Competitive Academic Agreement Program

Mitigating External Corrosion of Pipelines Through Nano-modified Cement-based Coatings

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Main Objective

- Explore the feasibility of a cement-based pipeline coating material that exhibits:
  - Superior hardened and sealing performance, through carbon nanotubes and supplementary cementitious materials
  - Ease of application, through nano-sized attapulgite clays

Project Team & Other Sponsors

- Department of Civil Engineering and Engineering Mechanics (CEEM)
- Shiho Kawashima (Principal Investigator, CEEM)
- Siwei Ma (PhD student, CEEM)
- Yu Xie (M.S. student, CEEM), Alyssa Ramos-Avila (B.S. student, CEEM), YoonJung Jo (H.S. student)

COLUMBIA | ENGINEERING
The Fu Foundation School of Engineering and Applied Science

Project Outline

① **Materials and Design**
② Mechanical and hardening properties
③ Permeability/porosity
④ Rheological properties
⑤ Conclusions and recommendations

Materials and Design

Additives:

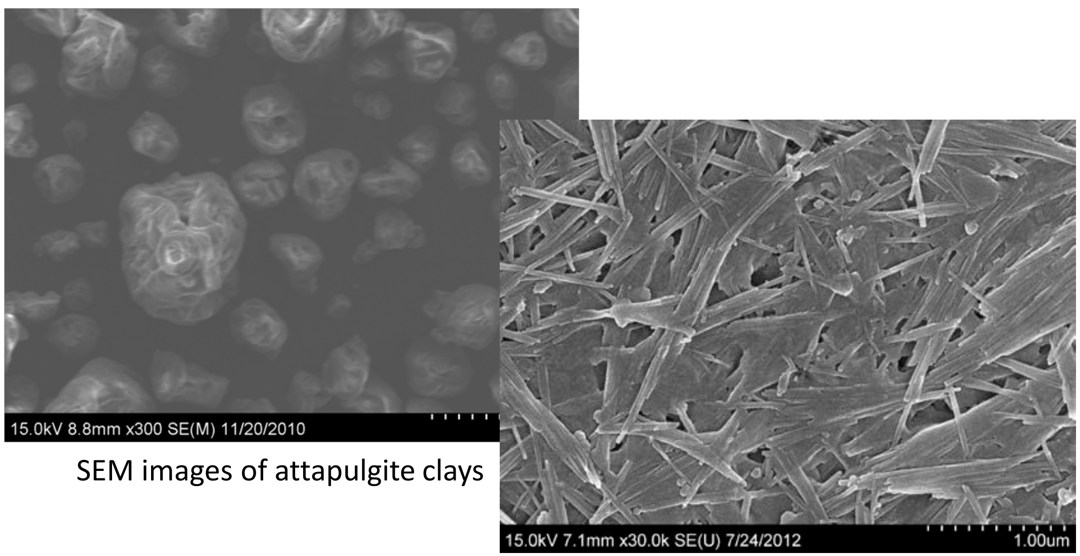
- Highly-purified attapulgite clay (Active Minerals)
- Carbon nano-tubes (Nanocyl)

Binder:

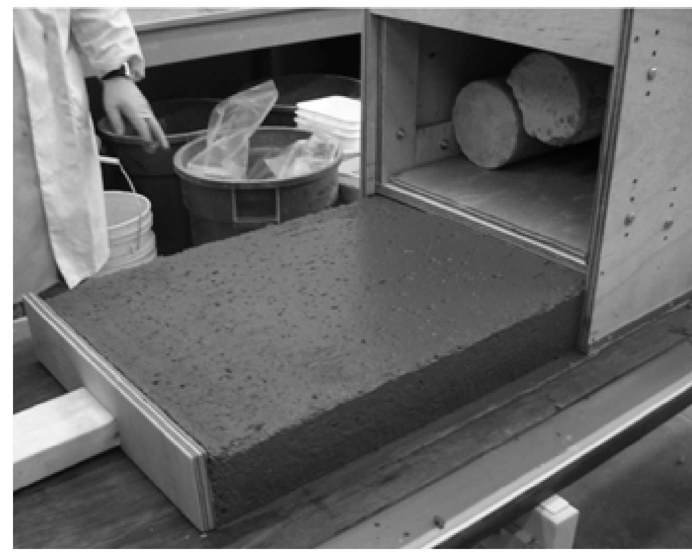
- Ordinary Portland Cement (Separation Technologies)
- Grade 120 Blast Furnace Slag (Lafarge)
- Type F Fly Ash (Separation Technologies)

Attapulgite Nanoclays (ATTs)

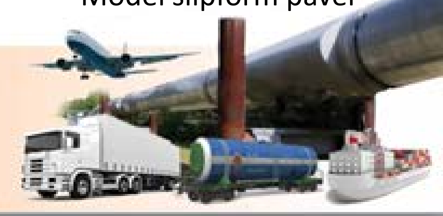
- 1.75 µm in length, 3 nm in diameter (average)
- Increases rate of structural rebuilding of fresh concrete mixes
- Applications: slipform casting/paving, reduce rebound of shotcrete
- Pipeline coating: rheological properties of fresh concrete can be tailored by clays to improve application process and improve uniformity



SEM images of attapulgite clays



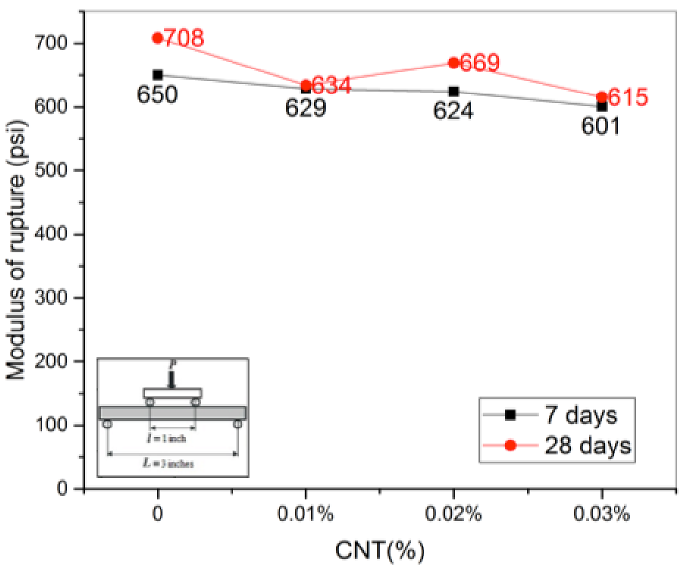
Model slipform paver



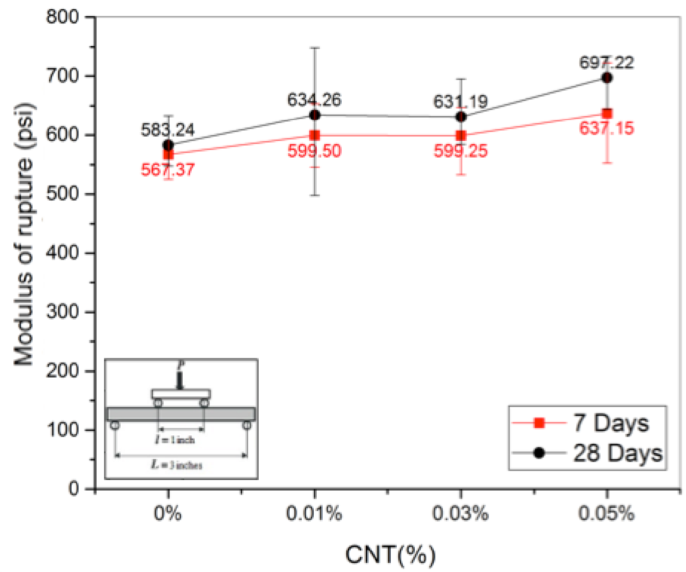
Carbon Nanotubes (CNTs)

