Novel concepts to construct cost effective geothermal wells with Electro Pulse Power Technology

Selection of material designs, based on literature review and modelling

Deliverable D5.1

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Review process

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Executive summary

The overall aim of the DEEPLIGHT project is to accelerate the growth of global geothermal production by a game changing drilling and well construction system. One of the main objectives is to develop contactless drilling with Electro Pulse Power (EPP) technology along with a design for casing placement drilling as to be a game changer being far superior to conventional drilling methods. The objective of Work Package 5 (WP5) is to investigate thermal flexible, smart cement tailored to the requirements of the integrated EPP-casing while drilling approach. The novel drilling technology enables the optimization of wellbore sealing solutions using graphene-enhanced cements, optimizing electrical and elastic cement properties to maintain integrity during cyclic thermal loading and enabling self-sensing cement integrity monitoring concepts as an integral part of the new approach leading to higher reliability and prolonged life of the well. This deliverable report is generated for the project's WP5 on well integrity approach for EPP drilled wells and focuses on the review, selection, design and characterization of geo-mimicry inspired cement slurries. A literature review has been completed with input from ongoing modeling work under Task 5.3 for guidance. Thus, this current report aims to provide a literature review towards designing self-sensing cements for geothermal wells, including EPP drilled wells.

The evolution of structural health monitoring in cement and concrete has advanced from traditional methods like strain gauges to modern techniques such as optical fiber sensors, piezoelectric ceramics, shape memory alloys, and non-destructive scanning methods like acoustic emissions. This research investigates the recent advancements in monitoring technologies, particularly cement-based sensors that integrate seamlessly into cement composites, offering enhanced compatibility, cost-effectiveness, and sensitivity. The conductive sensor used in this research is Graphene Nano-platelets (GNPs), selected for their exceptional electrical and thermal conductivity, which are leveraged for developing self-sensing cement composites.

In addition to enhancing electrical performance, GNPs have been shown to improve the ductility of cement composites, leading to better mechanical properties. This dual functionality not only boosts overall performance but also reduces costs and simplifies the complexities associated with traditional monitoring systems. According to the Effective Medium Theory (EMT), the conductive behavior of cement composites is influenced by the conductive additives, the cement matrix, and other components within the matrix. When GNPs are incorporated into Ordinary Portland Cement (OPC), they transform traditional composites into smart materials capable of real-time monitoring. Literature indicates that a GNP concentration of 1-2.4% by volume of cement is typically required to achieve effective self-sensing capabilities, while their mechanical benefits are most effective at concentrations below 1% by weight of cement. Striking an optimal balance in GNP concentration is critical to ensuring both functionalities are achieved without compromising either.

One of the primary challenges in developing OPC-graphene composites is ensuring the uniform dispersion of graphene. Due to strong van der Waals forces, graphene tends to agglomerate, leading to uneven distribution, weak points within the composite, and inconsistent electrical properties that diminish its self-sensing capabilities. Achieving homogeneous mixing is therefore essential and can be facilitated through optimized mixing procedures and the use of surfactants or dispersants. Advances in mixing technology, such as ultrasonic treatment and high-shear mixing, are being explored to further enhance graphene dispersion, ensuring a more uniform distribution. This is important for maximizing the potential of graphene-enhanced cements in advanced applications, particularly in smart, self-sensing infrastructure.

Contents

Abbreviations

AC/DC	Alternative Current / Direct Current
API	American Petroleum Institute
BWOC	By weight of cement
CCM	Cementitious Composite Materials
CNF	Carbon Nanofibers
CNT	Carbon Nanotubes
C-S-H	Calcium Silicate Hydrates
EMT	Effective Medium Theory
EGS	Enhanced Geothermal Systems
EPP	Electro Pulse Power
MLG	multilayer graphene
OPC	Ordinary Portland Cement

GNP	Graphene NanoPlatelets
PT	Percolation Threshold
SEM	Scanning Electron Microscope
SSC	Self-Sensing Cement Composites
TRL	Technology Readiness Level

Figures

1. Introduction

This first chapter introduces the background and scope of this report.

1.1. Background

One of the main objectives of the DEEPLIGH project is to develop contactless drilling with Electro Pulse Power (EPP) technology as to be a game changer being superior to conventional drilling methods. Within the DEEPLIGHT project different fields of research are combined to develop new technologies related to geothermal energy. These reach from the development of a new drill bit based on the Electro Pulse Power technology to a new borehole construction process. This construction process is based on a casing while drilling approach and expects to lead to improved wellbore stability, a faster drilling progress and superior cutting removal. As part of this research, Work Package 5 (WP5) is to investigate thermal flexible, smart cement tailored to the requirements of the integrated EPP-casing while drilling approach. The novel drilling technology enables the optimization of wellbore sealing solutions using graphene-enhanced cements, optimizing electrical and elastic cement properties to maintain integrity during cyclic thermal loading and enabling self-sensing cement integrity monitoring concepts as an integral part of the new approach leading to higher reliability and prolonged life of the well. Overall, a technology readiness level (TRL) 6 of this novel drilling technology is aimed for.

1.2. Scope

This deliverable report is generated for the project's WP5 on well integrity approach for EPP drilled wells and focuses on the review, selection, design and characterisation of geo-mimicry inspired cement slurries. A literature review has been completed with reference are made to ongoing modeling work under Task 5.3 for guidance. Thus, the aim for this current report is to provide a literature review towards designing self-sensing cements for geothermal wells, including EPP drilled wells.

The report begins with a brief introduction to geothermal wells and self-sensing cement, providing a broad overview of geothermal well technology and the importance of developing cement composites with self-sensing capabilities. This section establishes the context by discussing the operational challenges unique to geothermal environments and how innovative cement solutions can address these issues.

Following this, the review of cement properties and additives section discusses the fundamental properties of cement, particularly when subjected to the extreme conditions encountered in geothermal wells. The role of various additives, including carbon-based materials, is examined to understand their impact on the durability, thermal stability, and overall performance of the cement.

Next, the report explores Ordinary Portland Cement (OPC)-the base material used in most cementitious composites. The discussion highlights the inherent characteristics of OPC and how they serve as a foundation for more advanced formulations, particularly when modified with nanomaterials.

The subsequent section on carbon nanomaterials provides an in-depth analysis of materials like Graphene Nano-platelets (GNPs), focusing on their potential to enhance the physical and chemical properties of cement. The section emphasizes the transformative role of graphene in creating cement with superior strength, durability, and self-sensing capabilities.

In the Electrical Properties of Carbon Nanomaterials segment, the report shifts its focus to the conductive characteristics of graphene. This section discusses how graphene's electrical properties can be harnessed to develop cement composites that not only maintain structural integrity under thermal and mechanical stresses but also enable real-time monitoring of well conditions.

Then a brie status report is provided on the ongoing initial modeling of heat production and well integrity performed at LBNL. The modeling is conducted to investigate changes in temperature, pressure, stress and strain in the well assembly, including cement. Moreover, changes in electric properties of the cement are estimated for potential well integrity monitoring.

The Experimental Preparations chapter details the methodologies employed in preparing the experimental setups and testing protocols necessary to evaluate the performance of the resultant materials.

Finally, the report concludes with a section that reflects on the progress made towards developing self-sensing cements and the potential for further advancements, particularly in the context of EPP drilling.

2. Introduction to Geothermal Wells and Self-sensing Cement

Geothermal energy, sourced from the Earth's internal heat, is increasingly recognized as a sustainable alternative to traditional hydrocarbon-based energy sources. As global efforts intensify to reduce greenhouse gas emissions and combat climate change, geothermal energy is positioned to play an important role in the future energy mix. Despite its promise, geothermal energy currently accounts for only 0.4% of the U.S. energy market, according to the U.S. Department of Energy (2010). Expanding its role requires overcoming significant technical challenges, particularly in Enhanced Geothermal Systems (EGS).

