Electrochemical-Enabled Carbon Dioxide Mineralization (e-CO_2M) of Natural Brines and Wastes to Enable Carbon-Negative Value-Added Products

(DE-FE32258)

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2024 FECM/NETL Carbon Management Research Project Review Meeting

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Project Overview

- Funding
  - DOE: $2,000,000
  - Cost Share: $500,000
- Period of Performance: June 1, 2023-May 31, 2025
  - Budget Period 1: June 1, 2023 – May 31, 2024
  - Budget Period 2: June 1, 2024 – May 31, 2025
- Project Participants
  - Northeastern University, Tundra, Brown & Caldwell, AVN, CONSOL Energy, and Clear Skies

Project Objectives

– Overall

- The objective of this project is to develop an electrochemistry-enabled carbon dioxide mineralization (e-CO_2M) process to generate carbon-negative alkaline carbonate (AC) materials from natural brines for building, construction, and related applications.

– Budget Period 1

- Study process phenomena and alkaline carbonate recovery
- Characterize commercially available and e-CO2M alkaline carbonate products
- Evaluate corrosion of cathode materials
- Conduct initial techno-economic analyses (TEA) and lifecycle analyses (LCA)
- Establish project diversity, equity, and inclusion (DEI) outreach activities

Project Objectives

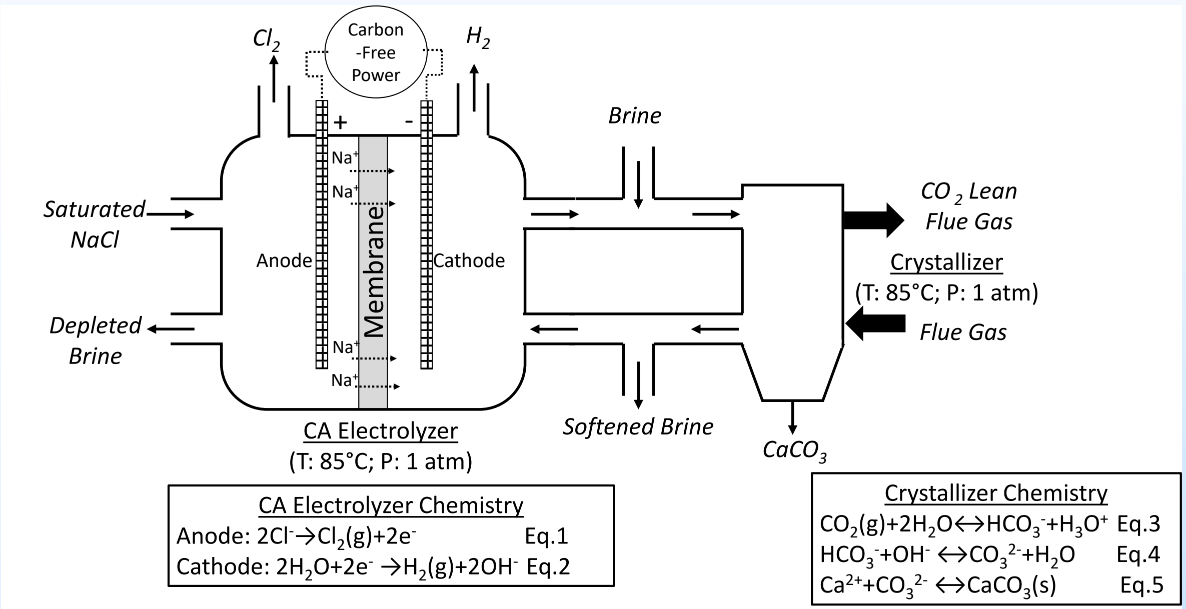
- Overall
  - The objective of this project is to develop an electrochemistry-enabled carbon dioxide mineralization (e-CO2M) process to generate carbon-negative alkaline carbonate (AC) materials from natural brines for building, construction, and related applications.
- Budget Period 2
  - Operate a 10 kg/day CO_2 conversion process to characterize process performance
  - Characterize engineered composites made from e-CO_2M product to assess market applicability
  - Update TEA and LCA studies for the e-CO_2M process and products
  - Identify building, construction, and related market applications best suited for e-CO_2M products

Technology Background

- $CaCO_3$ Market
  - Products: Ground calcium carbonate (GCC) & precipitated calcium carbonate (PCC)
  - PCC Chemistry
    - Calcination: $CaCO_3 \rightarrow CaO + CO_2$
    - Slaking: $CaO + H_2O \rightarrow Ca(OH)_2$
    - Precipitation: $Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$
  - Embodied carbon emissions
    - GCC: 8.37 kg_{CO2}/ton[1]
    - PCC: 1.1-1.8 ton_{CO2}/ton[2]
  - Value: $11.1 billion (2021)
  - Demand: 18.6 Mt/yr (2020); 23.5 Mt/yr (2025)
- Natural Brines
  - Produced water
    - Production: 20-25 billion bbls/yr (U.S.)
    - High divalent cation content
    - Existing collections infrastructure
  - Acid mine drainage
  - RO reject

1. DOI: 10.11578/GREET-Net-2023/dc.20230907.2
2. DOI: 10.2788/12850

Technology Background



e-CO_2M Process

e-CO_2M Process

- Modular CA electrolyzer technology
- Near ambient temperature (80-90 °C) and pressure (1 bar) operation
- Carbon-free power to enable carbon-negative products
- Potentially tailorable product properties
- Softens low-cost brine wastes
- Integration into existing facilities
- Valuable co-products: $Mg(OH)_2$, Cl_2 and H_2

Project Plan

- Task 1.0: Project Management and Planning
- Task 2.0: e-CO_2M Process R&D
  - Anode, cathode, and crystallizer testing
- Task 3.0: Alkaline Carbonate Product Characterization
  - Commercial and e-CO_2M material analyses
- Task 4.0: Cathodic Corrosion Analysis
- Task 5.0: Techno-economic (TEA) and Life-cycle Analyses (LCA)
- Task 6.0: Continuous e-CO2M Process Analysis
  - Continuous process design, fabrication, and operation

