

# Synthetic Calcium Carbonate Production by Carbon Dioxide (CO<sub>2</sub>) Mineralization of Industrial Waste Brines

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**Bu Wang**

**University of Wisconsin-Madison**

Collaborators: Raghavendra Ragipani (IIT Kanpur), Steven Bustillos (UCLA), Dante Simonetti (UCLA), Gaurav Sant (UCLA)

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# Project Overview

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- **Funding:** \$799,995 DOE share and \$199,998 Cost Share
- **Overall Project Performance Dates:** 2/15/2019 - 2/14/2023
- **Project Participants:** Bu Wang (PI, UW-Madison), Dante Simonetti (co-PI, UCLA)

# Project Overview

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## **Overall project objectives:**

Develop and evaluate the proposed methods for production of precipitated calcium carbonate (PCC) while simultaneously utilizing CO<sub>2</sub> and industrial solid and liquid wastes.

- Integration of CO<sub>2</sub> utilization with waste management
- Production of high-purity fine PCC

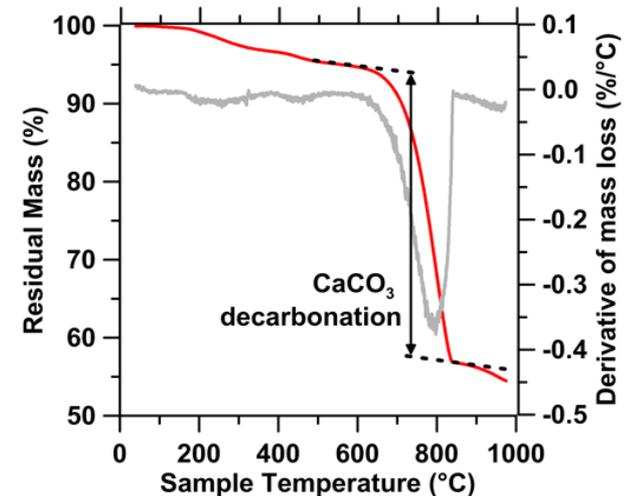
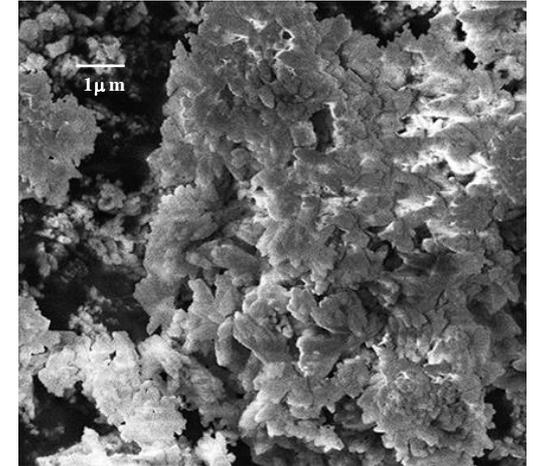
# Technology Background

## PCC Production by CO<sub>2</sub> mineralization

- Capture CO<sub>2</sub> into stable solid form
- Low energy input and can use flue gas as-is
- Potential to achieve negative life-cycle CO<sub>2</sub> 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

## 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



Red: coal power plants

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

# Project Scope/Success Criteria

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Enabling CO<sub>2</sub> mineralization and PCC production via the coal ash and produced water carbonation processes

- CO<sub>2</sub> uptake > 0.35 g CO<sub>2</sub> / g of dry product; CaCO<sub>3</sub> content > 85% (TGA/chemical analysis)

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

- Higher CO<sub>2</sub> consumption, lower life cycle cost and impact with respect to existing CO<sub>2</sub> 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

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## Produced water carbonation process

