

Review

Methods to Enhance Mechanical Properties of Cementitious Composites: Innovations at the Nanoscale for Humanitarian Impact

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Introduction

Ordinary Portland Cement, or OPC, is one of the most common materials employed in construction worldwide. While an attractive choice for its inexpensive production process and accessible raw materials, its manufacture can expose workers to toxic trace metals [1]. Total emissions from the cement industry contribute upwards of 8% of global CO₂ emissions, and OPC implementation, in particular, uses significant amounts of water [2]. According to a 2019 Nature assessment, 75% of the water necessary to produce OPC-associated concrete has been projected to originate in regions expected to experience significant drought and water stress 2050 [3, 4]. Despite these shortcomings, recent research has incorporated carbon nanotubes (CNTs) and superplasticizers into OPC matrices to enhance tensile strength. Although adverse impacts of OPC have been well-established, associated nanoscale level advancements improve mechanical properties of cementitious materials. With the widespread use of consumptive and harmful OPC constituting a major sustainability concern, the development of completely novel, greener alternatives to conventional building materials like OPC have become increasingly imperative.

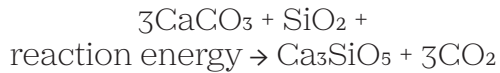
The purpose of this review is to characterize the effects of OPC additives, including various CNTs, surfactants, and superplasticizers, and innovate an alternative additive to enhance existing one-part, geopolymer cement composites. Geopolymer cement composites have emerged as marketable substitutes in place of carbon-rich OPC. Although the incorporation of additives into OPC to produce stronger concrete has been well-documented, little research has considered the

effects of the same OPC enhancers on geopolymer cement. Building off of this context, this review begins by synthesizing current understandings of CNT, surfactant, and superplasticizer properties in relation to cement durability. By summarizing the production process of geopolymer cement, this review underscores the need to develop compatible additives to ensure the material's higher resistance to crack formation, elevated tensile strength, and greater strain-withholding capacity [5]. We propose and devise one such improved nanomaterial based on the chemical characteristics of one-part and two-part geopolymer cement matrices. Through reviewing the resulting cyclic peptides that are equipped with piezoelectric properties, we suggest an application of the technology in homeless shelter design. In doing so, this review also aims to integrate nanotechnology insights from various sectors of the building sciences. By advocating for the implementation of enhanced geopolymer cement in higher-level construction, this review both highlights areas for further research as well as promotes an interdisciplinary approach to tackling social challenges.

OPC Production and Conventional Enhancements

Concrete, whose basic components include cement, water, and aggregates, such as sand, has often been viewed as a marker of economic development. Global per capita consumption of concrete has nearly tripled since the 1970s, a trend that mirrors the increase in the world's population [6]. This rising societal demand has necessitated improvements in concrete manufacturing and processing [6]. Worldwide, concrete has been commonly employed to rehabilitate and repair

existing, damaged structures [7]. A critical component of the concrete that is conventionally used in building construction is OPC, whose production requires high temperature combustion reactions to create calcium silicate “clinker” during a critical manufacturing step [8]. This process, referred to as calcination, also yields a carbon dioxide by-product. The net process is shown in Eq. (1) [9]:



A 2018 estimate attributed nearly half of the 8% of global CO₂ emissions from OPC manufacture to this step alone [3]. Later stages of cement production have attracted similar environmental concerns. The addition of water to OPC yields a chemically hydrated, solid cementitious mass. Although water-laden cement paste occupies only 10% to 15% of this final product, mechanical properties of cement are heavily influenced by the degree and duration of hydration [10]. A 2011 study investigating the effects of a sludge and sawdust composite on mortar stability revealed that high water content was inversely related to the strength of composite-containing concrete [11]. Other research indicates that water facilitates the formation of a three-dimensional structure in calcium-silicate-hydrate gel, a major component of cement-based materials, to influence shear strength [12]; Goracci et al. corroborated these findings in a 2017 study that reported water used to activate clinker into its major, semi-crystalline hydration product remains either chemically bound or otherwise confined within cement floccules [13]. While necessary for strengthening and curing, water also contributes to the physical degradation of OPC in nature. A 2017 publication determined that the interaction between concrete and aqueous media such as groundwater, freshwater, and precipitation can result in the physical degradation of associated structures in the built environment [14]. While further research is needed on reducing the effects of water in relation to enhancing OPC stability and lifespan, anhydrous nanoscale innovations have been shown to contribute to increased mechanical properties of OPC [15].