Milestones

Description	Planned Completion Date	Actual Completion Date
Updated Project Management Plan	8/31/2023	8/25/2023
Project Kick-Off meeting held	10/31/2023	10/6/2023
Technology Maturation Plan (TMP)	10/31/2023	10/31/2023
Commercial Carbonate Filler Characteristics	12/31/2023	12/31/2023
Alkaline carbonate precipitation rates	3/31/2024	3/31/2024
GO/NO-GO DECISION		
Commissioning of Continuous Lab-Scale Process	9/30/2024	N/A
Complete first 10 kg/day CO_2 conversion trial	12/31/2024	N/A
e-CO_2M Alkaline Carbonate Filler Characteristics	3/31/2025	N/A
TEA, LCA and Market Analyses	5/31/2025	N/A

Success Criteria

- Demonstrate chlor-alkali technology can be modified to serve as a CO_2 mineralization process,
- Establish alkaline carbonate products made from produced water possess desirable properties for building and construction applications,
- Verify alkaline carbonate products generated from produced water are occupationally and environmentally safe, and
- Demonstrate greater than 10 kg/day of CO_2 conversion into alkaline carbonates from produced water.

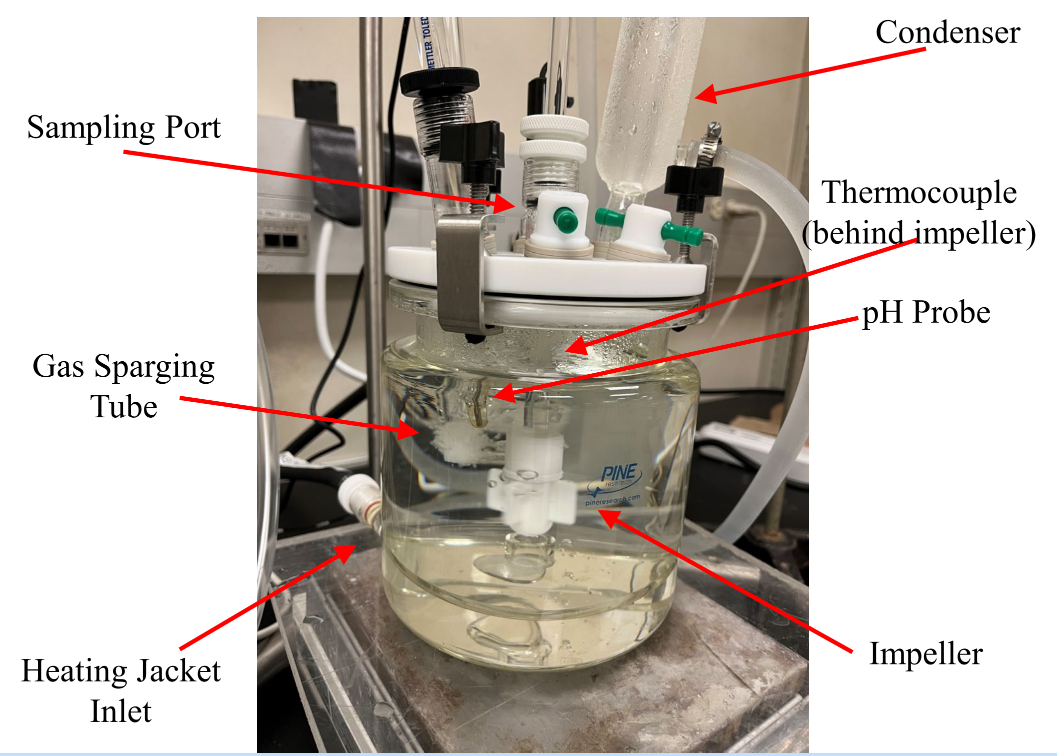
Risks & Mitigation Strategies

Perceived Risk	Risk Rating (Low, Med, High)			Mitigation/Response Strategy
	Probability	Impact	Overall	
Technical/Scope Risks:				
e-CO_2M Product Quality	Low	Medium	Low	Utilize chemistry and kinetics can be controlled to precipitate targeted products.
Cathode Corrosion	Medium	Medium	Medium	Evaluate existing and emerging corrosion-resistant chlor-alkali electrode materials for produced water treatment.
Product Performance	Low	High	Medium	Correlate product properties with operating parameters to identify envelopes to produce best performing products.
Product Leaching	Low	High	High	Products will undergo leachability tests to identify potential environmental releases alone and in composite materials.

Progress and Current Status

Task 2.0: e-CO_2M Process R&D

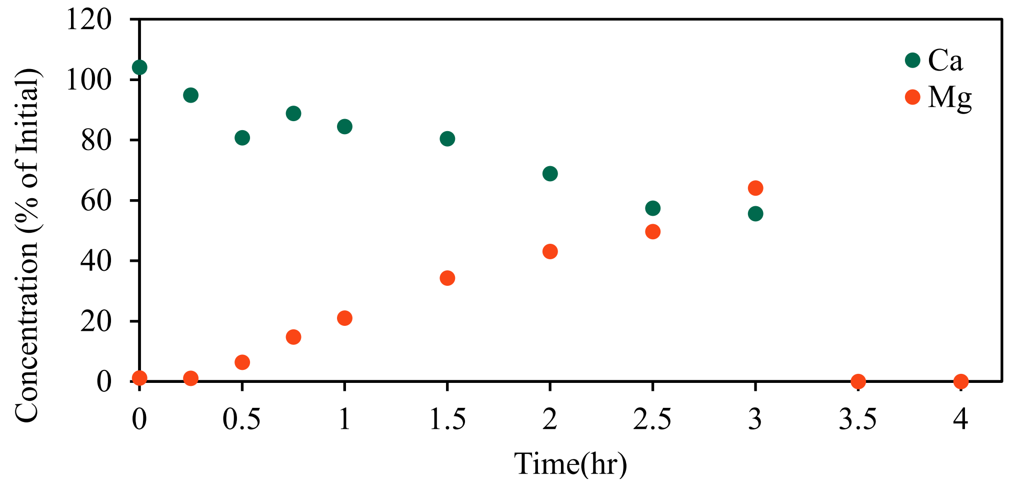
- Bench-top Crystallizer
- 1-liter jacketed reactor
- 20-90 °C
- pH monitored and controlled via NaOH dosing
- Utilized for determination of precipitation rates under semi-continuous operation.

