Development of an Advanced CO_2 Mineralization Technology for Coproduction of Value-Added Carbonate and Fertilizer Products (DE-FE0032256)

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2024 FECM / NETL Carbon Management Research Project Review Meeting

August 7, 2024

Presentation Outline

1. Project Overview
2. Technology Background
3. Technical Approach / Project Scope
4. Progress and Current Status of Project
5. Summary of CB/SCI
6. Lessons Learned
7. Plans for Future Work
8. Summary

1. Project Overview (1)

Overall Objectives:

Develop an advanced CO_2 mineralization technology using CO_2 from industrial sources and Flue Gas Desulfurization (FGD) byproducts for coproducing Precipitated Calcium Carbonate (PCC) and fertilizer products by

- conducting lab testing at a scale of 1 LB/hr of CO_2 mineralization,
- validating product properties, and
- evaluating its techno-economic and life cycle environmental performances

Project Participants

- University of Illinois at Urbana-Champaign: Tech development and testing; materials characterization; TEA; LCA
- Power plants and crop advisors/agronomists: Consulting on engineering analysis and fertilization use & assessment

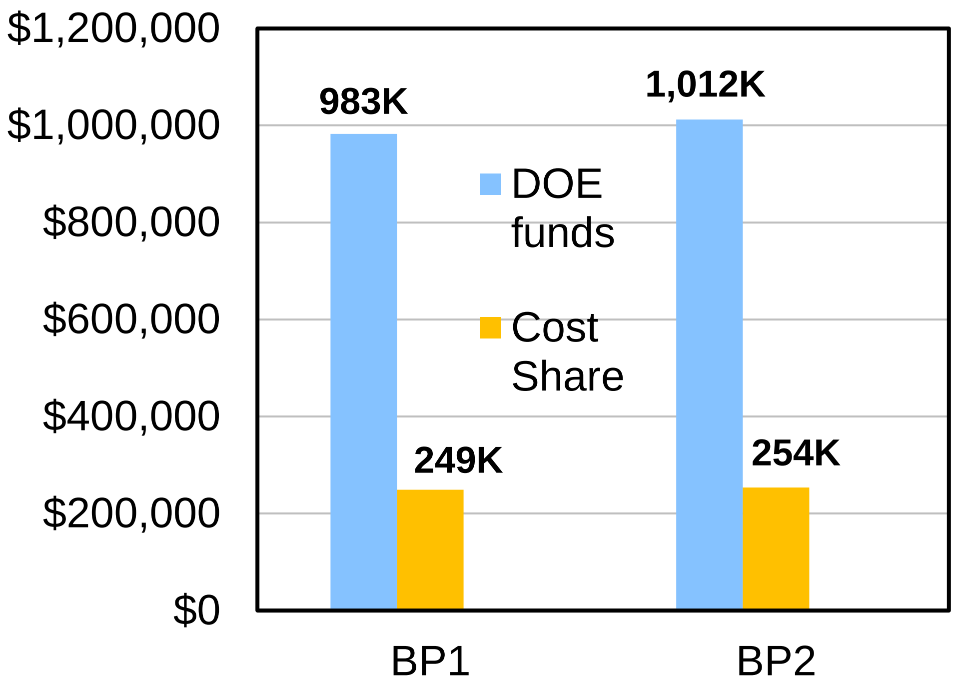
Project Overview (2)

Project Performance Dates

- BP1: 16 months, Aug 1, 2023 – Nov 30, 2024 (BP1 extended for 4 months)
- BP2: 12 months, Dec 1, 2024 – Nov 30, 2025)

Funding Profile

- DOE funding of $1,994,739
- Cost share (in-kind & cash) of $502,845 (~20.1%)



2. Technology Background

- **Chemistry of CO_2 mineralization with Flue Gas Desulfurization (FGD) byproducts**
  - With FGD gypsum feed:

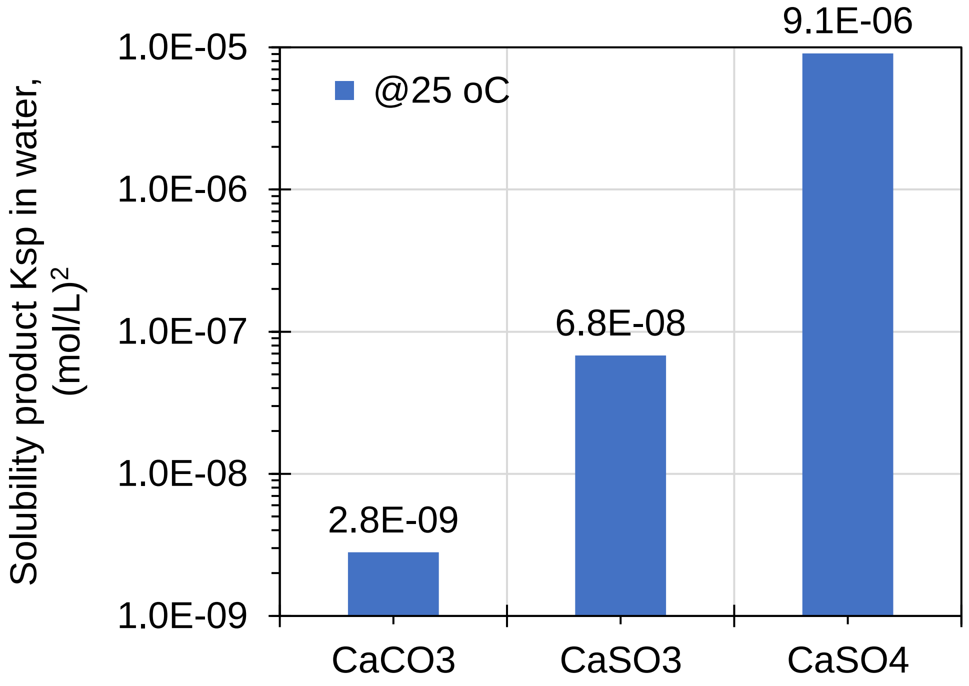
    $CO_2\ (g) + 2NH_4OH\ (aq) + CaSO_4{\cdot}2H_2O\ (s) = (NH_4)_2SO_4\ (aq) + CaCO_3\ (s) + 3H_2O$

  - With FGD non-gypsum feed:

    $CO_2\ (g) + 2NH_4OH\ (aq) + CaSO_3{\cdot}\tfrac{1}{2}H_2O(s) = (NH_4)_2SO_3\ (aq) + CaCO_3\ (s) + 1\tfrac{1}{2}\ H_2O$

