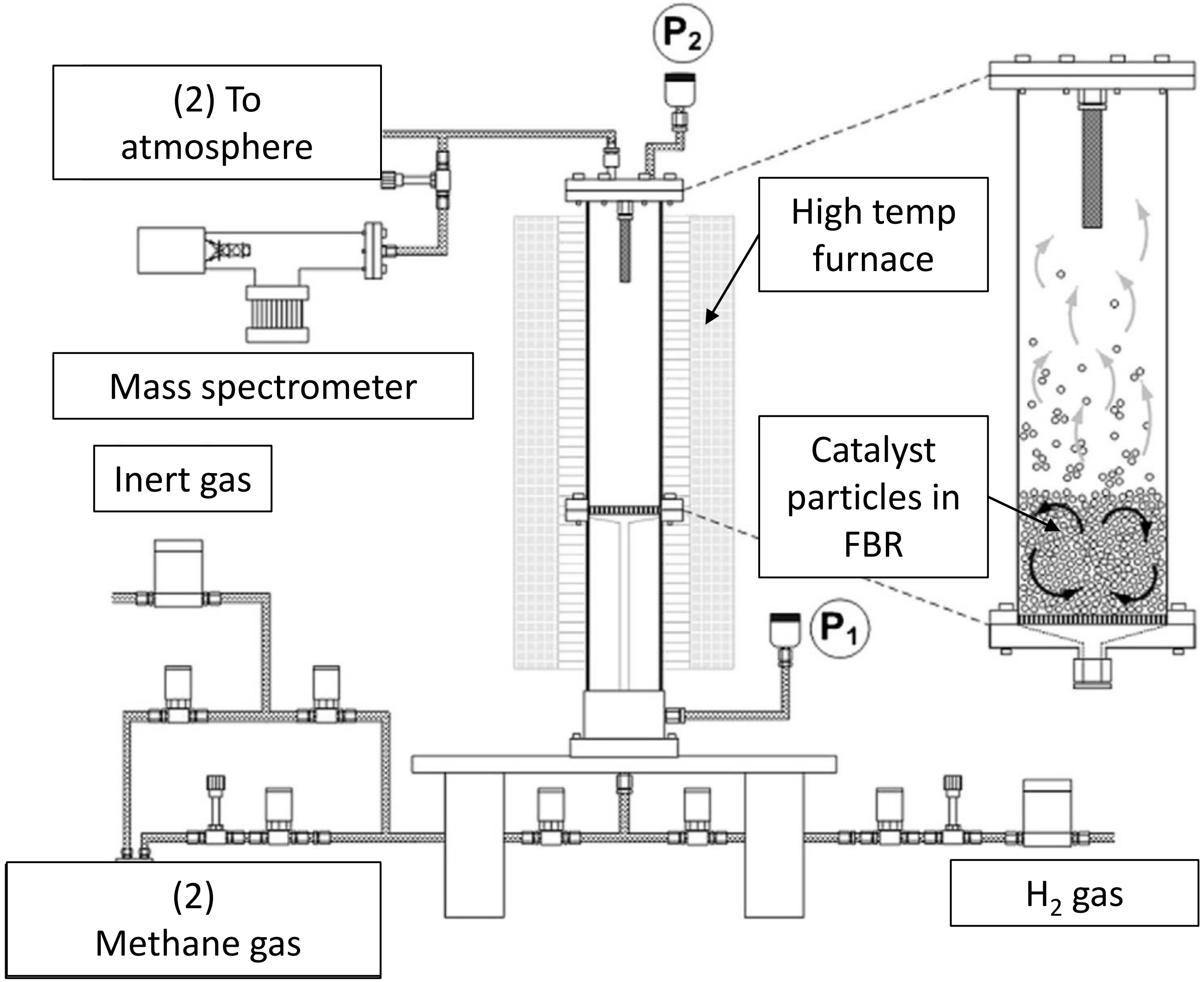
[1]Johanna Lehne, F. P. (2018). *Making Concrete Change Innovation in Low-carbon Cement and Concrete*.

Approach: Particle ALD/CVD catalysis system

- Use transition metal catalysts on a fumed silica support to grow CNFs
- Catalyst will be produced using particle atomic layer deposition (ALD) in a fluidized bed reactor
- Catalyst will **not** be separated from CNFs (sacrificial)
- CNF product will be used as a crack-bridging additive in high-performance concrete

Catalyst Metal	Catalyst Support	ALD Chemistry
Iron	Fumed silica	Ferrocene/H_2
Nickel	Fumed silica	Nickelocene/H_2

Approach: Particle ALD/CVD catalysis system



Step 1: ALD onto fumed silica particles (~300°C)

Step 2: CNF growth and hydrogen co-production from methane gas (500-750°C)

Approach: Safety Planning and Culture

- A hydrogen safety plan was submitted Fall 2020. Risks are identified below.

Item	Potential failure mode	Potential cause	Effect	Probability estimate	Severity	Detection	Risk Level	Mitigation
Viton O-rings	Leakage from poor seal	Degradation of O-ring due to high temperature	Loss of pressure and leaking of reaction gas	B	II	(1) Mass spec will detect change in gas concentration and baratrons detect deviation in pressure	Low	Inspect O-rings before every run and replace if damaged
Alumina reactor tube	Off-round condition	Manufacturer defect	Improper compression fitting seal around tube	C	II	(2) Reactor tubes checked for off-round when received	Low	Reactor tubes machined to resolve off-round
Reactor manifold system	Leak into or out of system	Loose Swagelok connection	Loss of pressure and leaking of reaction gas	B	II	(1) Mass spec will detect change in gas concentration and baratrons detect deviation in pressure	Low	Connections rigorously helium leak-tested and tightened/replace if leaking
Electrical control system	Spark/ignition	Short	Creation of electrical spark or fire	A	III	(3) Visible spark/small fire and failure of electronics	Medium	Placement of electrical components well below any area that contains H_2

SOPs are continually reviewed and updated for improved safety.

Achieved Go/No-Go Targets

CVD	*A 50% CH_4 conversion will be achieved while producing H_2 and CNFs having an L/D > 10 with a carbon content of 25 wt% of the combined CNF + metal catalyst + fumed silica support.*
Concrete Mix Design	*Samples containing CNFs from sacrificial metal catalyst will show: (1) maximum crack sizes ≤100 µm under drying conditions at 28 days; (2) an increased tensile ductility by 25% higher with CNFs in the optimized cement mix; (3) chloride permeability 25% lower when compared to standard accelerated-set high-strength cement obtained from cement manufacturers; and (4) no change in set time*
TEA	*On the basis of actual experimental results, an H2A analysis will be carried out including capex for H_2 purification and selling price for byproduct CNF to achieve DOE's cost target of \$2/kg H_2 selling price.*