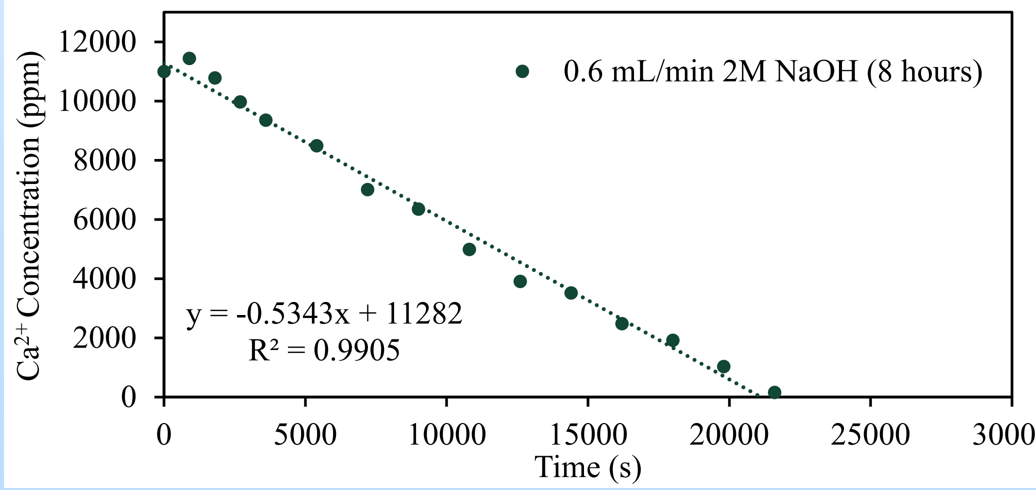


Progress and Current Status

Task 2.0: e-CO_2M Process R&D

- Cation concentrations are monitored versus reaction time by sampling the reactor contents
- Solid samples from each aliquot are also prepared for material characterization
- If Mg^{2+} is present, brucite ($Mg(OH)_2$) dissolves while $CaCO_3$ precipitates (top panel)
- The Ca^{2+} depletion rate is calculated through a linear fit (bottom panel)

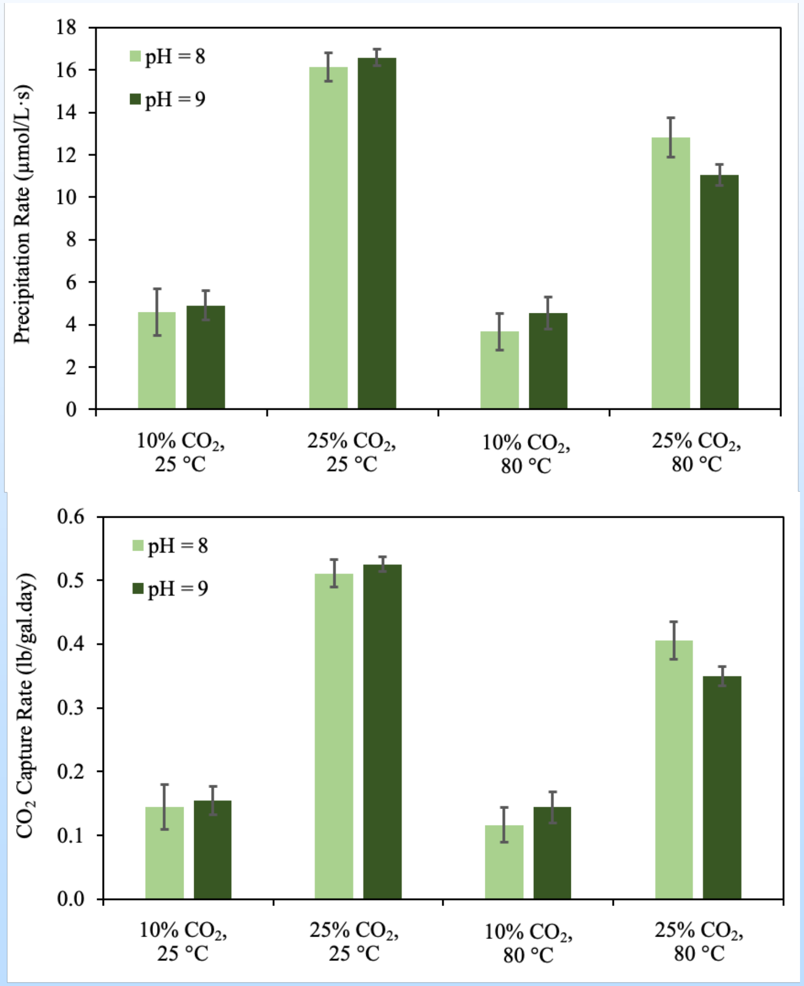




Progress and Current Status

Task 2.0: e-CO_2M Process R&D

- A design of experiments was conducted on three reactor variables (temperature, CO_2 composition, and pH) with two levels (high/low) and duplicates of each condition
- The mineralization rate of $CaCO_3$ was determined in units of µmol/L·s (top panel)
- The mineralization rate can also be used to determine the CO_2 capture rate (bottom panel)

