Graphene Oxide Modified Fly Ash Pervious Concrete

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Background

- Cement industry accounts for ~ 5% of global CO_2 emissions.
- The U.S. generated approximately 70 million tons of fly ashes in 2014, only 27% were recycled.

Cement Production
(photo by Shaila Dewan)

Air pollution from fly ash
(photo by Shaila Dewan)

Coal ash spill in Tennessee
(photo by Shaila Dewan)

Fly Ash Composition

	Cement	Fly ash
Specific gravity	3.2	2.7
Bulk Density (lbs/ft^3)	76	54
SiO_2 (wt. %)	21	23.5
CaO (wt. %)	**65**	**23.2**
Al_2O_3 (wt. %)	**4**	**13.8**
Fe_2O_3 (wt. %)	3.5	4.8
MgO (wt. %)	0.2	4.2

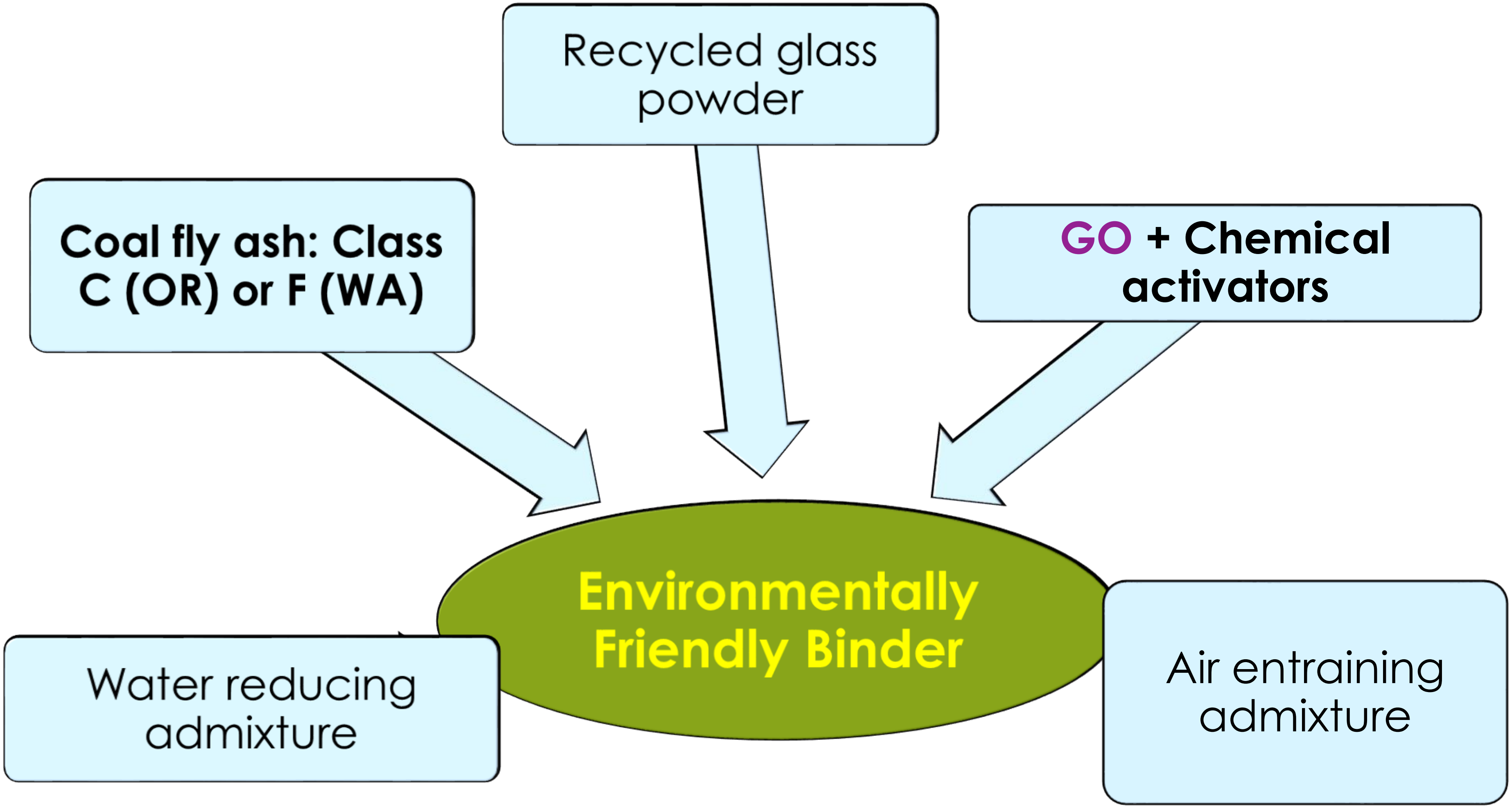
1. <u>Chemical Composition</u>

The contents of principal oxides are usually SiO_2, Al_2O_3, Fe_2O_3, CaO, MgO, K_2O, Na_2O and SO_3.

2. <u>Minerology Composition</u>

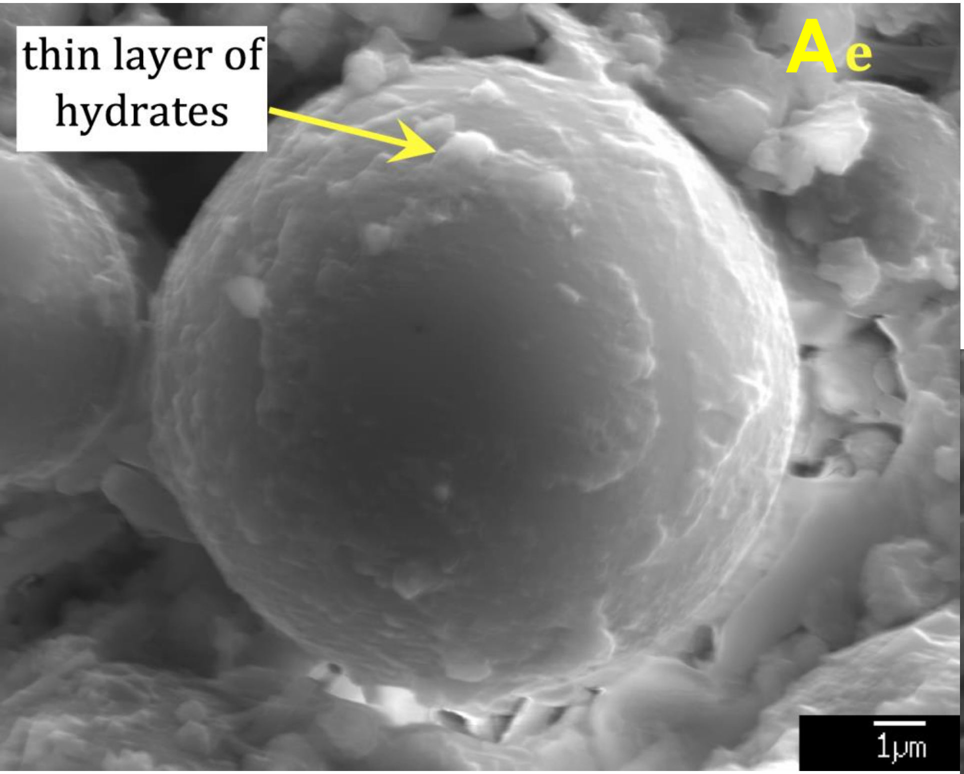
Fly ash has approximately 316 individual minerals and 188 mineral groups.

Turning Fly Ash into a Green Binder



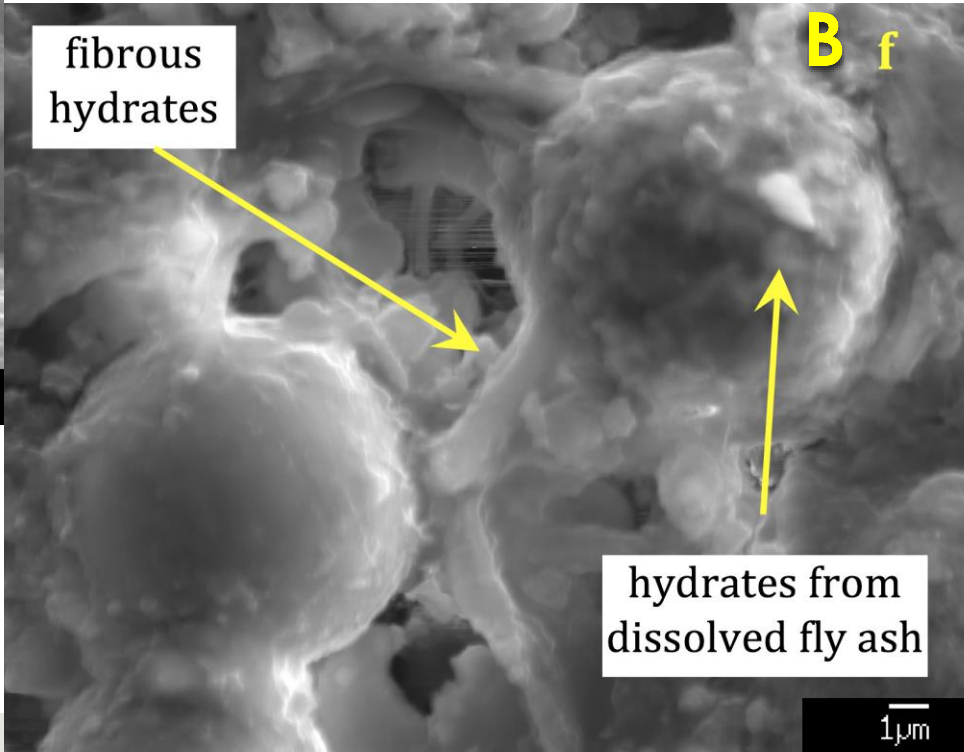
Chemical activators enhance fly ash hydration

