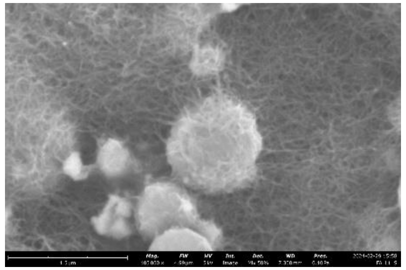
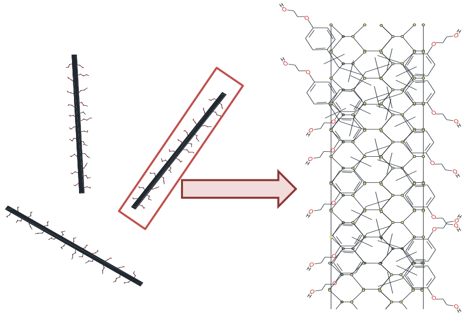
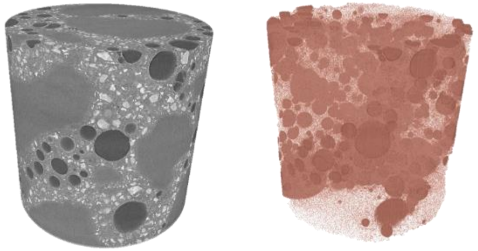
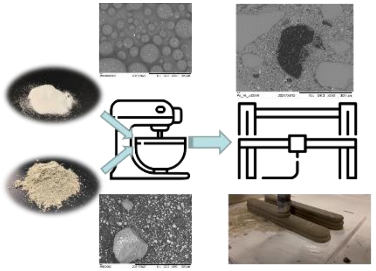
CO_2 Derived Carbon Nanotube in 3D Printable Cementitious Composites: Dispersion and Properties









Ehsan Moseni[1], Reese Sorgenfrei[1], Anna Douglas[2], Hongyu Zhou[1]

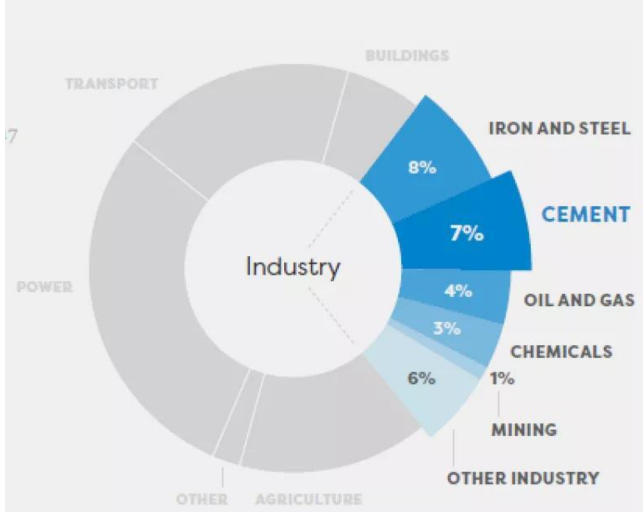
[1] University of Tennessee, Knoxville

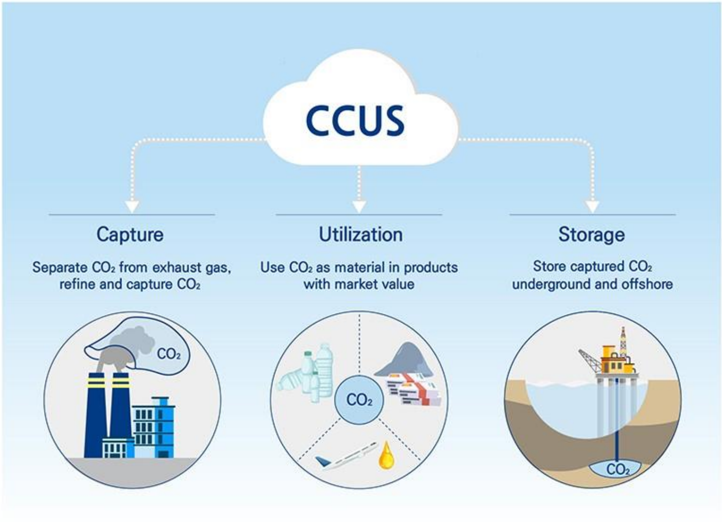
[2] SkyNano Technologies LLC

Outline

- Introduction
- CO_2 derived MWCNT and nanostructured carbon
- A novel technique to disperse MWCNT in cementitious composites
- Formulation of functional cementitious composite containing CO_2-derived MWCNT
- Conclusions

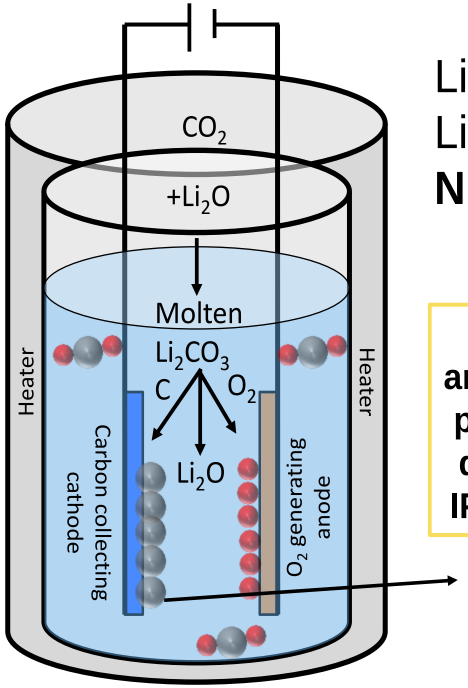
Introduction





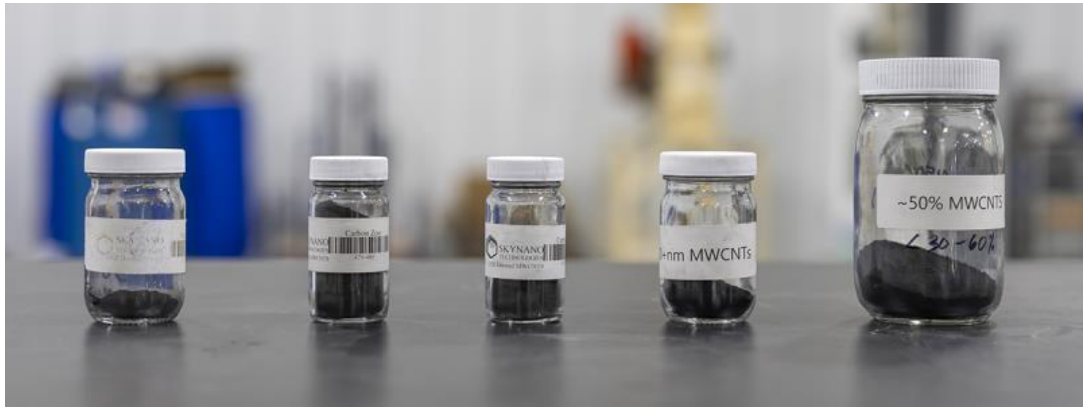
- Cement and concrete manufacturing is carbon intensive
- Beneficial utilization of CO_2 from cement manufacturing can be an effective means of decarbonization
- CO_2 emitted from the manufacturing process can be used as feedstock for value-adding products

Utilizing CO_2-derived CNT



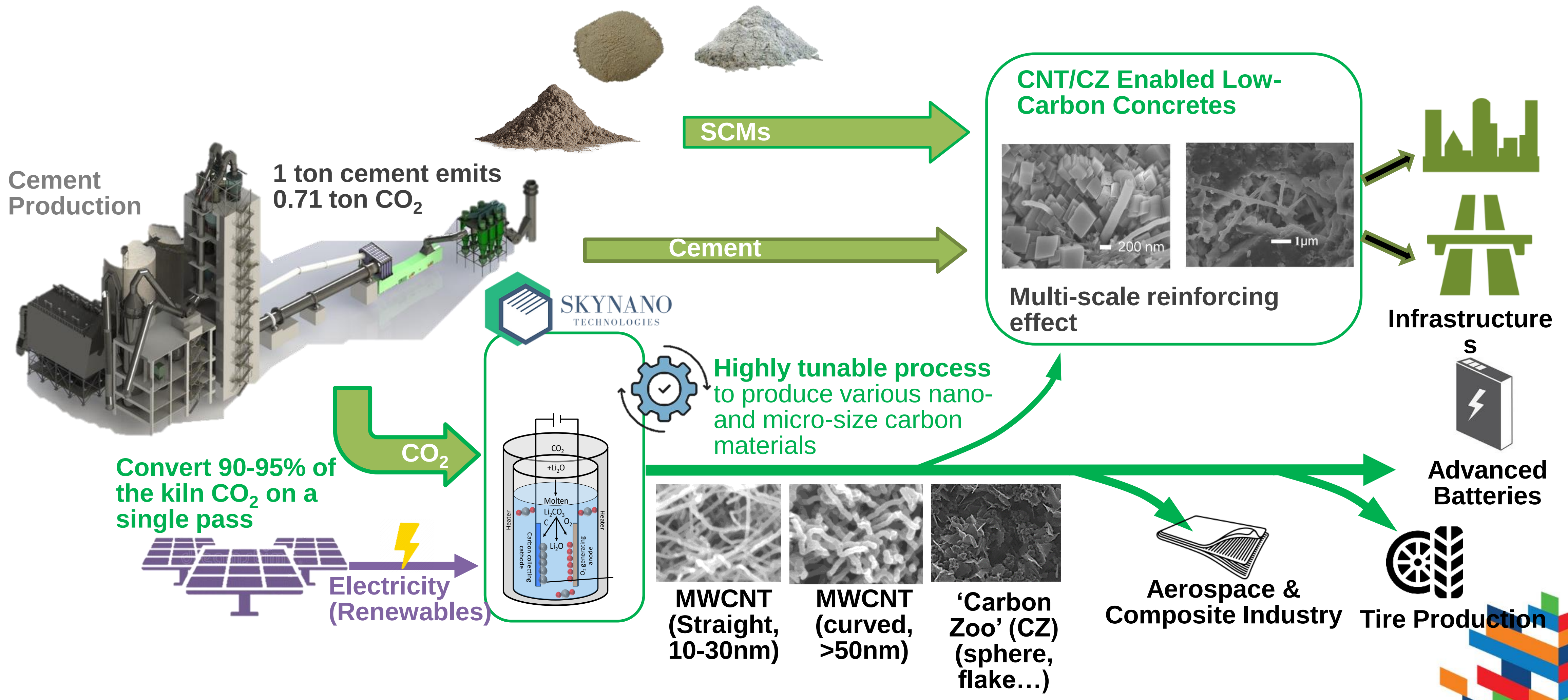
$Li_2CO_3 \rightarrow Li_2O + O_2 + C$
$Li_2O + CO_2 \rightarrow Li_2CO_3$
NET: $CO_2 \rightarrow C + O_2$

****Electrode architecture to produce high quality CNTs IP protected****

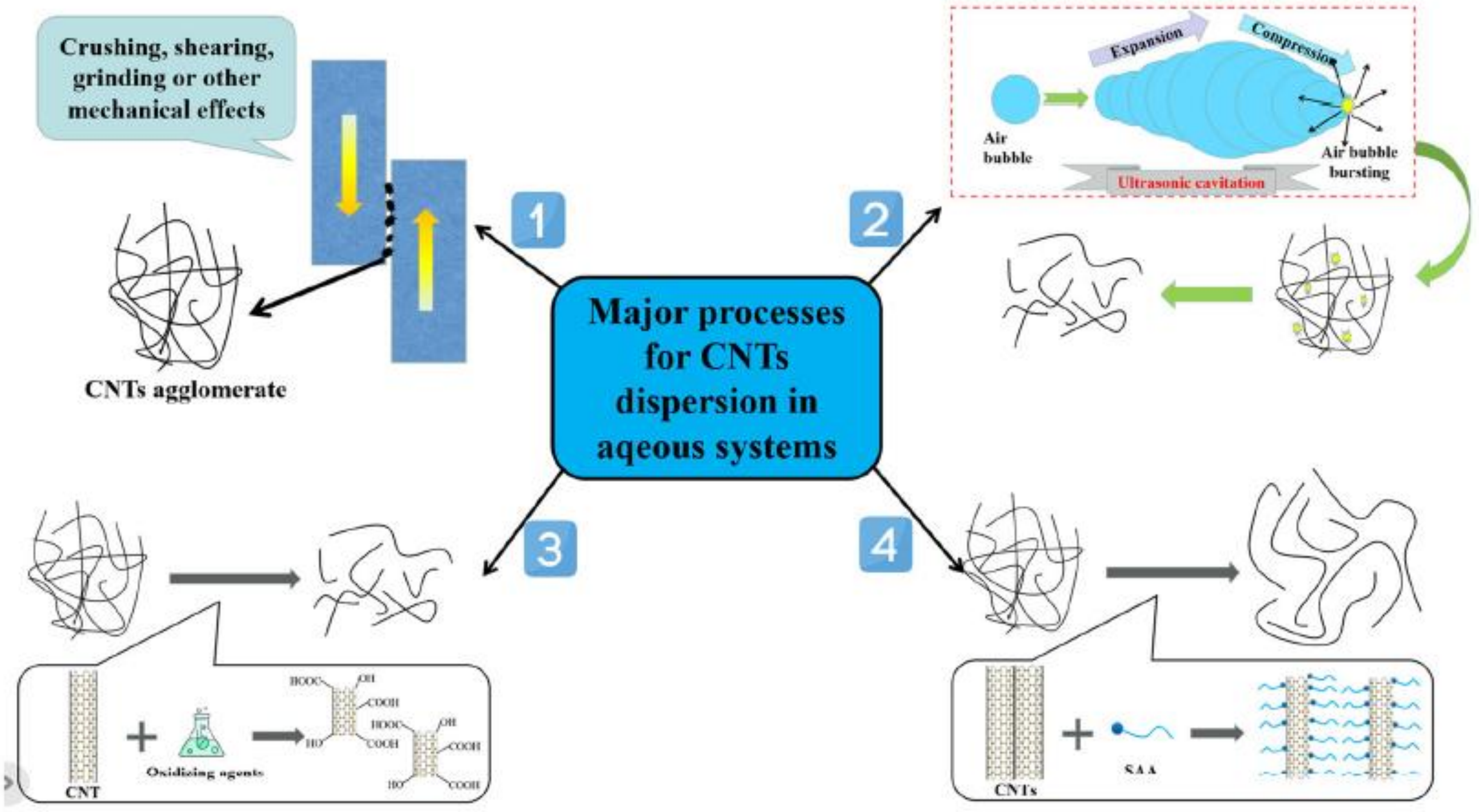


The SkyNano technology of MWCNT production is based on molten salt electrolysis, where carbonate-ion reduction occurs at the cathode and oxide-ion oxidation occurs at the anode. The captured CO_2 is then used to chemically regenerate the molten salt electrolyte by converting excess oxide ions back to carbonate ions.
The system may be run in semi-batch or continuous mode with the only inputs as CO_2 (atmospheric or a concentrated source) and electricity.