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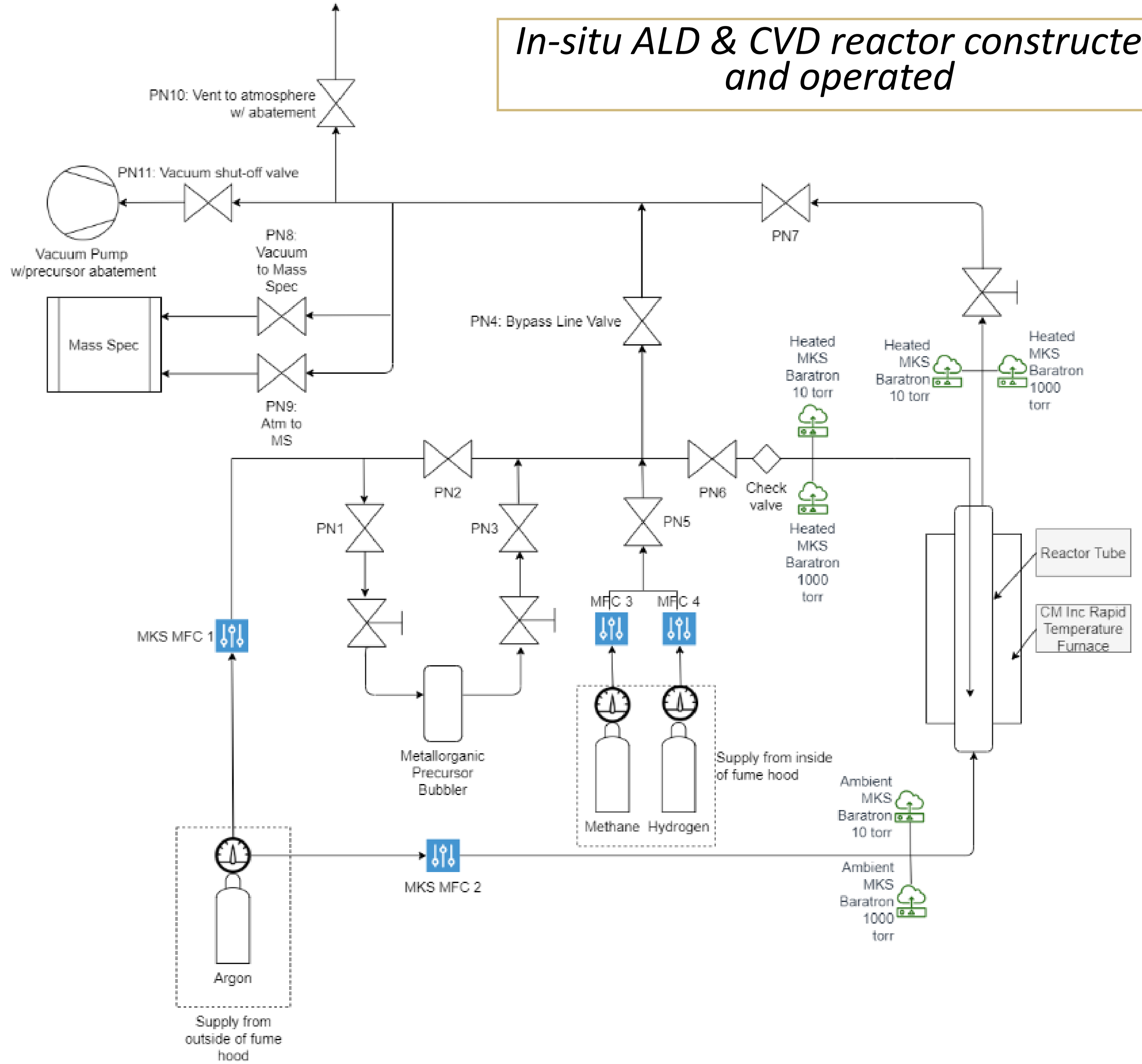
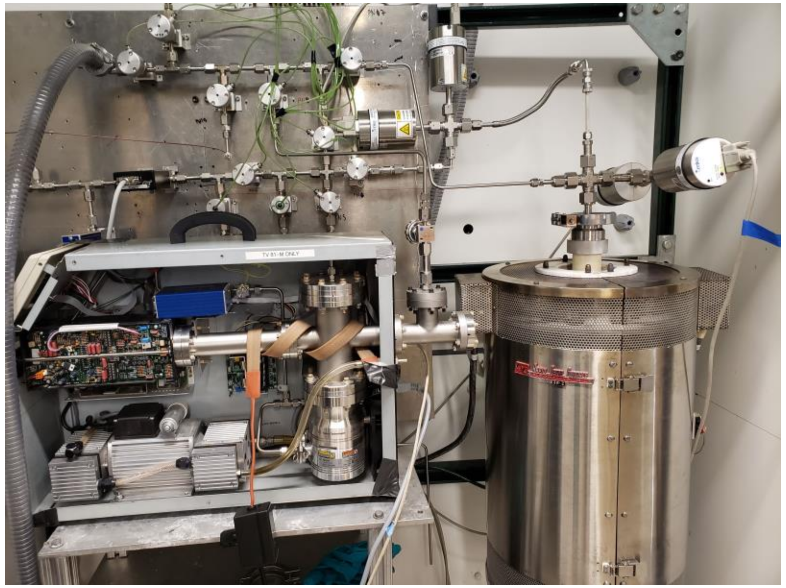
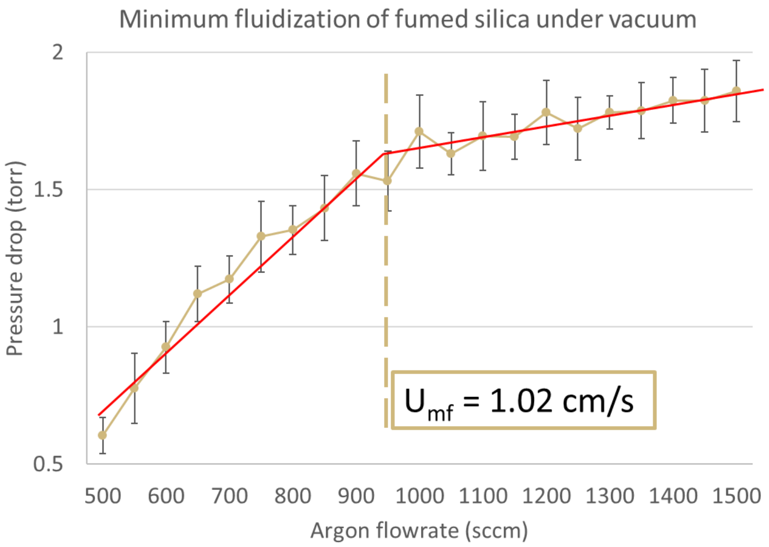
Accomplishments: Reactor design and construction

In-situ ALD & CVD reactor constructed and operated



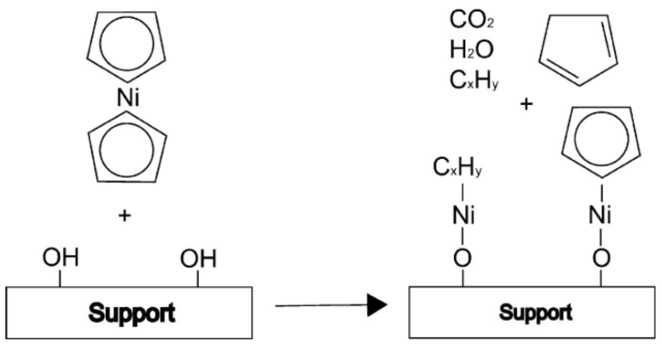




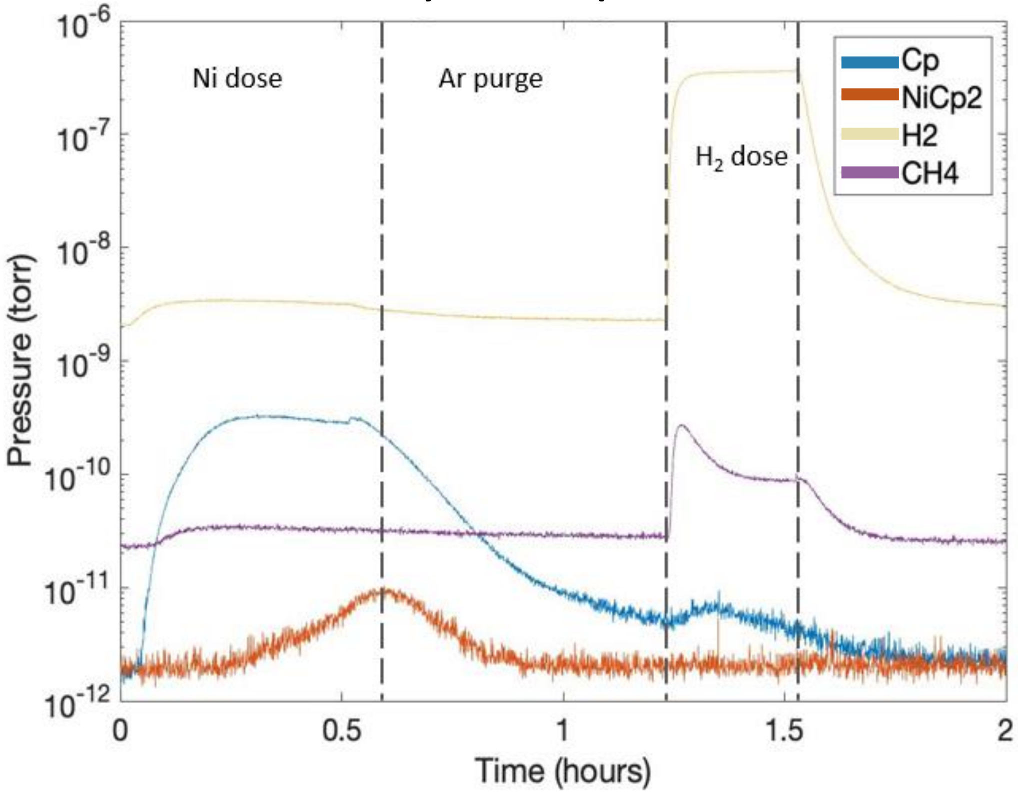
Accomplishments: Preliminary ALD Studies

