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

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05/29/2020

Project ID# P183

Overview:
Year 1 of 3-Year Project

Timeline

Project Start Date: 5/1/2020[1]

Project End Date: 5/1/2023

% Complete: 5%

Technical Barriers Addressed

S. High-temperature robust materials

W. Materials and catalysts development

X. Chemical reactor development and capital costs

Budget

Total project funding: $1,000,000

Sub-contract: $125,000

Total recipient cost share: $250,000

Total funds received to date: $306,731

Collaborators

ForgeNano, Thornton, CO

- Reactor/process design and technoeconomic analysis

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

- Concrete materials, mix design, and consulting

[1]Award made conditionally in 09/2019. Project official start date is 5/1/20. For the purposes of this presentation, FY19 refers to work starting 5/1/20 and ending 5/1/21

Relevance:
Hydrogen generation from decarbonization of methane

***Project Objective:* Develop a scalable low-cost CVD process to produce carbon nanofiber (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.**

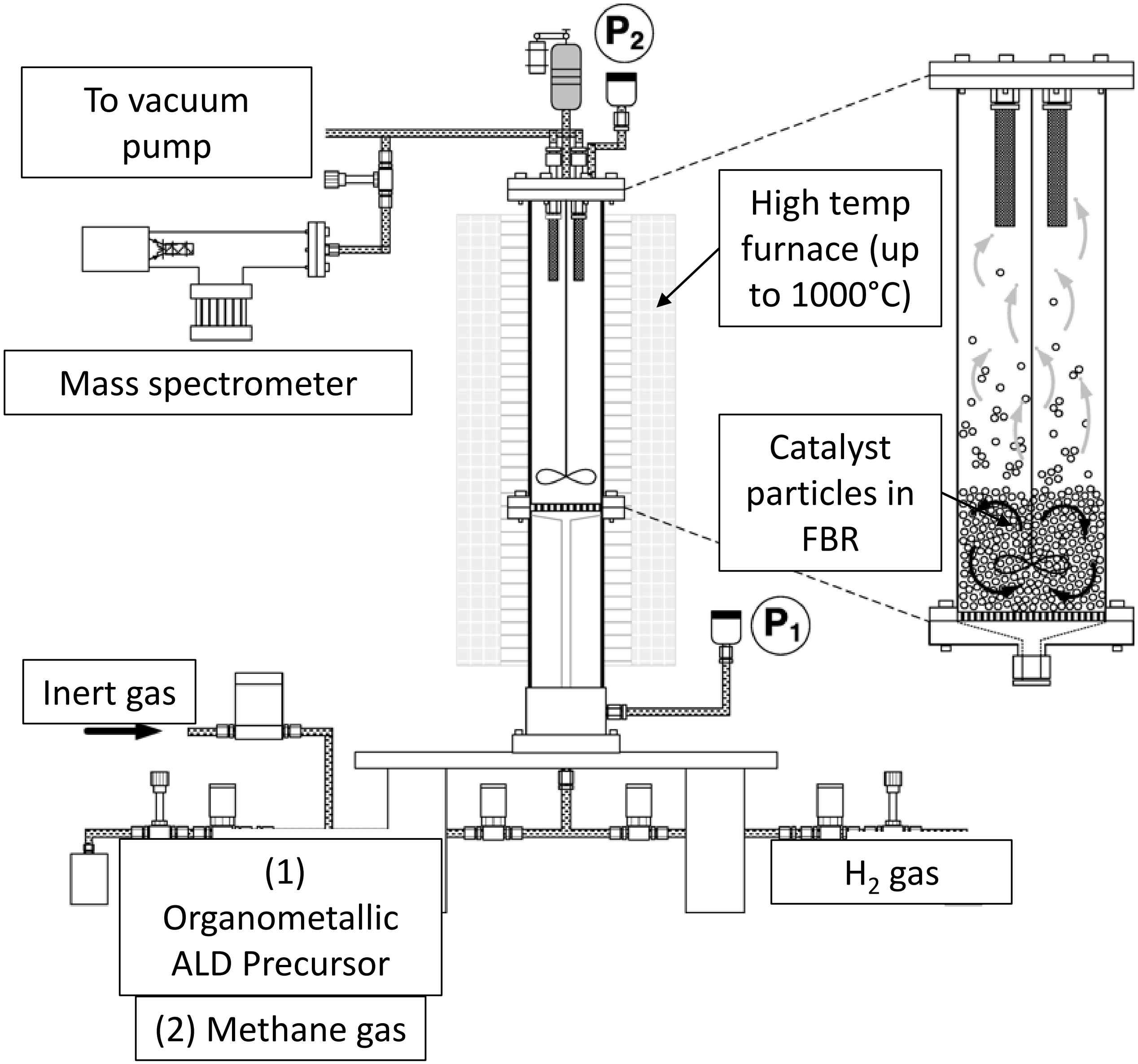
Technical Barrier	Objective	Progress this reporting period
(S) High-temperature robust materials and (W) Materials and catalysts development	Demonstrate co-production of H_2 (vol % H_2/vol % CH_4 > 0.2) and CNFs (L/D > 10; > 5 wt% Carbon) on sacrificial ALD catalyst	• Reactor design complete • Process flow diagram complete
(X) Chemical reactor development and capital costs	Develop preliminary process simulation and TEA to estimate CNFs selling price for a 10% IRR while selling H_2 at \$2/kg	• Preliminary TEA in progress