❑ Secondary Electron Imaging (SEI) Analysis



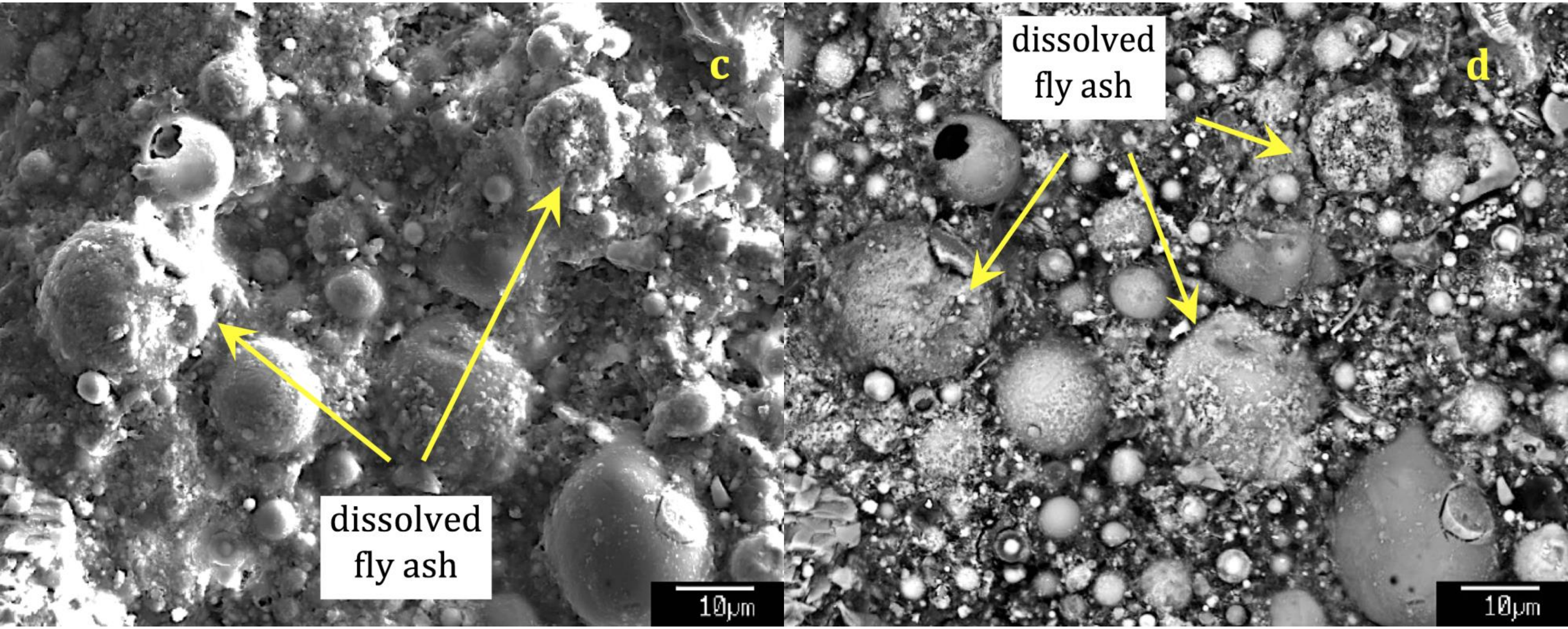
28-d f'_c: 20.5 MPa

vs. 33.6 MPa



A) Mortar without activators
B) Mortar with activators

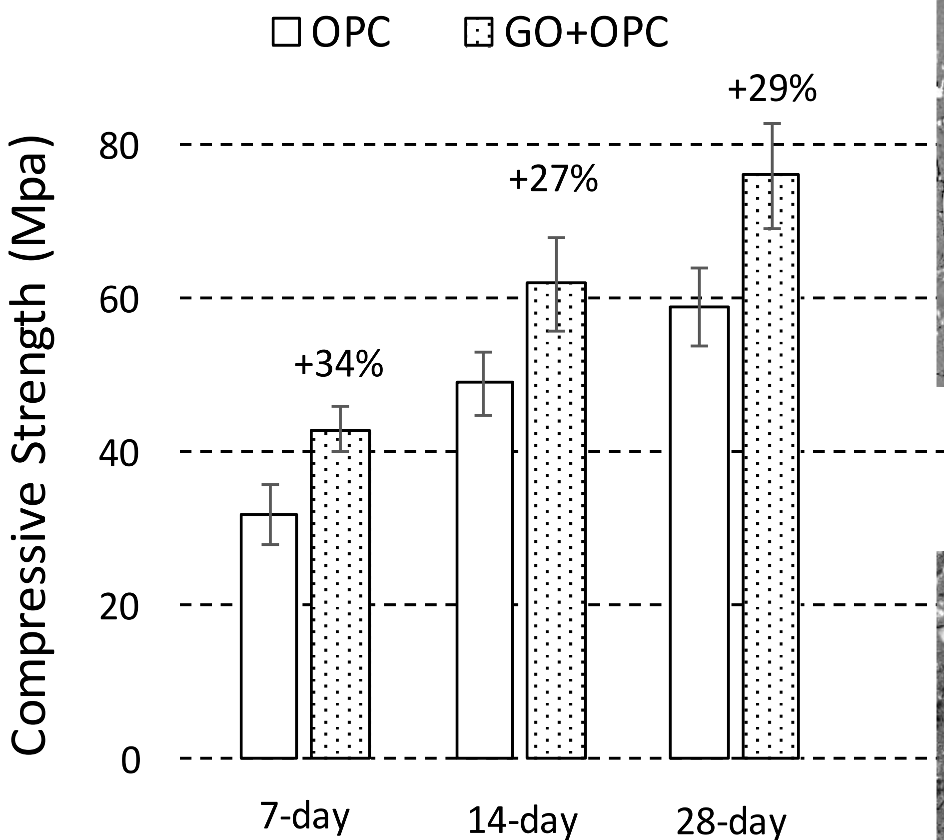
Chemically Activated Fly Ash Mortar



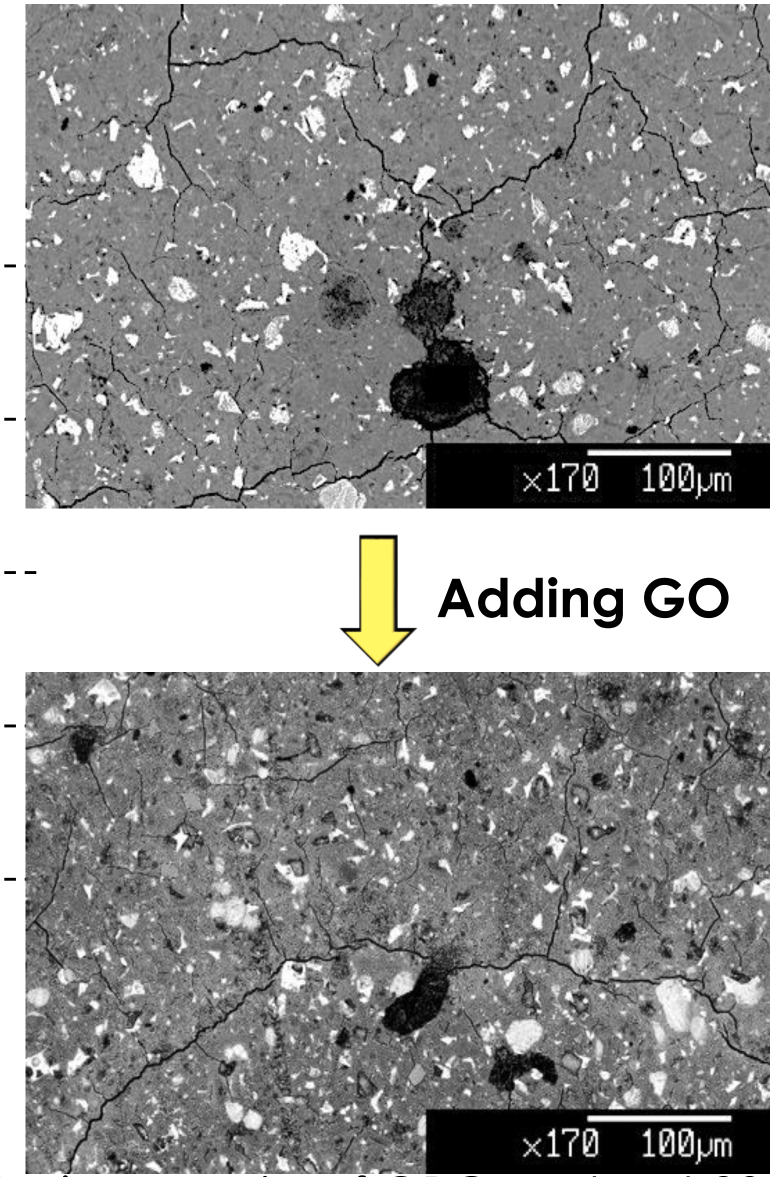
SEI (*left*); BSE (*right*) micrographs

Xu, G., Shi, X. Exploratory Investigation into A Chemically Activated Fly Ash Binder for Mortars. *ASCE Journal of Materials in Civil Engineering*, 2017, in press.

Function of graphene oxide in OPC

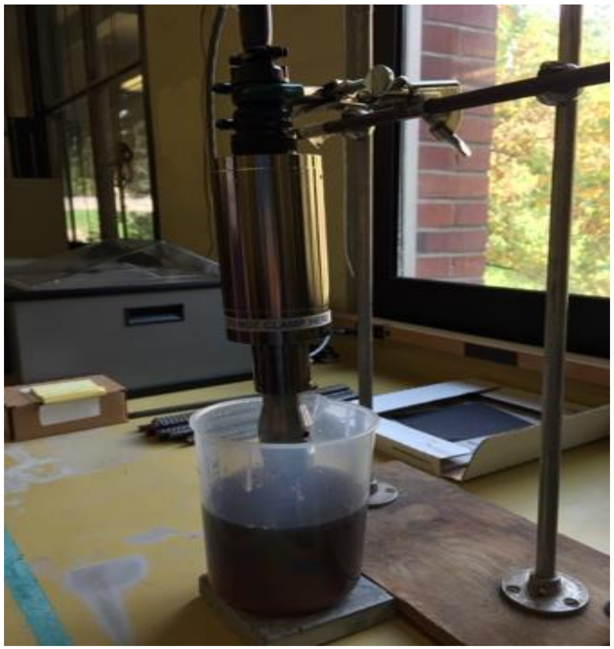


f_c' improvement with 0.03 wt% GO

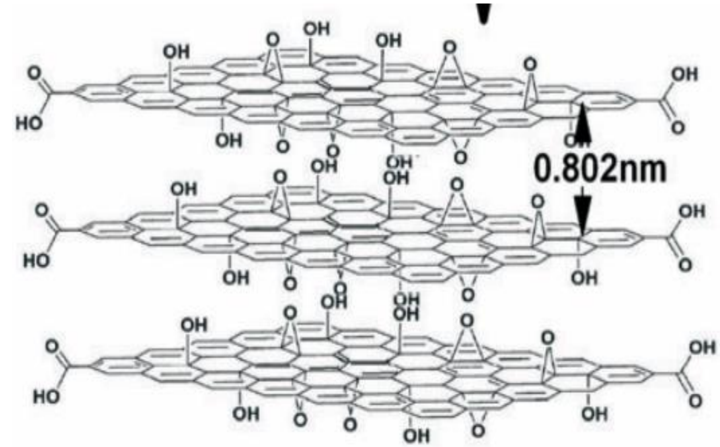


BSE micrographs of OPC paste at 28-d

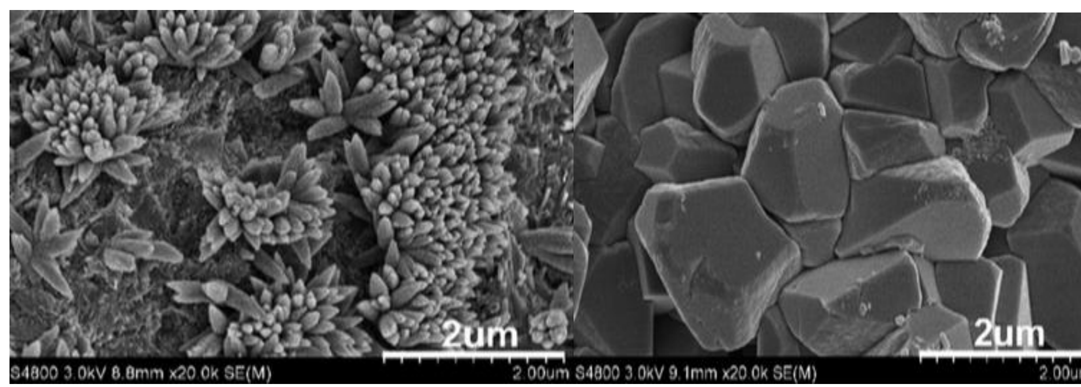
Graphene Oxide (GO) Modified Mortar



Ultrasonification of GO suspension

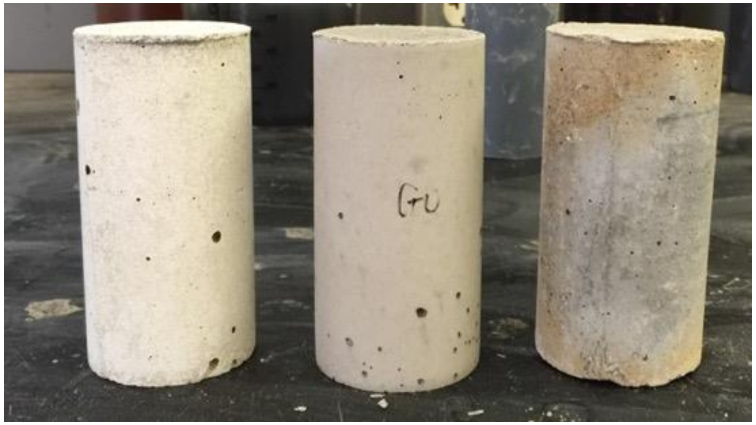


Molecular model of GO (Lv et al. 2014)



SEI image of cement hydrates at 7-days: (a) flower-like shape with 0.01% GO; (b) polyhedron-like shape with 0.05% GO (Lv et al. 2014)

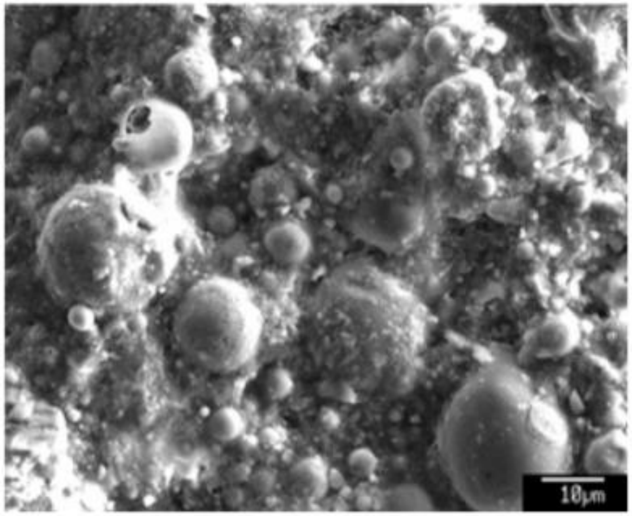
GO-Modified Fly Ash Mortar

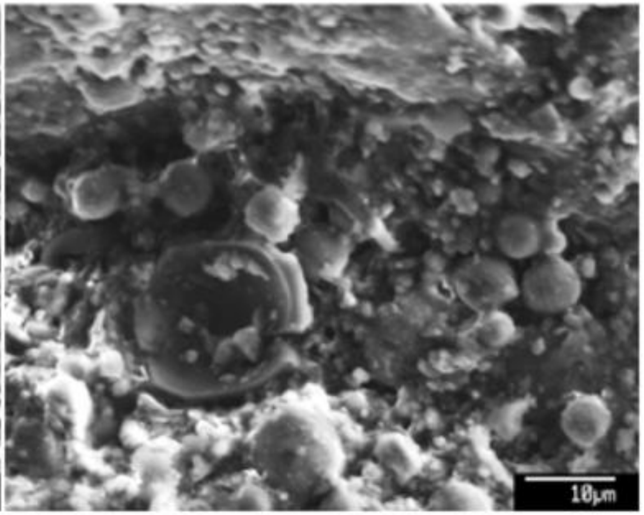


Cement mortar (left); GO-modified fly ash mortar (middle); fly ash mortar (right)

	0.03% GO-modified fly ash mortar	Regular fly ash mortar	f_c' increase
7-day f_c' (psi)	3353	2705.9	**24%**
14-day f_c' (psi)	4688	3721.1	**26%**
28-day *f'$_c$*	**5998 psi (41.4 MPa)**	**4878 psi (33.6 MPa)**	**23%**

Following ASTM C39/39M

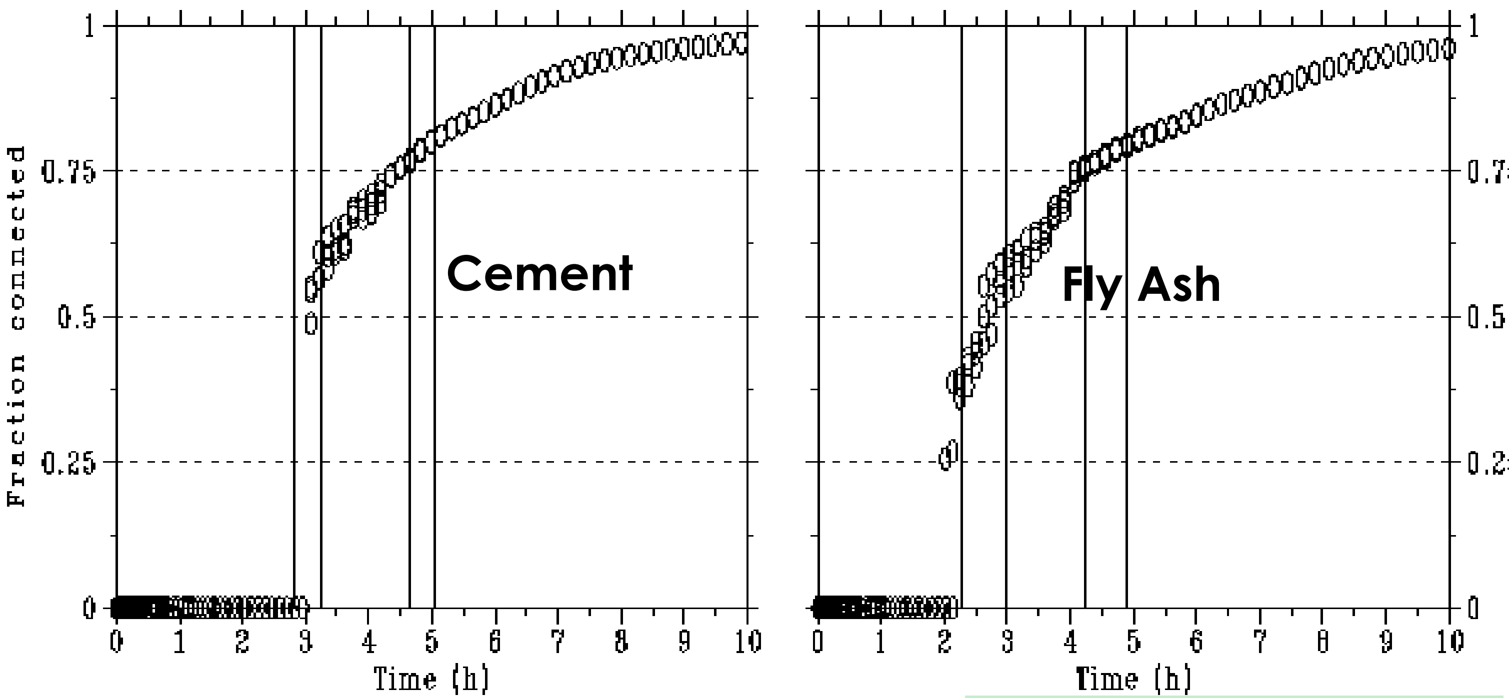




Fly ash mortar (left); **GO-modified fly ash mortar** (right)

Mortar Setting Time Test

Following ASTM C403/403M



1. Borax shows the ability to adjust the setting time of fly ash mortar.

2. 0.5 wt.% Borax is able to produce the similar setting time as cement.

