Converting CO_2 in Flue Gas and Alkaline Solid Wastes to Carbon-Negative Alternative Cement for Precast Concrete Units

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Xinhua Liang, Washington University in St. Louis
Hongyan Ma, Missouri University of Science and Technology
Shiguang Li, GTI Energy

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Project Overview

- **Funding**: \$2,500,000 (DOE: \$2,000,000, cost share: \$500,000)

- **Overall Project Performance Dates**: July 1, 2023 – June 30, 2025

- **Overall Project Objectives**: Develop an innovative and economical process for mineralizing CO_2 by producing a carbon-negative alternative cement (i.e., OxCem) and deliver a laboratory-scale, prototype system capable of converting 10 kg CO_2 per day for making precast concrete units

- **Project Participants**:

  Dr. Xinhua Liang — Washington University in St. Louis

  Dr. Hongyan Ma — Missouri S&T

  Dr. Shiguang Li — GTI Energy, solutions that transform

Technology Background

- The cement industry around the world emits >4 gigatonne (Gt) CO_2 from >4.5 Gt cement per year (e.g., Portland cement emits ~0.9 t CO_2/t cement) due to the requirement of $CaCO_3$ decomposition and kiln-processing at 1,450 ºC
- Limitation of CO_2 for curing Portland cement concrete to enhance CO_2 uptake via carbonation:
  - Low diffusion rate
  - Low capacity of CO_2 penetration/uptake due to low diffusion rate
  - Post-molding carbonation methods can only produce precast concrete, not adaptive to ready-mixed concrete that dominates the industry

Technology Description

CO_2 from point source, e.g., cement plant, steel plant

Alkaline solid wastes, e.g., steel slag

Cement-forming chemical

Cement-forming base phases by grinding, e.g., CaO/MgO, $(Ca,Fe)_2SiO_4$

Admixtures

Proportioning and **Co-Grinding**

Carbon-negative **Acid-Base Cements (OxCem)**

Precast Concrete Units (e.g., concrete blocks)

$$\mathbf{MO + H_2C_2O_4 + \mathit{x}H_2O \rightarrow MC_2O_4\cdot(\mathit{x}+1)H_2O}$$

$$\mathbf{(MO)_{\mathit{y}}\cdot SiO_2 + \mathit{y}H_2C_2O_4 + \mathit{xy}H_2O \rightarrow \mathit{y}MC_2O_4\cdot(\mathit{x}+1)H_2O + SiO_2\ (\mathit{gel})}$$

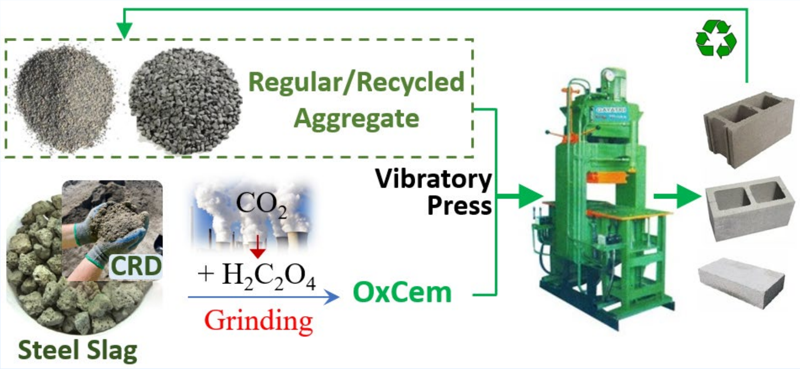
where M is Ca, Mg, Fe^{2+}, or other elements, $x = 0$, 1, or 2, and $y = 1$, 2, or 3

Technical Approach

Converting CO_2 to cement forming chemical

- Step I : $CO_2 + KOH \rightleftharpoons KHCO_3$
- Step II : $KHCO_3 + H_2 \rightleftharpoons HCOOK + H_2O$
- Step III : $2\ HCOOK \rightleftharpoons K_2C_2O_4 + H_2\uparrow$
- Step IV : $K_2C_2O_4 + 2HCl \rightleftharpoons H_2C_2O_4 + 2KCl$

OxCem formation



Member	Specific Project Roles
Washington University in St. Louis	• Lead on project management and planning • Lead on cement-forming chemical synthesis • Support techno-economic and life-cycle analyses
Missouri S&T	• Lead on synthesis of OxCem and development of OxCem-based precast units • Support techno-economic and life-cycle analyses
GTI Energy solutions that transform	• Lead on process model development, techno-economic and life-cycle analyses

Novelties and advantages compared to CO_2-absorbing cement and construction product technologies

- High performance catalysts for CO_2 conversion,
- Alternative cement produced by only grinding without calcination or carbonation,
- Permanent carbon mineralization by reacting oxalic acid with alkaline solid wastes one order of magnitude faster than carbonation reactions, and
- Two-fold carbon-uptake capacity by forming oxalates ($M^{2+}C_2O_4$) versus forming carbonates ($M^{2+}CO_3$).

In addition, OxCem will not change the existing practice of making concrete, since it can be used like Portland cement.

Project Scope

Tasks

Task 1	Project management and planning
Task 2	Community Benefits Plan
Task 3	Process model development and initial TEA and LCA
Task 4	Formate synthesis via bicarbonate hydrogenation
Task 5	Formate synthesis scaled up by 20 times
Task 6	Oxalic acid synthesis from formate
Task 7	Production and characterization of oxalate cement
Task 8	Preparation of one system for oxalic acid synthesis at a scale of 10 kg CO_2 converted/day
Task 9	Formate synthesis at a scale of 10 kg CO_2 converted/day
Task 10	Oxalic acid synthesis at a scale of 10 kg CO_2 converted/day
Task 11	Cement/concrete production at a scale of 10 kg CO_2 converted/day
Task 12	Final TEA and LCA

Decision points and success criteria

Decision Point	Success Criteria
Year one review	1) Convert CO_2 to formate with ≥80% formate yield from CO_2 2) Convert formate to oxalic acid with a yield of ≥75% and purity of ≥85% 3) Proof of setting time of OxCem fully controllable (10 min-to-60 min), compressive strength fully adjustable (20-80 MPa), and total shrinkage <200 με
Completion of the project	1) Complete formate synthesis on a scale of 10 kg CO_2 converted/day; 2) Make OxCem masonry blocks at a scale of 10 kg CO_2 converted/day and achieve compressive strength >6,500 psi/45MPa and cumulative mass loss <5.0% after 300 freeze/thaw cycles; and 3) Final TEA and LCA topical reports issued. Cost goal of $202/ton OxCem validated.

Progress and Current Status of Project: Efficient absorption of CO_2 by KOH solution

■ Step I： $CO_2 + KOH \rightleftharpoons KHCO_3$

- By using concentrated KOH solution as absorption solution, CO_2 can be fixed into $KHCO_3$ and saturated solution continuously.

- The obtained solid $KHCO_3$ can be directly used in Step II (hydrogenation reaction).

Example: After 24-hour absorption using 100 % CO_2, 8 L saturated $KHCO_3$ solution and 2.5 kg $KHCO_3$ solid were collected.

