Rapid Electrochemical Mineralization of Carbonates from Mine Tailings (TCF-NREL-22-FWP-REMINED)

August 5, 2024

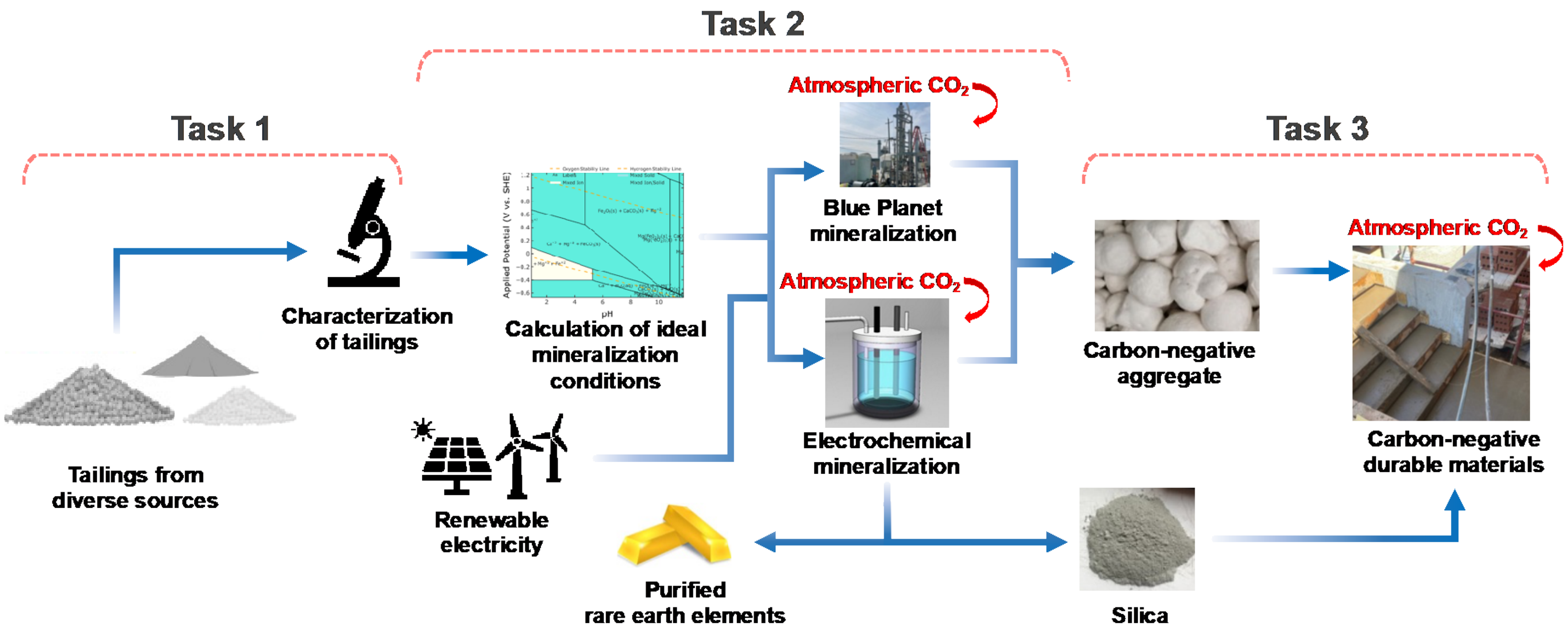
2024 FECM / NETL Carbon Management Research Project Review Meeting

PI: Kerry Rippy
Co-PI: Robert (Bob) Bell

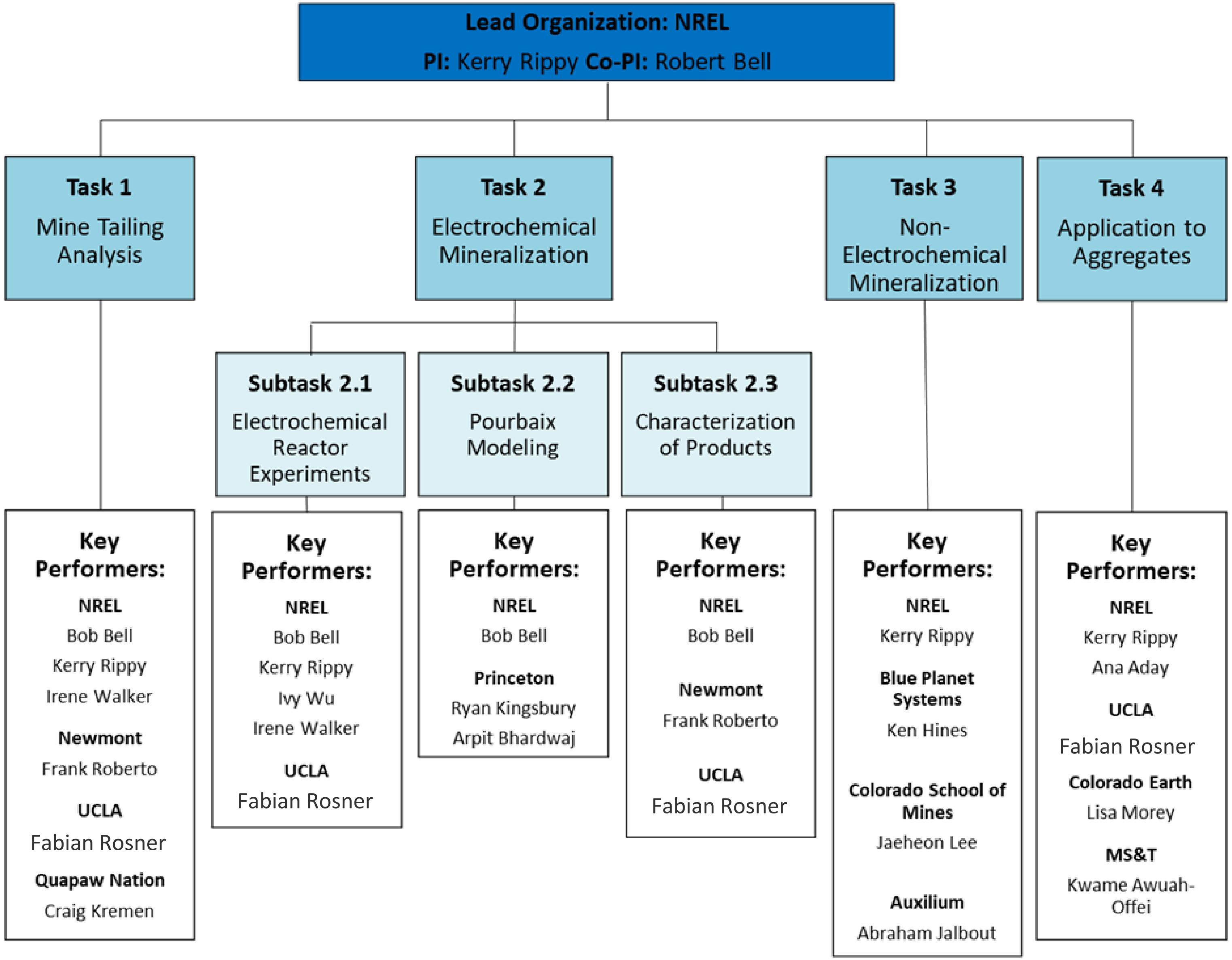
Rapid Electrochemical Mineralization to form Dolomite (REMineD)