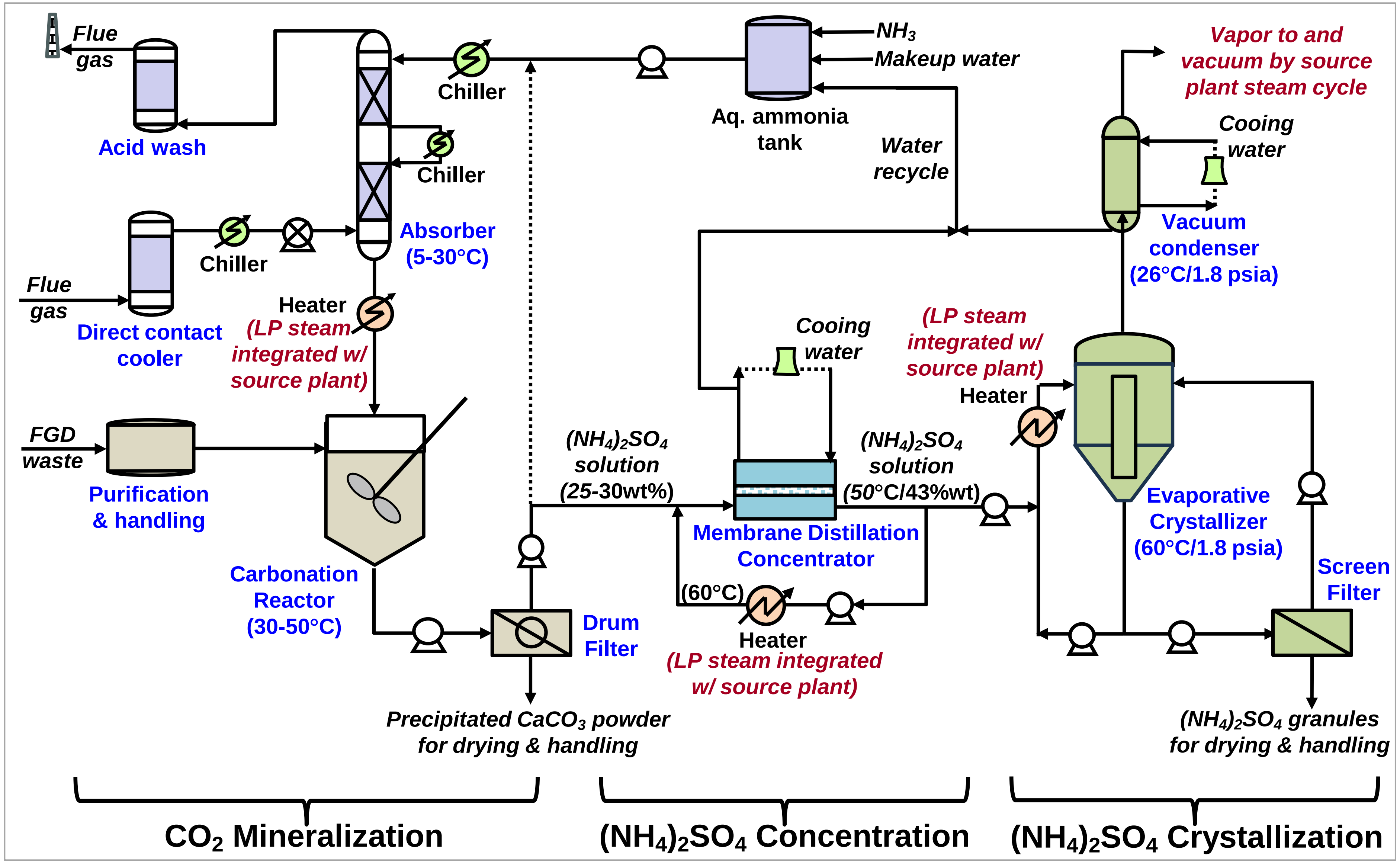
    $(NH_4)_2SO_3\ (aq) + \tfrac{1}{2}\ O_2 = (NH_4)_2SO_4\ (aq)$

- **Lower solubility of $CaCO_3$ vs. $CaSO_4$ and $CaSO_3$ (by 3,250 & 25 times, respectively) provides the driving force for the reaction equilibria to favor the formation of carbonate precipitates**



Solubility products (K_{sp}) of $CaCO_3$, $CaSO_4$ and $CaSO_3$ at 25 °C

Advantages of the Proposed CO_2 Mineralization Process

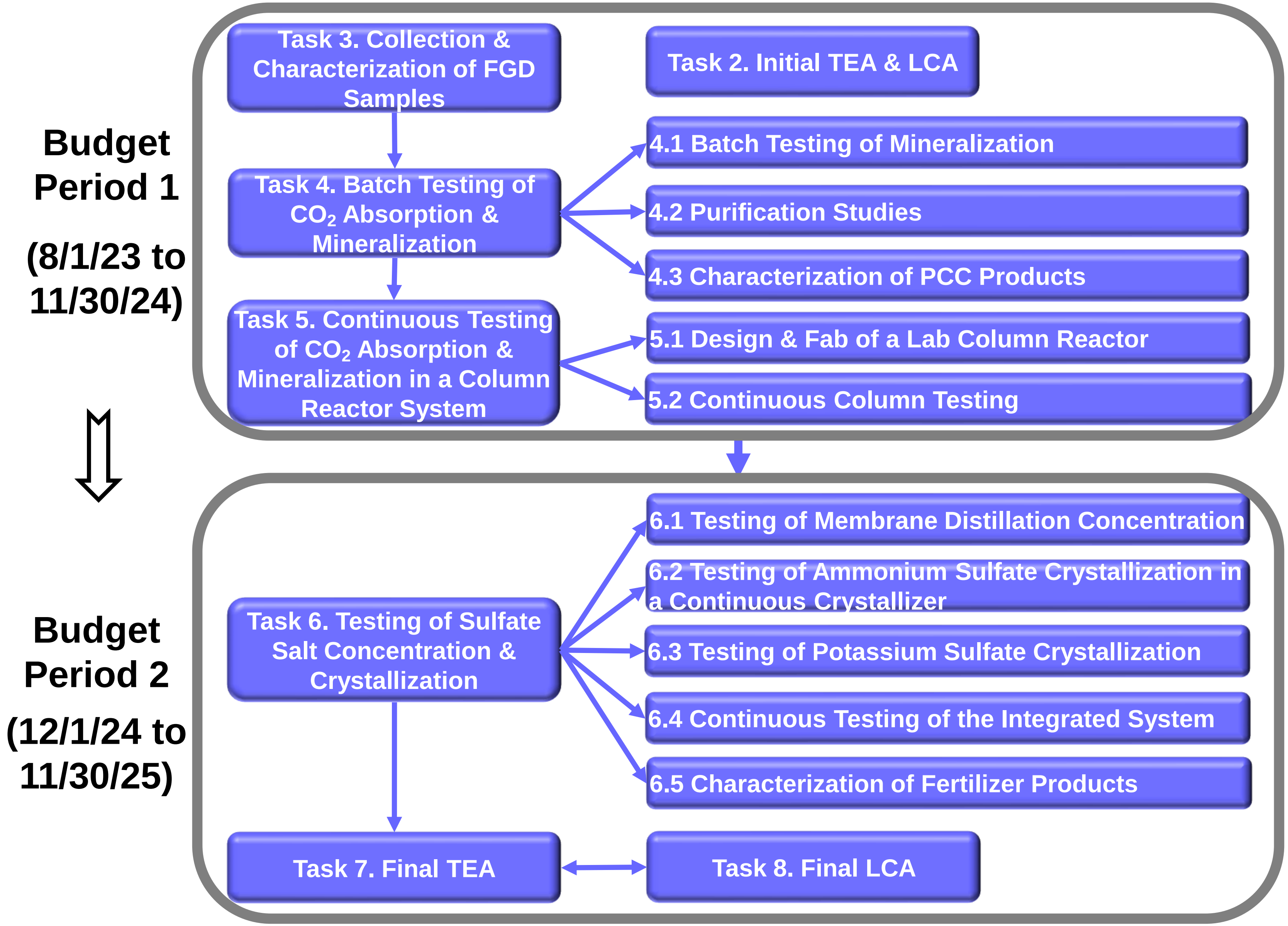


- Combined CO_2 capture & utilization from flue gas
- Beneficial utilization of industrial waste materials
- Purification incorporated to improve the purity of products
- Membrane distillation concentration reduces energy use vs. traditional evaporative concentration
- Use of low-quality steam from power plants to provide both heat and vacuum, improving energy efficiency

Technical and Economic Challenges of Technology Development

- Producing pure and uniform precipitated $CaCO_3$ powders are challenging (they may consist of a mixture of polymorphs and contain impurities
- Produce $(NH_4)_2SO_4$ crystals with a size of ≥1 mm and meet environmental requirements
- Few research conducted on utilization of non-gypsum materials (e.g., $CaSO_3 \cdot 1/2H_2O$ & $CaSO_4 \cdot 2H_2O$ mixture from wet scrubbers with inhibited oxidation and dry scrubbers)
- System integration to enhance energy efficiency, minimize ammonia emissions, maximize process water recycle, etc.