80% yield of HCOOK was achieved in one 1-L reactor

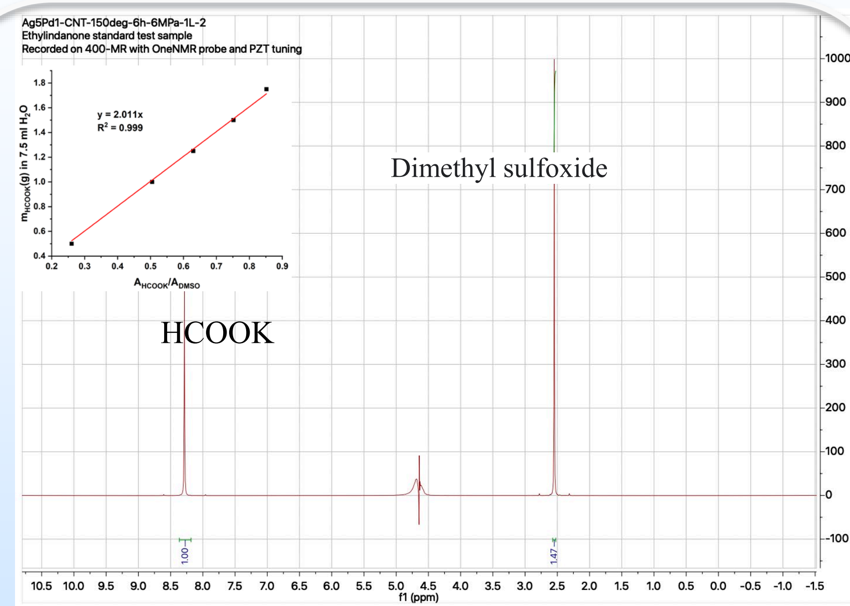
- Step II： $KHCO_3 + H_2 \rightleftharpoons HCOOK + H_2O$

Reaction Conditions:

Mass: 40 g $KHCO_3$

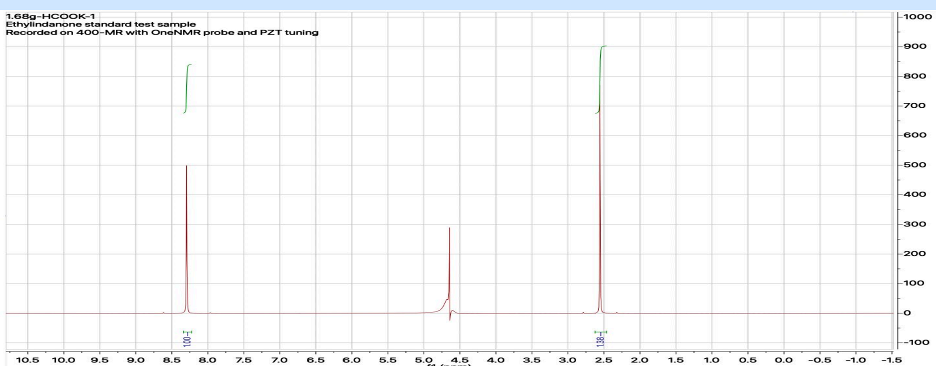
Temperature: 150 °C

Pressure: 6 MPa H_2



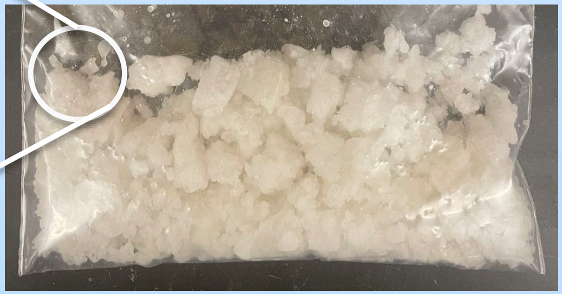
➢ HCOOK yield in solution is 81%.

1.68 g solid is dissolved in 7.5 mL H_2O for NMR test.



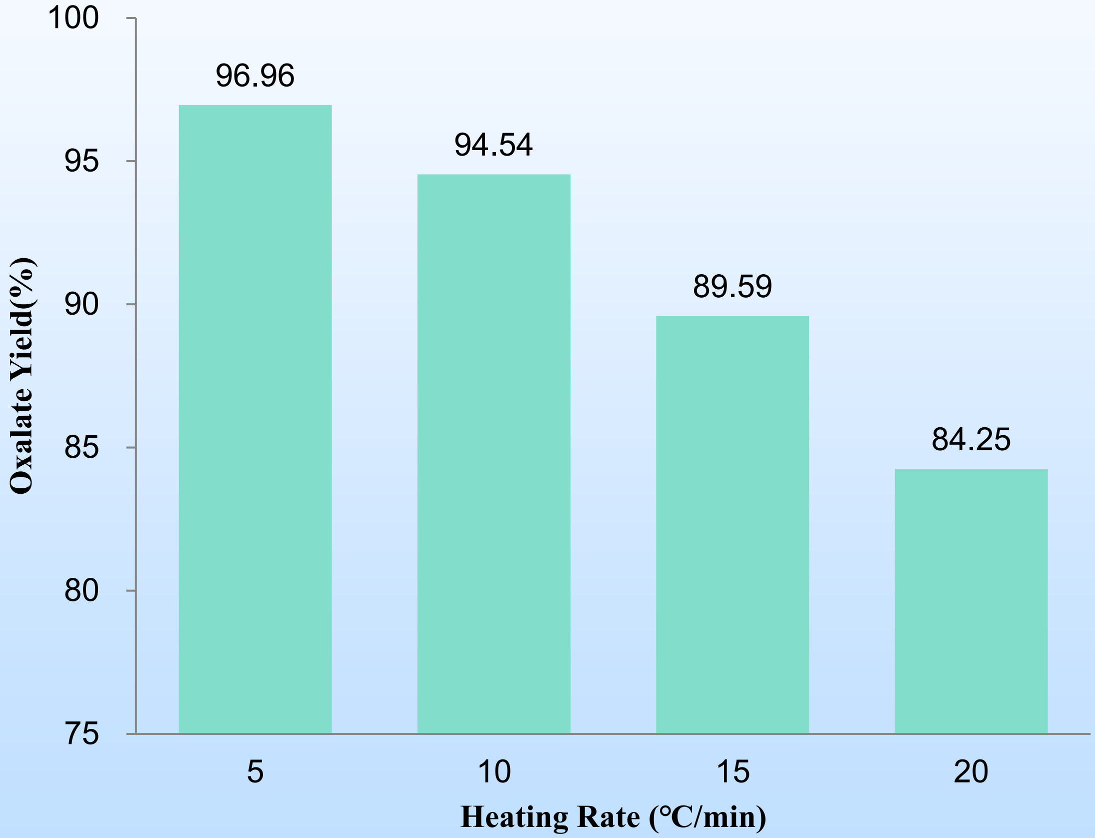
➢ HCOOK purity is 87%.