Concrete Pocket Penetrometer

Mortar Workability Test

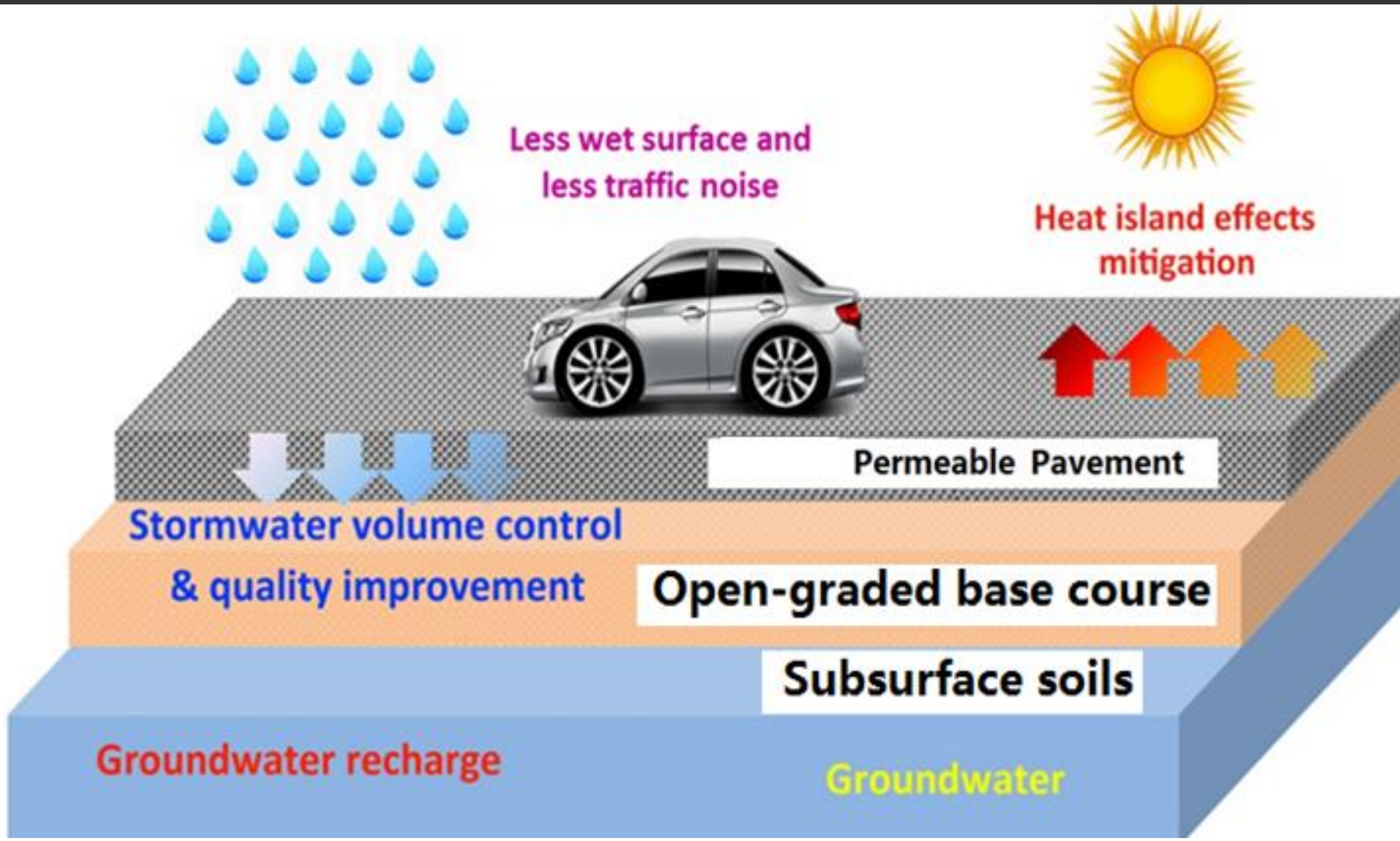
Following ASTM C230/230M

1. **HRWR is not effective for fly ash binder due to LOI content.**

2. **F-500 Encapsulate Agent shows the ability to increase the workability of fly ash mortar.**

3. **1% F-500 is able to produce the similar workability as cement (with same *w/b* ratio).**

Pervious Concrete is a LID Tool



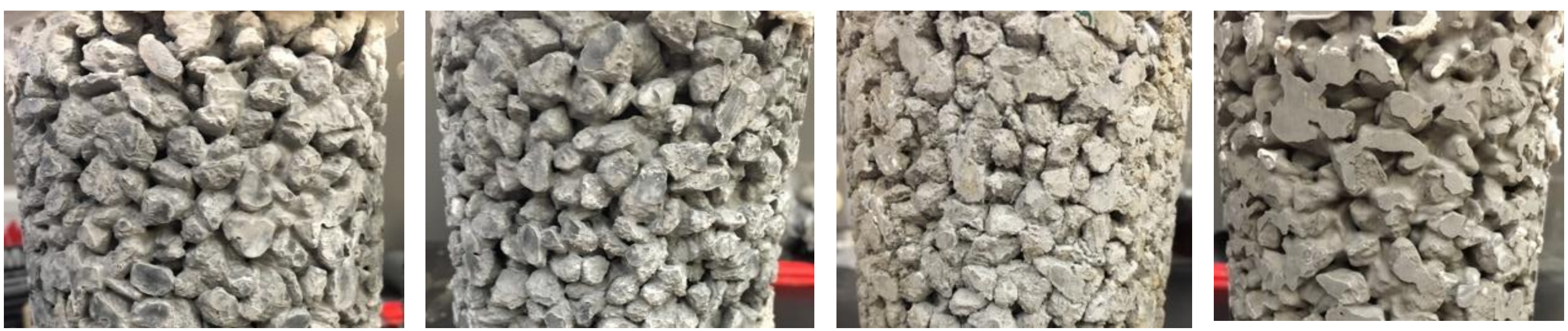
Developing Pervious Concrete with Fly Ash Binder

Mix Design	Agg. Size (inch)	Cement (kg/m^3)	Fly ash CFA1 (kg/m^3)	Water (kg/m^3) [w/b]	Na SO_4 (kg/m^3)	CaO (kg/m^3)	$CaCl_2$ (kg/m^3)	Water Glass (kg/m^3)	GO (g/100 kg binder)	HRWR (ml/100 kg binder)	AE (ml/100kg binder)
Cement	3/8	320	--	80 [0.25]	--	--	--	--	--	300	30
Cement + GO	3/8	320	--	**80 [0.25]**	--	--	--	--	96	300	30
Fly ash	3/8	--	358	97 [0.27]	3.6	17.9	3.6	25	--	1000	30
Fly ash + GO	3/8	--	358	**97 [0.27]**	3.6	17.9	3.6	25	108	1000	30

Fabrication of GO-FA-Pervious Concrete

(a)

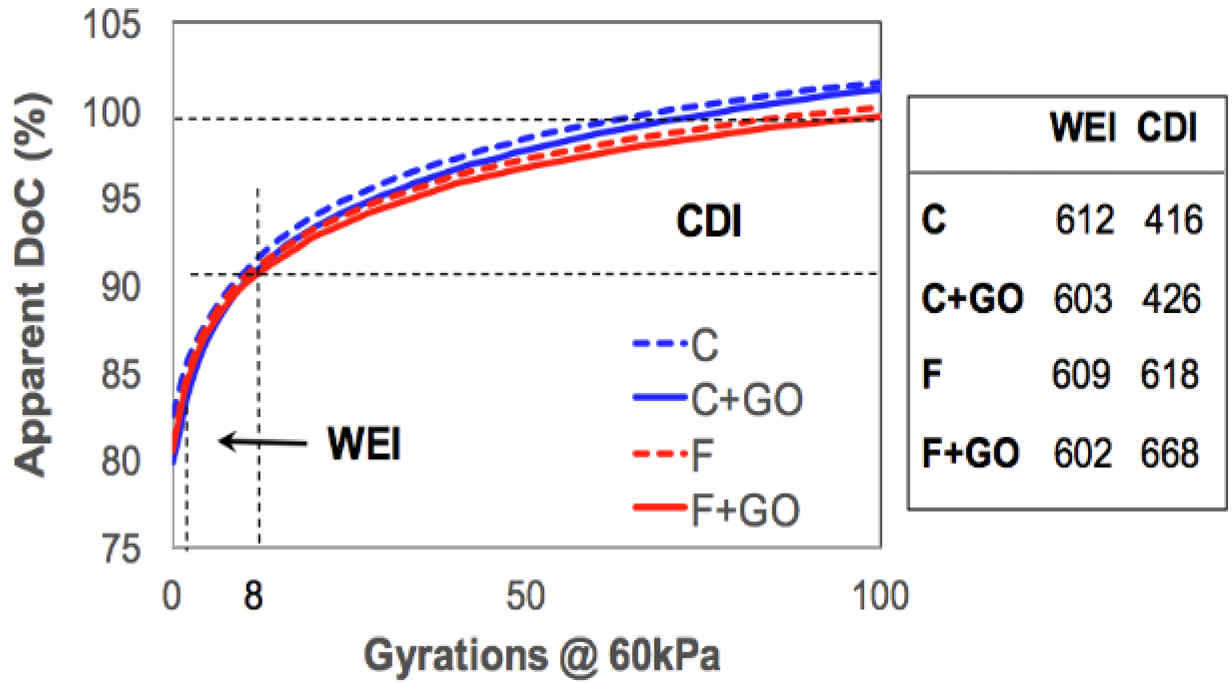
Pervious concrete 4”X8” cylinders (left to right) cement, cement + GO, fly ash, fly ash + GO
(a): cylinders with capping
(b): Close-up view of surface



(b)

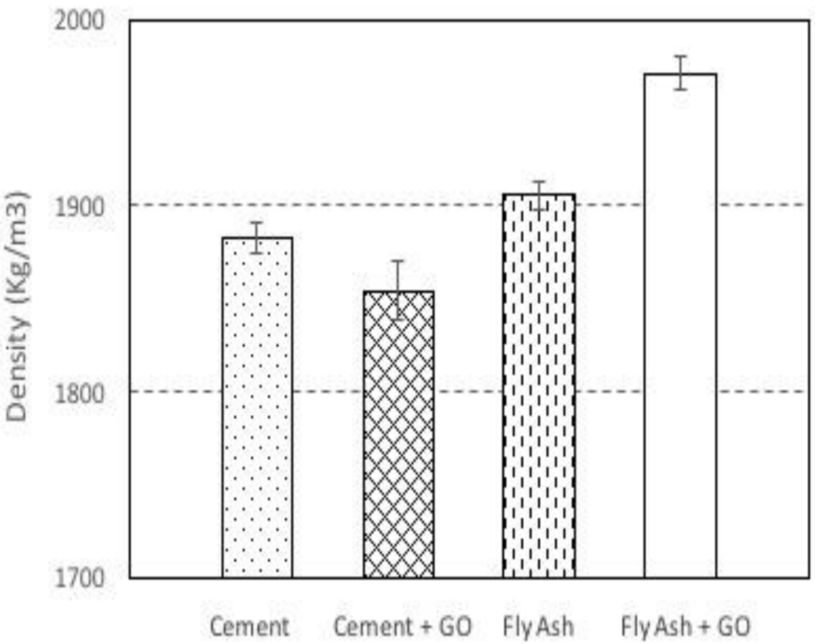
Workability of Pervious Concrete

Superpave gyratory compactor. (proposed by Kevern et al.)

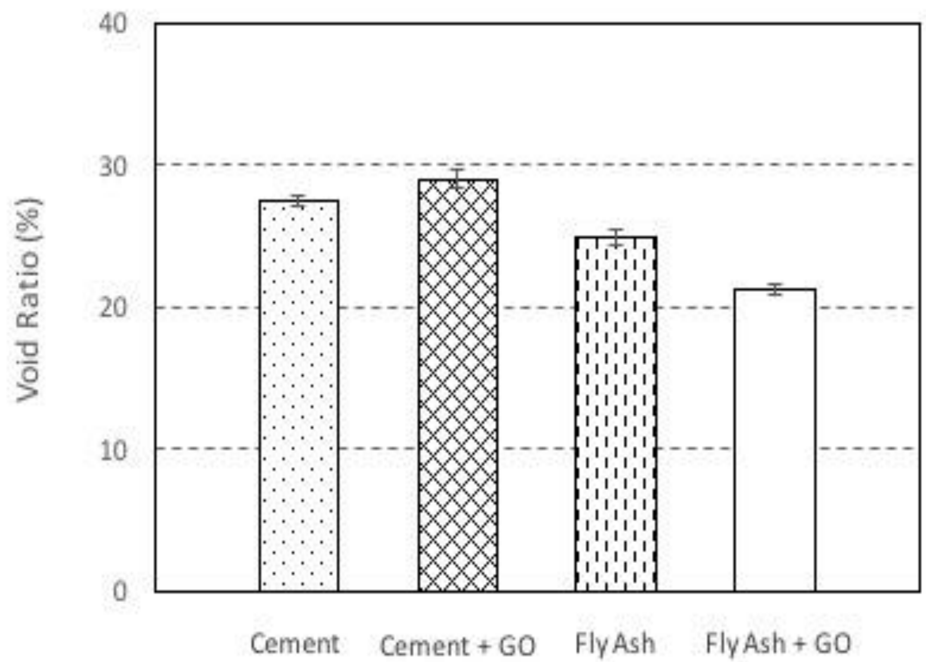


Workability (WEI)	
High workability	WEI > 640
Acceptable workability	640 > WEI > 600
Poor workability	WEI < 600
Compactability (CDI)	
Self-consolidating	CDI < 50
Normal compaction effort required	50< CDI < 450
Considerable additional compaction effort required	CDI > 450

Density and Void Ratio

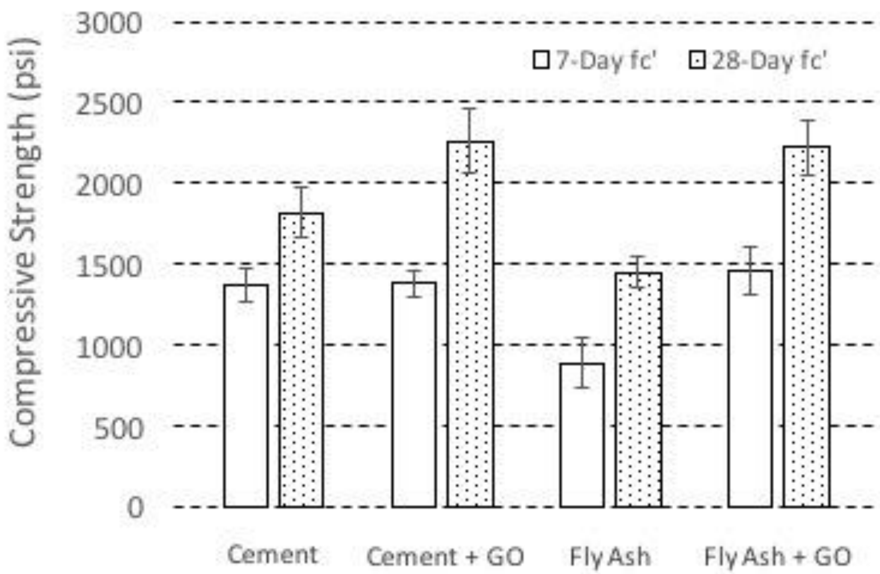


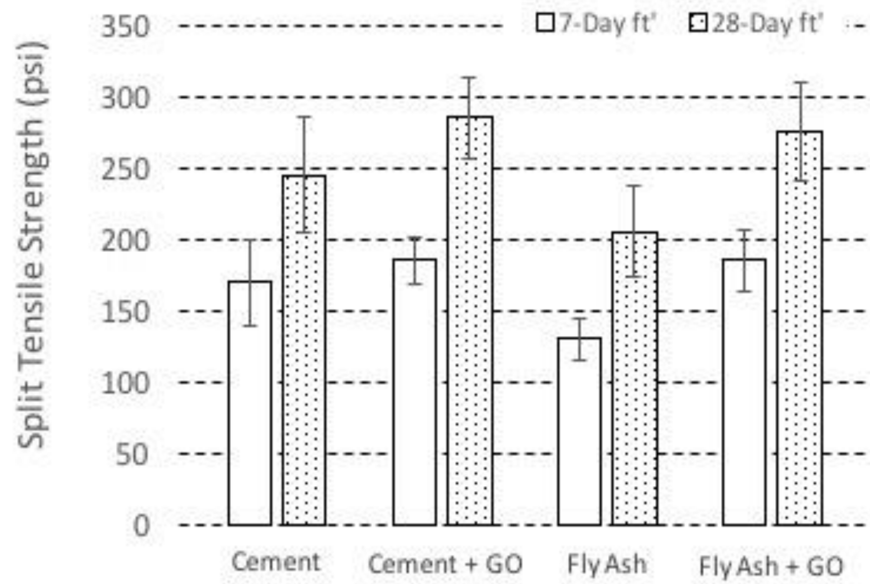
Density of hardened pervious concrete at 28 days

