

American Association of Petroleum Geologists
2021 Mid-Continent Section Meeting

Wellbore Cement Mechanical Enhancement by Addition of Zeolite and Graphene



Cody Massion

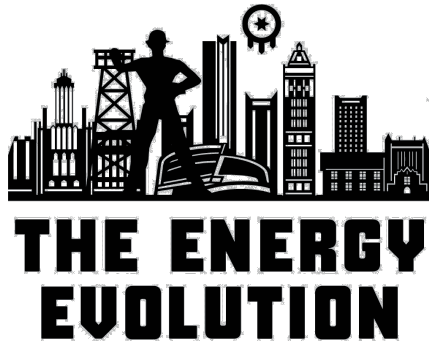


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Outline

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3. Methodology
4. Graphene Nanoplatelets and Results
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Relevance

- 281 kilotons of methane released by 3.2 million abandoned wells in 2018

Groom (2020)

- Methane gas leakage of oil and gas wells are 60-100% > U.S. Environmental Protection Agency Greenhouse Gas Inventory (GHGI)

Alvarez et al. (2018) and Gorchov Negrón et al. (2020)

- Bipartisan senate bill: ~\$4.7 billion for P&A projects and clean-up

Gardner (2021)

- 2021 infrastructure plan: \$8 billion towards P&A

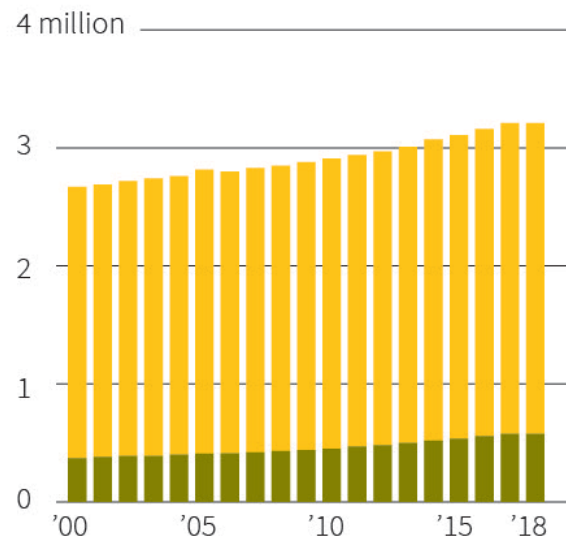
Gardner (2021)

Abandoned wells leaking methane

More than a century of oil and gas drilling has left behind millions of abandoned wells worldwide, many of which are leaching pollutants into the air and water.

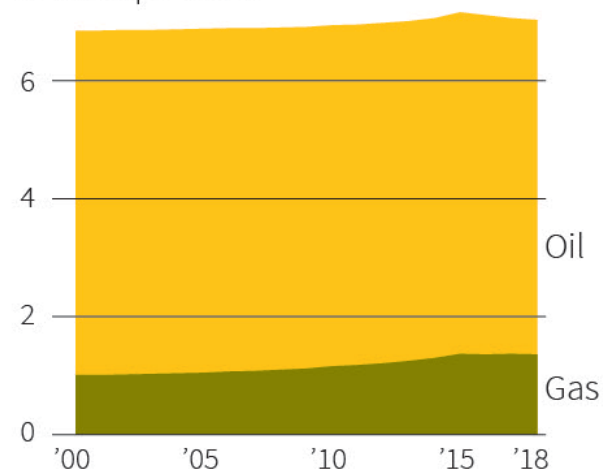
ABANDONED WELLS IN THE U.S.

Oil Gas



METHANE EMISSIONS FROM ABANDONED WELLS IN THE U.S.

8 million metric tons of CO₂ equivalents



Source: Environmental Protection Agency

Staff, 4/6/2020

REUTERS

<https://graphics.reuters.com/USA-DRILLING/WELLS/gjnpwylaapw/USA-DRILLING.jpg>

Introduction

Wellbore cement provides:

- Holds the casing in place
- Mechanical stability
- Zonal isolation
- Chemical protection for steel casing

Optimum properties:

- Long-term sealing capability
- Strong and ductile behaviour
- Impermeability
- Geo-compatibility

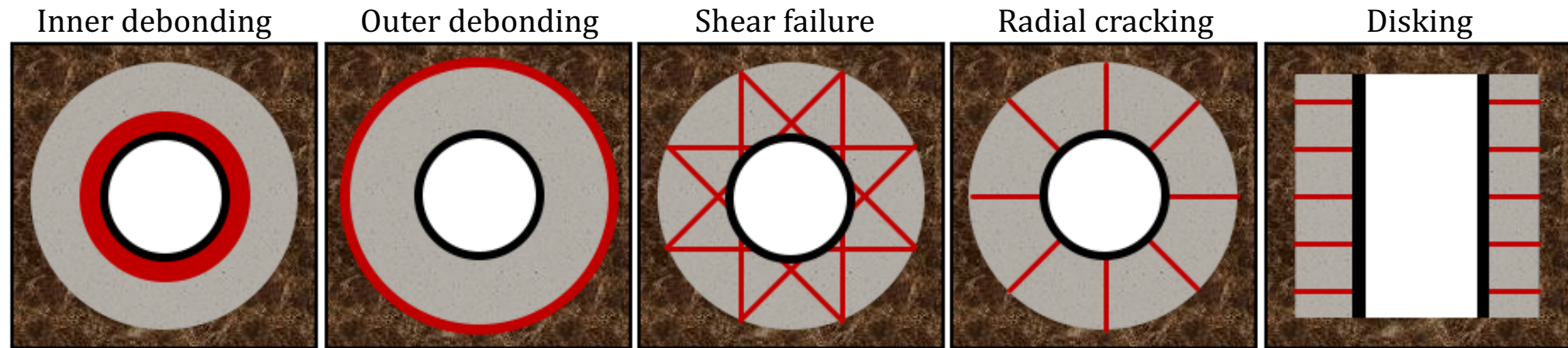


Figure 1: Common failure mechanisms of wellbore cement (red) creating leakage of subsurface fluids out of the well. Modified from Petty et al. (2003).

Materials and Methodology

Sample making:

- 16.4ppg (1.97 g/cm³) Class-H wellbore Additives of defoamer, friction reducer, and bentonite
- API Standard RP-10B
- Cement was demolded after 24hrs and hydrated at 90°C and 95%RH for 28 days
- Cement microstructure and mechanical properties evaluated with varying percentages
- Graphene added in different percentages of **0, 0.008, 0.016, 0.05%** by weight of cement.

Sample testing:

- Scanning Electron Microscopy (SEM)
- Micro indentation
- Porosimetry and Permeability
- Triaxial loading cell tests at simulated pressure and temperature
- Computed Tomography (CT) scanning
- Zeolite added in different percentages of **0, 5, 15, 30%** by weight of cement.

Scanning Electron Microscopy: *Morphology of Graphene*

Thinnest yet Strongest material currently known

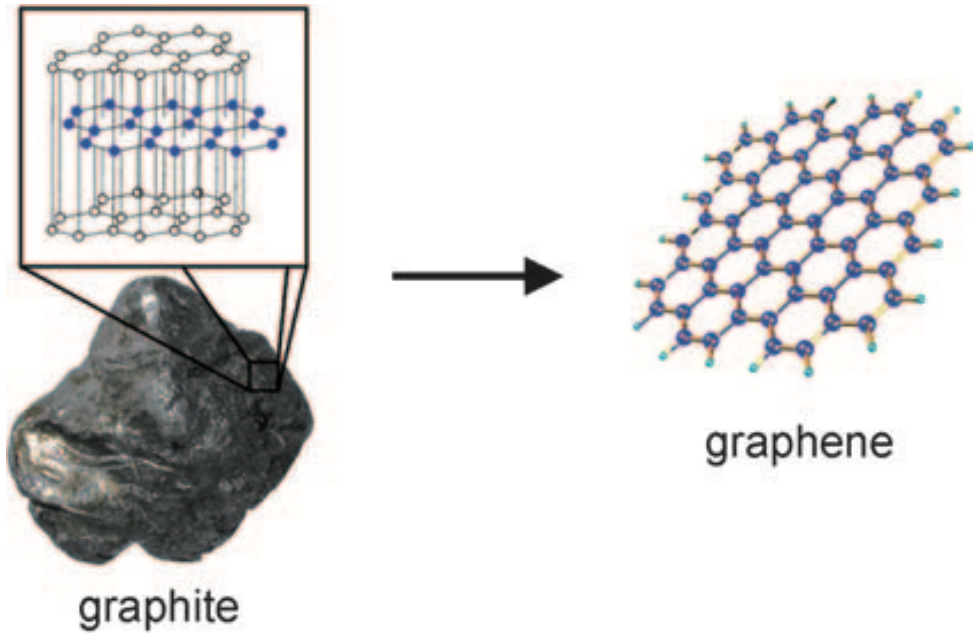


Figure 2: Graphic model of the transformation of graphene derived from graphite. Carbon atoms form hexagonal ring bonds that repeat to develop single graphene platelets with a thickness of one carbon atom. Dreyer et al. (2010).