- 1.5 µm in length, 9.5 nm in diameter (average)
- Increase flexural strength, reduce shrinkage
- Pipeline coating: refine pore structure to reduce permeability; enhance mechanical properties
- Key challenge is dispersion: compare dry form vs aqueous form

Aqueous form

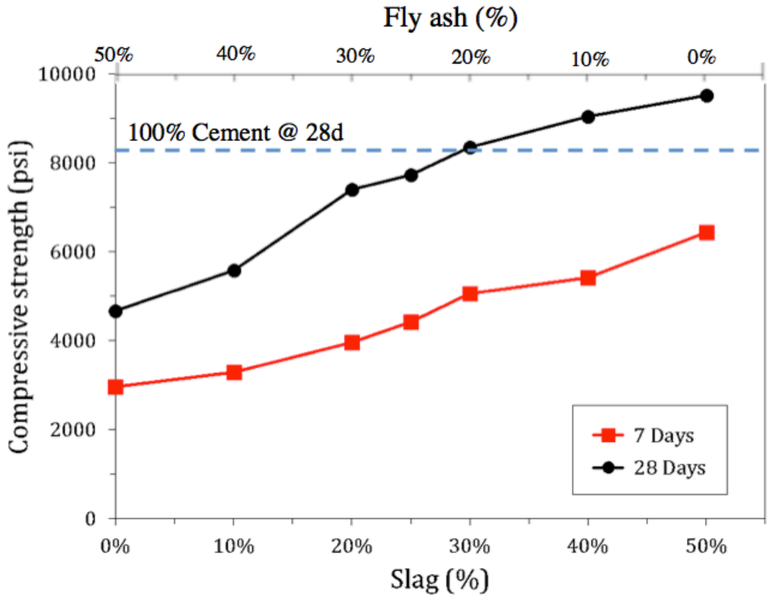


Dry form



Supplementary Cementitious Materials (SCMs)

- Replacement of cement with fly ash and blast furnace slag
- Refine pore structure to improve durability properties through pozzolanic reaction
- Pipeline coating: further refine pore structure to reduce permeability



Mix design

Mix	Cement	Fly Ash	Slag	Surfactant	CNT	Attapulgite Clay
	(% by mass of total binder)			(% addition by mass of binder)		
C	100	0	0	0	0	0
C_0	100	0	0	0.05	0	0
C_CNT	100	0	0	0.05	0.01	0
C_ATT	100	0	0	0.05	0	0.3
C_CNT_ATT	100	0	0	0.05	0.01	0.3
FS_0	50	25	25	0.05	0	0
FS_CNT	50	25	25	0.05	0.01	0
FS_ATT	50	25	25	0.05	0	0.3
FS_CNT_ATT	50	25	25	0.05	0.01	0.3

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④ Rheological properties

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Method: Isothermal Calorimetry

Figure. TAM Air Isothermal Calorimeter

- The heat flow of a sample measured through isothermal calorimetry provides the rate of cement hydration (exothermic reaction).

Results: Rate of Cement Hydration

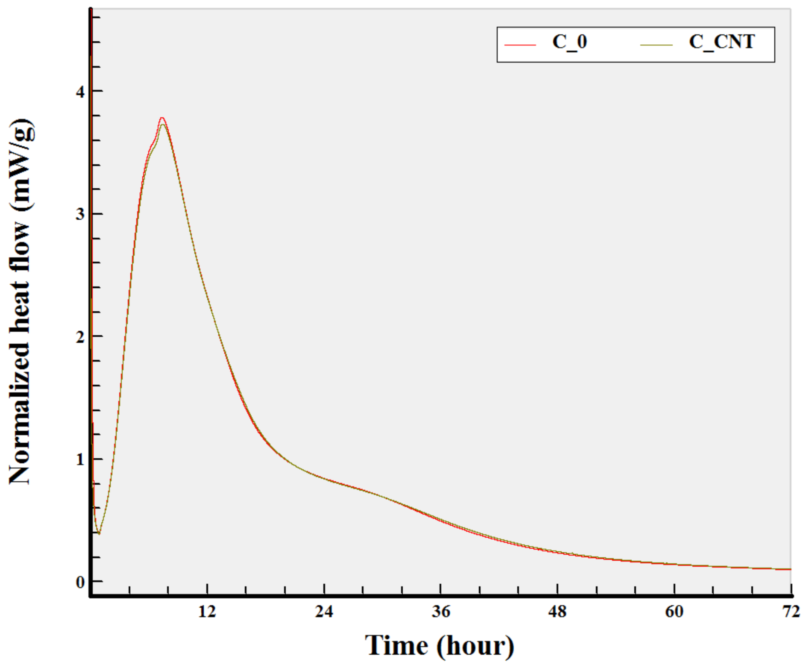

Figure. Paste with 0 and 0.01% CNTs

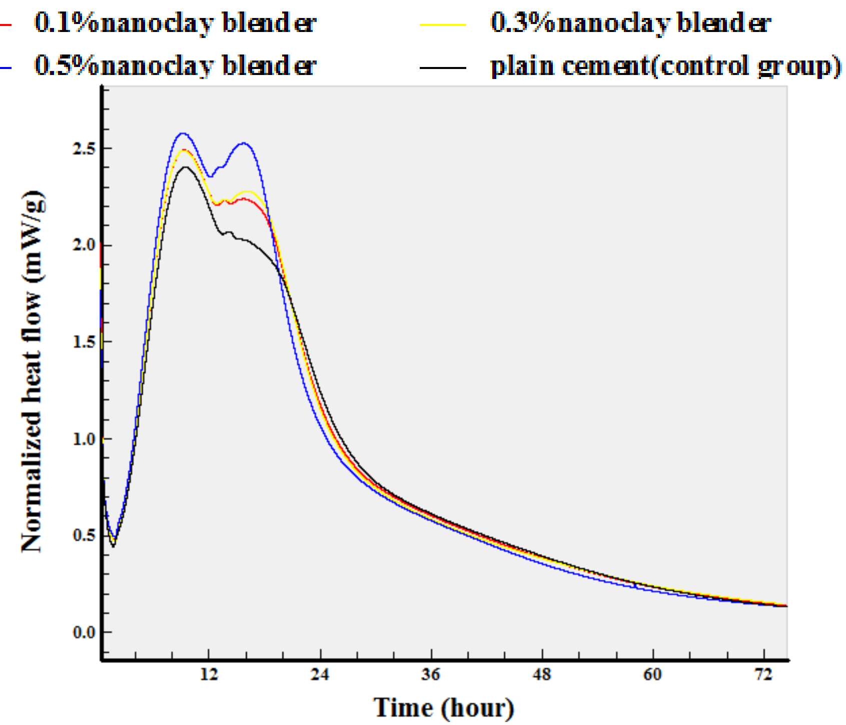

Figure. Paste with nanoclays.