In geothermal wells, cementing operations face unique challenges due to the extreme subsurface conditions. The geothermal gradient, typically ranging from 25°C to 30°C per kilometer of depth, results in substantial temperature variations that can impose severe thermal stresses on wellbore materials. These stresses are exacerbated in EGS, where the subsurface environment involves hot, dry rock formations that are fractured by the injection of lower-temperature fluids. The resulting thermal cycling can lead to mechanical degradation of cement, compromising the structural integrity of the well.

In addition to thermal stresses, geothermal wells are subject to various chemical and mechanical challenges that are less prevalent in conventional oil and gas wells. For instance, geothermal fluids often contain corrosive substances such as carbon dioxide (CO_2) and hydrogen sulfide (H_2S), which can chemically interact with ordinary Portland cement (OPC). These reactions can lead to the formation of expansive phases, such as ettringites, resulting in significant degradation of the cement matrix and a consequent loss of mechanical strength. Moreover, the high pressures encountered at depth further complicate the wellbore environment. The presence of high-pressure geothermal fluids can induce stress corrosion cracking and other forms of mechanical damage to the cement sheath, making it essential to develop materials that can maintain integrity under these harsh conditions. The high-temperature and high-pressure environment also accelerates the kinetics of deleterious chemical reactions, further threatening the long-term durability of cement in geothermal applications.

Given these challenges, the development of self-sensing cement, capable of real-time monitoring and diagnostics, represents a significant advancement in wellbore integrity management. Unlike traditional civil engineering structures, where deformations and failures are often visually detectable, wellbore issues in geothermal wells can be challenging to detect and locate. The incorporation of materials like graphene, with its exceptional electrical conductivity and mechanical properties, into cement composites offers a pathway to creating smart, self-sensing cement. These materials can sense and detect changes in the wellbore environment, such as temperature fluctuations or mechanical deformations, by monitoring variations in electrical resistance.

Systematic studies on cement health monitoring are significant for preventing potential safety and environmental disasters. The ability to assess and report the state of the cement in real time can enable timely interventions, reducing the risk of wellbore failure. The development of self-sensing cements tailored for geothermal applications, thus, not only enhances the safety and reliability of geothermal wells but also contributes to the broader adoption of geothermal energy as a key component of a sustainable energy future.

3. Review of Cement Properties and Additives

3.1. Cement Degradation

Cement degradation in geothermal environments is primarily driven by carbonation, where carbon dioxide (CO_2) reacts with portlandite [$Ca(OH)_2$] to form calcium carbonate ($CaCO_3$). While carbonation generally occurs at lower temperatures than those typically encountered in geothermal conditions, the resulting degradation mechanisms, such as dissolution and mechanical weakening of the cement matrix, remain similar. The CO_2 dissolves in water to form carbonic acid (H_2CO_3), which subsequently dissociates into bicarbonate (HCO_3^-) and carbonate (CO_3^{2-}) ions. These carbonate species react with calcium ions (Ca^{2+}) present in the cement, leading to the formation of calcium carbonate. In the initial stages, this process may reduce porosity and temporarily strengthen the cement by filling pores and micro-cracks. However, as carbonation progresses deeper into the cement matrix, it can create channels and pathways for fluid ingress, thereby compromising the integrity of the cement sheath (Chang et al., 2017).

In geothermal environments with elevated CO_2 levels or acidic conditions, calcium carbonate can dissolve, further weakening the cement structure. This dissolution is exacerbated by calcium leaching, which increases both porosity and permeability of the cement matrix, making it more susceptible to fluid migration and mechanical failure. Carbonic acid, being particularly aggressive, lowers the pH of the surrounding fluid environment, thereby enhancing the acidic attack on the cement. While calcium silicate hydrates (C-S-H) in the cement exhibit lower solubility compared to portlandite, providing some degree of resistance, the overall impact of prolonged carbonation tends to degrade the cement matrix, reducing its ability to maintain zonal isolation.

To mitigate this degradation, specific forms of silica can be incorporated into the cement mix, as silica reacts with calcium hydroxide to form additional C-S-H, thereby reducing the availability of free Ca^{2+} ions that can participate in carbonation reactions. However, this measure merely delays the onset of degradation and does not prevent it entirely. Additionally, geothermal fluids, often rich in salts and sulfates, can react with the aluminous phases in ordinary Portland cement (OPC), leading to the formation of expansive secondary minerals such as ettringite and thaumasite. These expansive phases induce internal stresses, causing cracking, spalling, and increasing porosity and permeability, which further compromise the structural integrity of the cement (Sakr et al., 2020; Batilov, 2016).

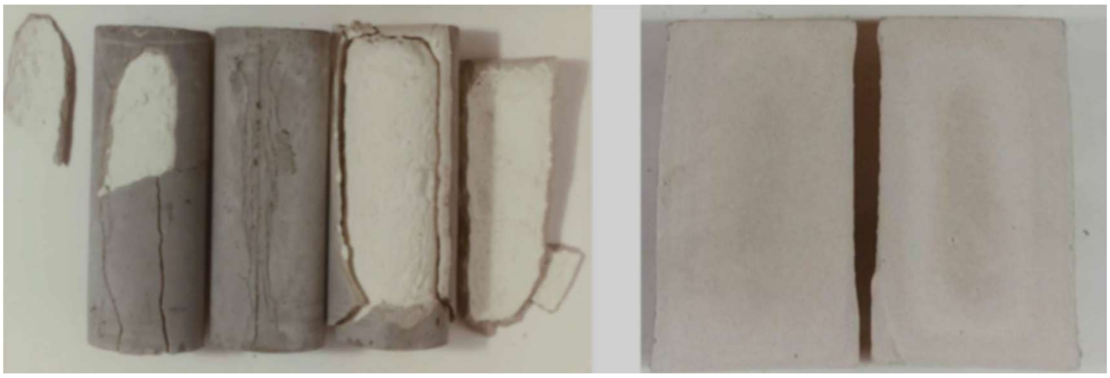

Figure 1. The impact of carbonation on the degradation of OPC cores. On the left, the figure shows neat OPC cement cores. On the right are sliced OPC cores with added silica flour. Both cores were subjected to 260°C for 4 months. Source: Milestone et al.

The thermal stresses resulting from cyclical exposure to cold and hot fluids within the wellbore, combined with mechanical stresses from hydraulic fracturing in Enhanced Geothermal Systems

(EGS) and drilling operations, can also contribute to various forms of cement degradation. Thermal cycling, in particular, can lead to debonding between the cement and the wellbore formation as well as between the cement and casing, exacerbating the risk of fluid migration. Other prevalent forms of cement failure include shear damage, radial cracking, and disking. Additionally, improper displacement during cementing operations can lead to contamination of the cement slurry by drilling mud, reducing the cement's effectiveness in forming a competent seal. Issues such as channeling and loss of circulation during cementing operations further undermine the integrity of the cement sheath (Nelson and Guillot, 2006).

The consequences of cement failure are not limited to the wellbore itself but can extend to surrounding geological formations and overlying aquifers. Compromised cement integrity can allow formation fluids to migrate into lower-pressure zones, potentially leading to the collapse of the wellbore structure. Such failures pose significant environmental and safety risks, including the potential contamination of overlying aquifers, which could have far-reaching consequences (Nelson, 1990).

This understanding of cement degradation mechanisms in geothermal environments emphasizes the critical need for selecting appropriate cement formulations and deploying robust cementing practices to ensure long-term wellbore integrity.