3. Technical Approach / Project Scope



Key milestones:

(Milestones in blue color completed)

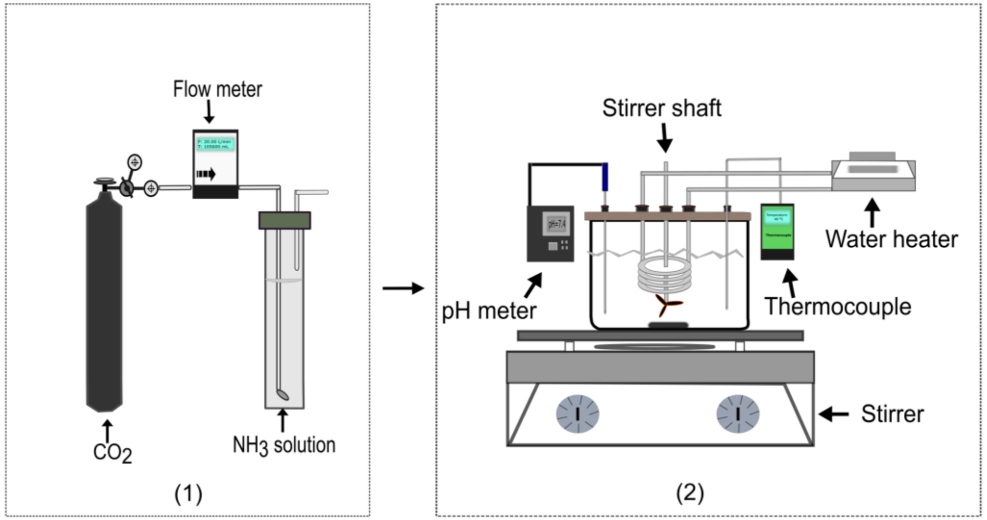
Task		Date
2.1	c. Initial TEA	11/30/23
2.2	d. Initial LCA	11/30/23
3	e. FGD samples collected & analyzed	12/31/23
4	f. Optimal conditions for CO_2 mineralization identified	2/29/24
5.1	g. A lab 1 LB/hr CO_2 column reactor system fabed	5/15/24
5.2	*h. Specs of PCC product meeting requirements*	*11/30/24*
6.1	*i. A lab MD concentrator fabed*	*1/31/25*
6.2	*j. A lab evaporative crystallizer fabed*	*2/28/25*
6.3	*k. Testing of crystallization completed*	*5/31/25*
6.4	*i. Testing of the integrated system completed*	*9/31/25*
7	*m. Final TEA*	*10/15/25*
8	*n. Final LCA*	*10/15/25*
	o. EJQ submitted	*10/15/25*
	p. Final TMP	*10/15/25*

Success Criteria

	Success Criteria
BP1	• Batch testing of CO_2 mineralization to identify optimal conditions and achieve >90% yield, <10 μm particle size, >97% purity for PCC product
	• Design, fab, & testing of a lab 1 LB/hr CO_2 mineralization system • Achieve >90% yield of PCC with required PCC properties
BP2	• Design, fab, & testing of a lab MD concentrator and an EC unit; Obtain ~1 mm fertilizer granules and meet fertilizer requirements • Testing of the integrated system producing PCC and fertilizer products with required specs
	• TEA shows cost-competitiveness for PCC and fertilizer production • LCA validates environmental sustainability vs. Comparison Production Processes

4. Progress and Current Status of Project

4.1 - Batch Testing of CO_2 Mineralization Reactions



Batch experimental setups

(1) CO_2 absorption

$2NH_4OH\ (aq) + CO_2\ (g) = (NH_4)_2CO_3\ (aq) + H_2O$

$2NH_4OH\ (aq) + CO_2\ (g) = NH_2COONH_4\ (aq) + 2H_2O$

$NH_4OH\ (aq) + CO_2\ (g) = NH_4HCO_3\ (aq)$

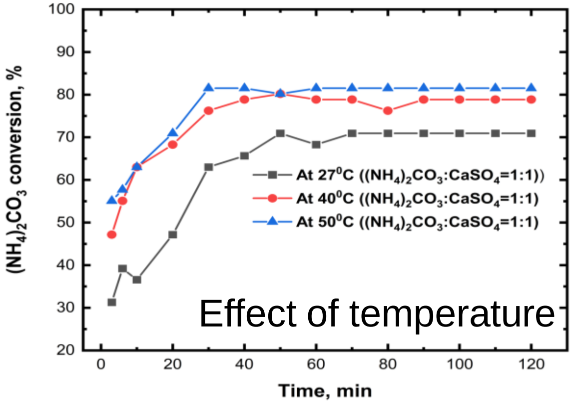
(2) Mineralization with gypsum

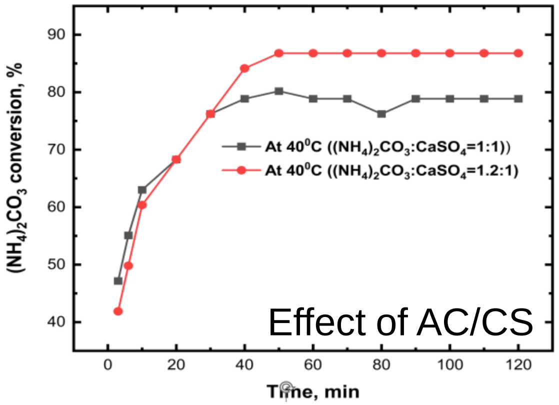
$(NH_4)_2CO_3\ (aq) + CaSO_4\ (s) = CaCO_3\ (s) + (NH_4)_2SO_4\ (aq)$

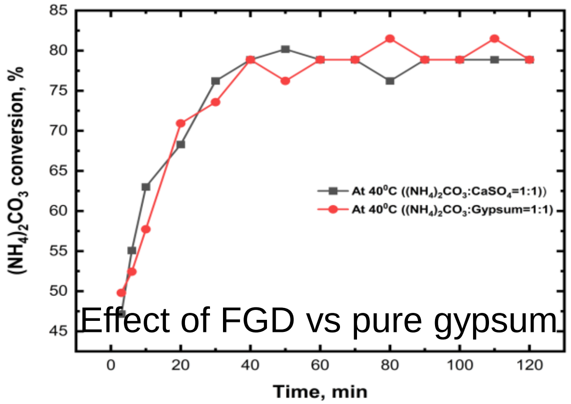
$NH_2COONH_4\ (aq) + H_2O = (NH_4)_2CO_3\ (aq)$

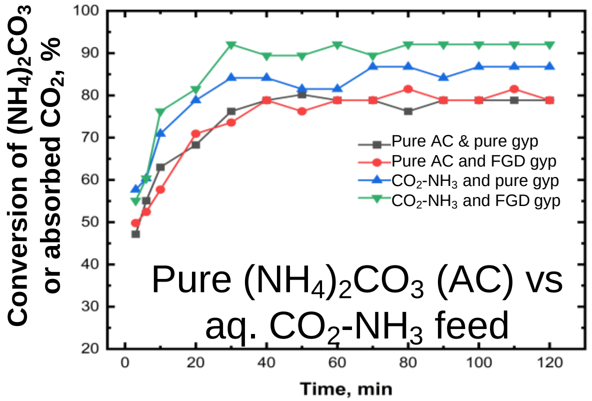
Parametric testing:

- Using analytical-grade $(NH_4)_2CO_3$ (AC)
- Using CO_2-loaded aq. ammonia
- Suitable conditions, such as T, $(NH_4)_2CO_3/CaSO_4$ (AC/CS) or CO_2 loading/CS, $(NH_4)_2SO_4$% (AS), feed materials, identified

