



CONCRETE INNOVATIONS
Session 15
September 13th 2023

On the multifunctional future of concrete

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 Massachusetts Institute of Technology

 Civil and Environmental Engineering

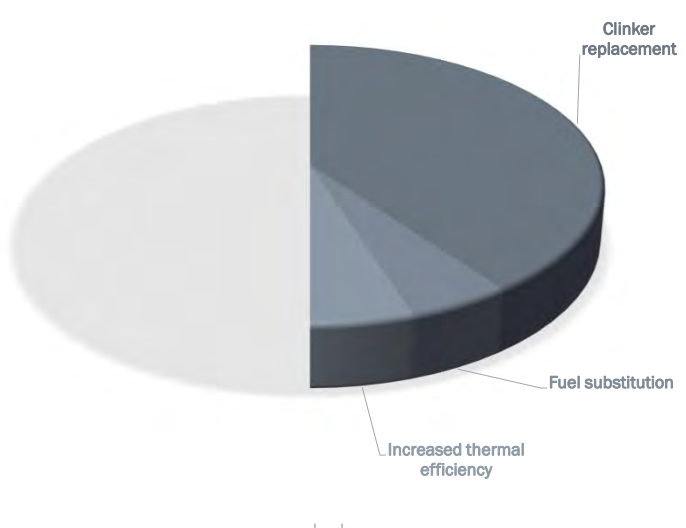
 Masic Lab @ MIT

 CSHub MIT CONCRETE SUSTAINABILITY HUB

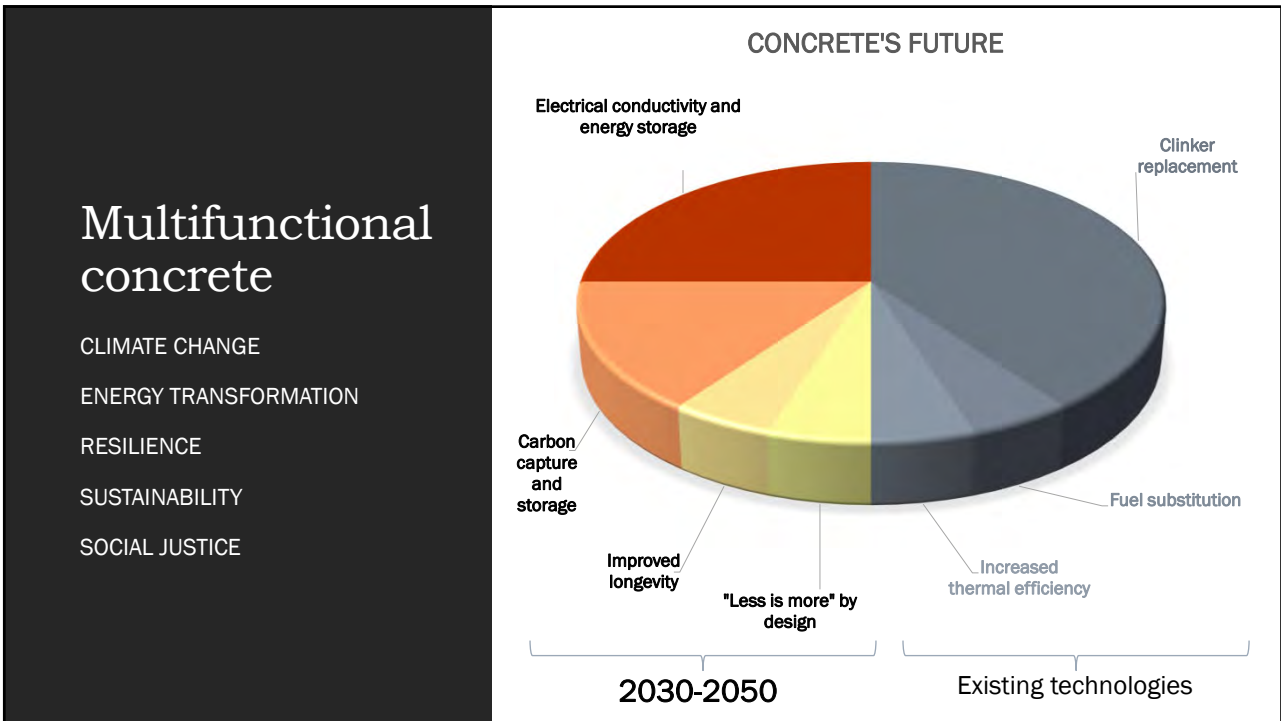
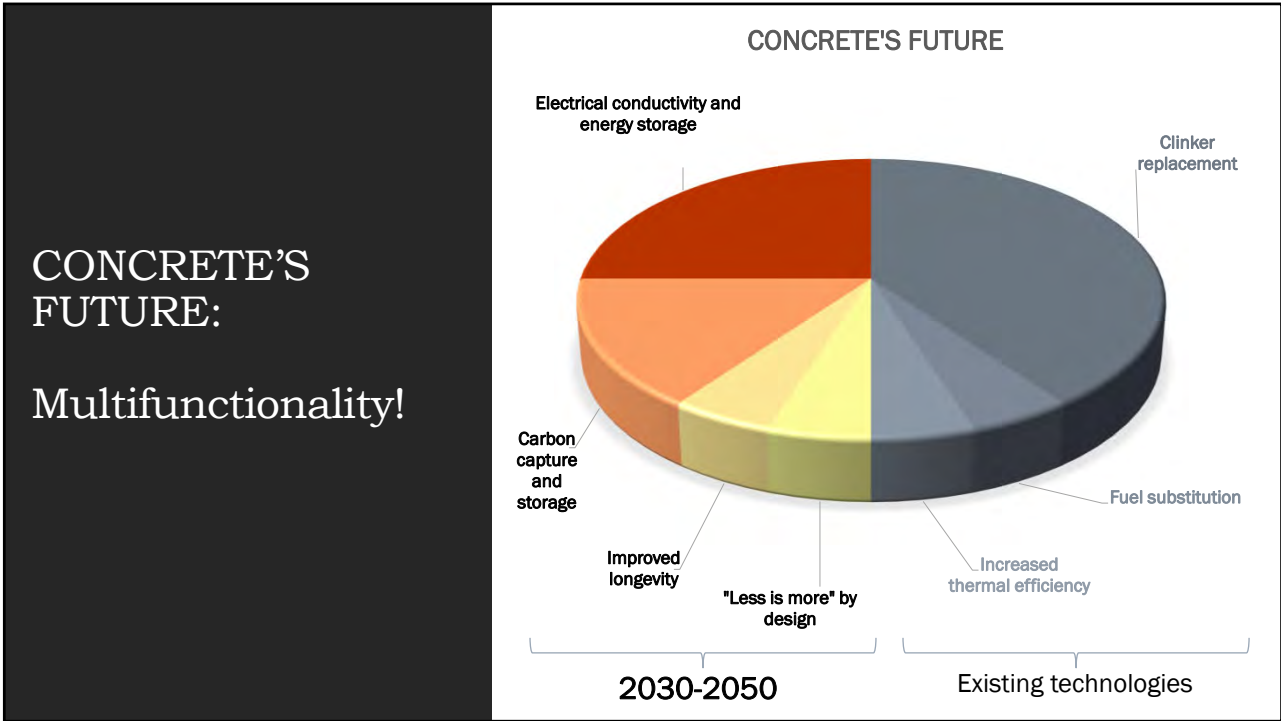
Why Materials Matter?

Portland Cement Association released in October 2021 the industries' 2050 carbon neutrality roadmap

CONCRETE'S FUTURE



Category	Strategy
2030-2050	Clinker replacement
	Fuel substitution
Existing technologies	Increased thermal efficiency

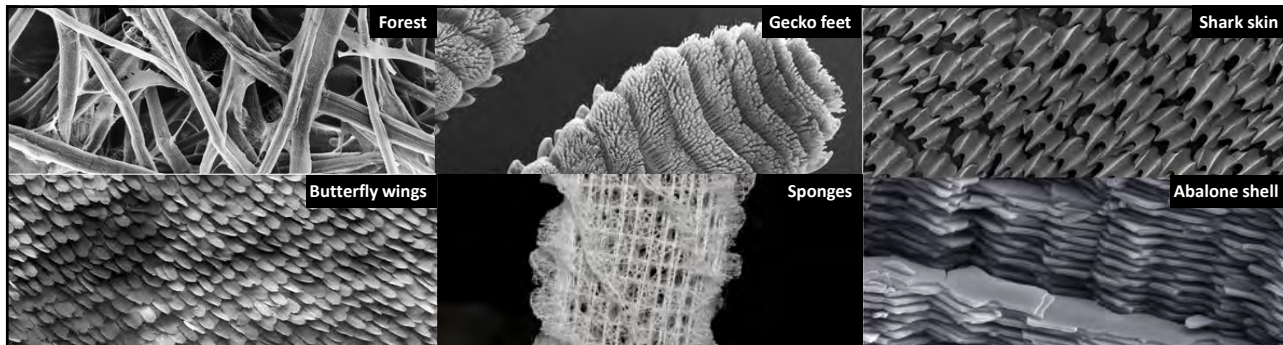




Biological materials/structures

- Organisms have evolved over millennia
- Hierarchical structure: from nano to macro
- Self-assembly
- Self-healing
- Synthesis under mild conditions (room temperature)

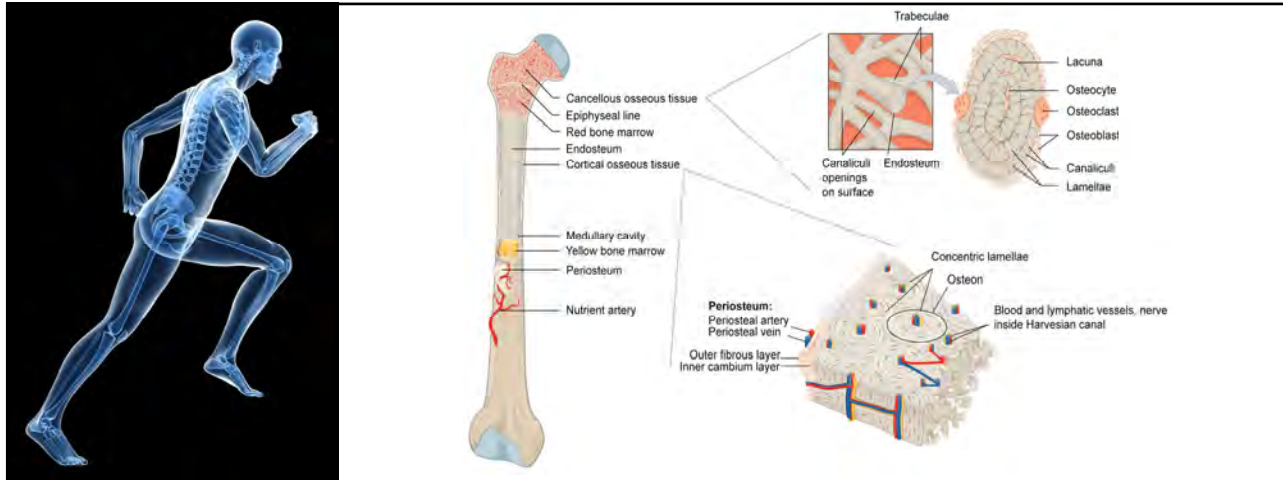
MULTI-FUNCTIONAL!