Studies have demonstrated a way to improve the weak fracture resistance of OPC through the

addition of CNTs [16]. Single-walled carbon nanotubes, or SWCNTs, are made from rolled-up sheets of graphene. SWCNTs can nest within each other to create multi-walled carbon nanotubes (MWCNTs) (Fig. 1) [17].

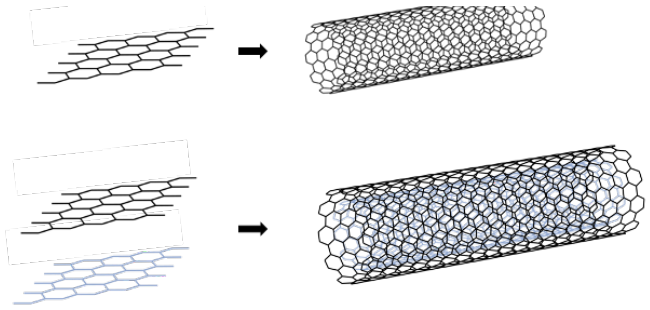


Figure 1: Assembly of carbon nanotubes from graphene. Industrial processes arc single and multiple layers of graphene sheets to produce (A) single-walled carbon nanotubes (SWCNTs) and (B) multi-walled carbon nanotubes (MWCNTs). ADAPTED FROM: https://commons.wikimedia.org/wiki/File:Eight_Allotropes_of_Carbon.svg#/media/File:Eight_Allotropes_of_Carbon.svg

Both SWCNTs and MWCNTs derive much structural stability from their regular, repeating lattices and wealth of electron delocalization. Consequently, CNTs have remarkable mechanical and thermal properties that allow them to effectively reinforce cementitious materials. According to a 2017 assessment, Young’s modulus of CNTs can reach around 1 TPa, approximately five times that of steel [18]. Using theoretical models, Che et al. demonstrated that the thermal conductivities of CNTs are comparable to that of diamond [19]. Because these two attributes also enable CNTs to have high conductivities and inherent piezoelectric properties, CNTs have been utilized as functional filler materials in OPC to sense strain, stress, and cracks, as well as to indicate sites of material disrepair [20]. The roles of such electrically conducting materials in non-conductive, cement matrices have been thoroughly investigated. A 2013 study revealed strong correlations between oscillatory applied axial strain—whose loading frequencies spanned those of typical civil structures—and measured electrical resistance in CNT-containing cement paste [21]. In a recent work concerning flexural behavior of reinforced concrete, Naji et

demonstrated the load-carrying capacity of OPC enhanced with MWNCTs is increased by more than 29% in comparison to unmodified reference materials [22].

While nanomolecular modifications to CNTs have been proposed to improve the electrical and mechanical properties of cementitious materials like OPC, studies have shown limitations to the widespread usage of CNTs as piezoresistive sensors [23, 24]. Although the high aspect ratio (fiber length to diameter) of CNTs, particularly MWCNTs, allows for additional contacts to form between nanoparticles and cement, such CNTs are more difficult to disperse throughout aqueous matrices [25]. Furthermore, because CNTs are highly nonpolar and hydrophobic, the van der Waals forces between the CNTs can cause them to aggregate within the dispersion. Nonrandom, nonhomogeneous dispersion of CNTs in cement can severely compromise the self-sensing ability of the overall material. According to Yang et al., the entanglement of CNTs has been frequently shown to inhibit the formation of a conductive network [26]. This inability of CNTs to reach the percolation threshold, or the minimum filler content necessary to promote conductivity, can yield insufficient changes in electrical resistance when subjected to external force [27].