- No measurable effect by the CNTS on the hydration kinetics.
- Higher rate of heat generation with higher additions of nanoclay, indicating acceleration in cement hydration (seeding effect).

Method: Mechanical Testing

- Direct tensile strength tests: dogbone-shaped paste samples 1” x 1” tapered cross-section

- Compressive strength tests: 2” x 2” x 2” cubic mortar samples (ASTM C-109)

- 7 and 28 d strength

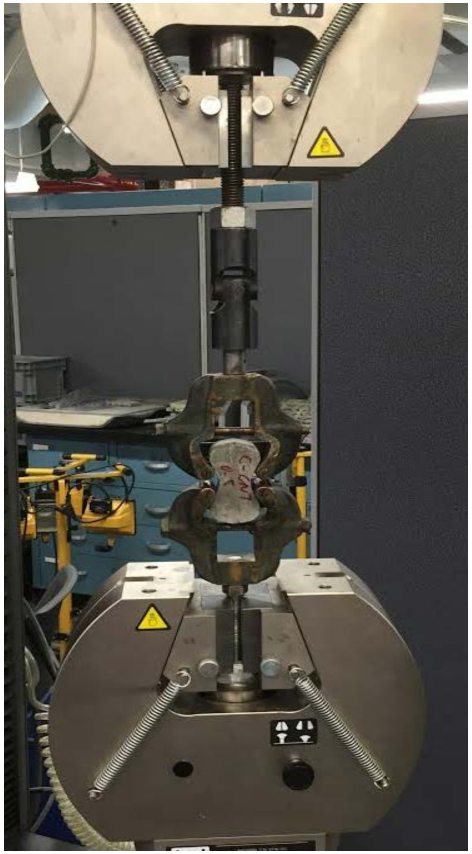

Figure. Tensile strength setup.

Results: Compressive strength

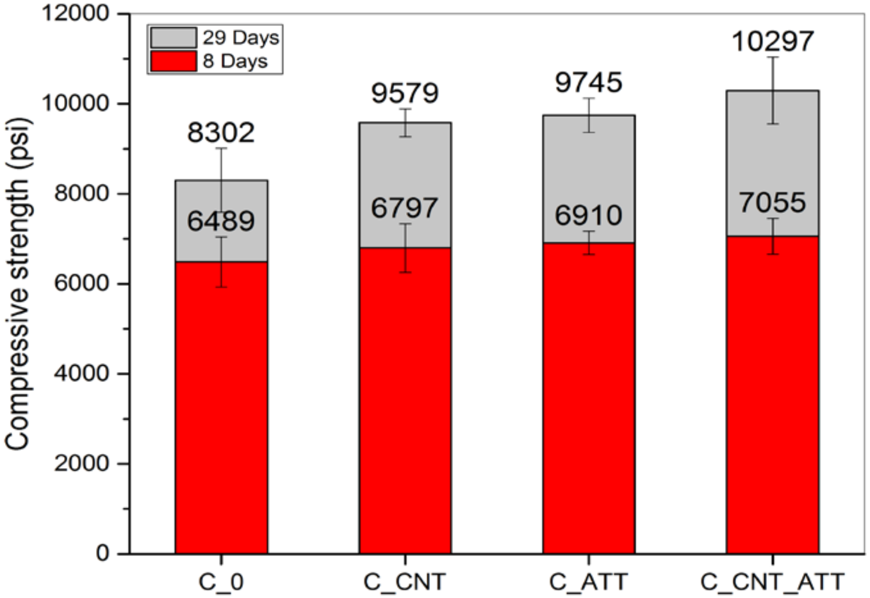

Figure. Cement mortar systems.

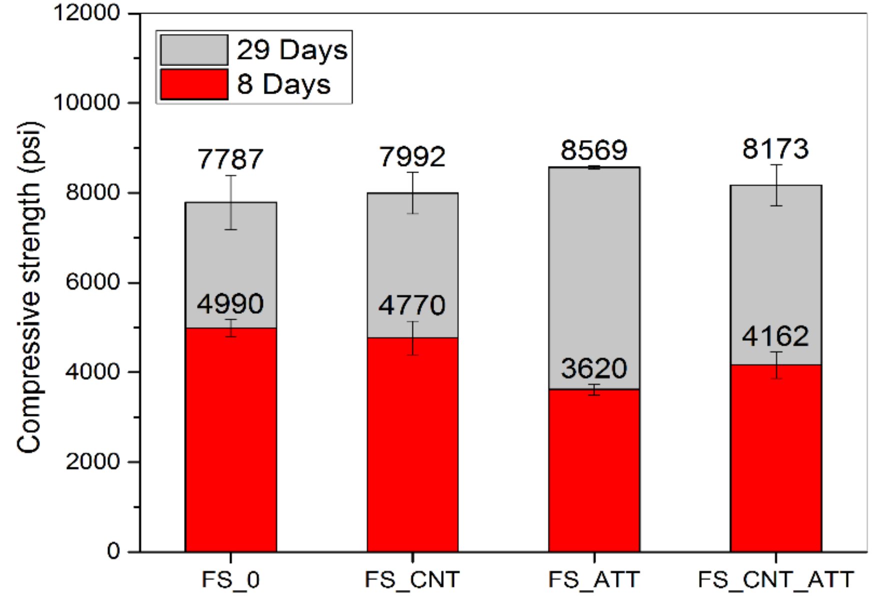

Figure. Cement-fly ash-slag mortar systems.

- Although attapulgite clays (ATT) are added as a rheological modifier, their effect on compressive strength is comparable to or greater than that of the carbon nanotubes (CNTs)
- Due to improved uniformity by ATT; dispersion issue of CNTs

Results: Tensile strength

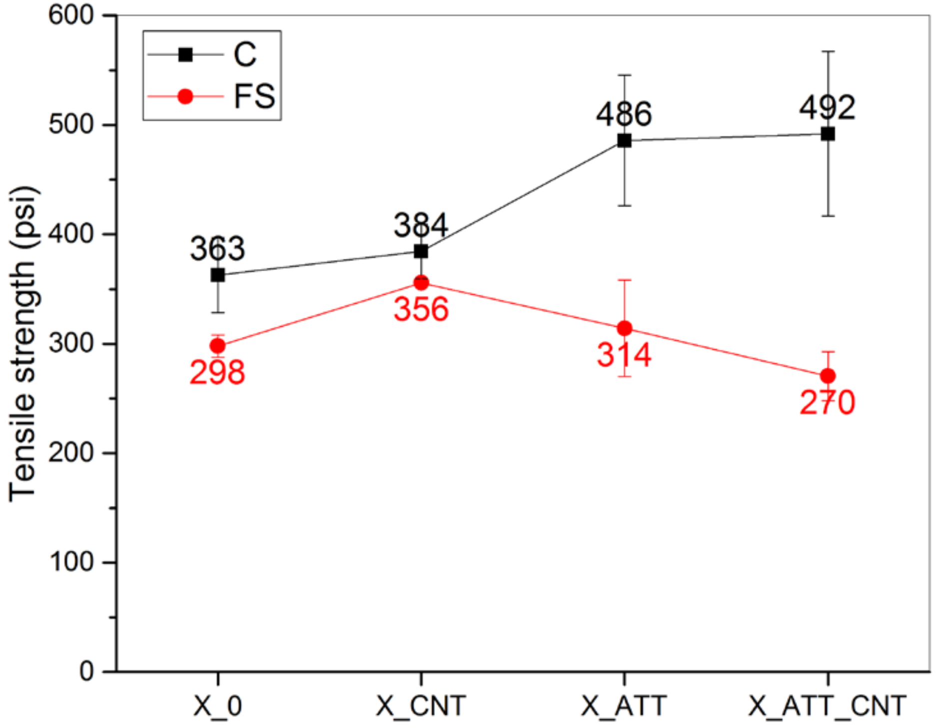

Figure. 28 day direct tensile strength
C: cement; **FS**: cement-fly ash-slag

- In agreement with compressive strength results, the effect of ATT on tensile strength is comparable to or greater than that of CNTs