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MULTI-FUNCTIONAL!



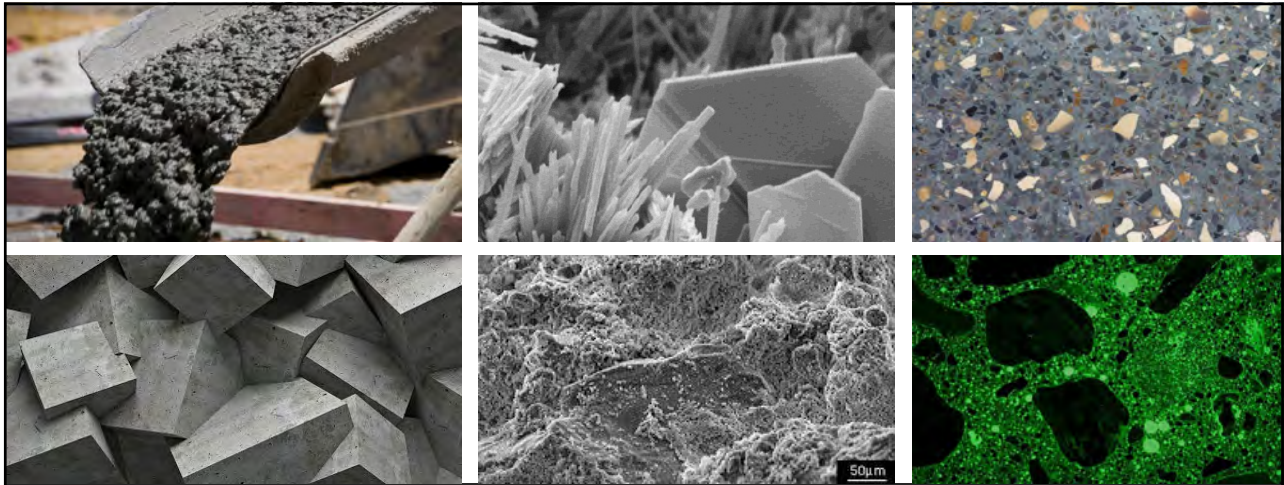
Bone as a MULTI-FUNCTIONAL material

Minerals=strength
blood vessels=energy supply
cells=self-healing
canaliculi = signaling

MULTI-FUNCTIONAL!

Concrete and multifunctionality

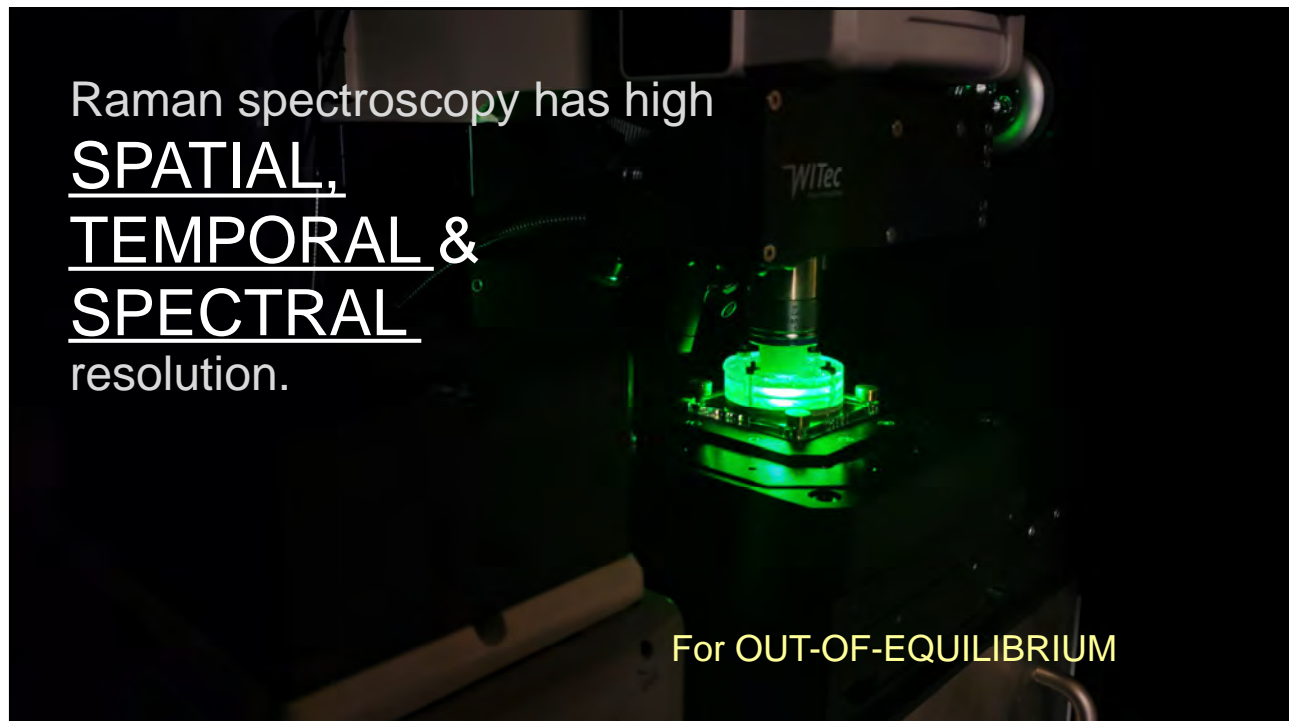




Capitalizing on cement chemistry: OUT-OF-EQUILIBRIUM

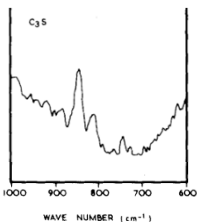
Concrete is a remarkably rich deposit of interesting and contemporary research questions, all contained in its ambiguities: granular or continuous?, liquid or solid?, crystalline or glassy?, smooth or rough?, “porous”, brittle or ductile?, material or process?

Henri Van Damme, CCR (2018)



+ Optical microscope, CCD

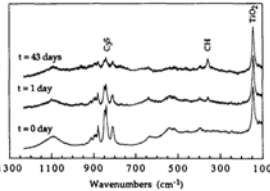
Clinker components



Bensted, JACeS (1976)
 Tarrida et al., ACBM (1995)

+ Confocal microscopy

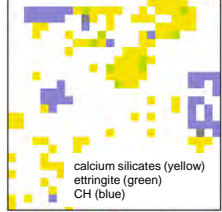
Hydration products



Liu and Sun, Front. Struct. Civ. Eng. (2016)

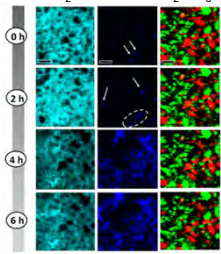
+ Underwater Raman

Raman mapping



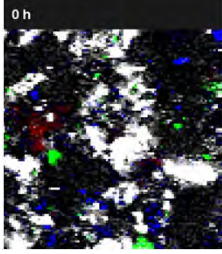
Torres-Carrasco et al., JRS (2019)

In-situ monitoring



Loh et al., Langmuir (2021)

Operando Real-world condition



Raman spectroscopy + Cement chemistry


Raman spectroscopy had limited applications due to its poor signal-to-noise ratio

Optical microscope added the **spatial resolution**

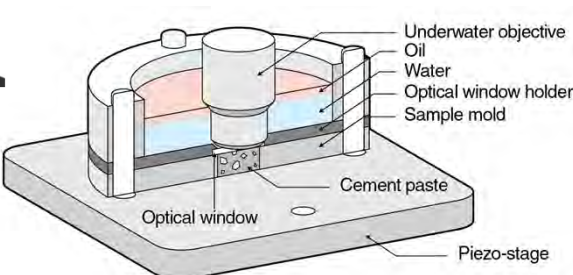
Confocal Raman micro-spectroscopy enabled fast acquisition → **temporal resolution**

Underwater Raman enabled monitoring in **real-world conditions** with **higher temporal resolution**

In-situ underwater Raman stage for cement hydration monitoring



Hyun-Chae Loh



- Allows *in-situ* Raman while the sample cures underwater
- Water dissipates heat and prevents sample damage
- Close to the real-world curing (hydration) conditions

Cement clinker	Reaction rate	Hydration products
C ₃ S (Alite)	Fast	C-S-H gel (50-60 vol%)
C ₂ S (Belite)		
C ₃ A (Celite)	Very fast	Ettringite, etc. (15-20 vol%)
Gypsum	Fast	
C ₄ AF (Ferrite)	Fast	