Filtered and concentrated



Efficient conversion of HCOOK to $K_2C_2O_4$

- Step III： $2\ HCOOK \rightarrow K_2C_2O_4 + H_2$



Reaction conditions: KOH as catalyst, 400℃

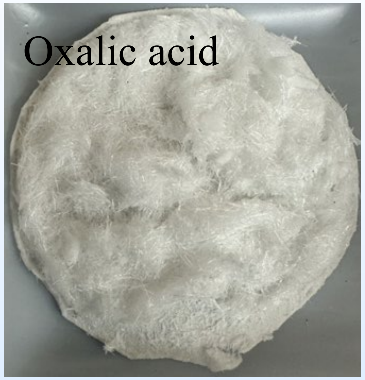
Efficient conversion of oxalate to oxalic acid

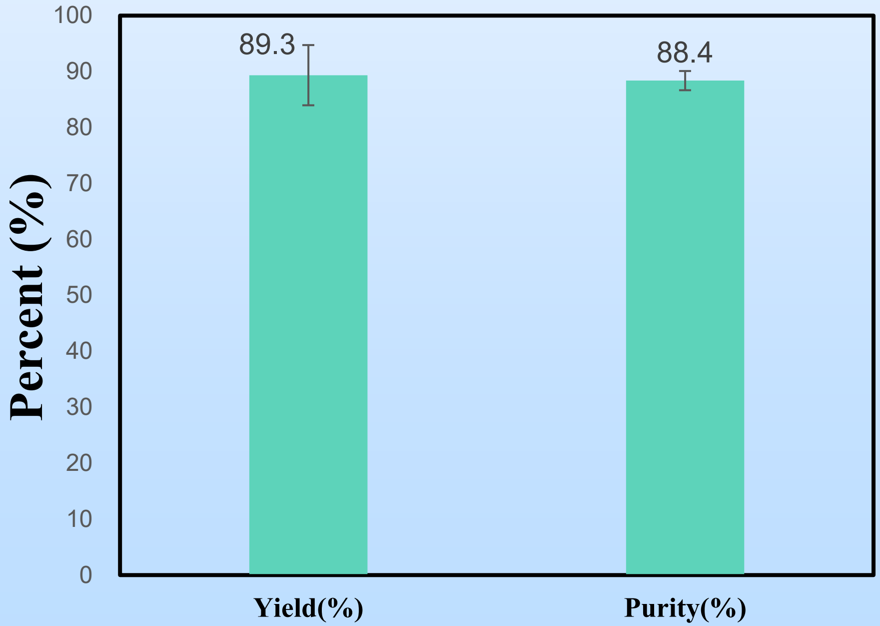
■ Step IV：Oxalate to oxalic acid

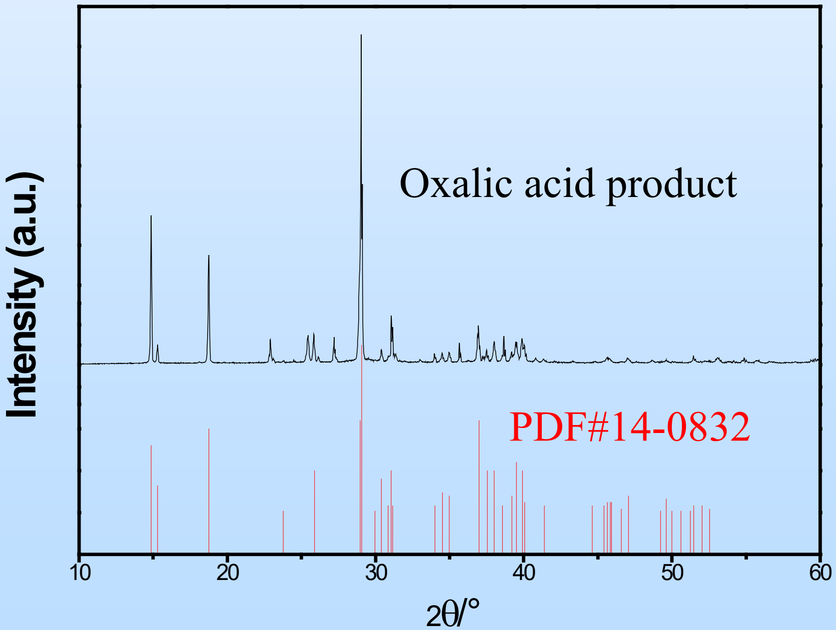
- The oxalic acid crystal was characterized by XRD, and the patterns was consistent with $H_2C_2O_4 \cdot 2H_2O$ (PDF#14-0832).

Acidification and Separation

Yield of oxalic acid:
89.3% (by weight)
(calculate as $H_2C_2O_4 \cdot 2H_2O$)
Purity of oxalic acid：
88.4%







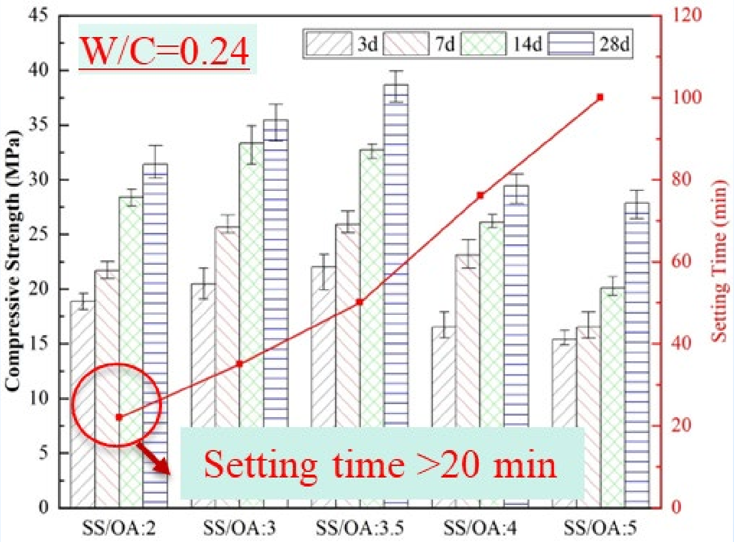
Oxalate cement formulated with steel slag: Raw material, proportions, & properties

EAF Steel Slag

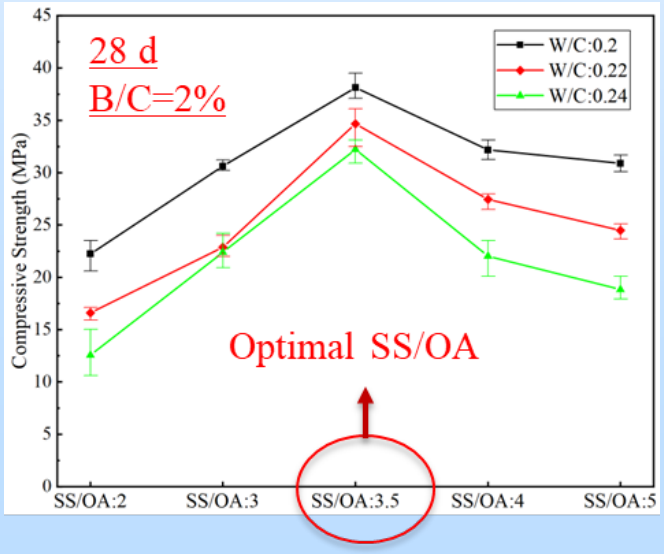
EAF steel slag

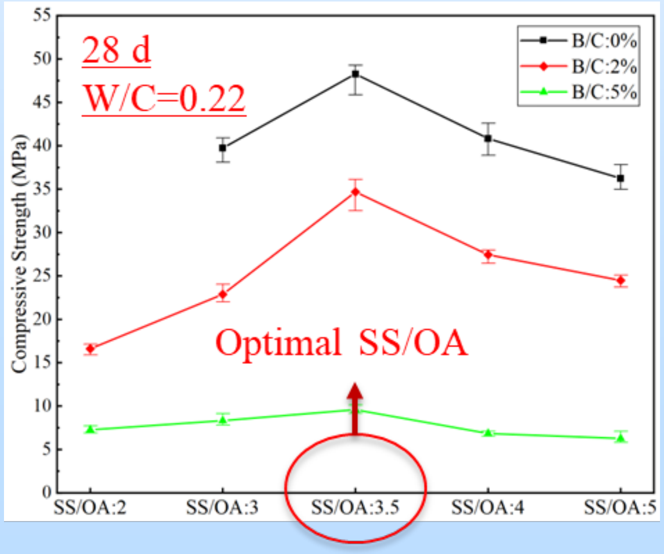
	wt%
MgO	**5.649**
Al_2O_3	10.161
SiO_2	14.977
CaO	**29.437**
MnO	5.576
FeO/Fe_2O_3	**30.362**
other	3.838