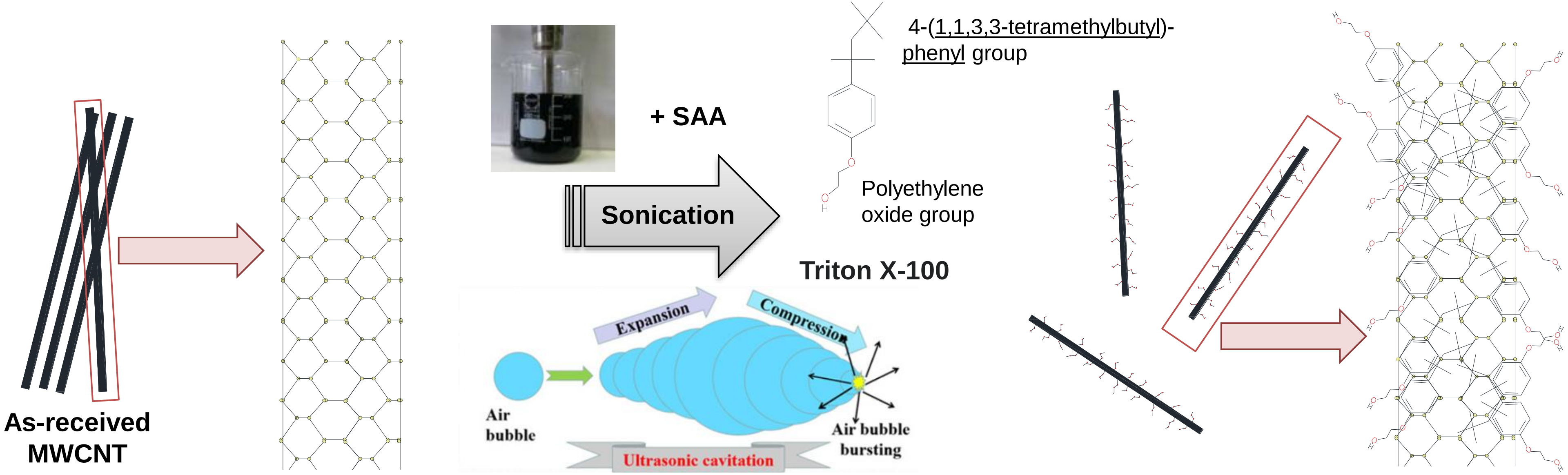
Utilizing CO_2-derived CNT



CNT Dispersion in Cementitious Materials

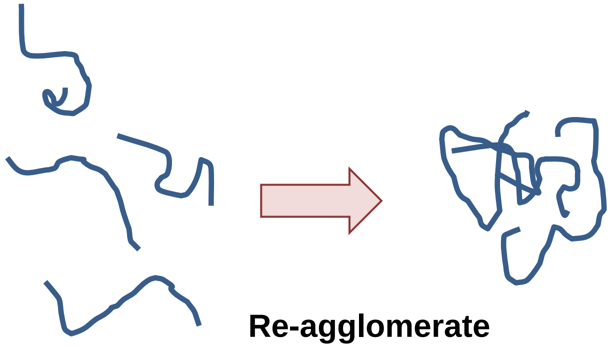


A novel strategy for CNT dispersion using SCMs as Carrier

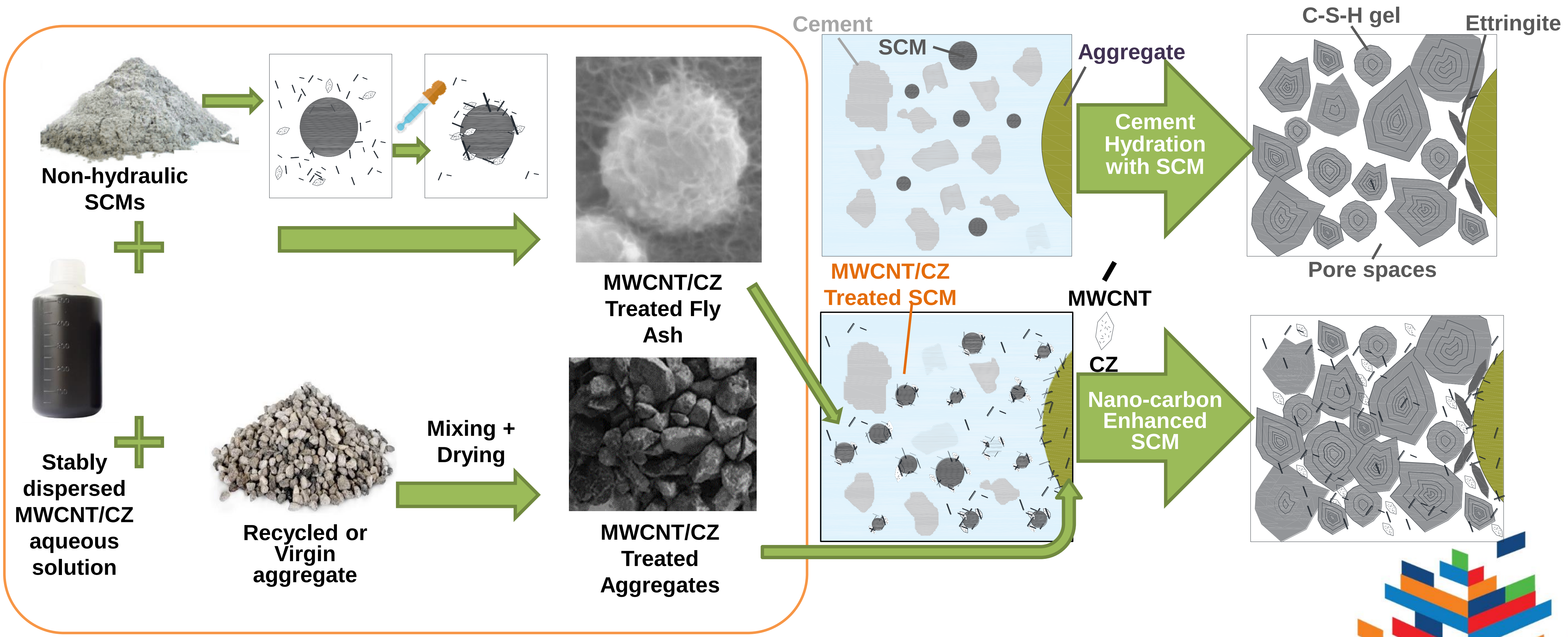


Problem?

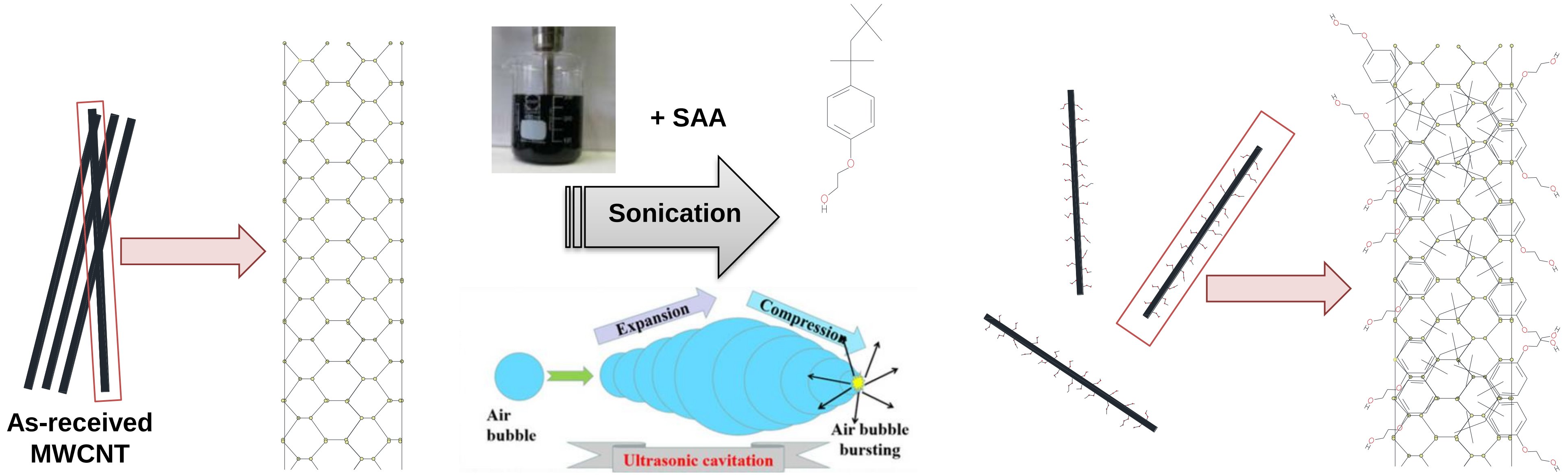
Over time

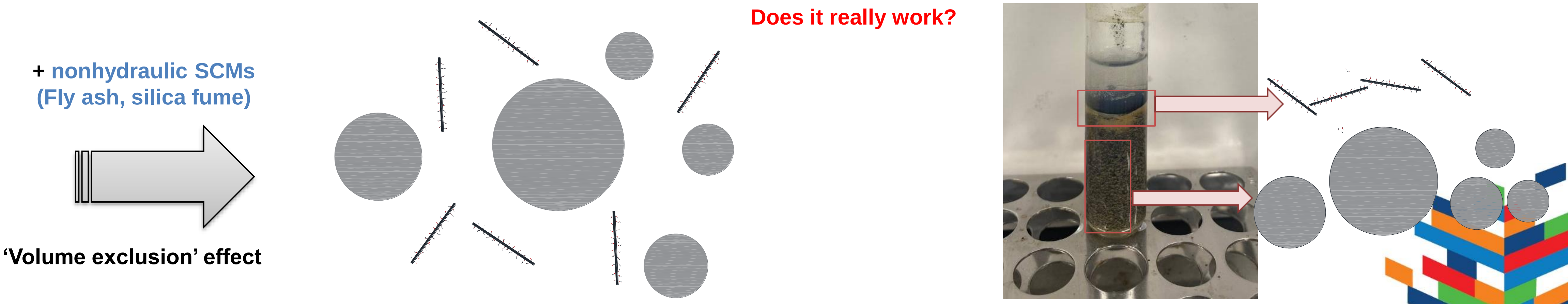


A novel strategy for CNT dispersion using SCMs as Carrier



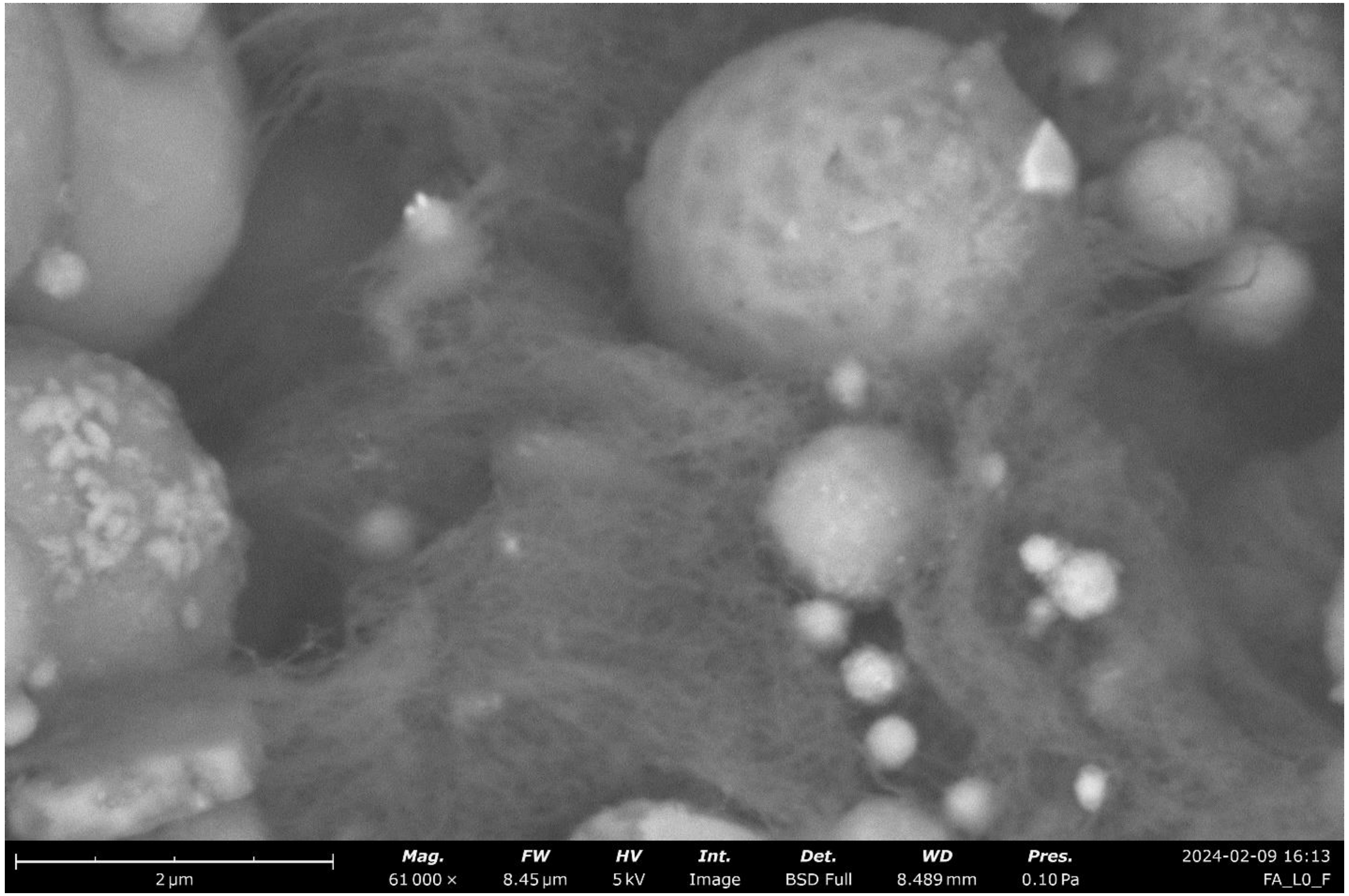
A novel strategy for CNT dispersion using SCMs as Carrier





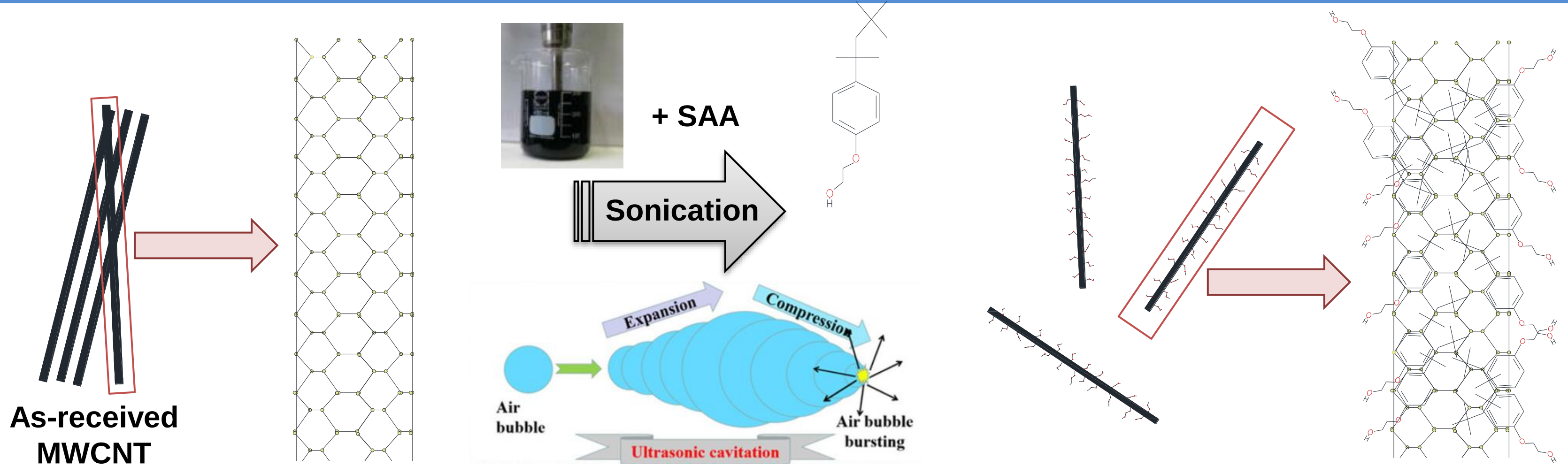
A novel strategy for CNT dispersion using SCMs as Carrier

