Synthetic Calcium Carbonate Production by Carbon Dioxide (CO_2) Mineralization of Industrial Waste Brines

DE-FE0031705

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U.S. Department of Energy

National Energy Technology Laboratory

Carbon Management and Natural Gas & Oil Research Project Review Meeting

Virtual Meetings August 2 through August 31, 2021

Project Overview

- **Funding**: $799,995 DOE share and $199,998 Cost Share
- **Overall Project Performance Dates**: 2/15/2019 - 2 /15/2019
- **Project Participants**: Bu Wang (PI, UW-Madison), Dante Simonetti (co-PI, UCLA), and JR DeShazo (co-PI, UCLA)

Project Overview

Overall project objectives:

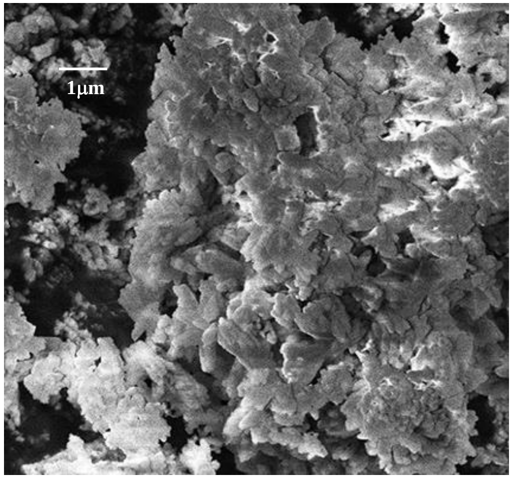
Develop and evaluate the proposed methods for production of precipitated calcium carbonate (PCC) while simultaneously utilizing CO_2 and industrial solid and liquid wastes.

- Integration of CO_2 utilization with waste management
- Production of high-purity fine PCC

Technology Background

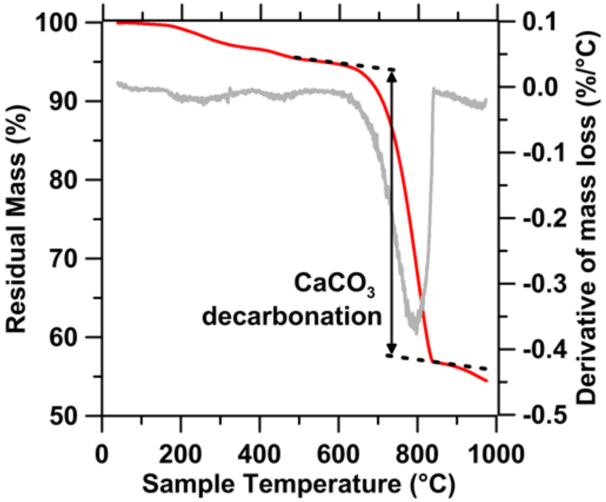
PCC Production by CO_2 mineralization

- Capture CO_2 into stable solid form
- Low energy input and can use flue gas as-is
- Potential to achieve negative life-cycle CO_2 emission



Market potential

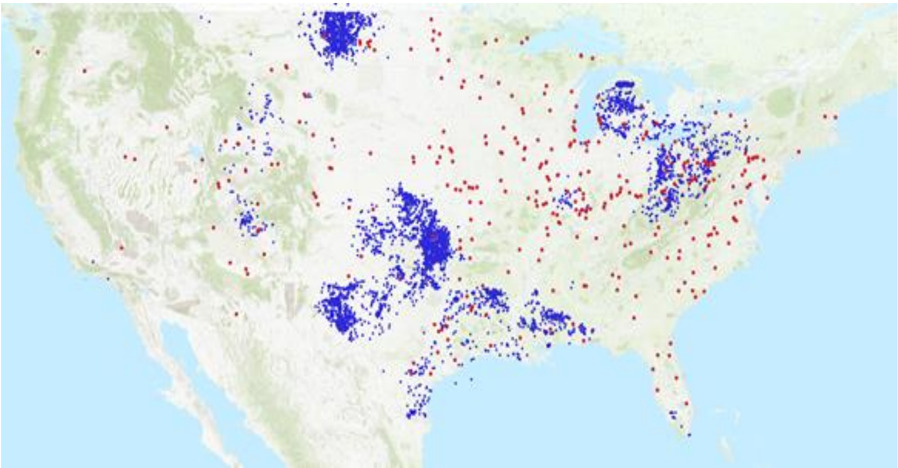
- Fine calcium carbonate (PCC/GCC): $230-$400 per ton
- Coarse GCC: $60 per ton
- Current market size: $5.9 B per year (additives for pharmaceuticals, paint, food, paper, cosmetics, etc.)
- Market may be further expanded into cement/concrete production