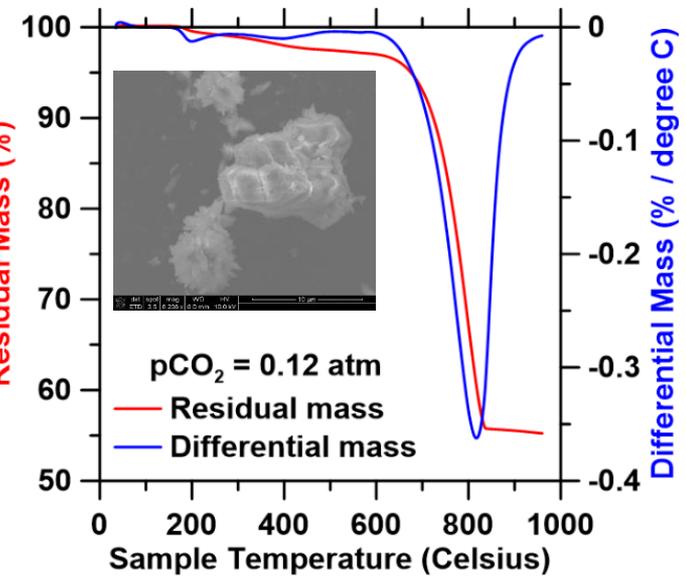
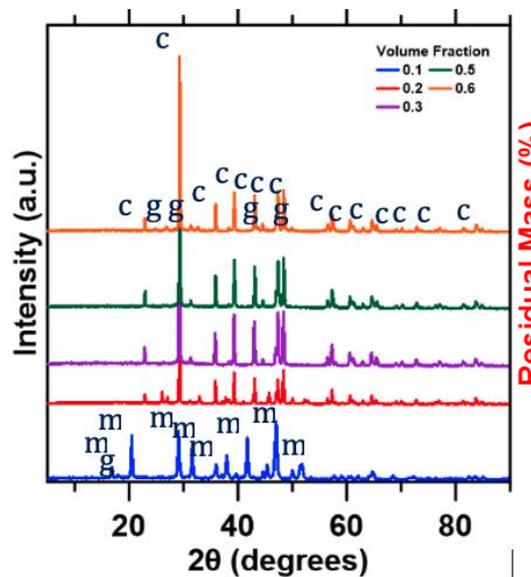
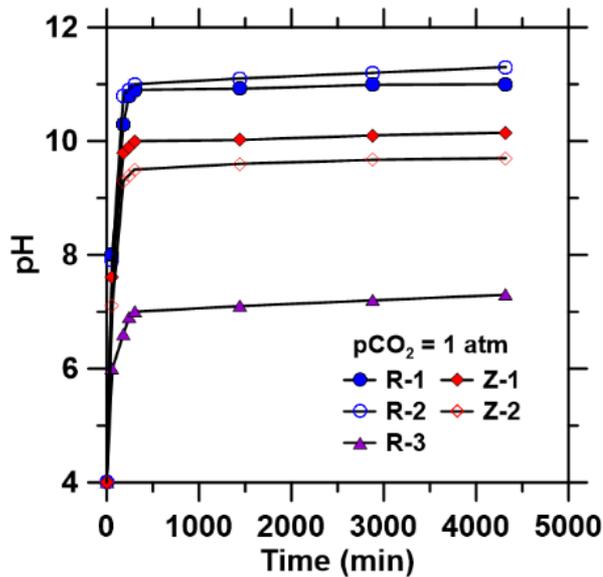
- Developed an ion-exchange (IEX) based PCC production process
- Tested on four IEX materials using simulated produced water

## Coal ash carbonation process

- Developed a new four-step process for PCC production from coal ash and CO<sub>2</sub>
- Tested the process on three different types of coal ashes