Ca/Mg/Fe >65%



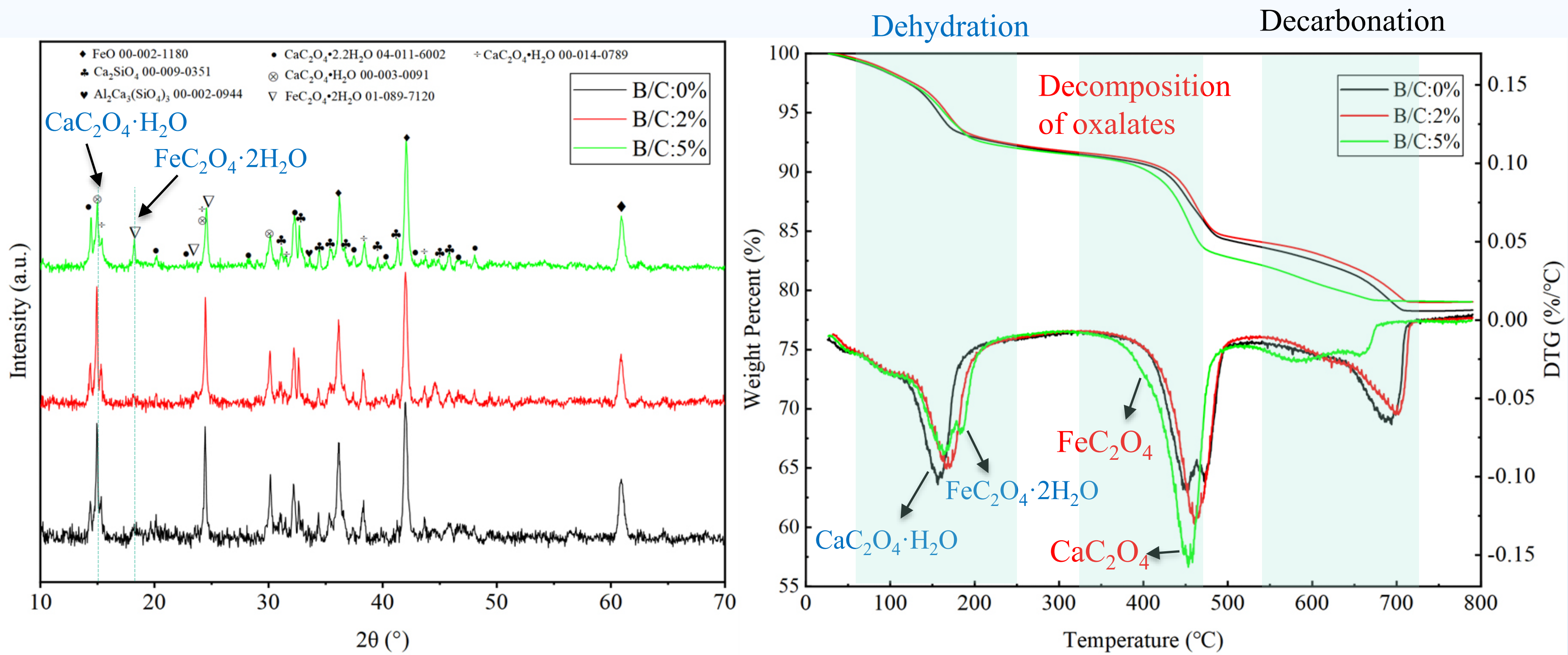
Proportions: **W/C,** water-to-cement ratio; **SS/OA,** steel slag-to-oxalic acid mass ratio; **B/C,** retarder dosage





Oxalate cement formulated with steel slag:
Effect of B/C on paste composition

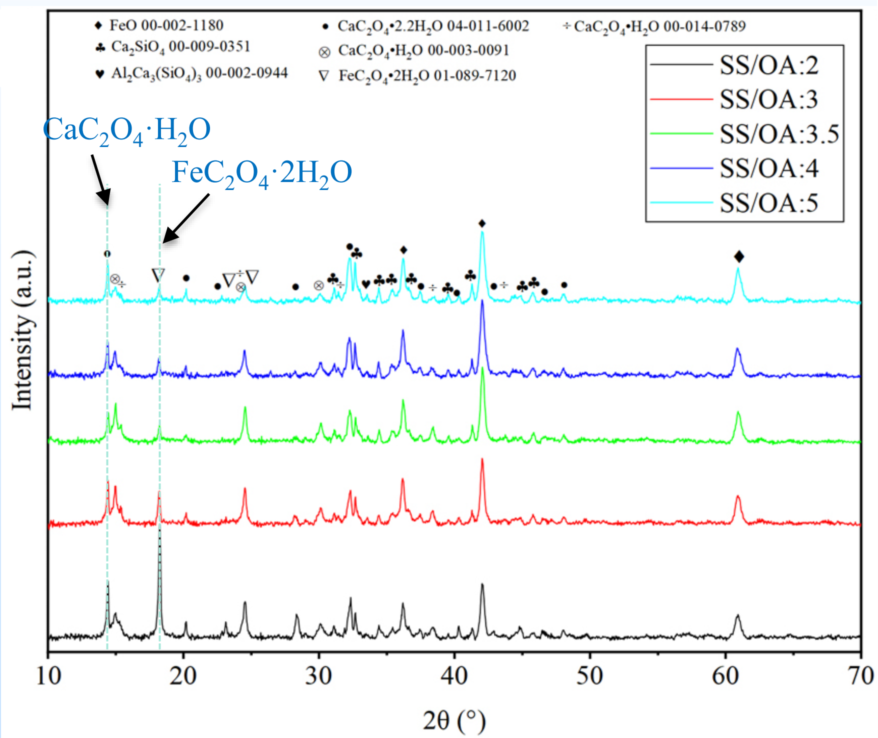
Phase composition (W/C=0.22, SS/OA=3.5)