Overview: We will develop a general electrochemical method to react alkaline mine tailings with CO_2 to form carbon-negative aggregate to be used in low-carbon concrete. Simultaneously, pozzolanic silica will be recovered from tailings which will be used to reduce OPC usage and trace rare earth elements will be purified and recovered, which can be sold to offset cost. The electrochemical method is guided by modeling, allowing a diverse range of tailings compositions to be processed. While reaction of alkaline mine tailings and CO_2 is thermodynamically favorable, it naturally occurs at a very slow rate. Utilization of electrochemistry will enhance reaction rate by orders of magnitude and will be compatible with atmospheric levels of CO_2 at low pressure, avoiding need for concentration and pressurization.

- **Budget:** $2,190,000 Federal, $2,190,000 Cost Share
- **PI:** Kerry Rippy
- **Prime Recipient:** NREL
- **Subrecipients and Partners:** Newmont USA, Colorado Earth, The Quapaw Nation, UCLA, Princeton, The Missouri University of Science & Technology, Colorado School of Mines



Project Team Structure



Key Team Members

NREL

PI: Kerry Rippy
Researcher IV - Chemistry

Co-PI: Bob Bell
Researcher IV - Chemistry

Ivy Wu
Postdoctoral Researcher

Irene Walker
Graduate student: Colorado School of Mines

Blue Planet

Brent Constantz
CEO

Jake Schneider
Director – R&D

UCLA

Gaurav Sant
Henry Samueli Fellow and Pritzker Professor of Sustainability

Fabian Rosner
Assistant Professor of Civil and Environmental Engineering

Newmont

Frank Roberto
Director, Processing

Toni Mika
Principal Advisor, Strategic Programs (Innovation & Decarbonization)

Princeton

Ryan Kingsbury
Assistant Professor of Civil and Environmental Engineering

CSM

Jaeheon Lee
Professor

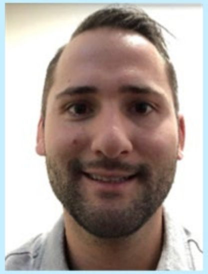
Colorado Earth

Lisa Morey
Owner

M S&T

Kwame Awuah-Offei
Rocky Mountain Energy Professor in Mining Engineering

Quapaw Nation



Craig Kremen
Environmental Engineer & Assistant Environmental Director

FY 24 Milestones

- On track for FY24 milestones

Task/ Subtask/ Milestone #	Milestone Title & Description	Planned Completion Date	Verification method
2.1.1	Fabrication of small-scale electrochemical reactors at NREL.	7/17/2023	***Completed.*** The reactor has been assembled, and experiments have begun.
1.1.1	Stoichiometric characterization of partner's stewarded mine tailings.	4/17/2023	***Completed*** Mine tailings from several sources have been characterized, establishing characterization capabilities. As needed, further tailings will be characterized.
3.1.1	Schedule three two-week focus periods during which Blue Planet shall evaluate opportunities for use of Newmont and/or Quapaw Nation mine tailings in CM-1.	10/17/23	***Completed.*** Focus periods planned for March 2024 and 2025 as well as September 2025. Dates subject to shift based on CM-1 operating schedule.
2.2.1	Generate Mg-Ca-CO_2 Pourbaix diagrams	1/17/24	***Completed.*** Pourbaix diagrams have been generated. These will be refined iteratively to provide insights for the electrochemical process.
2.2.2	Model the impact of key impurities on carbonation products.	6/30/2024	***Completed:*** Bulk energy calculations of 117 Ca-Mg-O-X materials were completed, where X = C, S, Na, K, Cl, and N . These elements are present in a sample of Newmont's mining waste.
3.1.2	Identify critical feedstock parameters for Blue Planet's processes	7/01/24	***Completed:***Provide a document to DOE summarizing findings on feedstock characteristics. No proprietary information shall be included.
2.3.1	**GNG**: Electrochemically increase carbonate formation rate by ≥50x via control of reaction conditions.	9/30/24	***On Track:*** Electrochemically induced carbonate formation occurred in a synthetic solution by applying 1.5V_{SHE} for 2.5 h. No carbonate formed in a static solution without applied potential for 4 days. Thermochemical precipitation tests are underway for comparison.

Upcoming Milestones

Task/ Subtask/Milestone #	Milestone Title & Description	Planned Completion Date	Verification method
2.3.1	**GNG**: Electrochemically increase carbonate formation rate by ≥50x via control of reaction conditions.	9/30/24	***On Track:*** Electrochemically induced carbonate formation occurred in a synthetic solution by applying 1.5V_{SHE} for 2.5 h. No carbonate formed in a static solution without applied potential for 4 days. Thermochemical precipitation tests are underway for comparison.
4.1.1	Demonstrate impact of dolomite in concrete aggregate on mechanical properties.	12/31/24	***On Track:*** Commercially available carbonate has been transferred to Colorado Earth to test their effect on building materials. The commercial carbonate is similarly sized as initial electrochemically mineralized carbonate.
3.1.3	Identify an NREL-developed method to optimize Blue Planet's thermochemical mineralization process	12/31/24	***On Track:*** Provide a document to DOE summarizing findings on optimization parameters. These parameters could include examining the effect of particle size on leach rate of desired ions. In addition to this summary, appendices may be provided as desired to detail relevant characterization data but are not required. No proprietary information shall be included in either the summary document or the optional appendices.
2.1.2	Experimentally test impact of key impurities on electrochemical carbonation.	3/31/25	***On Track:*** Relevant impurity compositions have been chosen based on active mining sites
2.1.3	**GNG:** Demonstrate electrochemical carbonation of mine tailings from Newmont and/or Quapaw Nation.	6/30/25	***On Track:*** Using either mine tailings from partners or, if necessary, near-identical simulated material, demonstrate conversion of Mg, Ca, Na, and /or other carbonate formers in mine tailings into solid carbonates.