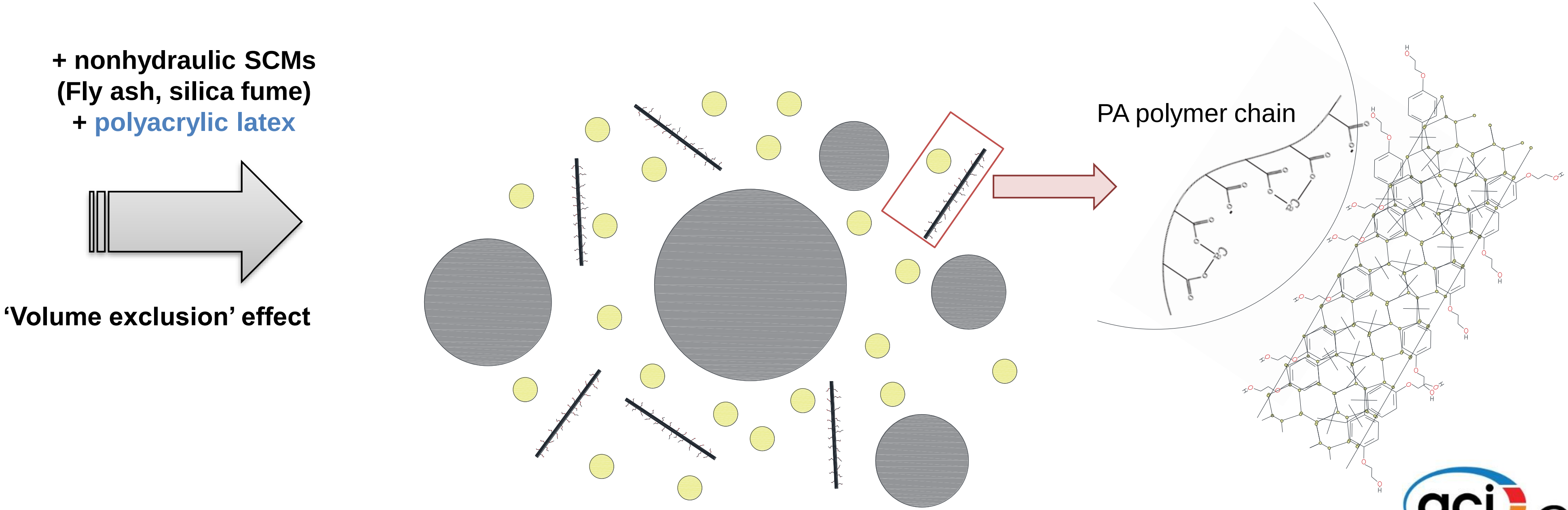
FA-L0 Slurry

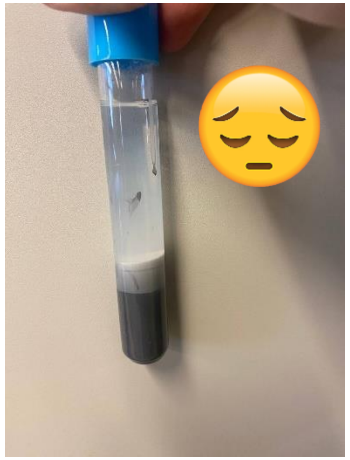


CNTs agglomerate and do not ‘coat’ the SCM surface

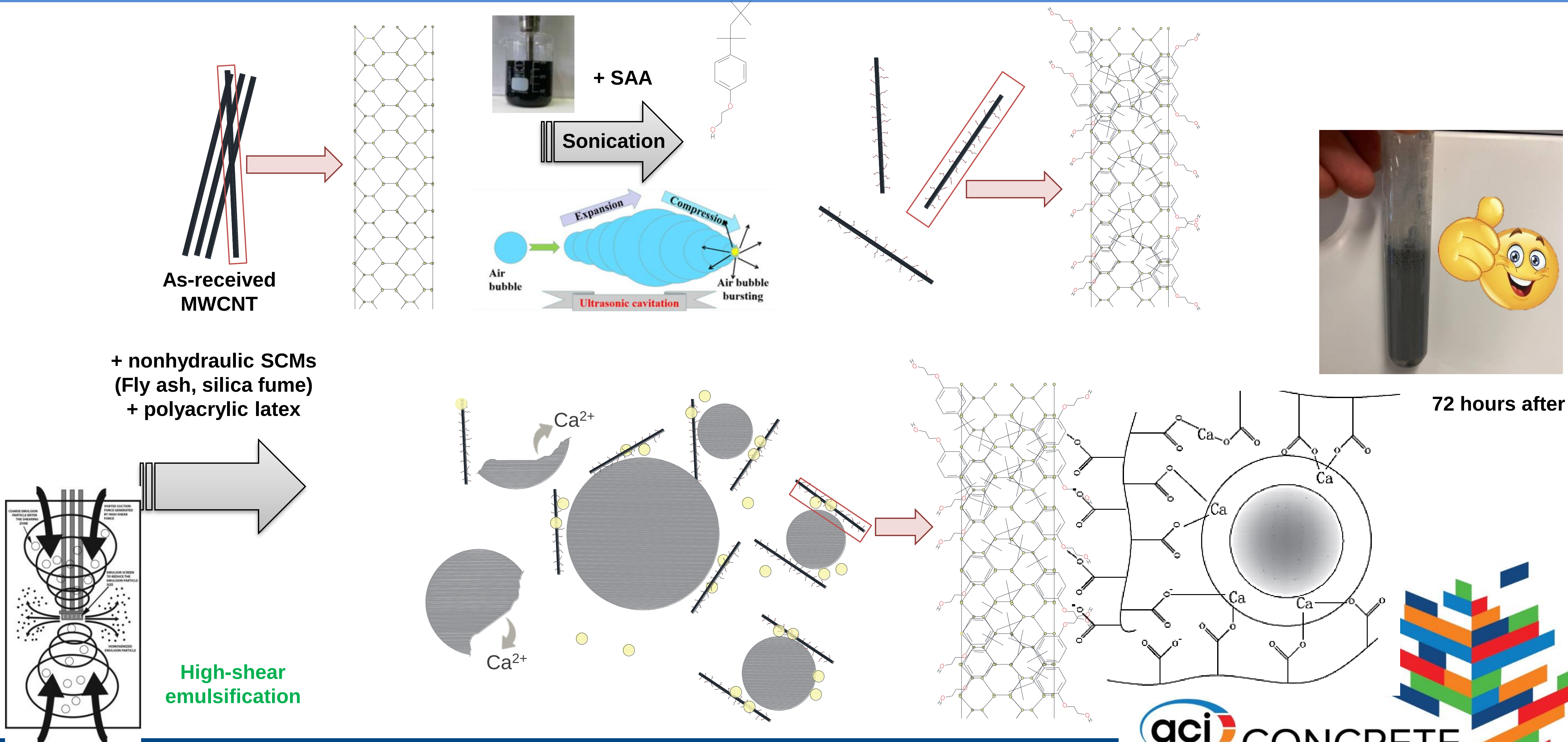
A novel strategy for CNT dispersion using SCMs as Carrier



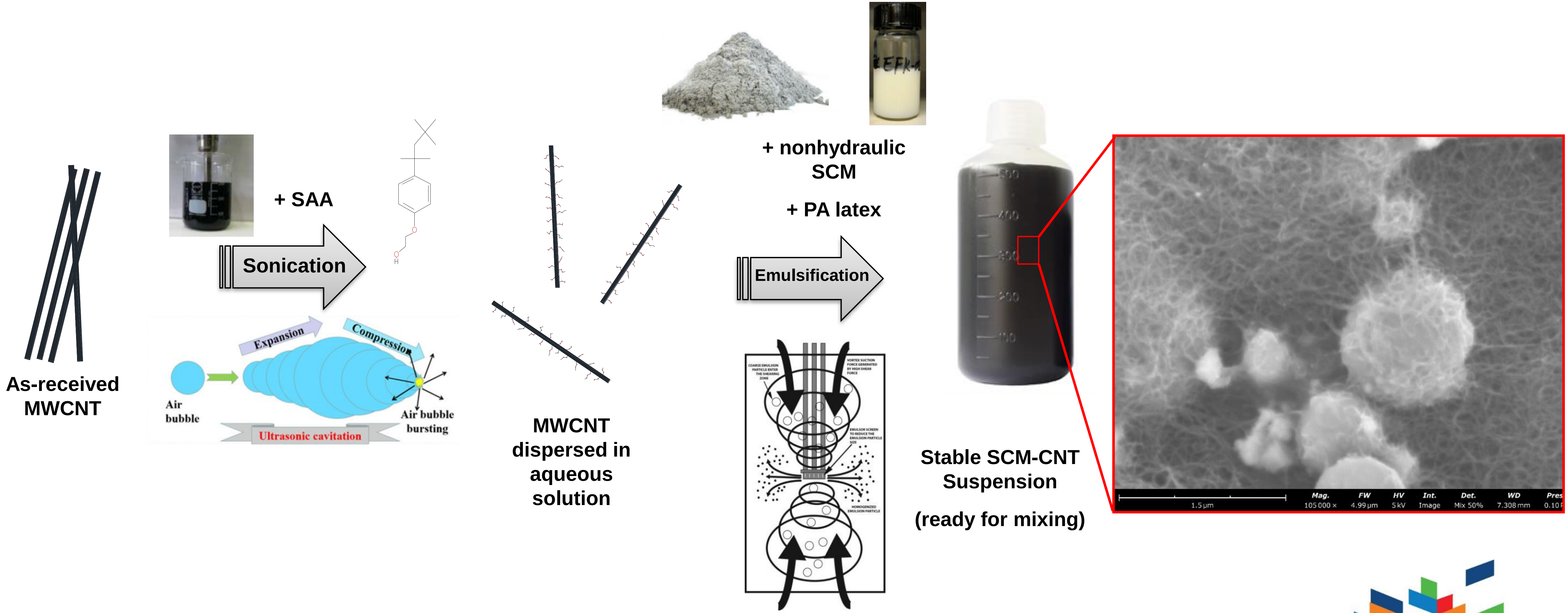




A novel strategy for CNT dispersion using SCMs as Carrier

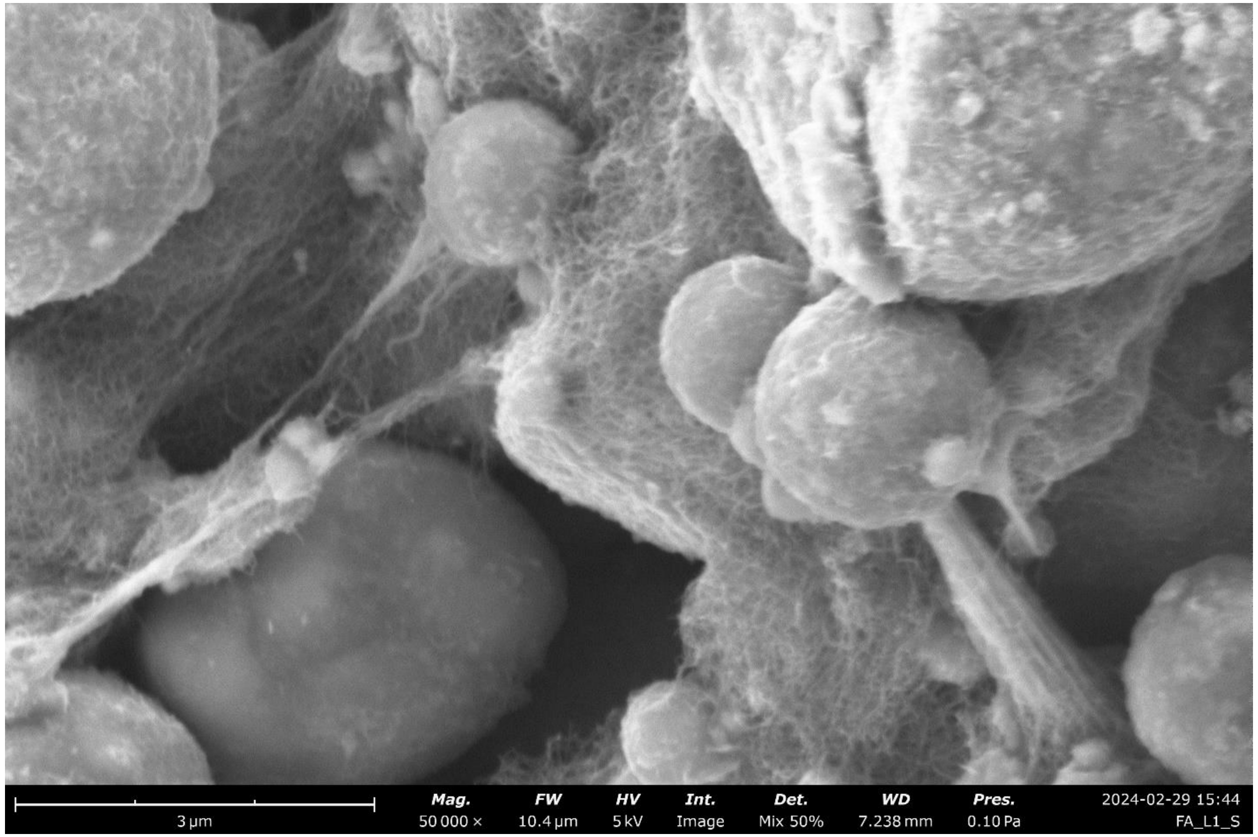


A novel strategy for CNT dispersion using SCMs as Carrier



A novel strategy for CNT dispersion using SCMs as Carrier

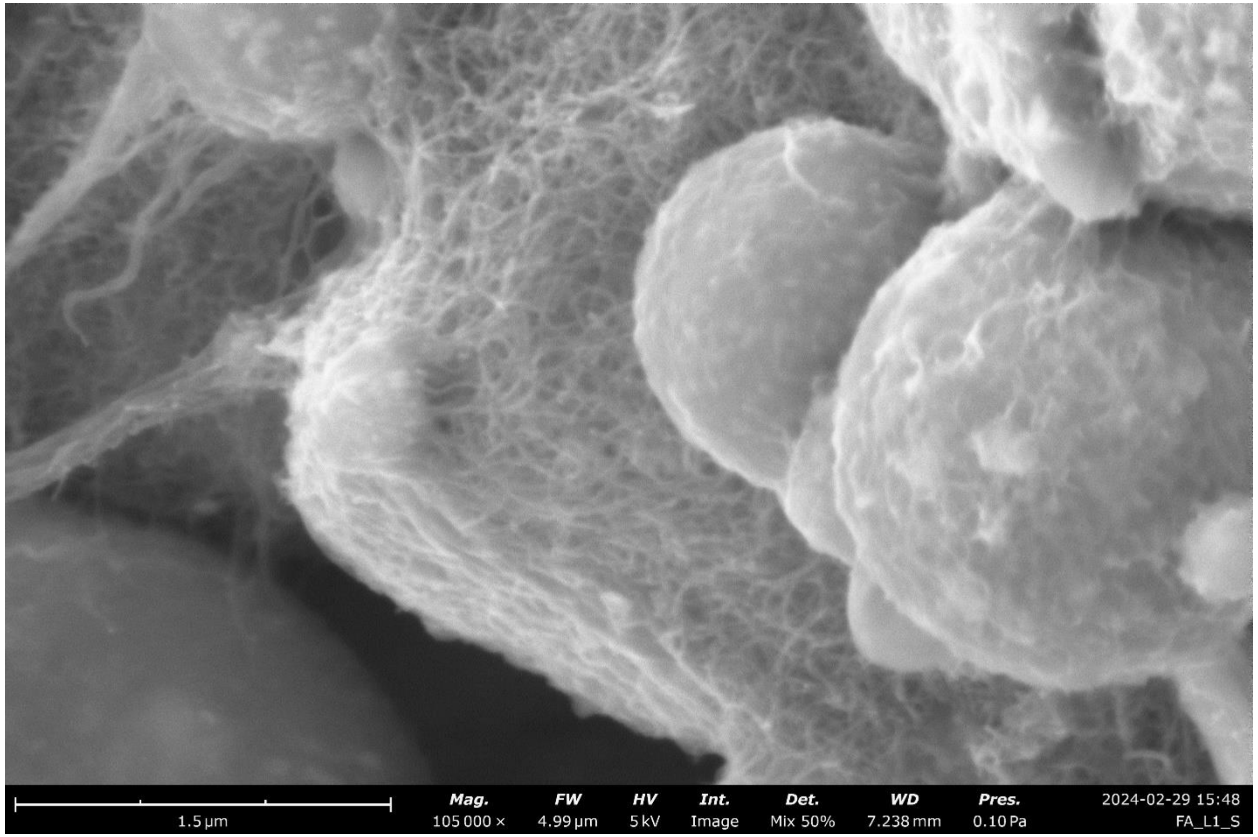
FA-L1 Slurry



Well dispersed with long ‘shelve life’