3.2. Ordinary Portland Cement

Ordinary Portland Cement (OPC) remains the preferred base cement for oil and gas wells due to its well-established properties, widespread availability, cost-effectiveness, and extensive track record in the industry. However, OPC's inherent brittleness makes it less suitable for geothermal wells, which are subjected to more extreme thermal and chemical conditions. To address these challenges in both oil and gas well operations, as well as in geothermal applications, various additives are introduced to mitigate cement strength retrogression, enhance durability, and improve overall performance.

The American Petroleum Institute (API) has classified oil-well cements into eight categories (Class A-H) as outlined in Specification 10A/ISO 10426-1:2000. Among these, Class G and Class H cements are particularly important for wellbore applications. Class G cement, characterized by its fine grind, is versatile and suitable for deep wells, promoting rapid strength development and shorter setting times. This class can be customized with additives to enhance its performance in high-temperature environments, making it ideal for a broad range of well conditions.

Class H cement, with its slightly coarser grind, is engineered for even deeper wells exposed to extreme temperatures and pressures. It offers higher long-term strength and durability, making it well-suited for applications that require extended working times and robust performance in harsh conditions. The coarser grind also contributes to its lower heat of hydration, reducing the risk of thermal cracking in massive cement structures.

Both Class G and Class H cements can be further tailored with various additives, including nanoparticles, extenders, chemical admixtures, mineral additives, and reinforcements, to optimize cement slurries for specific well conditions. Enhancing the mechanical properties of cement at the nanoscale is particularly critical, as it aligns with the non-classical theory of cement hydration. This theory emphasizes initiating calcium silicate hydrate (C-S-H) nucleation at the nanoscale, allowing it to develop into a robust microstructure that significantly improves the overall durability and performance of the cement (Mohamed et al., 2018; Yiying et al., 2023).

Among the innovative materials used to enhance cement performance, graphene nanoplatelets (GNPs) have gained significant attention. GNPs have been extensively studied for their ability to enhance the flexural strength of cement composites, improving their resistance to mechanical stress and crack propagation (Massion et al., 2022). Additionally, GNPs serve as a conductive material within the cement matrix, enabling the development of self-sensing cement composites. These composites possess the ability to monitor their own structural health in real-time, leveraging changes in electrical conductivity to detect variations in strain, stress, or damage within the cement structure.

The incorporation of conductive materials like GNPs into cement expands its functional properties beyond traditional structural applications. By embedding self-sensing capabilities, cement can transition from being a passive structural material to an active sensor capable of providing real-time information on its condition. This capability facilitates early detection of potential issues, such as cracking or debonding, allowing for timely preventive maintenance and enhancing the long-term integrity of wellbore systems. The integration of such advanced materials into cement formulations represents a significant advancement in ensuring the reliability and safety of both oil and gas and geothermal wells.

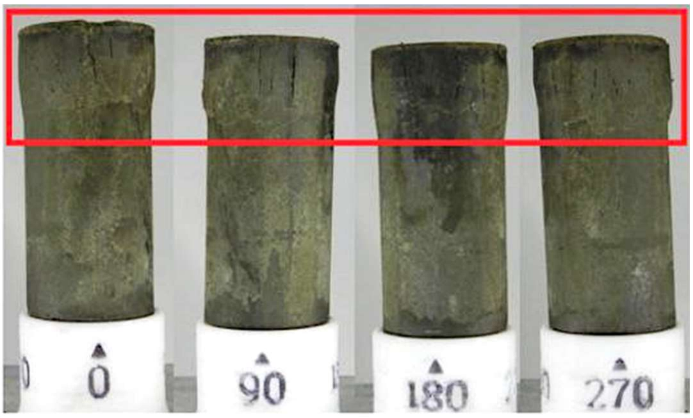

Figure 2. (unpublished work by Mileva Radonjic Research Group) shows OPC-based blended cement with Graphene Nanoplatelets (GNP) stored for 9 months in the Newberry geothermal well, demonstrating resistance to brittle fracturing after UCS testing.

3.3. Carbon nanomaterials

Carbon nanofibers (CNFs), with diameters around 100 nm and lengths from 10 to 50 μm, are derived from carbon fibers through graphitization, which imparts a highly ordered graphite crystal structure. This process enhances CNFs with high strength, low density, and excellent thermal and electrical conductivity, making them promising for self-sensing cementitious composites. Galao et al. (2017) explored the damage sensing capabilities of cement pastes with CNFs at concentrations of 0.5%, 1%, and 2%.

Carbon nanotubes (CNTs), developed in 1993, are one-dimensional lightweight nanomaterials with exceptional properties, including a Young's modulus of 1–5 TPa, tensile strength of ~100 GPa, and thermal stability up to ~2800°C (Metaxa et al., 2021). CNTs exhibit remarkable electrical conductivity, being 1000 times more conductive than copper, with an electrical resistivity of around 10^{-1} Ω cm (Jiang et al., 2024). These attributes make CNTs highly valuable for structural health monitoring (SHM) in construction, enabling strain mapping, damage detection, and crack monitoring (Kekez and Kubica, 2020).

Graphene, a two-dimensional honeycomb lattice of carbon atoms, is about 200 times stronger than steel with a thickness of approximately 6–8 nm. Its strength, elasticity, electrical, and thermal conductivity are attributed to its long-range π-conjugation, a unique electron arrangement (Jia-Yao et al., 2023; Allen et al., 2010). Despite its benefits, the high production cost of graphene limits its widespread use. As a cost-effective alternative, graphene nanoplatelets (GNPs) have been identified. GNPs, with thicknesses ranging from 5 to 25 nm and widths between 5 to 20 µm, share the same chemical structure as graphene but are more affordable (Kalaitzidou et al., 2007).

Although GNPs have a higher resistivity (~10^6 Ω cm) than copper or silver, their large-scale production and lower costs make them attractive for various applications. Liu et al. (2016) demonstrated that incorporating a high concentration of GNPs (6.4% by weight of cement) into mortar composites resulted in stable electrical conductivity and a sensitive piezoelectric response to compressive loading, crucial for damage detection in concrete. Sevim et al. (2022) further showed that cement composites with 7.5 wt% GNPs exhibited the lowest bulk resistivity, attributed to the enhanced conductive path formation from increased GNP proximity.

Graphene oxide (GO), a layered nanomaterial derived from graphite oxidation, improves cement composites' mechanical properties due to its higher dispersion rate in aqueous solutions compared to GNPs. The key difference between GNPs and GO lies in their electrical properties and dispersibility. GO's oxygen-containing functional groups enhance dispersion but reduce electrical conductivity, limiting functionalities such as self-sensing (Suo et al., 2022).

While GNPs can significantly enhance the mechanical properties and smart sensing capabilities of cement-based materials, the mechanisms behind these improvements remain unclear, primarily due to challenges in maintaining consistent experimental conditions, particularly in uniformly dispersing GNPs within the cement matrix (Chuah et al., 2014; Du and Pang, 2015; Yang et al., 2017; Zeng et al., 2023). Therefore, optimizing the concentration and ensuring uniform dispersion of GNPs are crucial for maximizing the effectiveness of self-sensing applications.

Graphene's incorporation into cement or polymer matrices enhances strength and durability through effective load transfer, facilitated by its high surface area and strong bonding capabilities. This extensive interfacial interaction promotes efficient stress distribution and crack bridging. However, carbon nanoparticles primarily act as inert fillers within the cement matrix, providing additional surfaces for hydrate growth without chemically participating in the hydration process (Awejori et al., 2023).

The amount of carbon nanomaterials used in concrete significantly differs from that in cement paste. In concrete, aggregates like coarse and fine particles influence composite behavior and nanomaterial distribution within the matrix. Aggregates contribute to mechanical strength but also challenge effective nanomaterial dispersion, making uniform distribution in concrete more difficult than in cement paste. In cement paste, nanomaterials can be evenly distributed, leading to consistent enhancements in mechanical properties, durability, and self-sensing capabilities. The smaller volume of cement paste allows for a higher concentration of nanomaterials without significantly impacting mixture rheology or workability. In concrete, the introduction of nanomaterials requires careful consideration of factors like aggregate size, volume fraction, and the potential for nanomaterial agglomeration, which can create weak spots and reduce overall performance.