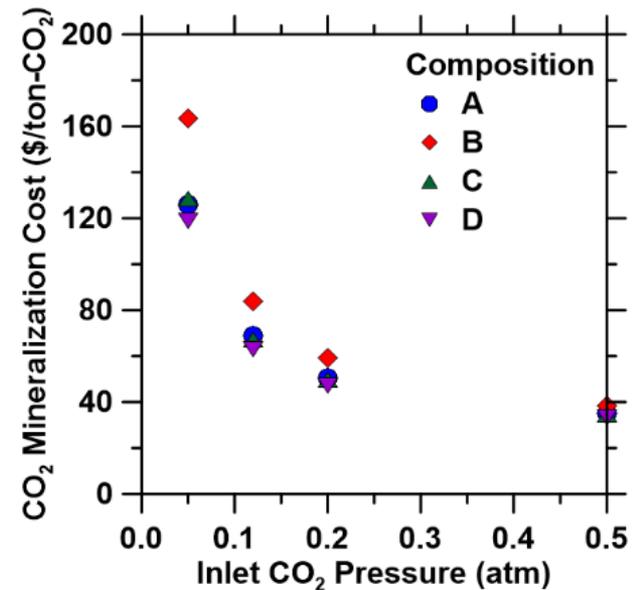
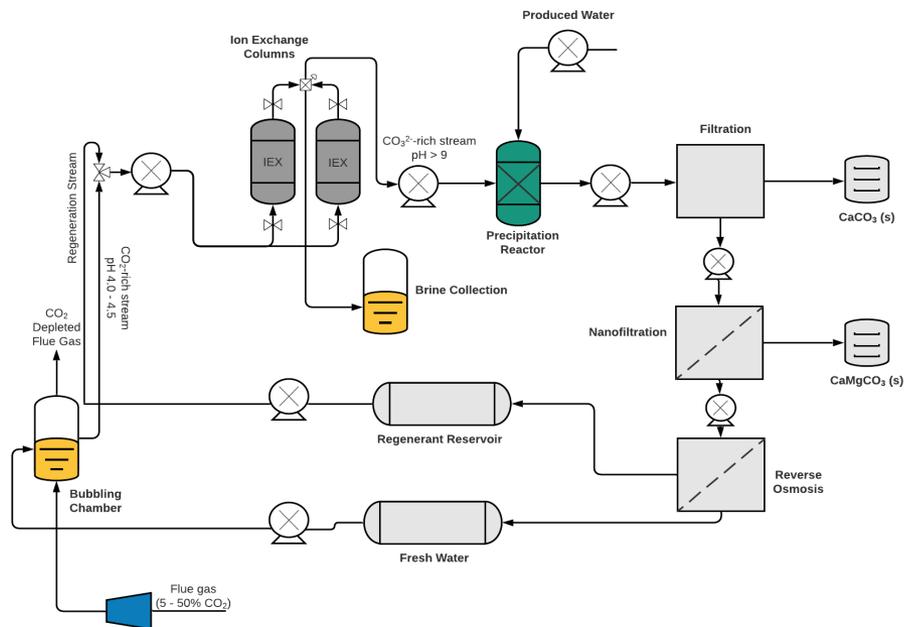
# Progress and Current Status of Project (Produced water carbonation)

- Use ion-exchange (IEX) materials to raise pH of the CO<sub>2</sub> equilibrated DI water from 4 to >8.
- PCC with purity >90% was produced using weak-acid IEX and produced water compositions from the USGS database.



# Progress and Current Status of Project (Produced water carbonation)

Process optimization and sensitivity analysis have been conducted based on experimental kinetic data.