Approach: Particle ALD/CVD Catalysis System

- Use single-atom (adatom) 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 Portland cement

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

Approach:
Particle ALD/CVD Catalysis System



Step 1: One ALD cycle onto fumed silica particles

Step 2: CNF growth and hydrogen co-production from methane gas

Approach:
Task 1, Particle ALD/CVD Catalysis System

Subtask 1.1 – Reactor design and build – 25% Complete

Q1 – Milestone 1.1.1
- ➓ Design of ALD/CVD reactor and PFD
- ➓ Pre-startup inspection and safety review audit

Q2 – Milestone 1.1.2
- ➓ Reactor start-up to 900°C
- ➓ DAQ process data collection and testing

Subtask 1.2 – Reactor start-up and CNF production

Q3 – Milestone 1.2.1
- ➓ Minimum fluidization velocity calculation
- ➓ Deposition of metal ALD film onto fumed silica

Q4 – Milestone 1.2.2
- ➓ Demonstration of CNF growth on metal ALD catalyst and production of hydrogen gas

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

Approach:
Task 2, Cement mix design using commercial CNFs

Subtask 2.1
Mix Design
60% Complete

Q1
Milestone 2.1.1

❿ 1st stage mix design including CNFs which show set times similar to standard cement, <3 min within set times without fibers

Q2
Milestone 2.1.2

❿ 2nd stage mix design including CNFs will show set times similar to standard cement as well as an improved ductility have >25% improved tensile ductility compared to the mixes without fibers

Subtask 2.2
Produce durable cement

Q3
Milestone 2.2.1

❿ Optimal CNF characteristics will be identified based on chloride permeability and set time

Q4
Milestone 2.2.2

❿ Optimal CNF characteristics will be identified based on maximum crack size and tensile ductility

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

Approach:
Task 3, Technoeconomic analysis

Subtask 3.1 – Process Modeling

- Q1 – Milestone 3.1.1: ❿ PFD developed for process
- Q2 – Milestone 3.1.2: ❿ Preliminary Aspen PLUS process simulation

Subtask 3.2 – Process simulation and TEA

- Q3 – Milestone 3.2.1: ❿ Aspen PLUS simulation outputs used for estimating capital costs
- Q4 – Milestone 3.2.2: ❿ Preliminary TEA to determine selling price of CNFs for H_2 at $2/kg and 10% IRR