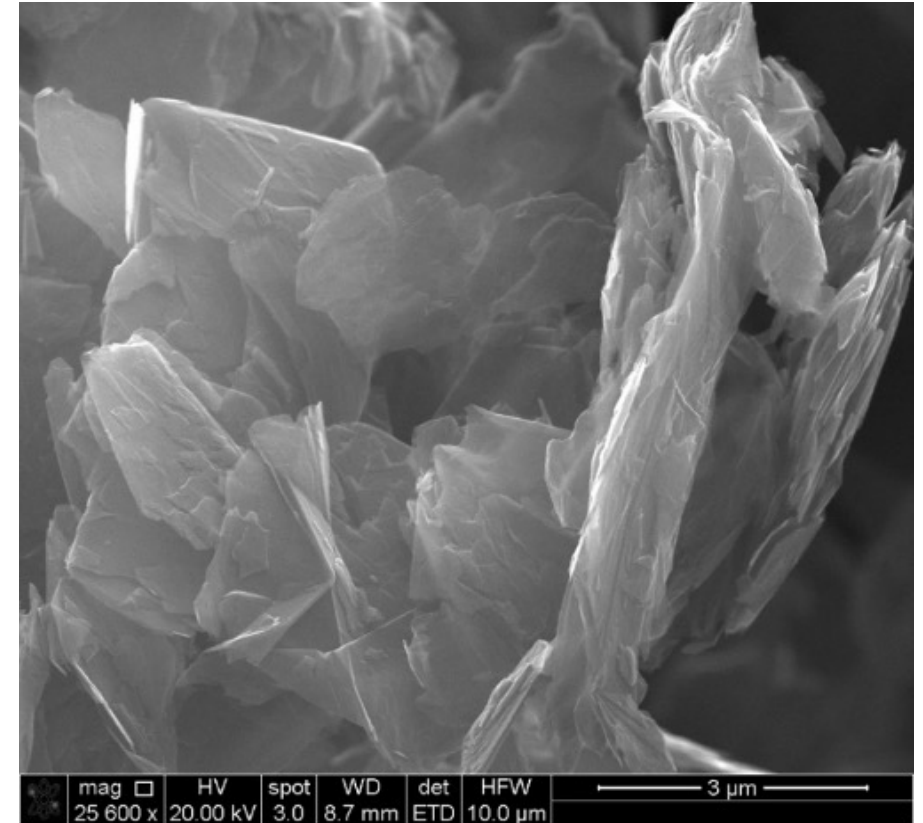


Figure 3: Graphene nanoplatelets at magnification of 25,600x depicts thin and nearly transparent individual platelets form layers.

SEM: Identifying Mechanisms of Graphene in Cement

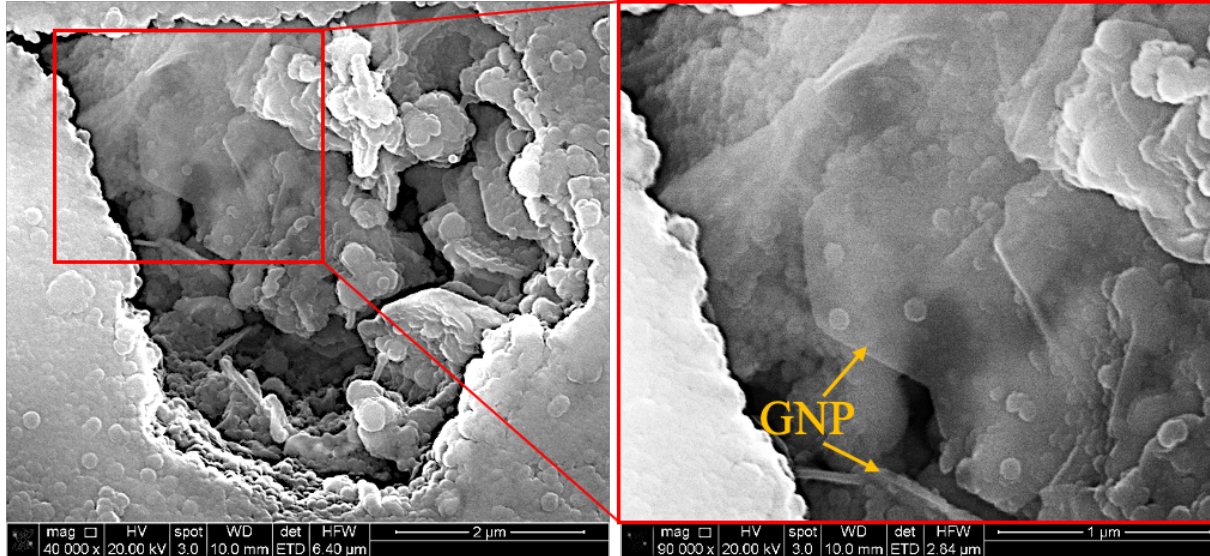


Figure 4: Graphene nanoplatelets imbedded into cement micropore space.

- Pore space is the weakest point in cement
- Graphene tends to accumulate within cement pore and reinforce the pore wall

- Global microstructure of cement is unaltered when graphene is added.
- Large partially hydrated grains surrounded in CSH matrix

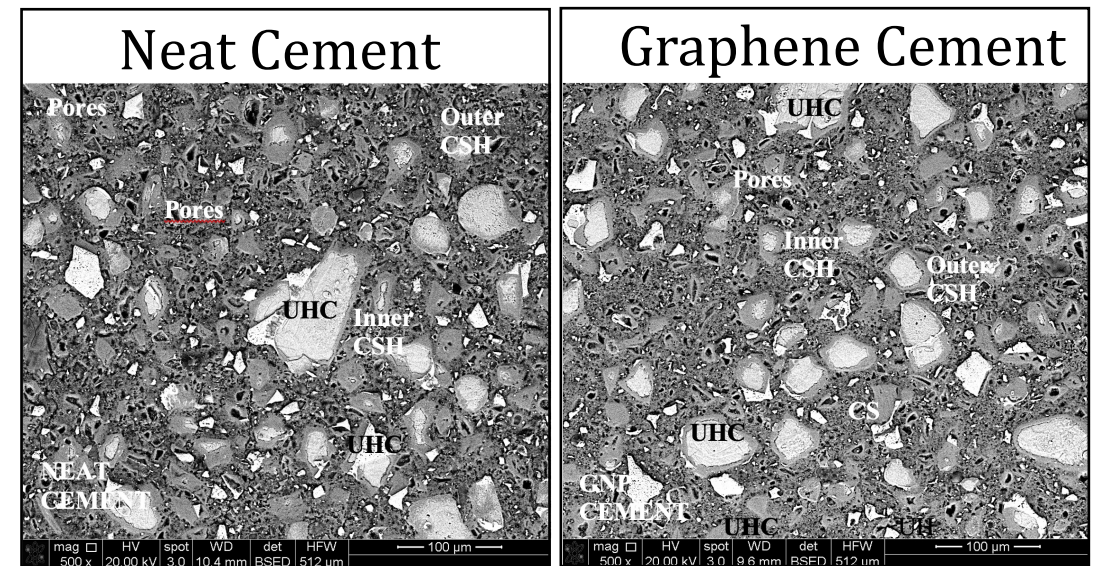


Figure 5: BSE micrographs with unhydrated cement clinker minerals (bright gray) with CSH hydration products outer rims (darker gray, within hydration matrix and porosity (black))