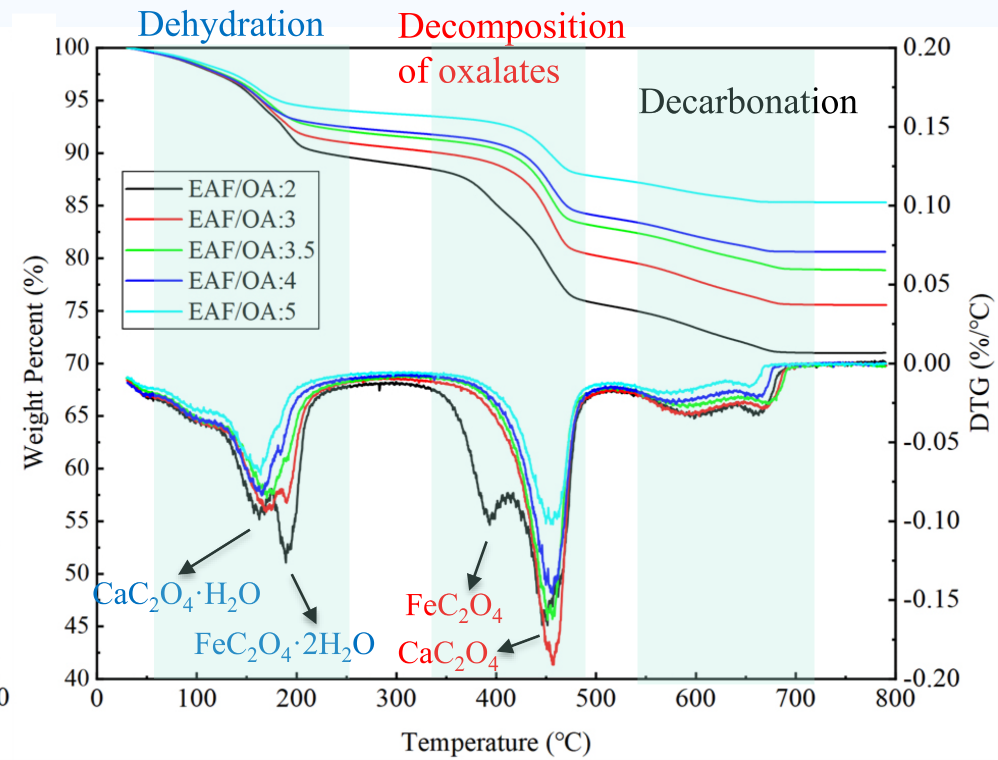


- Calcium oxalate hydrates are the dominant binder phases in the absence of retarder
- Addition of 5% retarder promotes the formation of ferrous oxalate dihydrate, suppressing the formation of calcium oxalate hydrates

Oxalate cement formulated with steel slag: Effect of SS/OA on paste composition

Phase composition (W/C=0.18, B/C=5%)





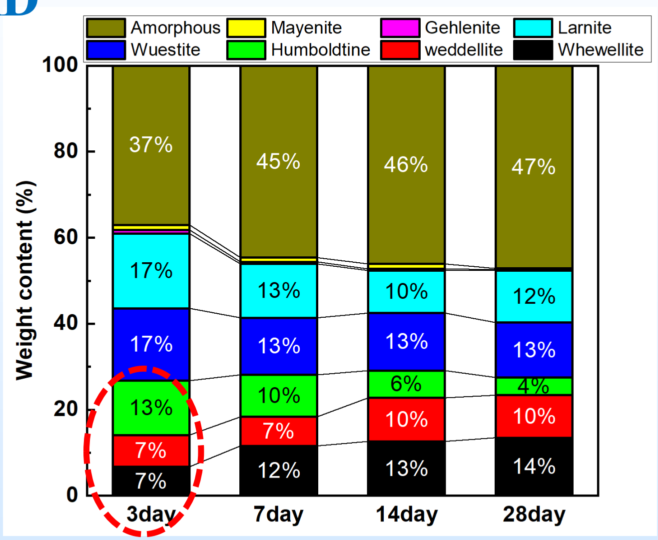
Quantification (wt.%)

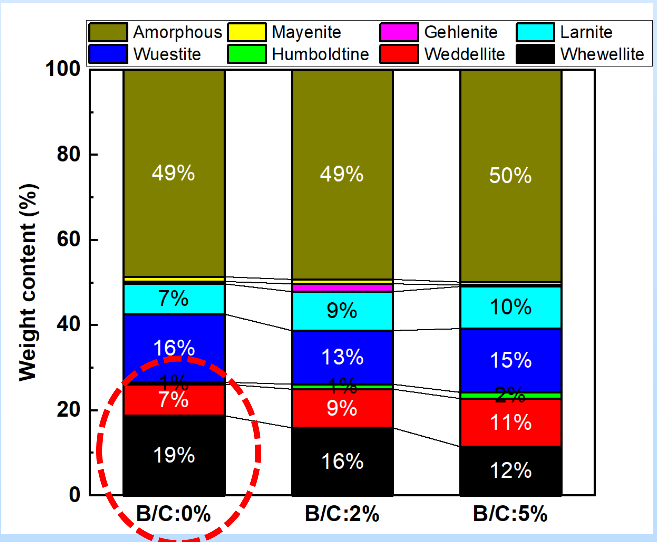
SS/OA ratio	Ca-Oxalates	Fe-Oxalate
2	29.06	16.67
3	24.68	7.45
3.5	22.95	4.95
4	20.68	4.13
5	16.65	3.80

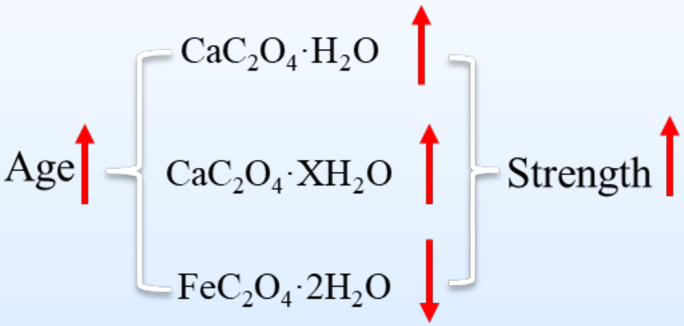
- More ferrous oxalate and calcium oxalate phases are formed at **lower SS/OA ratios**

Oxalate cement formulated with steel slag: Preferred binder phase

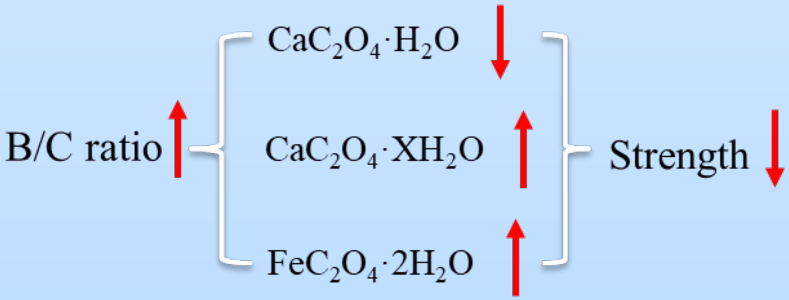
QXRD







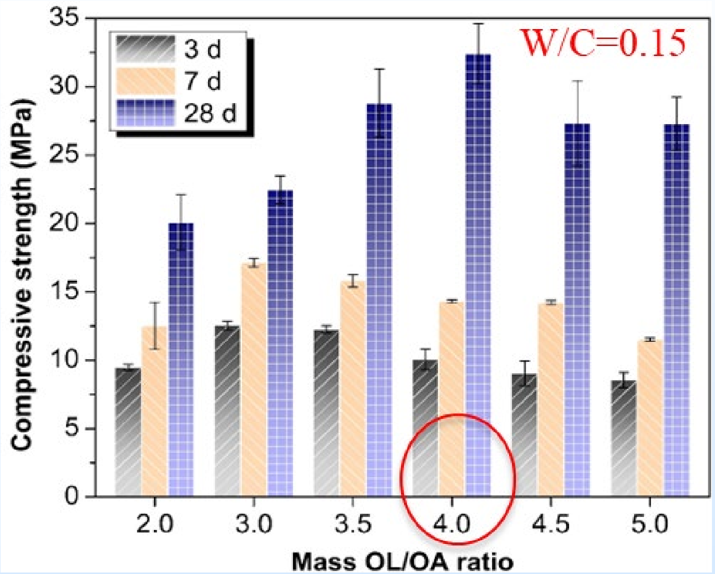
Whewellite ($CaC_2O_4 \cdot H_2O$) is more structurally stable and is responsible for the strength development