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① Materials and Design
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③ Permeability/porosity
④ Rheological properties
⑤ Conclusions and recommendations

Method: Mass change (direct method)

Figure. Setup to determine submerged mass.

$$\text{Void Content} = \left[1 - \left(\frac{K \times (A - B)}{\rho_w \times D^2 \times L}\right)\right] \times 100$$

A = dry mass of the specimen
B = submerged mass of the specimen
K = 1,273,240 in SI units or 2,200 in [inch-pound] units
D = average diameter of the specimen
L = average length of the specimen
ρ_w = density of water

Results: Mass change

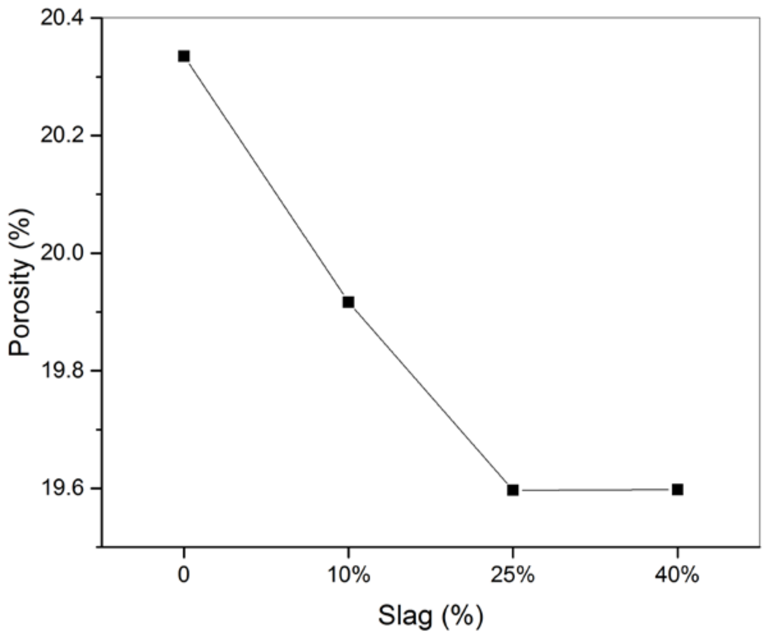


Figure. Porosity results of cement mortar with slag replacement.

- A decrease in porosity was capture, as expected, with increasing slag replacement, but the percent change is very low.

Method: Electrical resistivity

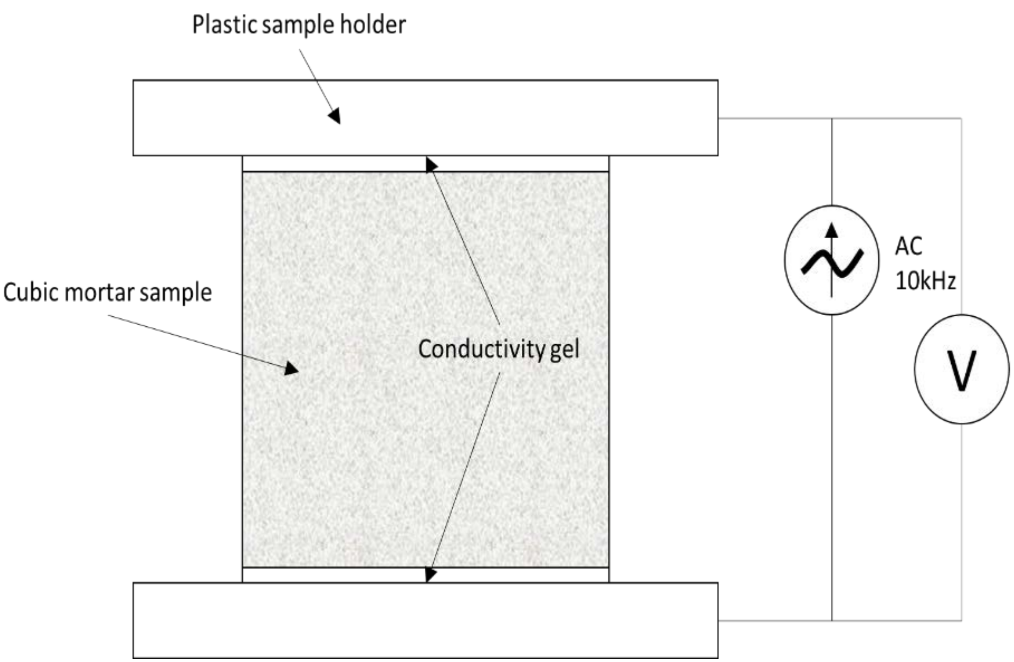


Figure. Schematic of electrical resistivity meter (RCON, Giatec). Uniaxial measurements performed at 1 kHz.

- 2-in cubic samples wet cured for 7 or 28 d, then air dried for 24 h prior to testing.
- Open microstructure will experience high moisture loss; highly percolated microstructure will experience limited moisture loss.
- As water is highly conductive compared to cement matrices, low resistivity is associated with a more percolated microstructure – low permeability – and vice versa.

Results: Electrical Resistivity

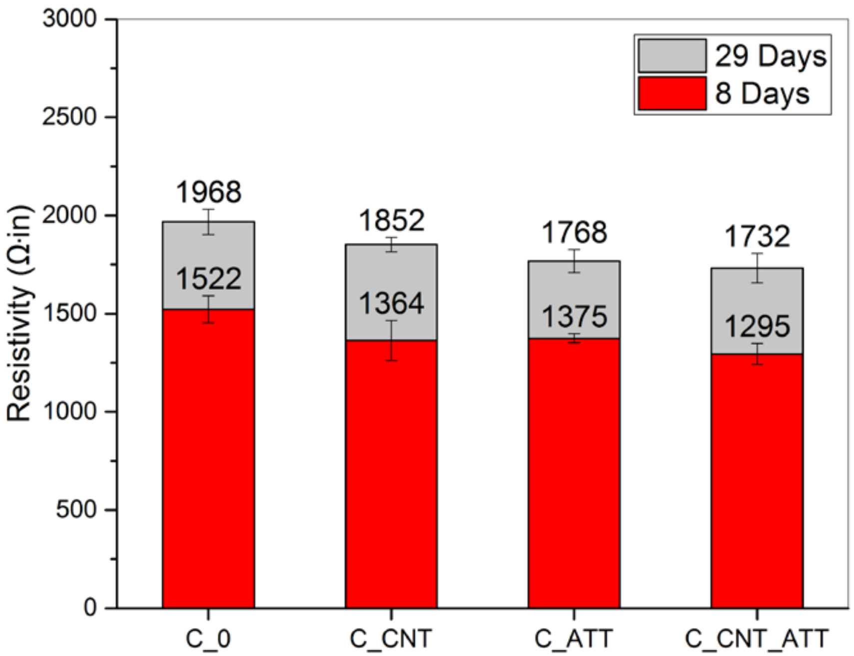


Figure. Cement mortar systems.