Technology Background

Calcium from waste streams

- Coal combustion wastes in the U.S.: 125 M t per year and 2 B t in landfills/ash ponds
- Produced water: 2230 B L per year in the U.S. with an average Ca concentration of >5500 mg/L



Red: coal power plants

Blue: sites of Ca-rich (≥10,000 ppm) produced water

Efficient processes to maintain alkalinity

- Alkaline solids: coal ashes
- Ion-exchange: a new process utilizing H^+/Na^+ exchanger and high ionic strength brines
- Integration with wastewater treatment

Project Scope/Success Criteria

Enabling CO_2 mineralization and PCC production via the coal ash and produced water carbonation processes

- CO_2 uptake > 0.35 g CO_2 / g of dry product; $CaCO_3$ content > 85% (TGA/chemical analysis)

Efficient process design for the proposed processes, that is scalable and economical

- Higher CO_2 consumption, lower life cycle cost and impact with respect to existing CO_2 mineralization-based PCC production technology (e.g., brine carbonation using NaOH/electrolysis)

Functional (benchtop) demonstration system

- System tested with simulated flue gas; real-time operation data for performance evaluation

Progress and Current Status of Project

Coal ash carbonation process

- Developed a new four-step process for PCC production from coal ash and CO_2
- Tested the process on three different types of coal ashes

Produced water carbonation process

- Developed a ion-exchange (IEX) based PCC production process
- Tested on four IEX materials using simulated produced water

Progress and Current Status of Project (Coal ash carbonation)

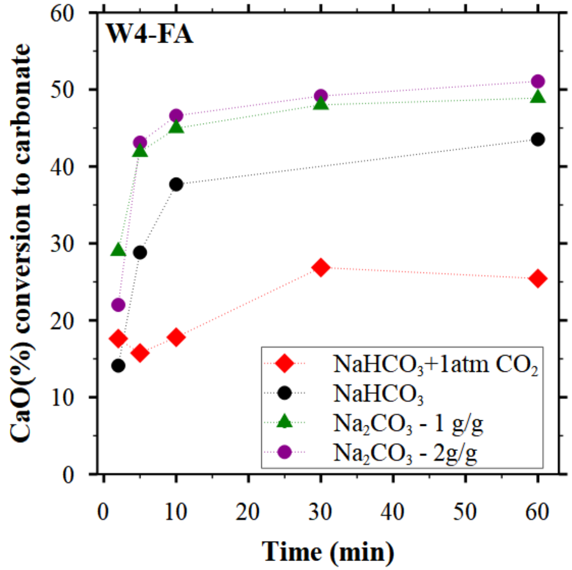
Accelerating ash dissolution through alkaline carbonation:

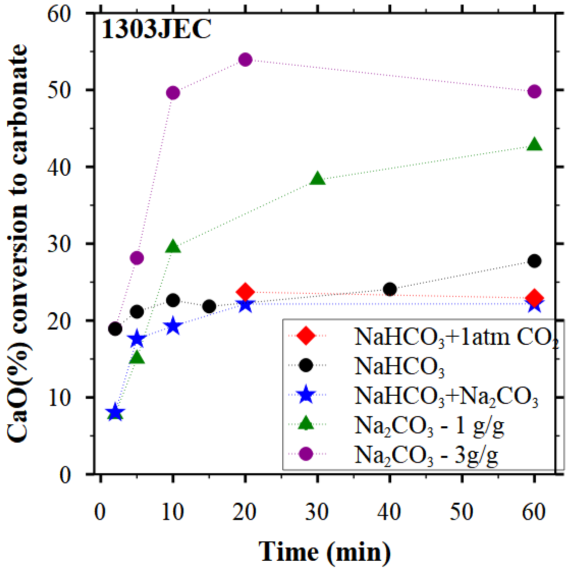
Aqueous carbonation:

$$2CaO.SiO_2(s) + 2Na_2CO_3(aq) + 2H_2O \rightarrow 2CaCO_3(s) + SiO_2(s) + 4NaOH(aq)$$

