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

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Andrew Broerman, Forge Nano
Colin Lobo, NRMCA
05/29/2020

Project ID# P183
### Overview:
Year 1 of 3-Year Project

<table>
<thead>
<tr>
<th>Timeline</th>
<th>Technical Barriers Addressed</th>
</tr>
</thead>
<tbody>
<tr>
<td>Project Start Date: 5/1/2020¹</td>
<td>S. High-temperature robust materials</td>
</tr>
<tr>
<td>Project End Date: 5/1/2023</td>
<td>W. Materials and catalysts development</td>
</tr>
<tr>
<td>% Complete: 5%</td>
<td>X. Chemical reactor development and capital costs</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Budget</th>
<th>Collaborators</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total project funding: $1,000,000</td>
<td>ForgeNano, Thornton, CO</td>
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<tr>
<td>Sub-contract: $125,000</td>
<td>• Reactor/process design and technoeconomic analysis</td>
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<td>Total recipient cost share: $250,000</td>
<td>National Ready Mix Concrete Association (NRMCA), Alexandria, VA</td>
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<tr>
<td>Total funds received to date: $306,731</td>
<td>• Concrete materials, mix design, and consulting</td>
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¹Award 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.

<table>
<thead>
<tr>
<th>Technical Barrier</th>
<th>Objective</th>
<th>Progress this reporting period</th>
</tr>
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<tbody>
<tr>
<td>(S) High-temperature robust materials and (W) Materials and catalysts development</td>
<td>Demonstrate co-production of H$_2$ (vol % H$_2$/vol % CH$_4$ &gt; 0.2) and CNFs (L/D &gt; 10; &gt; 5 wt% Carbon) on sacrificial ALD catalyst</td>
<td>• Reactor design complete</td>
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<tr>
<td></td>
<td></td>
<td>• Process flow diagram complete</td>
</tr>
<tr>
<td>(X) Chemical reactor development and capital costs</td>
<td>Develop preliminary process simulation and TEA to estimate CNFs selling price for a 10% IRR while selling H$_2$ at $2/kg</td>
<td>• Preliminary TEA in progress</td>
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</table>
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

<table>
<thead>
<tr>
<th>Catalyst Metal</th>
<th>Catalyst Support</th>
<th>ALD Chemistry</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iron</td>
<td>Fumed silica</td>
<td>Ferrocene/H₂</td>
</tr>
<tr>
<td>Nickel</td>
<td>Fumed silica</td>
<td>Nickelocene/H₂</td>
</tr>
<tr>
<td>Cobalt</td>
<td>Fumed silica</td>
<td>Cobaltocene/H₂</td>
</tr>
</tbody>
</table>
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

**Organometallic ALD Precursor**

**Methane gas**

**To vacuum pump**

**Mass spectrometer**

**Inert gas**

**High temp furnace (up to 1000°C)**

**Catalyst particles in FBR**

**H₂ gas**
Approach:
Task 1, Particle ALD/CVD Catalysis System

Subtask 1.1
Reactor design and build
25% Complete

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

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

Subtask 1.2
Reactor start-up and CNF production

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

Q4 Milestone 1.2.2
- 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

Milestone 2.1.1
1st stage mix design including CNFs which show set times similar to standard cement, <3 min within set times without fibers

Milestone 2.1.2
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

Milestone 2.2.1
Optimal CNF characteristics will be identified based on chloride permeability and set time

Milestone 2.2.2
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: PFD developed for process

Subtask 3.2 Process simulation and TEA
- Q2 Milestone 3.1.2: Preliminary Aspen PLUS process simulation
- Q3 Milestone 3.2.1: Aspen PLUS simulation outputs used for estimating capital costs
- Q4 Milestone 3.2.2: 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

- CNFs produced with L/D > 10, CH₄:H₂ (vol%:vol%) = 0.2, and carbon wt% > 5
- H₂ impurity identification and consultation with H₂ pumping experts
- CNFs produced with L/D > 10, 50% CH₄ conversion, and carbon wt% > 25
- TEA analysis to determine selling price of CNF to achieve $2/kg H₂ target
- Maximum crack sizes ≤100 µm under drying conditions at 28 days, increased tensile ductility, 25% lower chloride permeability, no change in set time

<table>
<thead>
<tr>
<th>Category</th>
<th>Key Milestones</th>
<th>Go/No-Go FY19 Progress</th>
<th>Go/No-Go FY20 Progress</th>
</tr>
</thead>
</table>
| 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 H₂ 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)

<table>
<thead>
<tr>
<th>Cement (kg/m^3)</th>
<th>Fly Ash (kg/m^3)</th>
<th>Silica fume (kg/m^3)</th>
<th>Coarse aggregate (kg/m^3)</th>
<th>Fine aggregate (kg/m^3)</th>
<th>Water (kg/m^3)</th>
<th>w/c</th>
<th>Superplasticizer</th>
</tr>
</thead>
<tbody>
<tr>
<td>320</td>
<td>80</td>
<td>44.5</td>
<td>1040</td>
<td>700</td>
<td>171</td>
<td>0.35</td>
<td>yes</td>
</tr>
</tbody>
</table>

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

Milestones: remainder of FY19

Task 1: Particle ALD catalysis system
• Reactor will be heated to max operating temperature of 900°C
• Minimum fluidization velocity of fumed silica up to 900°C 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

Task 2: Cement mix design using commercial CNFs
• 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

Task 3: Technoeconomic analysis
• 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, CH4:H2 (vol%/vol%) = 0.2, and carbon wt% > 5
• H2 impurity identification and consultation with H2 pumping experts

Future Work FY20
• CNFs produced with L/D > 10, 50% CH4 conversion, and carbon wt% > 25
• TEA analysis to determine selling price of CNF to achieve $2/kg H2 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
- Reactor design and PFD complete
- Reactor build and initial testing in progress

Task 2: Cement mix design using commercial CNFs
- 1st stage concrete mix design complete
- 2nd stage mix design in progress

Task 3: Technoeconomic analysis
- Preliminary TEA in development

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

<table>
<thead>
<tr>
<th>Fund-Receiving Collaborator</th>
<th>Project Roles</th>
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<tr>
<td>ForgeNano</td>
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