Nickel successfully deposited onto fumed silica support via $NiCp_2/H_2$ ALD

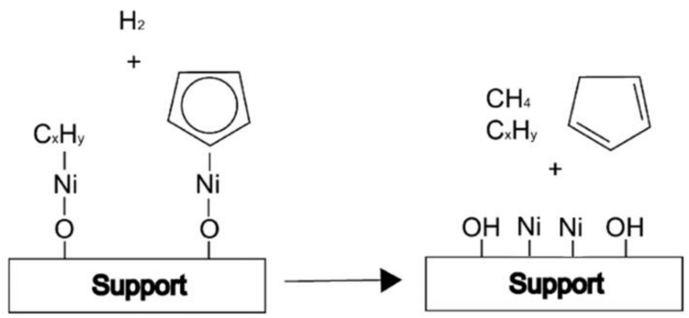
First Half Reaction[1]



First ALD Cycle Mass Spectrometer Trace



Second Half Reaction[1]



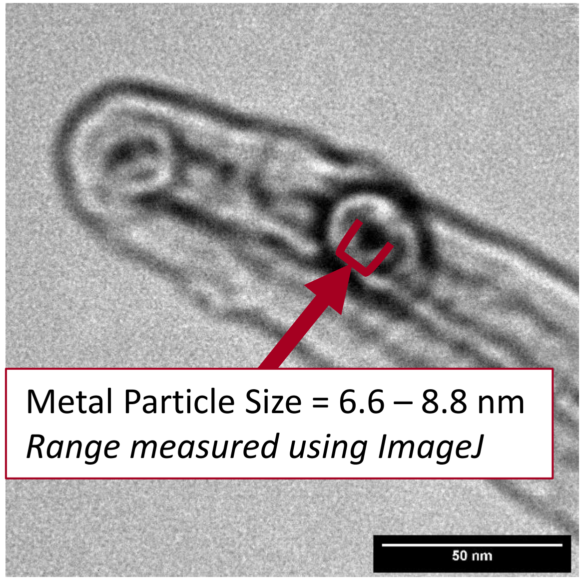
[1]Adapted from T.D. Gould et al., *Journal of Catalysis* 303 9-15. (2013)

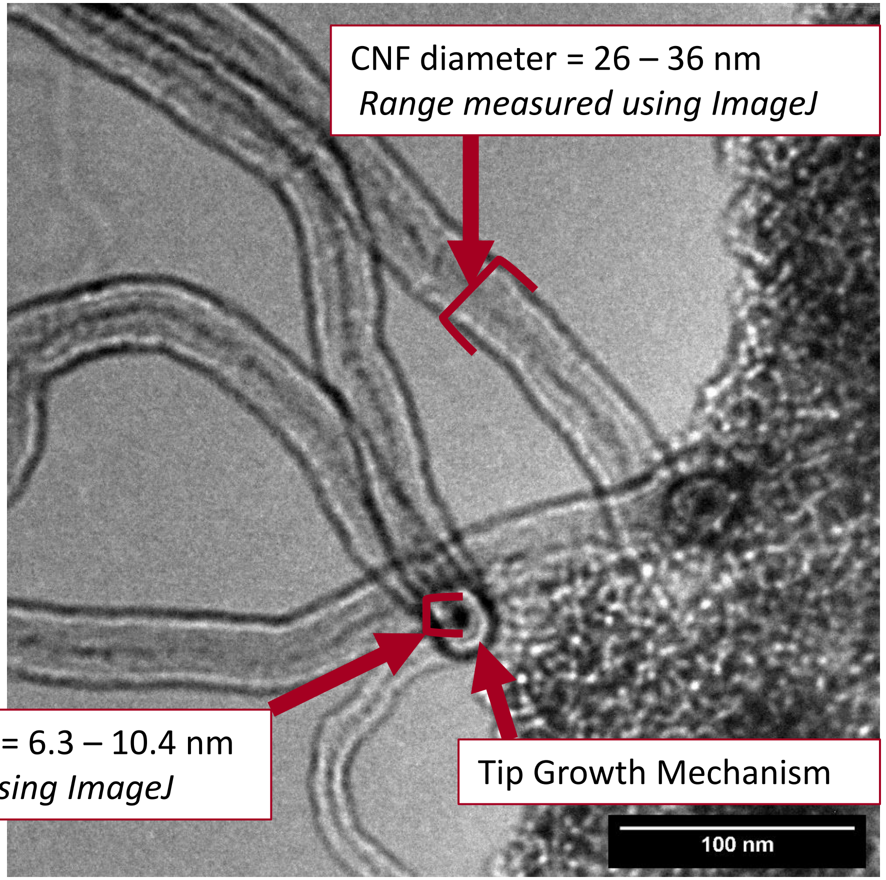
Accomplishments and Progress: CVD over ALD nickel catalyst

Carbon nanofibers can grow from CVD of methane on an ALD catalyst.
CNFs grow via tip growth mechanism.

CVD	
Temperature	550°C
Time of Reaction	3 hours
CH_4 Partial Pressure	0.10 atm
H_2 Partial Pressure	0.03 atm
$CH_4 : H_2$	3