SEM: *Observations of Graphene within Micropore Walls*

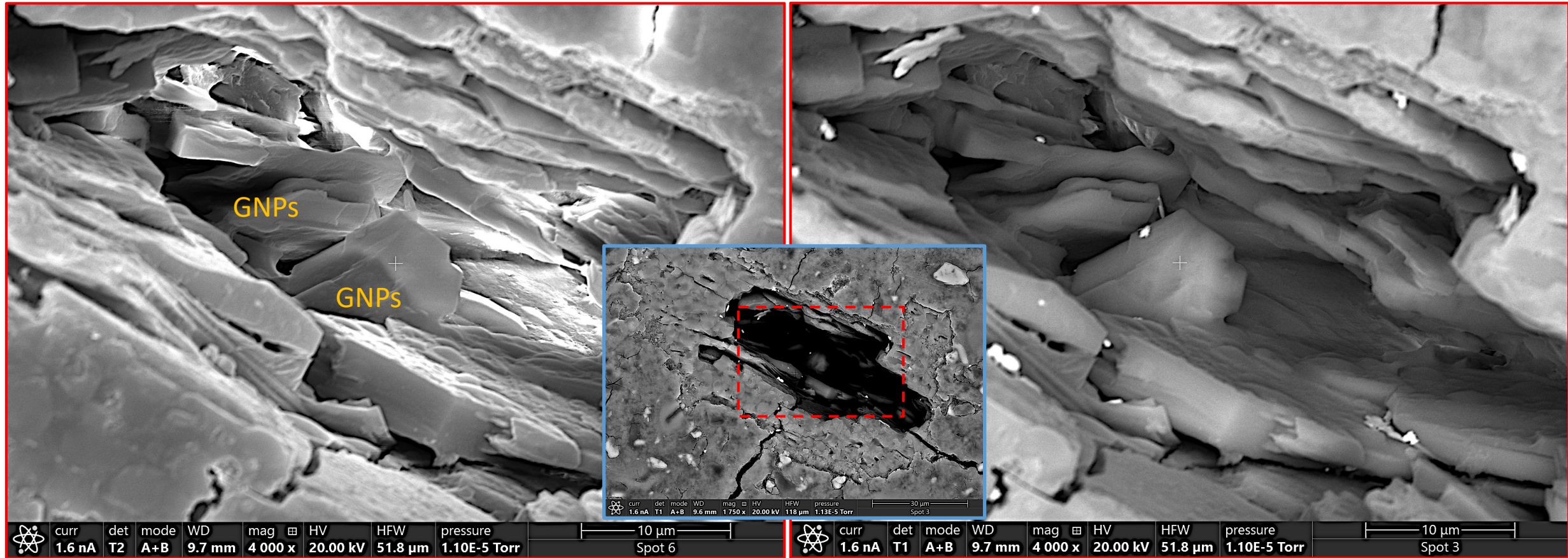
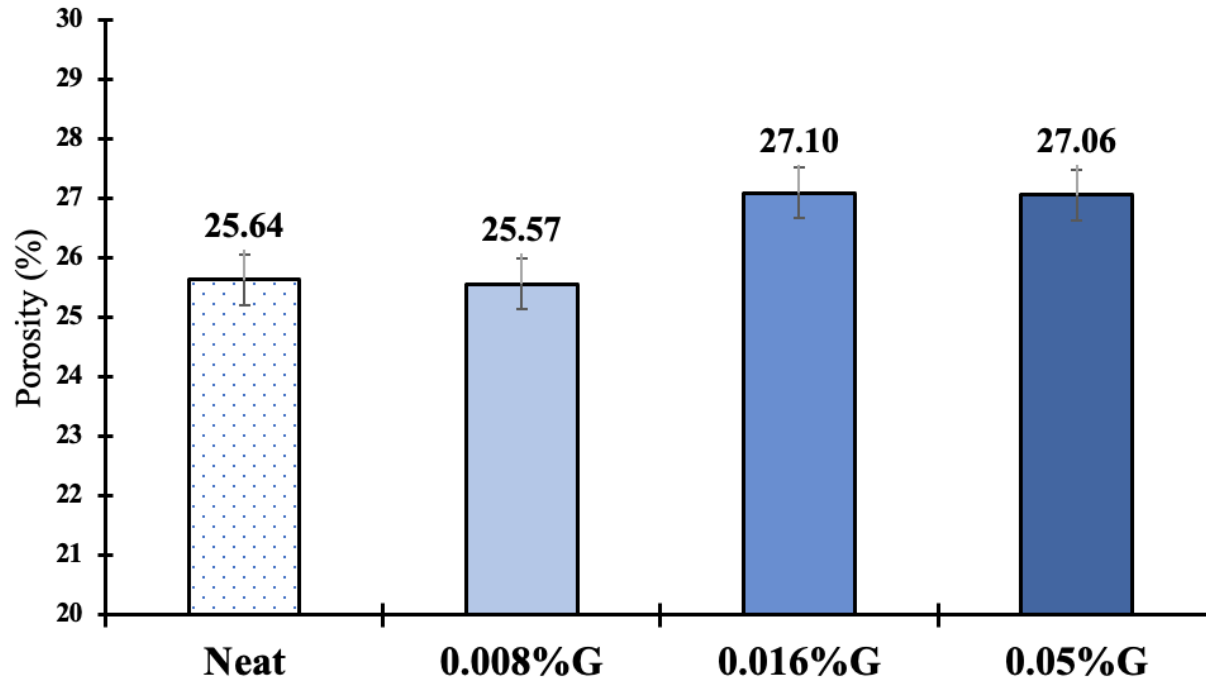


Figure 6: Graphene nanoplatelets reinforcing the micropore structure in secondary electron (left) and backscatter (right) imaging.

Porosimetry: *Porosity and Pore Throat Radius*

Helium Ultra-pore Porosimeter



Mercury Injection Petrophysical Properties

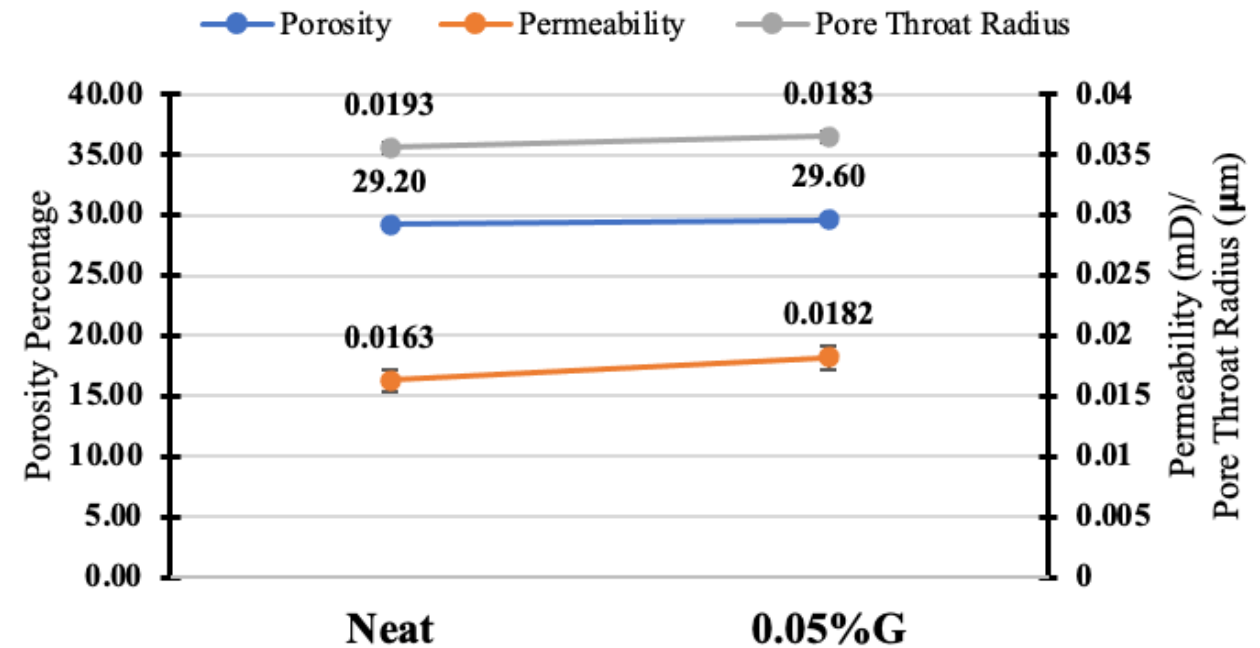


Figure 7: (Left) Ultra-pore porosimeter using helium gas. Measurements of 3 samples of each Neat Class-H, 0.008%, 0.016%, and 0.05%woc graphene in Class-H cement. (Right) Samples flooded with mercury at high pressure to measure the porosity, Swanson permeability, and pore throat size of both Neat Class-H and when 0.05%woc graphene added to the Class-H cement.