A novel strategy for CNT dispersion using SCMs as Carrier

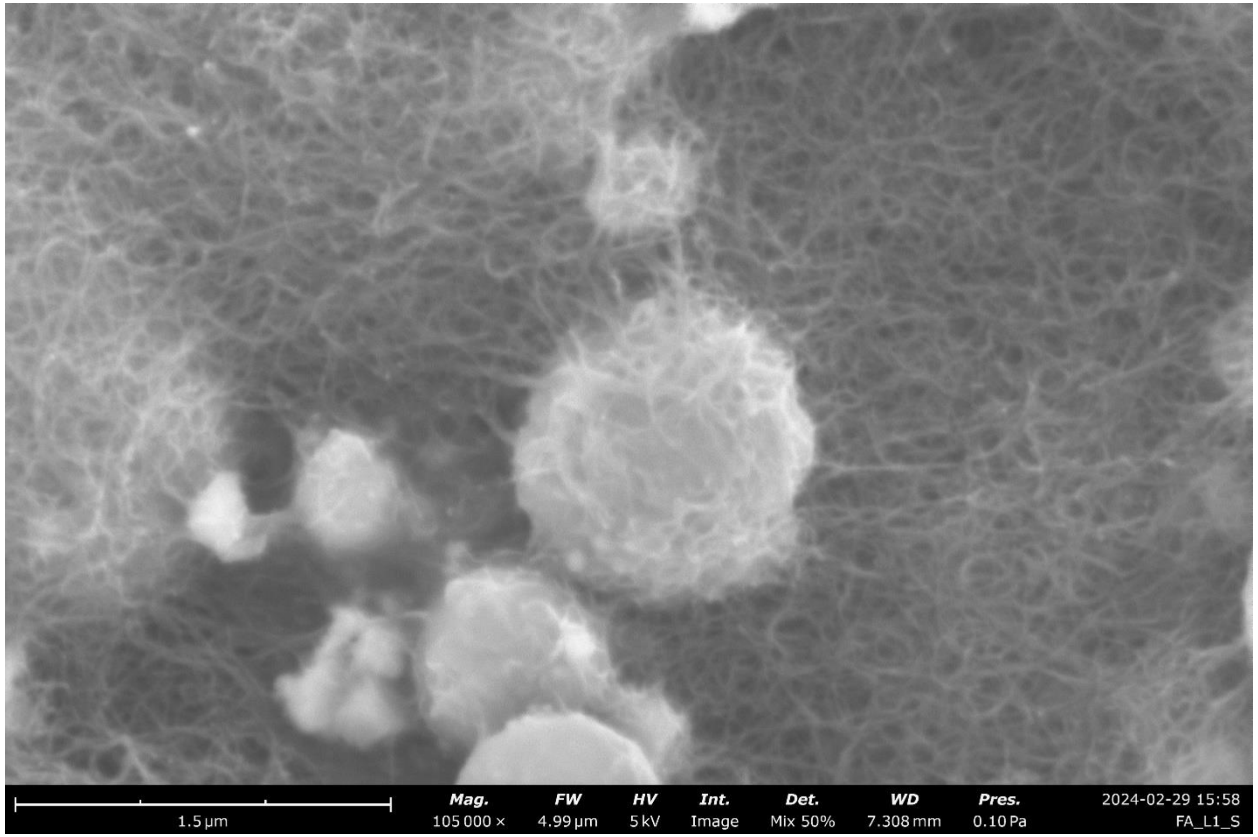
FA-L1 Slurry



Well dispersed with long 'shelve life'

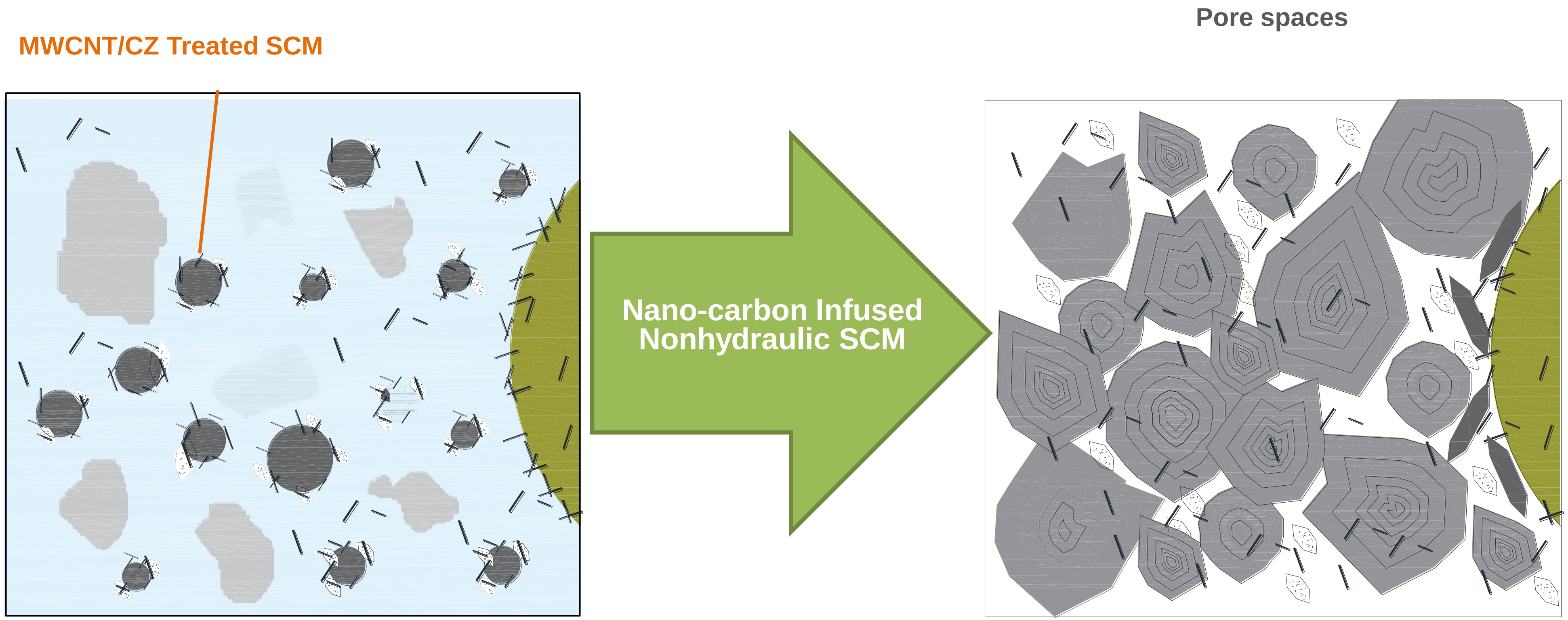
A novel strategy for CNT dispersion using SCMs as Carrier

FA-L1 Slurry



Well dispersed with long ‘shelve life’

Reaction with Cement



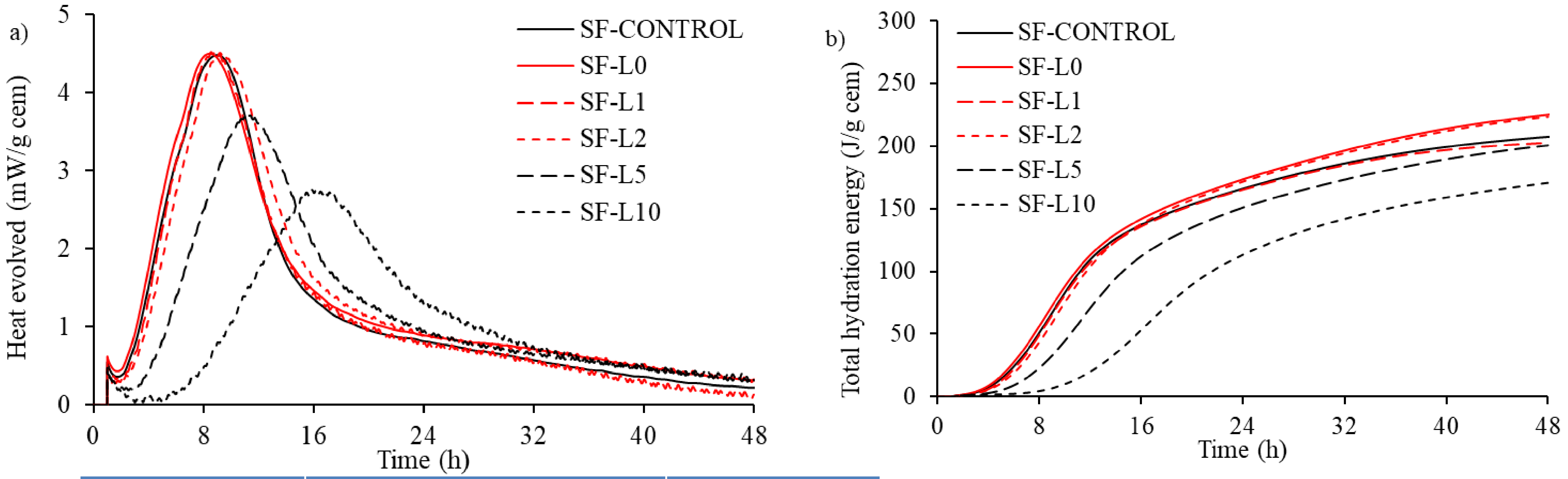
MWCNT/CZ treated unconventional SCMs acting as dispersant to improve MWCNT/CZ dispersion while densifying the microstructure of cement binder

Reaction in Cementitious Materials Sytem

Mix proportions of final mixtures in kg/m³

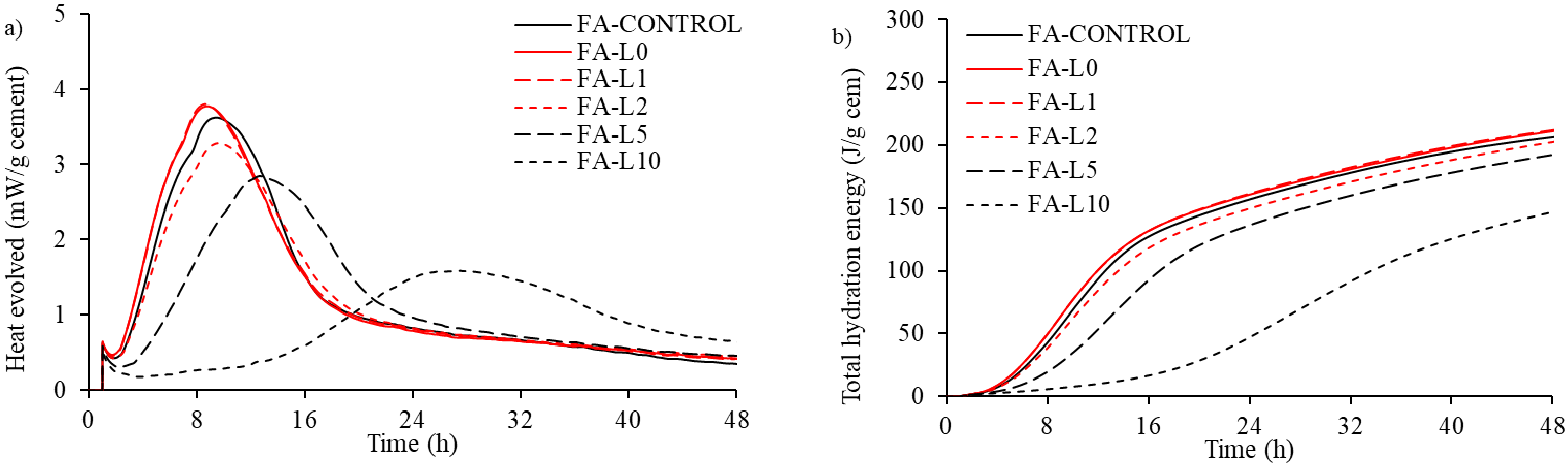
	Mix ID	Cement	Water	SCM	PA Latex	CNT	Surfactant
SCM Type Silica fume	SF-control	95	30	5	0	0	0
	SF-L0	95	30	5	0	0.5	0.5
	SF-L1	94	30	5	1	0.5	0.5
	SF-L2	93	30	5	2	0.5	0.5
	SF-L5	90	30	5	5	0.5	0.5
	SF-L10	85	30	5	10	0.5	0.5
SCM Type Fly ash	FA-control	90	30	10	0	0	0
	FA-L0	90	30	10	0	0.5	0.5
	FA-L1	89	30	10	1	0.5	0.5
	FA-L2	88	30	10	2	0.5	0.5
	FA-L5	85	30	10	5	0.5	0.5
	FA-L10	80	30	10	10	0.5	0.5