NREL FY24

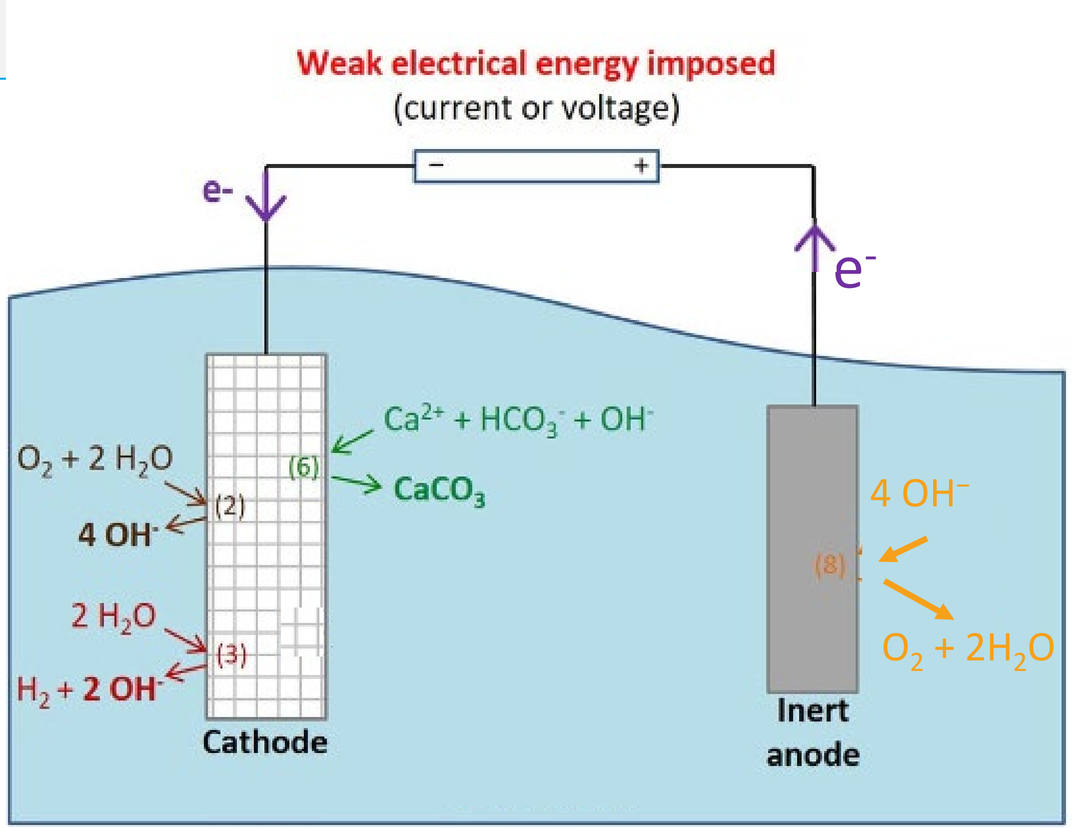
Accomplishments:

1. Review Paper accepted: Walker, I. *et al*. "Mineralization of Alkaline Waste for CCUS", *npj Mater. Sustain.* doi.org/10.1038/s44296-024-00031-x
2. Established baseline protocol for electrochemical mineralization experiments and precipitation collection

Electrode Choice:

RE	Notes
SHE	Bubbles cause noise
Ag/AgCl	*Current standard*

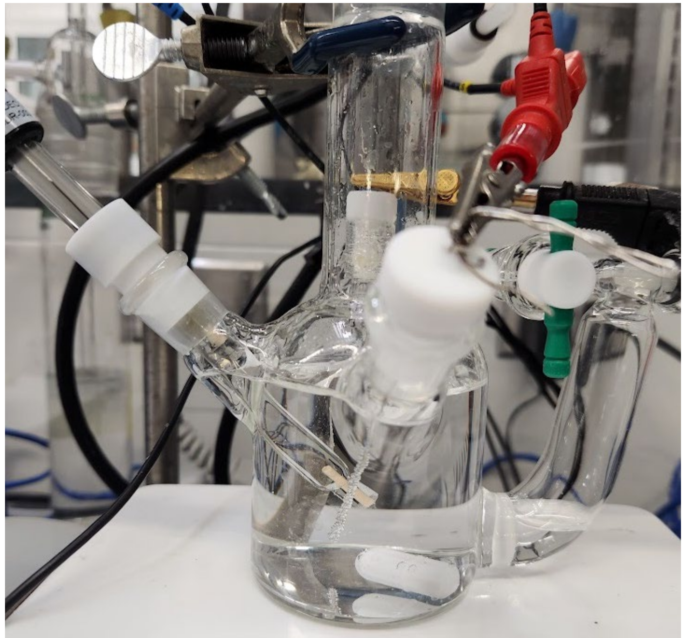
WE	CE	Notes
Pt wire	Pt wire	Negligible current
Pt mesh	Pt mesh	Pt complex issues
SS plate	Pt mesh	*Current standard*



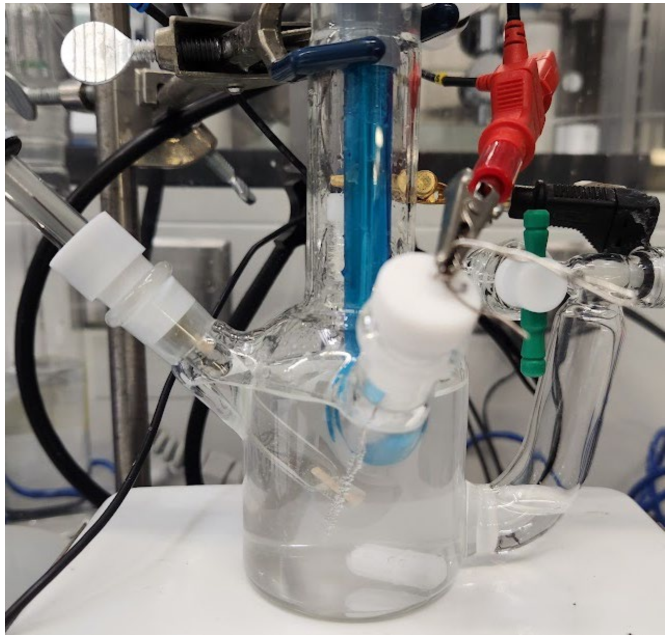
NREL small-scale electrochemical calcium carbonate mineralization