CO_2 capture:

$$CO_2(g) + 2NaOH(aq) \rightarrow Na_2CO_3(aq) + H_2O$$





Progress and Current Status of Project (Coal ash carbonation)

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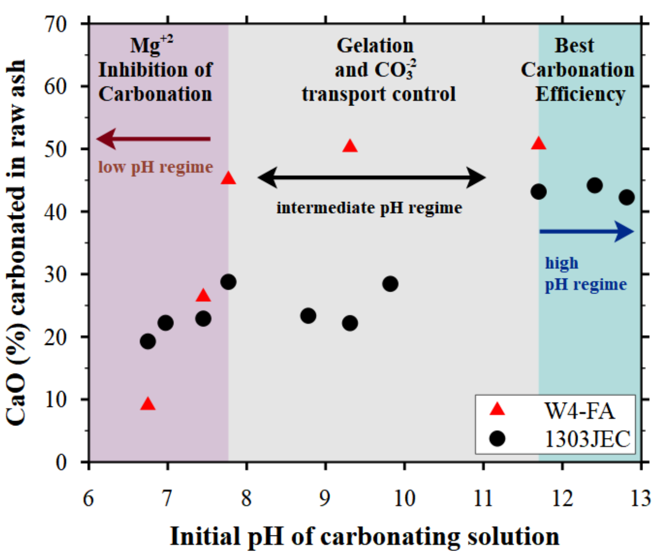
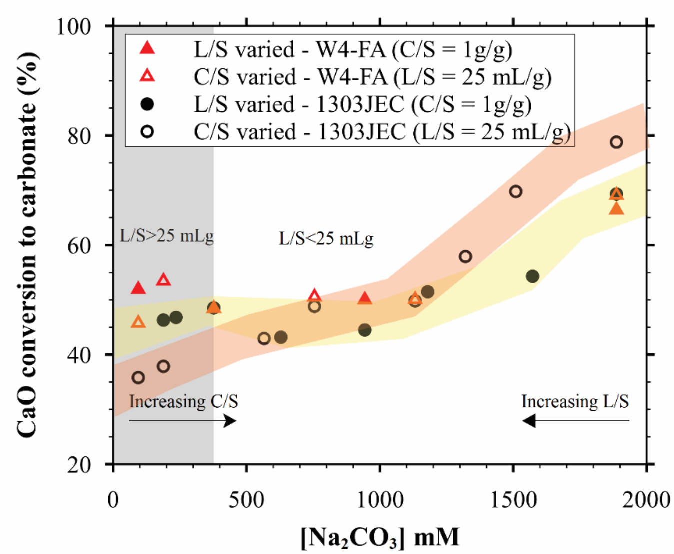




For reference, the CaO conversion efficiency obtained by:

- Direct carbonation of in 1 bar CO_2 is **4.25**%
- 24-hour carbonation under 5 bar CO_2 is **30**%

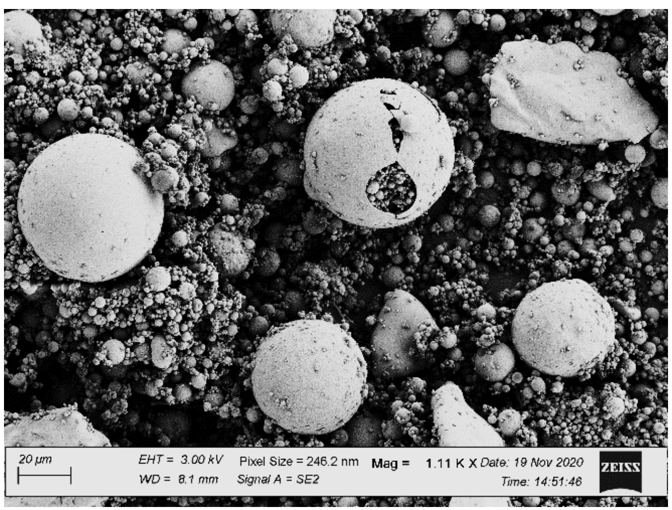
Progress and Current Status of Project (Coal ash carbonation)

PCC is separated from the carbonated ash residue by a pressure-swing process:

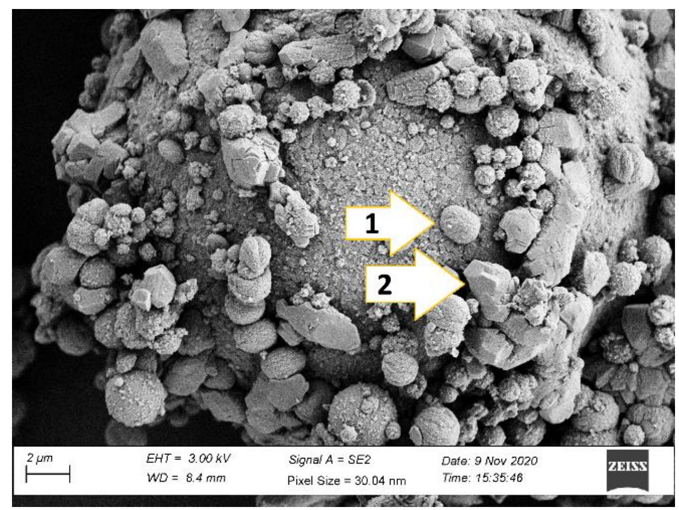
Calcium carbonate dissolution:

$$2CaCO_3(s) + SiO_2(s) + 2H_2O + 2CO_2(g) \rightarrow 2Ca^{+2} + 4HCO_3^- + SiO_2(s)$$

Calcium carbonate precipitation: $2Ca^{+2} + 4HCO_3^- \rightarrow 2CaCO_3(s) + 2H_2O + 2CO_2(g)$



Before carbonation

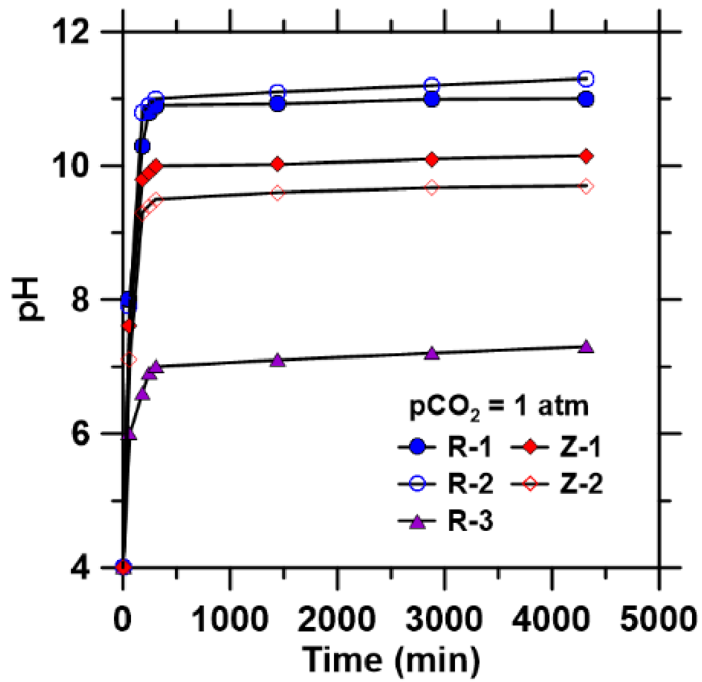


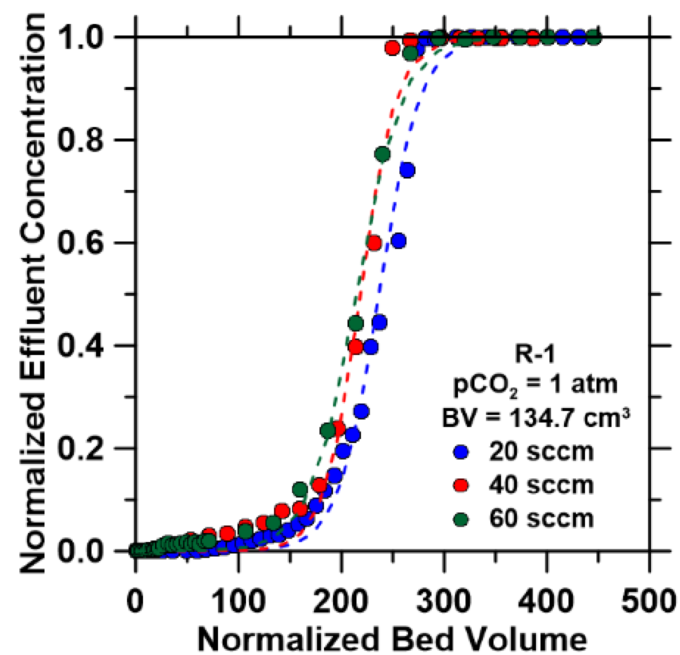
After carbonation

Progress and Current Status of Project (Produced water carbonation)

- Use ion-exchange (IEX) materials to raise pH of the CO_2 equilibrated DI water from 4 to >8.