# Progress and Current Status of Project (Produced water carbonation)

	Units	Measured/Current Performance	Projected/Target Performance
<b><i>Reaction Thermodynamics<sup>1,2</sup></i></b>			
Chemical Equation	mol <sup>-1</sup>	$\text{Ca}^{2+} + \text{HCO}_3^- + \text{OH}^- \rightarrow \text{CaCO}_3 + \text{H}_2\text{O}$	
<b><i>Reaction Conditions</i></b>			
CO <sub>2</sub> Source <sup>3</sup>		Simulated coal flue gas	Coal flue gas
Pressure	bar	1	
CO <sub>2</sub> Partial Pressure	bar	0.12	
Temperature	°C	25	<100
Alkaline Reactant Source <sup>5</sup>		pH swing by ion-exchange	
Process Route <sup>6</sup>	(direct/ indirect)	Indirect	
<b><i>Once-Through Performance<sup>7</sup></i></b>			
CO <sub>2</sub> Uptake Actual <sup>10</sup>	(g-CO <sub>2</sub> /g material)	0.40	0.35
<b><i>Product Properties<sup>11</sup></i></b>			
Desired Product		Precipitated Calcium Carbonate (PCC)	
Purity	(mass %)	>90%	>85%
Particle size, D <sub>50</sub>	(kg/h)	~10 microns	<15 microns
<b><i>Commercial Product Properties<sup>13</sup></i></b>			
		Current	
U.S. Market Size	(Tonnes/yr)	24.5 million	
Market Price	(\$/kg)	\$60-\$280; up to \$500 depending on the purity	

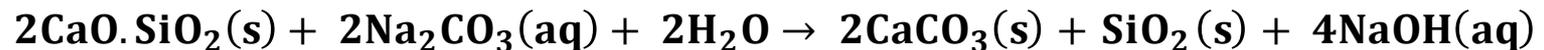
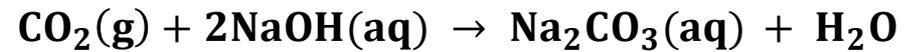
# Plans for future testing/development/ commercialization

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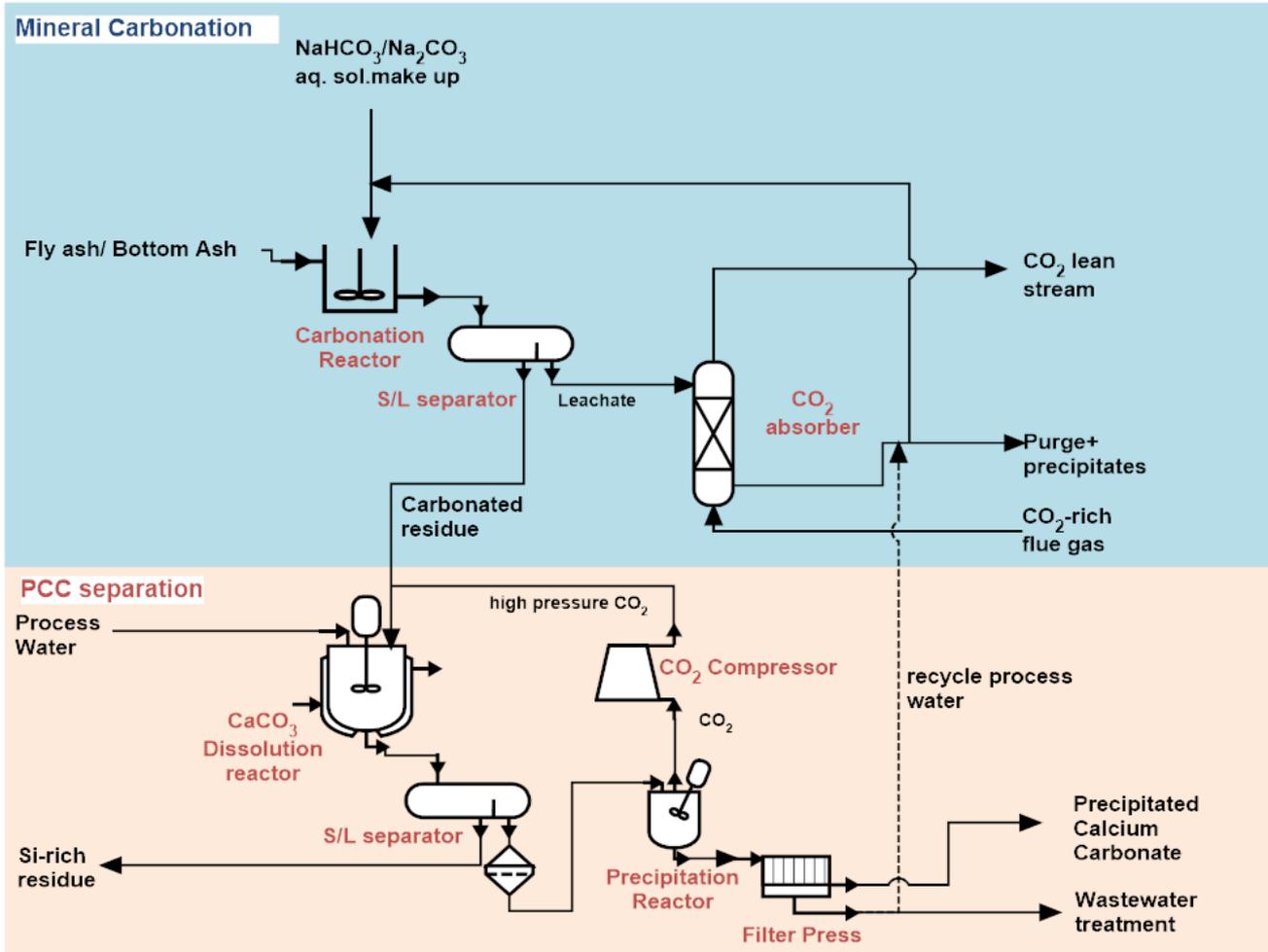
Demonstrate the optimized process using an integrated bench scale reactor system (on-going).