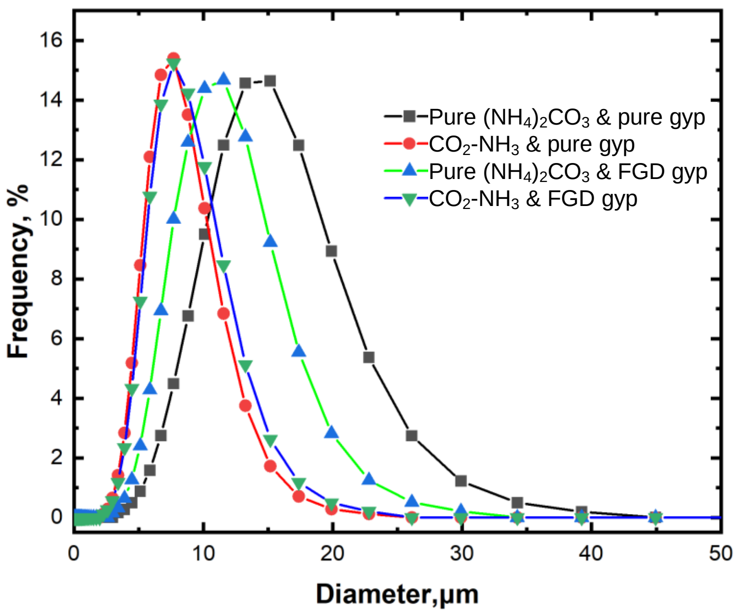




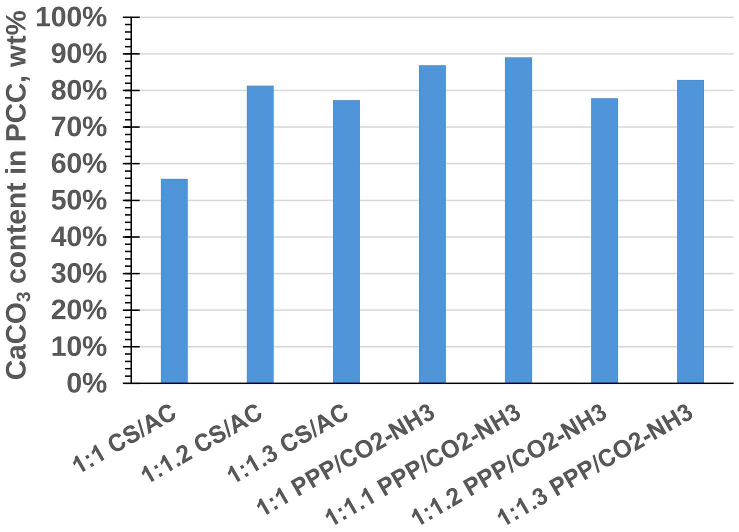




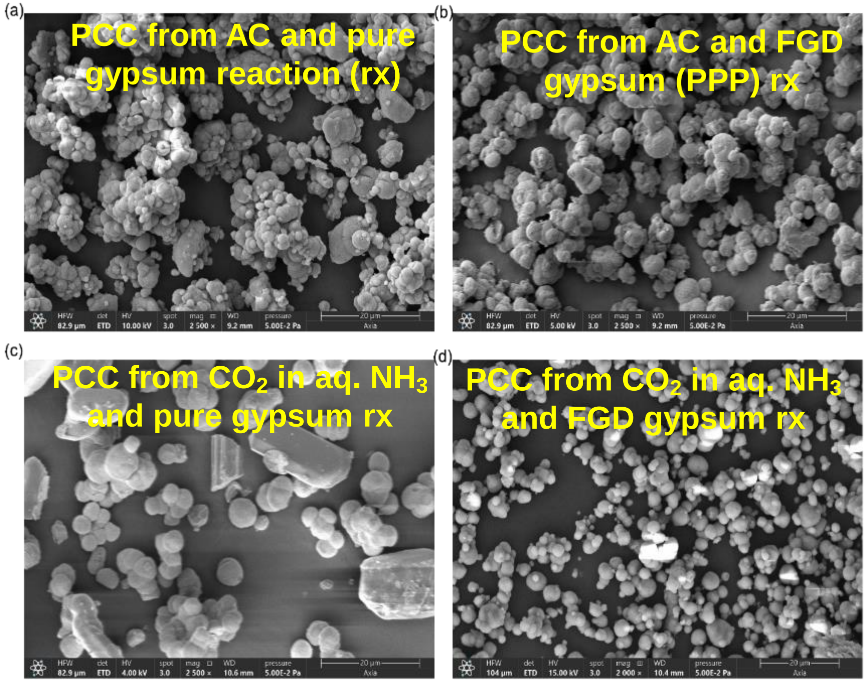
Batch Parametric Testing and PCC Product Characterization



Particle size distribution of synthesized PCC (40 °C, 1:1 CO_2 /$CaSO_4$, 25 wt% AS)



Purity of PPC synthesized with pure $CaSO_4.2H_2O$ (CS) or FGD gypsum (PPP) at different ratios to $(NH_4)_2CO_3$ (AC) or absorbed CO_2 in aq. ammonia (40 °C, 25 wt% AS)

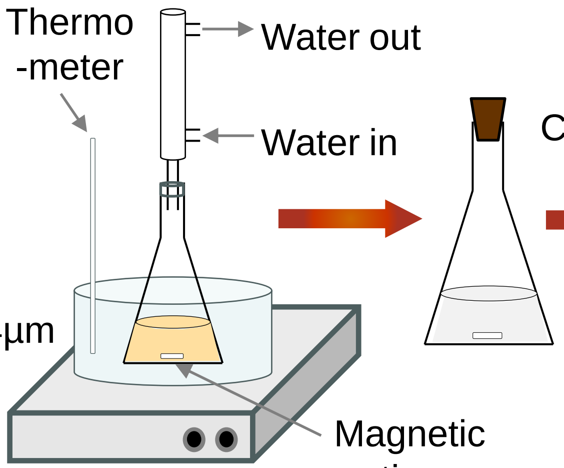


SEM images of synthesized PCC particles (40 °C, 1:1 CO_2/$CaSO_4$, 25 wt% AS)

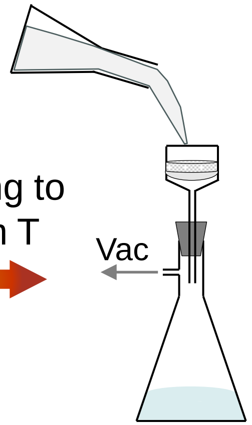
- From the reaction with CO_2 loaded in aq. ammonia, smaller PCC particles were formed [i.e., a geomean diameter of 7.7 µm vs. 11.1 µm obtained from that with pure $(NH_4)_2CO_3$] for PPP FGD gypsum
- PCC purity ranged from 55 to 90% depending on synthesis conditions
- Spherical vaterite particles were primary $CaCO_3$ in all PCC synthesized using either analytical-grade (pure) or raw FGD gypsum; Vaterite particles precipitated with CO_2 in aq. ammonia exhibited smaller spheres

4.2 Purification of Raw FGD Materials for PCC Synthesis: Methods

Acid extraction of FGD materials:
- H_2SO_4 was used for extraction
- Liquid/solid: 4, 3, 2
- Acid concentration: 25%, 30%
- Temperature: 80, 85, 90°C
- Particle size: 75-149, 44-75, <44µm
- Feedstocks: FGD samples from PPA and PPP power plants
- Duration: 30, 60 min



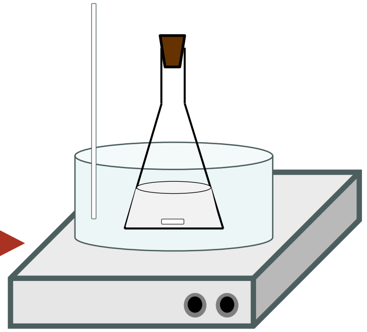
Cooling to room T



Vacuum filtration

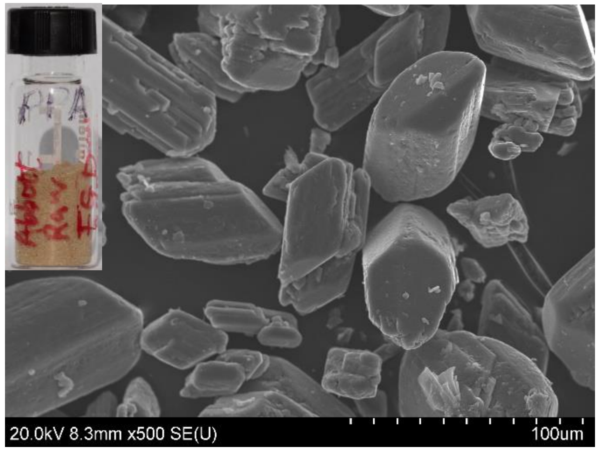
Dry purified FGD particles

Purified FGD characterizations:
- XRD (crystals);
- SEM (morphology);
- XRF (composition);
- TGA (hydrates)

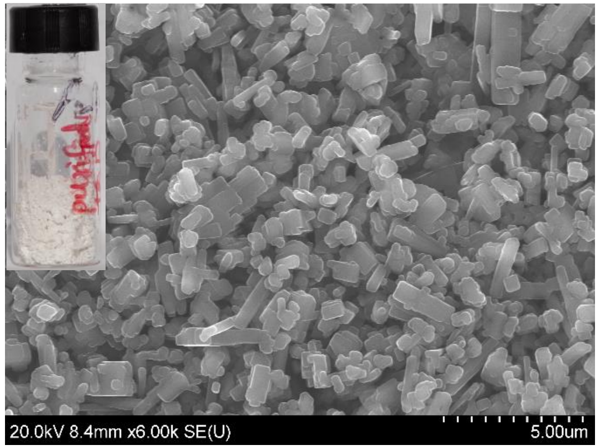


PCC synthesis:
- Temperature: 40 °C
- Feedstocks: P-PPA, P-PPP under various conditions
- Aq. $CO_2/CaSO_4$: 1:1, 1.2:1
- Duration: 30-60 min

