Integrated and Sustainable Pathways for CO² Capture and Mineralization with Recovery of High Value Metals and Filler Materials (INSPIRE) DE – FE0032398 (Managed by Kara Zabetakis)

Cornell

Engineering

Greeshma Gadikota | Sustainable Energy and Resource Recovery Group | Civil and Environmental Engineering | Cornell University DOE FECM Project Update Meeting | August 7, 2024

How do we innovate while managing the need to meet our energy and resource demand in response to a changing climate?

INSPIRE Team

Greeshma Gadikota PI, Cornell University Associate Professor

Key Personnel

T. Alan Hatton Co-PI, MIT Professor

David Heldebrant Co-PI, PNNL Chief Scientist

Julien Leclaire Co-PI, UCBL Professor

Deepika Malhotra Senior Scientist PNNL

Quin Miller **Geochemist** PNNL

Key Team Members

Deborah Romito, UCBL Franck Ulm, UCBL Yuan Jiang, PNNL

> **Industry Partners** Novelis Inc | Nucor

INSPIRE Team at Cornell University

Greeshma Gadikota PI, Cornell University Associate Professor

Porus Jadhav PhD student Cornell University

Dhruv Mehta PhD student Cornell University

INSPIRE Aim and Objectives

The *aim* of INSPIRE is to develop molecularly integrated CO₂ capture and mineralization pathways with inherent recovery of high value metals using multifunctional solvents and electrochemically mediated transformations.

The *two primary objectives* of the INSPIRE technology are to:

- (i) demonstrate the recovery of acids (alongside CaCO_3 , Mg(OH)₂ and H₂) from industrial wastewater for recovering Fe- and Al-rich solids followed by the use of CO_2 -bearing solids for recovering Ca- and Mg-carbonates, and electrochemical separation of base metals such as Ni, Zn, Co as carbonates, and Cu in Mode 1 in alkaline industrial residues bearing more than 5 wt% of (non-carbonate) Al, Fe, Mg, and Ca-components,
- (i) develop an integrated approach for the recovery of Ni, Zn, Co as carbonates, Cu metal, and solid carbonate product bearing Ca, Mg, Fe, or Al in Mode 2 in alkaline industrial residues where a single metal component is dominant (e.g., Al is at least 5-fold greater compared to other major elements such as Fe, Mg, Ca).

INSPIRE Mode 1: Metal Recovery and Carbon Mineralization

Schematic representation of the INSPIRE technology for selective metal recover

integrated with CO₂ capture and conversion.

(A) Mode 1: Compositions of Al, Fe, Schematic representation of the INSPIRE technology for selective metal recovery integrated with $CO₂$ capture and conversion.

(B) Mode 2: Compositions of one of the following elements: Al, Fe, Ca, Mg is at *Mg content exceeding 5 wt%*

INSPIRE Mode 2: Metal Recovery and Carbon Mineralization

 $\mathbf{r} \in \mathbb{R}$ **TO 10** Schematic representation of the INSPIRE technology for selective metal recovery integrated with $CO₂$ capture and conversion.

Mode 2 is applied for alkaline residues with Al, Fe, Ca, and Mg content at least 5 fold greater compared to other elements

Key Tasks and Subtasks

Milestones

Schematic representation of the INSPIRE technology for selective metal recovery integrated with $CO₂$ capture and conversion.

(B) Mode 2: Compositions of one of the following elements: Al, Fe, Ca, Mg is at *Mode 1 is applied for alkaline residues with Al, Fe, Ca, and Mg content exceeding 5 wt%*

Advances in Direct Electrolysis of Brine

How can we produce acids, bases, H² , and O² by harnessing brine and electricity while suppressing Cl² gas evolution?

Kim, Lu, Ochonma, and Gadikota, *ACS Energy and Fuels*, 2024 (Invited Article)

Advances in Direct Electrolysis of Brine

 $0.30 -$

100

 80_z

60

 $40₁$

68.5

46.6

NaOH and HCl yields normalized to charge are higher using MnMo/Ti vs. Pt electrode

Lower H² yield using MnMo/Ti electrode

13.7

Advances in Direct Electrolysis of Brine

Calculated oxygen evolution efficiencies using various electrodes and membrane configurations

Significant decrease in Cl² gas evolution efficiency and enhancement in O² gas evolution efficiency using MnMo/Ti electrode compared to Pt electrode

Energy consumption for producing NaOH is higher using MnMo/Ti electrode but economics are more favorable with brine electrolysis compared to water electrolysis!