# Progress and Current Status of Project (Coal ash carbonation)

Accelerating ash dissolution through alkaline carbonation:



# Progress and Current Status of Project (Coal ash carbonation)



- Can work with diluted  $\text{CO}_2$  sources (e.g, air)
- PCC production is not cost-competitive
- Using the carbonated residue as supplementary cementitious materials is a much more attractive utilization route.

# Progress and Current Status of Project (Produced water carbonation)

	Units	Measured/Current Performance	Projected/Target Performance
<b><i>Reaction Thermodynamics<sup>1,2</sup></i></b>			
Chemical Equation	mol <sup>-1</sup>	$2CaO \cdot SiO_2 + CO_2 \rightarrow 2CaCO_3 + SiO_2$	
<b><i>Reaction Conditions</i></b>			
CO <sub>2</sub> Source <sup>3</sup>		Air	
Pressure	bar	1	
CO <sub>2</sub> Partial Pressure	bar	.00041	
Temperature	°C	20-30	
Alkaline Reactant Source <sup>5</sup>		Mineral wastes (coal ash, cement kiln dust, slag, etc.) and calcium aluminosilicate minerals	
Process Route <sup>6</sup>	(direct/ indirect)	Indirect	
<b><i>Once-Through Performance<sup>7</sup></i></b>			
CO <sub>2</sub> Conversion <sup>8</sup>	(%)	10-20	
CO <sub>2</sub> Uptake Actual <sup>10</sup>	(g-CO <sub>2</sub> /g material)	0.10-0.17	
<b><i>Commercial Product Properties<sup>13</sup></i></b>			
Commercial Product		Supplementary cementitious materials (SCM)	
U.S. Market Size	(Tonnes/yr)	15.7 million tons (estimated based on 2021 cement production)	
Global Market Size	(Tonnes/yr)	775.5 million tons (estimated based on 2021 cement production)	
Market Price	(\$/kg)	\$50-\$100	

# Summary Slide

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- Two CO<sub>2</sub> mineralization processes, namely the coal ash carbonation and produced water carbonation, have been developed.
- The coal ash carbonation process can capture and sequester CO<sub>2</sub> 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.