Hydration Kinetics



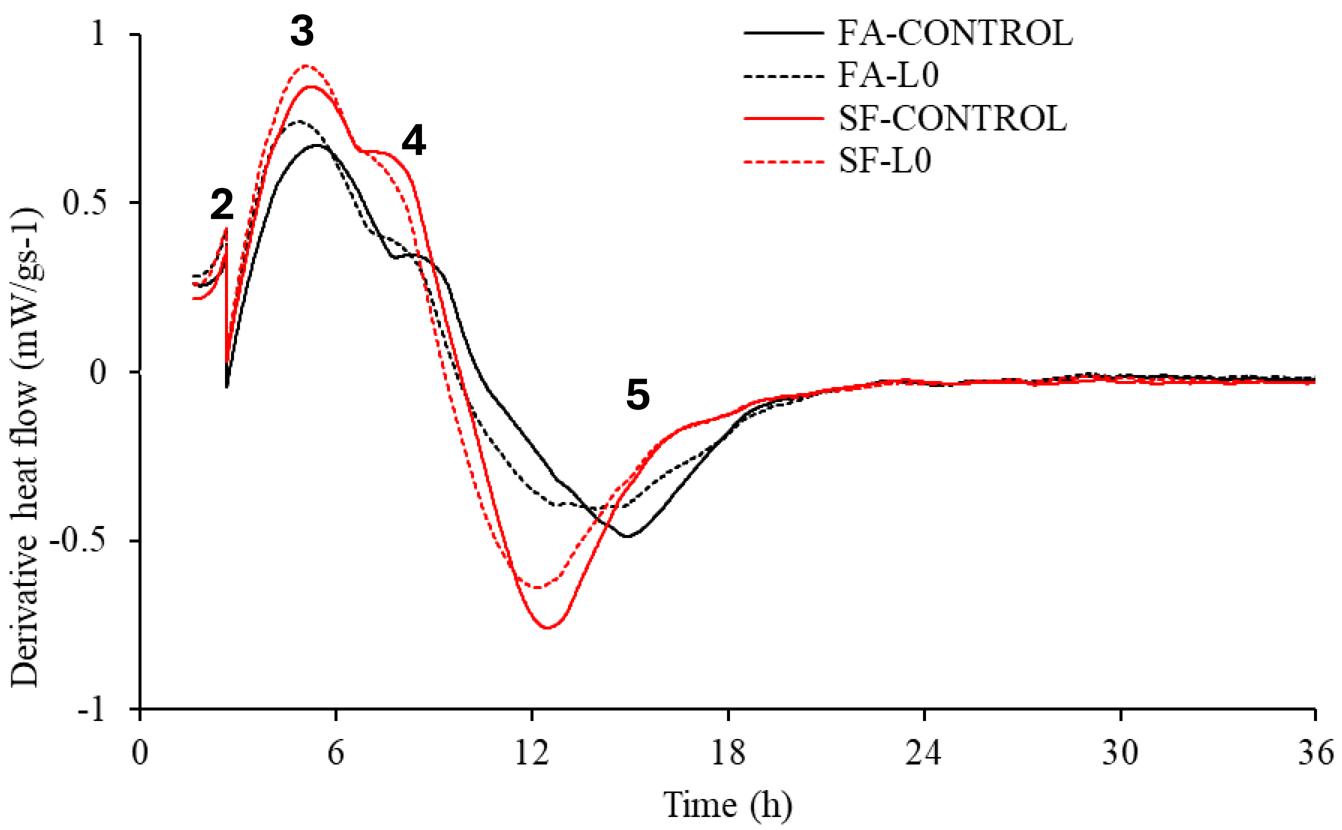
Mix ID	Peak		Total hydration energy (J/g cement)
	Heat flow (mW/g cement)	Time (h)	
SF-control	4.48	9.00	207.38
SF-L0	4.50	8.43	225.12
SF-L1	4.53	8.85	202.54
SF-L2	4.51	9.20	223.53
SF-L5	3.71	11.05	200.56
SF-L10	2.77	16.20	170.69

Hydration Kinetics



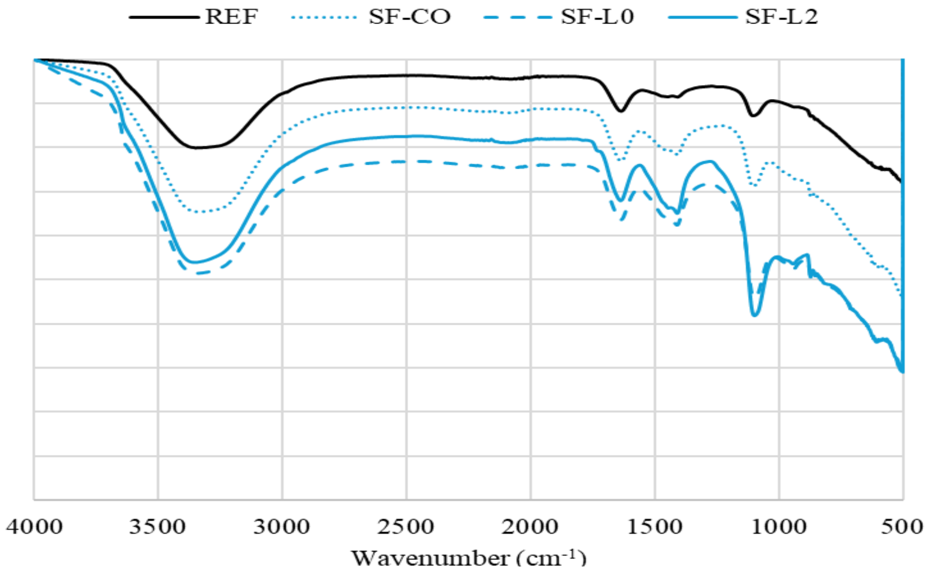
Mix ID	Peak		Total hydration energy (J/g cement)
	Heat flow (mW/g cement)	Time (h)	
FA-control	3.62	9.47	206.56
FA-L0	3.78	8.75	211.53
FA-L1	3.80	8.65	212.39
FA-L2	3.29	9.62	202.46
FA-L5	2.85	12.67	192.42
FA-L10	1.59	27.53	146.85

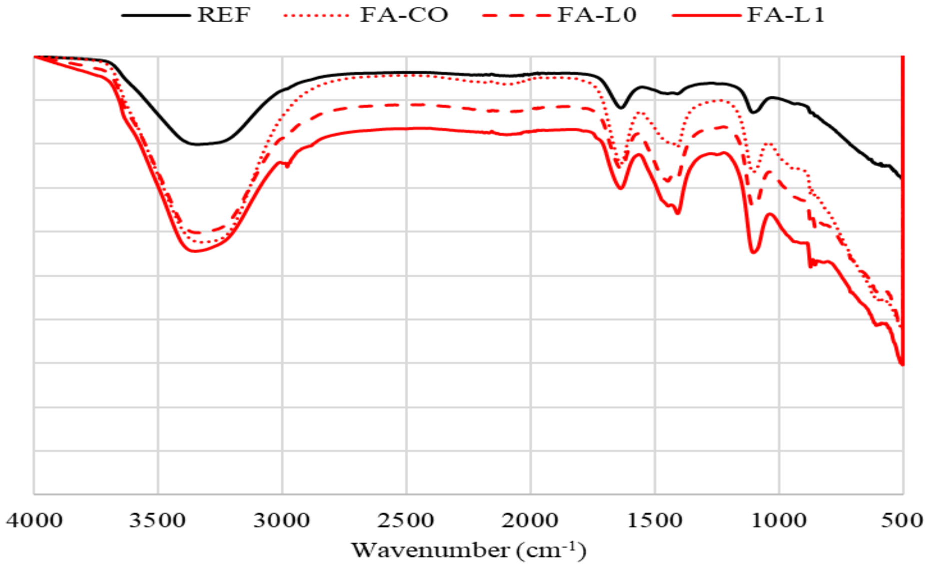
Hydration Kinetics



- The introduction of dispersed CNTs resulted in some acceleration in the primary heat evolution peaks.
- For SF-L0, the maximum of 0.98 mW/g s^{-1} was reached at 4.28 hours of hydration, compared to 0.89 mW/g s^{-1} at 4.52 hours for the reference mix, indicating an acceleration of 14.4 minutes.
- For FA-L0, the maximum of 0.81 mW/g s^{-1} occurred at 4.05 hours of hydration, compared to 0.73 mW/g s^{-1} at 4.67 hours for the reference mix, indicating an acceleration of 37.2 minutes.
- This acceleration was followed by a less pronounced shoulder at approximately 18 hours, is correlated with sulphate depletion.

FTIR



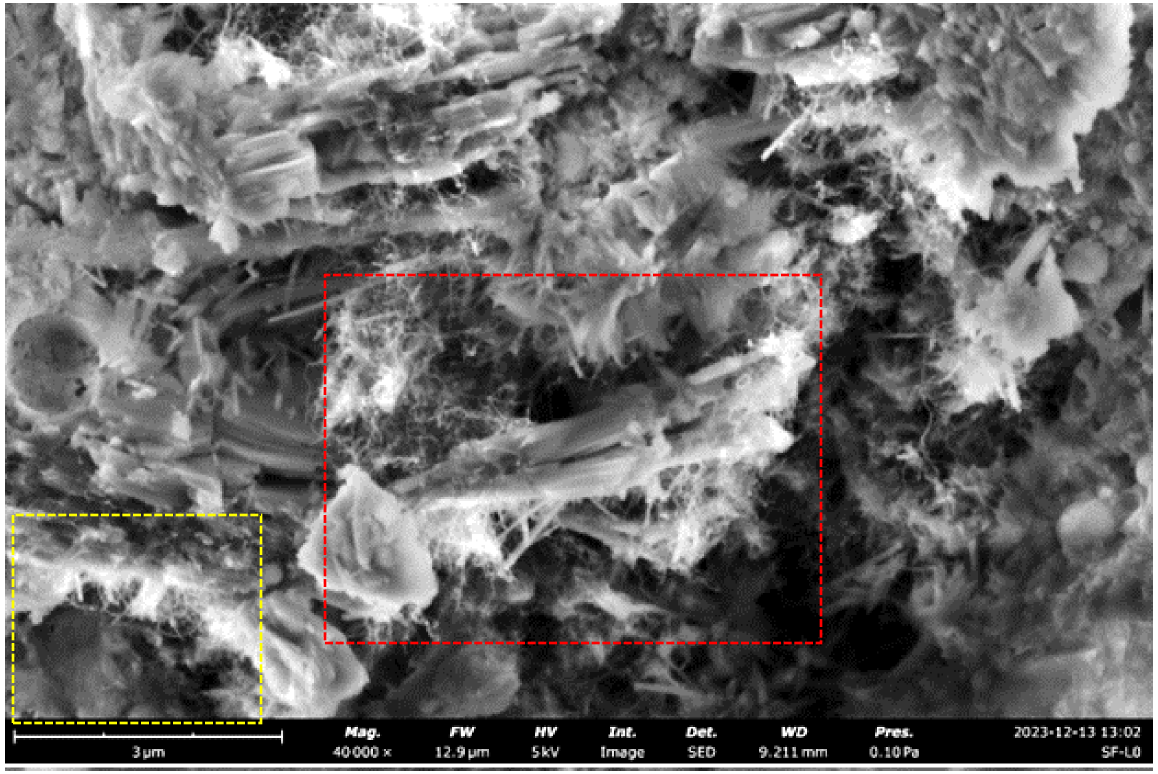


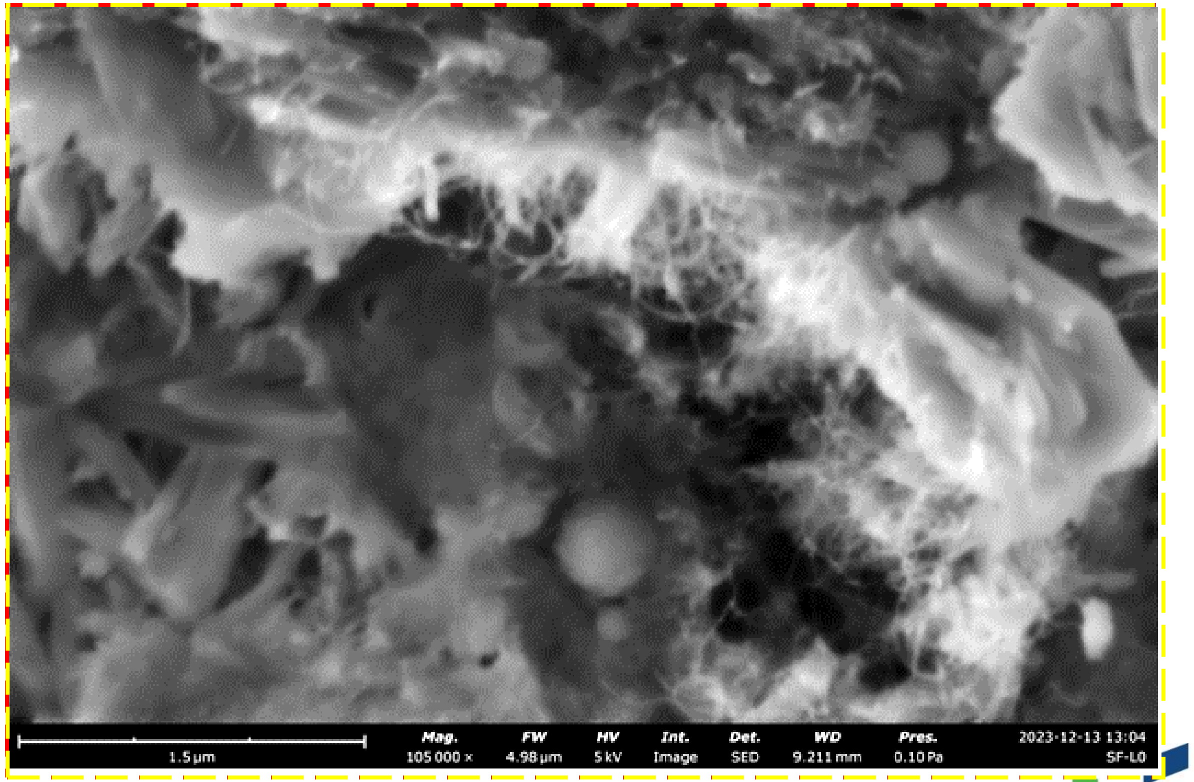
- Larger peaks at 1098 and 1408 indicates that CNT can inhibit the carbonation of cementitious composites to some extent

- Sharper intensity at 3392 indicates CNT accelerates the hydration of the cement and produces more calcium hydroxide crystals which can react with the carbon dioxide in the air to form calcium carbonate. It also indicates the increase of crystalline calcium hydroxide.