Water +

Notation
 C = CaO
 S = SiO₂
 H = H₂O
 A = Al₂O₃
 F = Fe₂O₃

Loh et al., Langmuir (2021) 12

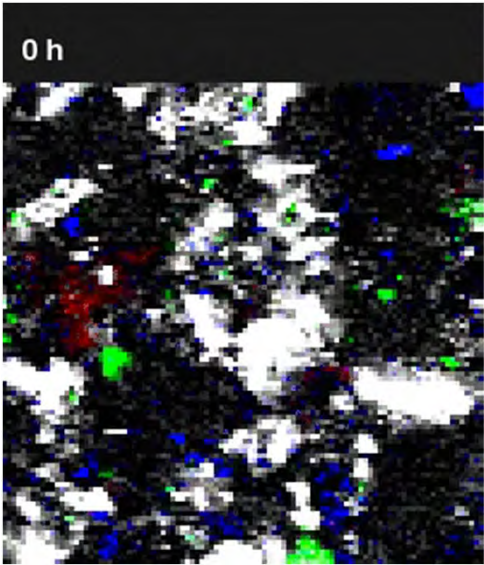
Raman spectroscopy + Cement chemistry

Underwater Raman enabled monitoring in **real-world conditions** with **higher temporal resolution**

+ Underwater Raman

Operando real-world condition OPC w/c=0.4

0 h



Loh et al., Langmuir (2021)

Schematic representation of early stage hydration

Reference sample

I **II** **III** **IV**

C₃S Pore water

Ca²⁺ DCH

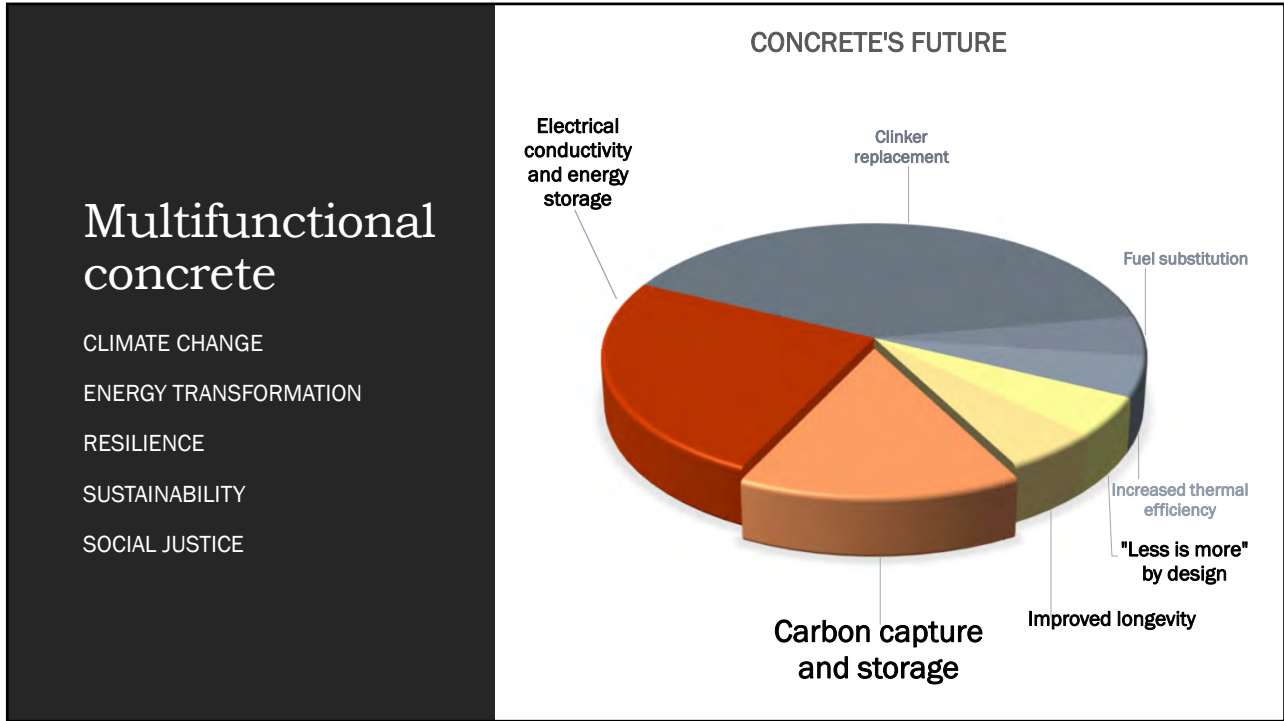
CH C-S-H

Loh et al., Langmuir (2021)

Early stages of cement hydration

Discovery of OUT-OF-EQUILIBRIUM/transient phases

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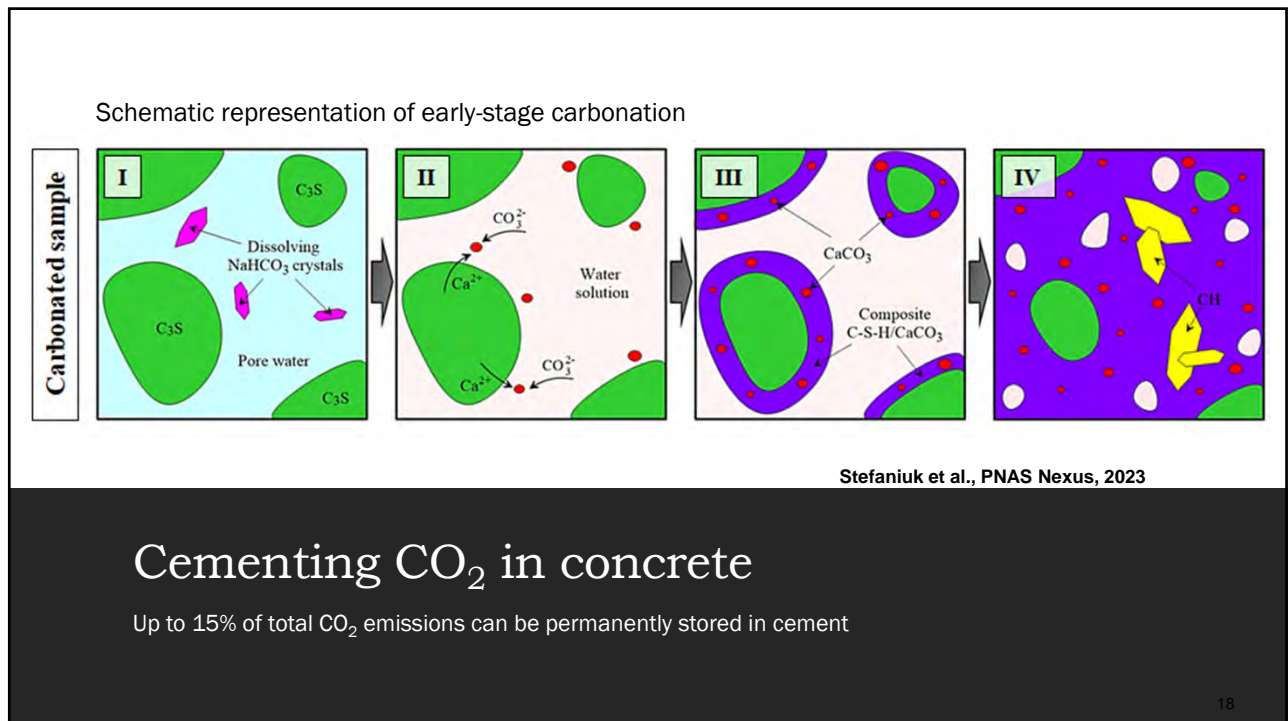
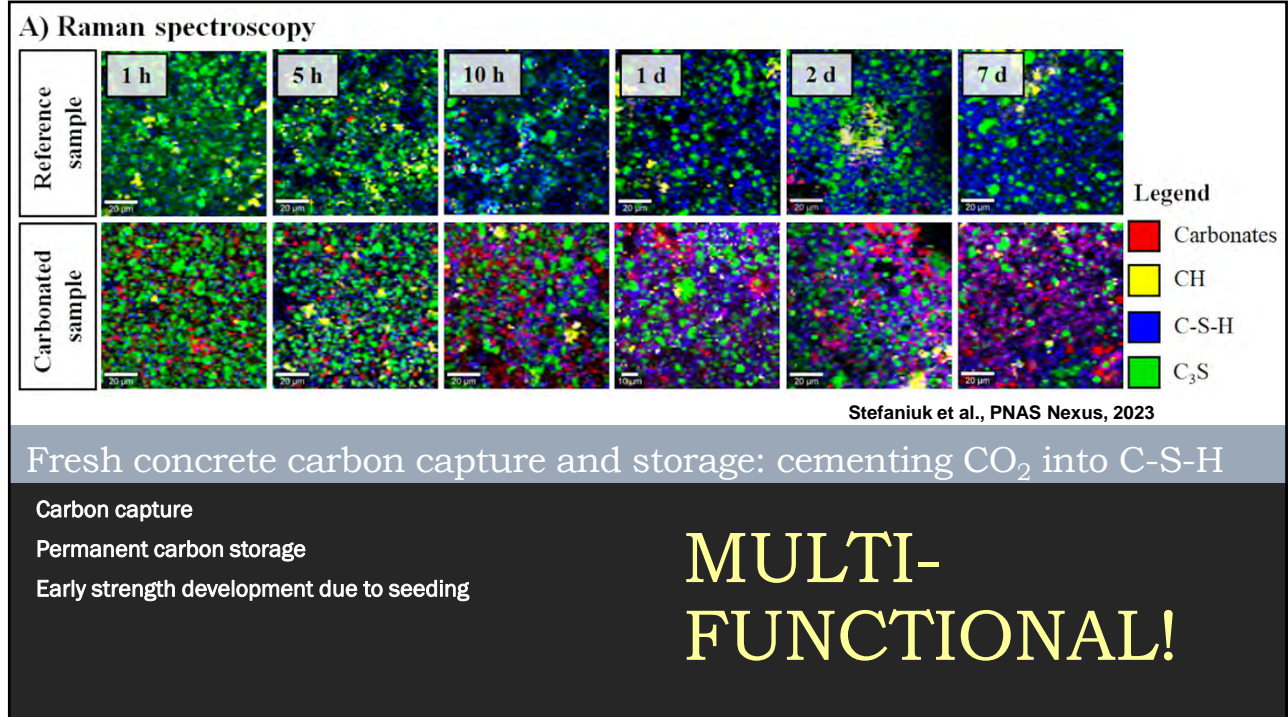
CO₂ uptake in concrete over time: problem or opportunity?