Other additives to OPC have been found to improve the wettability of these reinforcing nanotubes in polar solution and, thus, facilitate adequate conductive network production and strain detection [16]. Molecular dynamics simulations have indicated that anionic surfactants, including sodium dodecyl sulfate (SDS) and dodecyl-benzene sodium sulfonate (NaDDBS), may form a micellar layer surrounding CNTs to promote their uniform dispersion [28]. Nonionic surfactants have been proposed to stabilize nanoparticles by sterically hindering water-rich portions of cementitious matrices [29]. However, surfactants also have been shown to have disadvantages. For instance, Liu et al. found that cationic surfactants contribute to air bubble formation in cement, a result that has been theorized to complicate cement hydration and stability [30, 31]. To overcome discrepancies between surfactant function and maintenance of self-sensing properties in cement, polycarboxylate based superplasticizers have been employed [32].

Results from Kaur et al.'s 2020 study corroborate prior findings that superplasticizers can improve CNT dispersions in OPC more than ultrasonication and other mechanical methods [33]. Although superplasticizers were designed to enhance OPC rheology, increasing awareness of sustainability challenges associated with OPC production has prompted studies on leveraging these surfactants to enhance alkali activated materials [34]. So-called geopolymers have a production process that is estimated to reduce greenhouse gas emissions by upwards of 70% to 90% relative to emissions linked to conventional concrete manufacture [35]. This reduction largely stems from geopolymer concrete's substitution of limestone - responsible for 60% of CO₂ emissions during OPC production - with industrial by-products already produced in the production of materials in other industries [36]. These by-products are used as precursors that take on the role of OPC, except they are activated by alkali solution rather than water.

Geopolymer cement can be further differentiated from OPC on the basis of mechanical behavior and stability. Generally, studies have signaled that geopolymer cement has higher durability, tensile strength, and compressive strength compared to OPC [37]. Increased amounts of fly-ash, an industrial by-product, has afforded geopolymer cement greater resistance to aggressive environments compared with OPC [38]. While construction commonly utilizes OPC due to the accessibility of its raw materials and overall cost-effectiveness, non-Portland alternatives are garnering more scientific attention and commercial usage. Geopolymer cement, in particular, can be subdivided into two categories: one-part geopolymer composites aim to circumvent challenges encountered by two-part geopolymers, whose formation requires dangerous, corrosive alkali solutions [39]. The low-carbon production process of one-part geopolymers involves polymerization of aluminosilicate substrates in the presence of alkaline solids, followed by the addition of water [40]. For both geopolymer types, alkaline sources are crucial for providing basic cations that promote the dissolution of cement raw materials and hardening [41]. Because empirical evidence has shown that basic reaction conditions

promote the degradation of superplasticizers, alternative methods emphasizing the adequate incorporation CNTs into geopolymer matrices must be investigated [42].

One way to overcome these challenges is by incorporating nanowires with piezoelectric properties into geopolymer cement. Although studies have reported successful nanowire fabrication in aqueous solution, the carefully controlled reaction conditions under which synthesis must occur are unlikely to be achieved with the natural, raw materials that favor geopolymer formation. By introducing a biochemical method to scaffold nanowires inside water-soluble, cyclic peptide nanotubes, we propose a potential way in which geopolymer cement can attain comparable self-sensing abilities to CNT-enhanced OPC [43].

Proposed Cyclic Peptide Development

Cyclic peptides can form tubular structures from spontaneously self-assembling monomers of circularly arranged amino acids. The resulting constructs are visually analogous to the hollow cylinders of arced CNTs (Fig. 2) [44].