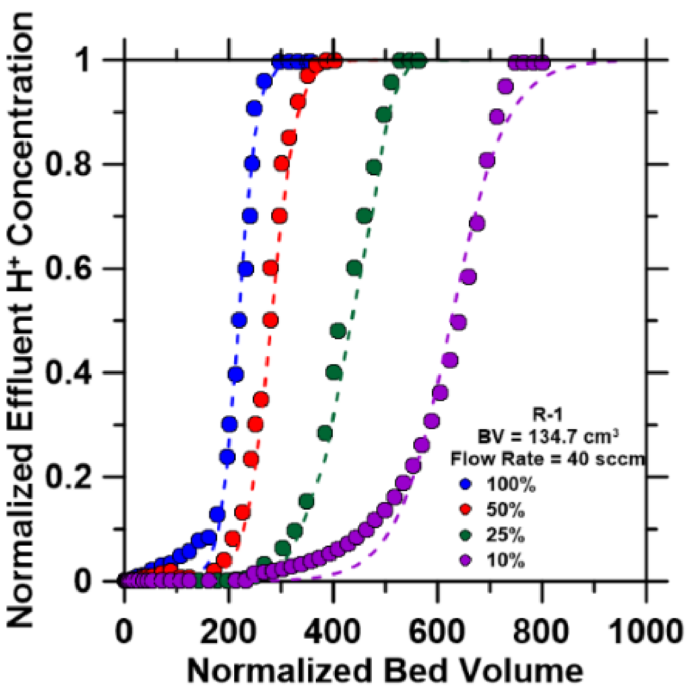
- Mixing IEX effluent with high-Ca produced water to precipitate calcium carbonate.

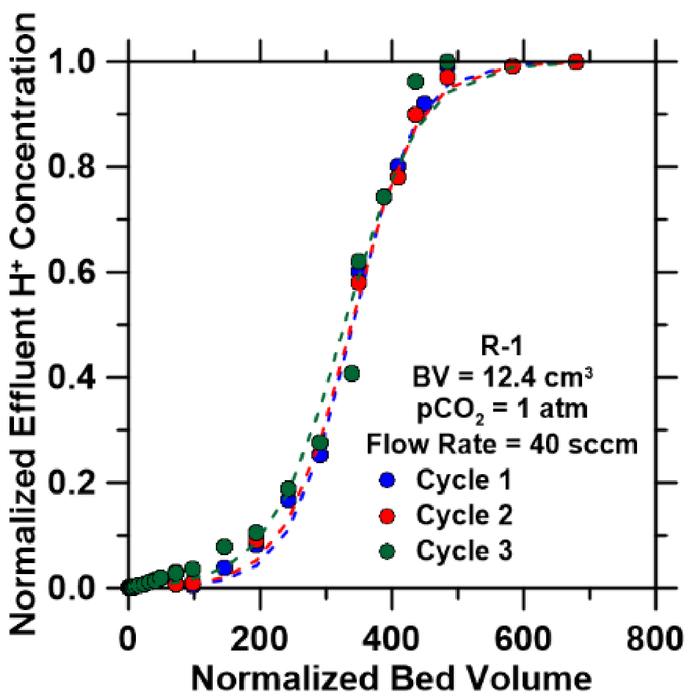




Progress and Current Status of Project (Produced water carbonation)