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

Approach: Milestone Summary

FY19 Q1 → FY19 Q2 → FY19 Q3 → FY19 Q4 → Go/No-Go FY19 → FY20 Q1 → FY20 Q2 → FY20 Q3 → FY20 Q4 → Go/No-Go FY20

Go/No-Go FY19

- CNFs produced with L/D > 10, CH_4:H_2 (vol%/vol%) = 0.2, and carbon wt% > 5
- H_2 impurity identification and consultation with H_2 pumping experts

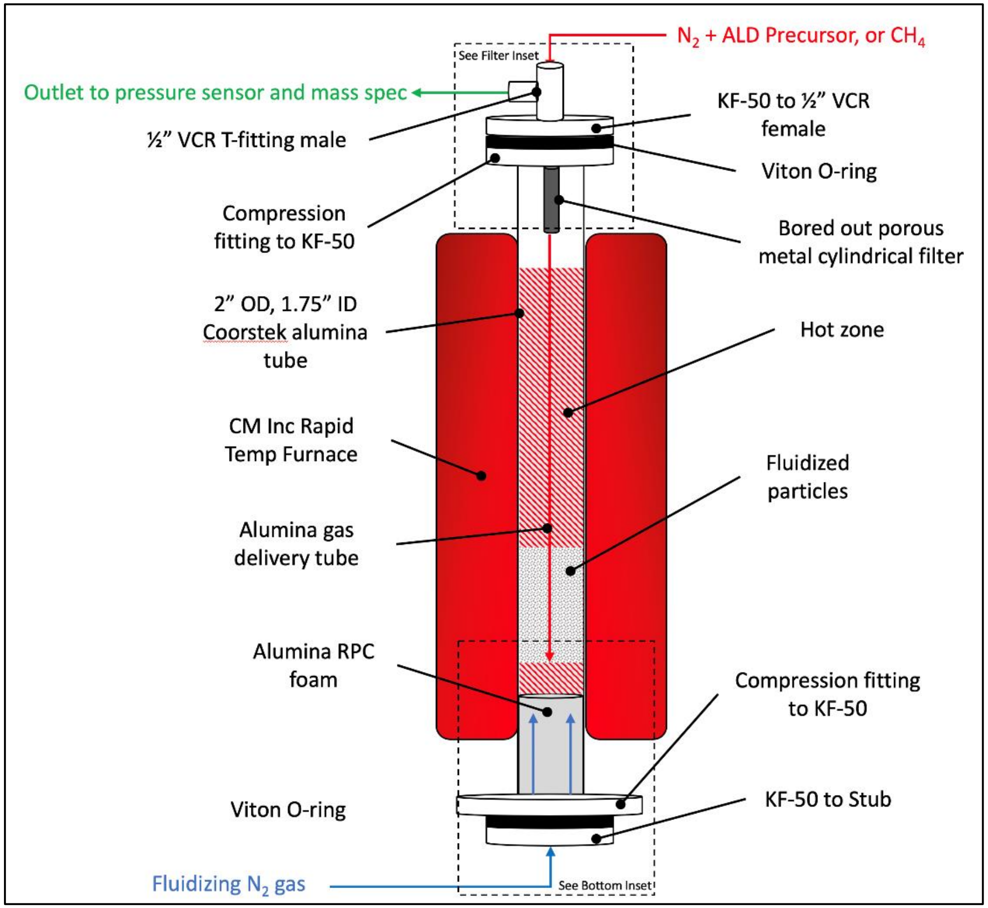
Go/No-Go FY20

- CNFs produced with L/D > 10, 50% CH_4 conversion, and carbon wt% > 25
- TEA analysis to determine selling price of CNF to achieve $2/kg H_2 target
- Maximum crack sizes ≤100 µm under drying conditions at 28 days, increased tensile ductility, 25% lower chloride permeability, no change in set time