Electrolyte: 0.5 M $CaCl_2$, saturated w/ CO_2, pH raised to >5 w/ 1M NaOH

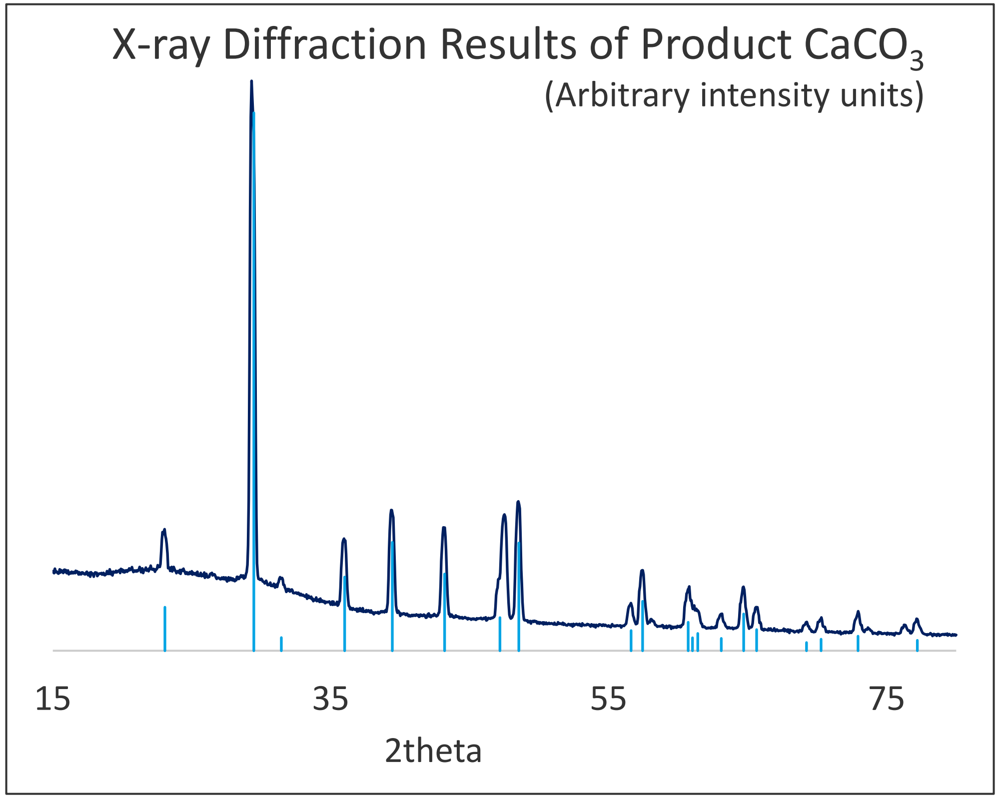
Applied 1.3 V



Beginning of test

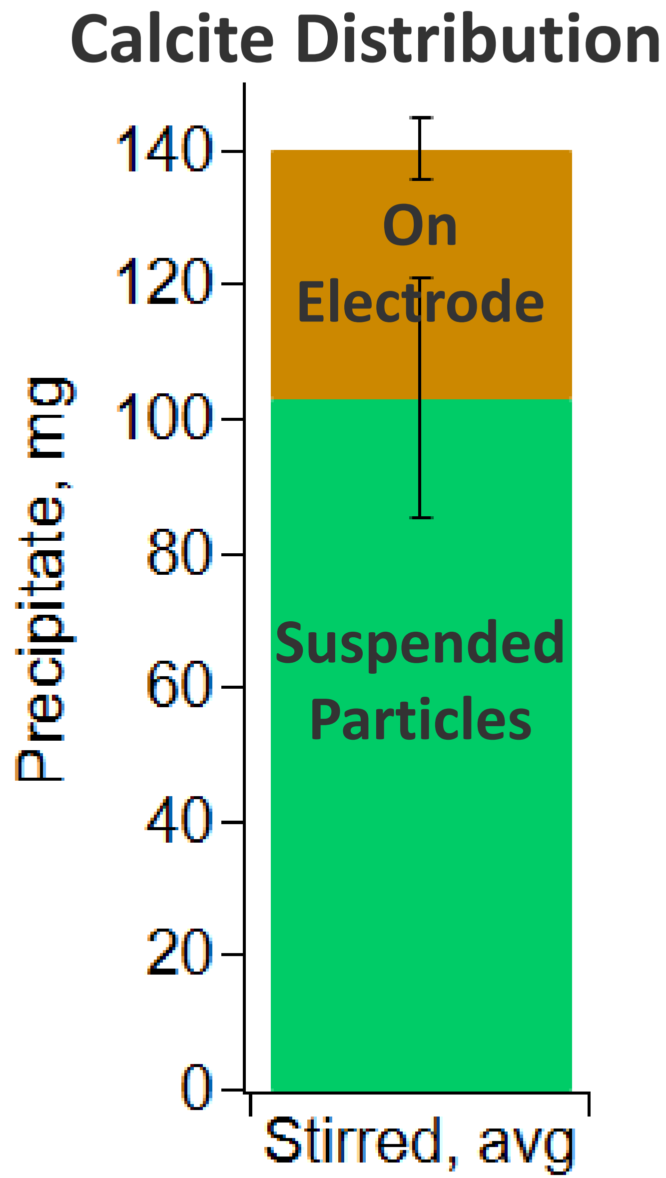


After test



Filtered solids identified as Calcite

Limited Fouling in High Purity Tests



- Most calcite in suspension
- H_2 bubbles may be clearing electrode
- Additional testing necessary in presence of impurities

NRE Small Reactor Overall Results

Bubble w CO_2

$CaCl_2$, M	mol CO_3/mol e^-	% Ca removed	% CO_3 conversion
0.5	3.06	4.9%	68.3%
0.25	0.81	2.1%	13.4%