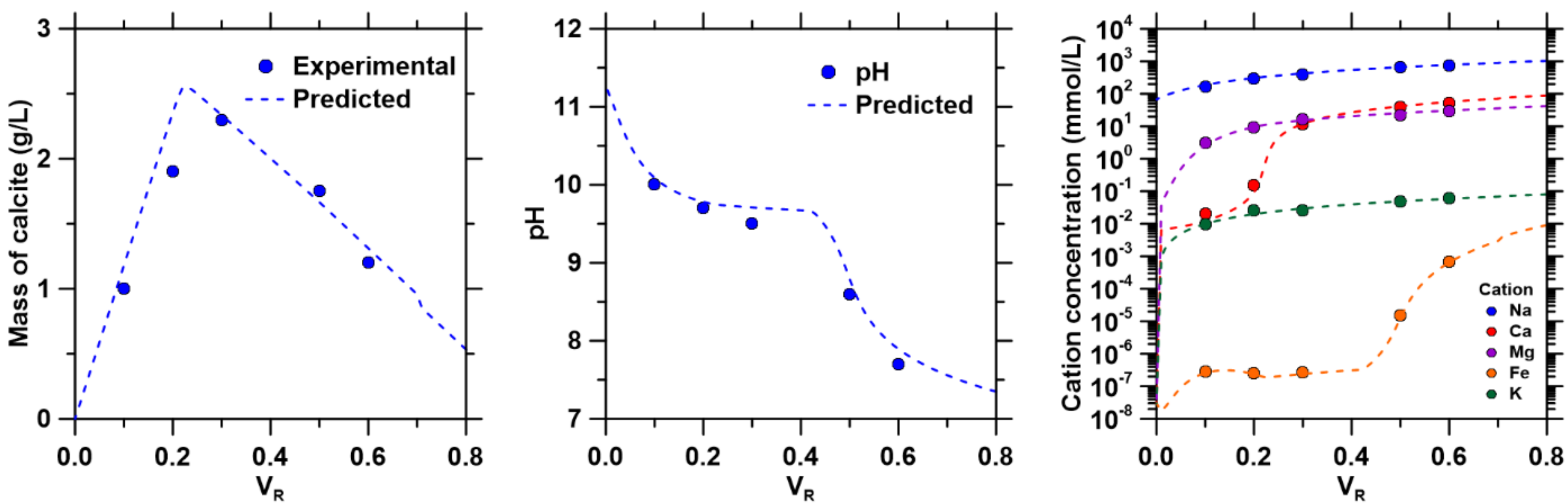
- IEX materials are regenerated using Na-rich produced water following calcium carbonate precipitation.
- No immediate degradation is induced by the IEX reactions.





Progress and Current Status of Project (Produced water carbonation)

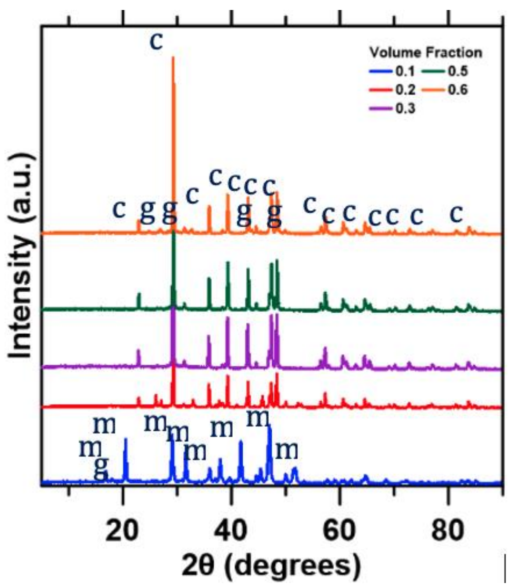
PCC production from IEX effluent and simulated produced water was investigated using both geochemical simulations and experiments.