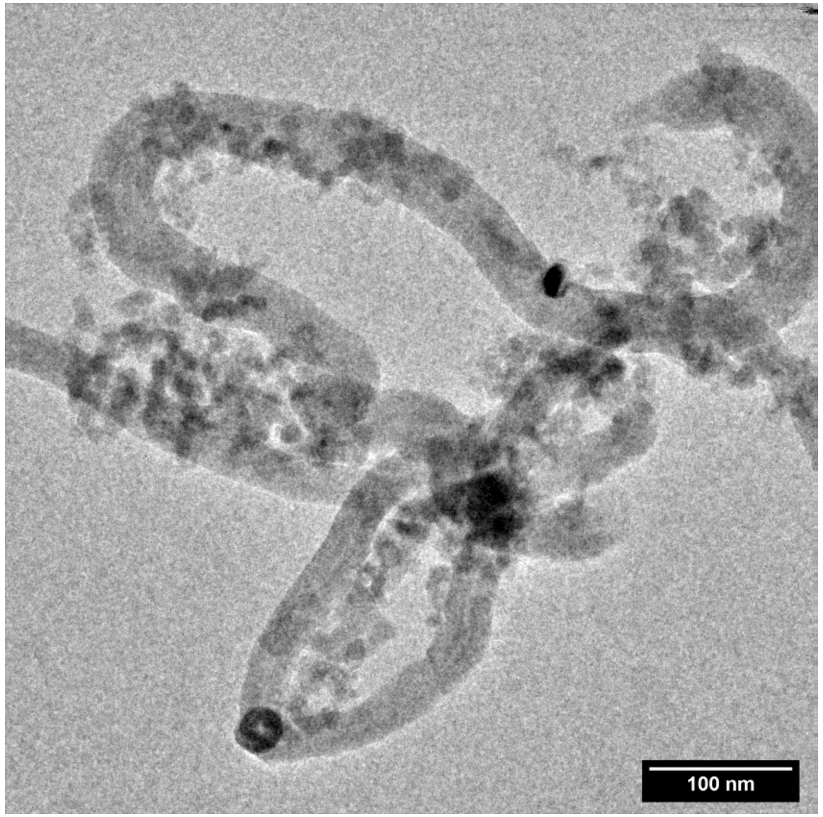
Product post-CVD

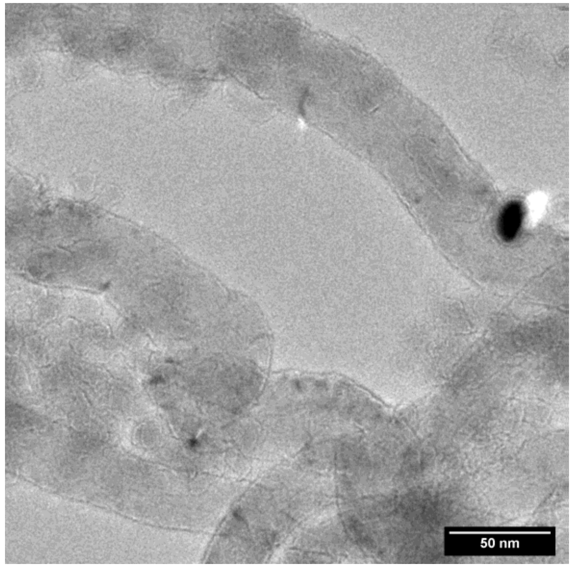


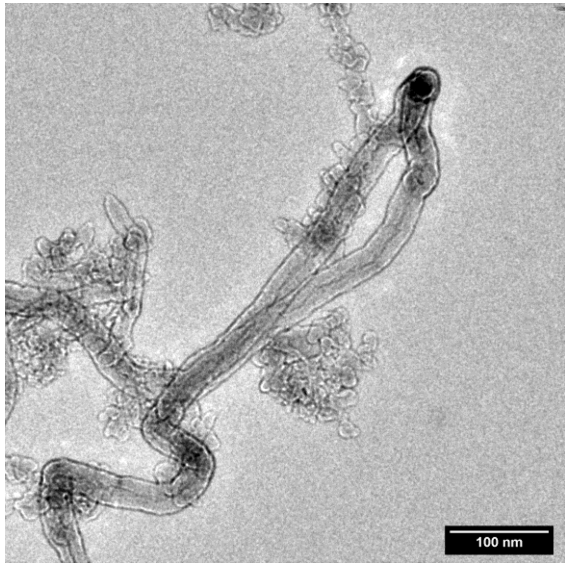


Accomplishments and Progress: Achieved Target Carbon Yields

✓CNFs with a L/D > 10



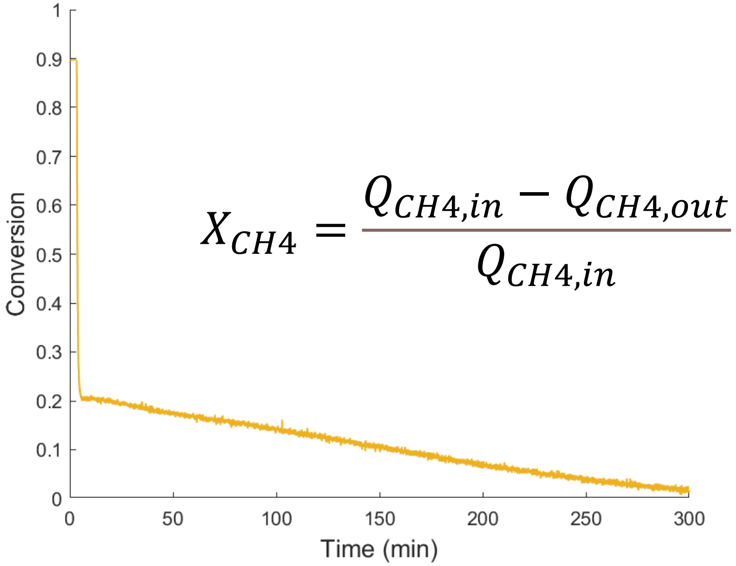




✓ Carbon content will be at least 25 wt% of the total mass of CNF + catalyst + substrate

	wt%	Determined by
Ni	9.8	ICP-OES
C	**26.5**	**Carbon LECO**
SiO_2	63.7	Difference

✓ 50% Conversion achieved



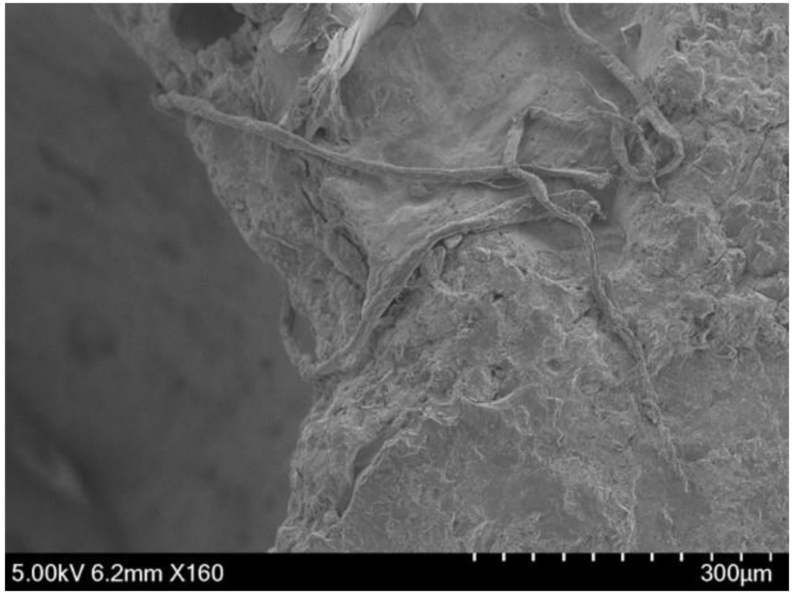
$$X_{CH4} = \frac{Q_{CH4,in} - Q_{CH4,out}}{Q_{CH4,in}}$$

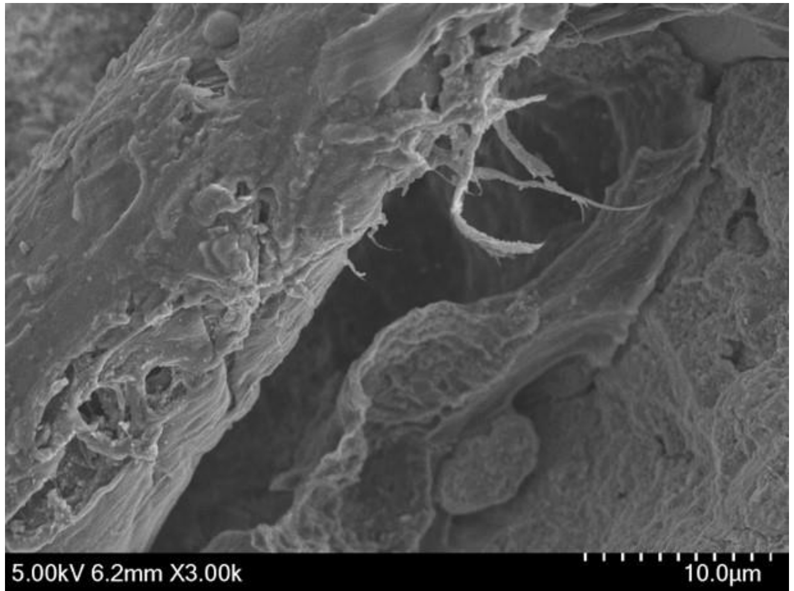
Achieved Go/No-Go Targets

CVD	*A 50% CH_4 conversion will be achieved while producing H_2 and CNFs having an L/D > 10 with a carbon content of 25 wt% of the combined CNF + metal catalyst + fumed silica support.*
Concrete Mix Design	***Samples containing CNFs from sacrificial metal catalyst will show: (1) maximum crack sizes ≤100 µm under drying conditions at 28 days; (2) an increased tensile ductility by 25% higher with CNFs in the optimized cement mix; (3) chloride permeability 25% lower when compared to standard accelerated-set high-strength cement obtained from cement manufacturers; and (4) no change in set time***
TEA	*On the basis of actual experimental results, an H2A analysis will be carried out including capex for H_2 purification and selling price for byproduct CNF to achieve DOE's cost target of \$2/kg H_2 selling price.*

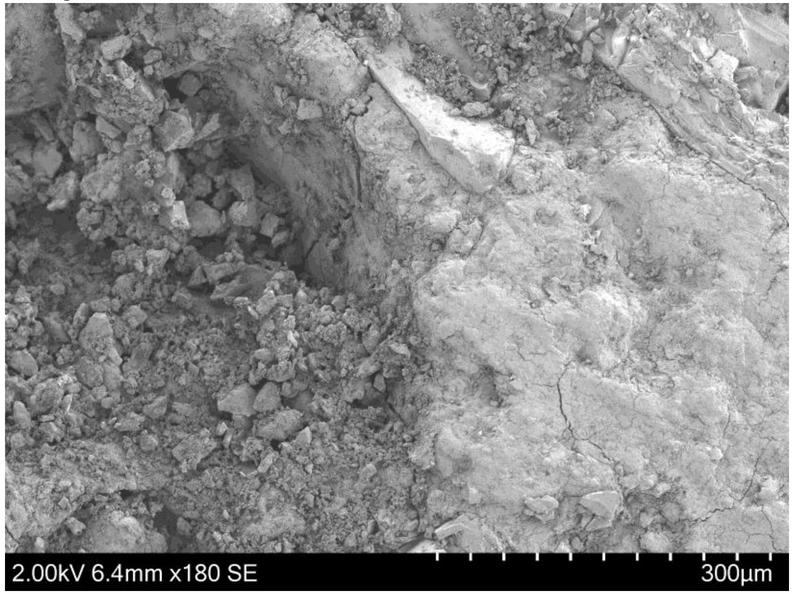
Accomplishments and Findings: SEM images