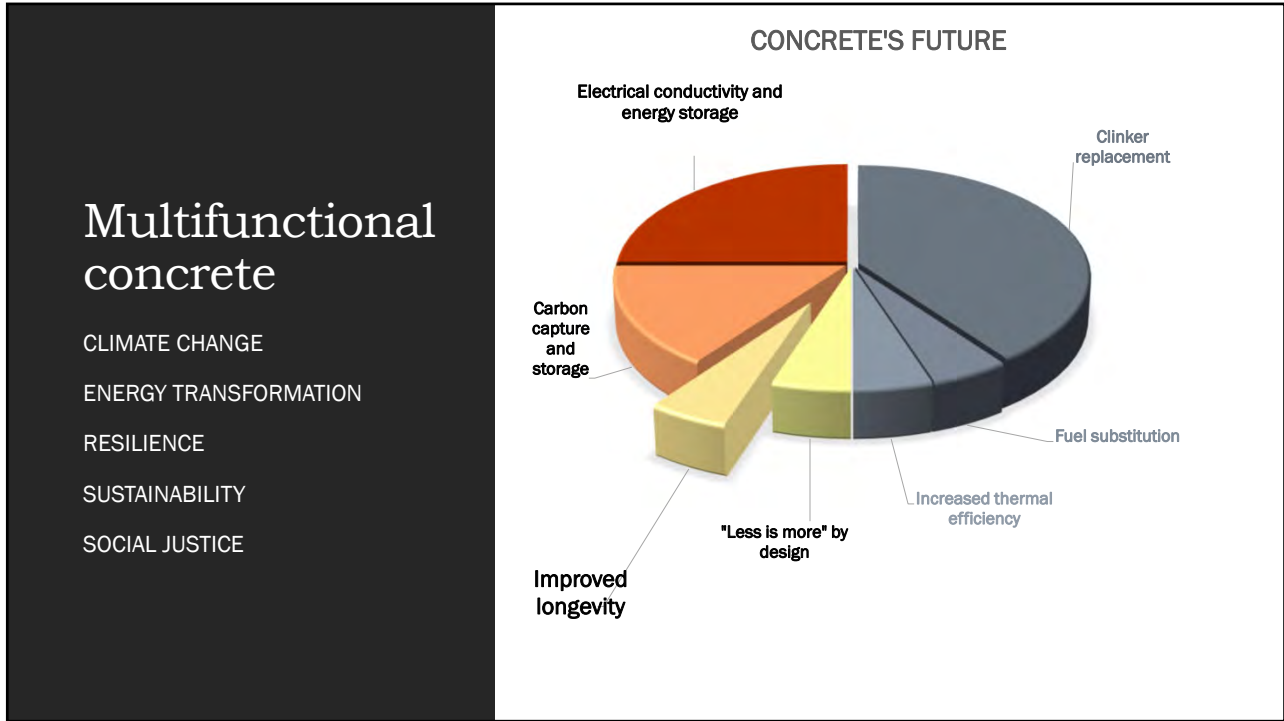
Late-stage carbonation leads to pH drop associated with reinforcement corrosion and concrete **spalling**.

But:
CARBONATION = CARBON SINK!

How to reconcile the two phenomena

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$$



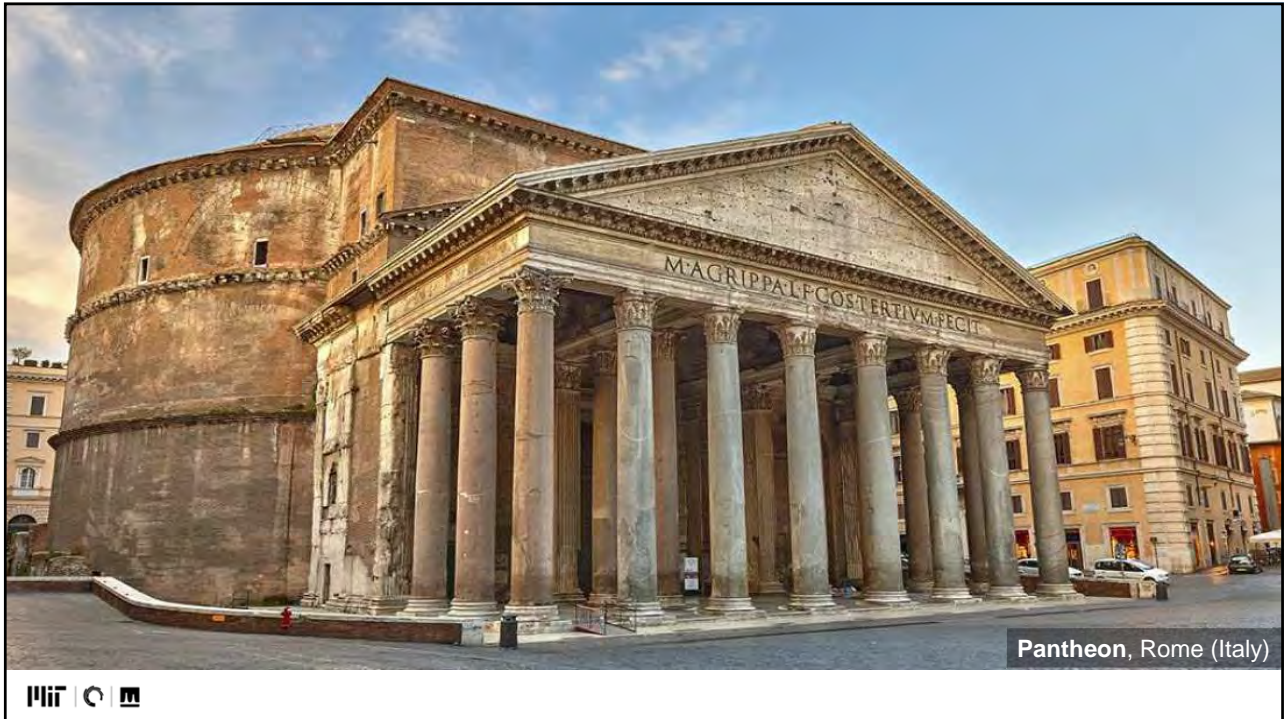




Roman aqueduct Pont du Gard

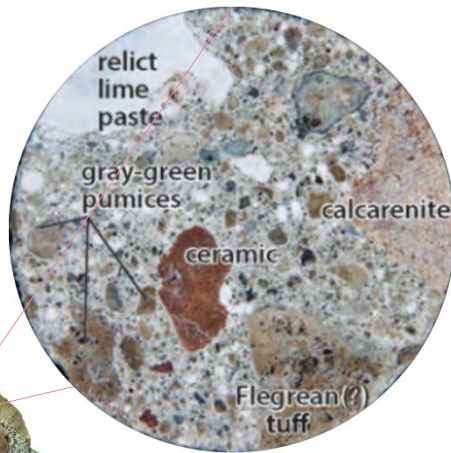
France 60 AD - today



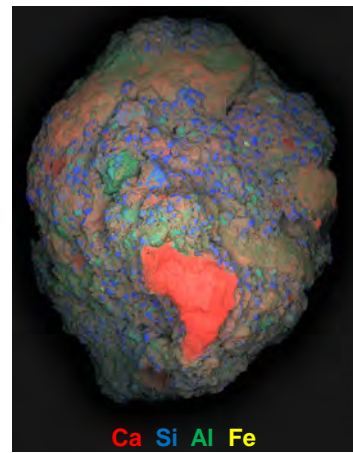


What are the origins of extreme long-term durability of ancient Roman concrete?

Roman concrete mix

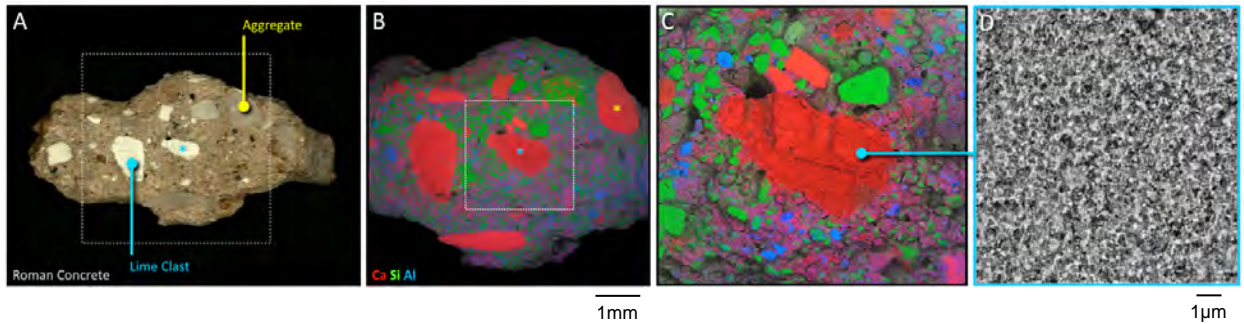


Jackson et al. (2016)



How relict lime clasts are formed in ancient samples and can they be the missing link in “self-healing” picture?