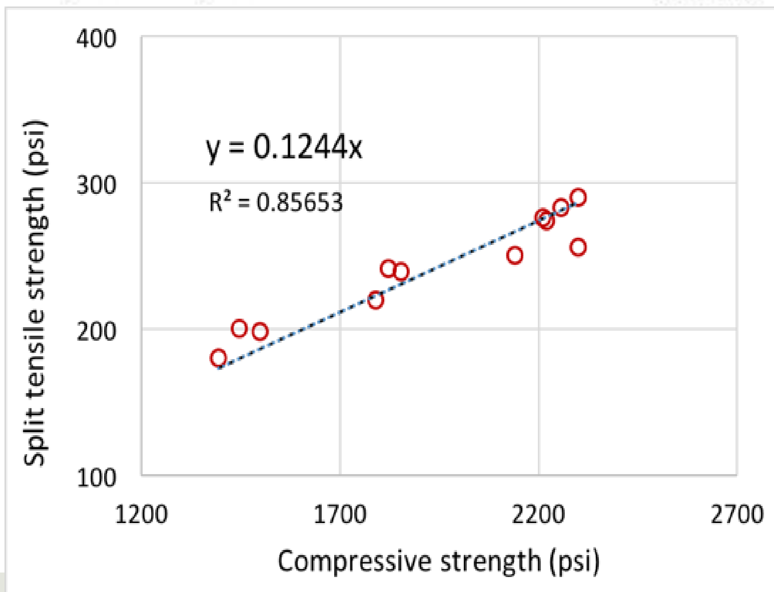


Void ratio of hardened pervious concrete at 28 days

Compressive and Split Tensile Strength

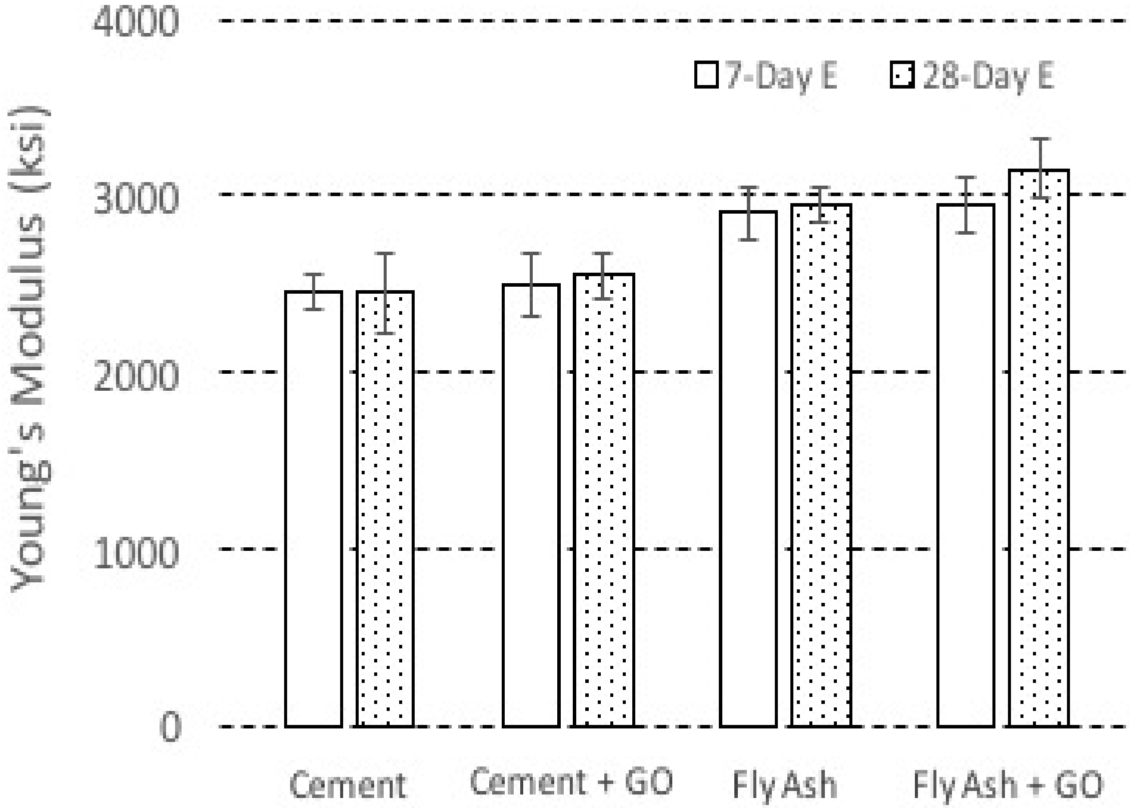






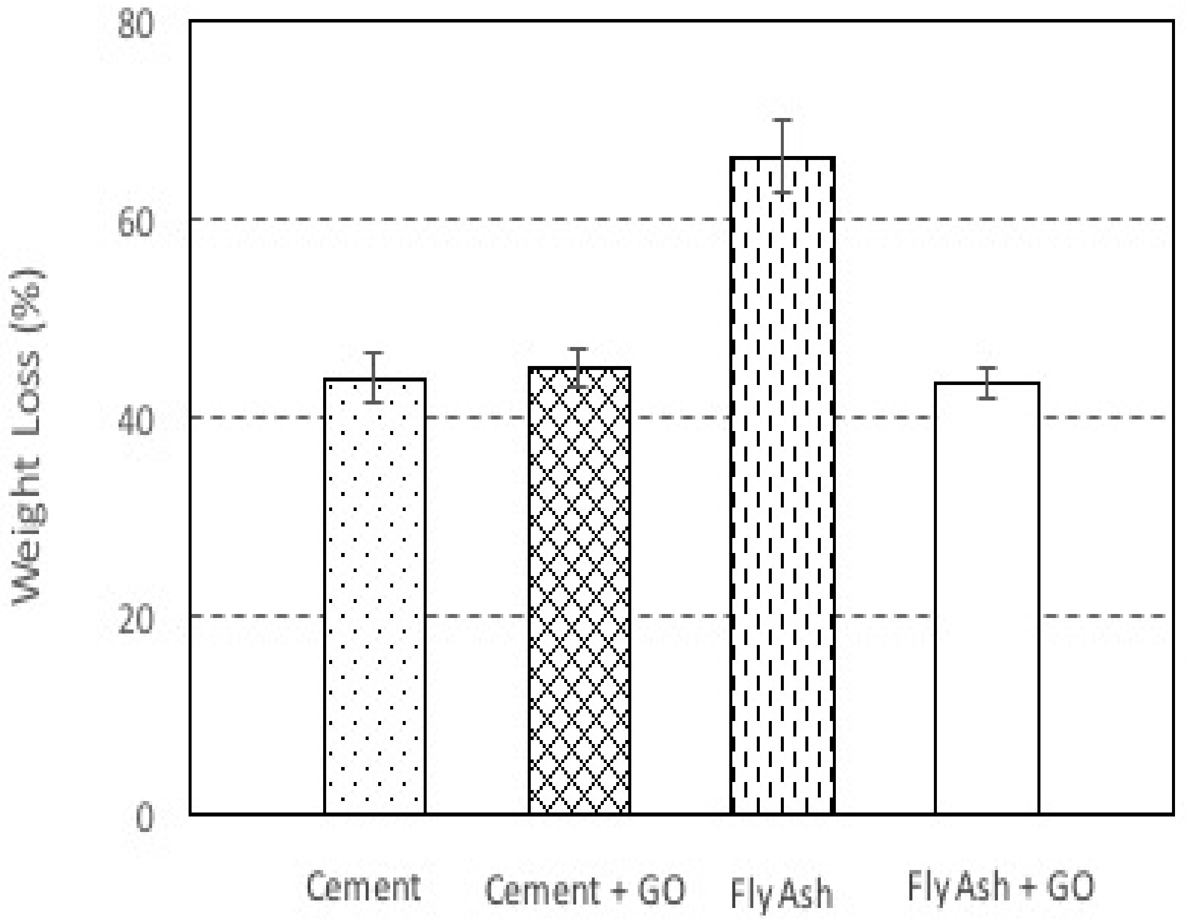
Relationship between split tensile strength and compressive strength at 28 days