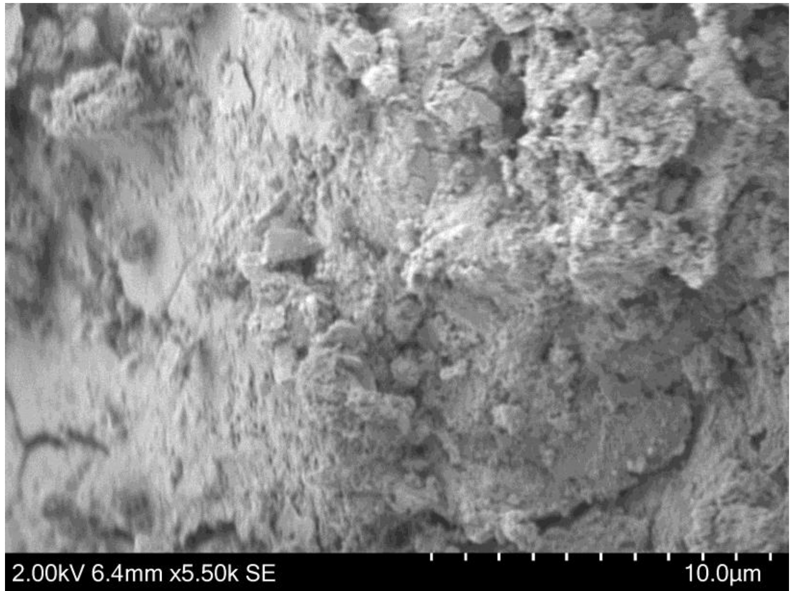
Poorly dispersed CNFs





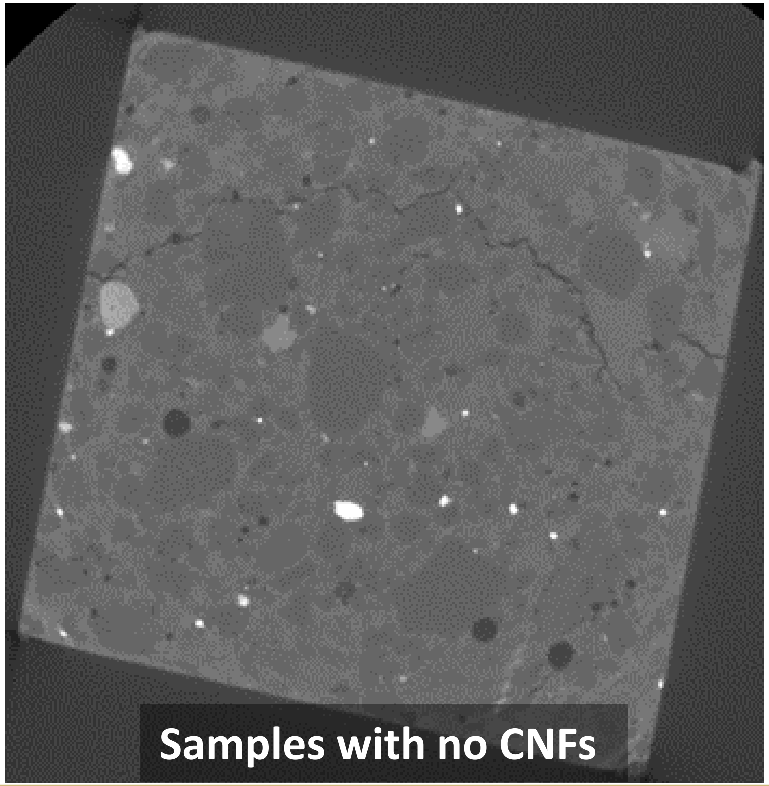
Well-dispersed CNFs with sacrificial metal catalyst

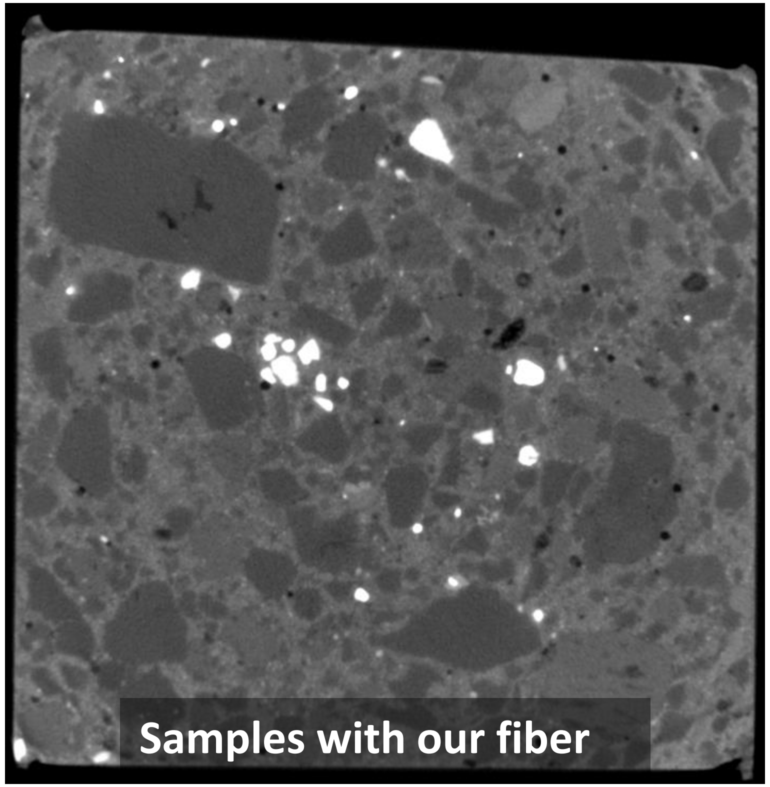




Accomplishments and Findings: Maximum crack size by XRM

✓ ***Maximum crack sizes ≤100 µm under drying conditions***





Results:

- For 1 cm mortar cube, after moist curing for 7 days under room temperature and oven drying for 7 days at 85°C,
  - Cracks ~50 µm visible in the cube without CNFs, **No cracks visible (at ~17.6 µm resolution) in the cube with CNFs from sacrificial metal catalyst**
- For 1 cm mortar cube reinforced with CNFs, after air drying for 28 days under room temperature,
  - Crack size: **still no cracks visible (at ~17.6 µm resolution)**

Accomplishments and Findings: Compressive strength and flexural toughness

Table 2 Compressive strength

Type of CNFs	7-day, psi	Increase	28-day, psi	Increase
No CNFs	10500±500	control sample	12450±600	control sample
PR-19	10700±1000	+2%	12700±1100	2%
Our fiber	9060±1000	-14%	9600±700	**-23%**

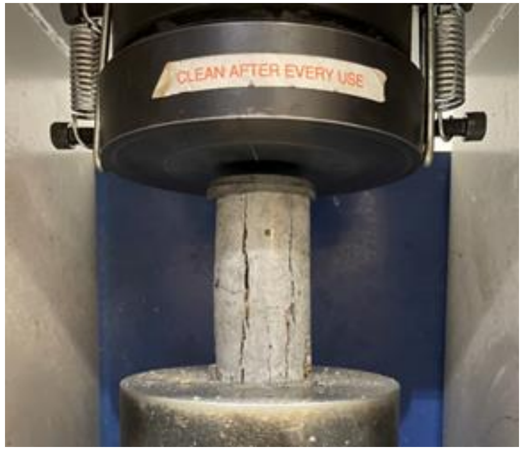
✓ ***Tensile ductility increased by 25%***

Table 3 Flexural toughness

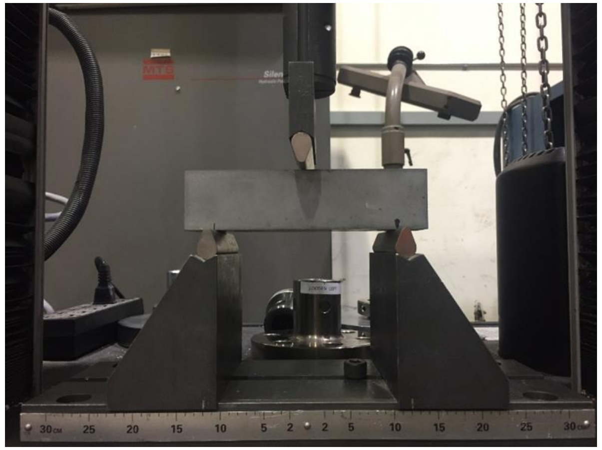
Type of CNFs	7-day, $N * mm$	Increase	28-day, $N * mm$	Increase
No CNFs	320.9±25	control sample	333±40	control sample
PR-19	398.6±20	+24%	441±70	+32%
Our fiber	321.2±25	0%	594.2±25	**+78%**