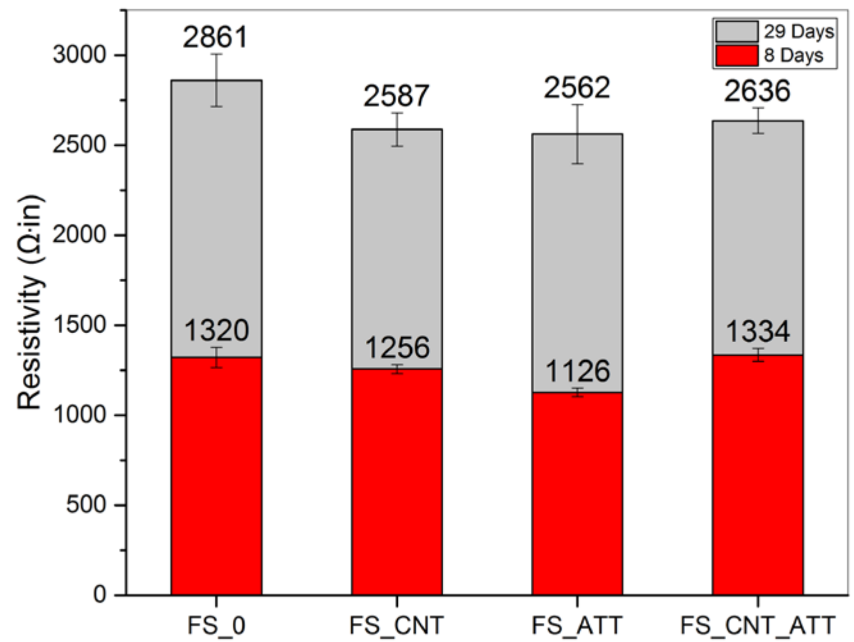
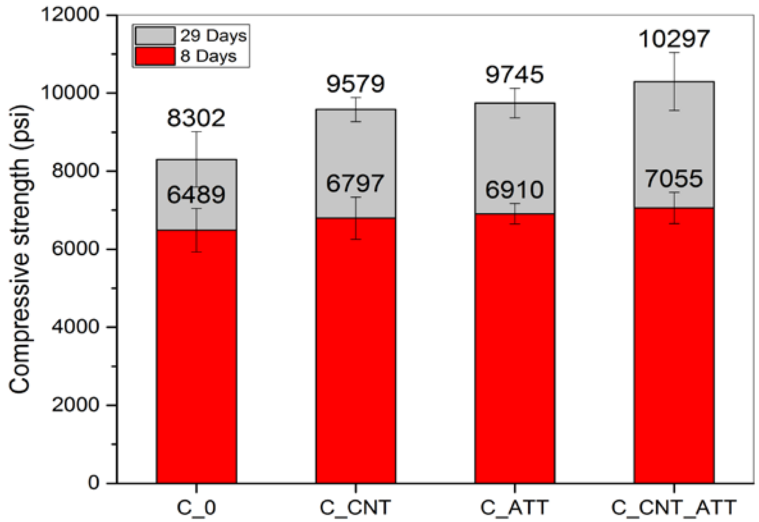


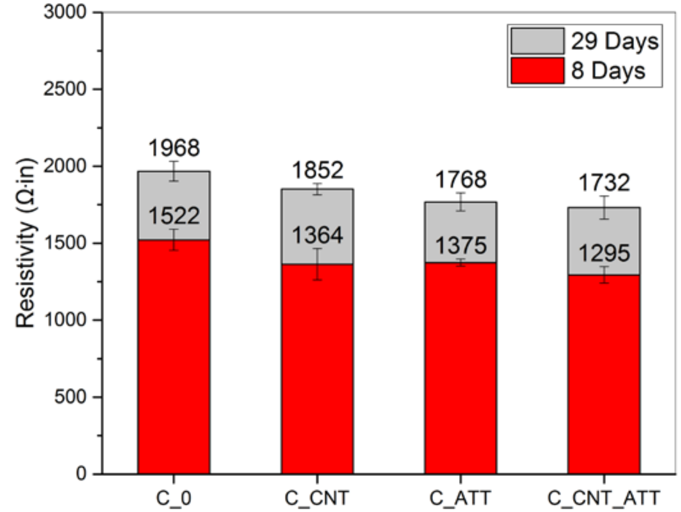
Figure. Cement-fly ash- slag mortar systems.

- Results indicate that ATTs and CNTs can reduce permeability, but effect was not significant.

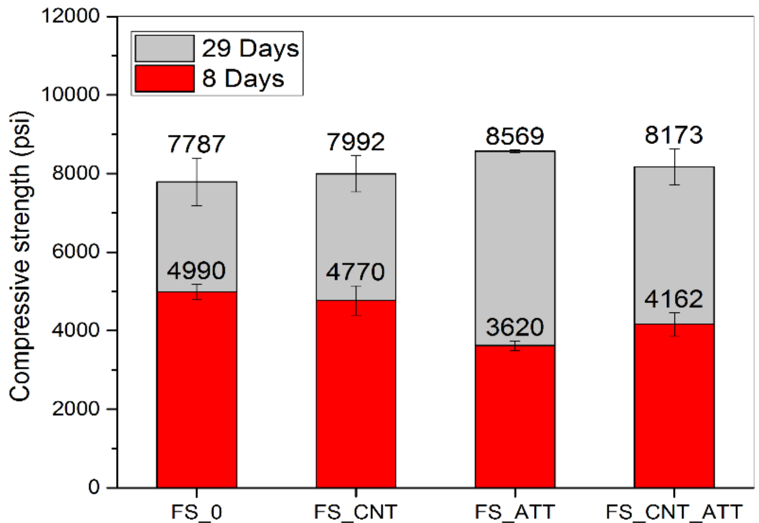
Compressive strength and electrical resistivity results

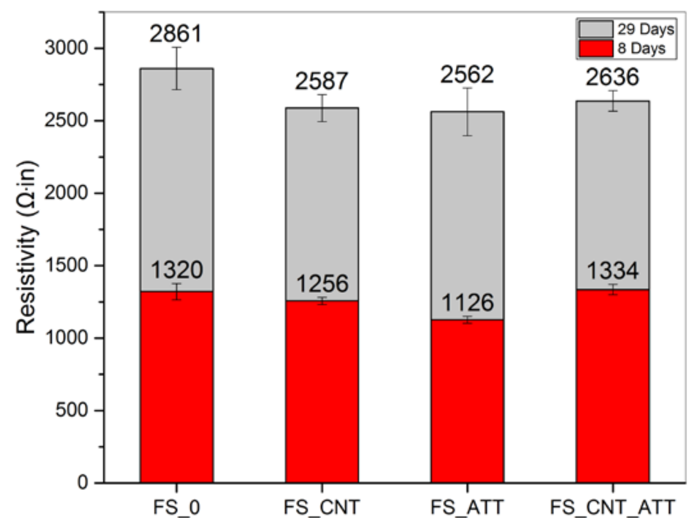
Cement





Cement-fly ash-slag





Similar trends: finer pore structure enhances strength and reduces permeability.