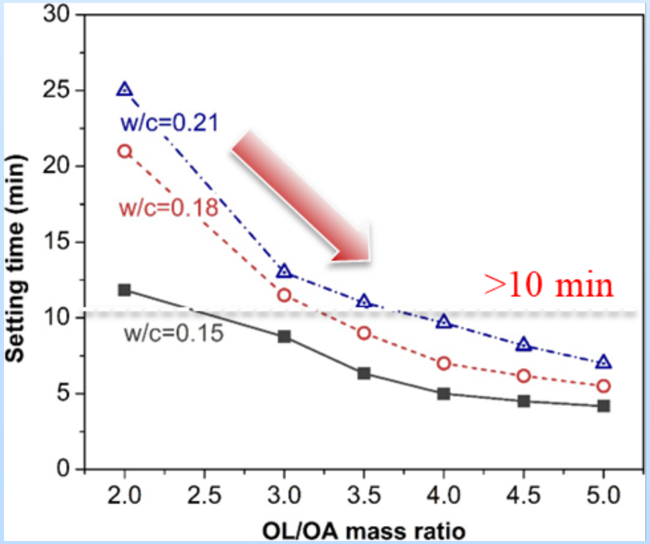
Oxalate cement formulated with olivine:
Raw material, proportions, & properties

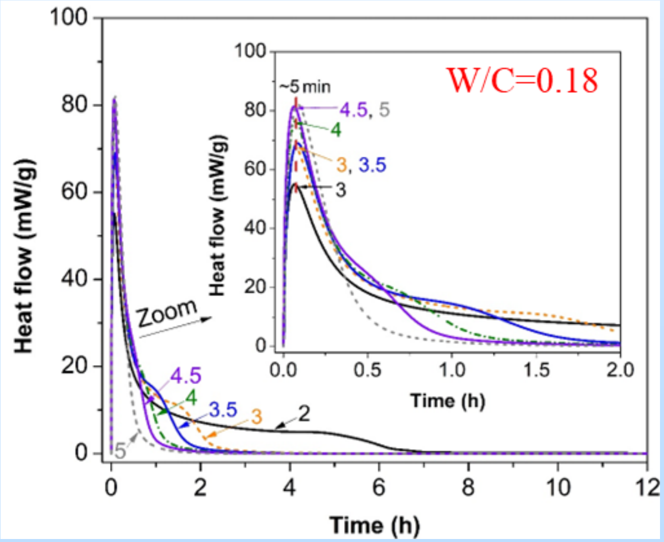
Raw materials

MgO	Al_2O_3	SiO_2	CaO	Fe_2O_3	Cr_2O_3	MnO	NiO	Others
48.38	0.25	**39.00**	0.17	**10.66**	0.73	0.17	0.52	0.12



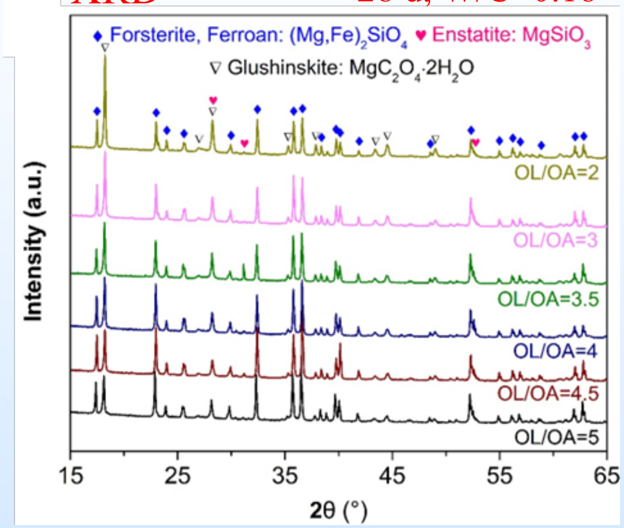
Proportion: **OL/OA,** olivine-to-oxalic acid mass ratio; **W/C**; **B/C**