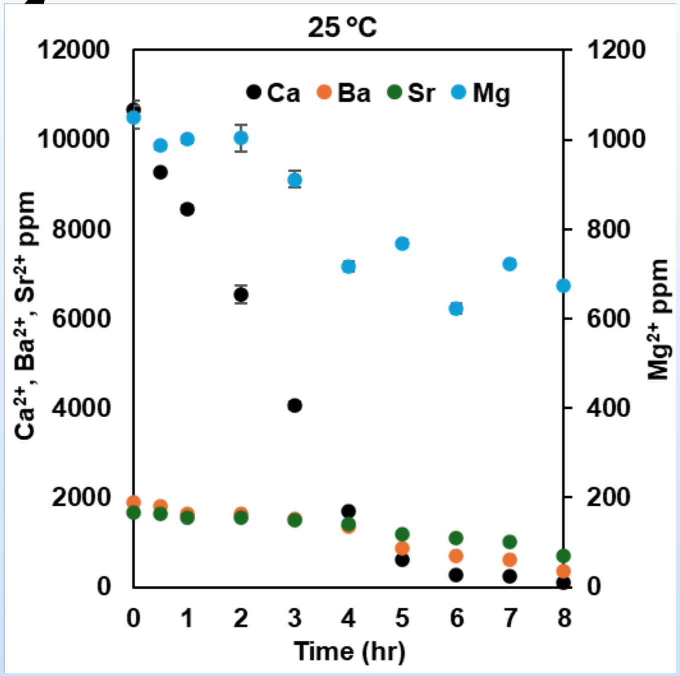


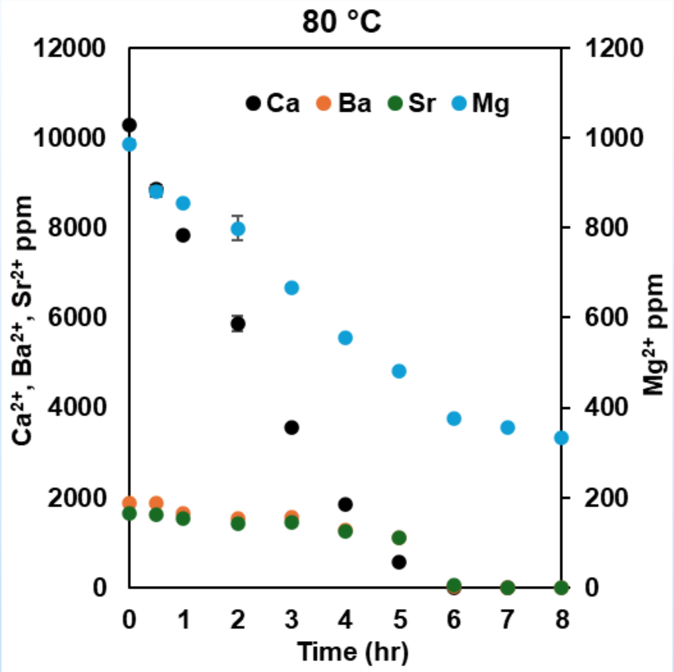
Progress and Current Status

Task 2.0: e-CO_2M Process R&D

Produced Water Composition

Cation	Concentration (mg/L)
Ca^{2+}	8,999
Na^{+}	28,000
K^{+}	398
Mg^{2+}	900
Sr^{2+}	2,001
Ba^{2+}	2,001





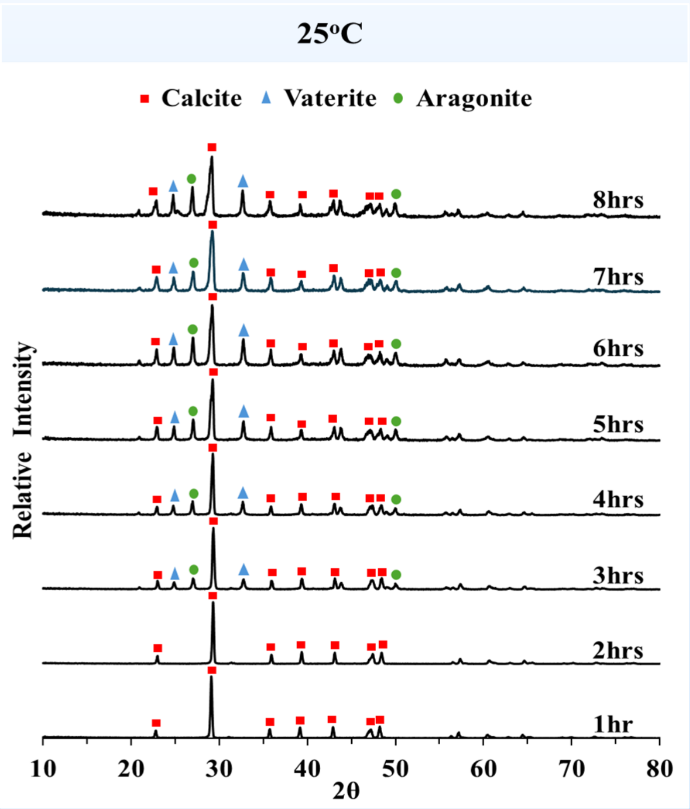
Observations:

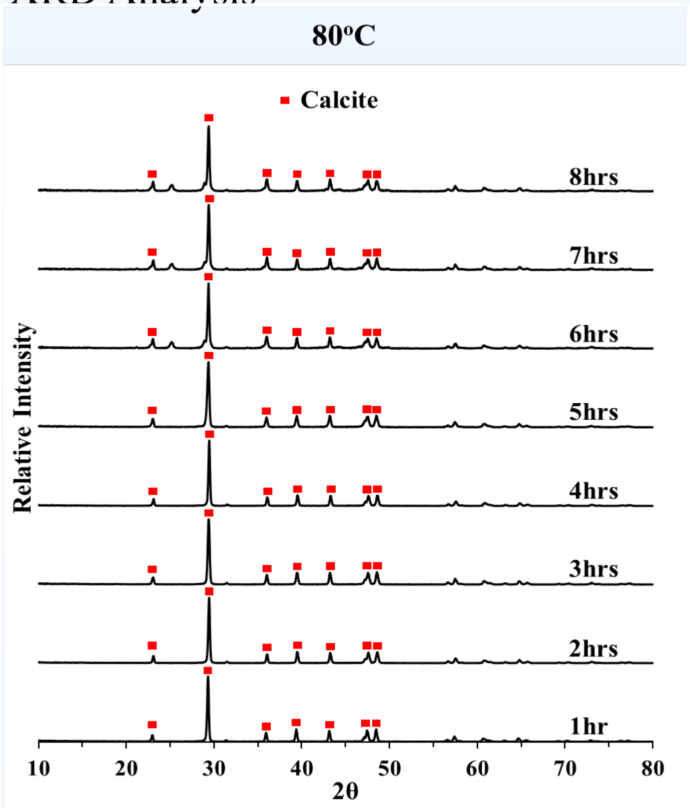
- Ca^{2+} and Mg^{2+} precipitation proceeds roughly linearly at both 25 and 80 °C
- Ba^{2+} and Sr^{2+} start precipitation only mid-way through run at both 25 and 80 °C
- The rates of Mg^{2+}, Ba^{2+}, and Sr^{2+} precipitation appeared to be faster at 80 °C

Progress and Current Status

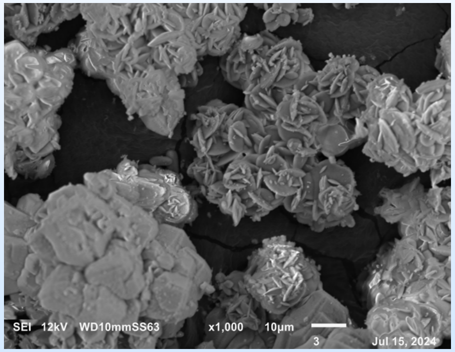
Task 2.0: e-CO_2M Process R&D

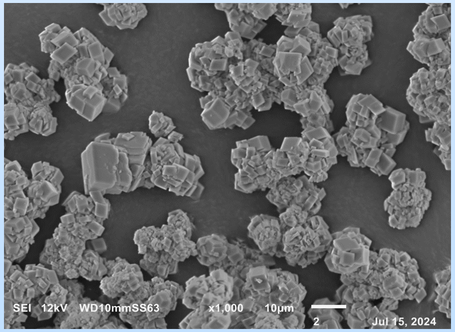
XRD Analysis





SEM Analysis



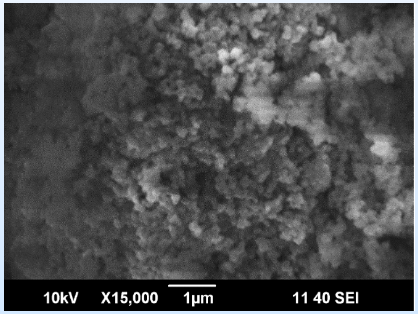


Progress and Current Status

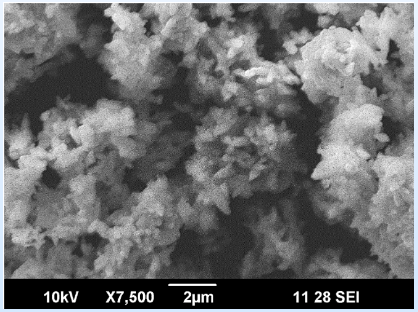
Task 3.0: Alkaline Carbonate Product Characterization

- Commercial materials: Precipitated calcium carbonate (PCC) & Ground calcium carbonate (GCC)

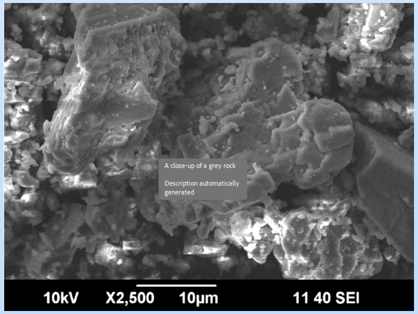
Property	PCC	GCC
Size (µm)	<0.1-1.5	<2.0-6.0
Surface Area (m^2/g)	5.4-21.3	1.3-4.1
Durability BET Increase (%)	17.8-90.0	3.8-5.1
Bulk Density (g/cm^3)	1.07-1.26	1.53-1.56
Flow via Repose (Height/Base)	0.57-0.77	0.77-1.18