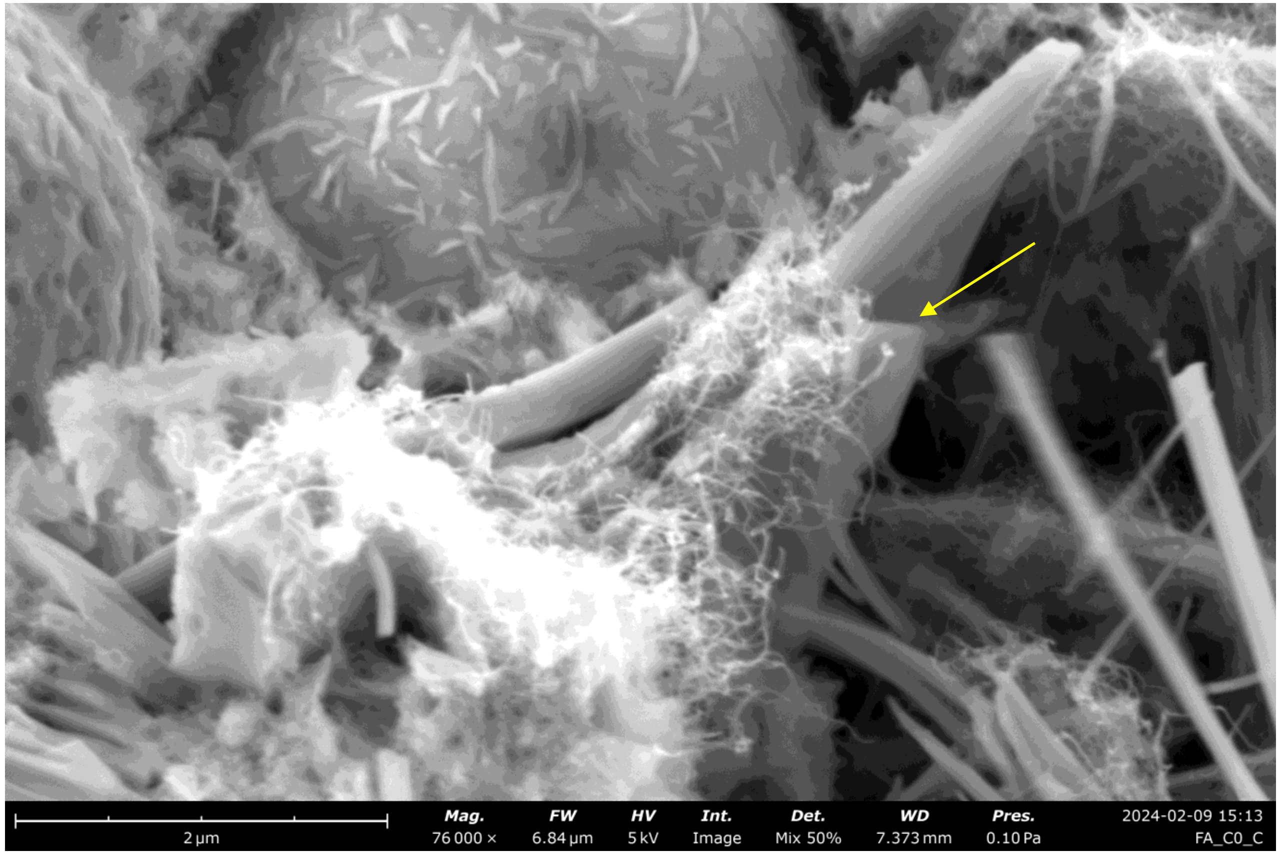
Microstructure

SF-L0 Cementitious Nanocomposite



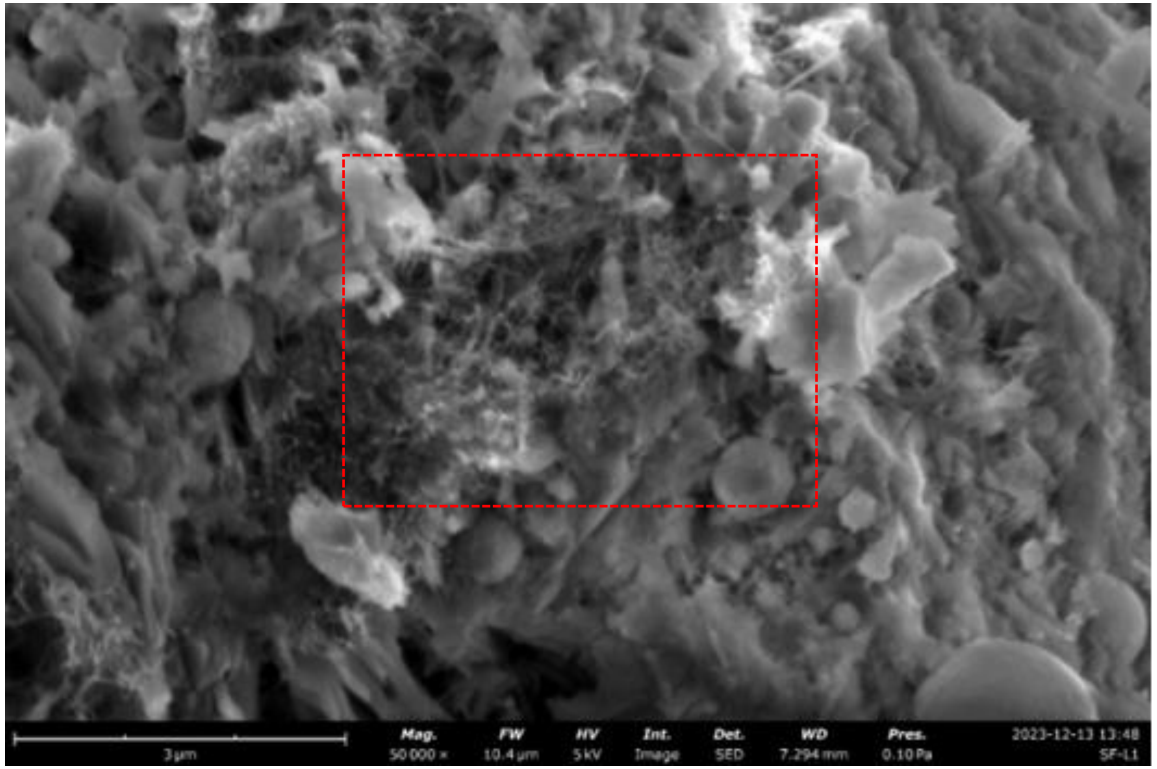


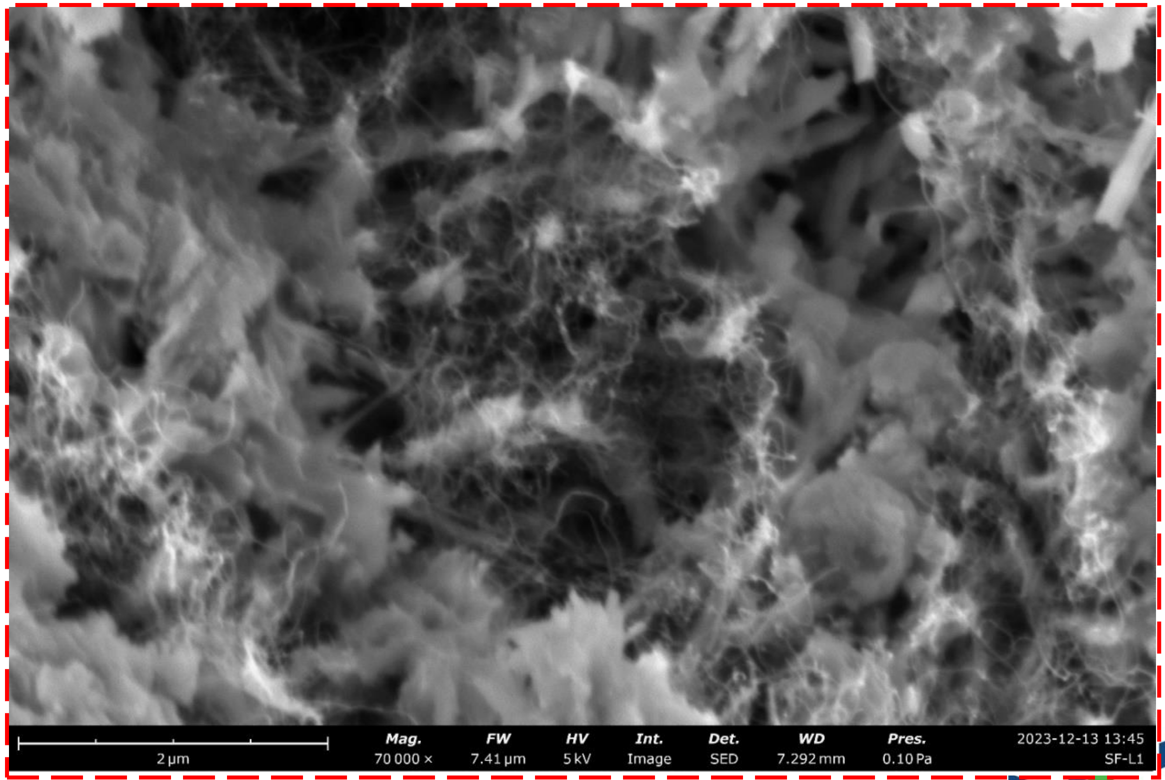
FA-L0 Cementitious Nanocomposite



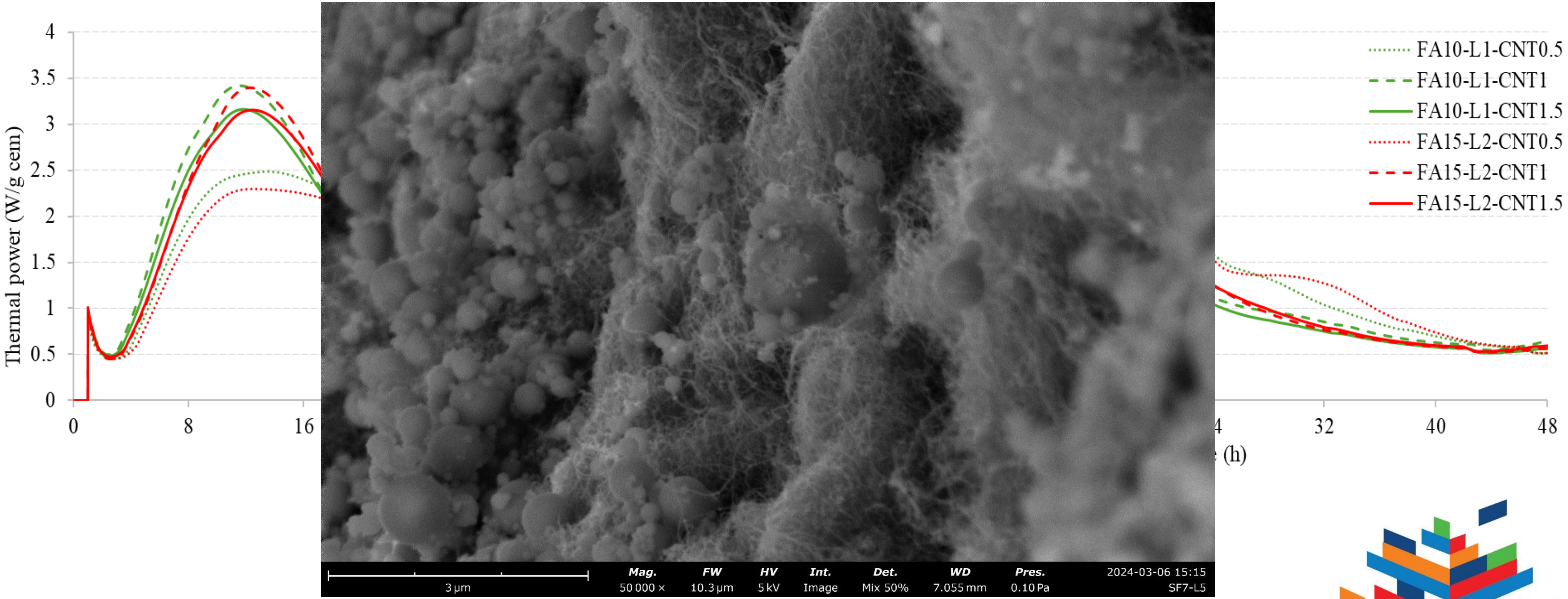
Microstructure

SF-L1 Cementitious Nanocomposite

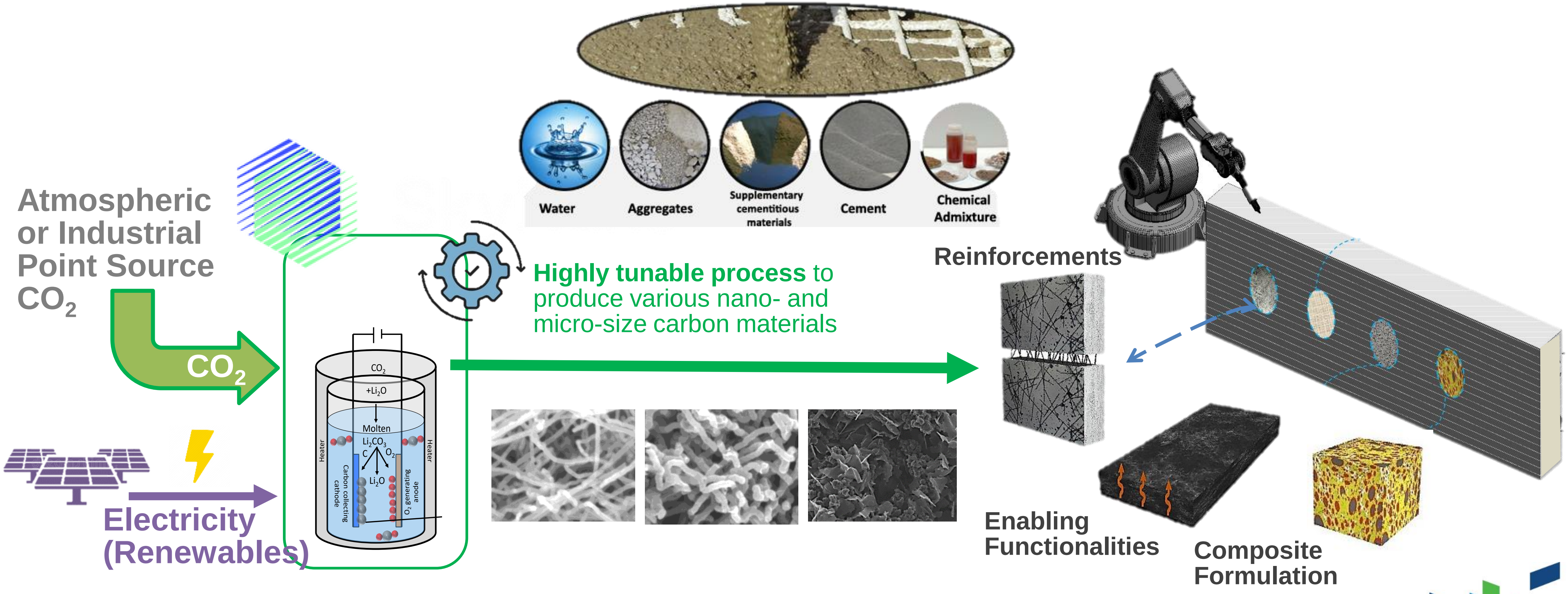




Synergistic Effect of SCM and PA Polymer

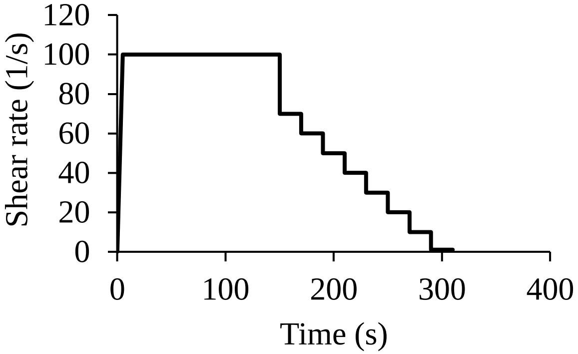


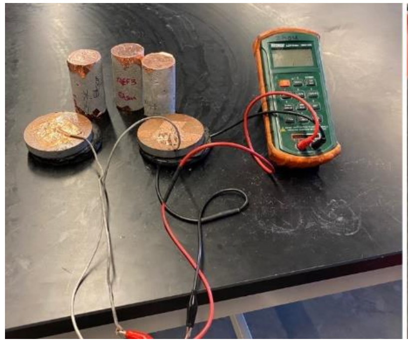
Utilizing CO_2-derived CNT in 3D Printable Cementitious Composites

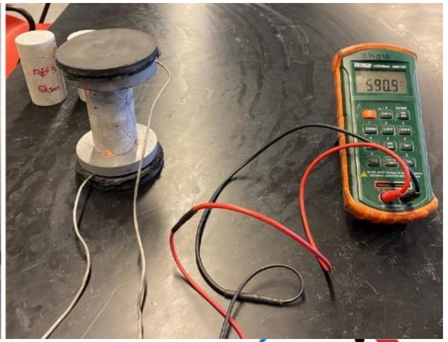


Utilizing CO_2-derived CNT in 3D Printable Cementitious Composites

Mix ID	Cement	Water	CNT	sand	SP	Cellulose Ether
Control	100	30	0	100	0.2	0.1
0.1CNT	100	30	0.1	100	0.2	0.1
0.2CNT	100	30	0.2	100	0.2	0.1
0.5CNT	100	30	0.5	100	0.2	0.1
1CNT	100	30	1	100	0.2	0.1