Experimental studies by Massion et al. (2022) have shown that adding less than 0.1% graphene by weight of cement (BWOC) can significantly increase the flexural strength of ordinary Portland cement (OPC). Cement samples cured at 90°C for 28 days with graphene nanoplatelets exhibited enhanced ductility and fracture toughness compared to neat cement. These improvements are attributed to graphene's ability to reinforce the cement matrix, effectively bridging microcracks and improving resistance to deformation. However, higher concentrations of graphene can negatively impact the rheology of fresh cement, leading to agglomeration, which may create voids and pathways for fluid migration, ultimately compromising the integrity of the cement sheath.

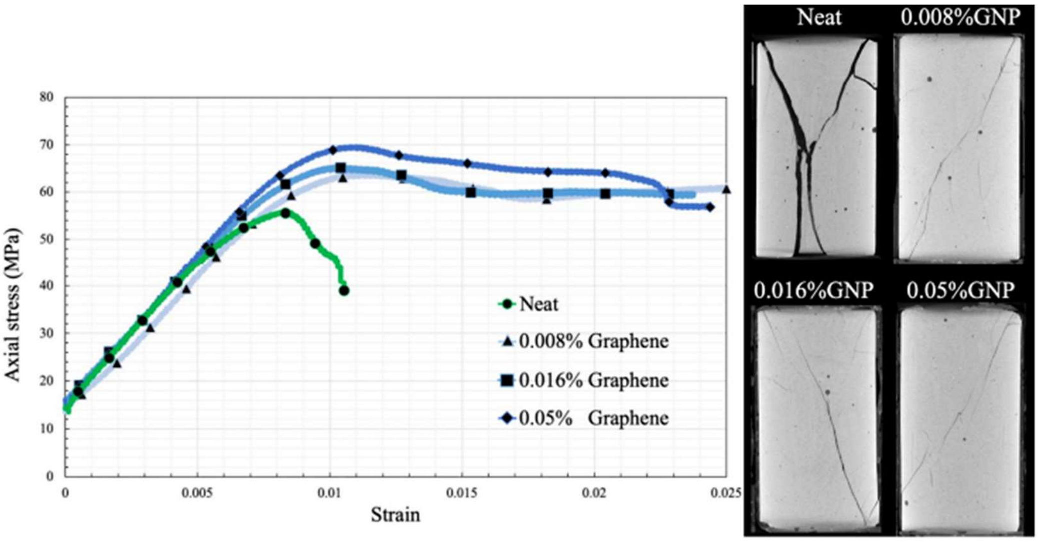

Figure 3. The stress-strain curves for neat cement and cement samples with 0.008%, 0.016%, and 0.05% graphene nanoplatelets (GNP) tested at 13.8 MPa and 90°C are presented. CT scan slice from post-triaxial mechanical testing shows the fracture patterns of the failed samples. It is observed that the introduction of graphene results in a reduced fracture network of failure (Massion et al., 2022).

Graphene's exceptional electrical properties, derived from its hexagonal lattice structure, allow for high carrier mobility and rapid electron transport, making it highly responsive to external stimuli. This characteristic makes graphene a promising material for developing self-sensing cement composites that can monitor structural health in real-time by detecting changes in electrical conductivity. However, ensuring uniform graphene distribution within the cement matrix and accurately identifying the percolation threshold— the point at which a continuous conductive network forms within the composite—remain significant challenges. Uneven distribution can lead to inconsistencies in material properties and performance, potentially undermining graphene incorporation's benefits.

Despite these challenges, graphene holds substantial potential for geothermal applications. Its ability to enhance the mechanical properties of cement, coupled with its self-sensing capabilities, positions graphene as a key material for improving cement performance in extreme environments and enabling real-time structural monitoring. This makes graphene-enhanced cement composites particularly valuable in geothermal wells, where maintaining cement integrity under harsh thermal and chemical conditions is crucial.

In summary, while CNFs, CNTs, and GNPs all offer unique benefits for improving the mechanical and electrical properties of cement composites, their differences in structure, cost, and conductivity must be carefully considered to optimize their use in specific applications.

3.4. Electrical properties of graphene

3.4.1. Electrical resistivity

Electrical resistivity can be categorized into surface resistivity and bulk resistivity. Surface resistivity (ρs) measures the resistance to electric current along a material's surface and is expressed in ohms per square (Ω/sq). This measurement is relevant for thin coatings and films used in touchscreens, sensors, and protective coatings. Bulk resistivity, on the other hand, focuses on the material's resistance in its three-dimensional bulk form, considering its microstructure, porosity, and additives. It is measured in ohm-meters (Ω·m) It reflects the intrinsic resistance of the material to electric current flow. Electrical resistivity (ρ) is defined by the formula $\rho = RA/L$, where R is resistance, A is the cross-sectional area, and L is the length.

According to the Effective Medium Theory (EMT), the conductive behavior of composite materials is influenced by both the conductive fillers and the matrix in which they are embedded. The effective conductivity depends on the content, conductivities, shapes, and distributions of each phase within the matrix. While dry cement is naturally highly resistant to electricity, incorporating conductive fillers such as graphene can transform the cement matrix into a conductive material. In conductive concrete, structural health monitoring relies on detecting changes in effective resistivity as fractures develop. An increase in resistivity indicates structural damage, allowing for early detection and intervention (Saafi, 2009).

A two-probe method measures electrical resistivity by applying a current through two probes placed on a material and measuring the voltage drop across those same probes, while a four-probe method uses two separate sets of probes - one to inject current and another to measure voltage drop, allowing for a more accurate measurement by eliminating the influence of contact resistance between the probes and the material being tested; making the four-probe method significantly more precise, especially for low resistance materials (Tiong et al., 2024).

(Liu et al., 2018) developed a simulation model to examine the percolation behavior of graphene nanoplatelet (GNP)/cement composites. Through detailed simulations, they identified the percolation threshold at 2.2 vol%, signifying the critical point where GNPs form a continuous, interconnected network within the cement matrix. At this specific concentration, the GNPs bridge the gaps within the pore structure, effectively establishing conductive pathways. This network formation leads to a significant enhancement in the composite's electrical conductivity, transforming the cement matrix from an insulator into a material capable of conducting electricity. The study's findings underscore the importance of reaching the percolation threshold for optimizing the electrical properties of GNP/cement composites, which is vital for applications in smart cementitious materials and structural health monitoring systems.

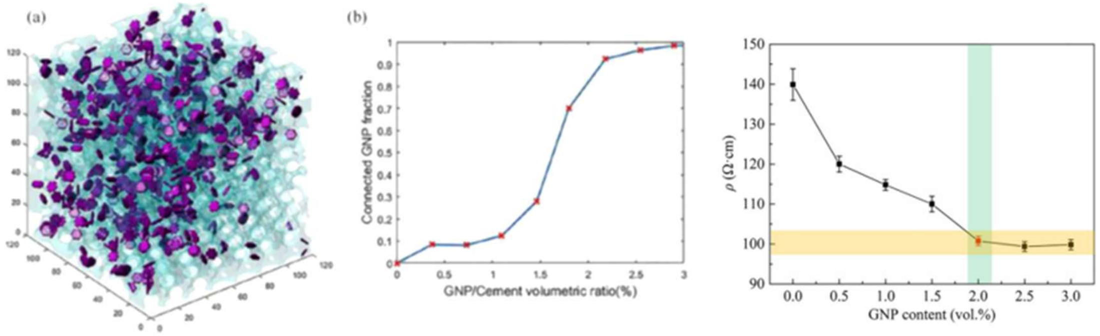

Figure 4. GNP/cement composites Simulation model and results (Liu et al., 2018).