Correlative Microindentation: *Linking microstructure to micromechanics*

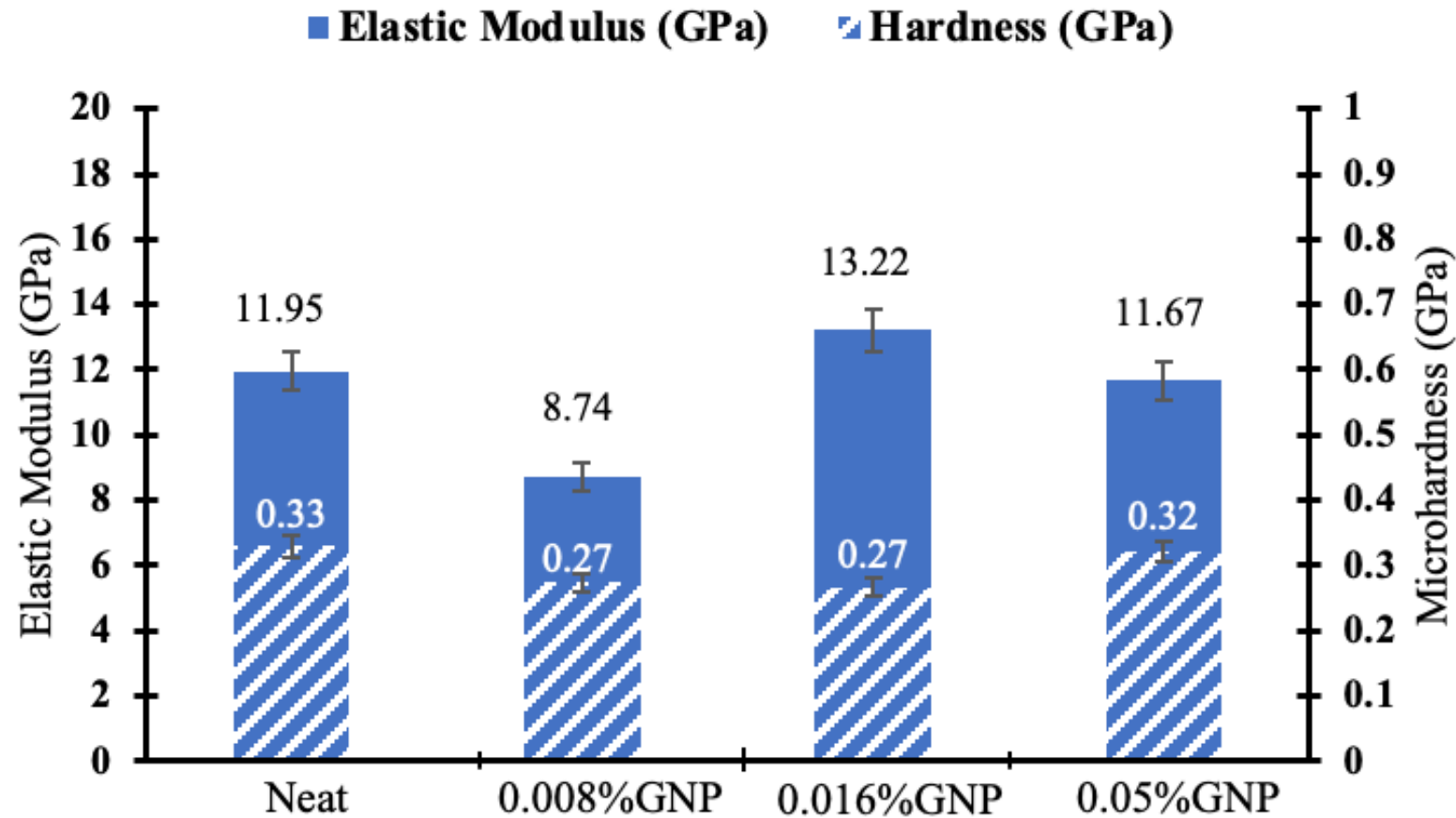


Figure 8: Micro-Vickers indentation conducted on a 5x5 matrix (25 indents) on neat, 0.008%, 0.016%, and 0.05% graphene addition.

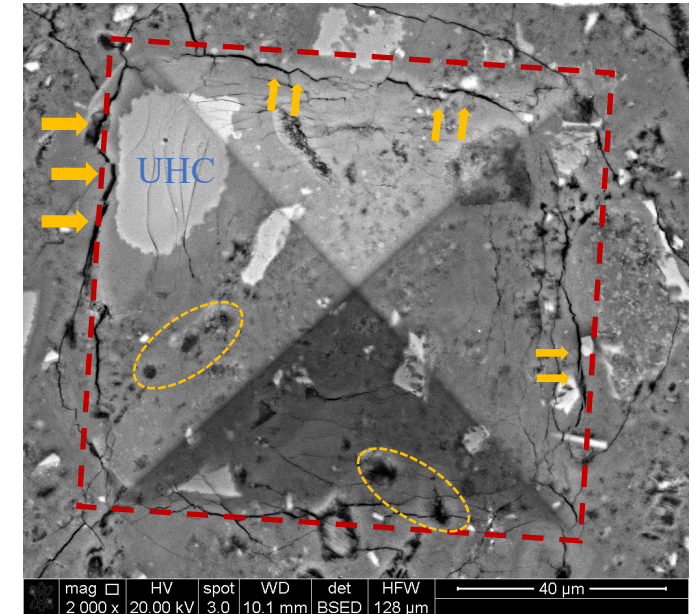
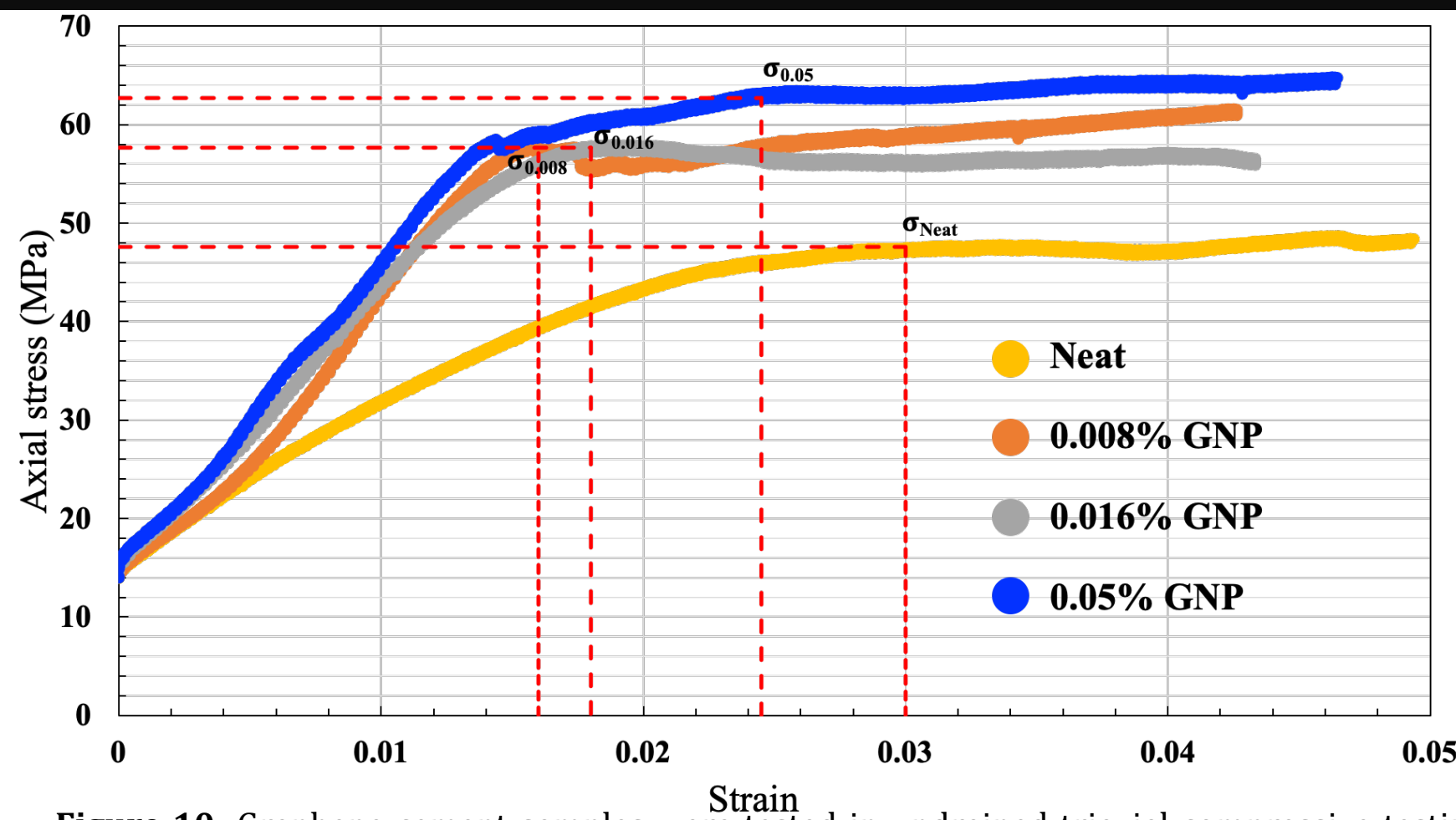


Figure 9: Backscatter electron image containing indentation by Vickers diamond indenter. Unhydrated cement (UHC) grain with pores (circles) and fractures (arrows) highlighted.