Pre-saturated w/ pure CO_2

Dosed w/ NaOH to increase initial pH to pH 5

Apply 1.5V vs Ag/AgCl

Bubble w air

$CaCl_2$, M	mol CO_3/mol e^-	% Ca removed	% CO_3 conversion
0.5	0.84	0.8%	5.7%

Pre-saturated w/ air

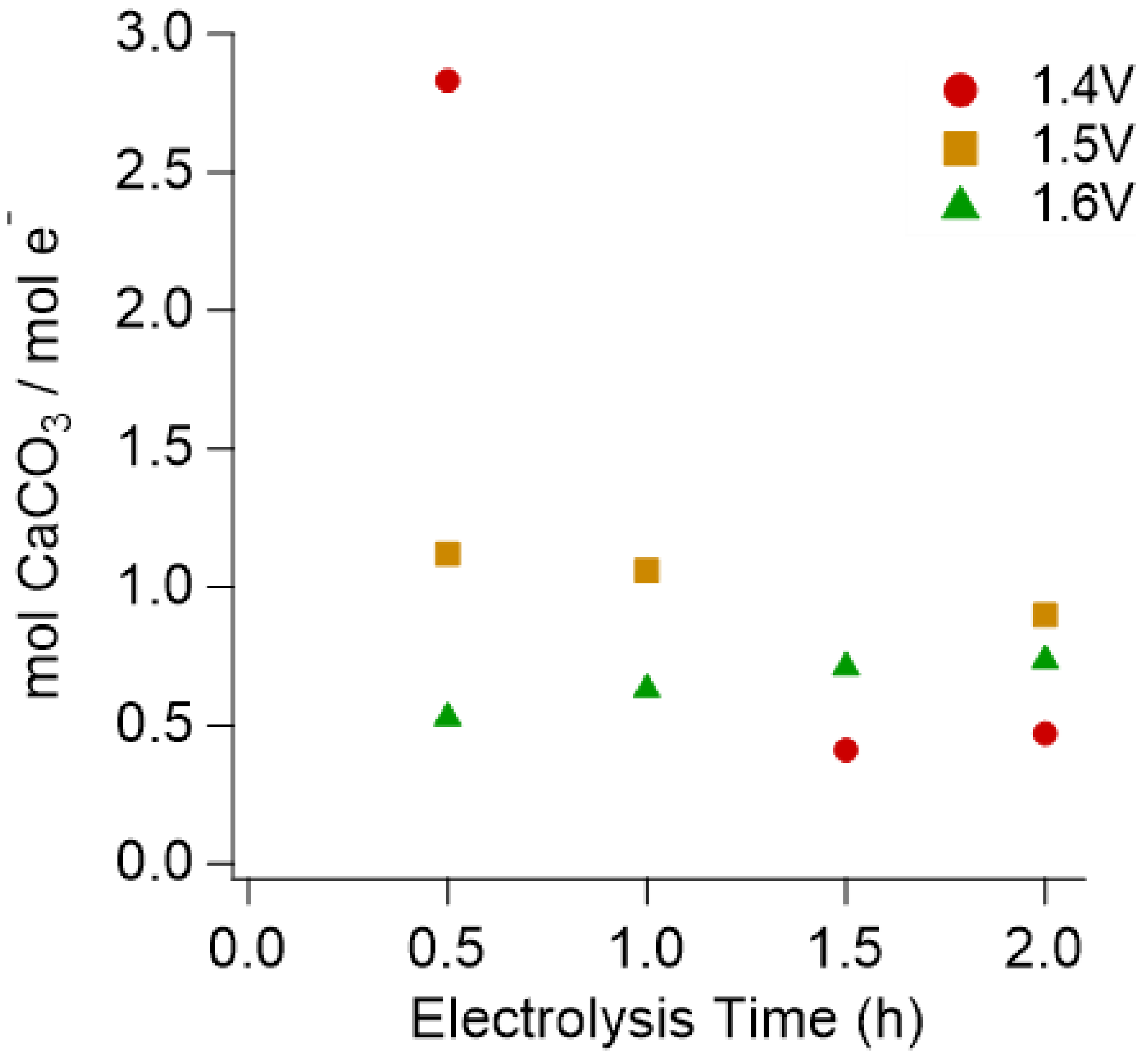
Apply 1.5V vs Ag/AgCl

Comparable electric efficiencies with pure CO_2 and air

- Non published results! Require duplication of results before publication

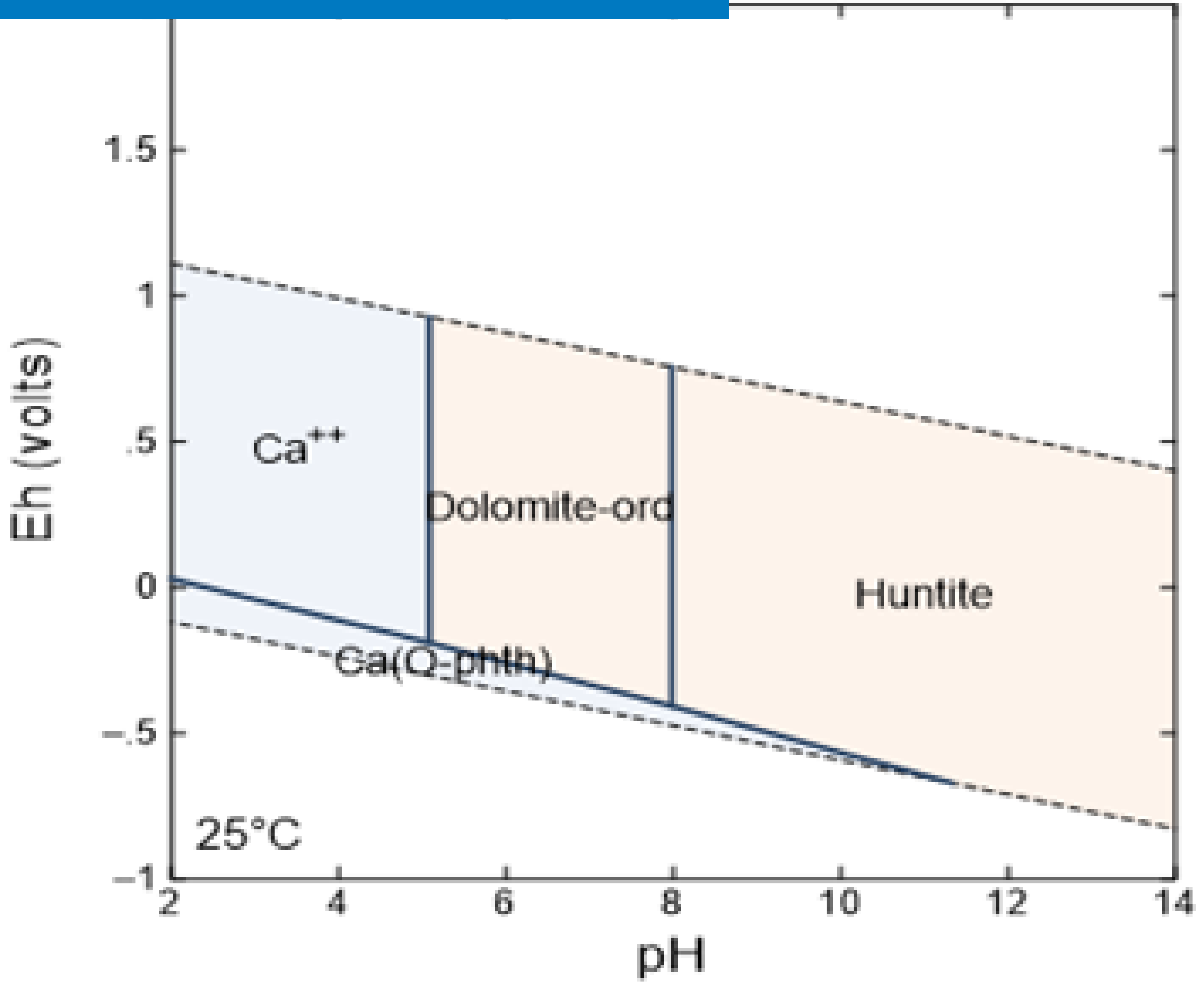
NREL Simple Reactor: Role of Potential

Working to identify optimal reactor operation for given feedstocks



Princeton Pourbaix Modeling

- Mg + Ca phases investigated
- At fixed concentrations, pH ranges determine thermodynamically preferred phase