Project Outline

1. Materials and Design
2. Hardening and mechanical properties
3. Permeability/porosity
4. **Rheological properties**
5. Conclusions and recommendations

Method: Rheology

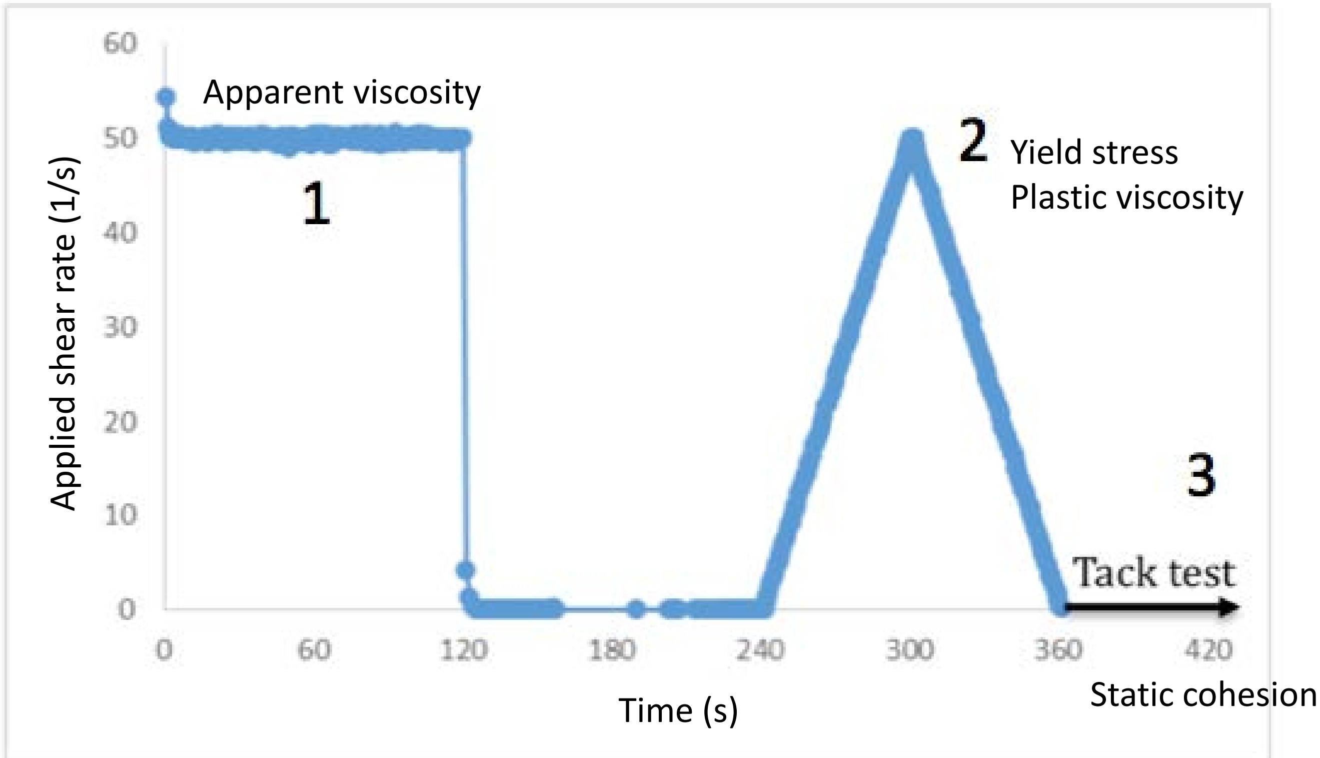
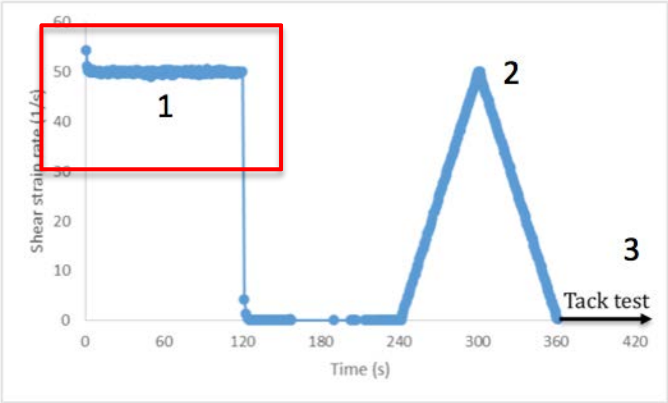


Figure. Rheological protocol.

Figure. Rotational rheometer (top); Parallel-plate setup (bottom)