Triaxial Load Cell: *Mechanical Testing at Simulated Reservoir Conditions*

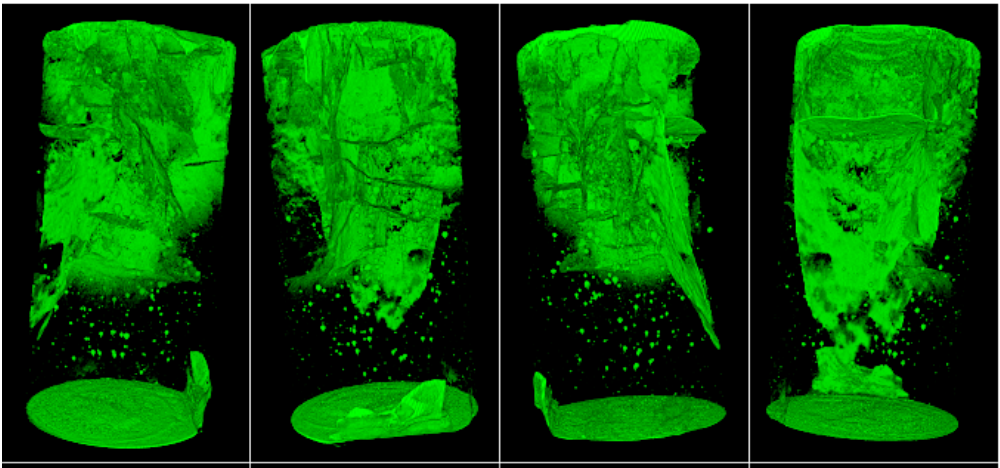


Graphene Percentage	Ultimate Stress (MPa)
Neat	47.57
0.008%	57.57
0.016%	57.64
0.05%	62.69

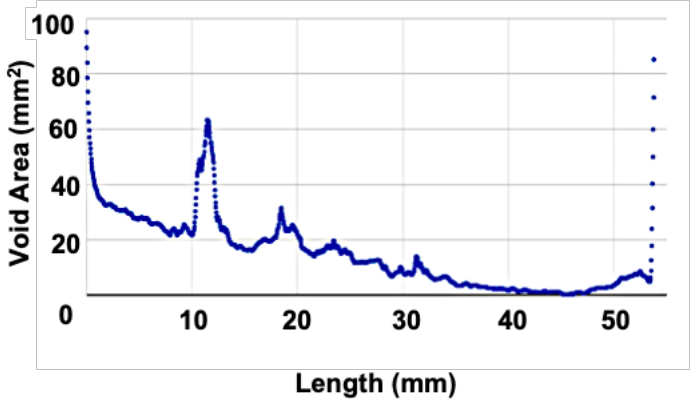
Figure 10: Graphene cement samples were tested in undrained triaxial compressive testing at simulated wellbore conditions and confining pressure of 13.7 MPa (2,000psi) and temperature 90°C (194°F). The graphene cement exhibited improvements in strength when compared with the neat cement. Failure stress and strength denoted by dotted line on the respective axes.

Computed Tomography: *Calculated Fracture Density of Post Triaxial test*

Neat Cement



1.18in x 2.4in
cement samples



- Reduction in fracture:
- Density
 - Conductivity
 - Propagations

Graphene Cement

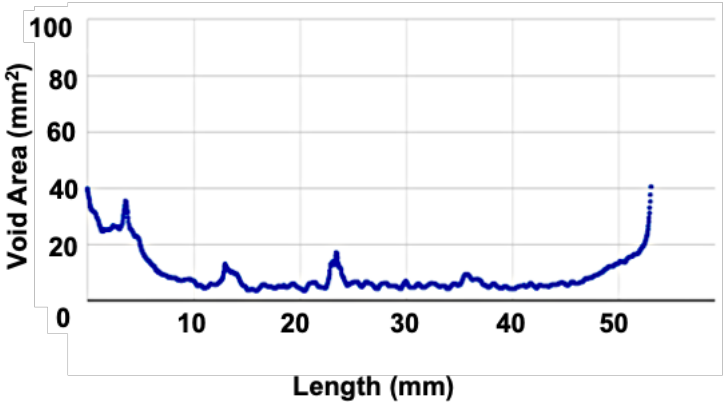
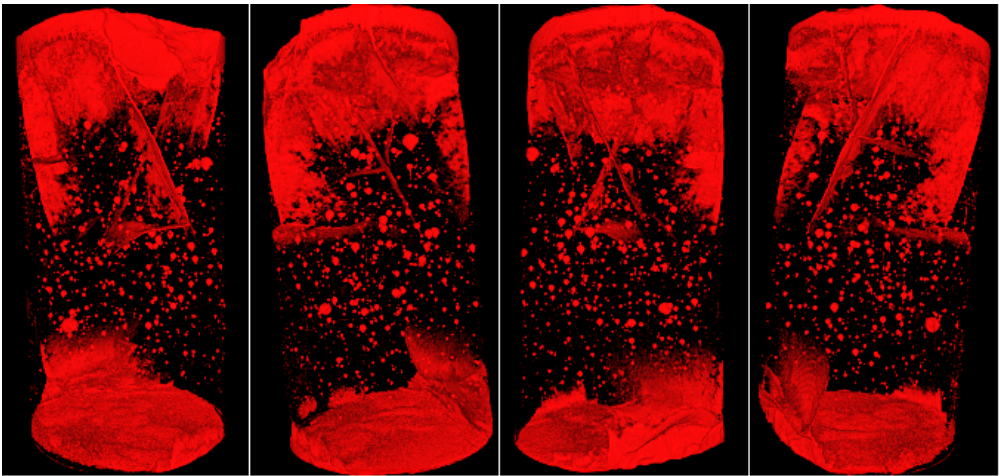


Figure 11: Calculated void space using CT scanning conducted after triaxial fracturing

Scanning Electron Microscopy: *Zeolite in cement*

- Morphology of cement matrix around a zeolite grain showing disjointed boundaries

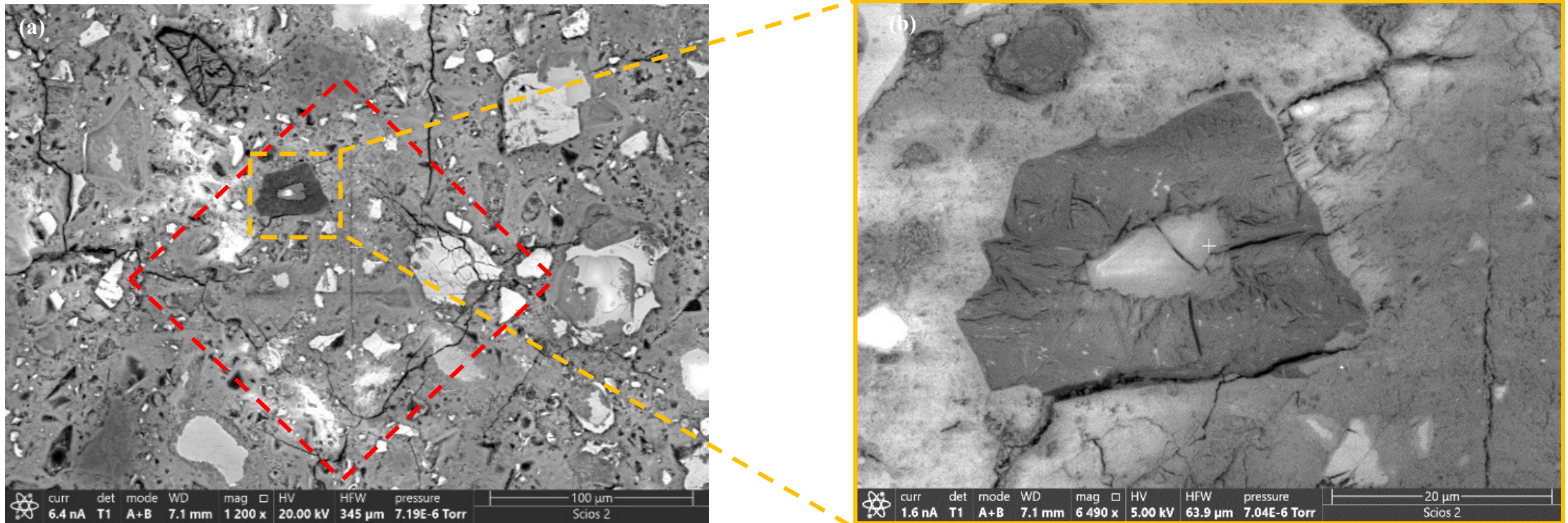


Figure 12: (a) An SEM image of an indenter mark on a polished uncoated 5% Ferrierite added sample. (b) A magnified SEM micrograph showing the ferrierite crystal right next to the indenter mark highlighting the failure of cement on indentation passing around the ferrierite crystal.