  - Dolomite, $MgCa(CO_3)_2$
  - Huntite, $Mg_3Ca(CO_3)_4$



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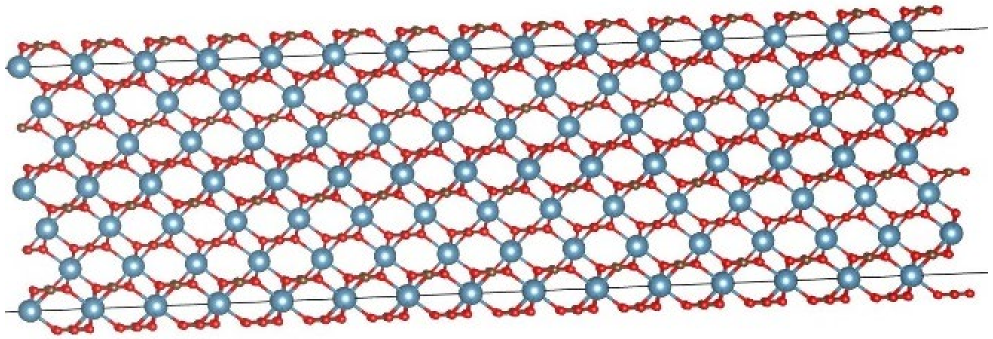
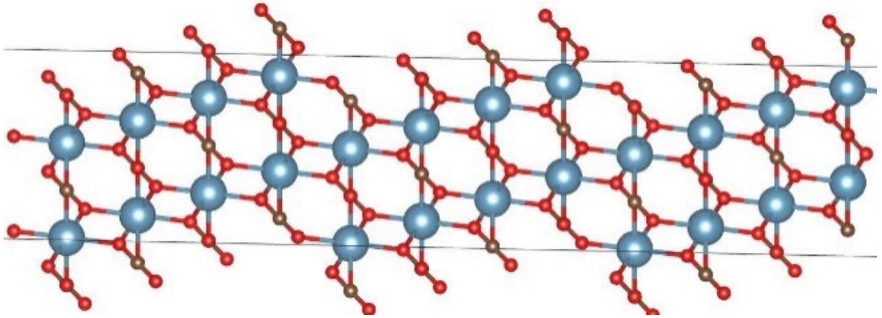
Princeton Modeling Results: Surface Energies

	(1,0,0)	(1,0,4)
		
Bulk energy	**-2.3 eV/atom**	**-2.3 eV/atom**
Slab energy	**-0.15 eV**	**-0.16 eV**
Surface energy	**0.44 J/m²**	**0.42 J/m²**

(1,0,4) facet is kinetically more favorable than (1,0,0)

Same as in literature[1]

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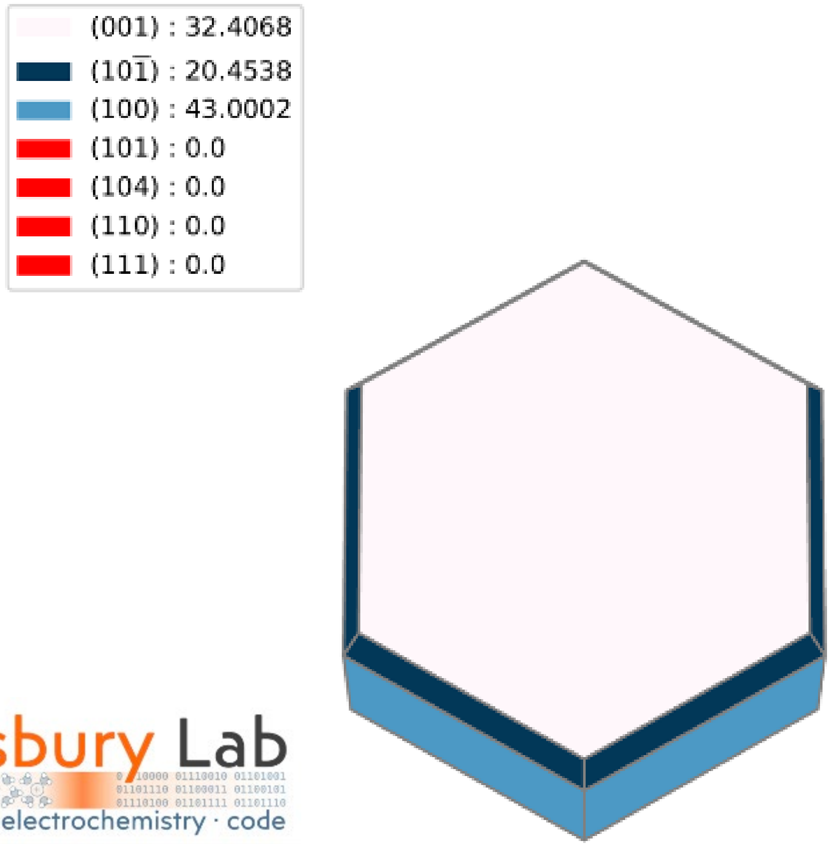
[1] Sun, Wenhao, et al. "Nucleation of metastable aragonite CaCO3 in seawater." Proceedings of the National Academy of Sciences 112.11 (2015): 3199-3204.