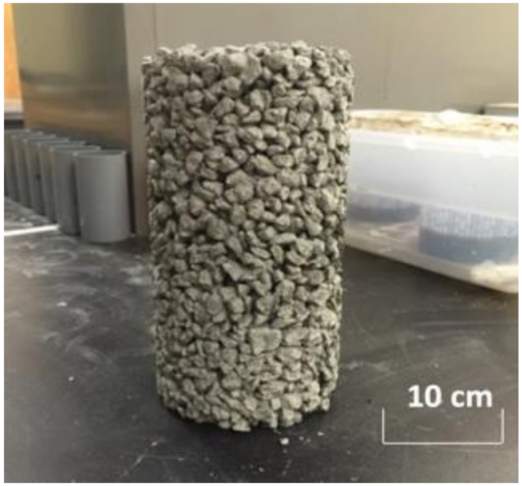
Young's Modulus

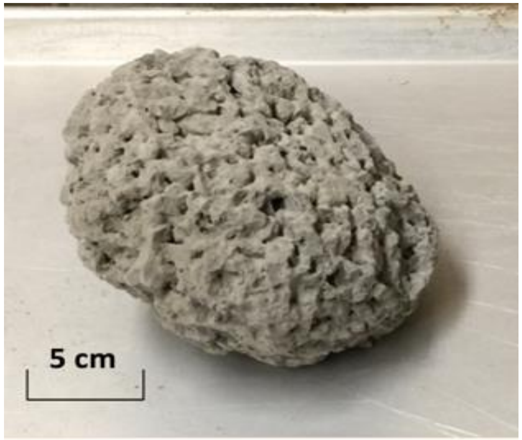


Abrasion Resistance

- (Abrasion) Degradation test results on 90-day







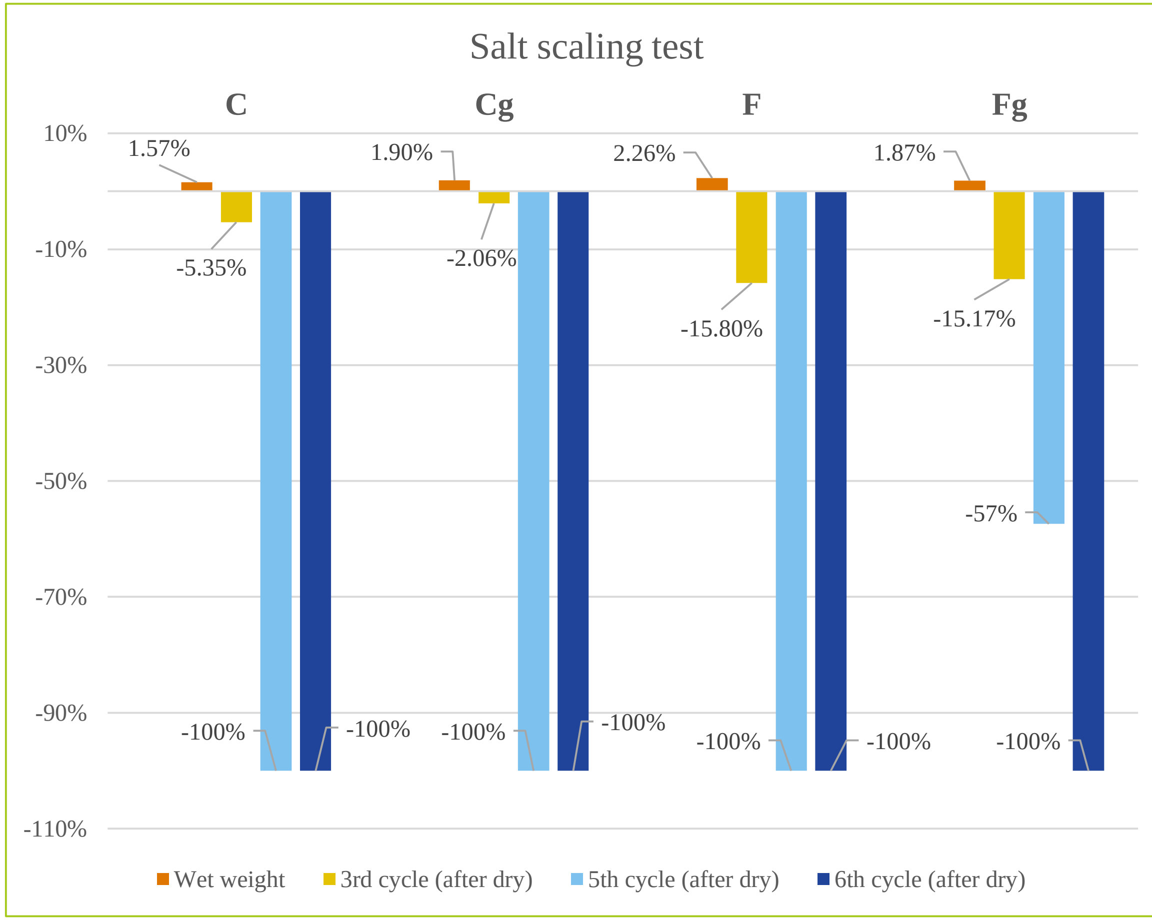
Sample before and after the test

Freeze-deicer Salt Scaling Resistance Test

Pervious concrete samples before freeze-deicer salt scaling test

Cement + GO

Fly ash + GO



Weight loss during salt scaling test

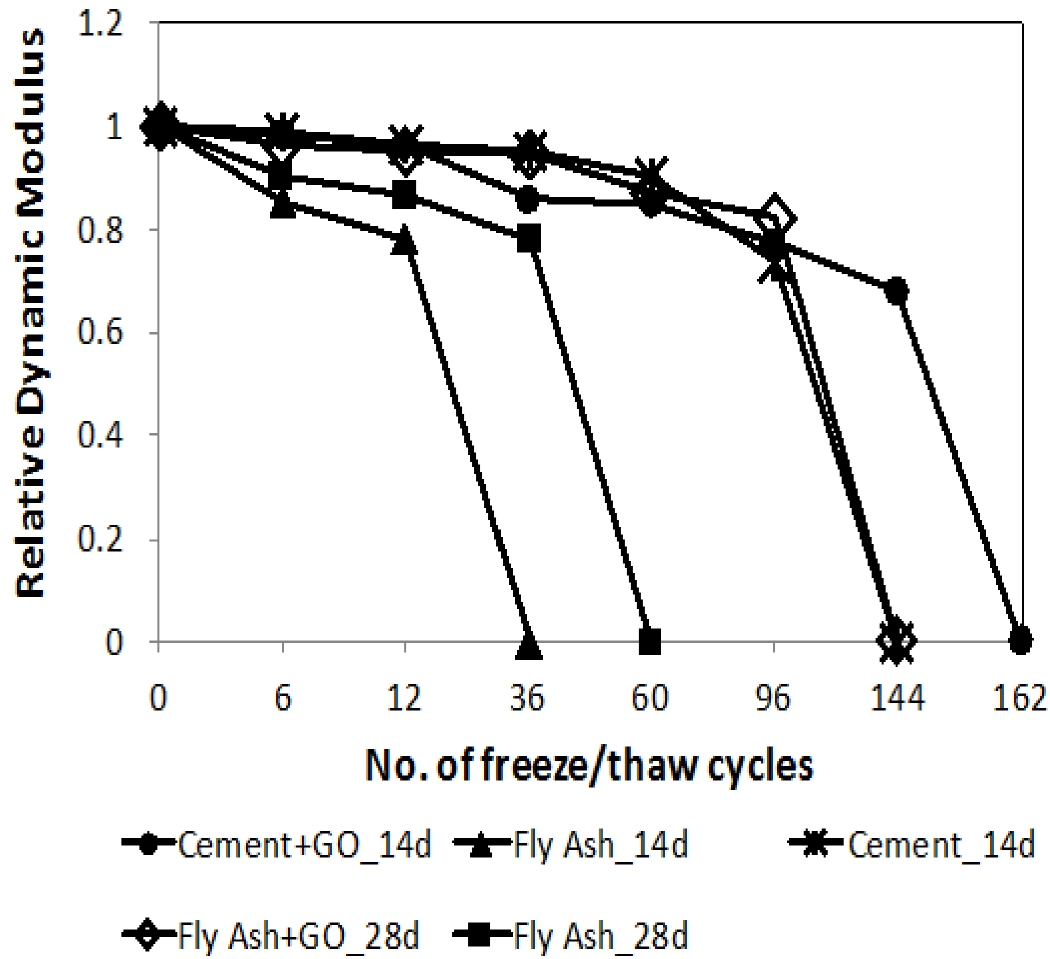
Samples after the 3rd cycle during test

Freeze-Thaw + Wet/Dry

Following ASTM C666/666M

Fly ash after 96 cycles

Cement after 96 cycles

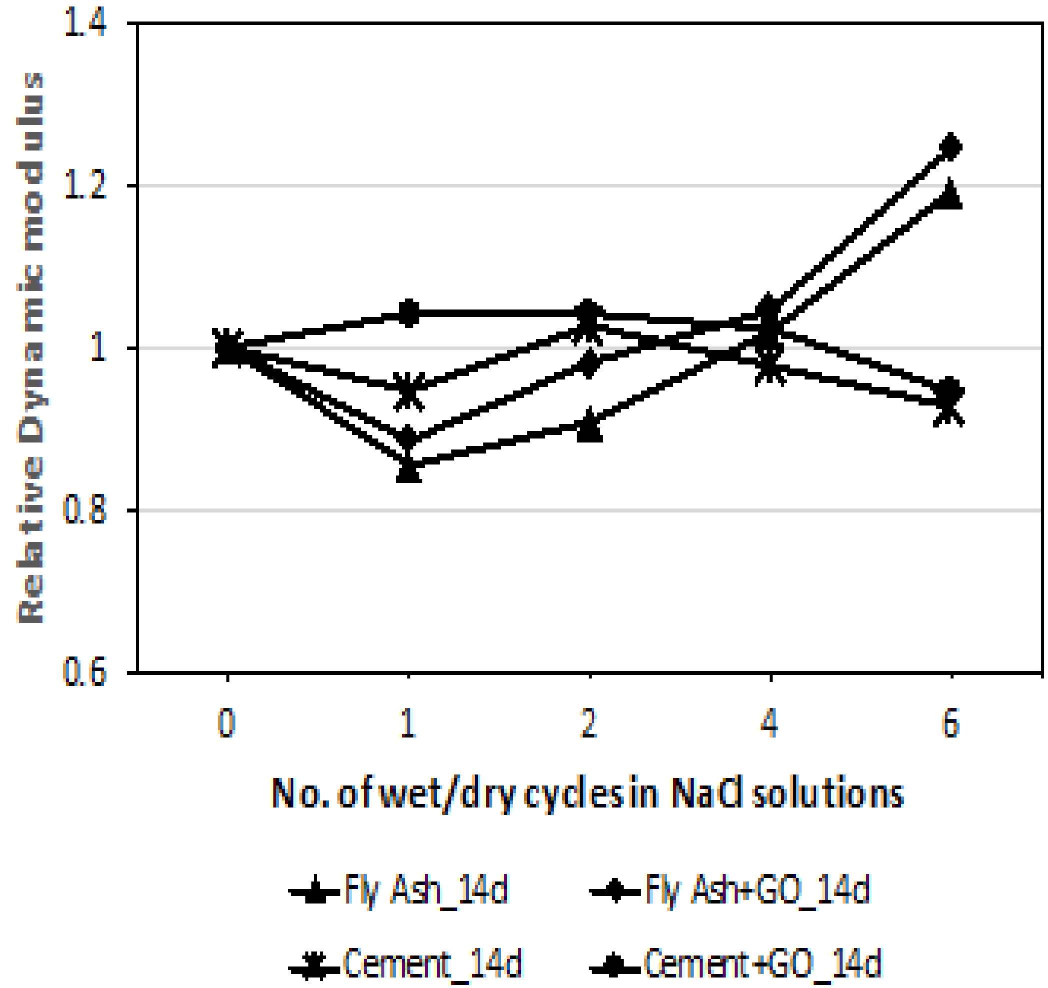


Salt Exposure + Wet/Dry

Following ACI Test

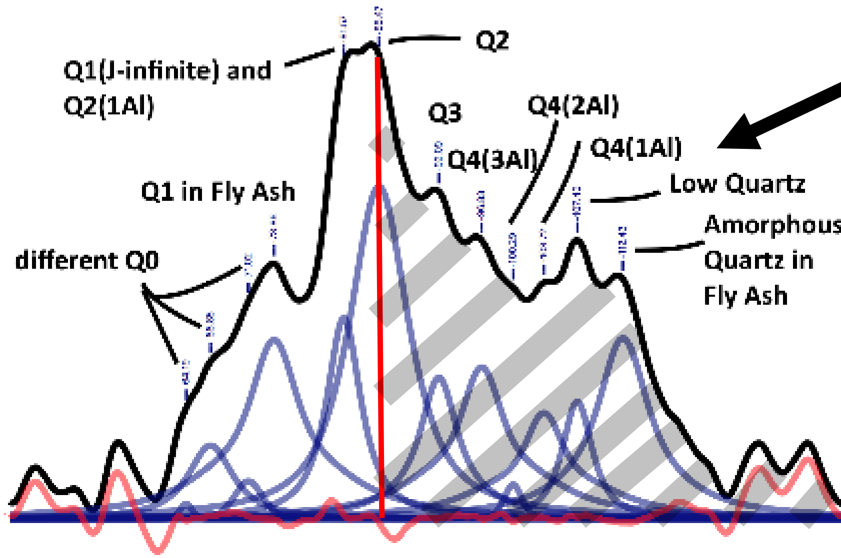
Fly ash after 4 cycles

Cement after 4 cycles

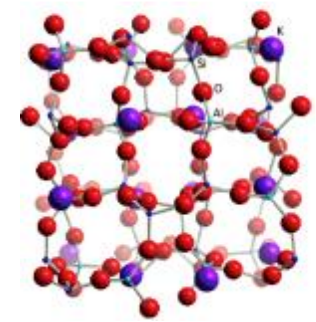


^{29}Si NMR Spectra Comparison

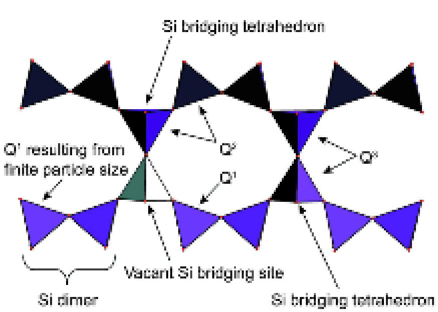
Fly ash hydrates



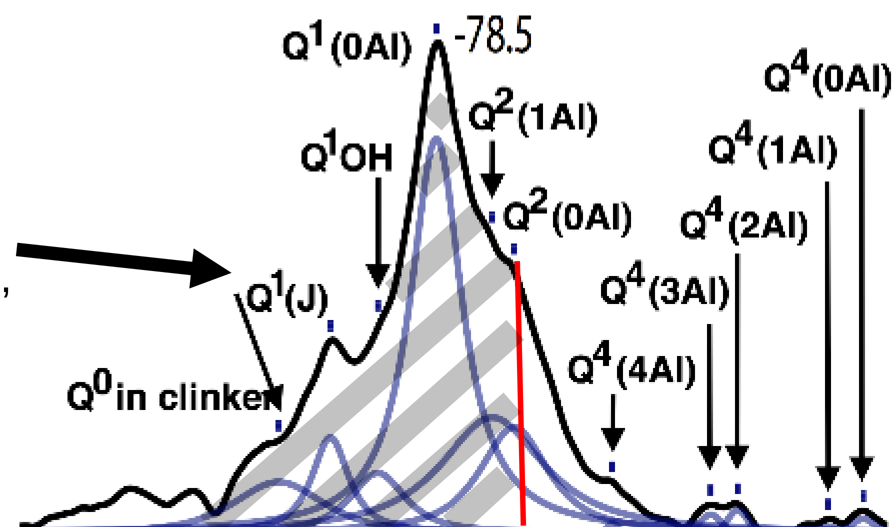
More than half of peak area is on the ***network structure*** side. Fly ash hydrates is essentially ***Geopolymer***



Cement hydrates

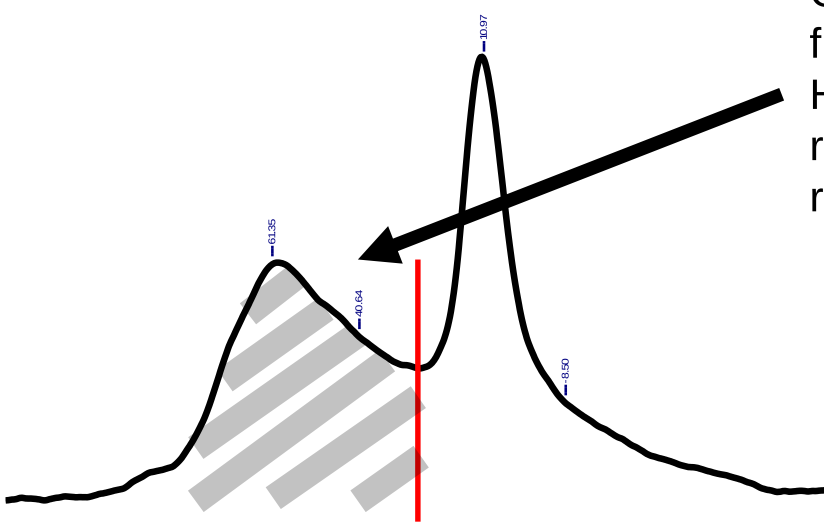


More than half of peak area is on the ***chain structure*** side, Cement hydrates is different from Geopolymer

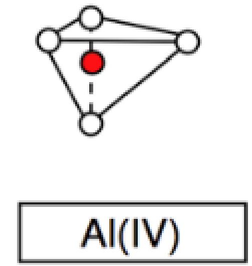


^{27}Al NMR Spectra Comparison

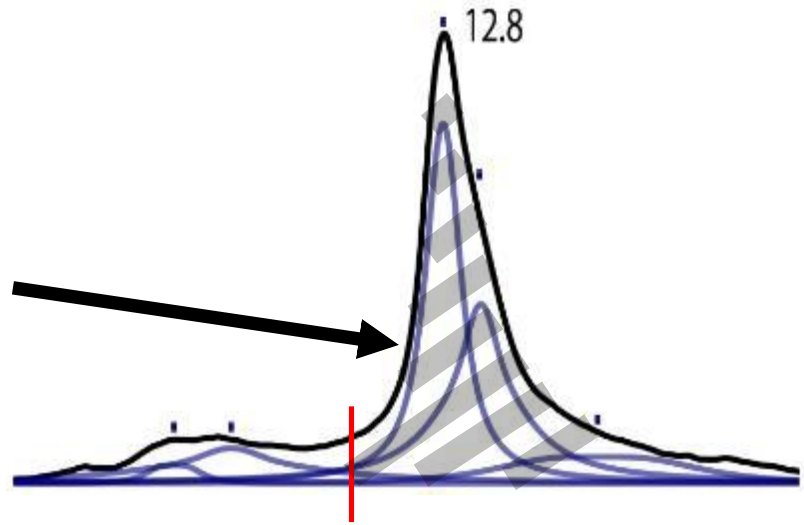
Fly ash hydrates

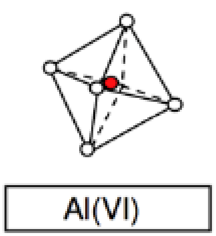


Great peak area of Al(IV) from fly ash itself and C-A-S-H hydrates. Al (IV) acts as reservoir to improve the resistance to sulfate attack.



Cement hydrates





Most of Al present as Al(VI) in AFt and TAH (amorphous Al hydroxide). No enough Al reservoir for later sulfate attack.

Summary

- A preliminary assessment showed that the fly ash binder was able to produce a pervious concrete with desirable densities, void ratios, infiltration rates and mechanical strengths.

- Freeze-thaw and deicer resistance of fly ash pervious concrete are better than the cement pervious concrete.

- Work is ongoing to employ waste carbon fibers to further enhance the durability of fly ash pervious concrete in cold climate.

Summary (cont'd)

- 0.03 wt.% GO improved overall performance of fly ash pervious concrete, e.g. the 28-day f'_c of fly ash pervious concrete was improved by more than 50%.
- GO accelerated the fly ash hydration and promoted the formation of low-Quartz and Jennite-like hydrates.
- GO increase the degree of polymerization of fly ash hydrates.
- EPMA and NMR are powerful tools that can shed light on the hydration mechanism of fly ash and on the role of GO.

Xu, G., Shi, X. Graphene Oxide Modified Pervious Concrete with Fly Ash as the Sole Binder. *ACI Materials Journal*, 2017.
Xu, G., Shi, X. Reaction mechanism of graphene oxide in a chemically activated fly ash binder, *Cement and Concrete Research*, 2017.

Acknowledgements

- Thanks for funding from CESTiCC and WSU Office of Commercialization
- Shi, X. and Xu, G. 2016. Fly ash cementitious compositions. Non-provisional Patent filed on 08/26/2016. PCT/US2016/049048.
- Shi, X. and Xu, G. 2016. Environmentally friendly pervious concrete with fly ash as a sole binder. Provisional Patent 62/330,427 filed on 05/02/2016.
- Shi, X. and Xu, G. 2015. 100% fly ash mortars. Provisional Patent 62/212,000 filed on 09/17/2015.
- BASF, Boral and Lafarge for donated materials
- Dr. Owen K. Neil, Dr. Mehdi Honarvarnazari, Jiang Yu, Sen Du, Jialuo He at WSU provided assistance in experiments

Questions?