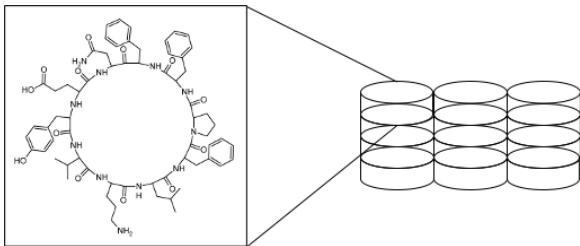


Figure 2: Cyclic peptide Tyrocidin A used to exemplify a general scheme for the spontaneous self-assembly of cyclic peptides into crystalline nanotubes. Quantity and identity of peptides can be adjusted to impact nanotube size and physiochemical properties. Adapted from: https://commons.wikimedia.org/wiki/File:Tyrocidin_A.png.

While cyclic peptide nanotubes have been discovered only recently, they constitute a growing, active area of biochemical and pharmaceutical research due to their alterable polarities, high surface areas, and cellular permeabilities [45]. These constructs have been employed in electronics, studied as versatile drug delivery

vectors, and used in tissue engineering, where nanotubes have been shown to repair injury by encapsulating neural stem cells and directing their differentiation [45, 46].

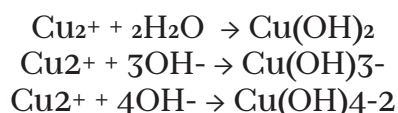
Nguyen et al. have shown that the energy-harvesting capacities of amphipathic peptide nanotubes are heavily dependent on the precise alignment of their electric dipoles [47]. Despite rigid hydrogen bonding networks along amino acid backbones, such proteinaceous structures have been found to have markedly reduced stiffness and stress tolerance compared to CNTs [48]. Accordingly, the utilities of cyclic peptide nanotubes alone as piezoelectric sensors appear limited by their lack of thermostability and mechanical stability. On the other hand, nanowires based on zinc oxide have been recorded to detect strain induced by mechanical deformation [49]. Because of the reported hydrophilicity, high electrical conductivity, and impressive strength of nickel (Ni) nanowires, literature indicates that certain metallic nanowires are promising piezoelectric materials in non-conductive matrices such as those of geopolymers [50, 51]. Xu et al. found that a Ni nanowire/OPC composite displayed higher strain sensing abilities than other cementitious ones, ultimately suggesting applications of nanowires in structural health monitoring provided their suitable dispersion [51].

Because superplasticizer-based additives are inadequate for nanoparticle dispersion in geopolymer matrices, we envision cyclic peptide nanotubes as having two distinct functions. First, polar, hydrophilic regions of cyclic peptide nanotubes can facilitate even distributions of nanowires. Findings from Resches et al. have indicated the secondary role of these constructs as serving as scaffolds for nanowires that are cast within the nanotubes' hollow interiors [52]. Nanowire formation can be aided by the ability of cyclic peptide nanotubes to selectively biomineralize hydrophilic metals at specific binding sites. For instance, proteins that selectively bind copper (Cu) are well-studied and play essential roles in cellular transport [53]. Amino acids that form copper-binding motifs, such as those found to comprise the copper-transporter ATP7B involved in Wilson's disease, can be incorporated into cyclic peptide nanotubes. Binding of Cu-

associated compounds to tubular sites can therefore constitute an effective way of trapping conductive metals. In 2007, Thilak et al. reported utilization of bacterial, peptide-based nanotubes to form cobalt, cadmium, palladium, silver, and copper nanowires [54]. More recent work has synthesized understandings of biologically-synthesized nanowires, made from stacked heme groups of cytochrome compounds, in *Geobacter* [55].

While nanowires have been the subject of much basic scientific research, insights from their applications in other fields are also revealing [56]. Cu nanowires have become a mainstay of the microelectronics industry due to their high conductivities [57]. Indicative of optimal metallic behavior, these reported properties can enable Cu nanowires to act as sensors, which may be able to detect strain, cracks, and damage extents in concrete upon embedment into the geopolymer's hydrophilic matrix. As concrete deformation has been demonstrated to occur—and worsen—at particular places over periods of time, changes in the nanowires' electrical impedance are expected to correlate with changes in mechanical strain due to cyclic compression [58].