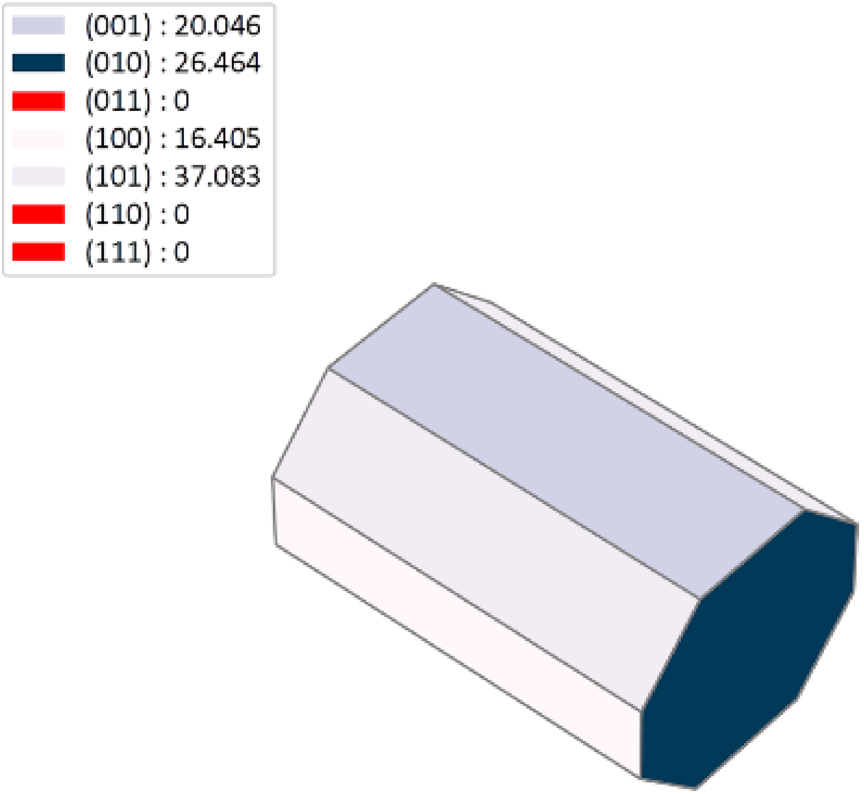
Princeton Modeling Results: Particle Shapes

Wolff Constructions of relevant phases

Calcite



Aragonite



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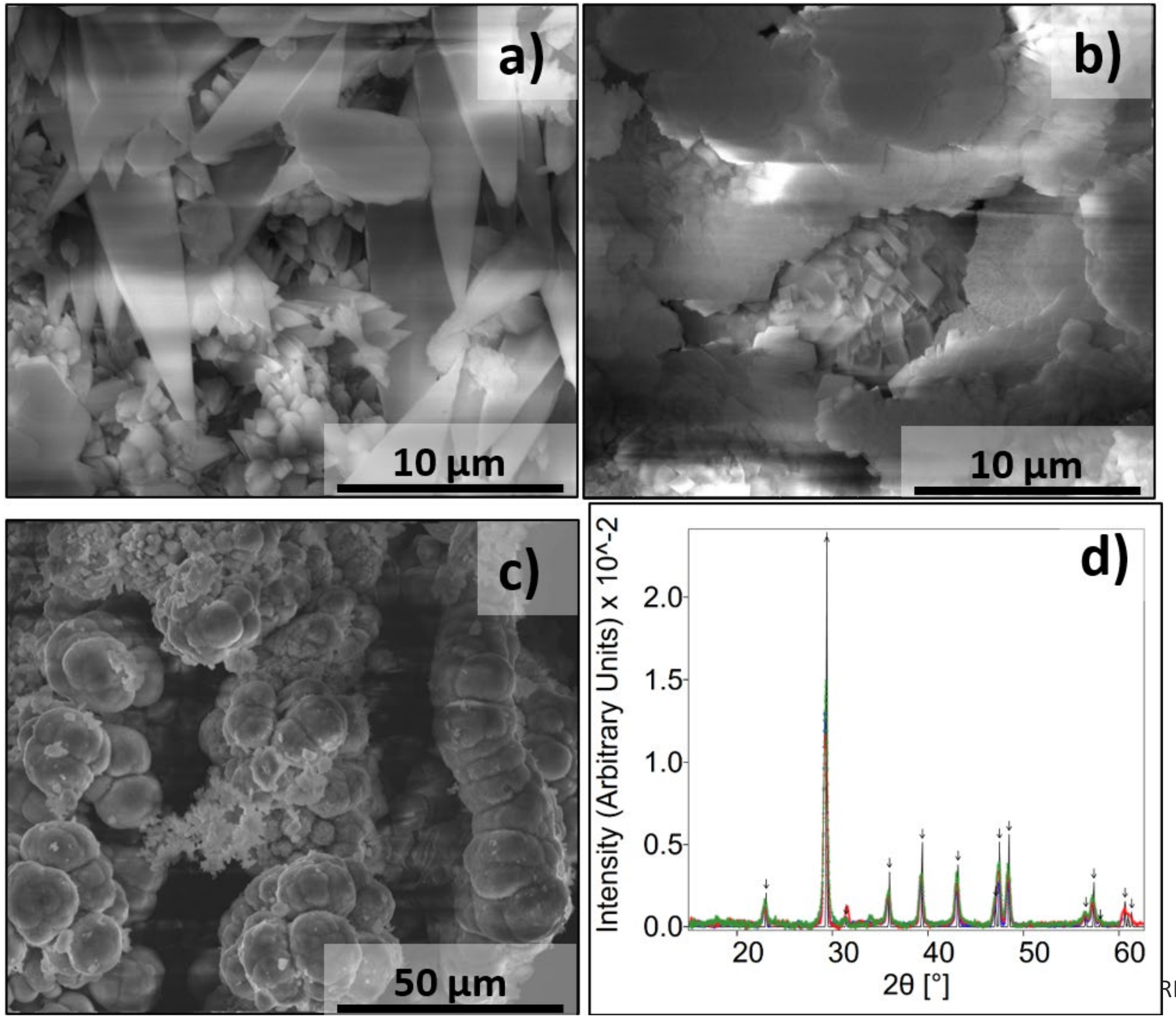
NREL Reactor Particle Shapes

- Applied voltage influenced phase and morphology of $CaCO_3$ formed.
- Morphology impacts utilization in building materials



Colorado Earth: Earthen Bricks with Carbonates

- Proof of principle $CaCO_3$ use in earthen bricks
  - 20 wt.% $CaCO_3$
  - 80 wt.% natural fines

Products: Review in Nature Partner Journal, Materials Sustainability Published

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Mineralization of alkaline waste for CCUS

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ABSTRACT

Ex-situ mineralization processes leverage the reaction of alkaline materials with CO_2 to form solid carbonate minerals for carbon capture, utilization, and storage. Annually, enough alkaline waste is generated to reduce global CO_2 emissions by a significant percentage via mineralization. However, while the reaction is thermodynamically favorable and occurs spontaneously, it is kinetically limited. Thus, a number of techniques have emerged to increase the efficiency of mineralization to achieve a scalable process. In this review, we discuss mineralization of waste streams with significant potential to scale to high levels of CO_2 sequestration.