Roman concrete: Long-lasting, self-healing ancient materials



Hypothesis: Relict lime clasts serve as the long-term source of reactive calcium

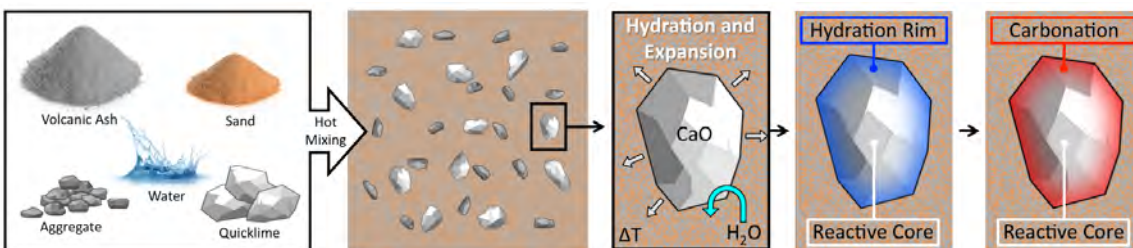


Linda Seymour



Seymour et al., Science Advances, 2023

Hot-mixing could create low-humidity conditions in lime clasts



Hot mixing
using
quicklime

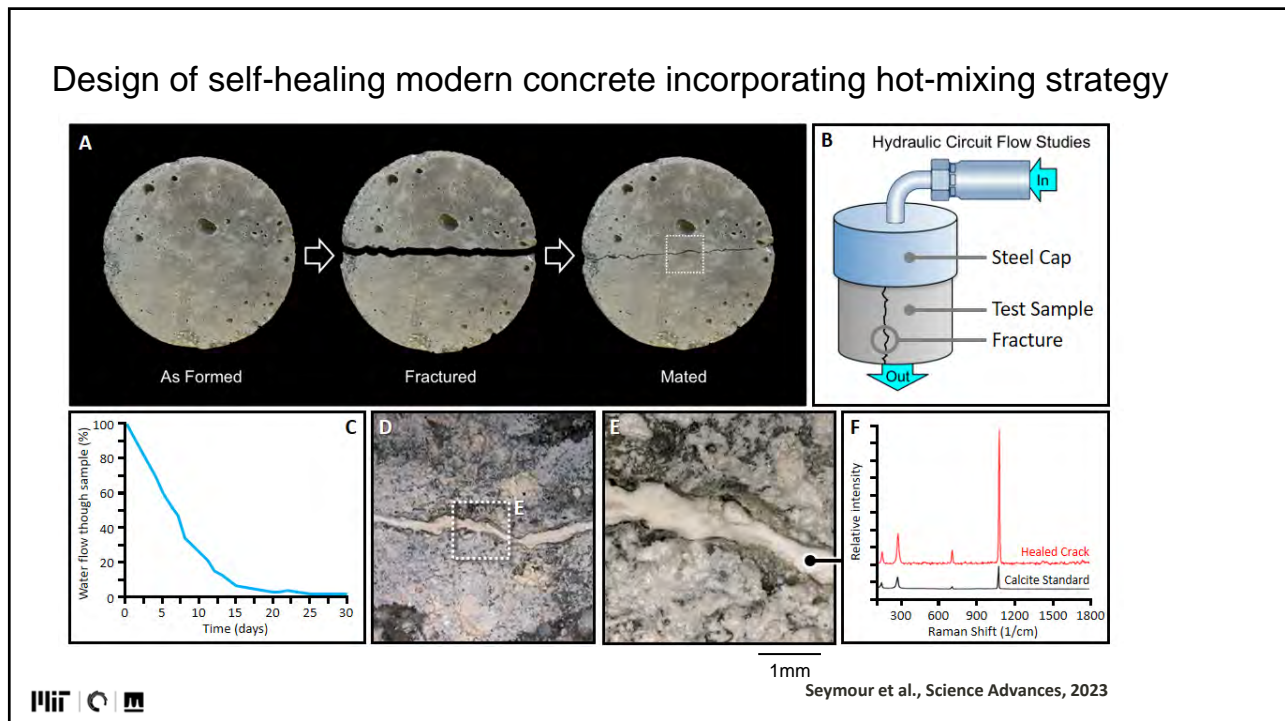
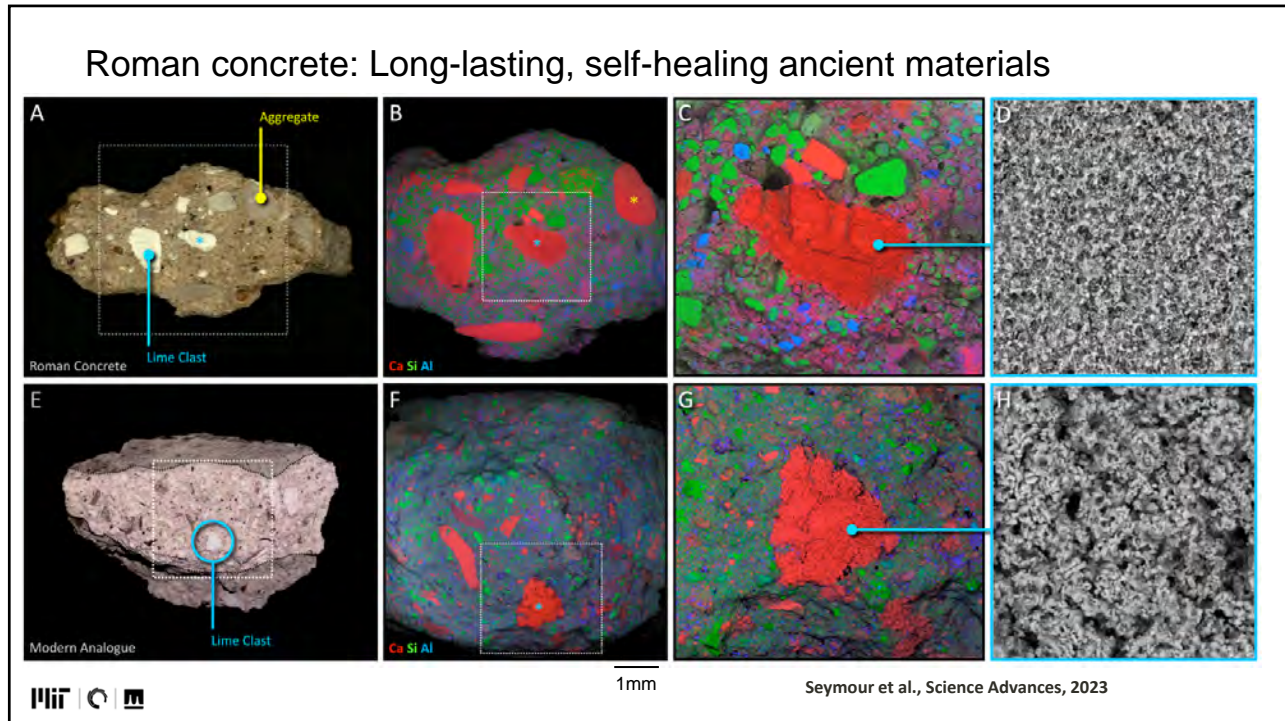
Exothermic hydration of quicklime in the mortar:

- Creates low-humidity conditions around lime particles preventing the dissolution.
- Promotes and accelerates hydraulic reactions (solving the issue of Roman concrete setting time)



Seymour et al., Science Advances, 2023

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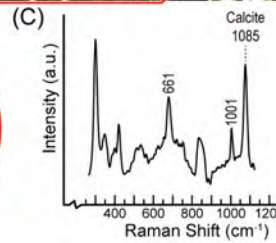
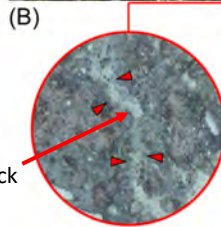
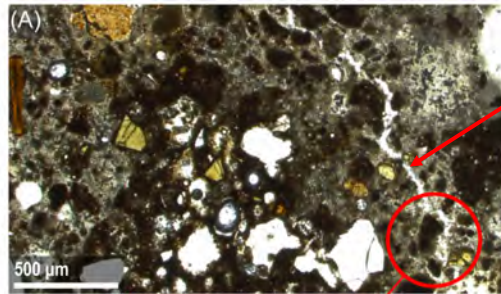
2,050-year-old Roman tomb offers insights on ancient concrete resilience



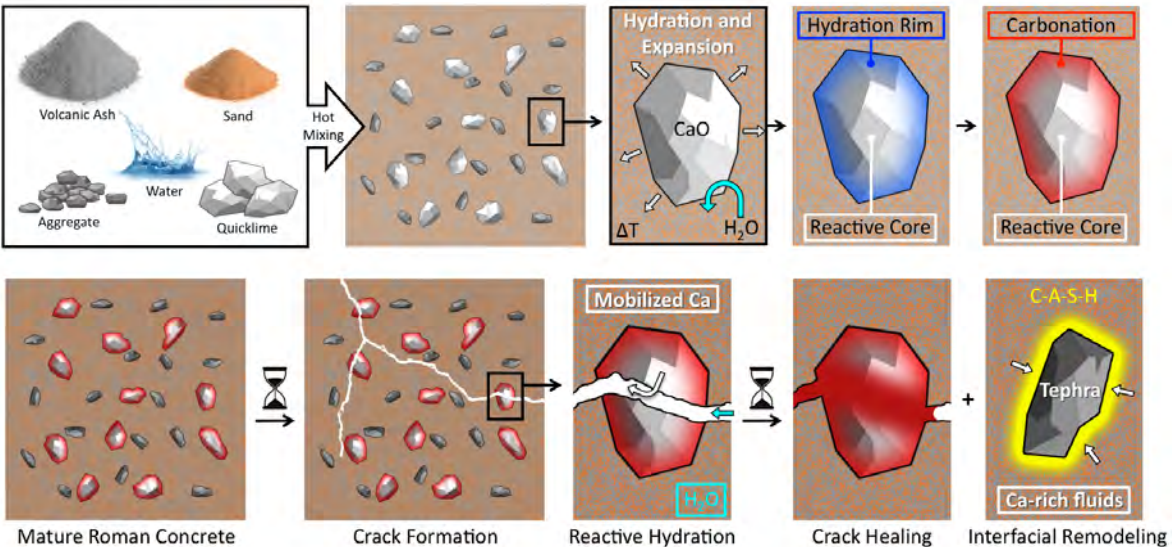
Linda Seymour



Seymour et al., JACerS, 2021



Self-healing mechanism



Seymour et al., Science Advances, 2023



Media coverage

Science Advances

Hot mixing: Mechanistic insights into the durability of ancient Roman concrete

Overview of attention for article published in Science Advances, January 2023


220 news outlets	5 Wikipedia pages	6 Dimensions	99 Mendeley
20 blogs	5 Redditors		
506 tweeters	2 video uploaders		
2 Facebook pages			

The MIT News article: **Riddle solved: Why was Roman concrete so durable** is the most-viewed article ever to appear on MIT News.