Energy Dispersive x-ray Spectroscopy: *Elemental analysis*

- EDS maps showing the phase stability of zeolite in the matrix after hydration

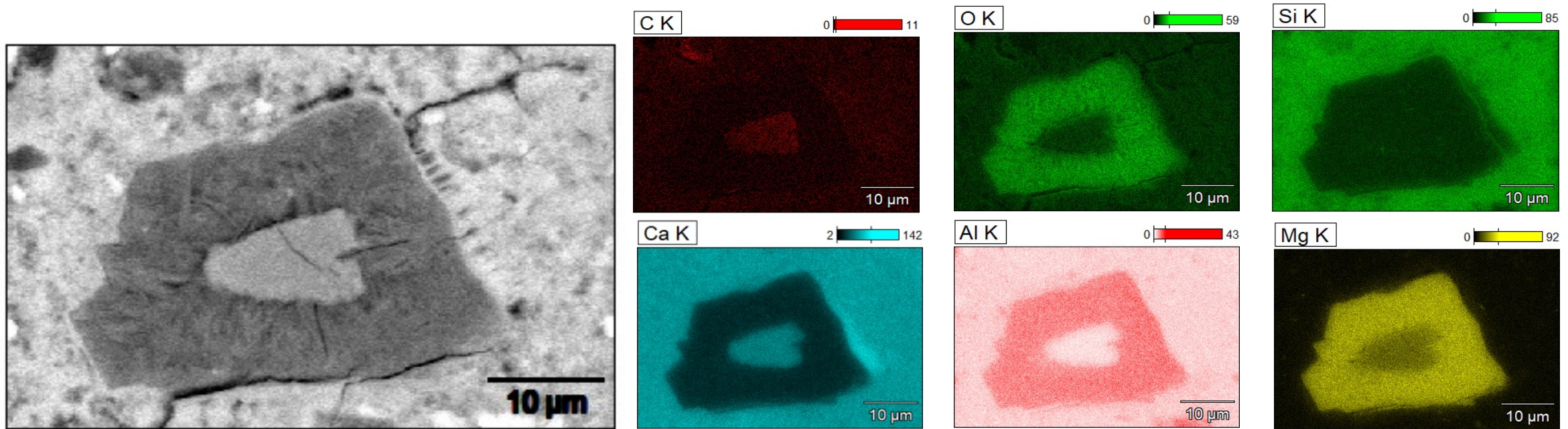


Figure 13: (a) EDS maps showing Aluminosilicate material (Zeolite) grain in the cement matrix. The grain interfaces need further high-resolution studies to show if Ferrierite has any pozzolanic activity like the other zeolites observed in literature.

Raman spectroscopy: *Zeolite percent variation in cement*

- Raman maps showing the phase distribution and distinct ferrierite peaks in the plots.

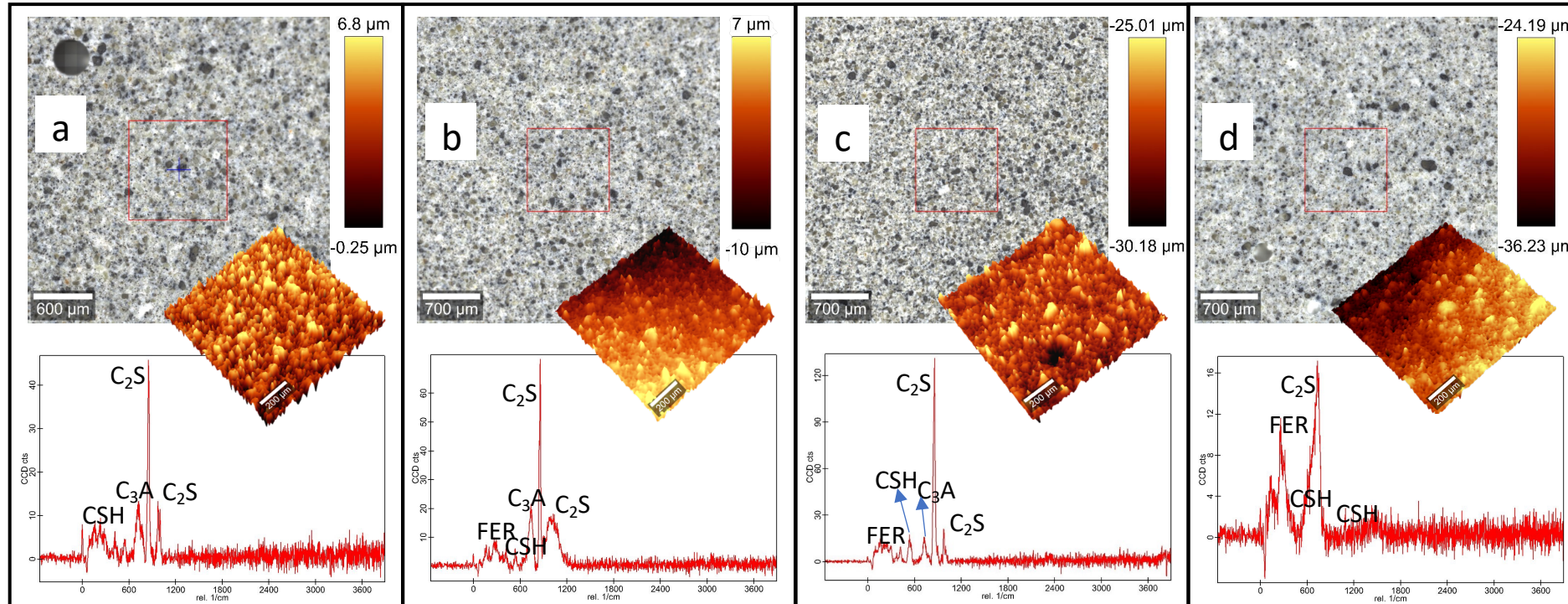


Figure 14: Raman results for polished cores Showing peaks for various cement phases : (a) Neat cement at 600-630nm,(CSH) 740nm, (C3A) 842nm and 972 nm(C2S) (b) 5% ferrierite added cement at 416nm,(Ferrierite) CSH ,C3A, C2S; (c) 15% ferrierite added cement- Ferrierite, CSH ,C3A, C2S ; (d) 30% ferrierite added cement Ferrierite, CSH (also at 1015nm), C2S. The ferrierite peaks observed fall in favor of the XRD studies done in earlier stages of this research which showed the phase stability of ferrierite which means that the ferrierite does not take part in hydration.

Strength Testing: *UCS vs indentation*

- Unconfined compressive strength (UCS) compared to hardness and elastic modulus results from indentation.