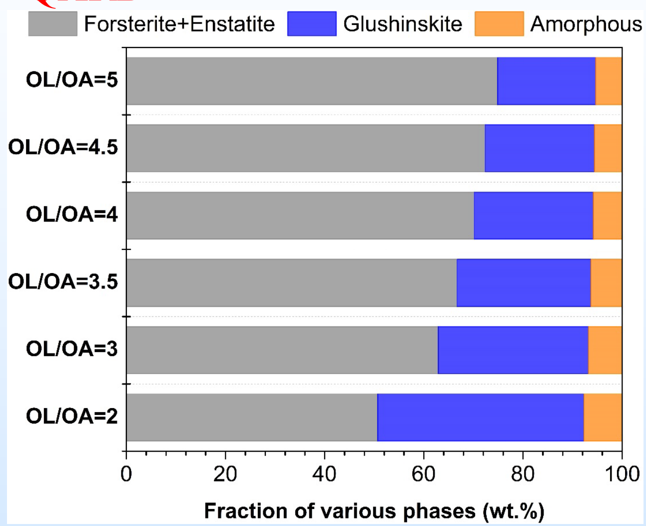


Oxalate cement formulated with olivine: Paste composition and microstructure

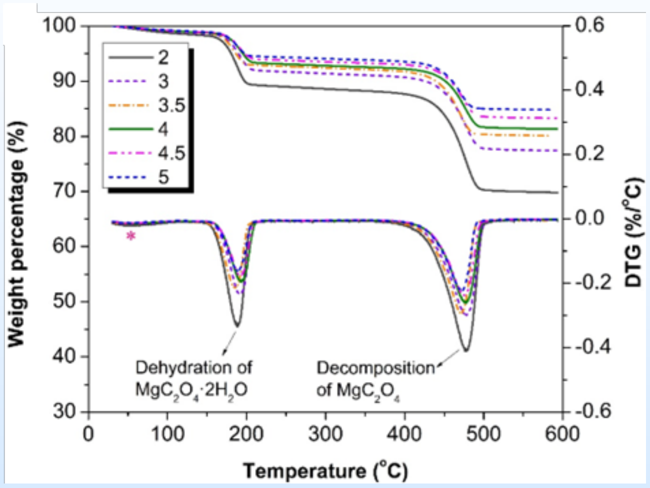
XRD 28 d, W/C=0.18

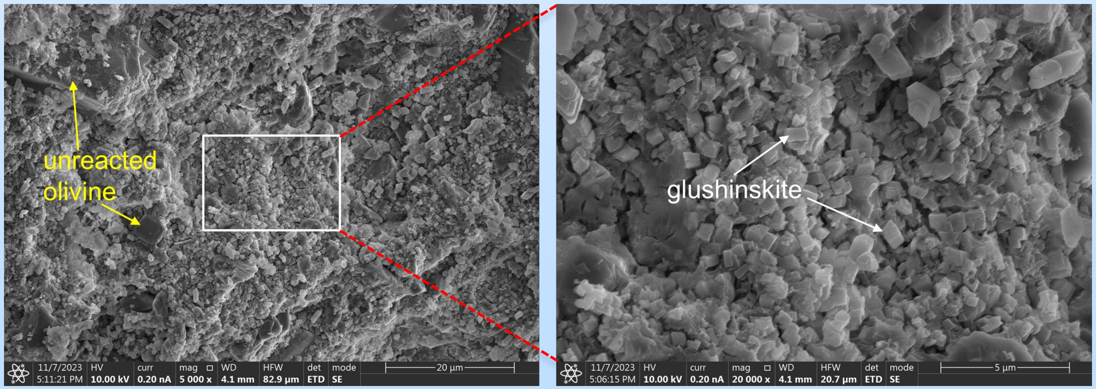


QXRD



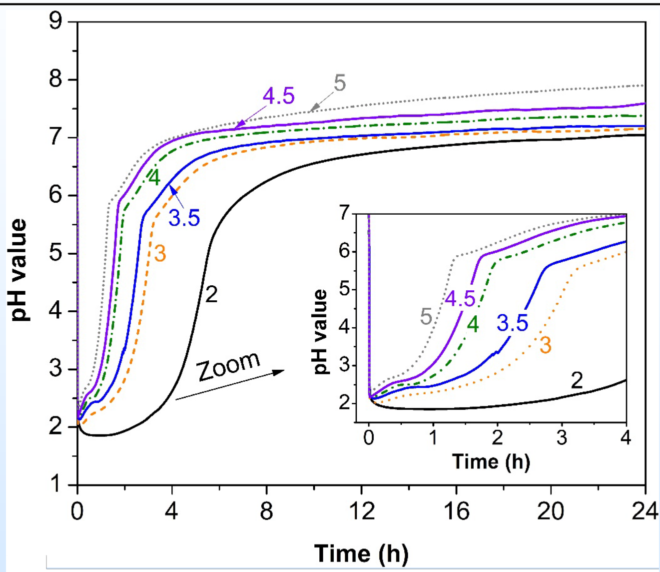
TG

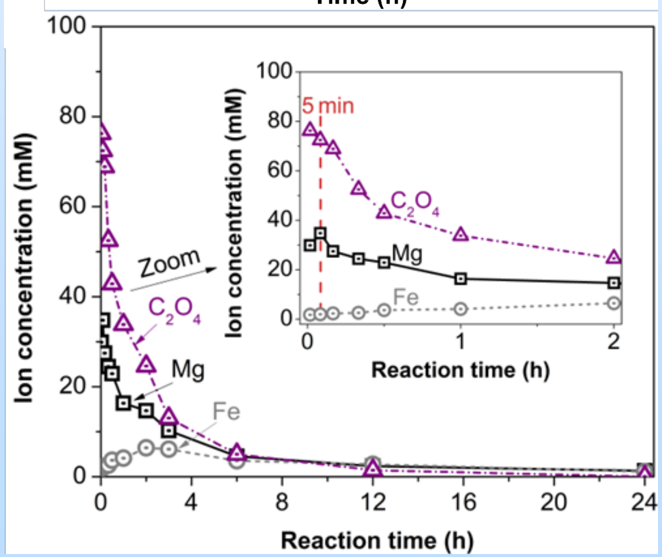




28 d, OL/OA=4, W/C=0.18

Oxalate cement formulated with olivine: Reaction mechanism





- **Dissolution of oxalic acid**

$$H_2C_2O_4 \rightarrow HC_2O_4^{-} + H^{+} + 2H_2O$$

$$HC_2O_4^{-} \rightarrow C_2O_4^{2-} + H^{+}$$

- **Dissolution of olivine minerals**

$$Mg_2SiO_4 + 4H^{+} \rightarrow 2Mg^{2+} + H_4SiO_{4\,(aq)}$$

- **Precipitation of glushinskite**

$$Mg^{2+} + HC_2O_4^{-} + 2H_2O \rightarrow MgC_2O_4{\cdot}2H_2O + H^{+}$$

$$Mg^{2+} + C_2O_4^{2-} + 2H_2O \rightarrow MgC_2O_4{\cdot}2H_2O$$

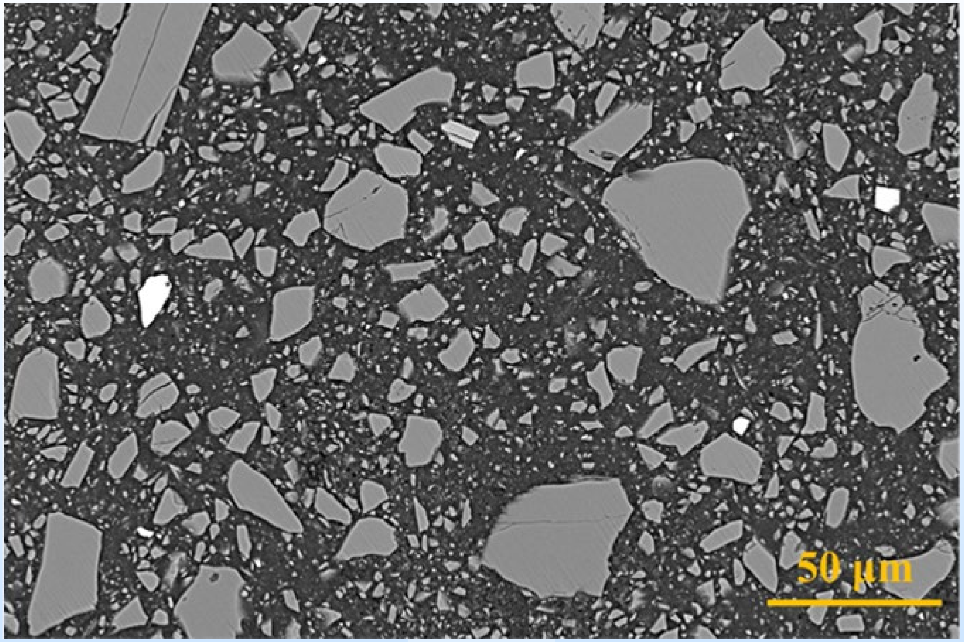
- **Formation of amorphous silica**

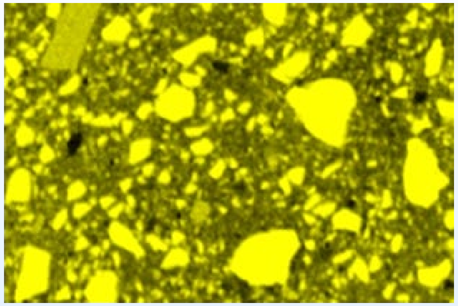
$$H_4SiO_{4\,(aq)} \rightarrow SiO_{2\,(gel)} + 2H_2O$$