Table 4 Dispersion methods w/ CNF containing metal catalyst

Dispersion methods	7-day compressive strength, psi	Increase
Control sample	8700±60	Control sample
2*dispersion time	8800±10	+1.1%
2*HRWR	9600±400	**+10.3%**



Compression test



Flexural test

Note:
- Compressive strength according to ASTM C39
- Flexural toughness according to ASTM C348
- Requirement for HPC is 8000 psi compressive strength

Accomplishments and Findings: Chloride permeability

✓ ***Chloride permeability 25% lower***

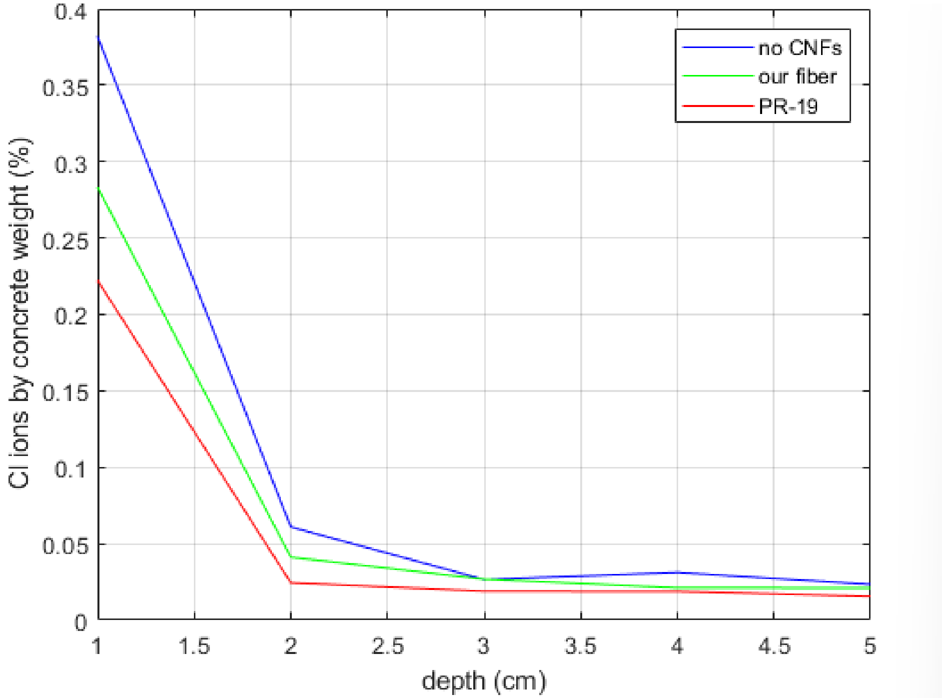
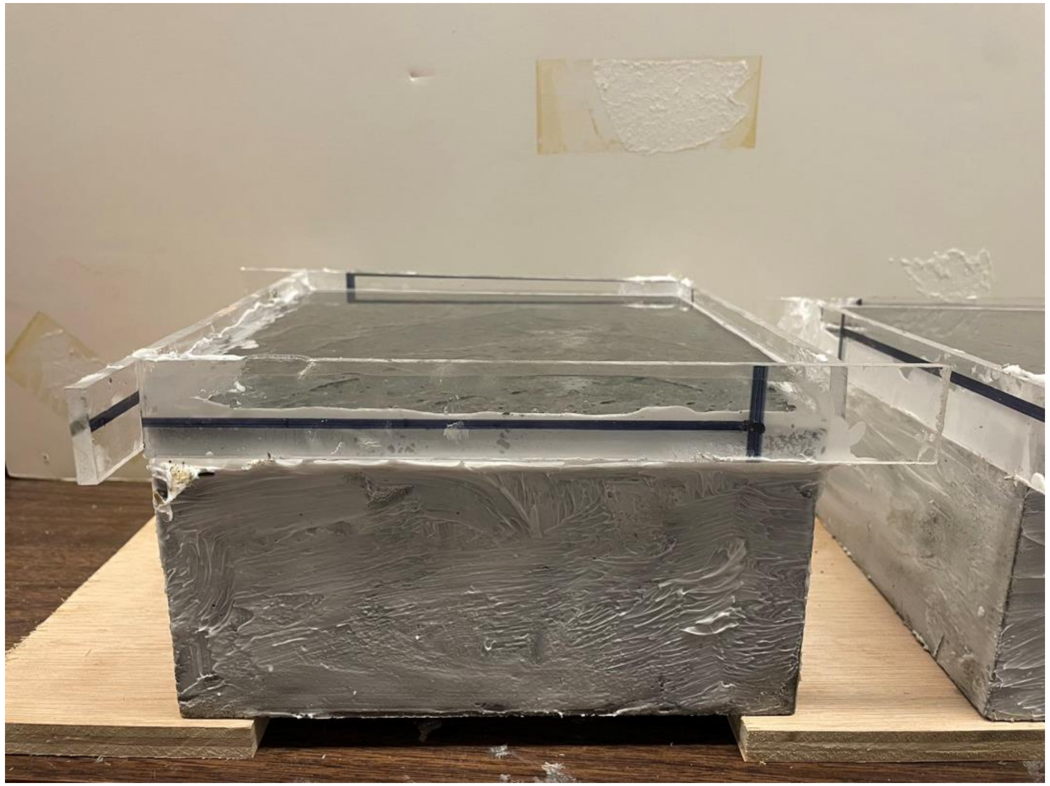


Table 5 Chloride permeability results

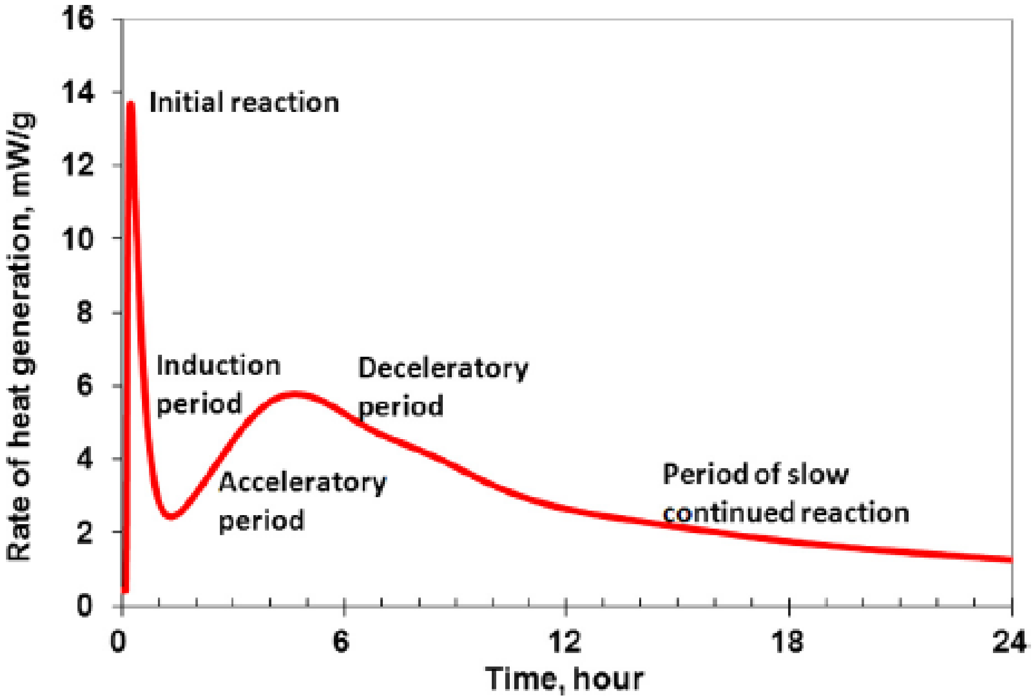
Samples	3-month chloride permeability
No CNFs	Control sample
Our fiber	**-24.9%**
PR-19	-42.7%