1. Apparent viscosity



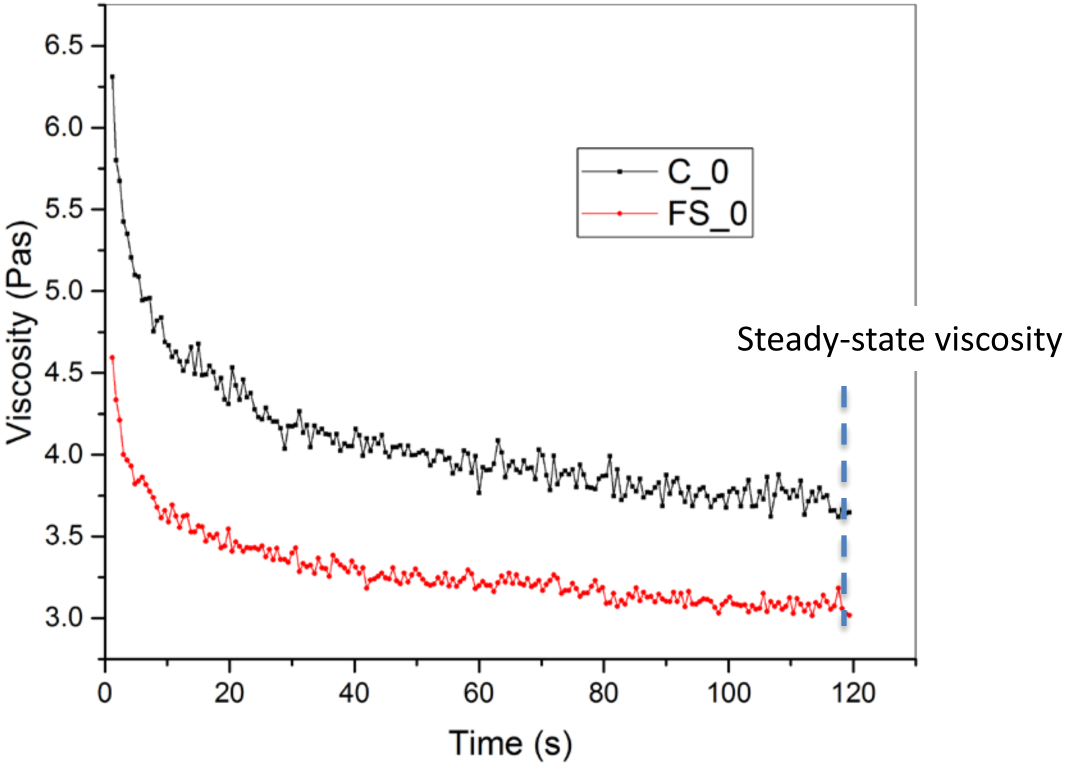


Figure. Viscosity evolution
C: cement; **FS**: cement-fly ash-slag

Results: Apparent viscosity

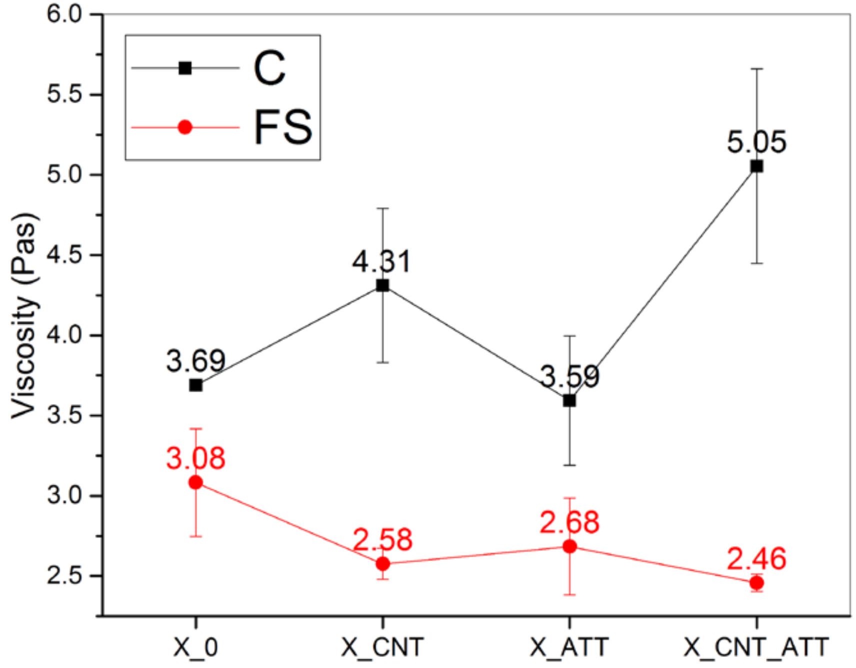
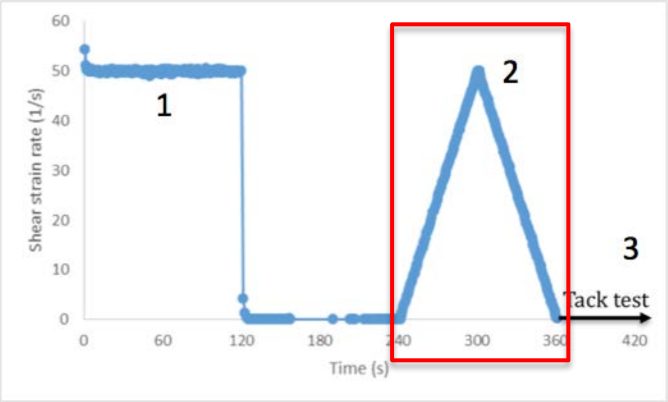


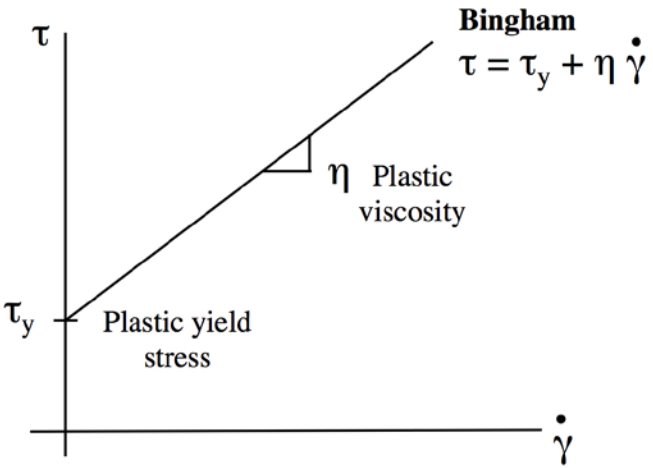
Figure. Apparent viscosity

C: cement; **FS**: cement-fly ash-slag **_CNT:** carbon nanotubes; **_ATT:** clays

- ATTs have little to no effect on viscosity in cement system; decreases viscosity in the ternary system → Flowability during casting
- CNTs (and CNTs+ATTs) have opposing effects → Dispersion issues

2. Yield stress





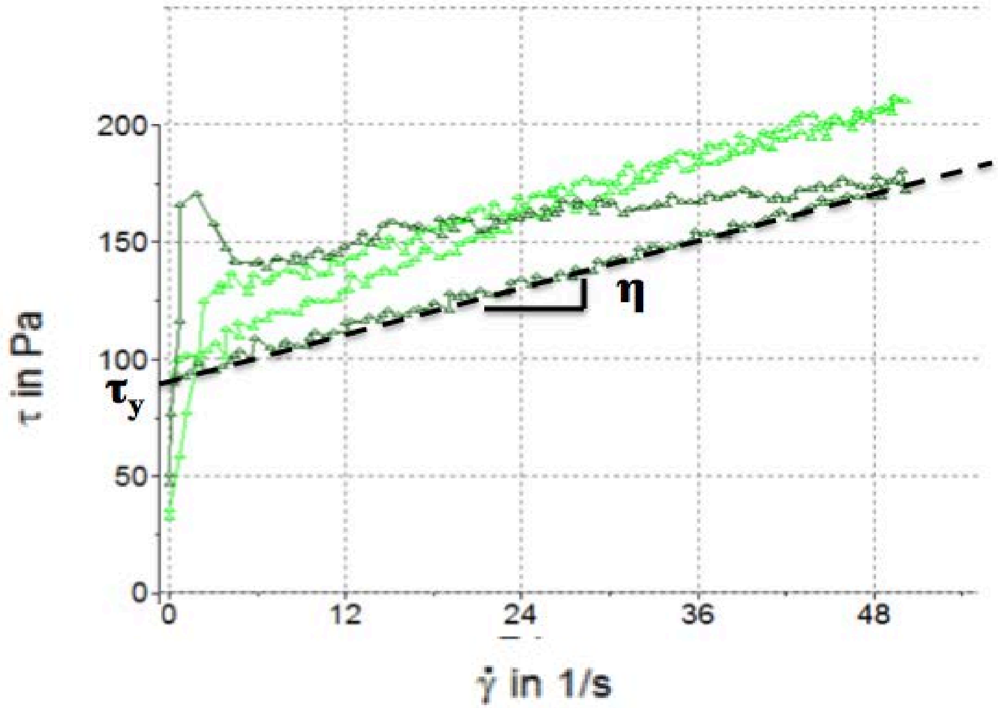
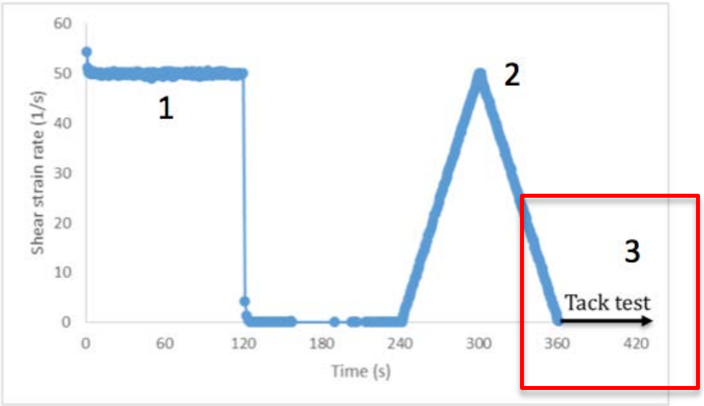


Figure. Flow curve fitted with Bingham model to obtain yield stress and viscosity.