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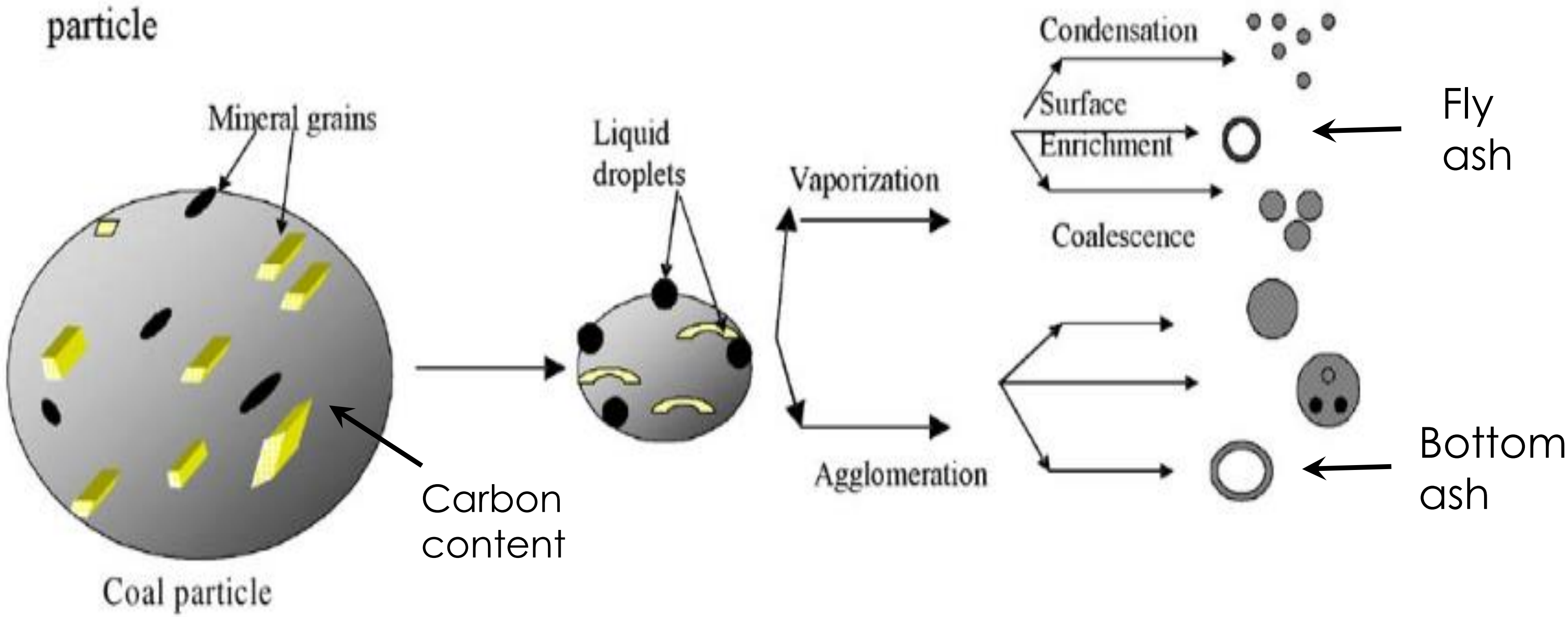
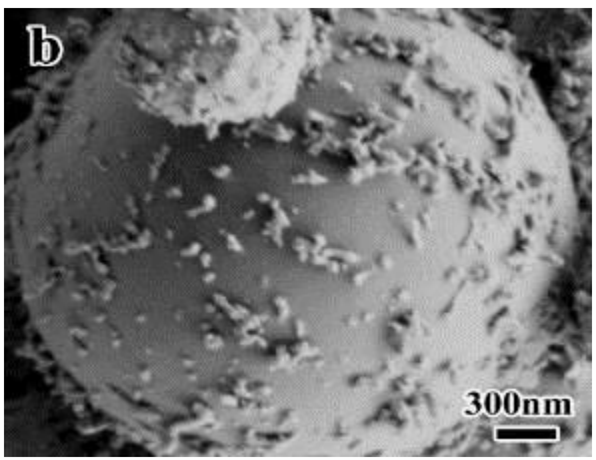
Fly Ash Formation

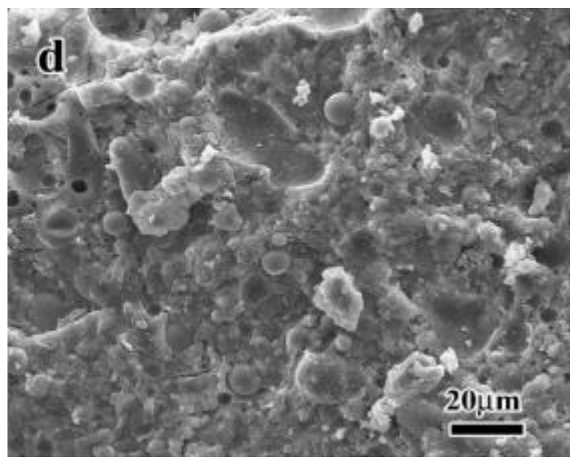


General transformation of coal during combustion (*Kutchko, 2006*)

Coal fly ash as the sole binder?

- Goal: Use coal fly ashes to make a durable, clinker-free concrete
- Our recent work has confirmed the possibilities of using class C coal fly ash (without activation) as the sole binder to make concretes of moderate strength.





w/b 0.20:

28-d f'_c: 38 MPa;

Surface resistivity: 130 KΩ.cm;

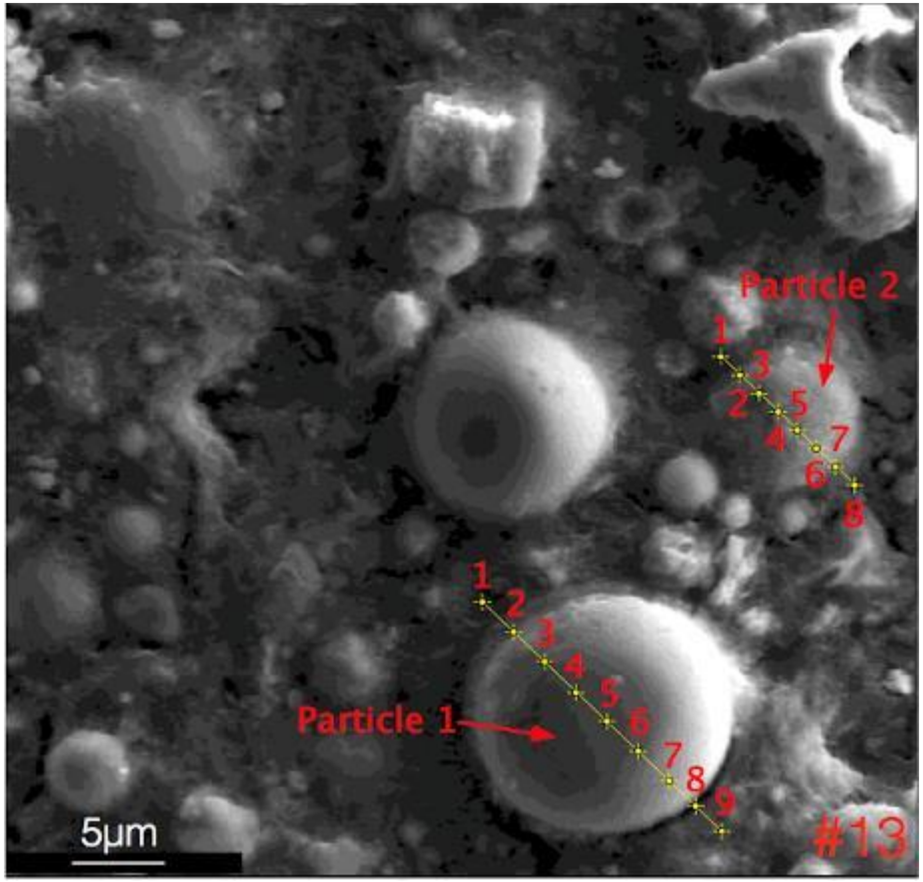
E_{nano}: 39.4 GPa;

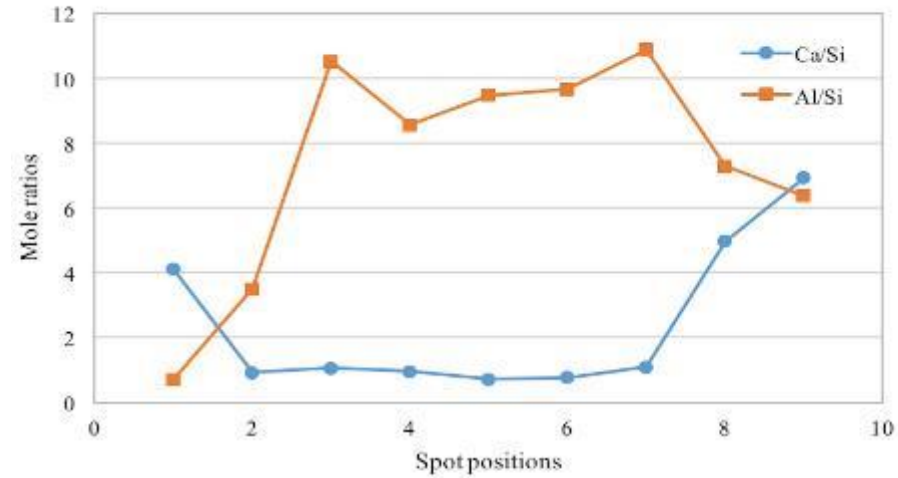
K: 4.1*10^{-17} m^2/s;

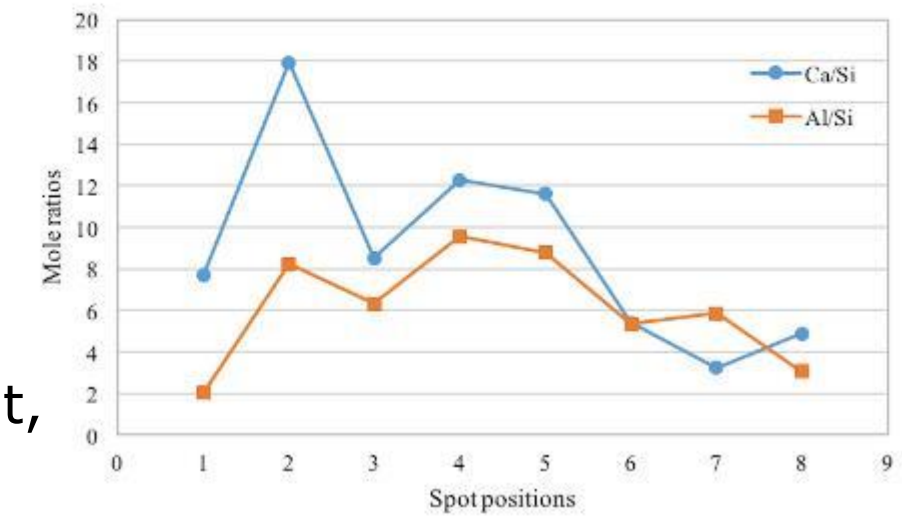
D_{Cl^-}: 1.9*10^{-12} m^2/s

Xie, N., Shi, X., et al. Upcycling of Waste Materials: Green Binder Prepared with Pure Fly Ash. *ASCE Journal of Materials in Civil Engineering*, 2016, 28(3), DOI: 10.1061/(ASCE)MT.1943-5533.0001414.

Coal fly ash as binder/aggregate?







w/b 0.27, 66% FA-C + 34% cement,

28-d f'_c: 35.1 MPa

Du, S., Shi, X., Ge. Y. Electron Probe Microanalysis Investigation into High-Volume Fly Ash Mortars. *ASCE Journal of Materials in Civil Engineering*, 2016, DOI: 10.1061/(ASCE)MT.1943-5533.0001854.

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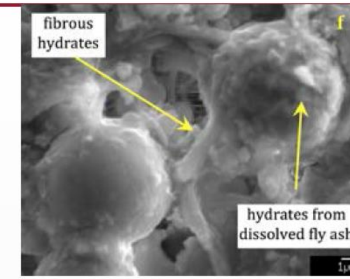
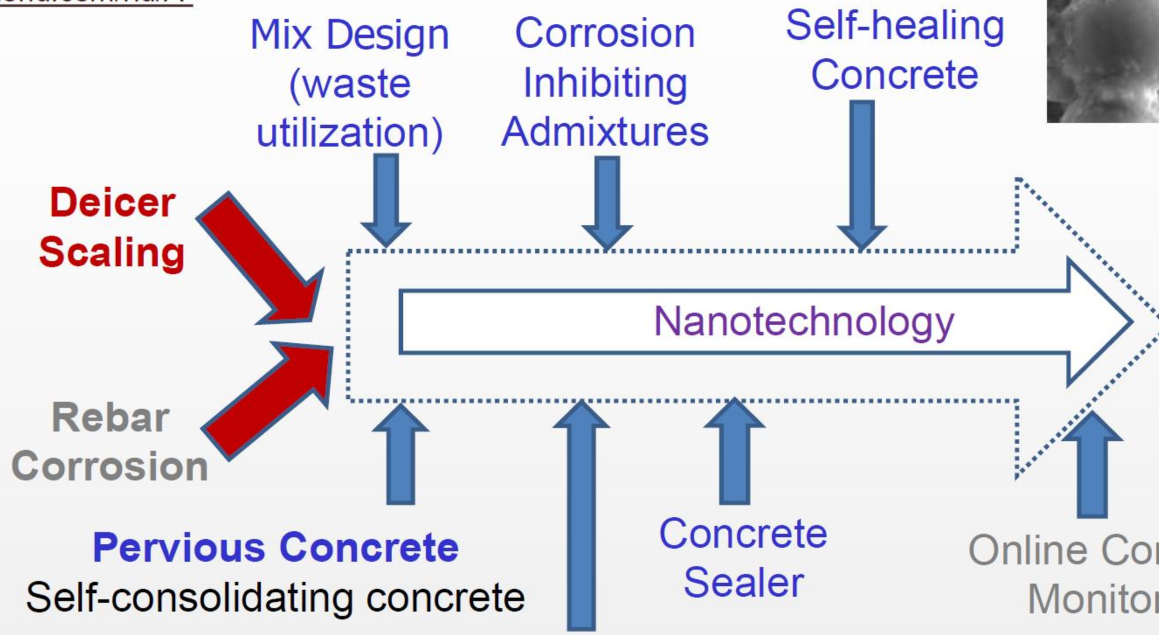
Smart and Green Infrastructure Enabled by Materials



Research Interests

- Durable, sustainable, and smart pavements
- Sustainable materials for the built environment: e.g., value-added utilization of industrial or agro-based byproducts and recycled materials, multiscale characterization and modification
- Corrosion protection, infrastructure preservation or rehabilitation techniques and practices



Electrochemical Preservation/Rehab.

- Anti-icing Overlays
- Bioenergy Harvesting

- Self-healing coating
- Nanocomposite coating …

NSF

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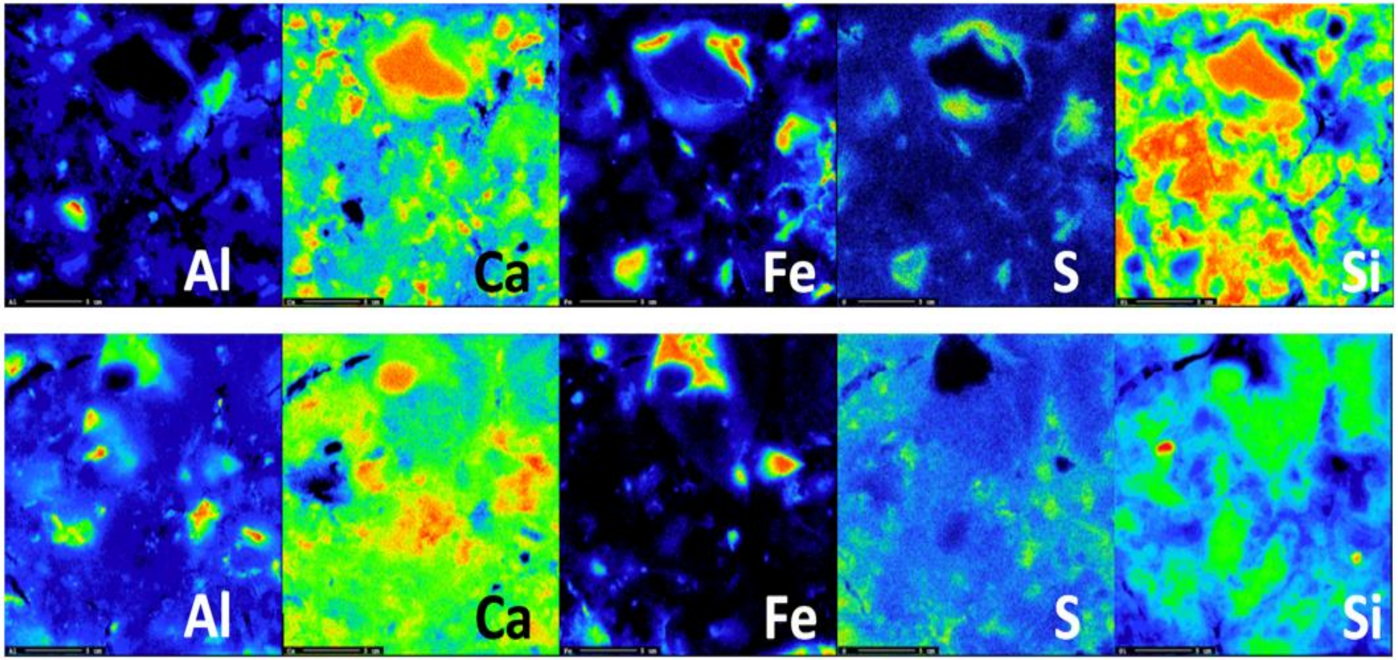
ILLINOIS CENTER FOR TRANSPORTATION