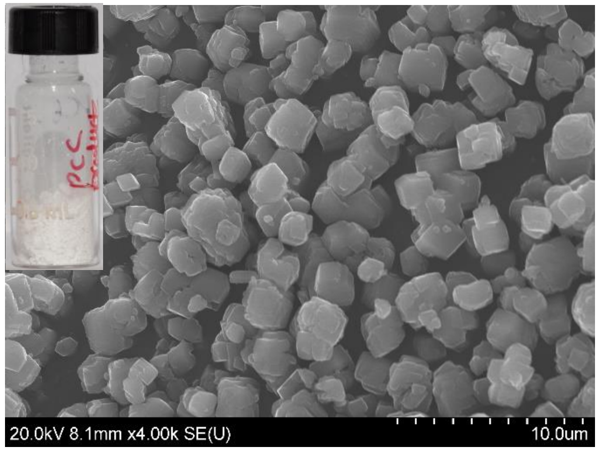
PCC characterizations:
- TGA (purity),
- XRD (polymorphs),
- SEM (morphology),
- PSD (particle size distribution)



Raw PPA



Purified PPA



PCC produced from purified PPA

Purification of Raw FGD Materials Significantly Increased PCC Purity

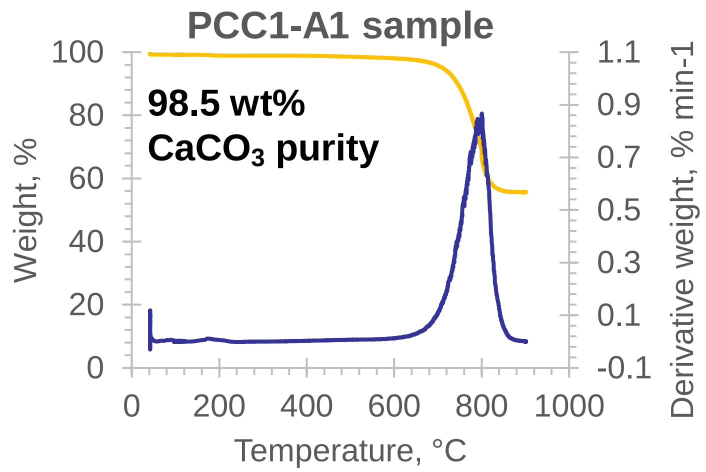
XRF and XRD results of raw PPA & PPP FGD byproducts and selected purified samples:

XRF results of raw and purified FGD byproducts

Sample#	CaO	SO_3	SiO_2	Fe_2O_3	MnO	K_2O	(Impurities/Ca) x 10^2
PPA-raw-air-dried	46.8	51.3	1.5	0.2	0.2	n.d.	2.8
P-PPA1 (purified)	44.1	55.1	0.8	0.1	n.d.	n.d.	1.3
PPP-raw-air-dried	47.0	51.0	1.6	0.4	n.d.	n.d.	3.0
P-PPP1 (purified)	43.7	55.5	0.7	0.1	n.d.	n.d.	1.3

XRD results of raw and purified FGD byproducts

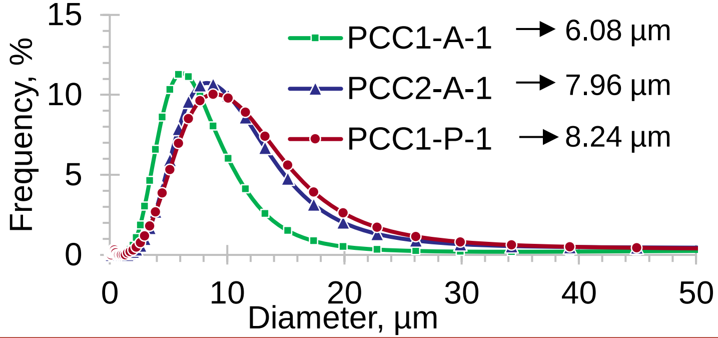
Sample#	$CaSO_4.2H_2O$	$CaSO_4.1/2H_2O$	$CaSO_4$	SiO_2	$CaSiO_3$
PPA-raw-air-dried	88	n.d.	n.d.	12	n.d.
P-PPA1 (purified)	n.d.	n.d.	96.0	2.0	2.0
PPP-raw-air-dried	94.0	1.0	n.d.	5.0	n.d.
P-PPP1 (purified)	n.d.	0.0	93.1	5.0	2.0



TGA of PCC1-A1 sample produced from the reaction of P-PPA1 with the stoichiometric amount of CO_2 loaded in aqueous ammonia

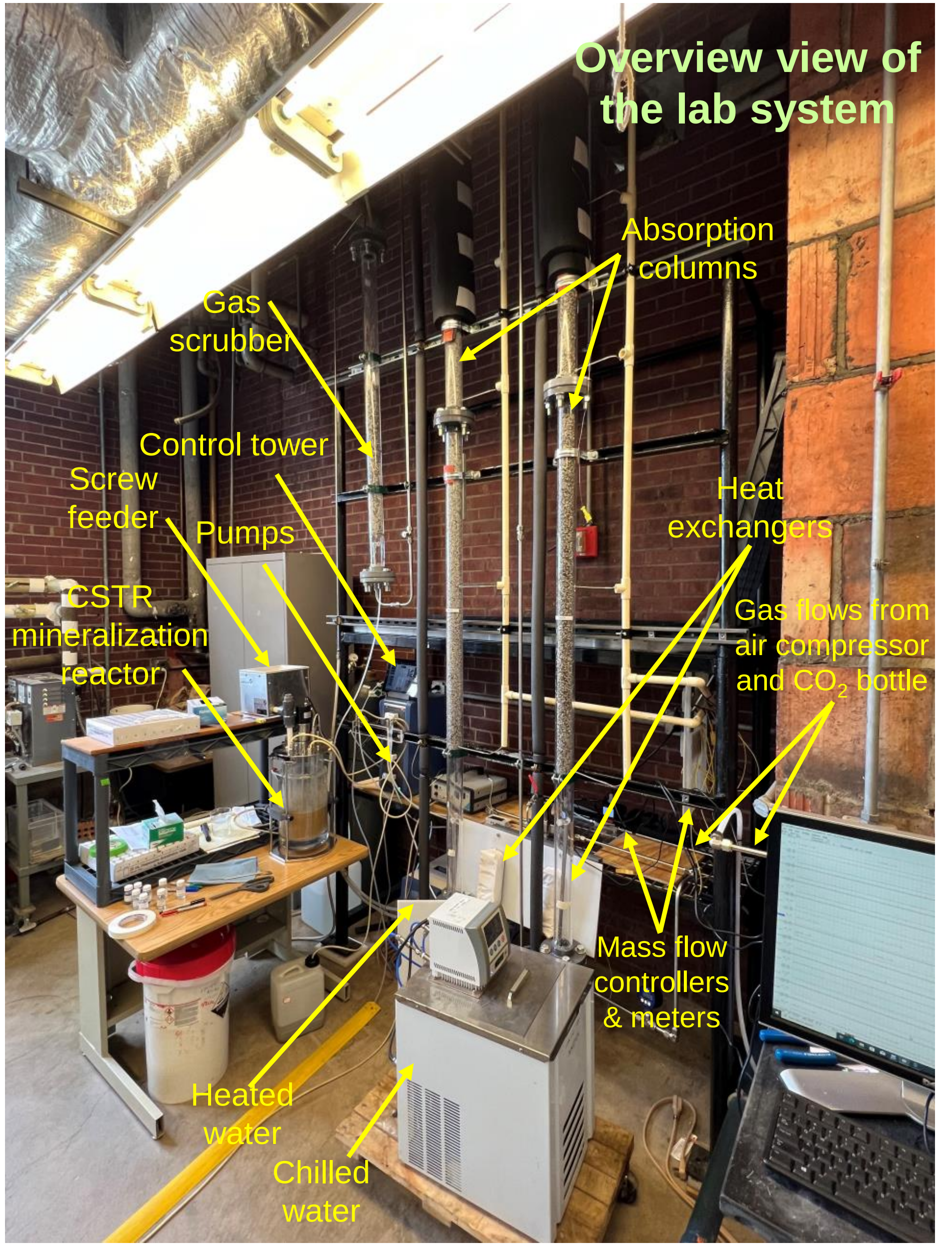
XRD results of the PCC produced from purified FGD byproducts under different synthesis conditions