Global reaction

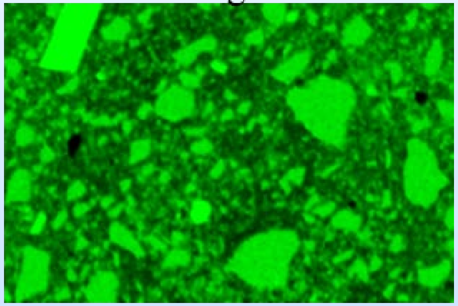
$$Mg_2SiO_4 + 2H_2C_2O_4 + 2H_2O \rightarrow 2MgC_2O_4{\cdot}2H_2O + SiO_{2\,(gel)}$$

Oxalate cement:
Microstructure and intensive carbon uptake

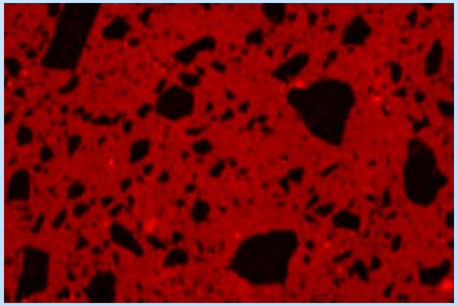




Mg



Si



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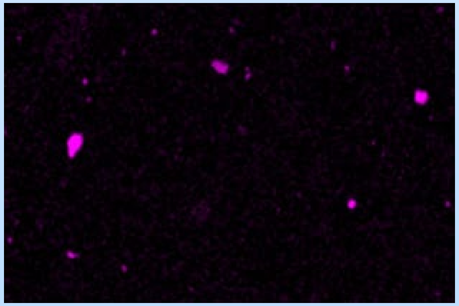
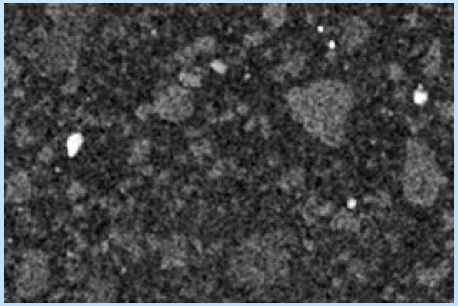


Al



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Summary of Community Benefits Plan

DEIA Plan

- Disseminating research results and development through outreach programs, such as organizing workshops
  - ✓ Completed an evidence-based implicit bias training for key personnel
  - ✓ Organized one half-day workshop (7/26/2024, "Storing CO_2 in Infrastructure Materials to Combat Climate Change") for high school students
- Inclusion of participants from underrepresented groups
  - ✓ One female summer intern joined the team
  - ✓ Recruited two female graduate students and will join the team in fall 2024

Education and Workforce Development Plan

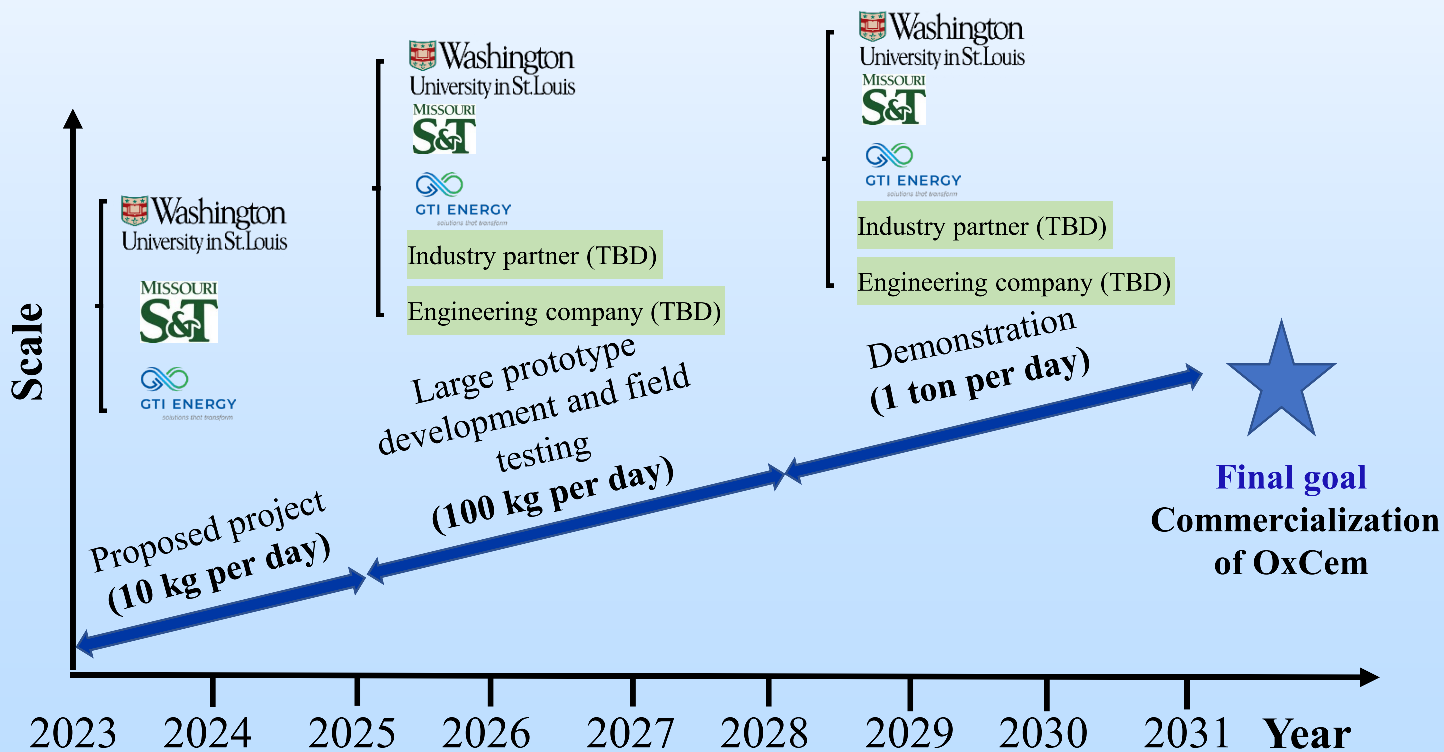
- Educate and train the future workforce so that they understand the significance and methodologies to covert CO_2 into cement-forming chemicals, manufacture new-concept cements, and integrate these cements into the cement toolkit of future engineers
  - ✓ Both undergraduate and graduate students are being trained

Plans for Future Testing/Development/ Commercialization

Plan for Future Testing of This Project:

- Oxalic acid synthesis from CO_2 at a larger scale
- Improve performance of OxCem

Technology Development Path:



Summary

- 100% CO_2 conversion could be achieved using base solution absorption.
- CO_2 could be efficiently converted to oxalic acid with overall yield >50%.
- Optimized OxCem attained sufficient setting time (>10 min) and robust compressive strength (20-50 MPa).
- Reaction between oxalic acid with olivine/steel slag led to the rapid formation of Mg/Ca/Fe oxalates that not only acted as the cementing phases but sequestered carbon stably.

Acknowledgements

- Financial and technical support

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- DOE NETL: Kara Zabetakis