PCC



PCC

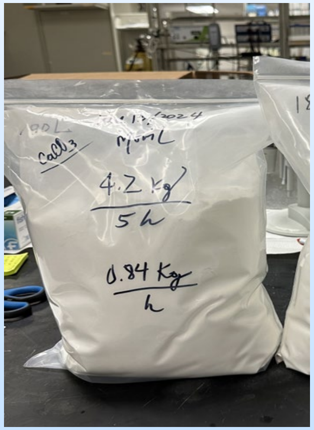


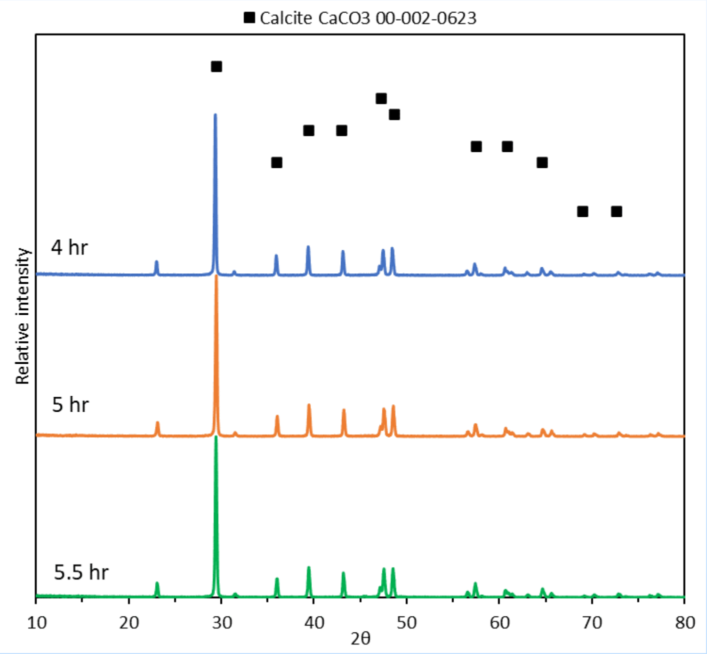
GCC

Progress and Current Status

Task 3.0: Alkaline Carbonate Product Characterization

- e-CO_2M materials:

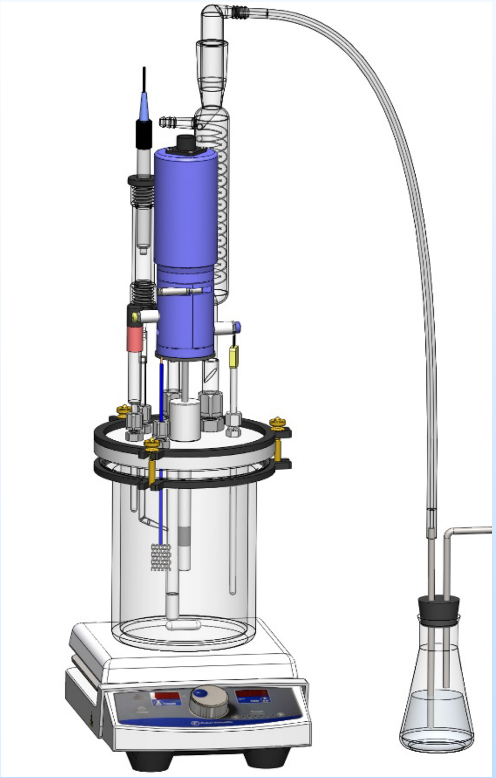




Progress and Current Status

Task 4.0: Cathodic Corrosion Analysis

- Conducted corrosion tests on Nickel (200) and Titanium (Grade 2) in Marcellus brine at pH 9.5 and 10, under OCP and electrolyzer conditions at 70°C.
- Both metals remained passive for 15-16 hours; Potentiodynamic Polarization indicated passivity breakdown with negative potential shifts.
- Titanium showed superior corrosion resistance compared to Nickel.
- At -1.5V vs Ag/AgCl, no corrosion was observed; Nickel was more active in HER, but both metals reduced HER activity over time.
- SEM analysis revealed surface precipitation on both metals, including calcium, magnesium, chloride, oxygen, potassium, and sodium.



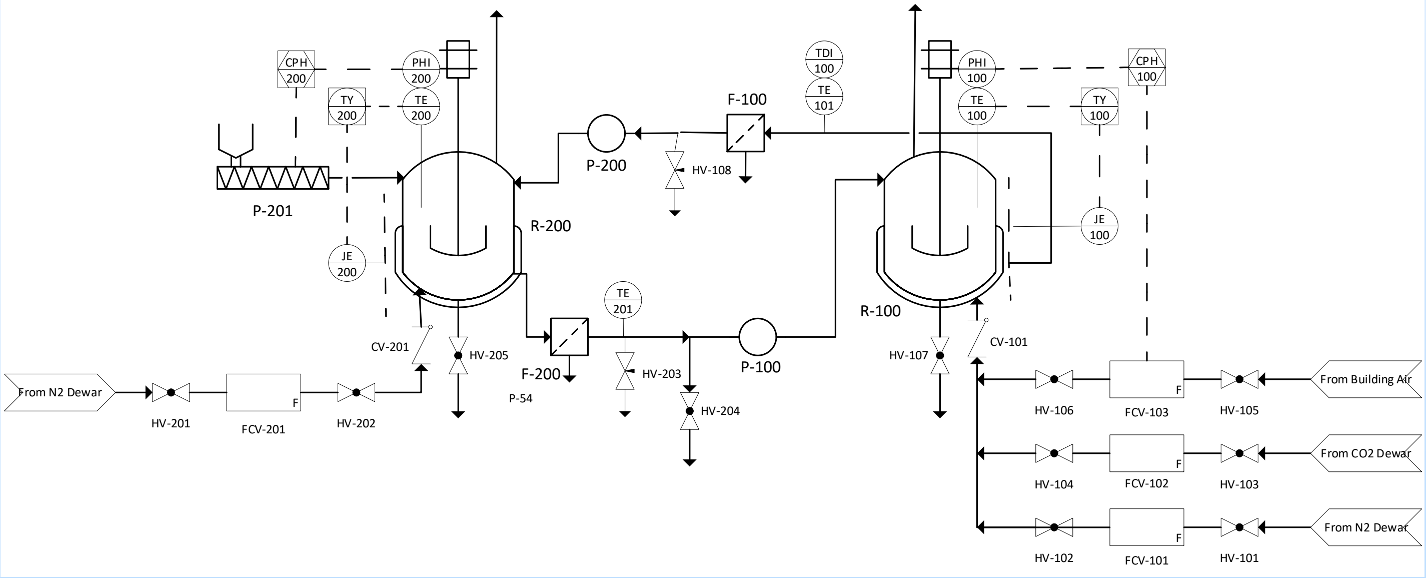
Cathode Testing Setup

Progress and Current Status

Task 6.0: Continuous e-CO2M Process Analysis

Design Parameters

- Capacity: 10 kg_{CO2}/day
- Temperature: 20-90 °C
- Pressure: 1 atm



Lab-Scale CO_2 Mineralization P&ID

Summary of Community Benefits

- Community Engagement
  - Trimble High School (Sep. ‘23)
  - Earth Justice and Regeneration Group (Dec. ‘23)
  - Green Project Camp (June ‘24)
- Undergraduate research opportunities
  - Mineralization testing and process simulation research