The Guardian


'Self-healing' Roman concrete could aid modern construction, study suggests

Research finds secret of durability of buildings such as the Pantheon could be in the techniques used at the time




REUTERS

Scientists chip away at how ancient Roman concrete stood test of time



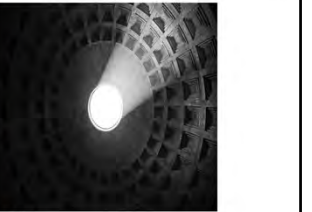
CNN

Mystery of why Roman buildings have survived so long has been unraveled, scientists say



WIRED

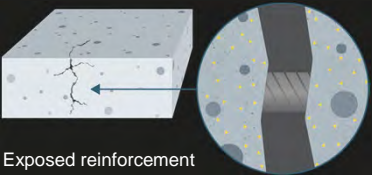
The Secret to Making Concrete That Lasts 1,000 Years



MIT | C | M

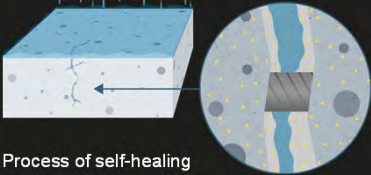
DMAT
PERFORMANCE MATTERS

MICROFRACTURE



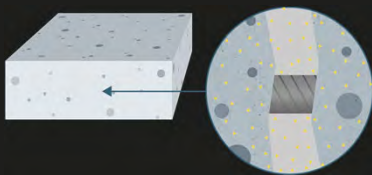
Exposed reinforcement

WATER INFILTRATION



Process of self-healing activated by water

SEALED CRACK

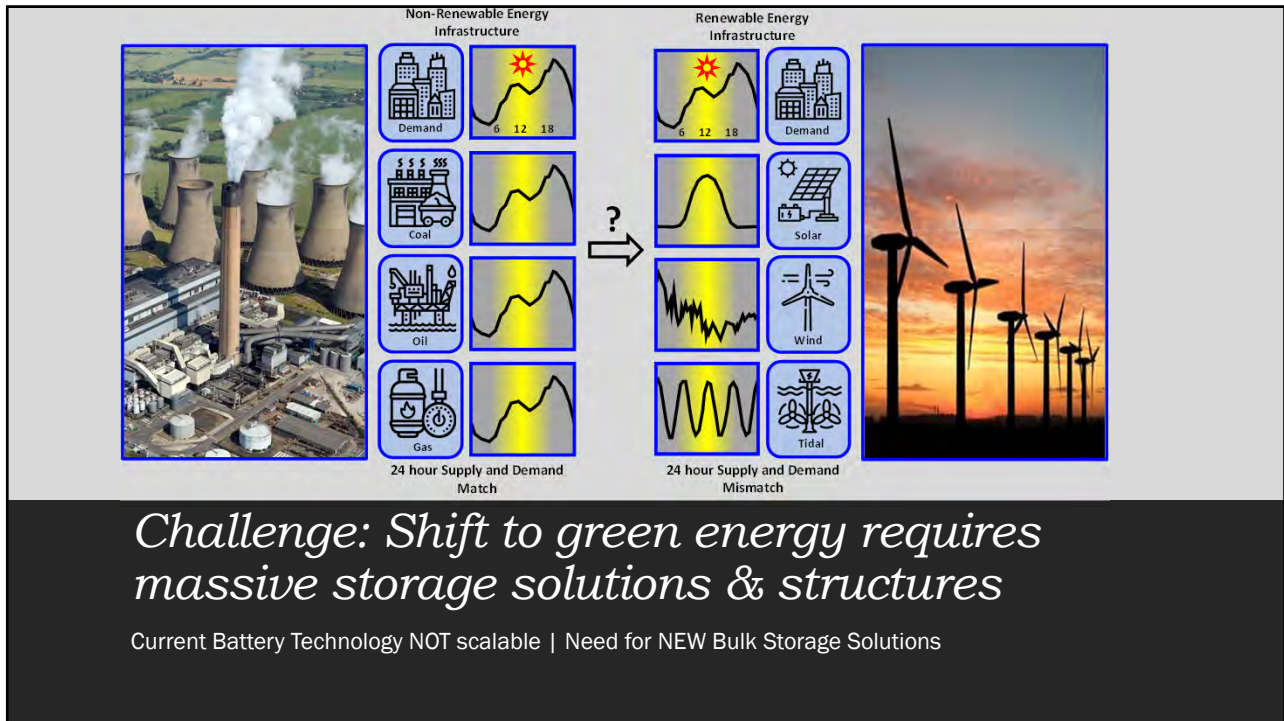
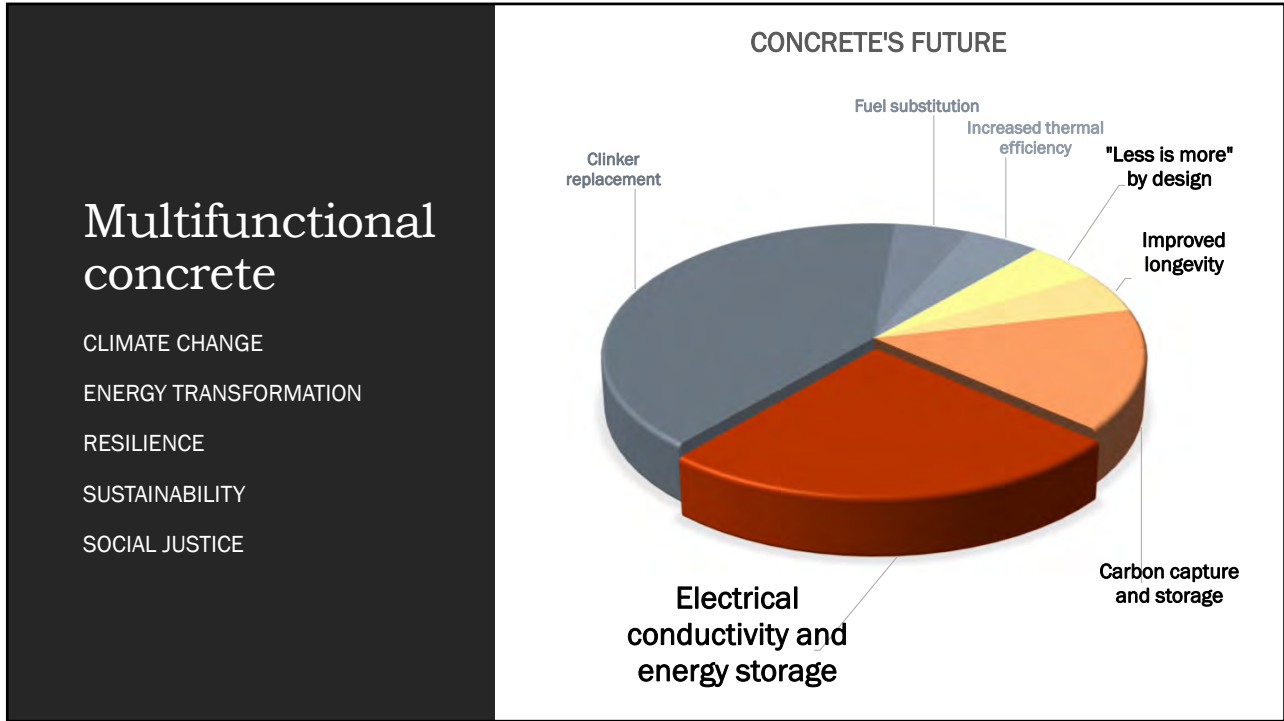


Fractures up to 0,6 mm

Technology made of inexpensive and readily available material precursors

Roman-inspired self-healing concrete (50% lifespan extension at 50% cost reduction compared to other self-healing solutions)

MIT | C | M



Electron Conductivity? –

*Get Real: Concrete is Strong,
Everybody can make it... & it has a
huge environmental footprint.*

But it's an Insulator –

IS THERE ANY CHANCE TO ADD THIS FUNCTIONALITY TO
CONCRETE?

Know how: a proper dispersion of nCB particles is the key

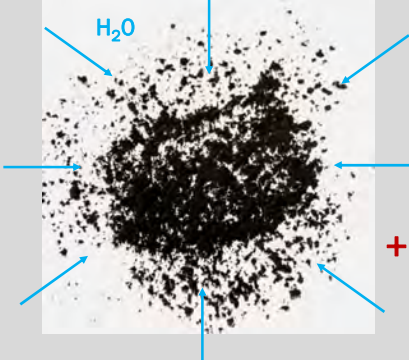
How to mix and disperse hydrophobic nCB particles in water?



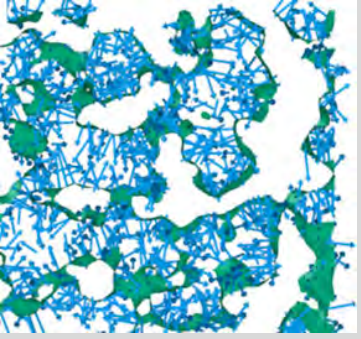
[1] Pellenqu et al. (2018-2020). Electron conducting carbon-based cement, method of making it as supercapacitor. Patent.



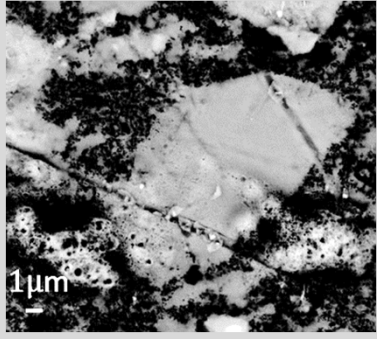
Hydrophobicity of Carbon
Leads to clumping



Hydrophilicity of Cement leads to
Hydration (solid formation w water)



Competition of (1) and (2) lead to
Volumetric Wire



Percolation of a Volumetric Wire through a load-bearing cement skeleton

A Physical Chemistry Driven Process = Highly Repetitive

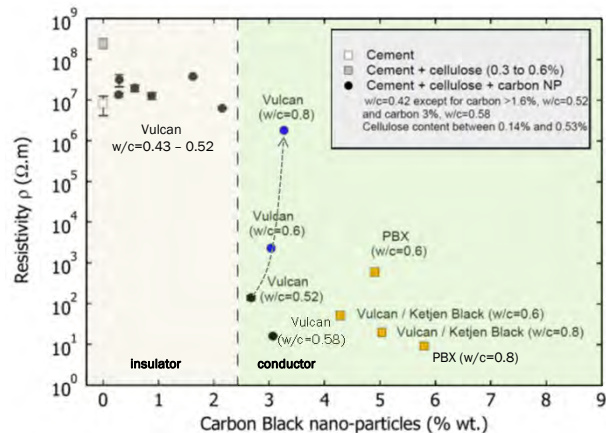
Patent pending

PROPERTY:

Electron
Conductivity

At 2-3%wt VOLUMETRIC WIRE
percolates through the solid
skeleton

Electron Conductivity ~ 1/Resistivity



Patent pending

Opportunities of electron conducting carbon concrete ec^3

Resistivity vs. cost [1]

Freeze-thaw resistance
(Hydrophobicity)
Longevity of structures

Self-heating
(Joule effect)
De-icing bridges, sidewalks, airport runways, etc.
Radiant floor heating

ec^3 (electron conducting concrete)

Energy storage
(Structural supercapacitor)
Renewable energy buffer
Autonomous housing
Smart charging roads

HPEM* shielding
(Faraday cage effect)
Military structures
Data storage
Human health

References
 [1] <http://www-materials.eng.cam.ac.uk>
 [2] <https://www.militaryaerospace.com/power/article/14072339/>
 [3] The New York Times; Photographs by SCIEPRO and mikromani6, via Getty Images

Cement + Carbon + Porosity = Supercapacitor

Battery = Change electrical energy into chemical energy


Supercapacitor = Electrical Charge stored in a shell around the carbon (no chemical reaction)

HOW DOES A SUPERCAPACITOR WORK?