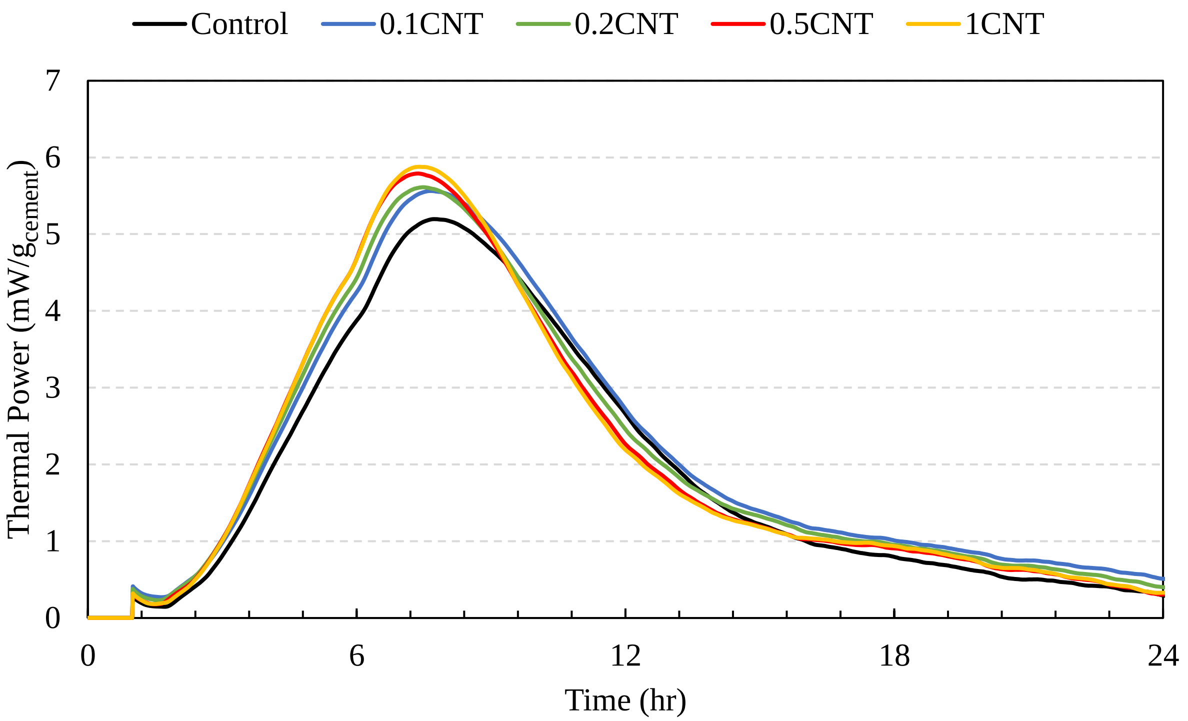


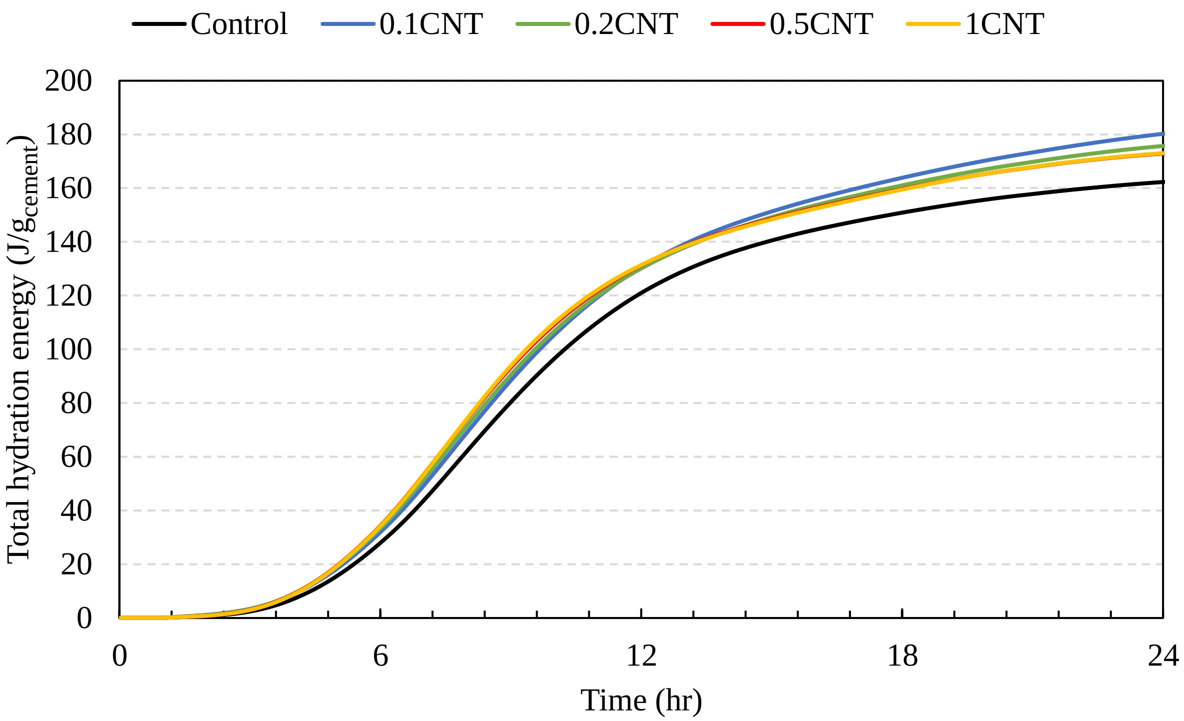




Evaluating CO_2-CNT in 3DP CC

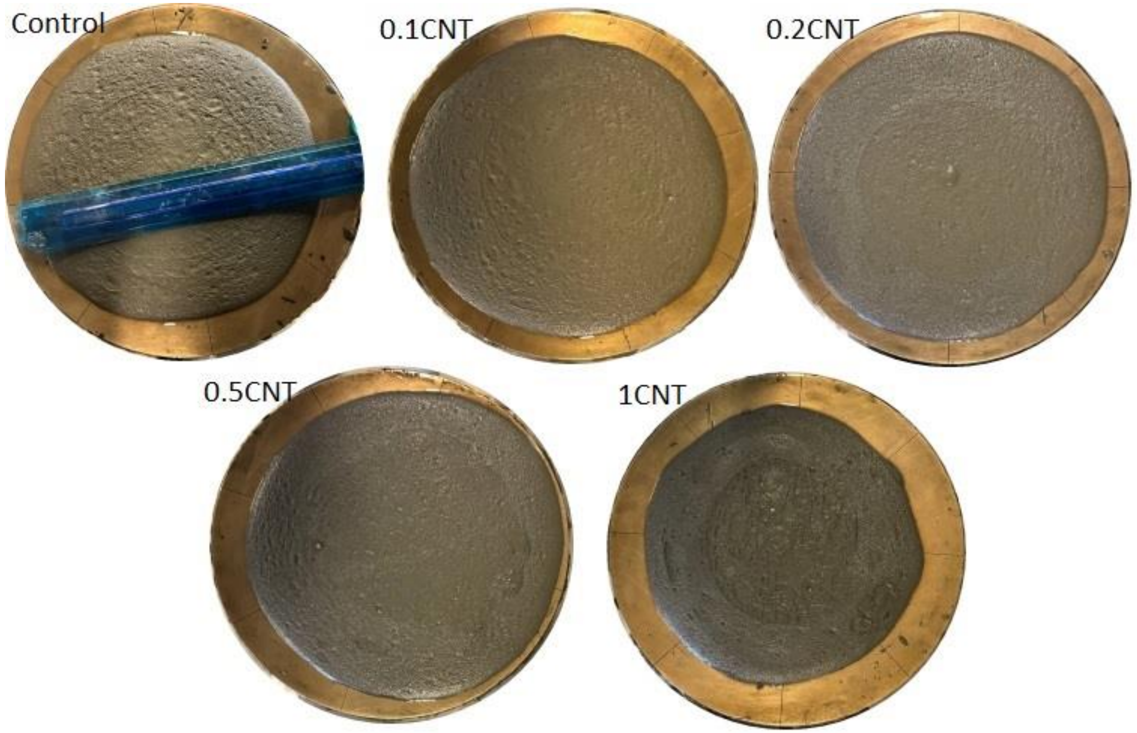
Hydration Kinetics

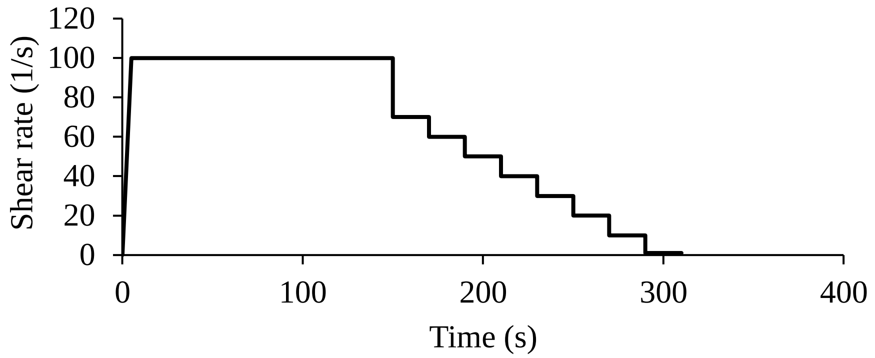


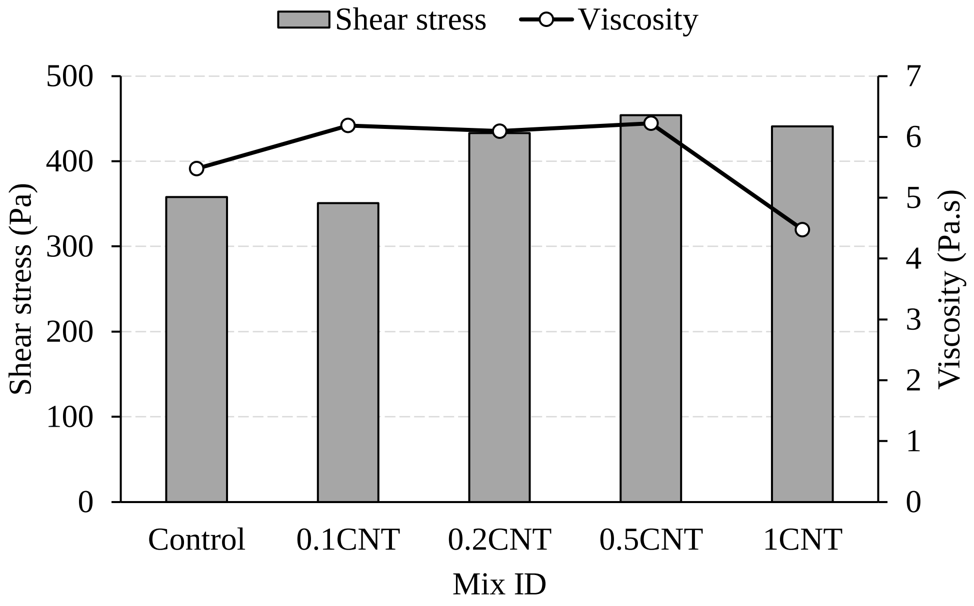


Evaluating CO_2-CNT in 3DP CC

Fresh Properties

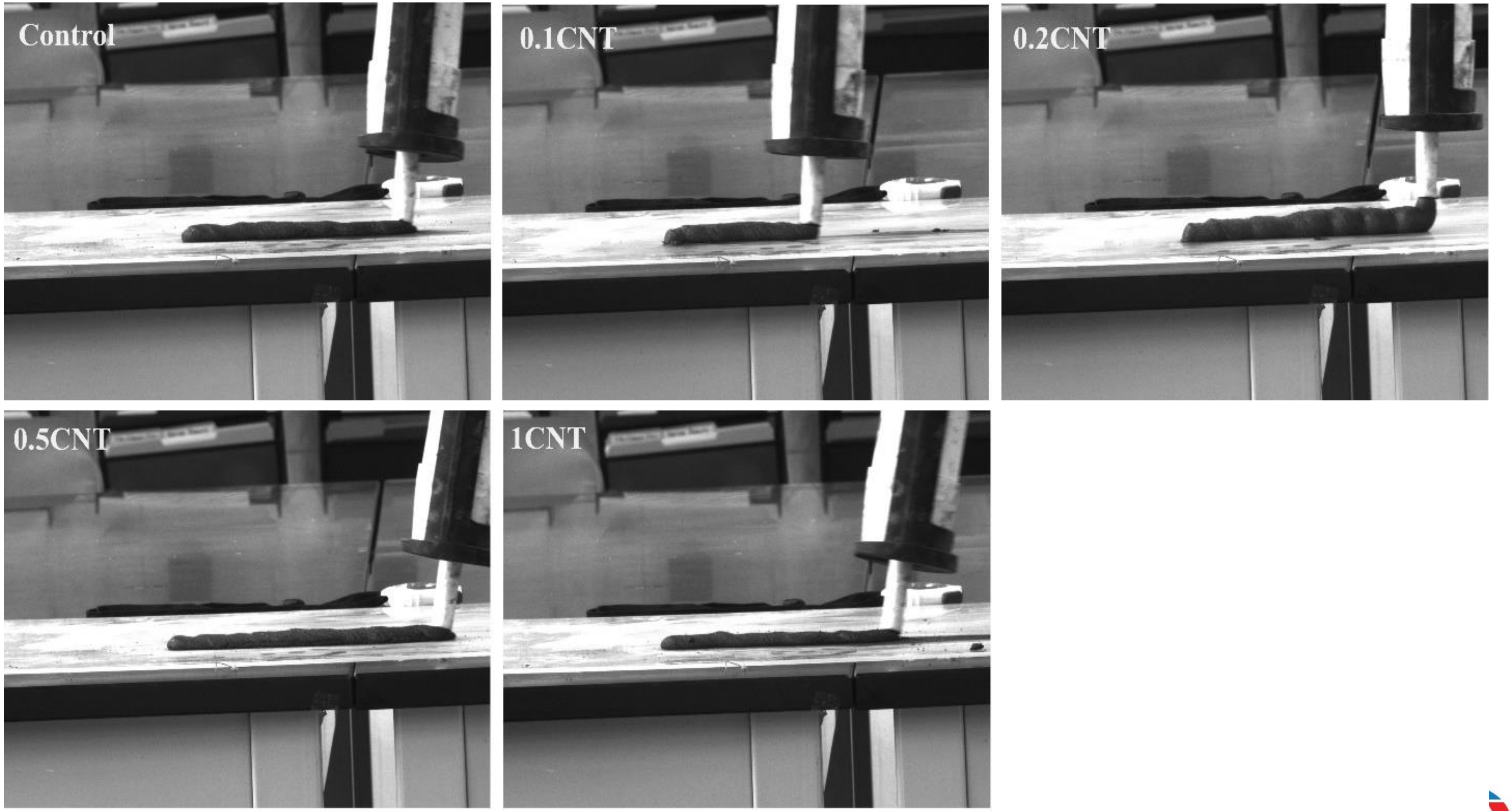






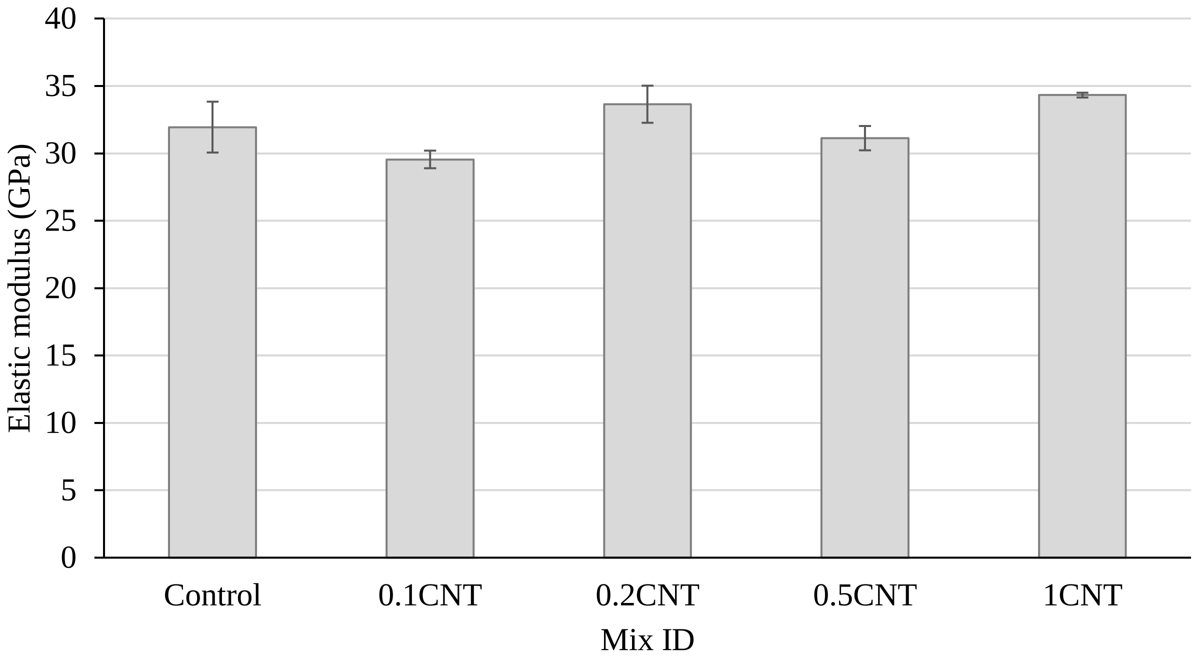
Evaluating CO_2-CNT in 3DP CC

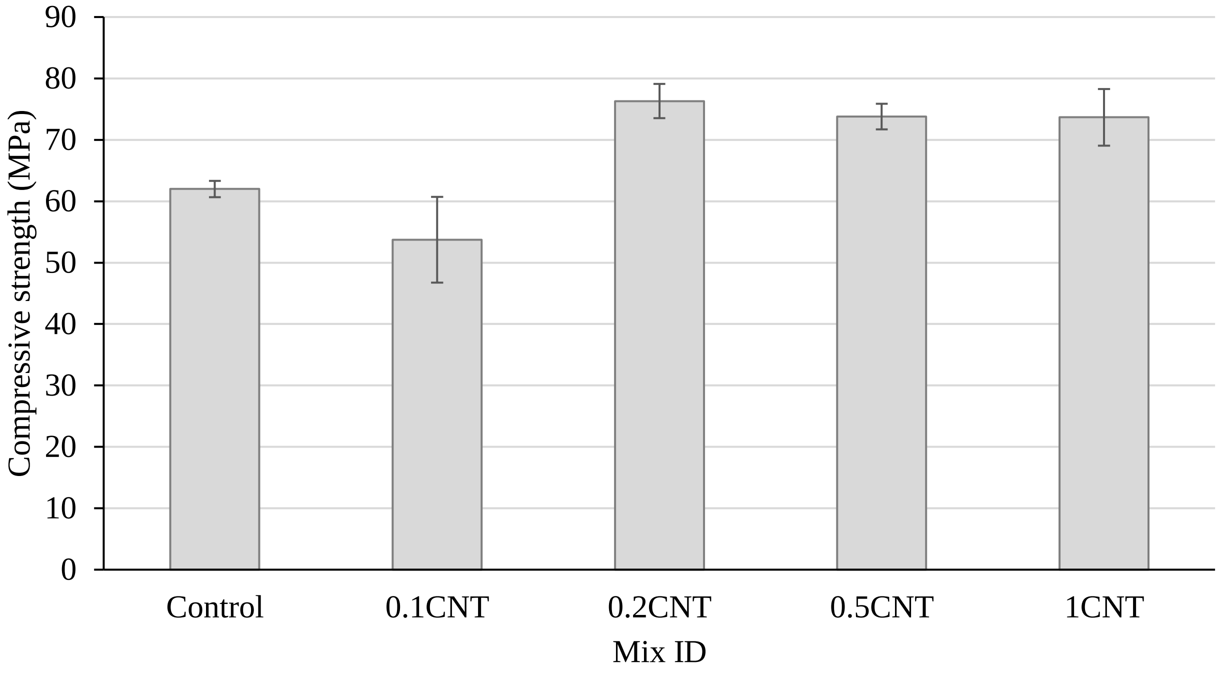
Printability



Evaluating CO_2-CNT in 3DP CC

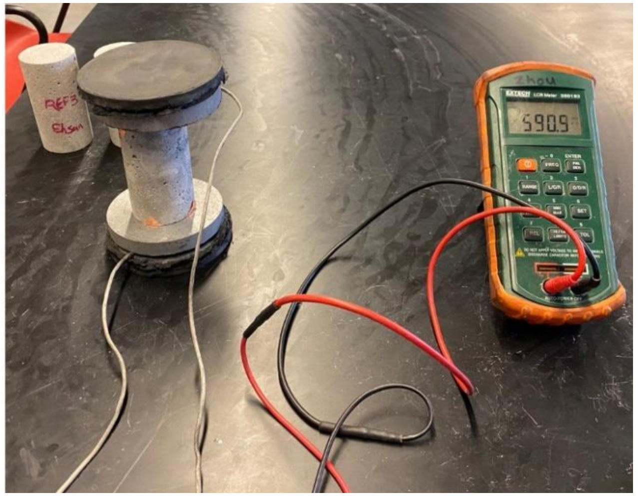
Mechanical Properties

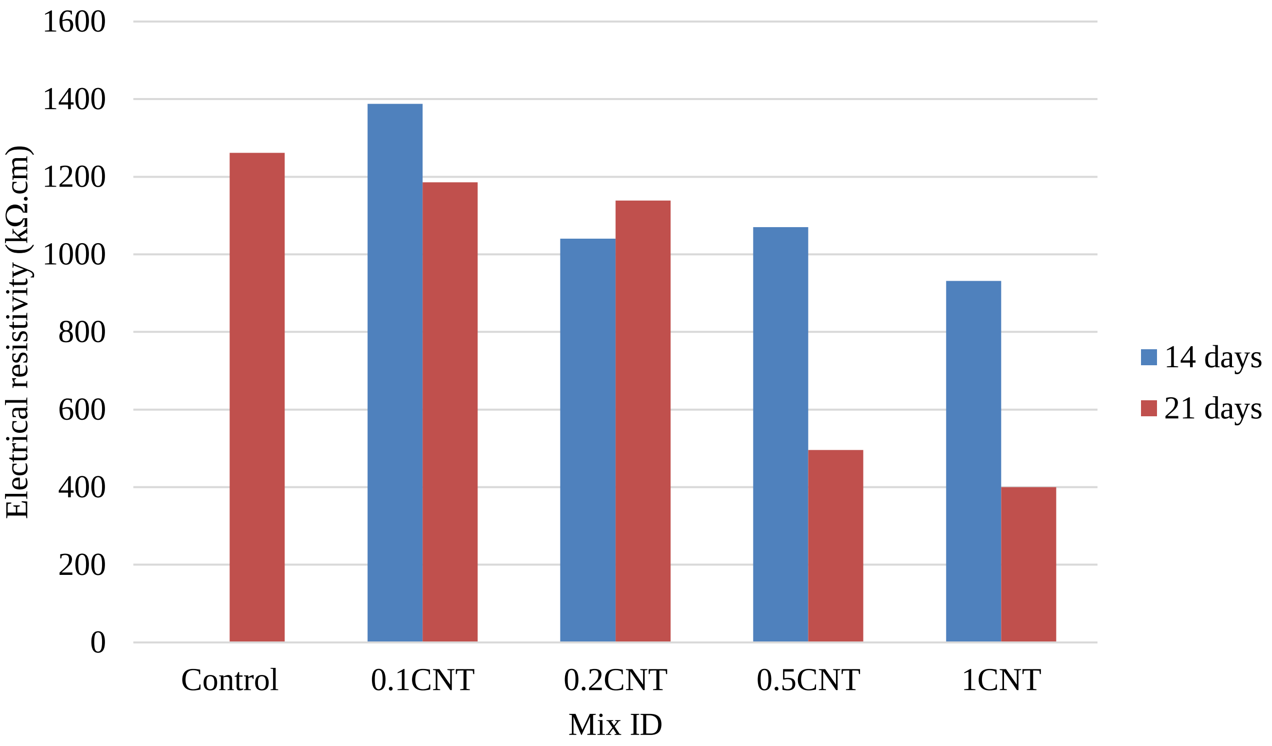




Evaluating CO_2-CNT in 3DP CC

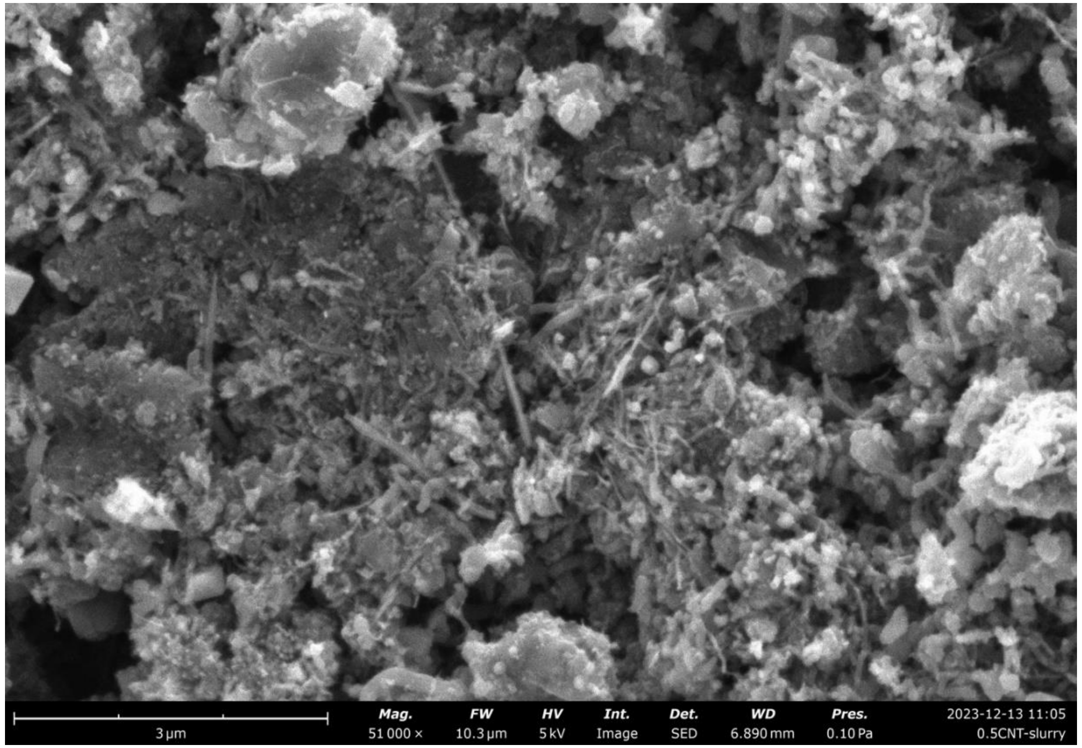
Electric Conductivity

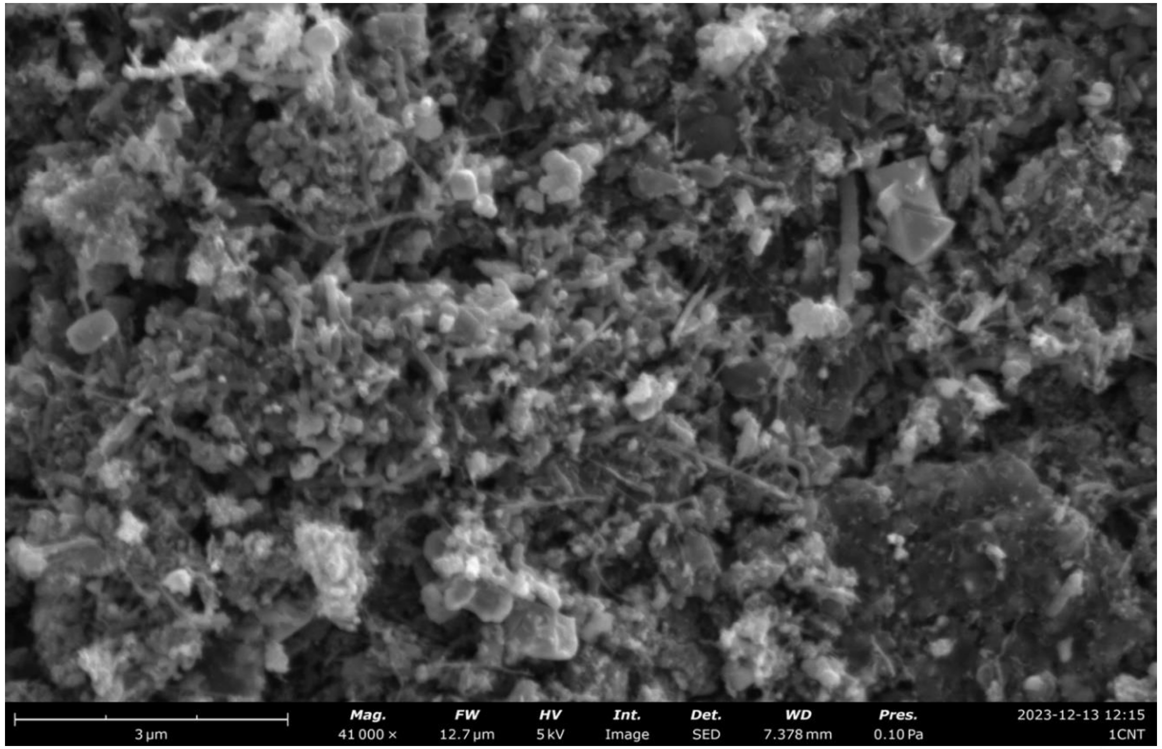




Microstructure

Microstructure





Conclusions

- A novel strategy was proposed to effectively disperse CNT and other forms of nanostructured carbon (e.g., graphene) in cementitious composites using SCMs as ‘carriers’
- The synergistic effects of SCMs, dispersants (e.g., surfactants), and PA latex was investigated.
- The feasibility of utilizing CO_2-derived CNTs in 3D printable cementitious composites was explored
- The effects of C-CNTs on hydration kinetics, fresh properties (e.g., rheology and flowability), hardened properties (mechanical and electrical), and printability are investigated.

Conclusion

This work is partially sponsored by the U.S. Department of Energy (DOE) Industrial Efficiency and Decarbonization Office (IEDO) and Office of Navel Research (ONR) through project N68335-23C-3047.

The authors would also like to acknowledge:

Dr. David Wood, SkyNano LLC
Dr. Chengqing Qi, Ash Grove
Dr. Peyman Zandifeaz, University of Tennessee Knoxville
Dr. Heather Willauear, US Naval Research Laboratory

THE WORLD’S GATHERING PLACE