Category	Key Milestones	Go/No-Go FY19 Progress	Go/No-Go FY20 Progress
Particle ALD/CVD catalysis system	✓ Reactor design and PFD ❑ Reactor start-up and initial testing ❑ CNF growth on metal ALD catalyst	• 25% accomplished • Reactor and PFD design complete • Build will be completed in Q2 • CNF growth demonstrated in Q4	• Process optimization will occur after initial CNF growth demonstration
Cement mix design	✓ 1st stage mix design ❑ 2nd stage mix design ❑ Optimal CNF characteristics identified	• N/A	• CNF product from experiments will be incorporated into cement mix designs
Technoeconomic analysis	❑ Process PFD ❑ Aspen Plus simulation ❑ Preliminary TEA	• Consultation carried out with H_2 pumping experts to determine the ultimate purity anticipated for the product H2	• Experimental results will inform TEA developed in FY19 Q4

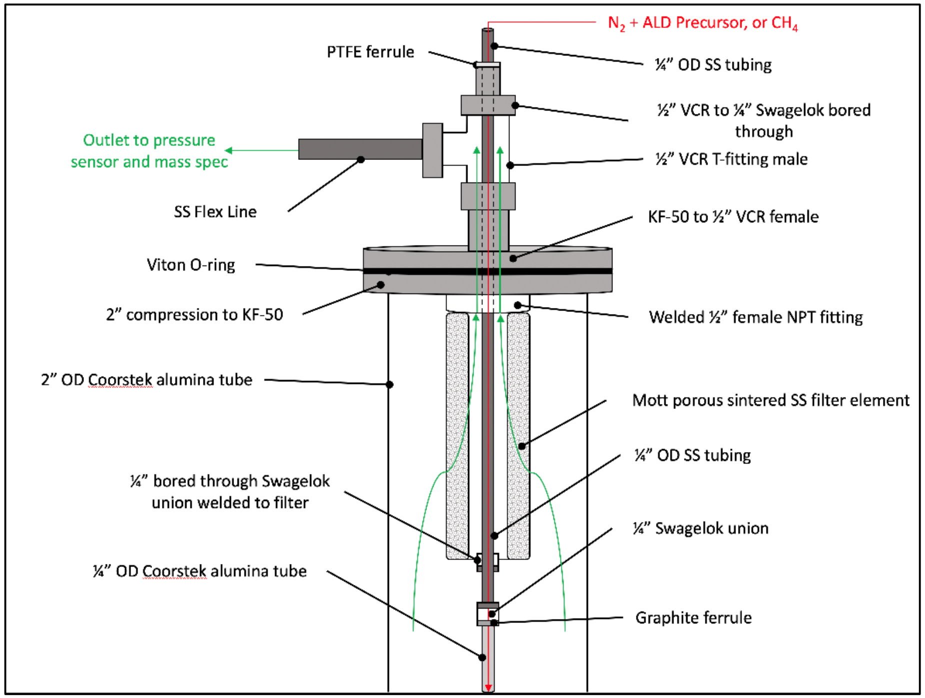
Accomplishments and Progress: Reactor design

- Ceramic alumina reactor tube
- Reaction and carrier (N_2) gases delivered through metal tube
- Nitrogen delivered through bottom as fluidizing gas
- Compression fittings kept outside hot zone