CLEAR ROADS — research for winter highway maintenance

CAMMSE

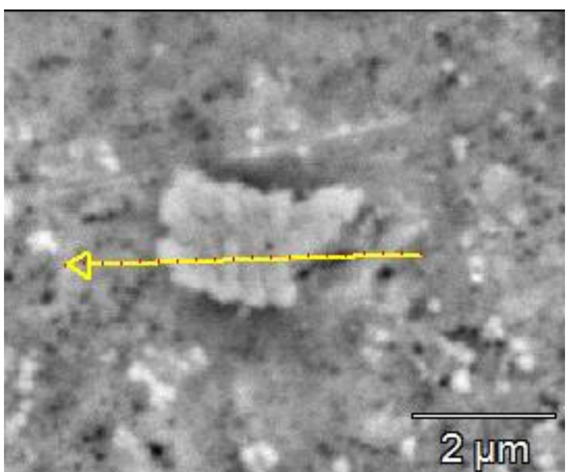
ACRP — AIRPORT COOPERATIVE RESEARCH PROGRAM

GO-OPC: Elemental maps & SEM

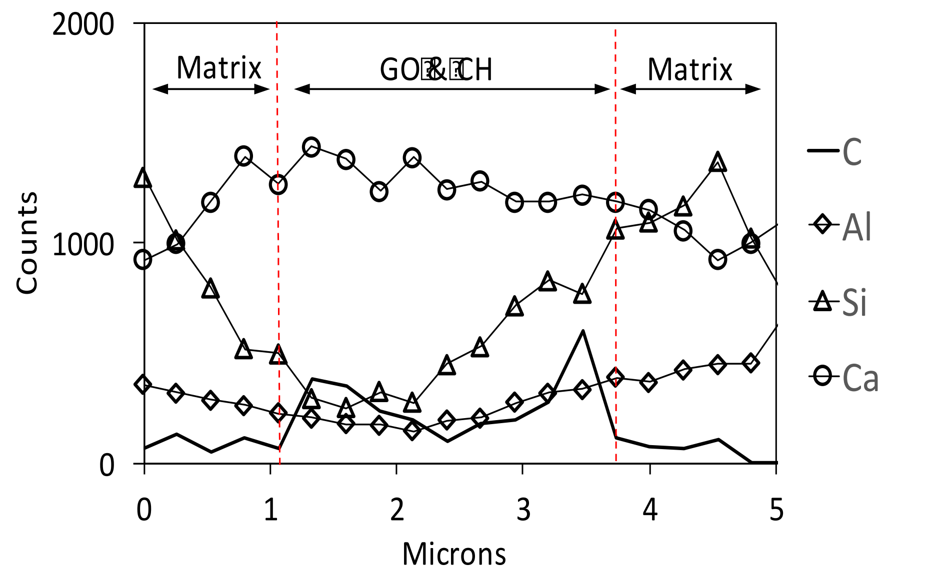


Elemental maps (10x10 μm) for selected sites at 28-d

(top) OPC paste; **(bottom)** OPC+GO paste

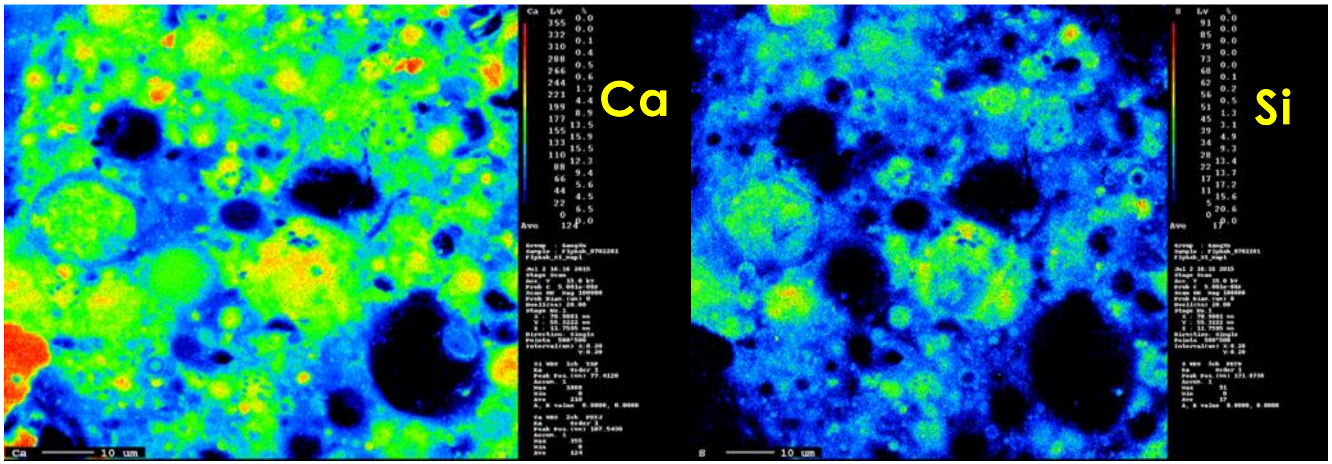


GO-induced crystalline $Ca(OH)_2$

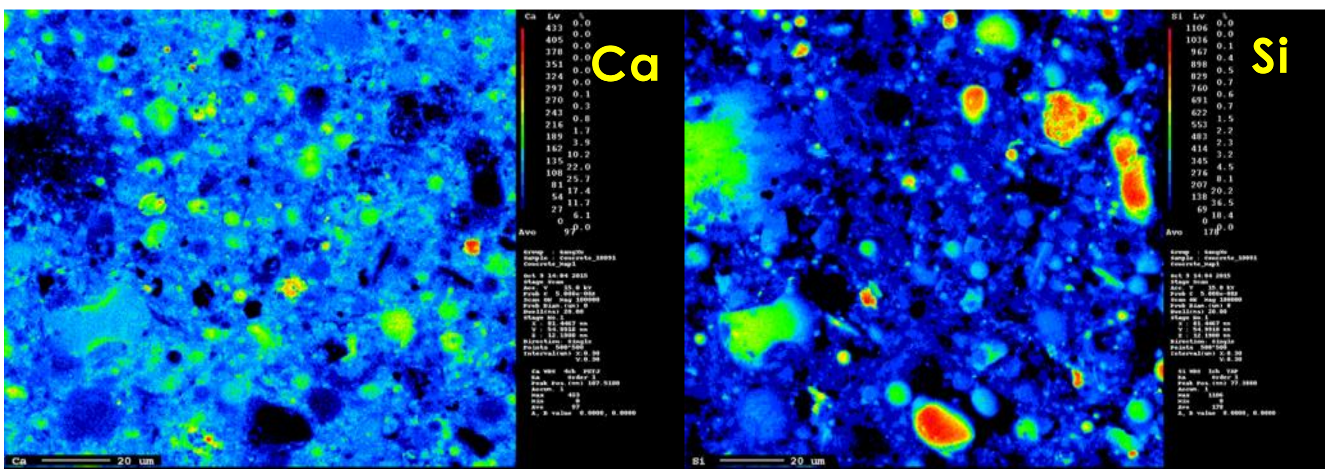


GO Modified Fly Ash Mortar

❑ EPMA (Electron probe micro-analyzer)



(a)



(b)

Element mapping (Ca and Si)
(a) mortar without GO;
(b) **GO-modified mortar**

GO in the hydration system

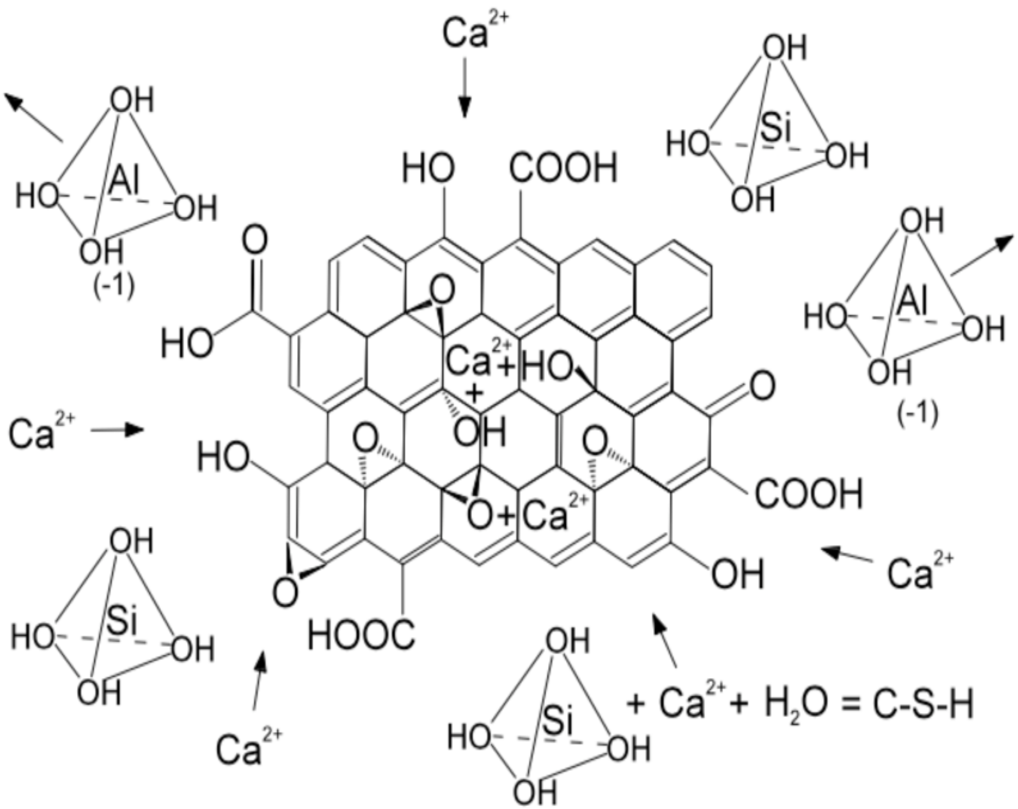
Group	Modifier		Intermediates				Former		Bridging	
	Ca		Al		Fe		Si		S	
	Mean	Std. dev.	Mean	Std. dev.	Mean	Std. dev.	Mean	Std. dev.	Mean	Std. dev.
OPC	14.3	1.39	3.85	2.52	0.58	0.69	15.3	4.40	0.42	0.18
OPC+GO	13.5	1.57	4.23	2.91	0.62	0.71	15.1	4.52	0.19	0.12
GO effect		+13%		+15%		+3%		+3%		-33%

1. The GO increased σ of Ca distribution by 13%. The boxplot also indicated that GO reduced the Ca-concentration.

2. The GO increased σ of Al and Fe distribution by 15% and 3% respectively. e.g., **repelling $Al(OH)_4^-$**

3. The effect of GO on the Si distribution was considered weak (increased by 3%). This is due to the presence of neutral $Si(OH)_4$ units in addition to $SiO(OH)_3^-$ and $SiO_2(OH)_2^{2-}$ anions, as the electronegative GO does not repel neutral $Si(OH)_4$ units.

Function of GO

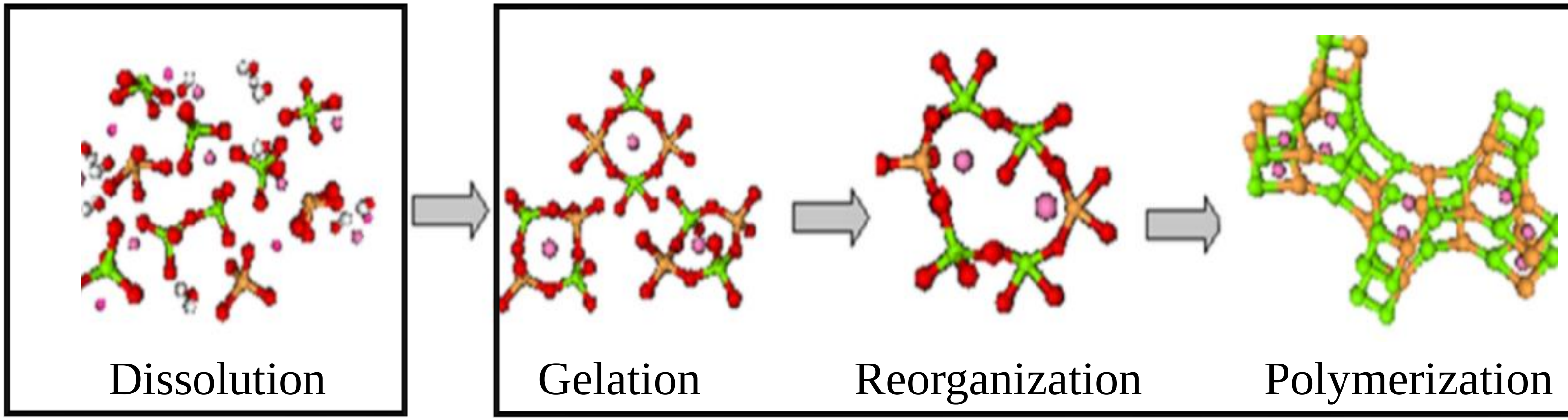


1. Exclude the intermediates
2. Consume network modifiers
3. Not affect network formers

	Cement	Fly ash
SiO_2 (wt. %)	21	23.5
Al_2O_3 (wt. %)	**4**	**13.8**
Fe_2O_3 (wt. %)	3.5	4.8
CaO (wt. %)	**65**	**23.2**

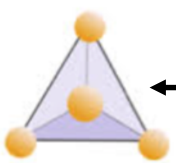
Element	**Function in structure**
Ca	Network Modifiers
Fe	Intermediates
Al	
Si	Network Formers

Unlock the potential of fly ash!