Both alternate current (AC) and direct current (DC) voltages are used in measuring resistivity, but they come with distinct challenges. Research has shown that DC can cause significant polarization within the composite, which can lead to errors in resistance measurements (Banthia et al., 1992; Reza et al., 2001). (Sun et al., 2017) research on the effect of multi-layered graphene on the electrical resistivity of cement composite using AC and DC voltages. It was observed that the percolation threshold was the same for both voltages (Figure 32). This is an indication that the percolation phenomenon is not subject to AC and DC voltages. However, the AC method reveals a notably lower resistivity values and a clearer distinction between the percolation and conduction zones. This discrepancy is due to polarization effects observed under DC voltage, which cause charging at the capacitor formed on the C-S-H gel surface and at the interface between the multilayer graphene (MLG) and the cement matrix. This polarization results in an opposing current when a DC voltage is applied, making the MLGs act as insulators at DC or low AC frequencies, thereby increasing resistivity. In contrast, high AC frequencies, with their sinusoidal variations, do not induce polarization effects, leading to lower resistivity values.

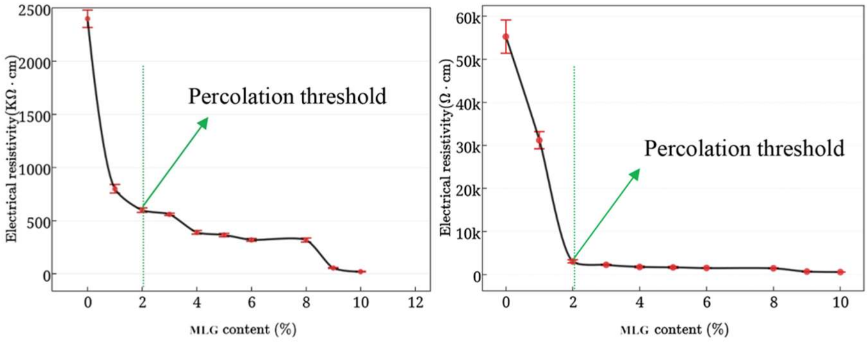

Figure 5. The relationship between electrical resistivity and graphene volume fraction using both DC (left) and AC (right) methods (Sun et al., 2017). Both have the same percolation threshold of 2% BVOC.

(Xu et al., 2021) investigated the microstructure of a graphene/cement composite before and after carbonation. The flat flakes represent graphene, which are either tiled or embedded in the cement matrix. After carbonation, there is minimal morphological change in the graphene flakes. In Figure 27(a), graphene is in close contact with the gel. Post-carbonation, irregularly shaped prominences or sporadic crystals, mostly $CaCO_3$, form around the graphene due to the chemical reaction between H_2CO_2 and $Ca(OH)_2$, AFt, and gel. These carbonation products partially fill the pores, obstructing the connections between graphene flakes. In 27a, the system conducts mainly through the gel, increasing electrical conductivity due to carbonation. In 27b, the graphene conductive path begins to form, contributing more to the system's conductivity, where carbonation effects shift from strengthening to weakening. In 27c, the system conducts mainly through an intact graphene network, but carbonation disrupts these connections, reducing conductivity. Figure 28 presents a schematic plot of the conductive path in the graphene/cement composite after carbonation.

Before carbonation, the primary conductive paths were the gel matrix and continuous or discontinuous paths formed by graphene. After carbonation, the products fill the pores, adhere to the graphene surface, and embed between the flakes. This enhances the conductivity of the gel but impairs the graphene's conductive path, generally leading to high resistivity of the cement matrix. SEM observations provided evidence supporting the proposed microstructure changes and their impact on the variation in electrical conductivity caused by carbonation.

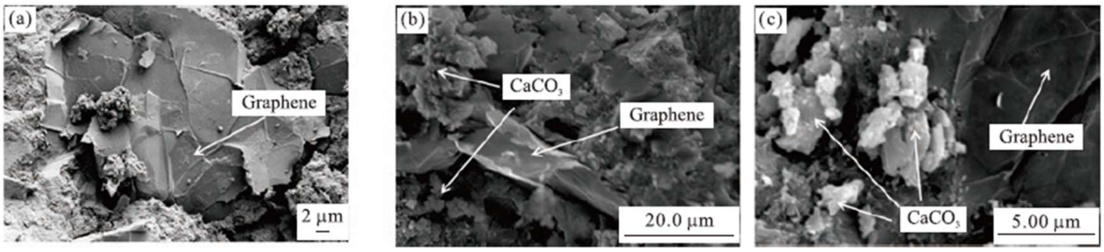

Figure 6. SEM images of graphene/cement composite: (a) Before carbonation; (b) and (c) After carbonation (Xu et al., 2021).

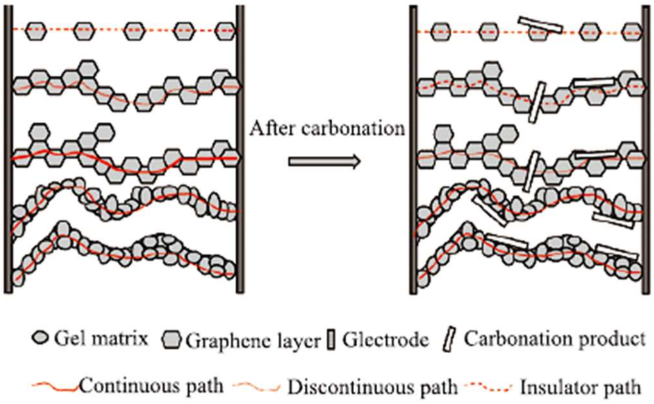

Figure 7. Schematic plots depicting the conductive paths of graphene/cement composite after undergoing carbonation (Xu et al., 2021).

Conductive materials such as carbon fibers, graphite, or carbon nanotubes create interconnected networks within the cement matrix. These networks facilitate the flow of electrical current, making the cement responsive to changes in its structure. When the cement undergoes stress or strain, the conductive networks are disrupted, leading to measurable changes in electrical resistivity. The presence of conductive materials enhances the signal-to-noise ratio in resistivity measurements. Small changes in the internal structure of the cement, such as the development of microcracks or minor deformations, cause significant changes in resistivity. This heightened sensitivity allows for the detection of early signs of damage, enabling timely maintenance and repair. Conductive additives help in distributing stress more uniformly throughout the cement. This uniform distribution ensures that the changes in resistivity are representative of the overall health of the cement, rather than being localized to specific areas. A more consistent and reliable self-sensing capability is achieved.

(Guo et al., 2020) developed high-performance cementitious composite materials (CCMs) by incorporating graphene nanoplatelets (GNPs) as reinforcing fillers. Their findings showed that adding GNPs lowered the resistivity of the CCMs from 18.85 kΩ·m to 6.26 kΩ·m, as illustrated in Figure 5. Cement without GNPs exhibits higher resistivity compared to graphene-infused cement due to the absence of conductive networks, lower electron mobility, lack of percolation networks, and higher contact resistance. Graphene, with its exceptional electrical conductivity and ability to form continuous conductive paths within the cement matrix, significantly reduces the resistivity of the composite material.

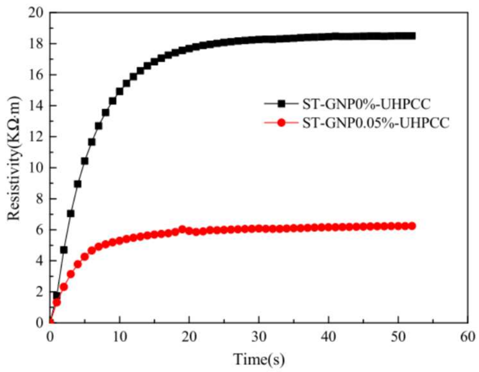

Figure 8. (Guo et al., 2020) shows the variation of electrical resistivity with time cement samples with and without graphene.