# Appendix

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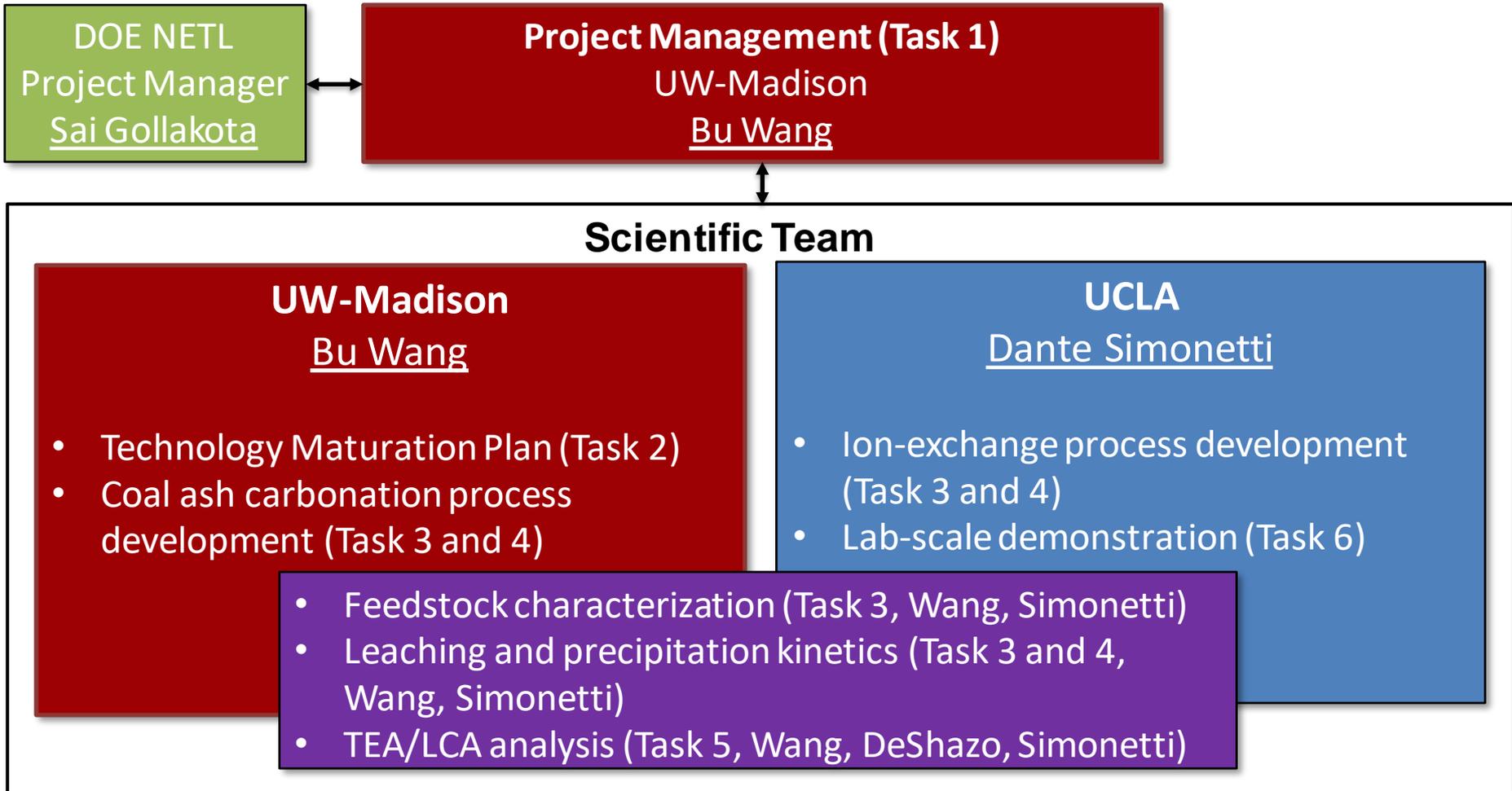
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# Organization Chart



# Gantt Chart