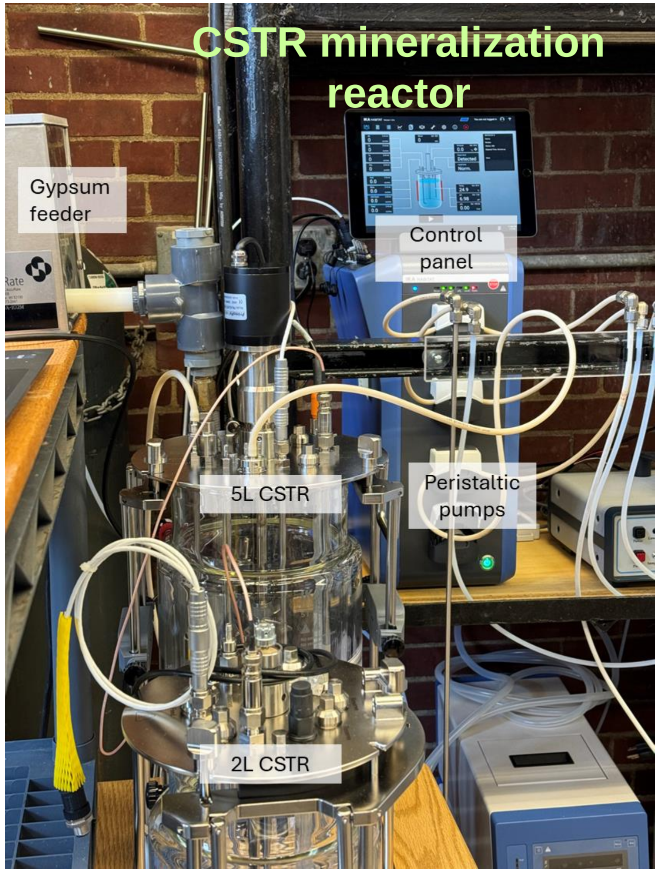
Sample#	Calcite	Aragonite	Vaterite	SiO_2
PCC1-A1	98.0	0.4	n.d.	1.6
PCC2-A1	98.3	0.3	n.d.	1.4
PCC1-P1	96.2	0.3	2.6	0.9

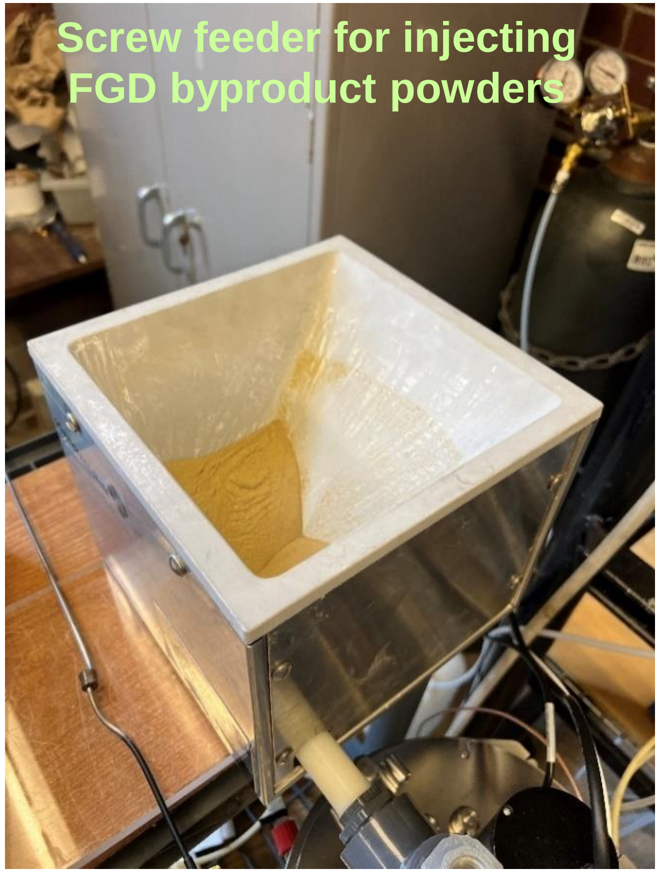


Particle size distribution of PCC particles produced from purified FGD byproducts

4.3 A Lab 1 LB/hr CO_2 Mineralization System Built for Continuous Testing







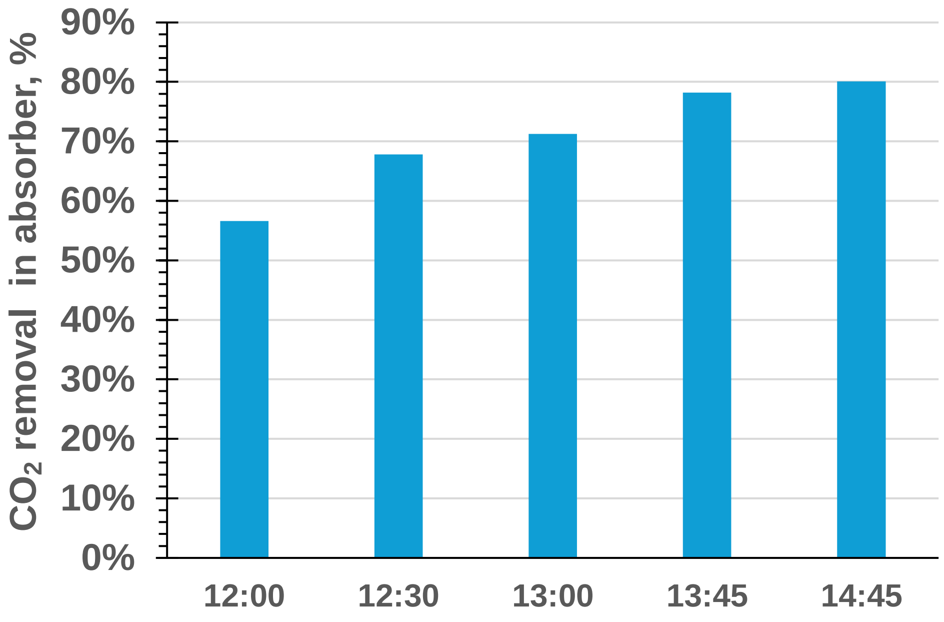
1 LB/hr CO_2 mineralization system:

- CO_2 absorption: 2 columns installed in sequence; each is a 2"ID ×11'H packed bed with 7.5'H Pro-Pak packing
- CO_2 mineralization: 2 CSTR units (5L & 2L) with a Control Tower for controlling and monitoring T, liquid level, flow rates, stirring, etc.
- Instrumentation and controllers

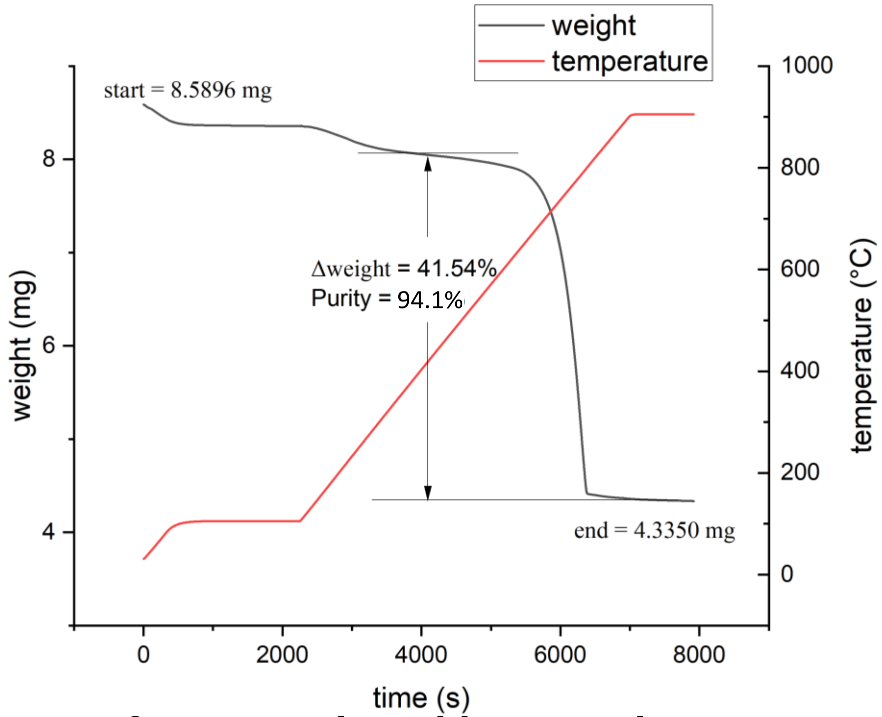
Testing with the Lab Continuous System Has Been Initiated; Testing will Continue to Study Parametric Effects and Process Performance

Operating conditions in an initial test:

Aqueous ammonia flow rate	66	ml/min
Ammonia concentration in solvent	9	wt%
Total gas flow rate	43	L/min
CO_2 concentration in feed gas	10	vol%
FGD gypsum (PPA) injection rate	16.6	g/min