Mechanical loading affects the resistivity of graphene nanoplatelet (GNP)-cement composites by altering the conductive pathways within the material. Under compression, resistivity typically decreases as GNPs are brought closer together, enhancing conductivity. In contrast, tensile stress increases resistivity by disrupting these pathways. Microstructural changes, like the formation of microcracks, further impact resistivity, especially when cracks interrupt the GNP network. The material's sensitivity to strain, quantified by the gauge factor, makes it effective for structural health monitoring. Additionally, the rate and duration of loading influence resistivity, with dynamic loading causing temporary changes and static or prolonged loading leading to more stable or cumulative resistivity shifts. These effects highlight the potential of GNP-cement composites as self-sensing materials capable of monitoring structural integrity in real time.

(Guo et al., 2020) in their work observed that under cyclic loading, ST-GNP0.05%-UHPCC experiences variations in compressive stress and corresponding changes in specific resistance. As compressive stress is applied, the specific resistance decreases due to enhanced conductivity from the closer alignment of graphene nanoplatelets. Upon unloading, the resistance may partially recover, but permanent microstructural changes like microcracks could lead to cumulative increases in resistance over time.

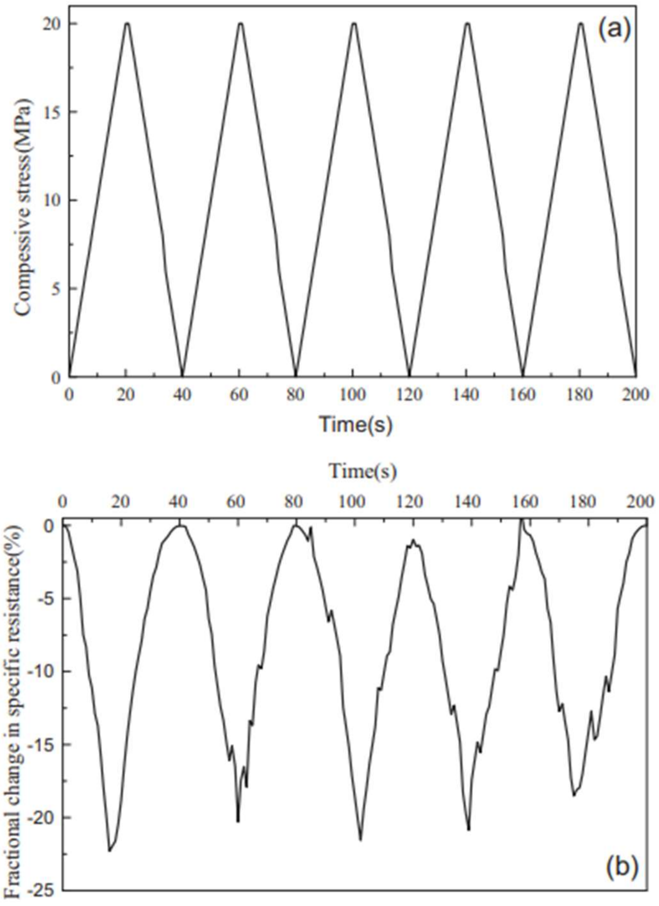

Figure 9. (Guo et al., 2020) displays the compressive stress (a) and the corresponding fractional change in specific resistance (b) of ST-GNP0.05%-UHPCC during cyclic loading.

Different percentages of conductive materials can significantly impact the sensitivity of cement to stress, strain, and damage. Experimenting with various amounts allows for identifying the optimal concentration that balances conductivity and mechanical properties for accurate health monitoring. The concentration of conductive material determines the overall electrical conductivity of the cement. Insufficient conductive material may result in low conductivity, making it challenging to detect resistivity changes accurately. On the other hand, excessive conductive material can compromise mechanical integrity and increase costs. Finding the right percentage ensures that the cement is sufficiently conductive for effective self-sensing while maintaining its structural properties (Saafi et al.,2009).

3.4.2. Electrical Conduction

Electrical conduction in cement composites is generally classified into three distinct types: contacting conduction, tunneling conduction, and ionic conduction.

Contacting conduction arises when neighboring conductive fillers within the composite make direct contact, thereby forming a conductive network. This direct contact allows electrons to flow freely across the composite, enabling electrical conductivity. The efficiency of this conduction type is heavily dependent on the concentration and distribution of conductive fillers, such as carbon nanotubes or graphene, within the cement matrix. As these fillers come into direct contact, they create pathways that facilitate the movement of electrons, thereby reducing the electrical resistivity of the composite.

In contrast, tunneling conduction, also known as the quantum tunneling effect, occurs when the distance between disconnected conductive fillers is extremely small, typically ranging between 1 and 10 nanometers. Despite the lack of physical contact, electrons can "tunnel" through the insulating barrier separating the fillers due to quantum mechanical effects. This type of conduction becomes particularly significant in composites where the conductive fillers are close enough to allow tunneling but not in direct contact. The presence of a strong local electric field, often caused by conductive fillers with unique morphologies like spiky spherical nanoparticles, can enhance this tunneling effect. Research by Alamusi et al. using a 3D resistor network numerical model demonstrated that tunneling conduction plays a dominant role in the electrical performance of composites, especially under low external force conditions.

Ionic conduction in cement composites is more complex and varies significantly depending on the moisture content within the matrix. Under dry conditions, the cement matrix functions as an insulating material, preventing the free movement of ions and, consequently, electrical conductivity. However, when the cement is hydrated, the water within the capillary voids or pores dissolves ionic species such as Ca^{2+} and OH^{-}. These dissolved ions facilitate ionic conduction through the cement matrix. The effectiveness of this conduction type is closely linked to the amount of free water present, as it directly influences ion mobility within the pore solution. Under saturated conditions, ionic conduction, supported by a conductive networking mechanism or micro-conductive paths, predominantly governs the composite's overall conductivity. Conversely, in dry conditions, electronic conduction, which relies on electron flow rather than ion movement, becomes the dominant mechanism.

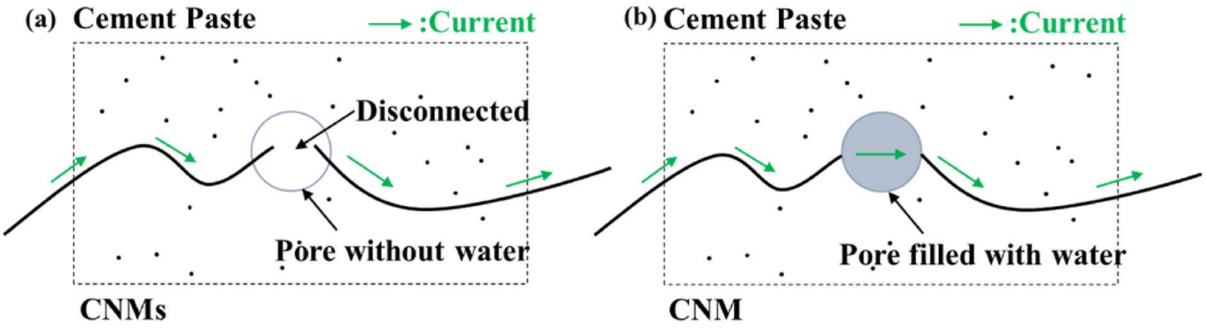

Figure 10. Effect of pore water on electrical current flow; (a) non-saturated, (b) saturated (Tian et al., 2019; Wen and Chung, 2006)

Overall, the conduction mechanisms within cement composites are highly intricate and interrelated. The three conduction types—contacting, tunneling, and ionic—can coexist and interact in complex ways, making the real conduction mechanism challenging to delineate. At lower filler concentrations, contacting conduction, tunneling conduction, and/or field emission conduction, along with ionic conduction, are likely to dominate the composite's electrical conductivity. However, as the filler concentration increases beyond a certain threshold, known as the percolation threshold (PT), the nature of the conduction changes. Nalon et al. further classified these mechanisms into three distinct zones: insulation, percolation, and conductive zones.