Past attention placed on Cu as a component of nanowire and as a target of pharmaceutical drug development suggests precedent for the scaffolding of Cu nanowires within cyclic peptide nanotubes. A proposed reaction scheme involves the sequestration of metal species, such as Cu^{2+} , Cu^+ , and Cu, inside cyclic peptide nanotubes. Through this method, Cu ions are likely to interact with molecules in the geopolymer concrete's aqueous activating solution [59, 60]. Based on our review of the literature, we highlight Eqs. (2-4) as pH-dependent reactions, involving water and the polar charged molecules, that may predominate as a consequence of Cu-based nanowire formation in this manner.



Empirical studies indicate insoluble $\text{Cu}(\text{OH})_2$ is a prominent copper form when NaOH is used as an alkaline activator at basic pH levels of 6.5 to 12 [61].

Cyclic peptide residues that stabilize interactions between Cu^{2+} and OH^- will contribute to $\text{Cu}(\text{OH})_2$ precipitation at pH values ranging from 10.9 to 11.6. Because this is the approximate pH span over which geopolymer concrete synthesis occurs, methods to convert $\text{Cu}(\text{OH})_2$ into a chemically useful form are necessary to develop Cu-based nanowires [62]. As confirmed by Zeng et al., a highly efficient way to reduce $\text{Cu}(\text{OH})_2$ into uncharged, metallic Cu via hydrazine has been well-characterized under extremely high pH and otherwise ambient reaction conditions [46]. Altogether, these mechanisms use peptide nanotubes as a cast for the production of polycrystalline Cu nanowires, which we propose can be separated from the surrounding hydrophobic protein core through enzyme-mediated degradation (Fig. 3) [52].

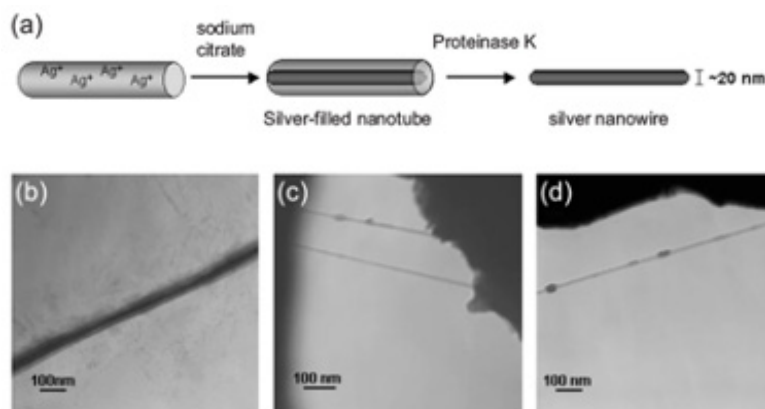


Figure 3: Casting of silver (Ag) nanowires within peptide nanotubes. Filling hollow, nanotubular interiors with metallic ions and proceeding to enzymatically degrade the peptide mold has been demonstrated to construct metallic nanowires. Adapted from Reches and Gazit (2003).

Because negatively charged amino acid side chains contribute to electrostatic repulsion between peptides, we anticipate potential challenges for nanotube formation. Studies have reported the dissociation of peptide-based nanotubes at basic pH. A 2003 study investigating the effects of histidine-rich peptides on Cu nanocrystals growth at variable pH found that higher pH levels corresponded to less nanoparticle formation [63]. While the spontaneous assembly of cyclic peptides may be disfavored at the alkaline pH needed for geopolymer production, chemical tools offer ways to bolster the feasibility

of nanotubular formation [64]. Several methods for generating and screening cyclic peptide libraries exist and can be utilized to understand the effects of pH dependence on nanotube assembly [65]. Furthermore, assessing the peptides' associated crystal structures can also help identify targets for site-directed mutagenesis, where negatively charged residues can be substituted with neutral or positively charged ones to prevent nanotube dissociation [66]. Beyond considering cyclic peptides as nanowire scaffolds, these proteinaceous molecules can be equipped with specialized properties to enhance the sustainable impacts provided to the cementitious material. Slight modifications in peptide identities may lead to the addition of proteins that immobilize heavy metals within geopolymer concrete, thus contributing to environmental remediation efforts. Other possible adjustments can yield water-absorbing concrete that has had utility in flood-prone areas or light-emitting concrete that reduces reliance on electricity [67].