Ongoing work involves developing novel electrodes for direct electrolysis!

INSPIRE Mode 1: Metal Recovery and Carbon Mineralization

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(B) Mode 2: Compositions of one of the following elements: Al, Fe, Ca, Mg is at *Mode 1 is applied for alkaline residues with Al, Fe, Ca, and Mg content exceeding 5 wt%*

Milestone 2.1: Quantify the chemical compositions and morphological features of the alkaline industrial residues from secondary aluminum processing and steel making

Compositions of Ca- and Mg-bearing content exceeds 40 %.

Compositions of Ca- and Mg-bearing content is less than 20 %.

Ultramafic mine tailings can contain ~ 40 – 50% SiO² , and 30 – 40% Mg-oxide, 5 – 15% Fe-oxides in addition to ~ 100 – 2000 ppm of Ni

 $Cu \sim 200 - 500$ ppm; $Ni \sim 50 - 100$ ppm; $Cr < 50 - 200$ ppm

Milestone 2.1: Quantify the chemical compositions and morphological features of the alkaline industrial residues from secondary aluminum processing and steel making

- ❑ **Evidence of Ca-, Mg-, and Fe-silicates, silica, and** (Forsterite) **iron oxide phases in EAF slags**
- ❑ **Evidence of soluble KCl and NaCl phases in addition to insoluble Al2O³ , Al, MgO, and MgAl2O⁴ phases in black dross**
- ❑ **Evidence of metallic Al, Al2O³ , MgAl2O⁴ , and MgO phases in white dross.**
- ❑ **Significant differences in the compositions of the slags and dross materials motivate advances in customized pathways to recover high value products**

Schematic representation of the INSPIRE technology for selective metal recovery integrated with $CO₂$ capture and conversion.

(B) Mode 2: Compositions of one of the following elements: Al, Fe, Ca, Mg is at

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Task 2. Material Characterization, Solvent Synthesis, and Determination of Key Solvents

Water-lean solvents are a prime medium for integration of capture *and mineralization and metal recovery.*

- Overall process is catalytic with respect to solvent
- Catalytic exothermic mineralization offsets endothermic solvent regeneration
- Bypasses CO₂ compression
- PNNL's single-component water-lean solvents are tunable bi-dentate ligands for cation chelation

e.g. EEMPA: N-(2-ethoxyethyl)-3 morpholinopropan-1-Amine

Brickett et al. Chem. Sci., **2022**,13, 6445-6456

Task 2. Material Characterization, Solvent Synthesis, and Determination of Key Solvents

Towards Designing Candidate Solvents: **PNNL has libraries of available solvents from three classes to select from and reduced-order models enable us to quickly design and synthesize solvents with tailored properties (as needed).**

 λ

N

N

Syntheses are designed for use of off-the-shelf reagents.

2-EEMPA w/wo $CO₂ + Ni$ and Co

 $\left.\begin{array}{c} \mathsf{H} \\ \mathsf{H} \\ \mathsf{H} \end{array}\right\}$

 $\frac{N}{H}$

H

^H OH

N H

 $\widehat{O}CH_3$

 $\frac{1}{2}$ $\frac{1}{2}$ **Nucleophilicity**

Design Criteria:

Hardness

• pKa

- **Conductance**
- Binding enthalpy
	- -60 to -85 kJ/mol

Cantu et. al. *ChemSusChem.*, **2020**, DOI: 10.1002/cssc.202000724.

Milestone: 2.2: Synthesize third generation solvents and quantify CO₂ capture behavior and **2.3:** Identify 2 – 3 appropriate solvent systems

Water – lean solvents developed at PNNL

Evidence of the carbon mineralization of Ca(OH)₂ and Mg(OH)₂ using 2-EEMPA in gas – liquid – solid mode. Experimental conditions include $pCO₂$ of 1 atm, 15 wt% solid in a well-stirred slurry environment

The team will build on these studies for the selective separation of Mn, Ca, and Mg-bearing carbonates in INSPIRE.