CO_2 removal % in the absorber in an initial run



TGA of PCC produced in a continuous run

Raw FGD byproduct feed (PPA)

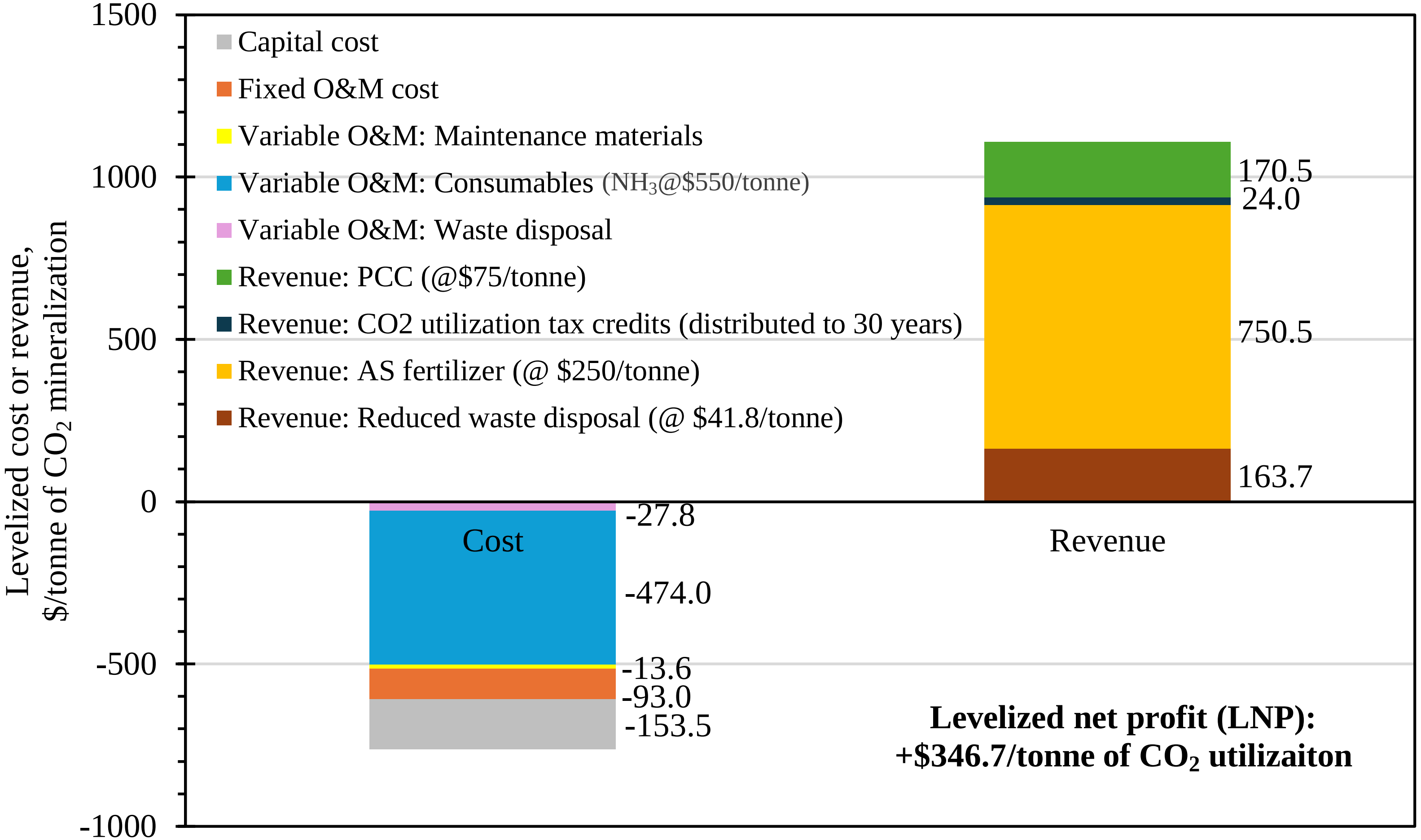
PCC produced with raw unpurified FGD feed

- Initial runs with the lab continuous system confirmed steady-state operation
- Initial runs used raw, unpurified PPA FGD byproduct as feed:
  - PCC purity reached ~94% (impurities from FGD byproduct)
  - Achieved ~100% conversion of FGD gypsum content

4.4 Initial Techno-Economic Analysis

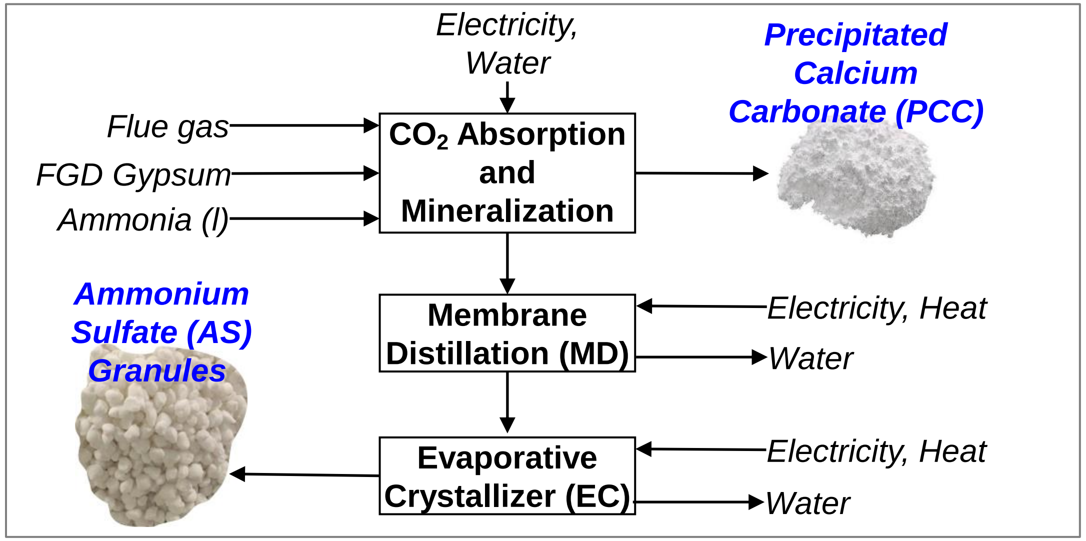
- Mass & energy (M&E) balances and stream tables generated from process modeling for a 51,000 TPY CO_2 mineralization plant

- Equipment sizing, capital and O&M costs, and net profit assessed:
  - The process is profitable, with a levelized net profit (LNP) of \$346.7/tonne of CO_2
  - NH_3 use is a major cost; Profitability remains unaffected if NH_3 and AS fertilizer prices change simultaneously
  - PCC sales price assumed at \$75/tonne; More profitable at higher PCC prices