Future Plans

- Mineralization testing
  - Evaluate field-derived and simulated brines, RO reject, and acid mine drainage
  - Assess characteristics of e-CO_2M materials and identify applications
  - Assess corrosion of dimensionally stabilized and antimonate materials
- TEA and LCA
  - Assess the availability of PW brines and chemistries
  - Evaluate direct and indirect CA integration strategies and conduct TEA and LCA
- Fabricate continuous mineralization system and conduct testing

Summary Slide

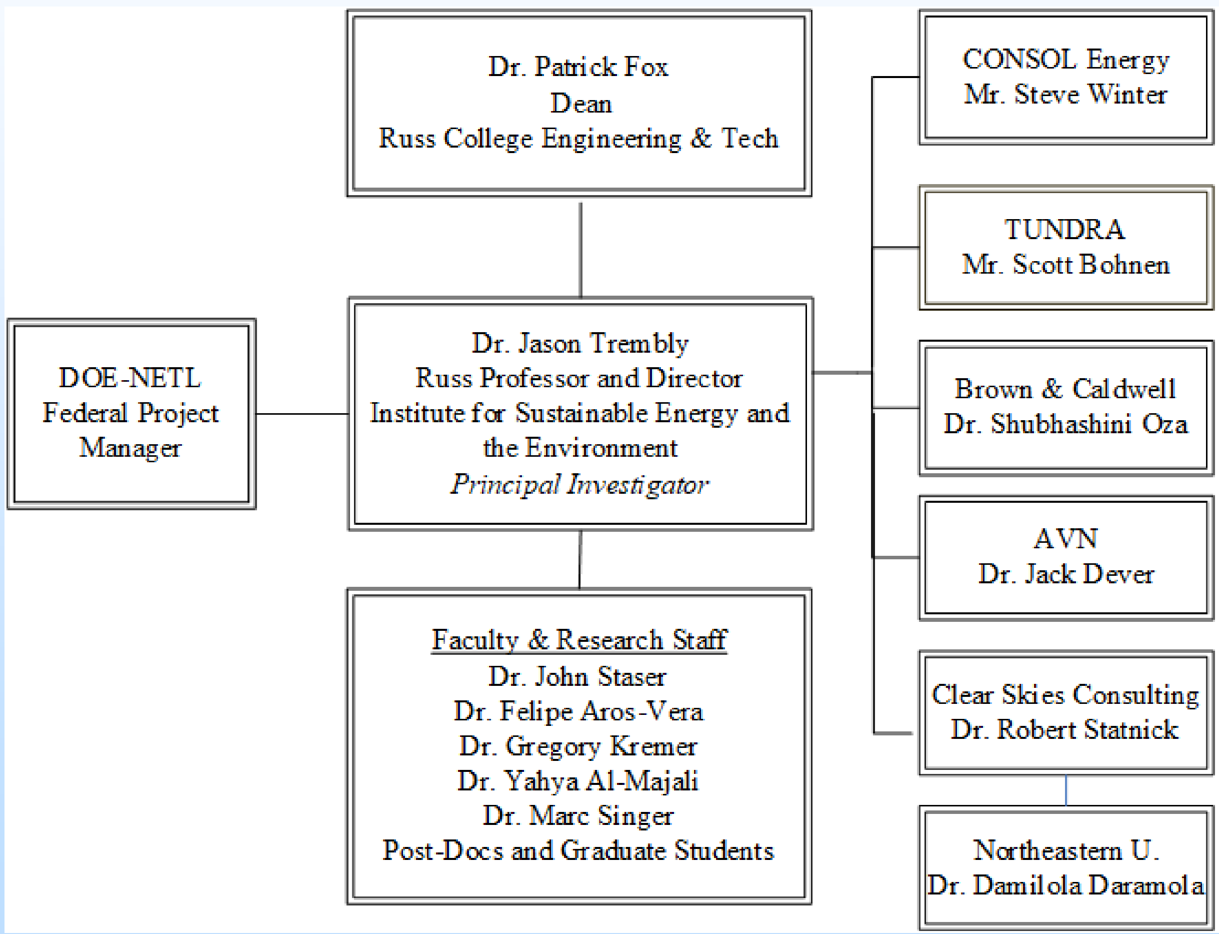
Accomplishments

- Established mineralization rates and potential with simulated shale brines
- Identified envelopes for production of $CaCO_3$ polymorphs with shale brines
- Evaluated properties of commercial PCC and GCC materials
- Evaluated corrosion of cathodic materials in the presence of simulated shale brine
- Developed design package for 10 kg/day CO_2 mineralization system

Acknowledgments

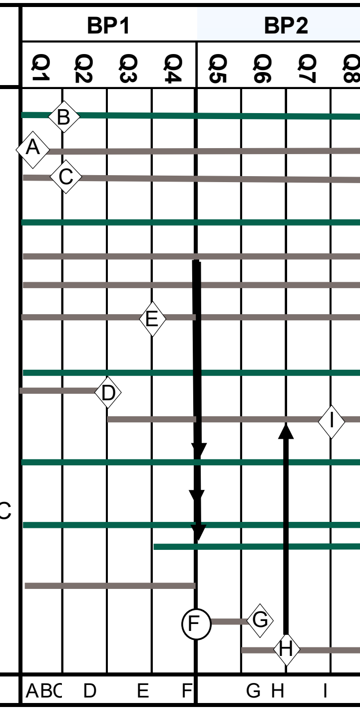
- OHIO: John Staser, Kody Wolfe, Omar Movil-Cabrera, Marc Singer, and Srdjan Nesic, Edward Nyamekye, Andrew Kasick, and Quinn Bennett
- Northeastern University: Dr. Damilola Daramola
- Tundra: Mr. Scott Bohnen and Mr. John Kroll
- Brown & Caldwell: Dr. Shubhashini Oza