Milestone 3.1: Leach > 60% of Ni and > 80% of Ca from select alkaline industrial residues - SMART; Go – No Go Milestone

Inorganic acid driven leaching

Dissolution of black dross in a 2 M HCl solution at 50 °C and 300 rpm for two hours

Task 3. Metal Recovery

Decreasing concentrations => precipitation of dissolved ions

Recovered (%)

- ❑ High content of Al in the solid recovered at pH 5 is noted.
- ❑ Similar quantity of Al is noted in the recovered product with S:L::1:50 and 1:10

Task 3. Metal Leaching using CO₂-Bearing Solvents and Electrochemical Approaches

harnessing selective chelation ability of specific ligands.

Task 3. Metal Leaching using CO₂-Bearing Solvents and Electrochemical Approaches

Harness differences in the binding affinities of various metals for ligands to drive metal separations

Thermodynamic constants of competing solvent-metal complexation (columns) vs hydroxylation (black line) (a-c) and carbonation (d-f) (black line).

Bottom: water-lean solvent models (A3), polyamines (A2) and aminoacid solvents (A1) reported in the literature.

Next steps: Advance experimental efforts to determine the effectiveness of various solvents in effectively capturing energy relevant metals.

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Task 4. Extractive carbon mineralization of Mn, Ca, and Mg recovery

Milestone 4.1. Achieve selective separation of Mn, Ca, and Mg-carbonates

How do we quantify solvent regeneration?

¹³C NMR comparison for solvents recovered after mineralization of $Ca(OH)$ ₂ using CO₂ pre-loaded 2.5 M Na-Glycinate at: a) 25° C, b) 50° C and c) 75° C.

 $H_2NCH_2COO^+ + CO_2 \rightleftarrows \cdot OOCNCH_2COO^+ + H^+$ $-OOCNCH_2COO + H_2O \rightleftarrows H_2NH_2COO + HCO_3$ $CO_{2(aq)} + OH \rightleftharpoons HCO₃ \rightleftharpoons CO₃² + H⁺$

Task 4. Extractive carbon mineralization of Mn, Ca, and Mg recovery

- ❑ Extent of mineralization, solvent regeneration and effective solvent regeneration for mineralization of $Ca(OH)_2$ using CO_2 pre-loaded 2.5 M Na - Glycinate at 25 $\mathrm{^0C}$, 50 $\mathrm{^0C}$ and 75 $\mathrm{^0C}$.
- Extent of carbon mineralization \sim 92% and solvent regeneration \sim 92% is realized using Ca(OH)₂
- \Box Solvent regeneration \sim 94% is achieved on the mineralization of by-product obtained on slag dissolution

Milestone 6.1. Complete the TEA framework for INSPIRE

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- ❑ The annual slag processing volume amounts to 8,640 tons, based on plant operation for 360 days per year. Each ton of slag yields a profit of \$220,662.44, predominantly derived from the sale of carbonates and metal oxides. Additionally, revenue is generated from the recovery of critical metals.
- \Box About 338 tons of CO₂ captured per ton of slag.

Milestone 6.2. Complete the LCA framework for INSPIRE

LCA is based on processing 1 ton of slag coupled with the electrochemical co-generation of NaOH, HCl, H² , and O² for extracting energy critical metals and producing inorganic carbonates via CO² capture and mineralization.

Milestone 6.2. Complete the LCA framework for INSPIRE

CO² emissions are predominantly from electricity, brine, and solvent. Negative emissions arise from co-product generation.

Switching to electricity from renewable energy resources and crediting the products can result in carbon – negative products.

Outreach Activities

C1. Engage K – 12 community in science education and communication

The REACT (Research Education and Activities for Community Teachers) program connects K-12 educators with cutting-edge research at Cornell University. Organized by graduate students, this initiative highlights the latest research techniques and advancements for teachers, aiming to bring cutting-edge research into their classrooms. Dhruv Mehta participated in the virtual lab tour, where he showcased various equipment and analytical instruments in the lab used for research on carbon capture and metal recovery.

Upcoming activities

We are organizing the ACS Women in Energy Symposium in the ACS Fall Meeting in Denver, Colorado from August 18 – 22, 2024.

We welcome you to attend!

Key Tasks and Subtasks

The team has made significant progress on Tasks 1 – 6 during the first year

Milestones

Milestones 1.1, 2.1, 2.2, 6.1, and 6.2 are achieved.

Significant progress is being made towards Milestones 2.3, 4.1, 5.1, 6.1, and 6.2.

Green: completed | Blue: In Progress | Black: To Begin

Thank you!