Ponding test

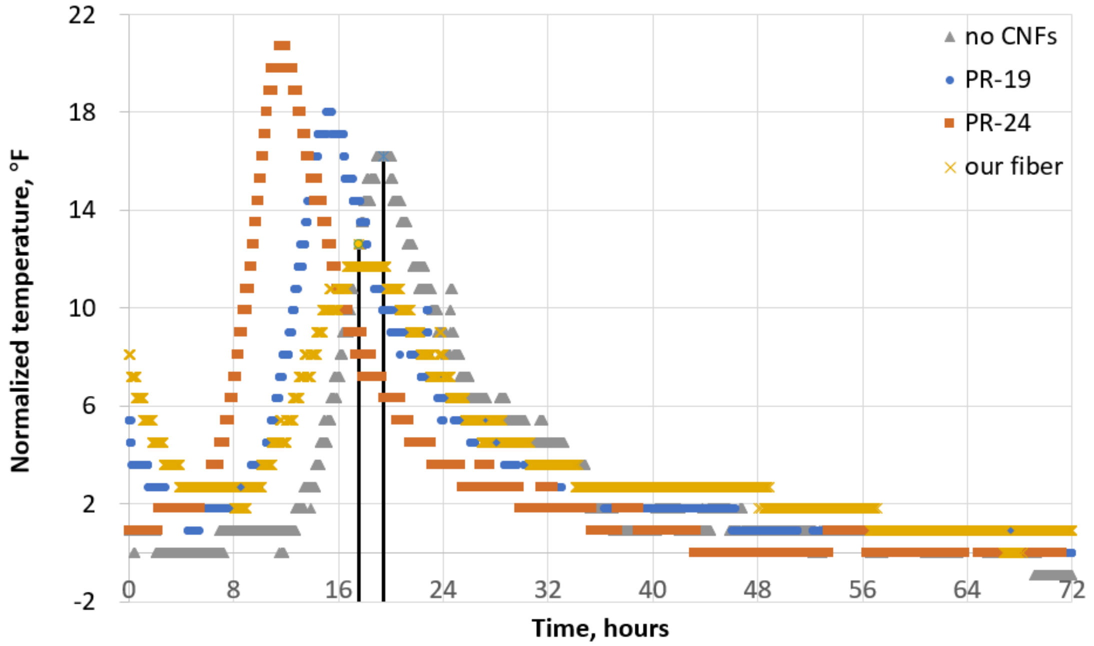
Note:
- The chloride permeability test – ASTM 1543.

Accomplishments and Findings: Setting time



Example of heat of hydration curve[1]

✓ ***Minor change in setting time***



Maturity test ASTM C1604

Results:

- CNFs accelerate the hydration process. Concrete with our CNF set 1.8 hours earlier. This is a smaller change than seen with commercial fiber.
- Within this range optimization of set time can be achieved with chemical admixtures. This is part of the proposed BP3 tasks.

Note: Normalized Temperature = T_sample – T_environment

[1] *J. Hu, etc. (2014) "Influence of cement fineness and water-to-cement ratio on mortar early-age heat of hydration and set times". Construction and Building Materials 50 (2014) 657–663.*

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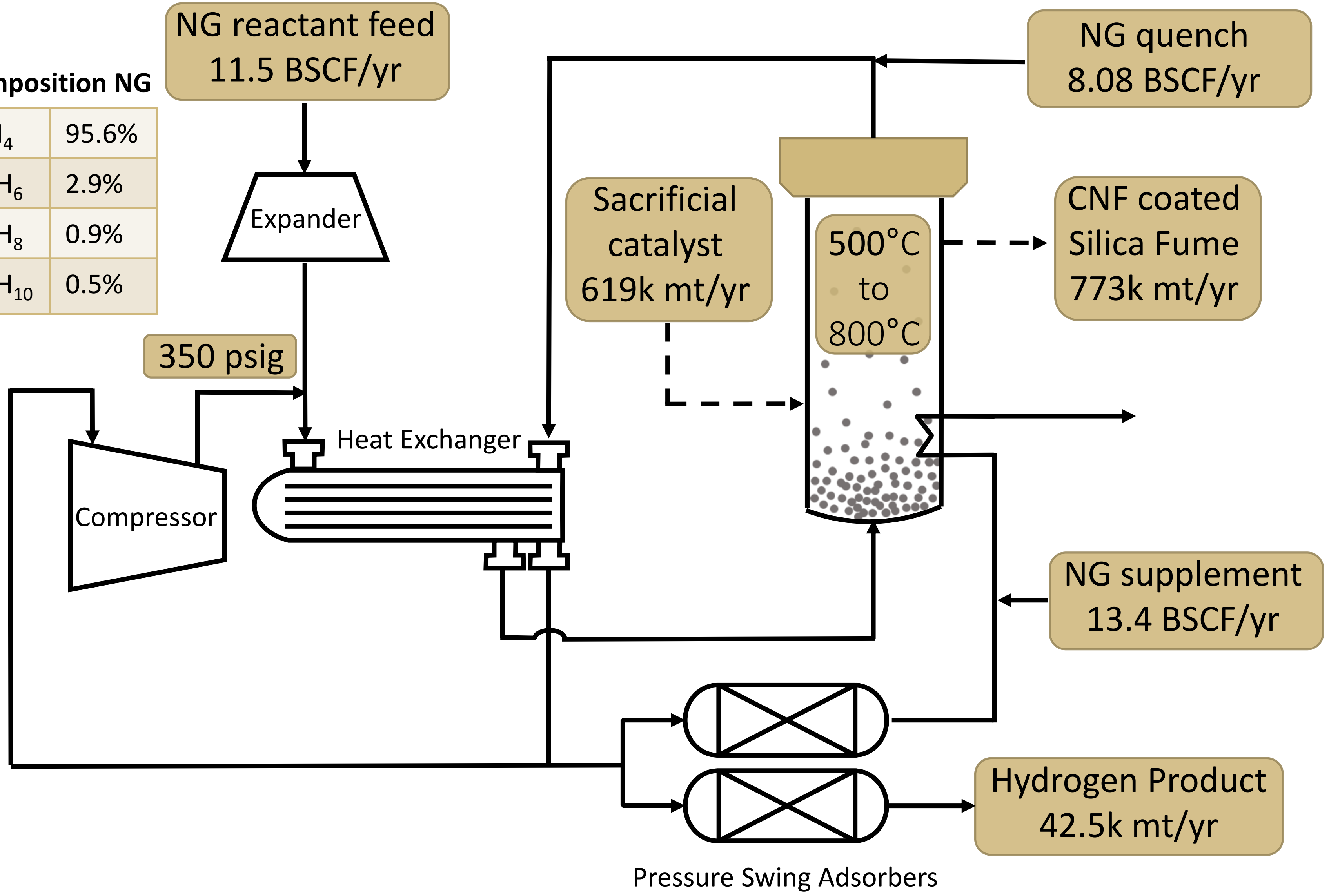
Concrete Mix Design	*Samples containing CNFs from sacrificial metal catalyst will show: (1) maximum crack sizes ≤100 μm under drying conditions at 28 days; (2) an increased tensile ductility by 25% higher with CNFs in the optimized cement mix; (3) chloride permeability 25% lower when compared to standard accelerated-set high-strength cement obtained from cement manufacturers; and (4) no change in set time*
TEA	***On the basis of actual experimental results, an H2A analysis will be carried out including capex for H_2 purification and selling price for byproduct CNF to achieve DOE's cost target of \$2/kg H_2 selling price.***

Accomplishments: Technoeconomic Analysis

Composition NG

CH_4	95.6%
C_2H_6	2.9%
C_3H_8	0.9%
C_4H_{10}	0.5%



Parameters

Hydrogen cost: $2.00/kg

NG cost: $3.00/KSCF

IRR: 10%

Lifetime: 40 years

Results

CNF coated silica, price range:

$4.00 - $8.00 per kg

Pure CNF, price range:

$20.00 - $30.00 per kg

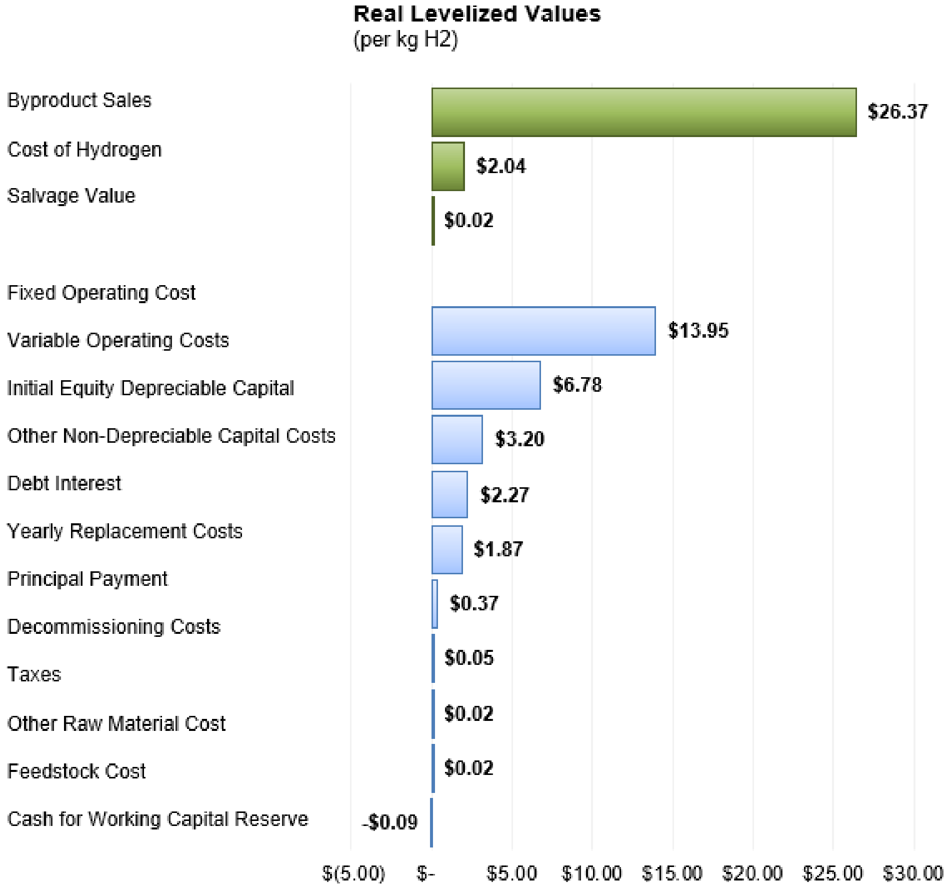
Pure CNF, current technology:

$300 per kg[1]

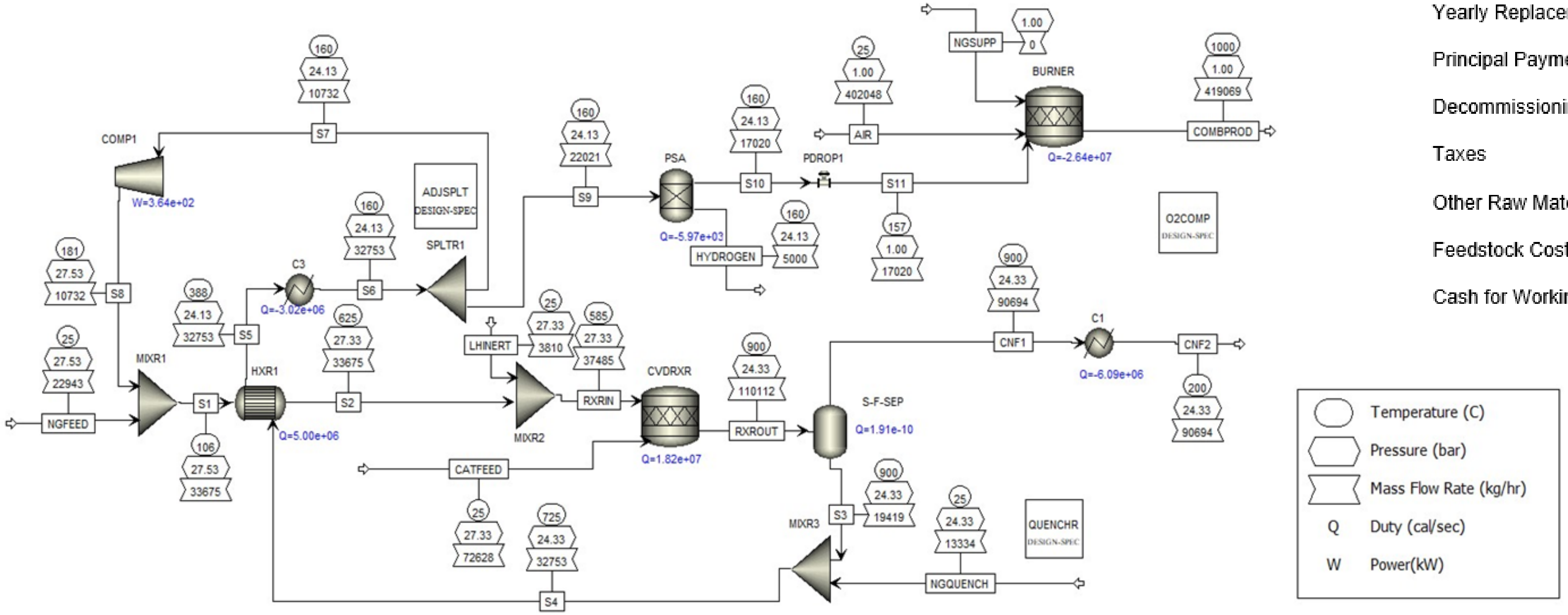
1 Pyrograf quote, personal correspondence 10/21/2020

Main Accomplishments and Findings: TEA

- Previous technoeconomic analysis cost inputs were adjusted for inflation
  - $CEPCI_{2020} = 615 \rightarrow CEPCI_{2022} = 831$



Real levelized costs output from DOE's H2A model, accounting for 2022 inflation values



Responses to Previous Year Reviewers' Comments

- Project was not reviewed in 2023

Collaboration and Coordination

- Alan Weimer (Chemical Engineering) PI — 1, 3
  - Kent Warren, Postdoctoral Fellow — 1, 3
  - Jessica Hauck, PhD Student — 1, 3
  - Samantha Harshberger, Undergraduate — 1
- Mija Hubler (Civil Engineering) co-PI — 2
  - Boning Wang, PhD Student — 2
  - Bola Odunaro, PhD Student — 2
- Collaborators
  - Forge Nano — 1, 3
    - Andrew Broerman, Principal Engineer
    - Christopher Gump, Principal Scientist
    - Caitlin Czernik, R&D Jr. Engineer
  - National Ready Mixed Concrete Association (NRMCA) — 2
    - Colin Lobo, VP

1. Methane Decarbonization at Lab-Scale
2. HP Concrete Mix Design
3. Technoeconomic Analysis

Current Focus Areas/Barriers to Overcome

	CVD	Concrete Mix Design	Technoeconomic analysis
Current Focus Area(s)	• Optimizing catalyst morphology (particle size, dispersion) for CNF formation • Optimize cost/ performance (metal loading) for CVD	• Optimize co-product CNF characteristics based on improved (reduced metal) CNF product and their effect on dispersion and mechanics	• Incorporate impact of IRA and reduced metal content on TEA
Barriers to overcome	• Generate enough product for civil engineering team for different CNF yields	• Integration of *a variety of* co-product CNFs	• Large-scale CCVD reactor design • Limited knowledge of industrial prices • Sensitivity to CNF yield, catalyst loading etc.

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Proposed future work

Milestones: remainder of budget period 3

CVD	Concrete Mix	Technoeconomic analysis
• Large batches of CNF product with varying yields will be produced based on prior research • Optimizing catalyst morphology (particle size, dispersion) for CNF formation	• Summary of targeted material design objectives for product integration at scale • Strength, modulus of elasticity and full stress-strain response of the final concrete containing the co-product CNF will be reported	• Incorporate impact of IRA on hydrogen pricing • Incorporate catalyst optimization into TEA • Create comprehensive report assessing commercial viability of this process at scale, including market end-users

Final Project Deliverable

A scalable low-cost CVD process to produce CNFs and H2 from CH4 using a sacrificial ALD catalyst deposited on a fumed silica substrate will be demonstrated. A minimum 10% Investors Rate of Return (IRR) for a process selling CNFs at an acceptable identified cost while selling H_2 for < $2/kg.

Summary

Synthesis of H_2 and CNFs

- Carbon yields >25wt%C achieved with CNF L/D >10
- Sufficient quantity of product generated for initial civil engineering explorations.

Concrete mix design using lab-made CNFs

- Met or exceeded performance expectations with small batches of CNFs containing metal catalyst

Technoeconomic analysis

- Updated TEA for 2022 inflation still results in economically promising process

Any proposed future work is subject to change based on funding levels

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

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