Organization Chart



Gantt Chart

Task	Responsible Organizations
Task 1.0 – Project Management and Planning	OHIO
Sub-task 1.1 - Project Management Plan	OHIO
Sub-task 1.2 - Technology Maturation Plan	OHIO
Task 2.0 – e-CO2M Process R&D	OHIO, BC, MATRIC, CE
Sub-task 2.1 - Anode Testing	OHIO, MATRIC
Sub-task 2.2 - Cathode Testing	OHIO, BC, CE, MATRIC
Sub-task 2.3 - Carbonate Crystallizer R&D	OHIO, BC, MATRIC
Task 3.0 – Alkaline Carbonate Product Characterization	OHIO, Tundra
Sub-task 3.1 - Commercial Alkaline Carbonate Material Analyses	OHIO, Tundra
Sub-task 3.2 - e-CO2M Alkaline Carbonate Material Analyses	OHIO, Tundra
Task 4.0 – Cathodic Corrosion Analysis	OHIO
Task 5.0 – Techno-economic (TEA) and Life-Cycle Analyses (LCA) of e-CO2M Process	OHIO, Tundra, CE, MATRIC, BC, CSC
Task 6.0 – Continuous e-CO2M Process Analysis	OHIO, CE, MATRIC, BC, CSC
Sub-task 6.1 - Continuous Lab-Scale Process Design and Continuation Application Package	OHIO, MATRIC
Sub-task 6.2 - Fabrication of Continuous Lab-Scale Process	OHIO
Sub-task 6.3 - Continuous e-CO2M Process Analyses	OHIO, CE, MATRIC, BC, CSC
Milestone Log	



Ohio University (OHIO), Tundra Companies (Tundra), Brown & Caldwell (BC), CONSOL Energy (CE), MATRIC, Clear Skies (CSC)

Milestones: A: Updated Project Management Plan; B: Project Kickoff Meeting; C: Preliminary Technology Maturation Plan; D: Commercial Carbonate Filler Characteristics; E: Alkaline carbonate precipitation rates; F: GO/NO-GO DECISION POINT; G: Commissioning of Continuous Lab-Scale Process H: Complete first 10 kg/day CO2 conversion trial; I: e-CO2M Alkaline Carbonate Filler Characteristics; J: TEA, LCA and Market Analyses

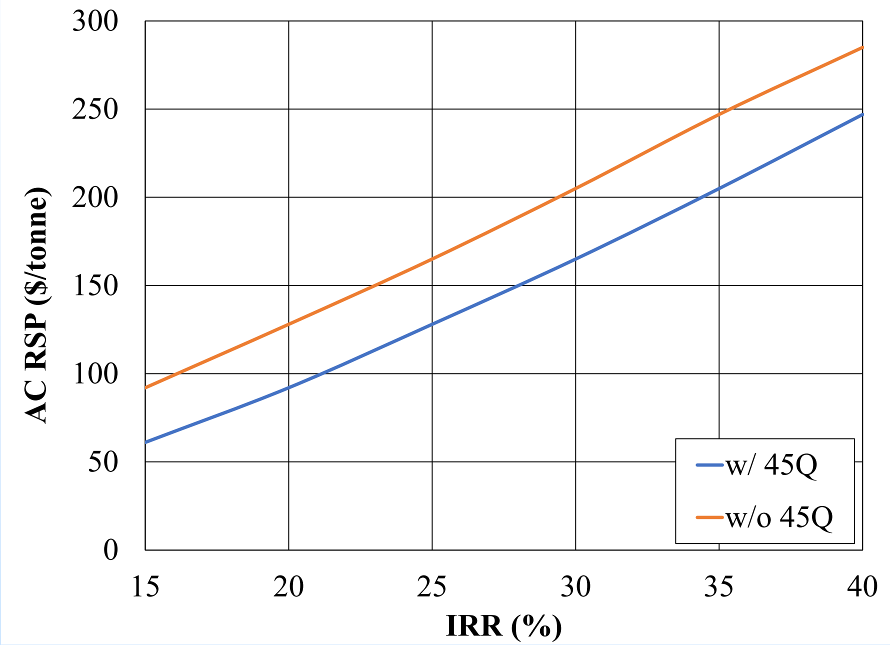
Progress and Current Status

Task 5.0: TEA & LCA

TEA Parameters

- PCC Capacity: 65,700 tonnes/yr
- $[Ca^{2+}]$: 15,000 mg/L
- Co-products
  - Cl_2: 46,575 tonnes/yr
  - H_2: 1,310 tonnes/yr
- Gross Revenue: $27.5-30.0 MM/yr

Material Streams	Value
PW Treated (m^3/yr)	$3.48 \cdot 10^6$
AC Product (lt/yr)	65,745
Cl_2 Product (lt/yr)	46,575
H_2 Product (lt/yr)	1,310
Costing Parameters	**Value**
Capital Cost ($MM)	$40.2
Electricity ($/MWh)	42
Maintenance (%CapCost)	3%
Taxes (%CapCost)	2.5%
Wages (%CapCost)	3%
Cl_2 Price ($/lt)	160
H_2 Price ($/lt)	1,000
CO_2 Credit ($/lt)	85



Commercial PCC Pricing

- THIXO-CARB 500: $3,800/$lt_{AC}$
- ALBAFIL PCC: $1,400/$lt_{AC}$

Cradle-to-Gate LCA Results

- Scenario 1: -0.42 to 0.78 t_{CO2}/lt_{AC}
- Scenario 2: -0.25 to 0.45 t_{CO2}/lt_{AC}