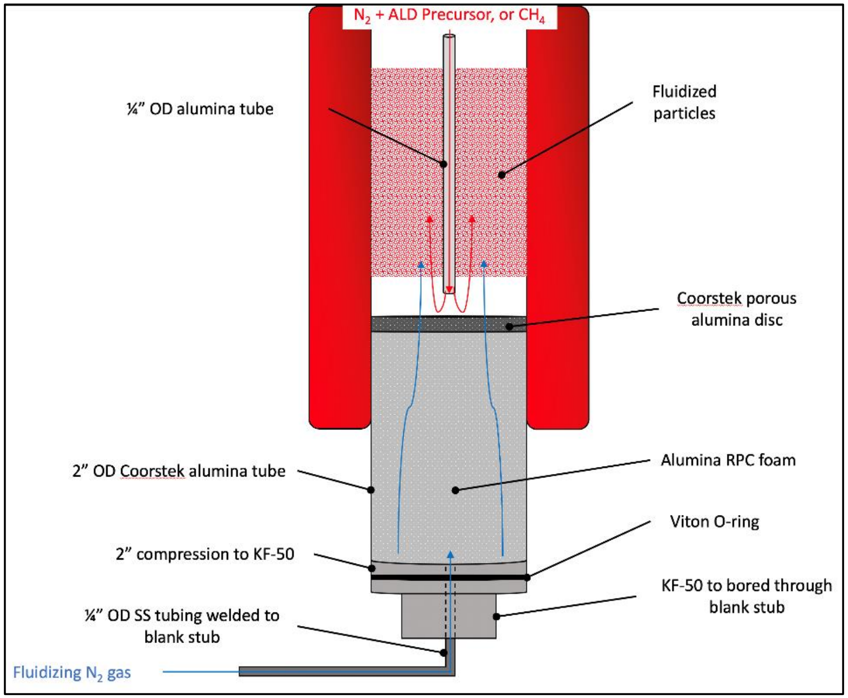


Accomplishments and Progress:
Filter and bottom inset from reactor design

Filter assembly inset

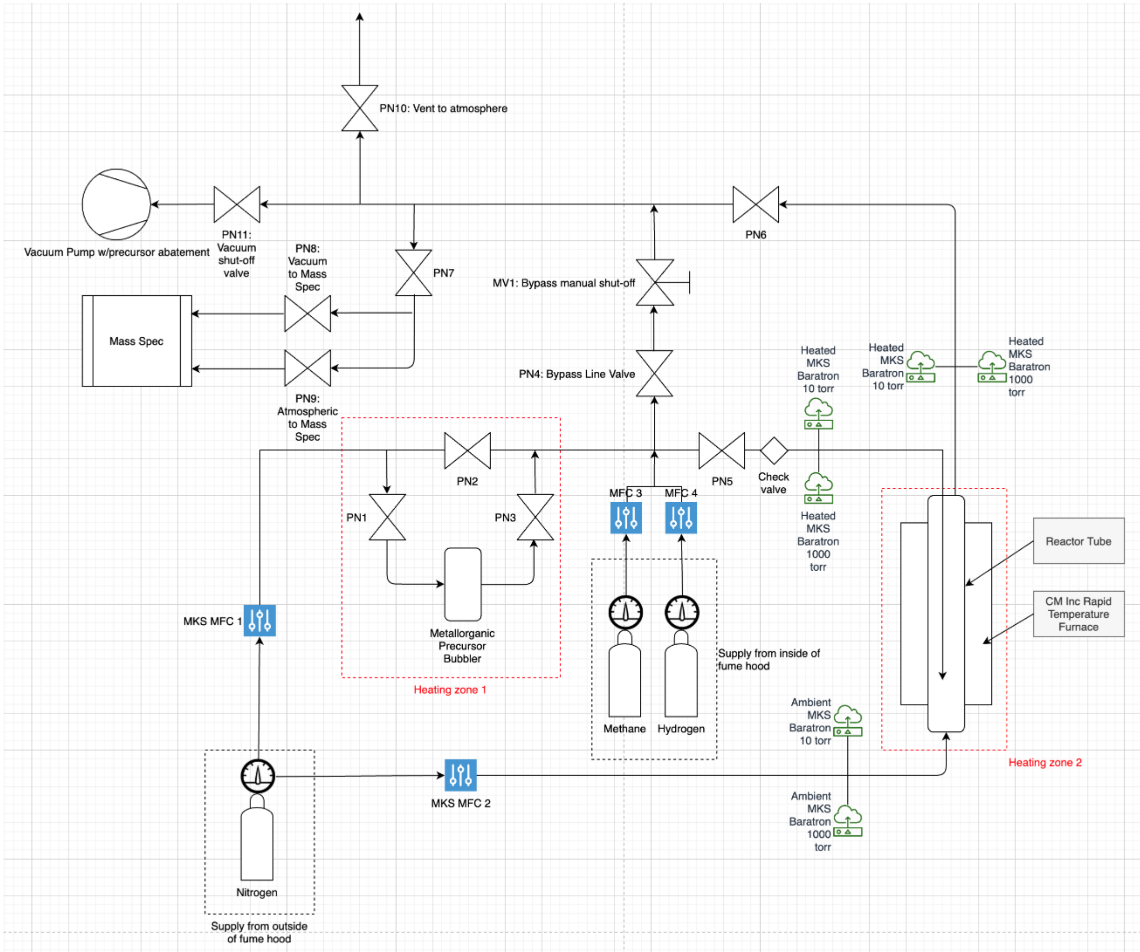


Bottom assembly inset



Accomplishments and Progress: Process flow diagram

- All-in-one system capable of operating under vacuum and atmospheric pressure
- Lines heated by PID controlled heat tape
- Mass flow controllers interface with LabVIEW
- Nitrogen delivered as carrier and fluidizing gas



Accomplishments and Progress: Cement mix design using commercial CNFs

1. Preliminary concrete mix design (Based on research papers and commercial mix designs)

Cement (kg/m^3)	Fly Ash (kg/m^3)	Silica fume (kg/m^3)	Coarse aggregate (kg/m^3)	Fine aggregate (kg/m^3)	Water (kg/m^3)	w/c	Superplasticizer
320	**80**	**44.5**	**1040**	**700**	**171**	**0.35**	**yes**

2. Three-point-bending tests on concrete samples embedded with carbon nano-fibers)

Proposed Future Work

Milestones: remainder of FY19[1]

Task 1: Particle ALD catalysis system	Task 2: Cement mix design using commercial CNFs	Task 3: Technoeconomic analysis
• Reactor will be heated to max operating temperature of 900ºC • Minimum fluidization velocity of fumed silica up to 900ºC will be determined • CNFs will be grown on ALD catalyst. Carbon content will be at least 5 wt% of the total mass of CNF + catalyst + substrate while producing H2 having a volume ratio to CH4 of at least vol %H2/vol % CH4 = 0.2	• Optimal CNF characteristics will be identified based on chloride permeability and set time. CNF containing samples will show: (1) chloride permeability 25% lower when compared to standard accelerated-set high-strength cement obtained from cement manufacturers; and (2) no change in set time • CNF containing samples 