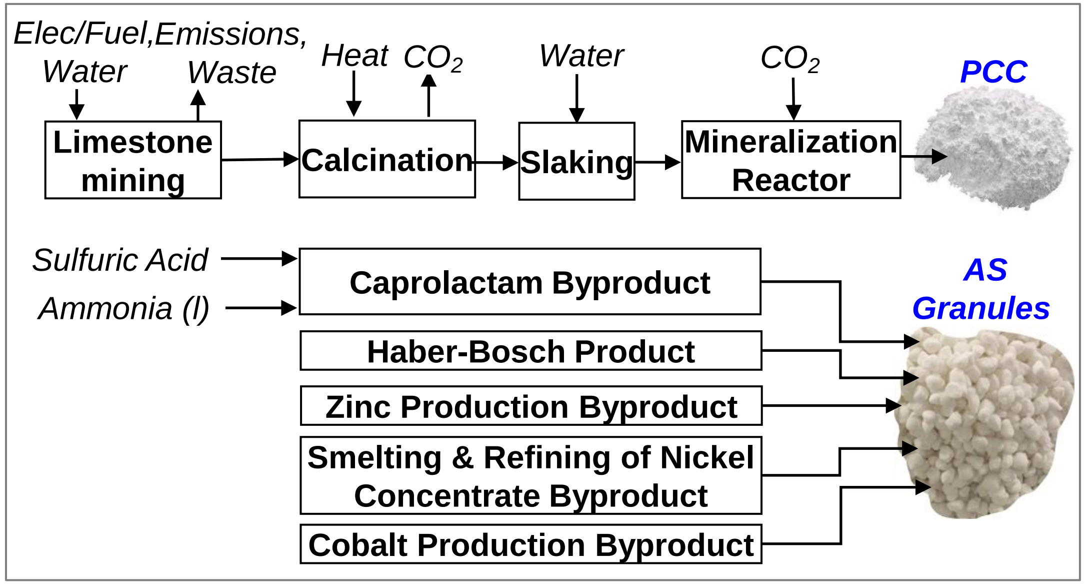


Cost and revenue analysis

4.5 Initial Life Cycle Assessment

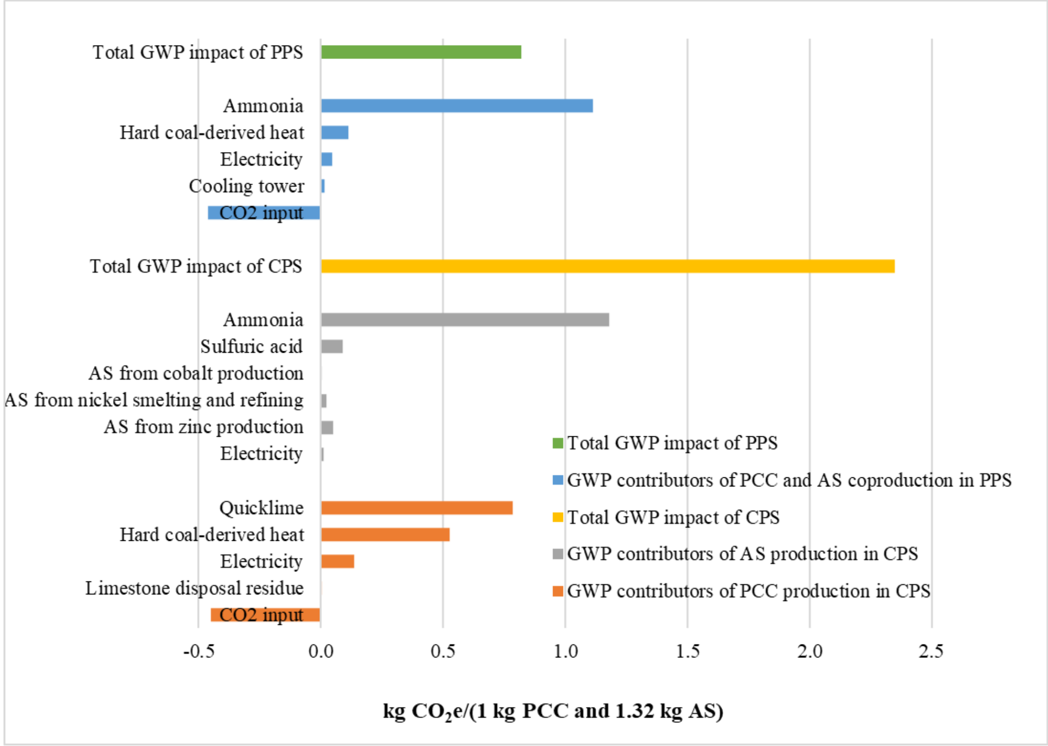


Proposed Production Process (PPS)



Comparison Production Process (CPS)

- LCA modeling using openLCA software and NETL CO2U LCI databases (v2.1)
- LCA inventories based on process modeling from TEA
- PPS showed significant environmental advantages vs CPS
  - GWP impact of 0.82 kg CO_2-Eq /(1 kg of PCC + 1.32 kg of AS), ~2.9 times < CPS
  - Other environmental impacts 1.5-8.6 times < CPS



Comparison of the GWP impact between PPS and CPS

5. Community Benefits / Societal Considerations & Impacts (CB/SCI)

CB/SCI for this lab-scale project primarily involves DEIA planning and execution

	DEIA Goals / Milestones	Progress
1	Engage 2 employees from underrepresented backgrounds in key roles on the project	Goal 1 achieved: 2 employees from underrepresented backgrounds played major roles in Project Team
2	Recruit and engage student(s) underrepresented in STEM for ≥ 500 hours in each BP	Goal 2 in progress as the project proceeds: • One underrepresented/women STEM student recruited since the project began (since July 2023); • One underrepresented/women STEM student through the ISGS' Paul Edwin Potter Internship Program for 10 weeks in 2024 summer
3	Recruit and develop career opportunities for employee(s) from underrepresented backgrounds or early career stage	Goal 3 in progress as the project proceeds: • Two employees from underrepresented backgrounds or early career stage recruited in BP1
4	Collect one or more FGD byproduct samples from sites in rural or disadvantaged areas	Goal 4 achieved: • One FGD sample collected from an industrial site in a rural / underserved area

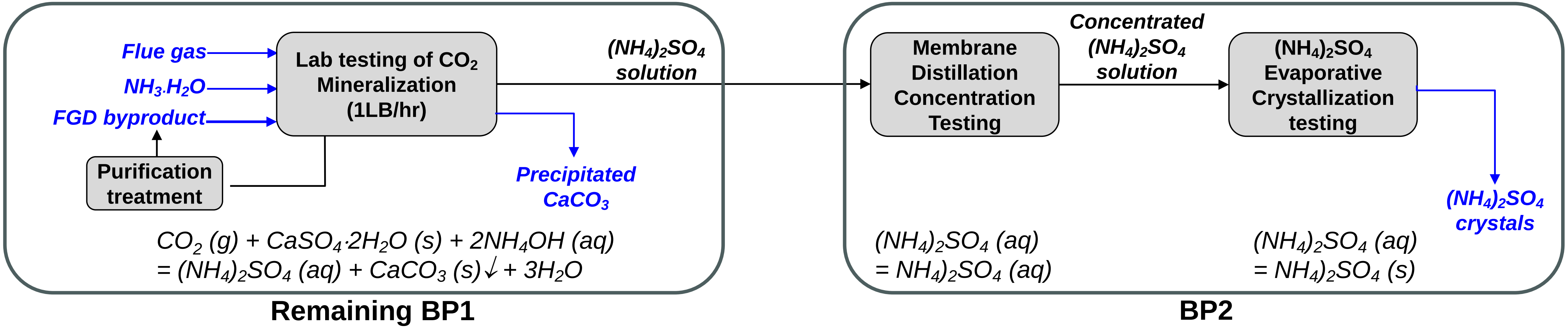
6. Lessons Learned

	Lessons learned	Mitigation Strategies
1	**Different time scales** occur between the CO_2 absorption reaction and the mineralization reaction (seconds vs. minutes). A combined process configuration might impose process control risks and compromise process performance	• A combined process step should be assessed in comparison to that of separate steps based on both process performance and equipment cost; • Kinetics studies and materials characterization can aid in the assessment and comparison
2	Without **purification treatment**, initial PCC products showed relatively low purity of less than ~80%	• Purification of raw FGD materials with acid extraction has been effective in improving the purity and whiteness of PCC (achieved >97% purity); • PCC synthesis under optimized process conditions can further improve its purity
3	Process performance (e.g., conversion, yield) and product specs (e.g., size, purity, morphology) are affected by multiple factors. Work is needed to identify **optimal operating conditions** to achieve the best performance and product specs	• Detailed parametric studies are required to optimize the process design and operation; • Temperature control is critical to ensure the performance of CO_2 absorption into aqueous ammonia and to minimize emissions

7. Plans for Future Testing/Development/Commercialization

Future work in this project

- Testing of membrane distillation (MD) concentration and evaporative crystallization (EV)
- Continuous testing of the integrated system (mineralization + MD + EC) in the laboratory
- Finalize TEA and LCA



Aimed to reach TRL4 at the end of this project

Future work after this project

- Upon successfully completion of this project, efforts to be furthered to seek support and partnerships to design and test a bench-scale or small pilot-scale prototype unit in a power plant or an FGD waste disposal site to reach TRL5/6

8. Summary

- Lab batch experiments were conducted to study various parametric effects on mineralization reactions, and optimal conditions were identified for the process
- Purification of raw FGD byproduct materials with acid extraction significantly improved PCC purity, reaching >97% compared to ~80% for PCC produced from unpurified raw FGD materials
- A 1 LB/hr CO_2 mineralization system was built at an ISGS lab; Testing with the lab system was initiated and will continue in the following months
- Initial TEA showed that the proposed CO_2 mineralization process was profitable, with a levelized net profit of $346.7/tonne of CO_2 mineralization
- Initial LCA revealed the environmental advantages of the proposed process; The Global Warming Potential (GMP) impact is 2.9 times lower than conventional processes

Acknowledgements

- DOE/NETL Funding Support under Agreement #DE-FE0032256
- DOE/NETL Project Managers: Sai Gollakota, Kristy Hahn

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