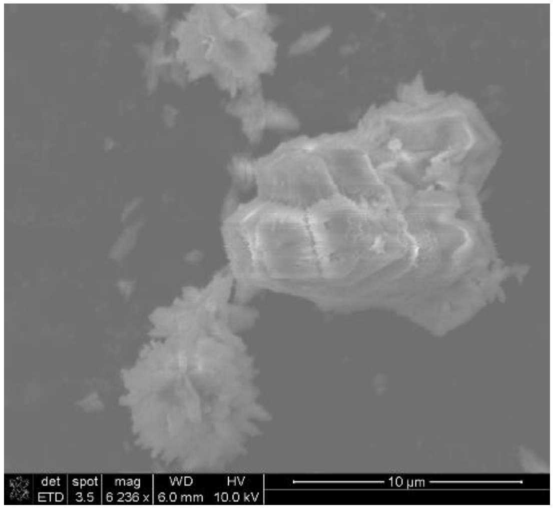


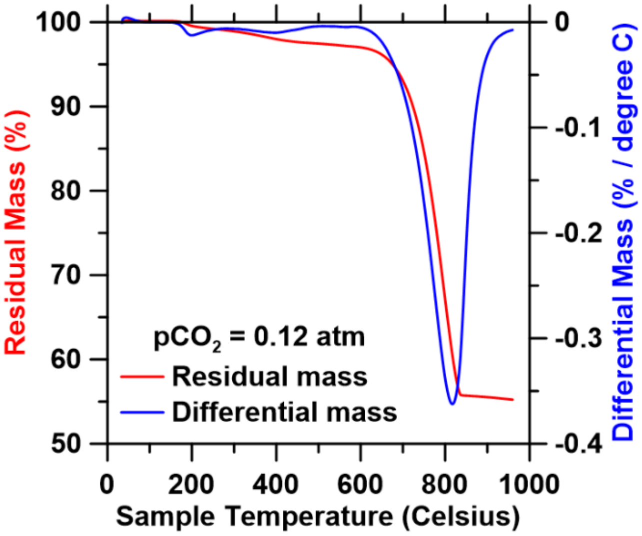
$$V_R = V_{PW} / (V_{PW} + V_{IEX})$$

Progress and Current Status of Project (Produced water carbonation)

PCC with purity >90% was produced using weak-acid IEX and produced water compositions from the USGS database.







Plans for future testing/development/ commercialization

- Optimize process parameters for different feedstocks
- Complete techno-economic analysis including capital cost estimates and scalability assessment
- Quantify life-cycle carbon footprint using the NETL CO2U LCA Toolkit
- Demonstrate the optimized process using an integrated bench scale reactor system

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Summary Slide

- Two CO_2 mineralization processes, namely the coal ash carbonation and produced water carbonation, have been developed.

- The coal ash carbonation process can capture and sequester CO_2 from dilute sources while upcycling waste materials for secondary applications (e.g., calcium sulfate and supplementary cementitious material).

- The produced water carbonation process can produce PCC at low cost from waste brines and coal fired power plant flue gas. This process can provide attractive value to produced water treatment facilities that has access to flue gas stream.

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Appendix

Acknowledgment
This material is based upon work supported by the Department of Energy under Award Number DE-FE0031705.

Disclaimer

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Organization Chart

DOE NETL
Project Manager
Sai Gollakota

Project Management (Task 1)
UW-Madison
Bu Wang

Scientific Team

UW-Madison
Bu Wang

- Technology Maturation Plan (Task 2)
- Coal ash carbonation process development (Task 3 and 4)

UCLA
Dante Simonetti

- Ion-exchange process development (Task 3 and 4)
- Lab-scale demonstration (Task 6)

- Feedstock characterization (Task 3, Wang, Simonetti)
- Leaching and precipitation kinetics (Task 3 and 4, Wang, Simonetti)
- TEA/LCA analysis (Task 5, Wang, DeShazo, Simonetti)

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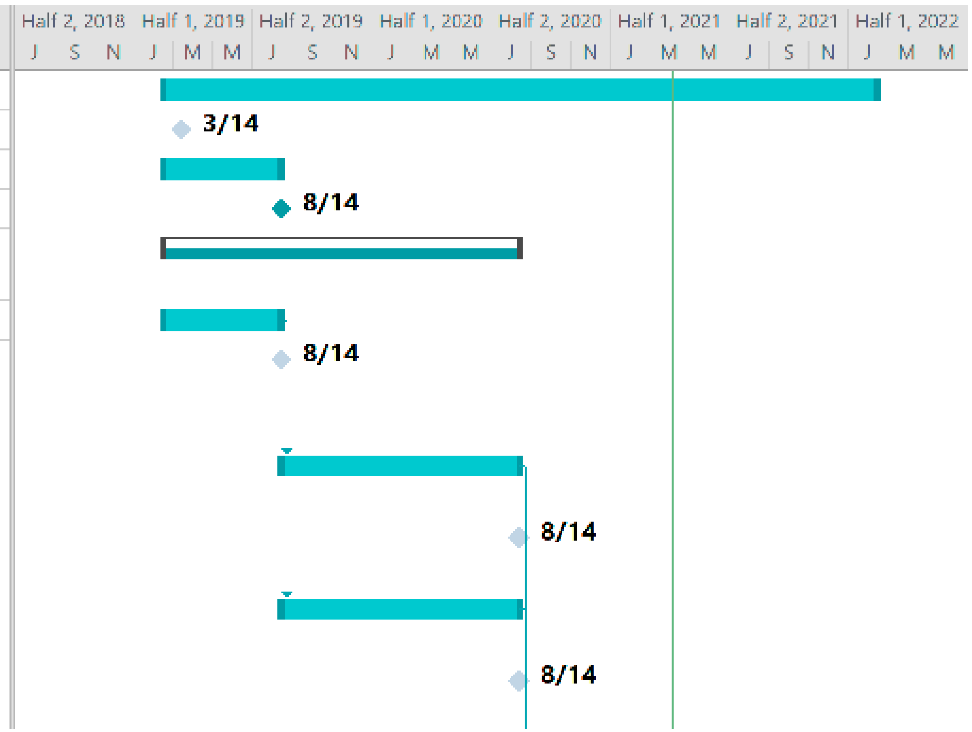
Gantt Chart