In the insulation zone (Zone A), ionic conduction is predominant, leading to high electrical resistivity in dry conditions, where electron conduction dominates. However, in the wet state, the situation is reversed due to the presence of free water facilitating ionic movement. This zone is also characterized by a significant capacitive response due to the polarization phenomenon. As the concentration of conductive fillers increases, the composite transitions into the percolation zone (Zone B), where the conduction mechanism gradually shifts from ionic to tunneling and contacting conduction. Finally, in the **conductive zone (Zone C)**, the distance between conductive fillers becomes short enough for direct contact, which significantly reduces the electrical resistivity to its minimum possible value.

To determine which conduction mechanism governs the electrical conductivity of self-sensing cement composites (SSC), the DC electrical resistance-time relationship is often used. For instance, if ionic conduction prevails, the DC electrical resistance will noticeably increase over time due to the polarization effect. In contrast, for other conduction types, the resistance remains relatively constant over time.

In summary, the electrical conduction in cement composites is a multifaceted process influenced by the interplay between contacting, tunneling, and ionic conduction mechanisms. Each type of conduction plays a crucial role depending on the composite's filler concentration, moisture content, and external conditions, making the understanding and optimization of these mechanisms essential for the development of advanced self-sensing cementitious materials.

4. Input from Initial Production Modeling

This section provides a brief status report on the ongoing initial modeling of heat production and well integrity performed at LBNL. A large diameter geothermal well model has been developed based on the linking of LBNL's T2Well simulator for multiphase fluid flow and heat transfer in wells with the FLAC3D mechanical simulator for well integrity. The model has been tested and demonstrated to be able to model geothermal production through a 3-km deep well, 0.5 m in diameter, along with well casing and cement mechanical responses. The model is currently being applied for initial modeling of heat production, well integrity modeling and cement strain–resistivity. At this stage, preliminary results of the model can be used to inform about the potential for the application of self-sensing cement in a geothermal well, including what are the temperature, pressure, stress and strain changes that can be expected. This may inform the selection of additives and guide laboratory the testing. The ongoing modeling include production from a hot steam reservoir, including assumed daily production cycles to investigate potent cyclic mechanical responses in the well cement. Preliminary results are stated as follows:

- The biggest risk of mechanical cement failure occurs during the initial start-up of production because of a large and rapid temperature increase from an initially cool temperature near the ground surface.
- During variable production with assumed daily production cycles, temperature fluctuations also result in fluctuations in pore pressure and stress with a relatively larger impact when producing from a very hot steam-dominated system.
- Both tensile and compressive cement failure can occur as a results temperature increase and thermal pressurization as a result the thermal expansion of fluids trapped in the cement.
- Key mechanical parameters for the stress and strain evolution in the cement are Young's modulus and cement strength, including compressive strength and tensile strength.

Figure 11 shows example of changes in temperature and fluid pressure in the well assembly near the ground surface two days after the start of steam production. Temperature changes of up to 223°C in 2 days, causes thermal pressurization with pressures up to 5 MPa.

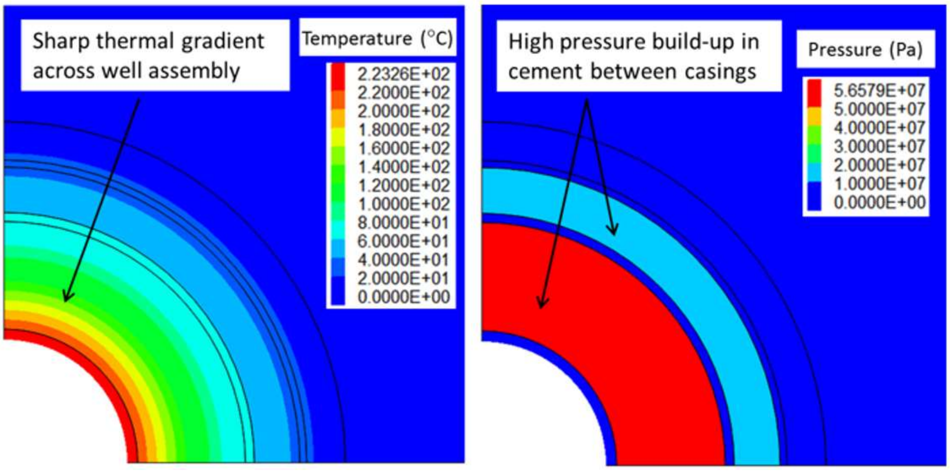

Figure 11. Simulated temperature and pressure changes in the well assembly near the ground surface after 2 days of production from a deep geothermal reservoir.

Figure 12 shows examples of changes in maximum and minimum principal stresses. As a results of thermal pressurization with high pressure increase, tensile failure can occur and the and the maximum principal stress can be as high as 3 MPa, which is equal to the assumed tensile strength for the cement. Show in the figure is also the minimum principal effective stress, which is equal to the maximum compressive effective stress with a maximum of 11 MPa. The compressive effective stress is causes by thermal expansion of the cement that is mechanically confined by host rock and casings.

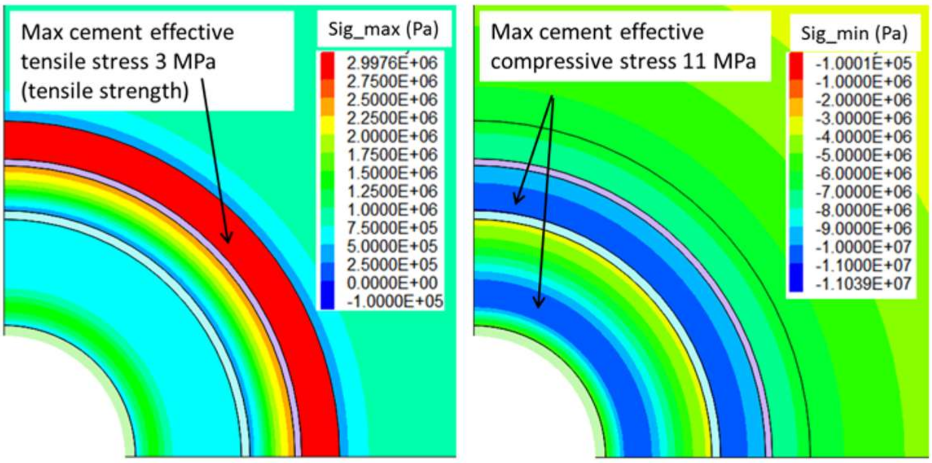

Figure 12. Simulated stress changes in the well assembly near the ground surface after 2 days of production from a deep geothermal reservoir.

Figure 13 presents results of volumetric and shear strain in the cement. The inner cement is expanding caused by thermal expansion and thermal pressurization. The expansion near the inner casing is the largest with volumetric strain exceeding 0.03.The entire inner cement experience a volumetric strain of close to 0.01 or higher.