Cyclic Peptide Application

While usage of the engineered peptides and nanowires in construction has not been widely considered, nanoscale biosynthetic innovations are gaining traction and suggest the wealth of research results that can be leveraged towards improving self-sensing materials [68]. A 2012 study revealed that a CNT/OPC composite generally showed higher detection accuracy than strain gauges when installed as pavement and monitored for voltage changes in response to vehicular stress [69]. Other work has similarly emphasized potential applications of sensors in concrete for traffic monitoring and road design [70]. However, few studies have investigated the implementation of nanotubular-based, piezoelectric sensors in cementitious materials involved in higher-level construction. Although scientific innovations have helped create more environmentally friendly building materials, these have been scarcely adopted and employed in mainstream home construction.

OPC-based concrete is used in the majority of new and old construction in the place of greener, geopolymer-based alternatives [71]. Poorly maintained and deteriorating structures, such

as homeless shelters, are thus vulnerable to the adverse impacts of OPC, whose high permeability disadvantages overall structural integrity and contributes to building corrosion [72]. A clear application for utilizing cyclic peptide nanotubes as a geopolymer cement additive appears in improving aged construction and design of buildings or renovations [73, 74]. The self-sensing ability of the material, stemming from nanotubular piezoelectricity, promises to reduce repair costs of buildings in the long-term by pinpointing damaged regions within the structure itself. The enhanced geopolymer concrete also lessens operational costs by detecting structural defects before they begin to seriously threaten building integrity. In the context of homeless shelter programs, this is a crucial consideration. Redistributing funds to support services to uphold the well-being of residents and assist them with reintegration is just one downstream, humanitarian effect of the innovative material [75].

Further Directions and Conclusion

Although many state-of-the-art reviews have underscored the favorable properties of geopolymer-based cementitious materials relative to those containing OPC, the civil engineering and building science spheres have not implemented geopolymer cement on a large, commercial scale. This trend may be explained by the lack of studies highlighting effective methods to promote the uniform dispersion of nanotubular constructs in cement matrices. When homogeneously incorporated, CNTs have been shown to improve stability and equip OPC with piezoelectric, strain-sensing characteristics, the latter of which can be applied towards "smarter" building materials [76]. Capitalizing on findings from studies that have shown the incompatibility of conventional superplasticizers with CNTs in geopolymer cement, this review prompts closer scientific attention on cyclic peptide nanotubes by highlighting their roles as both surfactants and nanowire scaffolds.

We propose a sample reaction scheme for the formation of Cu nanowires within cyclic peptide nanotubes to illustrate the potential uses of highly conductive metals in cement innovations. Furthermore, mere modifications in peptide

identities can lead to drastically altered cyclic peptide nanotube functions and customizable properties. While these attributes appear advantageous, more research into the influence of the micro-level environment on cyclic peptide nanotubes should be undertaken to ensure stable formation of the nanoparticles in response to pH changes. Although real-world applications of nanoscale-based, piezoelectric sensors are scarce, increasing research on cement may spur studies investigating their impacts on higher-order civil structures.

By pointing out the vulnerability of current and planned buildings due to OPC-based construction paradigms, this review underscores the benefits of geopolymers in modern-day building projects for its low environmental impact and potential for strain detection. With the development of usable construction innovations occurring at a relatively slow pace compared to the urgent nature of ecological and social stressors globally, alternative innovations and approaches are necessary to generate stronger, longer-lasting building materials. This review indicates that nanoscale engineering can offer immense support for the adoption of geopolymers in the industry. A myriad of sectors can benefit from geopolymers upon further refinement of and research into its technical attributes.

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