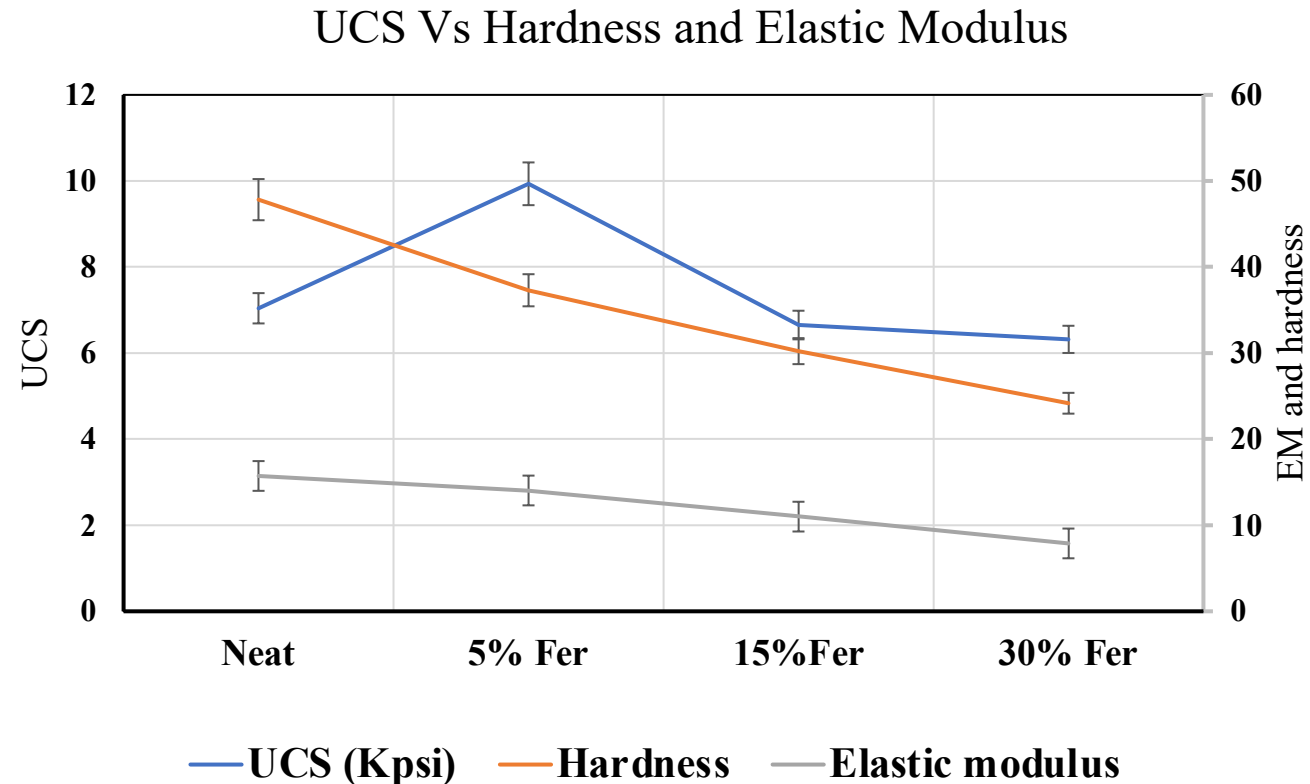


Figure 15: UCS Vs Indentation for Neat Class-H, 5%,15%,30% ferrierite added Class-H cement cores showing slightly similar trends. However, indentation is a representative of microscale properties and increasing the sample size affects the magnitude of the properties.

Correlative Microindentation: *Linking microstructure to micromechanics*

- Indentation performed on a 5% Fer added sample which had the best UCS results.

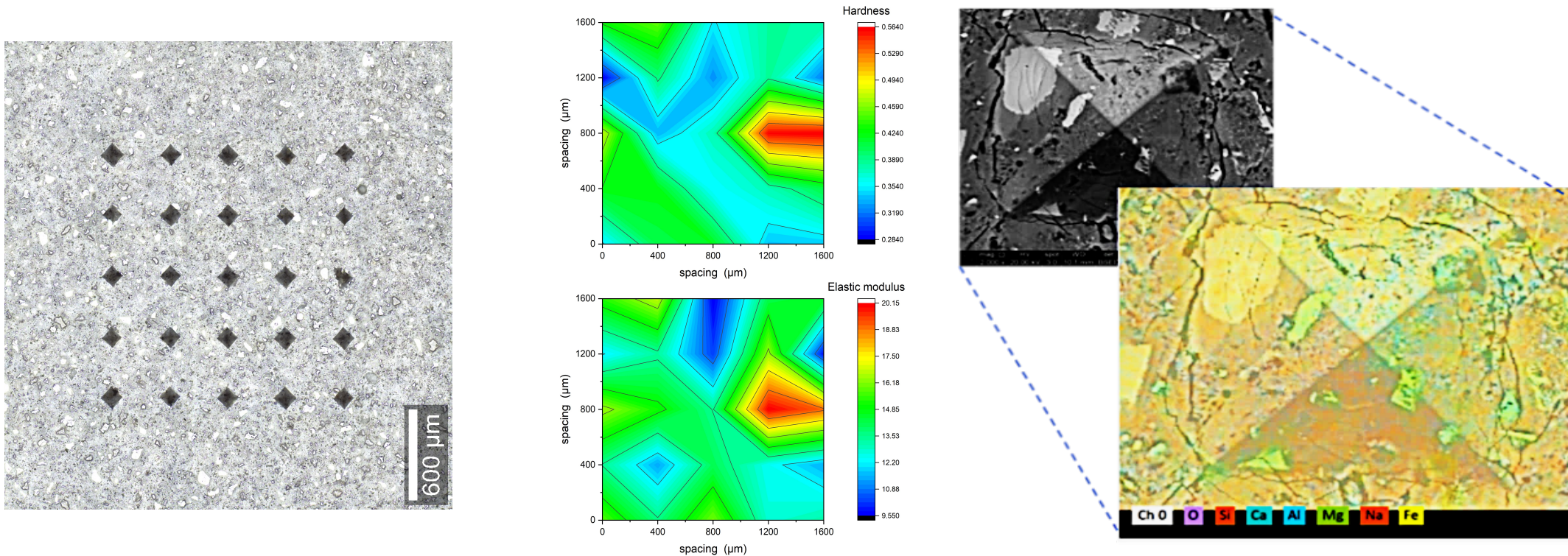


Figure 16: (a) Indentation results for 5% Fer added cement polished cores with 25 indents and maps of hardness (Avg 0.506 GPa) and elastic modulus (Avg 15.72 GPa). (b) An EDS map overlapping and SEM image showing a single indent. Indentation was done for all the formulations (for 5%, 15%, 30% ferrierite added Class-H cement) as well, and SEM and EDS studies are under progress to see if there is any noticeable surface chemical change on failure.

Triaxial Load Cell: *Mechanical Testing at Simulated Reservoir Conditions*

- Triaxial test results showing best performance for the 5% Fer added sample.

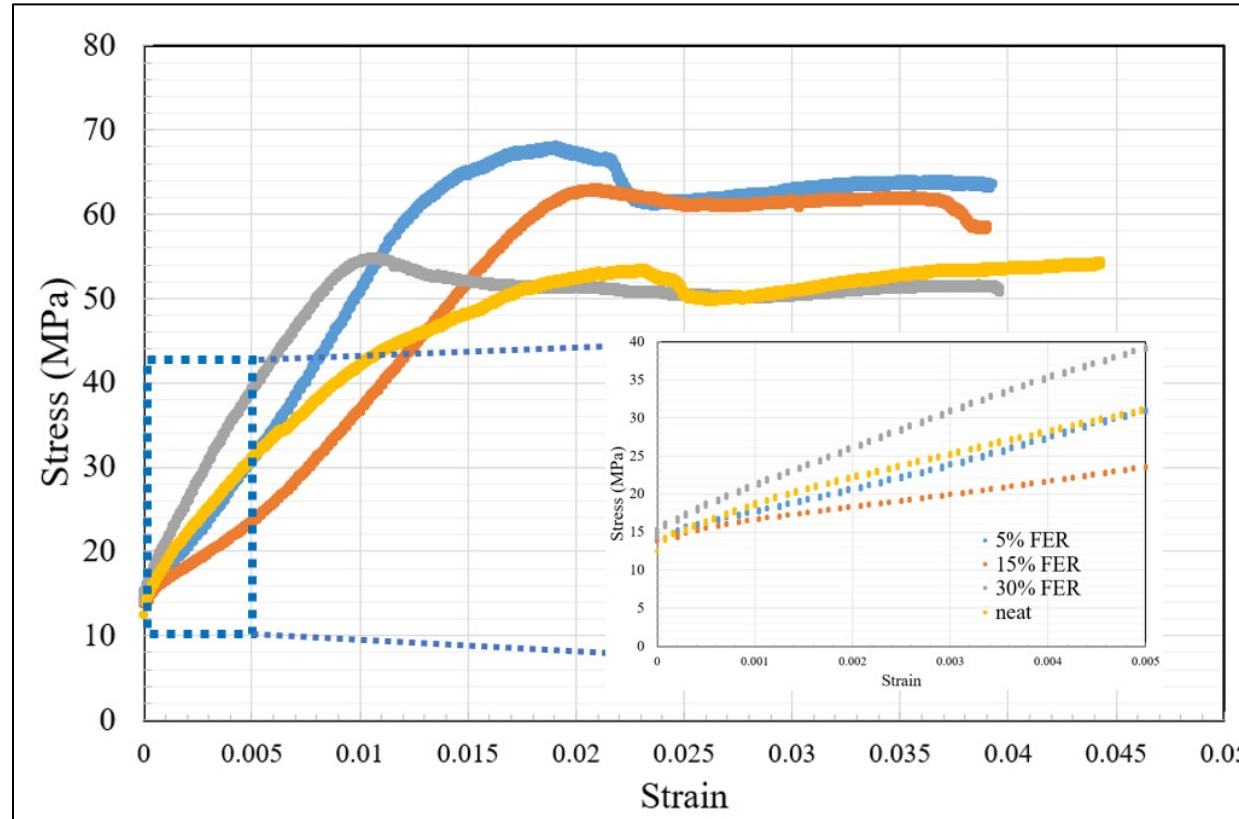


Figure 17: Triaxial test results for 5%, 15%, 30% ferrierite added and neat class-H cement at 13.7M.Pa and 90°C. 5% ferrierite added cement the highest axial stress which coincides with the UCS results showing a similar trend. The initial linear regime is shown in a magnified scale in the inset and the slope of this initial linear regime is used to calculate the Young's modulus.