CONCRETE AS “structural” SUPERCAPACITOR:

- Porosity of cement paste (for Electrolyte)
- Carbon-Cement Composite for Energy Storage

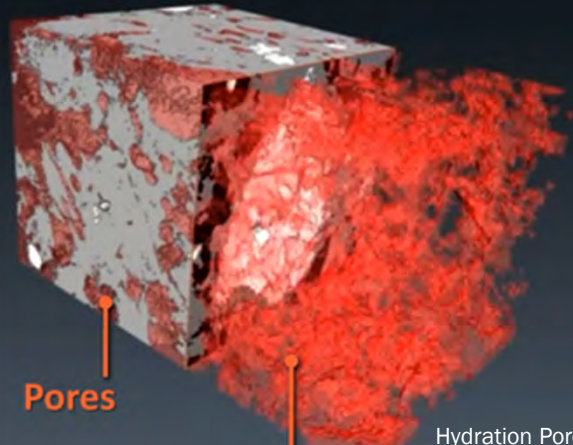
We use the “natural” porosity of cement as transport porosity (electrolyte)



Transport Porosity

Patent pending

How does it work?

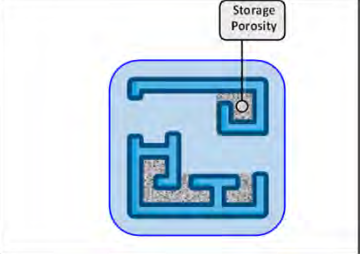


Pores

3D Pore Network

Hydration Porosity In a normal cement paste

We use the nanoporosity of carbon black for charge storage

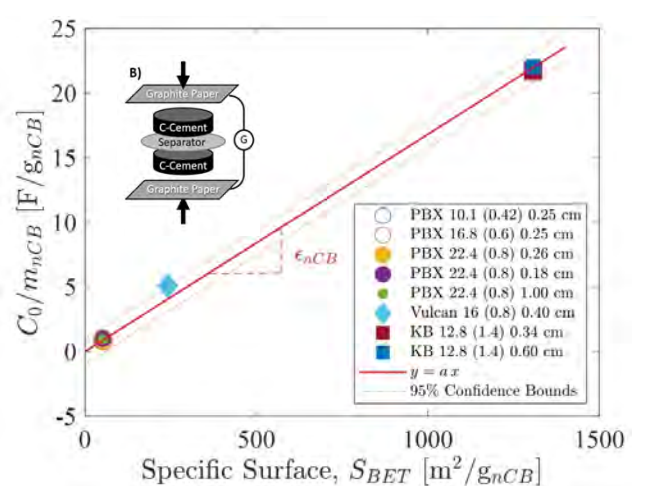


Storage Porosity

Patent pending

How does it work?

Energy Storage Capacity Increases linearly with surface area of disordered nanocarbon.



C_0/m_{nCB} [F/g_{nCB}]

Specific Surface, S_{BET} [m²/g_{nCB}]


~ ENERGY STORAGE CAPACITY

Carbon Black	Specific Surface (m ² /g)	Thickness (cm)
PBX 10.1	0.42	0.25
PBX 16.8	0.6	0.25
PBX 22.4	0.8	0.26
PBX 22.4	0.8	0.18
PBX 22.4	0.8	1.00
Vulcan 16	0.8	0.40
KB 12.8	1.4	0.34
KB 12.8	1.4	0.60


B) Graphite Paper
 C-Cement
 Separator
 C-Cement
 Graphite Paper

$y = ax$
 95% Confidence Bounds

For more details see the recent paper in PNAS
(Proceedings of the National Academy of Sciences)

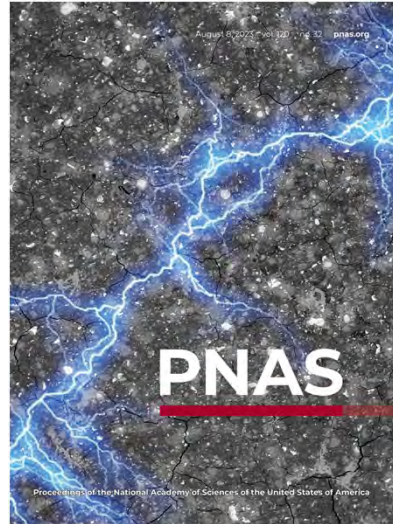
RESEARCH ARTICLE | ENGINEERING | 

Carbon–cement supercapacitors as a scalable bulk energy storage solution

Nicolas Chanut, Damian Stefaniuk, James C. Weaver, Yunguang Zhu, Yang Shao-Horn, Admir Masic, and Franz-Josef Ulm  [Authors Info & Affiliations](#)

Edited by Yonggang Huang, Northwestern University, Glencoe, IL; received March 23, 2023; accepted June 22, 2023

July 31, 2023 | 120 (32) e2304318120 | <https://doi.org/10.1073/pnas.2304318120>



PNAS cover by James C. Weaver



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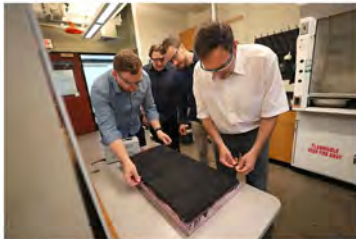
Increasing global interest

The Boston Globe

Is cement the solution to storing renewable energy? Engineers at MIT think so.

Supercapacitors could make powering your home and electric vehicles easier and more sustainable

By [Nancy Fisher](#) | [Climate Change](#) | [Environment](#) | July 31, 2023



At the Massachusetts Institute of Technology, from left to right, Professor Admir Masic, visiting professor James Weaver, assistant Professor Nicolas Chanut, and Professor Franz-Josef Ulm examine a supercapacitor, which can store renewable energy using cement, water, and carbon. (S.2304318120) (12/31/23)

MIT researchers say they have developed an energy storage system that could allow homes to store their own power without external batteries and highways to charge electric vehicles as they traveled on the road — no charging stations needed.

And the best part, the researchers say, is their system, called a supercapacitor, could be built from three of the world's most abundant materials: cement, water, and carbon.

The researchers, who work at MIT's Concrete Sustainability Hub, recently reported their breakthrough in the *Proceedings of the National Academy of Sciences*, a peer-reviewed scientific journal. They detailed how a tiny prototype — around a centimeter wide and a millimeter thick — powered an LED light at least 10,000 times.

WORLD ECONOMIC FORUM

World Economic Forum
4,764,058 followers
Ad · 

These scientists are using widely available materials to create an alternative to batteries

Learn more about sustainable battery chains: <https://ow.ly/phaL50P9khe>

Massachusetts Institute of Technology



MIT News

ON CAMPUS AND AROUND THE WORLD

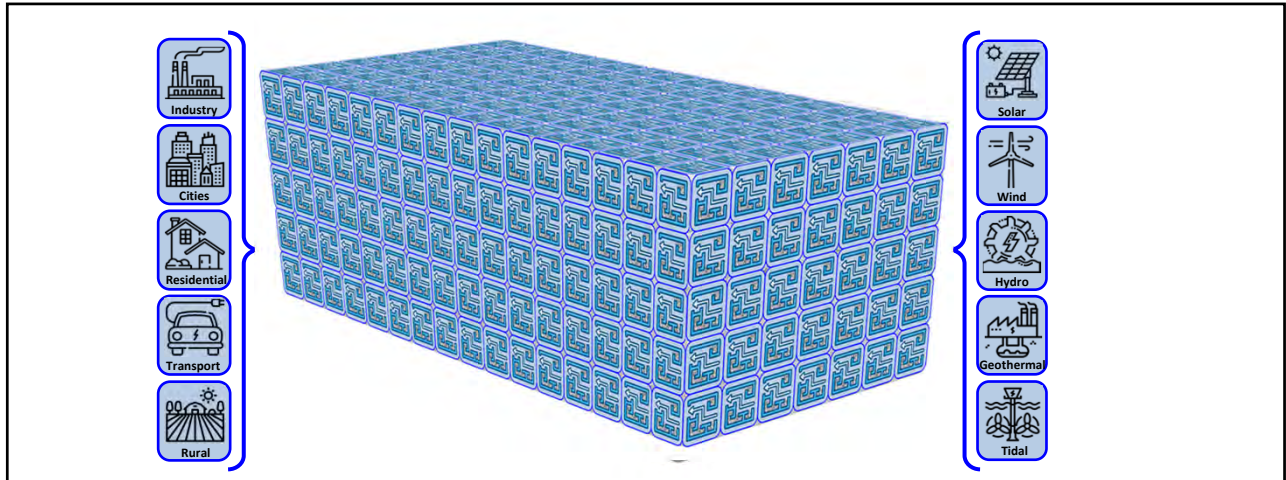
MIT engineers create an energy-storing supercapacitor from ancient materials

Made of cement, carbon black, and water, the device could provide cheap and scalable energy storage for renewable energy sources.