Completed tasks

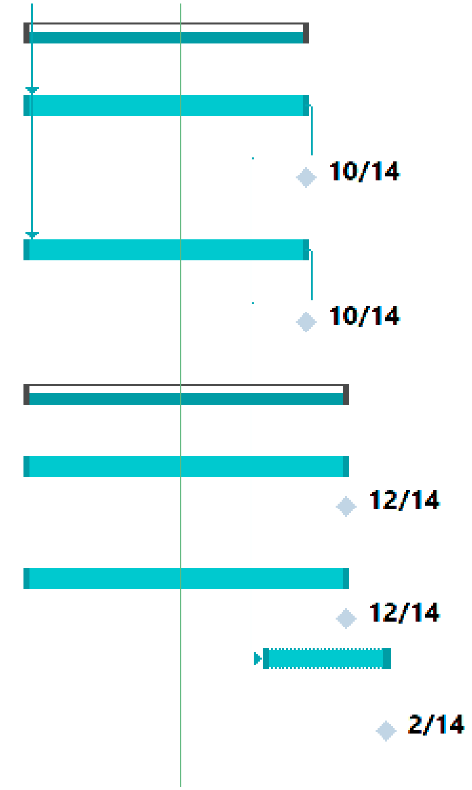
Task Name	Start	Finish
Task 1.0 - Project management and planning	**2/15/19**	**2/14/22**
Update Project Management Plan	3/14/19	
Task 2.0 - Technology Maturation Plan	2/15/19	8/14/19
Finalize Technology Maturation Plan	8/14/19	8/14/19
Task 3.0 - Production of high-purity calcite from solid and liquid waste streams	**2/15/19**	**8/14/20**
Subtask 3.1 Feedstock characterizations	2/15/19	8/14/19
Acquire physical and chemical characteristics of representative coal ash and produced water samples	8/14/19	
Subtask 3.2 Aqueous-state carbonation of coal combustion byproducts	8/15/19	8/14/20
Establish kinetic characteristics of coal ash dissolution and brine carbonation	8/14/20	
Subtask 3.3 Carbonation of produced water through ion-exchange process	8/15/19	8/14/20
Establish kinetic characteristics of ion-exchange and calcite precipitation	8/14/20	



Gantt Chart

On-going and planned tasks

Task 4.0 - Establishment of suitable approaches to scalable production of high purity calcite	**8/15/20**	**10/14/21**
Subtask 4.1 Process development for aqueous carbonation of coal ashes	8/15/20	10/14/21
Establish process parameters for the coal ash carbonation process	10/14/21	
Subtask 4.2 Process development for produced water carbonation	8/15/20	10/14/21
Establish process parameters for the ion-exchange process	10/14/21	
Task 5.0 - Completion of Technical and Economic Feasibility Study and Life Cycle Analysis	**8/15/20**	**12/14/21**
Subtask 5.1 – Technical and Economic Feasibility S	8/15/20	12/14/21
Complete Technical and Economic Feasibility Study	12/14/21	
Subtask 5.2 – Life Cycle Analysis	8/15/20	12/14/21
Complete Life Cycle Analysis	12/14/21	
Task 6.0 - Laboratory-scale demonstration of high-purity PCC production	**8/15/21**	**2/14/22**
Integrated system demonstration with simulated flue gas	2/14/22	



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