3. Static cohesion



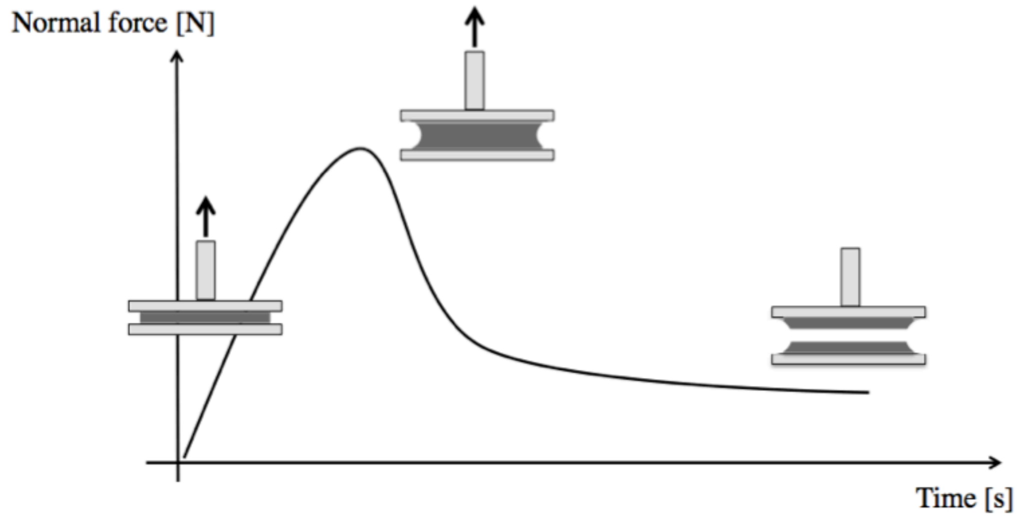


Figure. Tack test results.

Project Results: Rheological properties

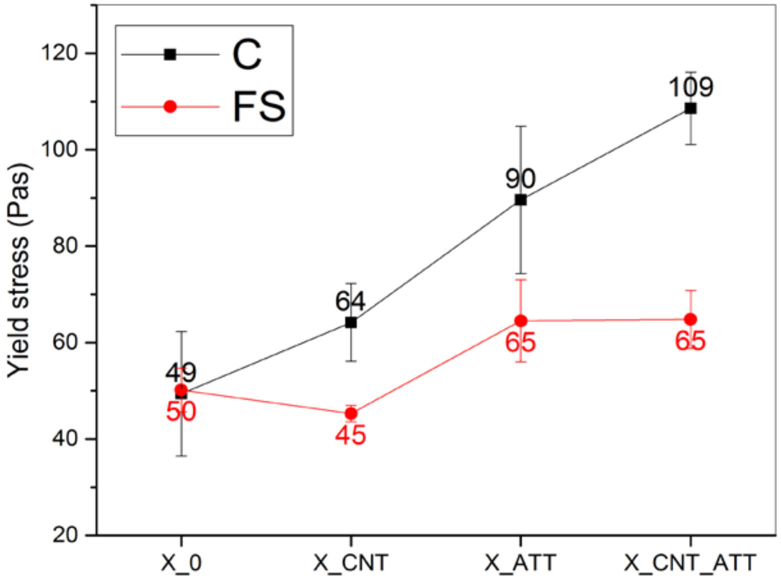


Figure. Yield stress

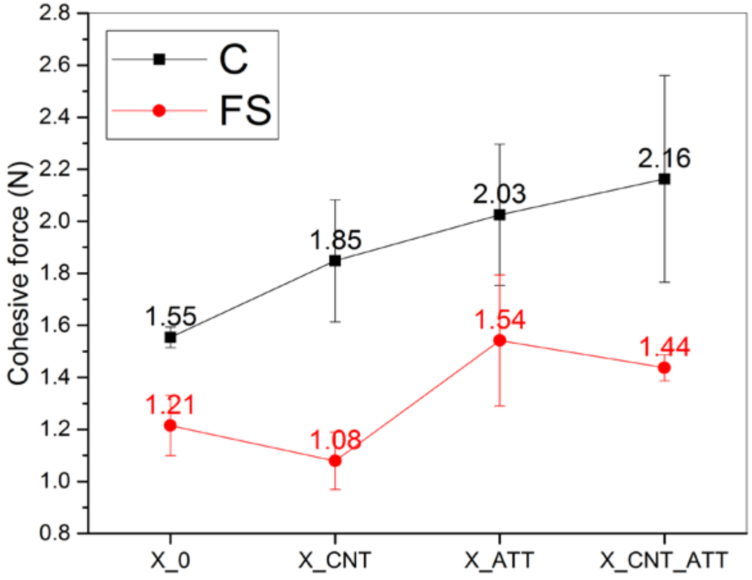


Figure. Static cohesion.

C: cement; **FS**: cement-fly ash-slag **_CNT:** carbon nanotubes; **_ATT:** clays

- Yield stress and cohesion were found to exhibit similar trend.
- ATTs enhance yield stress and cohesion in both systems → Ability to adhere onto pipeline surface
- CNTs have opposing effects → Dispersion issues

Other Project Results

- 1 PhD student
- 1 MS student, 1 BS student, 1 HS student (independent study for credit, summer internships)
- One technical journal manuscript– submitted for review

* R&D Program performance metrics reported to Congress

Summary of results

Testing methods	Attapulgite Clay		CNT		Summary
	Cement	Ternary	Cement	Ternary	
Compressive strength	↑	↑	↑	–	Attapulgite clays introduce enhancing effects on mechanical and hardening properties that are comparable to or greater than those by CNTs.
Tensile strength	↑↑↑	–	–	↑↑	
Isothermal calorimetry	↑		–		
Permeability	↓	↓	–	↓	CNTs and attapulgite clays can reduce permeability, but results indicate that the degree is moderate.
Apparent viscosity	–	↓	↑	↓	The effect of attapulgite clays on rheology is positive, as it is desirable to keep viscosity low during casting and static yield stress and cohesion high after placement.
Yield stress	↑↑↑↑↑↑↑↑	↑↑↑	↑↑↑	–	
Cohesion	↑↑↑	↑↑	↑↑	–	

*Note: − : <10%; ↑ : 10%-20%; ↑↑:20%-30%; ..... ↑↑↑↑↑↑↑↑: 80%-90%

Summary of results (conti.)

- Ternary (cement-fly ash-slag) systems with attapulgite clays can lead to beneficial properties, i.e. improved processing, permeability, and mechanical strength

- Potential future direction: System explored in the present project can be utilized for a dual coating system – cement-based top coating and polymer-based base coating – using two coating protection technologies to provide a viable solution to significantly increase protective performance and processing while alleviating the disadvantages of a single approach (not a simple superposition of materials and costs)

Future Program Improvements

- Overall great support/feedback from Program and Program Directors
- Longer project periods (> 18 months)
- More information on level of industry acceptance for new and emerging technologies and industry needs (tied to improved description of research areas)
- More opportunities for program awardees to interact with other awardees and attend industry meetings (prior to start date or early on during the project period)

Project Reporting

- Final Reporting and any student poster papers are available from:

https://primis.phmsa.dot.gov/matrix/PrjHome.rdm?prj=510

THANK YOU!