1. INTRODUCTION

In recent centuries, atmospheric CO_2 levels have risen from less than 250 ppm to roughly 420 ppm. Levels continue to rise, as we emit an additional 37 gigatons of CO_2 each year. [1,2] To avoid global temperature increases above 1.5 C, carbon dioxide emissions need to be reduced to 18 gigatons of CO_2/year by 2030 [1,2]. Carbon capture, utilization, and sequestration (CCUS) has emerged as an important route toward achieving this goal.

Mineralization, or reaction of alkaline materials with CO_2 to form solid carbonate minerals, is a promising CCUS technology. The reaction is thermodynamically favorable and occurs spontaneously, albeit slowly. Current research efforts focus on enhancing the rate and efficiency

-Invited submission to *npj Materials Sustainability,* submitted Jan 31st, 2024.

-Detailed survey of current efforts for mineralization at scale

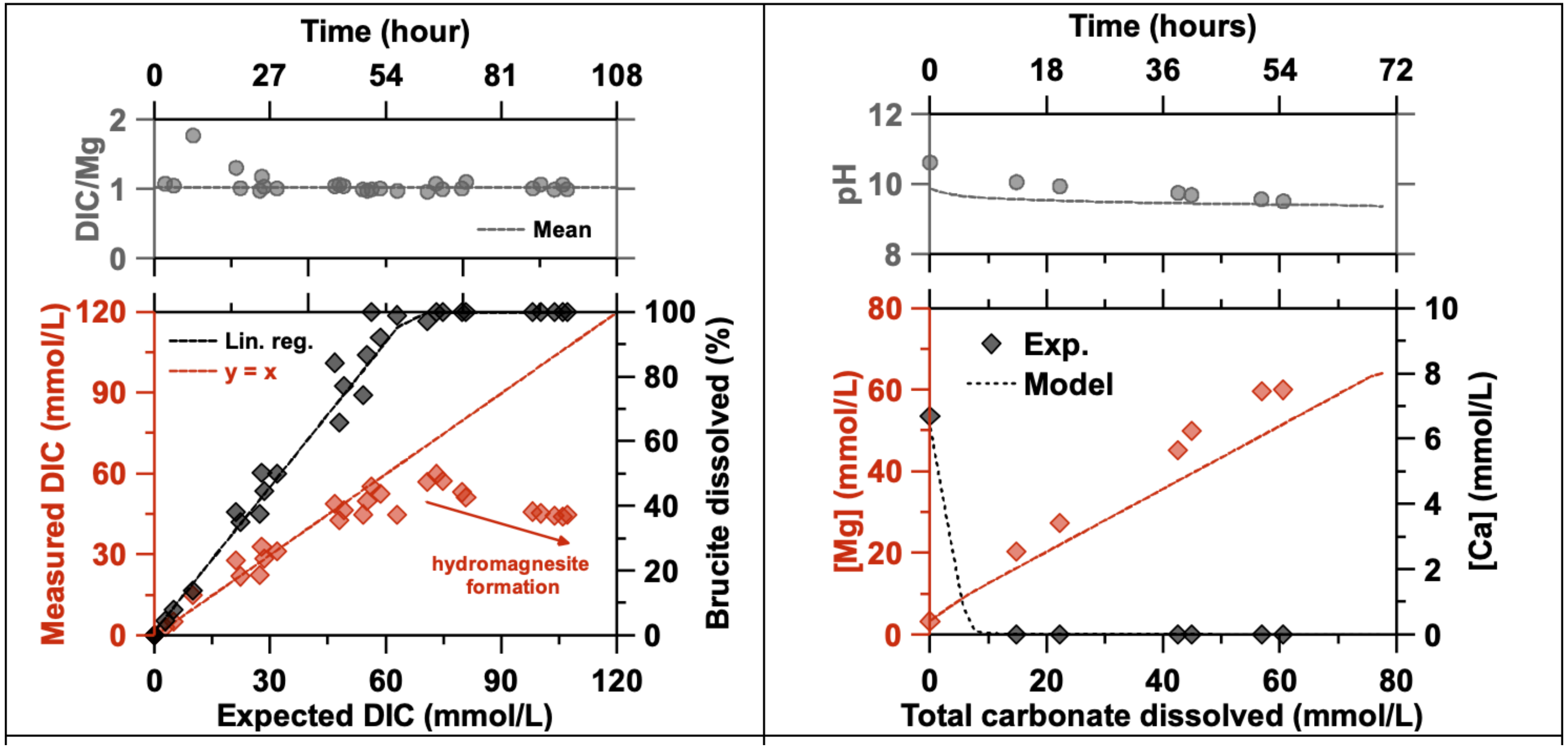
-Includes tables discussing current approaches and feedstocks

Method	Tailings - Mineral	Temperature	Pressure	Particle Size	Time	Liquid/Solid (L/S) ration	Carbonation content	Carbonation efficiency	Author/Year
Direct gas-solid	Chrysotile - Mg	Ambient	0.1 MPa, 14% CO2	<2 mm		35% liq sat.	56.8 mmol/g/h		Assima 2013
Direct gas-solid	Serpentine residue - Mg	258 C	5.6 bar flue gas (pCO2=1 bar	<2 mm	310 min		0.12 g/25 g	37%	Veetil 2014
Direct solid-gas	Chrysotile waste - Mg	375 C	0.1 MPa, 60% CO2			Moist conditions			Larachi 2010
Direct gas-solid	Chrysotile mining waste - Mg	22 C	Ambient, 10% CO2 flue gas	1 mm, 1.3 g/cm3	28 days	40% humidity			Hamilton 2020
Direct gas-solid	Steel slag	600 C	10 vol% CO2	<74 um	1 hr		88.5 kg CO2/t	55.5%	Tian 2013
Direct gas-solid	AOD/EAF	300 C	0.4 MPa	48-75 um	90 min		8.2 wt%	16% (Degree)	Zhang 2018
Direct gas-solid	Waste cement paste	Ambient	.2 MPa	80 µm	2 hr	-	19.8 wt%		Fang and Chang 2015
Direct gas-solid	*CKD, CBD*	*Ambient*	*2 bar*		*24 hr*	*10% moisture*			*Gunning 2009*

doi.org/10.1038/s44296-024-00031-x

UCLA: Dissolution of Mg and Ca Containing Phases

- Methods of dissolving solid tailings into solution.
- Kinetics of Mg and Ca entering solution.



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- TCF-OTT funding
- FECM