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	• A preliminary Aspen process simulation will be completed, and equipment will be designed for the purpose of estimating capitalized cost in a process model • A preliminary H2A analysis will be completed for process economics including capital and variable and fixed operating costs along with a cash flow scenario and identifying a selling price of H2 to achieve an IRR of 10%. The selling price of CNFs will be determined in order to sell H2 at $2/kg for a 10% IRR

Go/No-Go FY19

- CNFs produced with L/D > 10, CH_4:H_2 (vol%/vol%) = 0.2, and carbon wt% > 5
- H_2 impurity identification and consultation with H_2 pumping experts

Future Work FY20

Go/No-Go FY20

- CNFs produced with L/D > 10, 50% CH_4 conversion, and carbon wt% > 25
- TEA analysis to determine selling price of CNF to achieve $2/kg H_2 target
- Maximum crack sizes ≤100 µm under drying conditions at 28 days, increased tensile ductility, 25% lower chloride permeability, no change in set time

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

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Summary

Task 1: Particle ALD catalysis system	Task 2: Cement mix design using commercial CNFs	Task 3: Technoeconomic analysis
• Reactor design and PFD complete • Reactor build and initial testing in progress	• 1st stage concrete mix design complete • 2nd stage mix design in progress	• Preliminary TEA in development

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

Collaborations

Fund-Receiving Collaborator		Project Roles
FORGE NANO	ForgeNano	Reactor/process design and technoeconomic analysis
NRMCA NATIONAL READY MIXED CONCRETE ASSOCIATION	National Ready Mix Concrete Association (NRMCA)	Concrete materials, mix design, and consulting

Acknowledgements