By using activators

Release

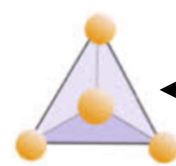


Network formers and intermediates: (SiO_4, FeO_4, AlO_4 or MgO_4)

Network modifiers: (Ca, Na or K)

By GO

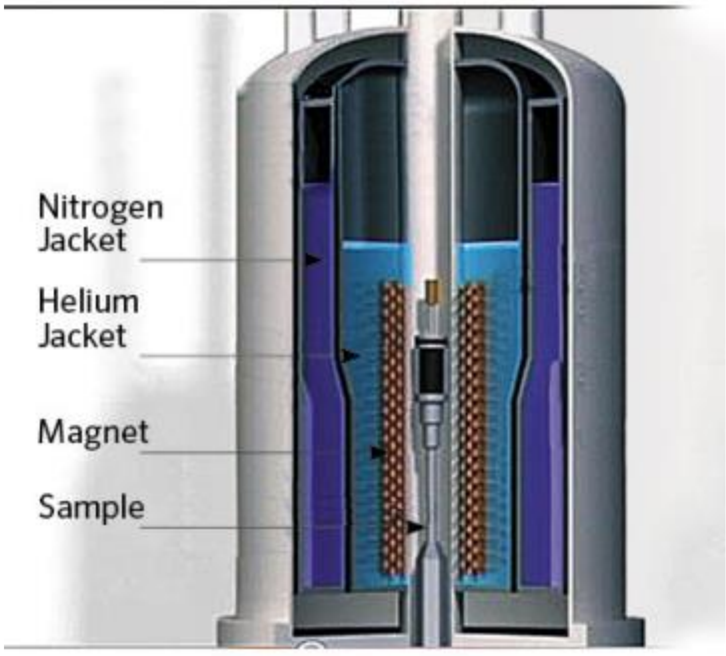
Directional selection



(SiO_4, ~~FeO_4~~, ~~AlO_4~~, ~~MgO_4~~)

Consume Network modifiers: (Ca, Na or K)

NMR Instrument

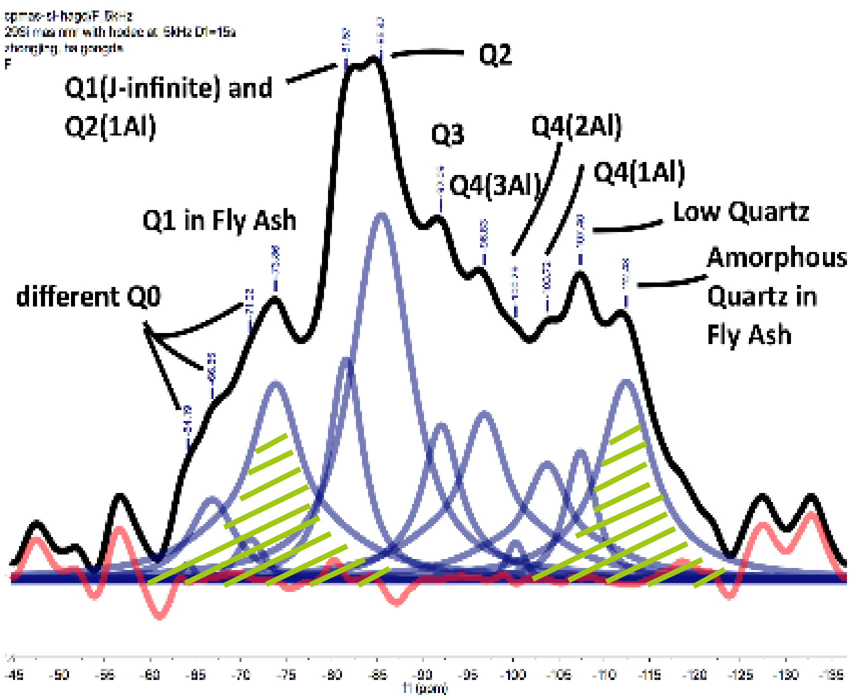


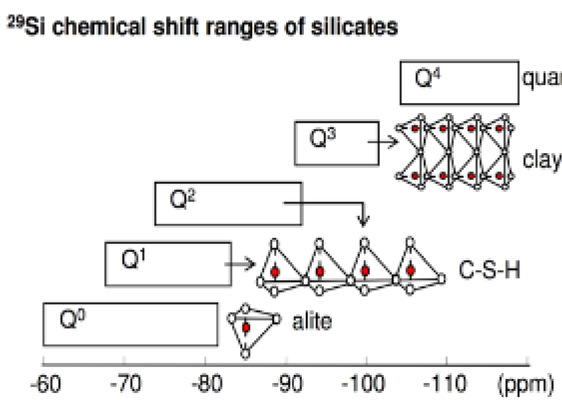
Bruker Avance III 400MHz NMR machine

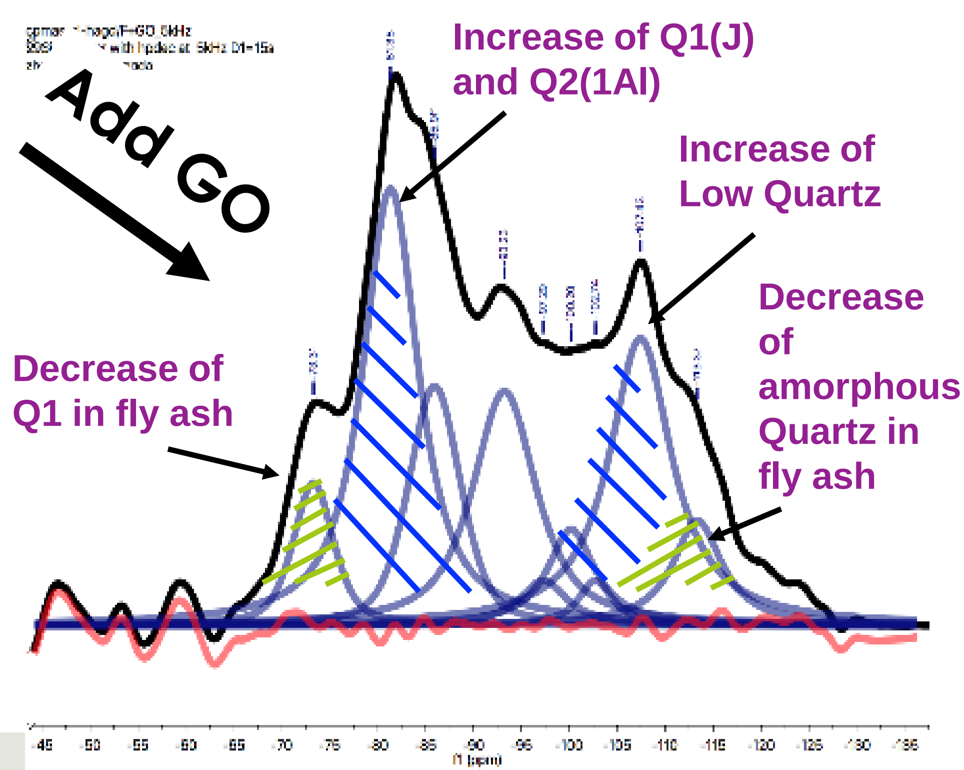
(photo by Bruker Inc.)

^{29}Si NMR Study of Fly Ash Hydrates

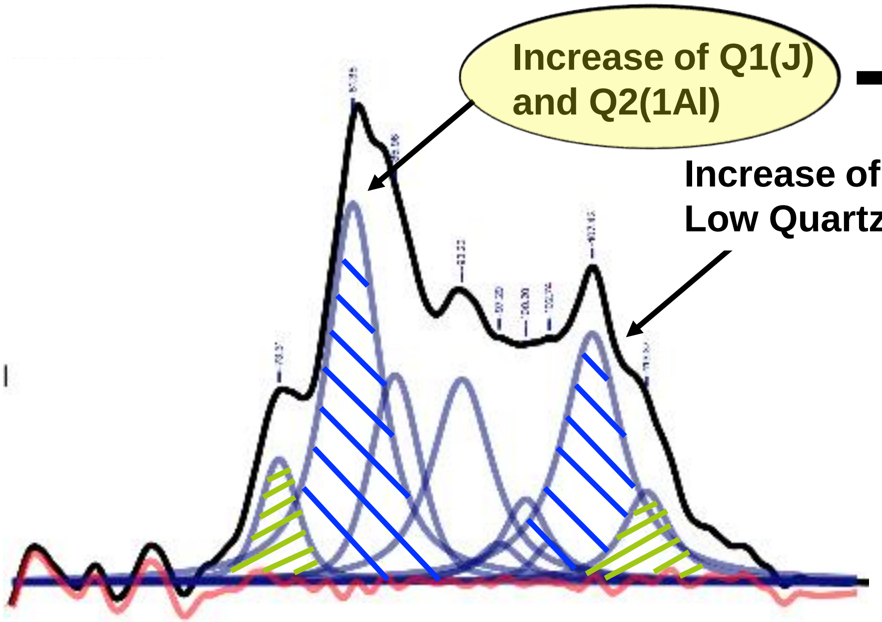
^{29}Si NMR spectra at 56-day

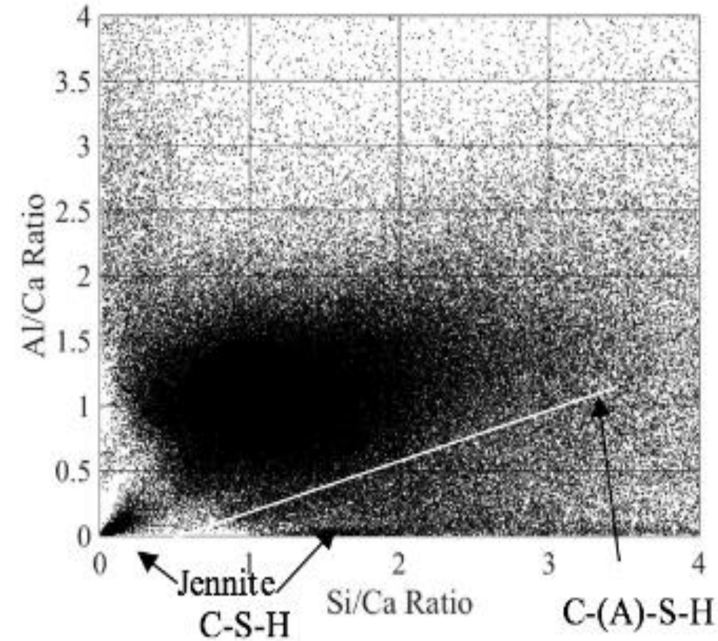


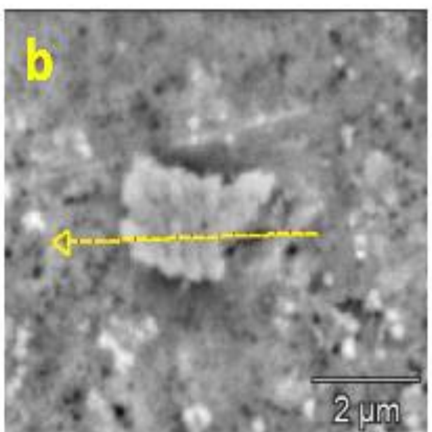


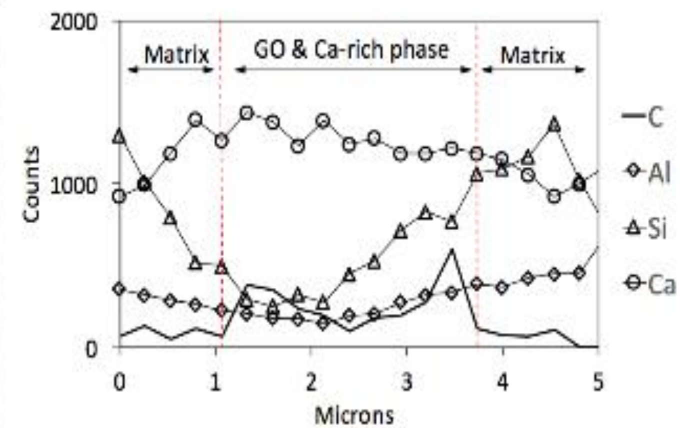


^{29}Si NMR Coupling with EPMA



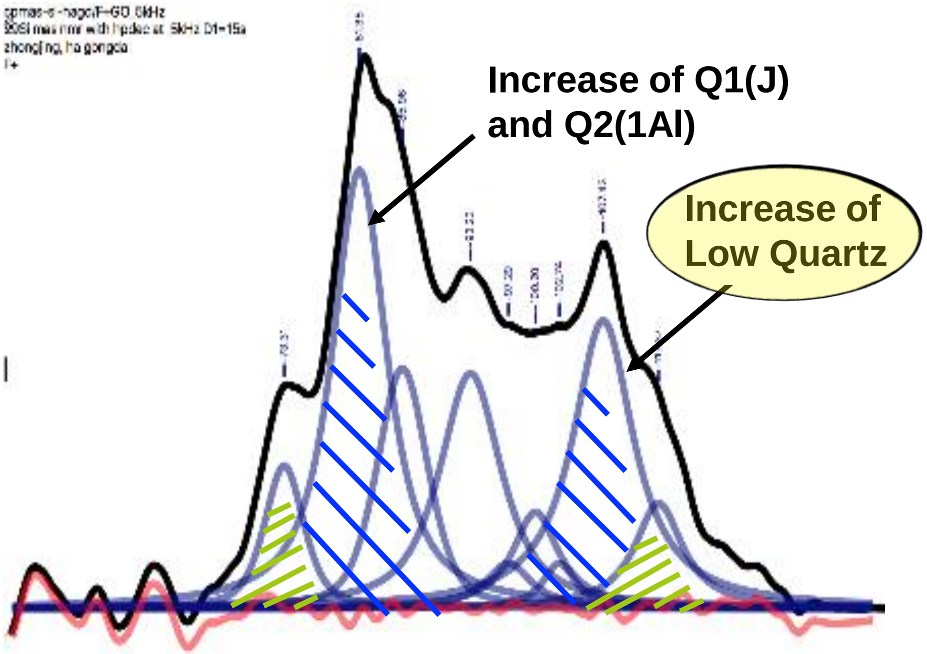


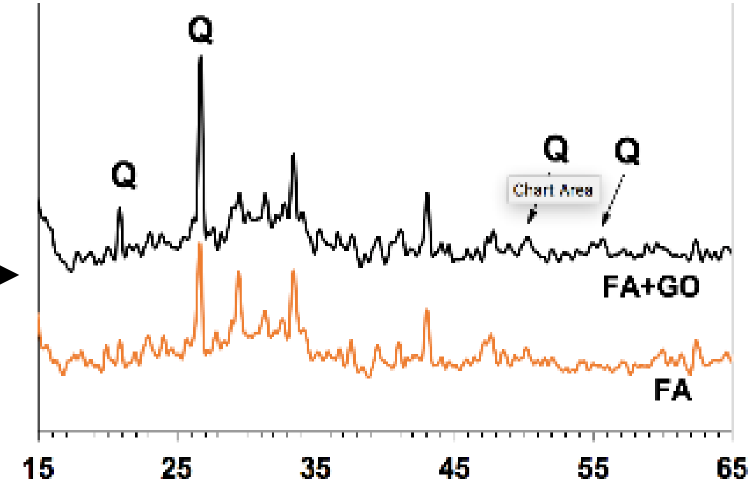




BSE image of GO-induced Jennite

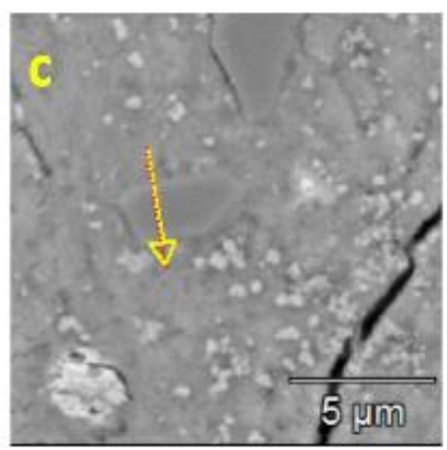
^{29}Si NMR Coupling with XRD

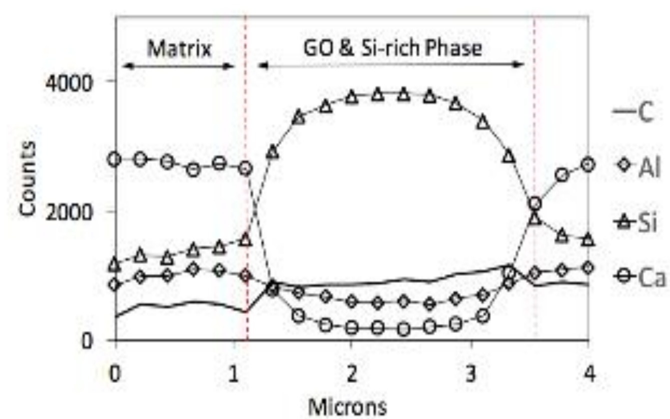




XRD confirmed increase of Low Quartz

BSE image of GO-induced Low Quartz





^{27}Al NMR Study of Fly Ash Hydrates

^{27}Al NMR spectra at 56-day