Petrophysical properties: *Porosity and Permeability*

- Permeability and porosity measured for the 5%, 15% and 30% Zeolite (Fer) added cement samples

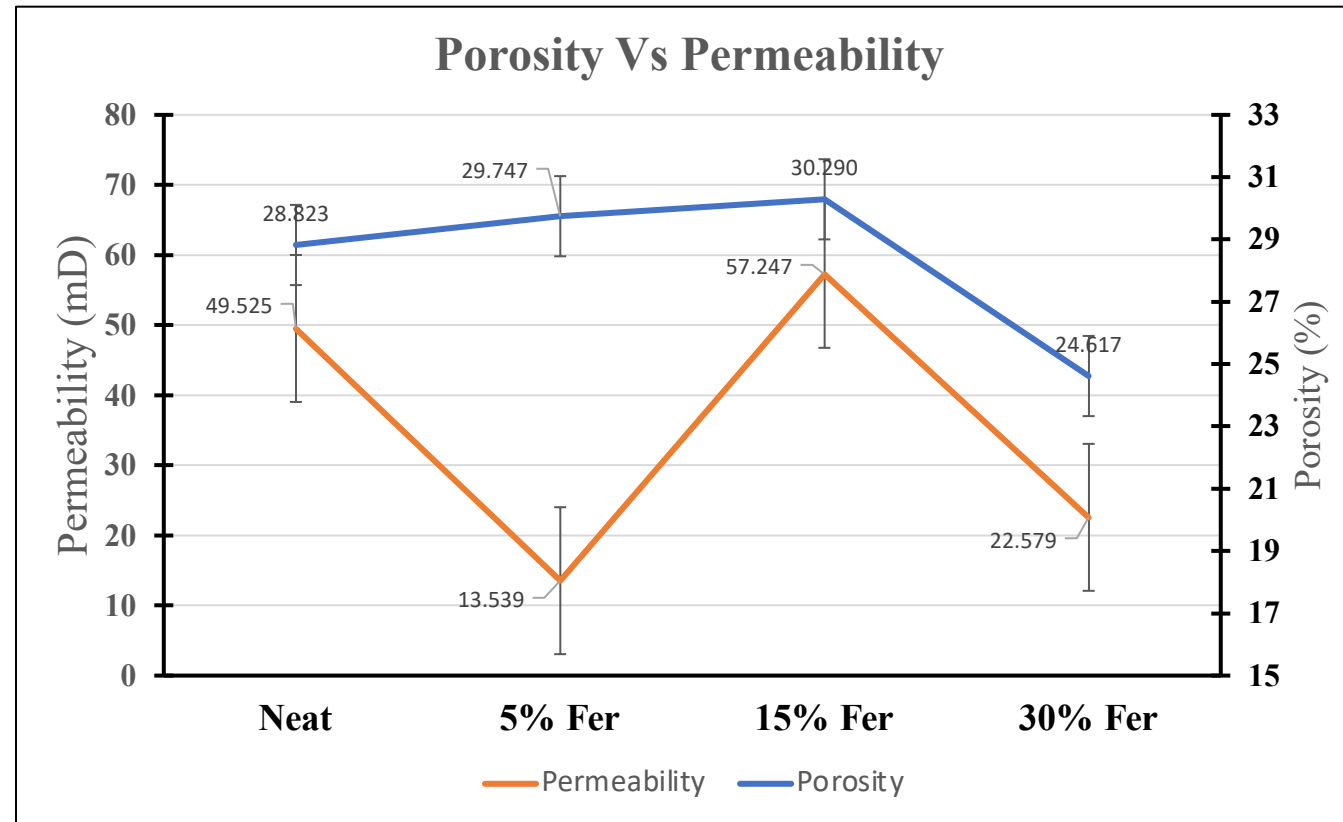


Figure 18: Average porosity and permeability values of 5%, 15%, 30% ferrierite added, and Neat class-H cement measured using Corelab ultrapore 300 porosimeter and Nanoperm permeameter

Discussion (*Graphene Nanoplatelets*)

This study's hypothesis on how graphene nanoplatelets enhance cement properties based on literature:

1. Cement hydration crystal morphology can impact the overall cement Young's Modulus (Dunant et al., 2020).
 - Higher aspect ratios of crystal length to width, such as needle-shaped crystals, result in smaller Young's Modulus
 - Shorter and wider crystals result in a higher Young's Modulus
2. Stacking graphene platelets slide against one another under load due to weak Van der Waal forces between, acting as nano springs within the matrix Berman et al. (2014).

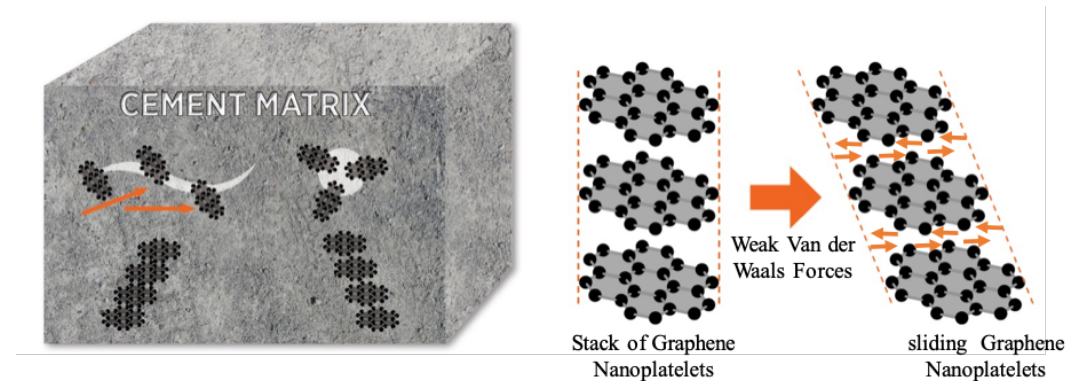


Figure 19: Proposed mechanisms of graphene nanoplatelets within the cement matrix by bridging fracture propagations, reinforcing pore structures, and stack and sliding due to Van der Waals forces between the platelets.

Discussion (*Zeolite*)

- SEM,EDS and Raman studies show the phase stability of zeolites in cement.
- UCS and Triaxial tests indicate superior performance in 5% ferrierite added cement.
- Indentation results show optimum results of hardness and elastic modulus for 5% Fer added cements.

	Indentation		Triaxial		UCS
	Hardness (Gpa)	EM (GPa)	Axial peak stress (psi)	EM (GPa)	Comp. strength (psi)
Neat	0.506	15.72	7730	9.65	7041
5% Fer	0.394	14.03	9882	8.82	9934.3
15% Fer	0.319	11.006	9133	7.72	6652
30% Fer	0.256	7.88	7944	11.29	6319

- Permeability is also superior in cores made of 5% Fer added cement slurry.
- Porosity is gradually increasing for increasing amounts of zeolites but decreases for 30% Ferrierite added cement owing to its increased water to cement (w/cm) ratio due to correction from absorbed water in zeolite pore structure.

Conclusion

Preliminary results for the addition of these additives into wellbore cement indicate:

Graphene cement:

1. Graphene reinforces cement pore walls and matrix
2. No significant alterations to the cement microstructure or petrophysical properties
3. All graphene percentages increase ultimate axial stress over 20% at simulated reservoir conditions
4. Reduced cement brittleness and Young's modulus in microstructure at 0.008%GNP.

Zeolite cement:

1. Zeolite acts as a substrate for hydration to take place without actively taking part in hydration.
2. Zeolite addition enhances the cement properties like strength and petrophysical properties. 5% zeolite addition had lower permeability – essential for zonal isolation.
3. 41% increase in UCS for 5% zeolite addition compared to neat class-H cement.
4. Highest peak axial stress in 5% zeolite addition.

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Future work

- Examine how additives interact with pure unhydrated cement phases (C3S, C2S, etc).
- Investigate the self healing in zeolite added cements for subsurface applications.
- Combination of these two additives into one cement design to further improve performance.

Thank you

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