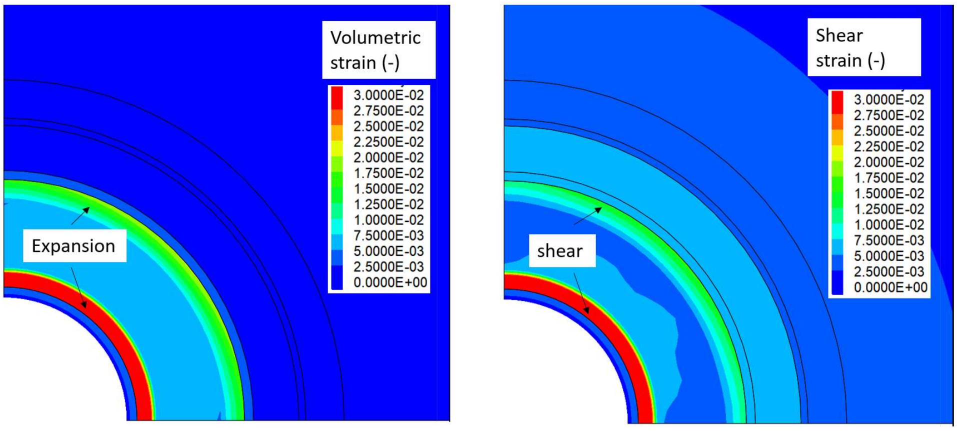

Figure 13. Simulated strain changes in the well assembly near the ground surface after 2 days of production from a deep geothermal reservoir.

For the self-sensing potential, we may relate the obtained stress and strain changes with potential changes in resistivity as reported from experiments in the literature. For example, Gawel et al (2021), measured resistivity of Portland G—oil and gas well cement with carbon nanofibers (CNF) to axial load during uniaxial compressive strength test. The experiments showed fractional resistivity changes ranging from 50% - 150% when loading the samples through compressive failure. That is, the samples were loaded to a peak compressive stress of about 14 MPa and with axial strain about 0.03 at failure. This is similar to the stress and strain evolution in the simulation results with the results in Figure 12 to 13. However, at this point it is not clear how to relate the calculated and stress and strain to those in compression experiments. Moreover, we might have to look for irreversible strain that could indicated permanent damage. In this context, Wen and Chung (2007), presents experimental results of carbon fiber reinforced cement showing up to 40% fractional resistivity change associated with irreversible strain on the order of 1×10^{-4}. The amount of irreversible strain will be investigated in the continued modeling. That is, the production will be stopped to let the well cool down to ambient temperature and irreversible strain can be extracted from the simulation results.

From the preliminary results presented here, the potential for self-sensing has been indicated by relating calculated stress and strain changes to experimental observations of stress and strain induced resistivity changes. Moreover, the simulations clearly show the importance of the mechanical properties, i.e. cement deformability and strength that are properties that can be modified by additives considered in this study.

5. Experiment Preparations

This research investigates the recent advancement in monitoring, including cement-based sensors that integrate directly into the cement composite, offering improved compatibility, lower costs, and greater sensitivity. The conductive material for this research is graphene.

5.1. Expected Outcome

- ✓ Stress-induced microcracks could disrupt the conductive pathways within the cement matrix, increasing electrical resistivity.

- ✓ The thermal and mechanical stress tests are expected to demonstrate the resilience of the cement composite under simulated geothermal conditions.

- ✓ To determine a clear correlation between cement failures and the measured resistivity values.

5.2. Materials and equipment

- ✓ The RCON2 device from Giatec Scientific Inc. was recently acquired for this research to measure electrical (bulk) resistivity of cement samples.

- ✓ All materials, tools, and equipment are available at OSU except for tools measuring some mechanical properties of cement composites. This will be outsourced.

- ✓ The cement materials were donated by Mr. Lance Sollohub from Cudd Energy Services.

Figure 14. Cement Materials donation from Mr. Lance Sollohub of Cudd Energy Services

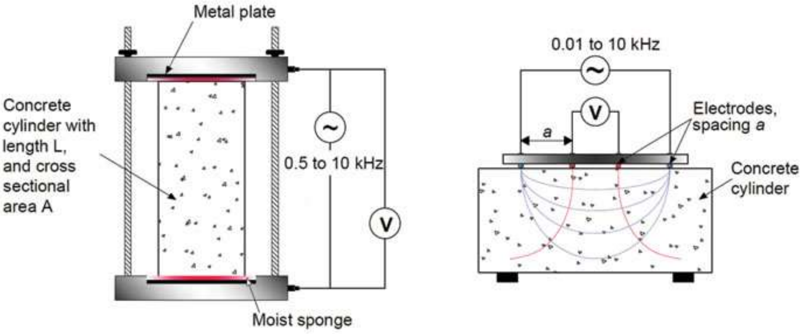

Figure 15. Bulk resistivity measurement. Source: Giatec Scientific Inc.

6. Conclusion

The composition of wellbore cements, primarily as blended cements, dictates their setting and strength development based on the reactivity of the predominant component. In cases where pozzolanic materials dominate, the hydration of C_3S (tricalcium silicate) is crucial as it provides the necessary calcium for pozzolanic reactions. For blended cements with a significant proportion (over 50 wt%) of a hydraulic supplementary cementitious material (SCM), such as granulated blast furnace slag, the hydration process is critical in determining the long-term performance of the cement. This process influences the composition of the reaction products, microstructure, porosity, and overall mechanical properties.

Effective self-sensing in cement composites is characterized by a direct correlation between resistivity changes and structural failures induced by thermal or mechanical stresses and strains. This research aims to advance the field of smart materials, particularly in geothermal well applications, by showcasing the potential of graphene-enhanced cement composites as self-sensing materials. The findings are expected to pave the way for future innovations in smart infrastructure, with significant implications for the design and maintenance of structures in extreme environments. This contribution is anticipated to enhance the safety and resilience of infrastructure systems in challenging conditions.

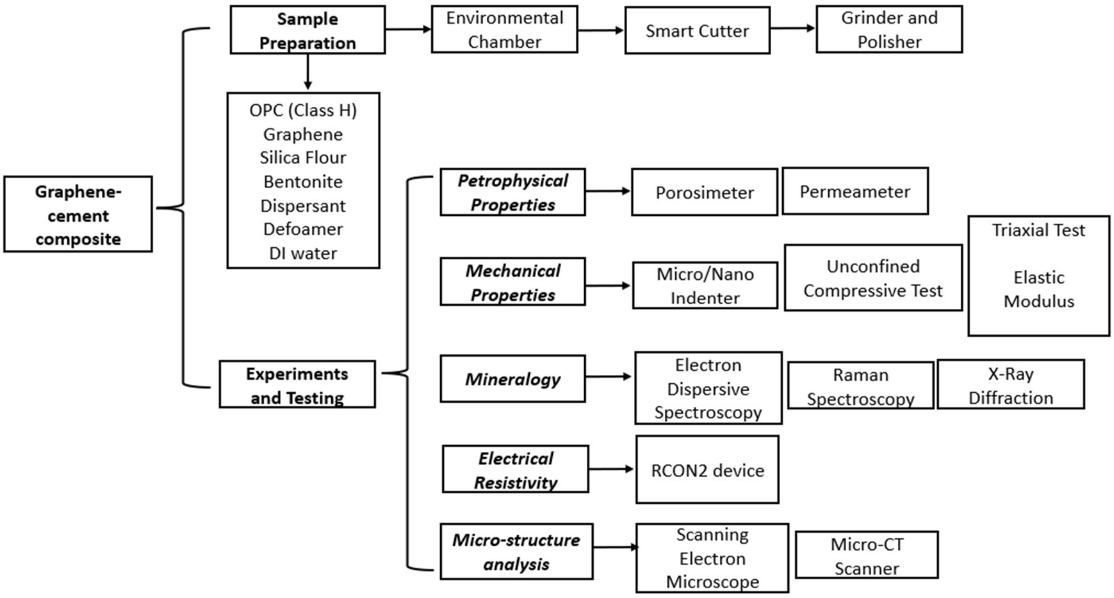

Figure 16. Preliminary Schematic Summary of Planned Experimental Workflow, Tools, and Materials Required

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