David L. Chandler | MIT News
July 31, 2023

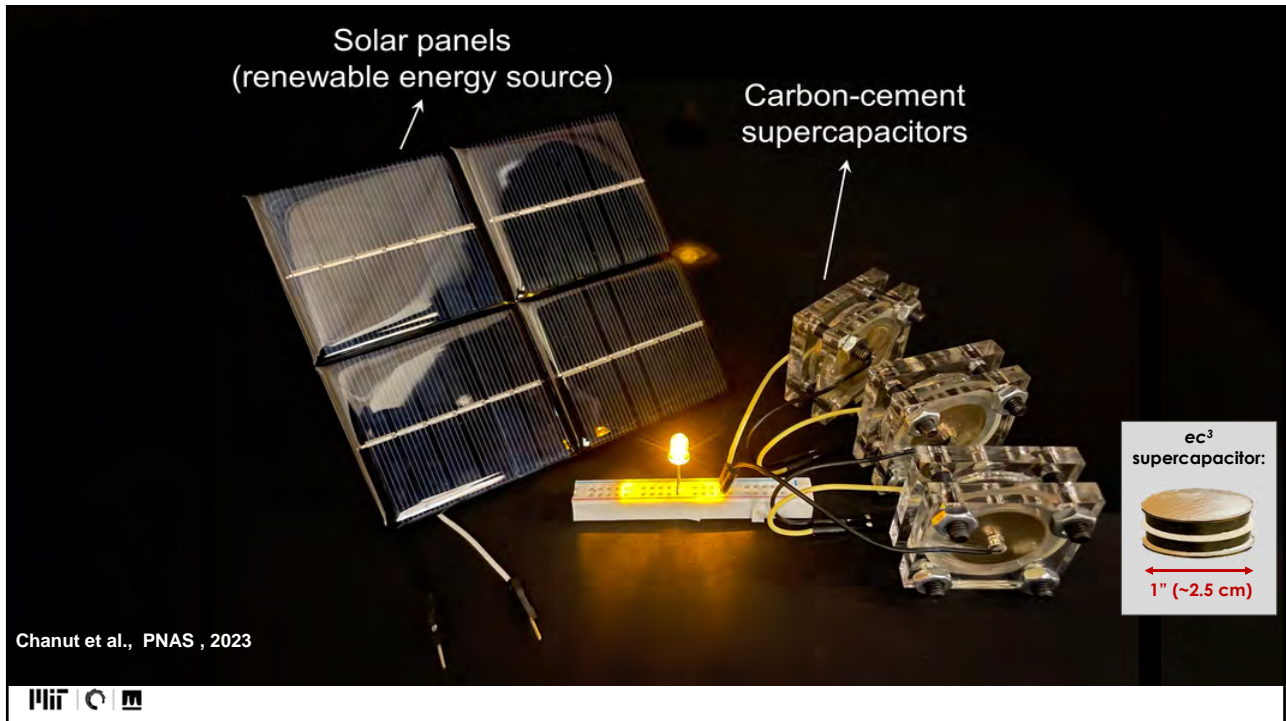


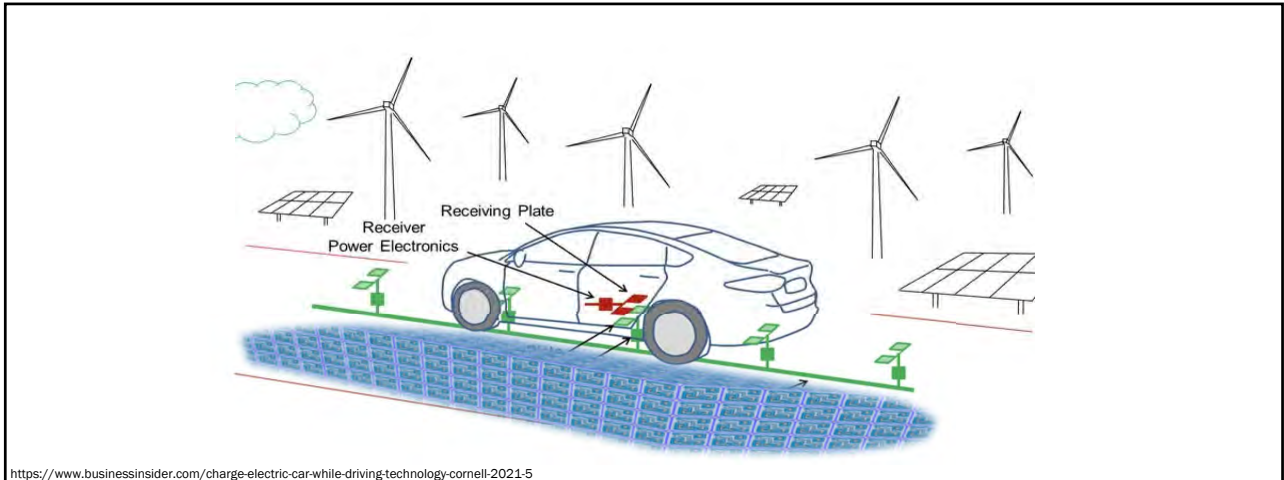
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Multifunctionality: Concrete as a “Battery”

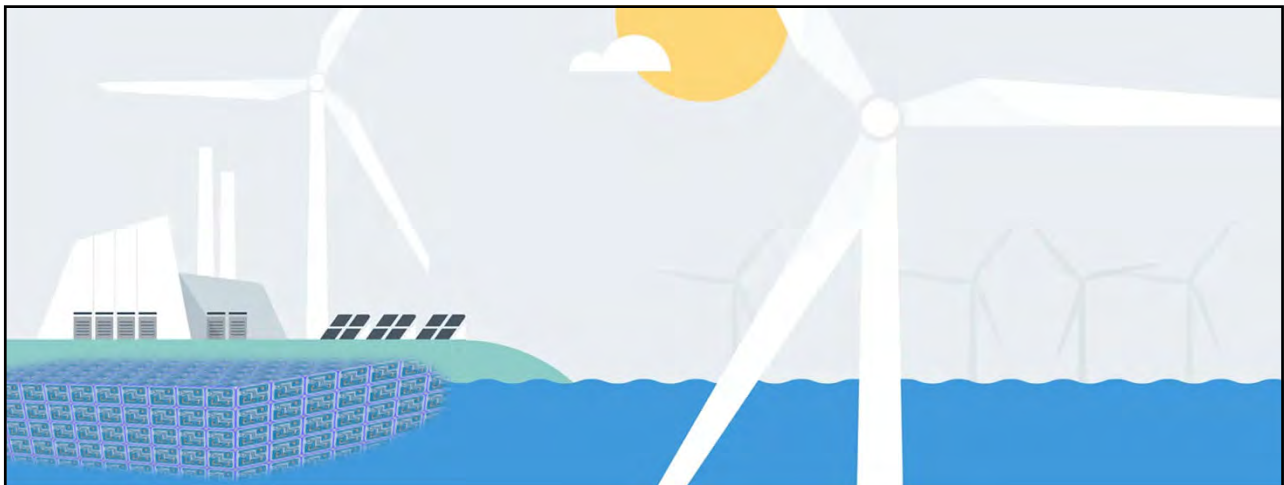
Electron-Conducting Cement-Based Materials





Future: Smart charging roads

Road as a renewable energy storage
Wireless charging of cars



Future: Energy Storage Everywhere

Scalable bulk supercapacitors for renewable energy storage

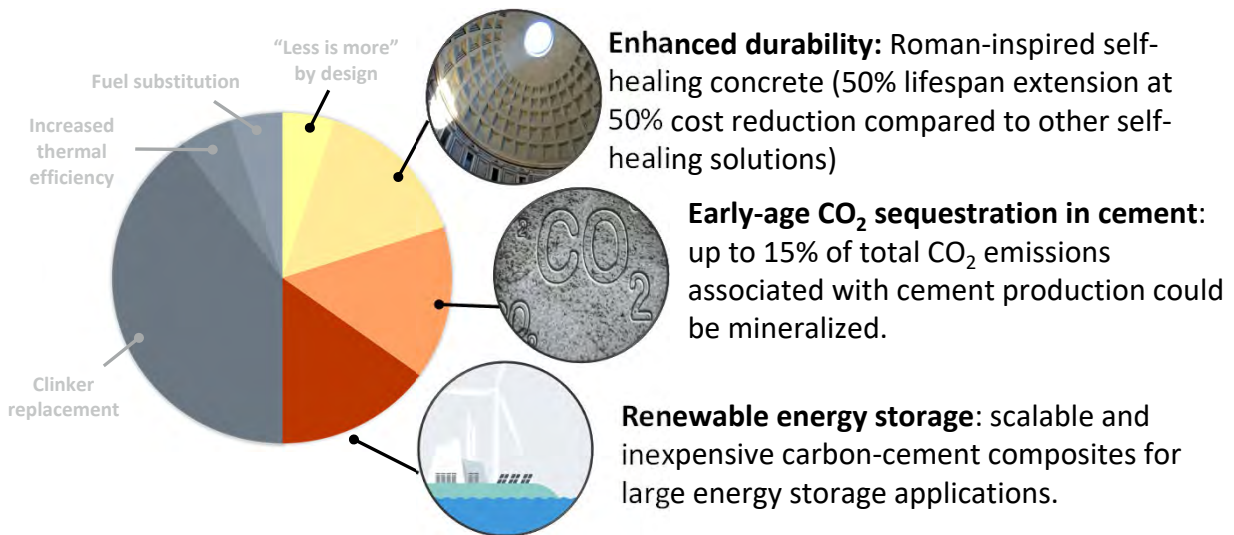


Future: decentralized electrical energy supply

Integrated Vascular Networks | Home foundations and walls as batteries

For reference:
Daily residential energy consumption: ~10 kWh ~ 40 m³ EC³-Concrete

Multifunctional concrete



Acknowledgments – Collaborators



Dr. Damian Stefaniuk
Marcin Hajduczek
Dr. Hyun Chae Loh
Dr. Linda Seymour
Dr. Janille Maragh
Dr. Rachel Kim
Dr. Nicolas Chanut
Dr. Thibaut Divoux
Sophia Mittman

Prof. Franz-Josef Ulm
Prof. Markus Buehler
Prof. Vladimir Bulovic
Prof. Heather Lechtman
Prof. Linn Hobbs
Randolph Kirchain
Stephen Rudolph

Dr. Marco Nicola
Prof. Roberto Gobetto



Dr. James Weaver



Tavis Ezell
Dr. Ute Schmidt



Paolo Sabatini



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THANK YOU!



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