Current development of geopolymer cement with nanosilica and cellulose nanocrystals

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Abstract. The cement industry has contributed large amounts of CO₂ emissions and is responsible for the consumption of non-renewable natural resources. Geopolymer based cement has emerged as an environmentally friendly alternative to construction materials because it can be produced from industrial waste. Similar to ordinary portland cement, geopolymer cement can be strengthened with nanomaterials. This paper presents a review of nanosilica and cellulose nanocrystals in geopolymer cement. The addition of nanosilica can improve the properties of pozolana which is able to bind calcium-hydroxide so that the resistance to sulfate corrosion will also be better and nanosilica can also increase chemical reactions due to its surface area. Nano-sized cellulose-based particles can fill the smallest gaps in cement paste that cannot be treated by other micro or macro sized materials. This paper also presents an overview of the latest advances in the production of geopolymer cement that reinforced by nanosilica and cellulose nanocrystals as promising sustainable construction materials.

Keywords: geopolymer, nanosilica, cellulose nanocrystals, cement

1. Introduction

Geopolymer cement is a binder made without using Portland cement but using high silica (Si), and Alumina (Al) precursor reacted with alkaline solutions [1]. The advantages of geopolymer cement compared to Original Portland Cement (OPC) include high mechanical strength in the early and later age, stable under thermal and chemical conditions, strong adhesion on various surfaces, low permeability, low cost, etc [2][3]. The use of OPC has caused CO₂ emissions; thus, the development of geopolymer cement is necessary. The amount of research on geopolymer cement continues to grow, which shows the growing interest among researchers in this particular issue. It is worth to note that most of the references from 2010 to 2020 are focused on geopolymer cement. Figure 1 shows that the development of geopolymer cement continues to be carried out with various material modifications to produce high-strength concrete. Some of the development of geopolymer cement undertaken are the modification of carbon nanotubes [4] [5], nano-SiO₂ [6] [7], nano-Al₂O₃ [8] [9], nano-TiO₂ [9] [10], nano-Fe₂O₃ [11], nano-clay [12][13].
Figure 1. Overview research about geopolymer cement

The latest development and never been conducted is geopolymer cement modified with nanosilica and cellulose nanocrystals (CNCs). A schematic diagram of geopolymer cement with nanosilica and CNCs can be developed, as shown by Figure 2.

Figure 2. Schematic diagram of geopolymer cement with nanosilica and cellulose nanocrystals

2. Nanosilica in Composite Material

Nanosilica is the most widely used material in cement and concrete to improve performance due to its pozzolanic reaction and the influence of its pore-filling. Nanosilica has been developed as a cement composite that is strong, durable, sustainable and environmentally friendly. Nanosilica in cement paste was studied to determine the hydration process, microstructure changes and mechanical properties. The surface area of nanosilica particles influences the cement hydration process by accelerating the hydration and the binding processes of cement paste [14].

The compressive strength of cement paste containing 5% nanosilica was 64% higher in 1 day and 35% in 28 days than that of the control cement [15]. Utilization of 2% nanosilica increases the compressive strength from 53.2 MPa in the control specimen to 86.1 MPa in 90 days, and the addition of 10% microsilica and 2% nanosilica enhance the compressive strength to 92.1 MPa [16]. The addition of nanosilica results in an increased amount of C-S-H gel formed and can increase the compressive strength at the percentage of 5 to 10% nanosilica [17].

The purpose of adding nanosilica to the cement mixture is to increase durability because micro silica and nanosilica particles can fill the gaps between cement particles. The right composition will contribute to increased strength due to reduced capillarity. Moreover, the addition of nanosilica has significantly higher pozzolanic reactivity compared to silica fume. Thus, these two effects are necessary in developing
high-performance concrete [18][19]. Another benefit of using nanotechnology in cement is to improve the performance of cement paste, mortar and concrete by combining nanomaterials. Nanosilica (nano-SiO$_2$) is a good example of how nanoparticles can increase the compressive strength and flexural strength of concrete. Figure 3 shows the addition of silica fume can improve the performance of concrete. The addition of nanosilica and nanocellulose materials will enhance the concrete into nanoengineered concrete.

![Figure 3. Relationships between particle size and specific surface area in concrete material 18.](image)

The synthesis of nanosilica was realized with either a top-down or bottom-up approach. In the top-down approach, nanosilica synthesized by cutting the bulk material via different mechanical procedures to produce nano-sized structures, whereas the bottom-up approach is a process undertaken chemically. The synthesis of nanoparticles (top-down) with high energy ball milling works easily. The Ball milling is a grinding machine containing tiny rigid balls, in which the collision between the tiny rigid balls in a concealed container will generate localized high pressure. The machine can produce relatively fast nanoparticles. Based on the research, using ball milling at 600 rpm for 3 hours was able to create nanosilica up to 70-75 nm size [20]. Nanozeolite 74 nm size can be obtained by extracting rice husk ash smoothing rice husk ash and passing a 200 mesh sieve then calcined at 600°C for 2 hours, and put in ball milling for 10 hours [21].

### 3. The Effects of Cellulose in Composite Materials

Adding synthetic fibers (carbon, polymer fibers, etc.) to concrete, has been widely done to increase the strength of concrete, however, these fibers addition may result in weak concrete-matrix interface bond, low corrosion and alkali resistance, high cost and lower compressive and flexural strength [22]. Synthetic fibers are made by a heating process at very high-temperatures; therefore, they are not environmentally friendly. Unlike natural fibers, these fibers have good mechanical properties at a low cost.

The addition of rice husk and bamboo cellulosic fibers with a concentration of 2-16% led to an increase of flexural strength by 24.3%, and bulk density increased from 12.4 to 37.3% [23]. Wood cellulose reinforcement using a concentration from 0.05 to 0.5% showed an increase in the mechanical properties of concrete at a percentage of 0.15% CNCs by 90 MPa with a flexural strength of 25 MPa [24]. There are several problems related to the use of natural fibers in concrete matrices, namely lignin, hemicellulose, pectin and glucose degraded in alkaline solutions which cause low-strength concrete. Therefore, natural fibers with good mechanical strength must be carefully selected. The flexural strength of cement paste can be increased by the addition of cellulose nanocrystal (CNCs) [24]. Cellulose nanocrystals are produced by acid hydrolysis by removing amorphous cellulose regions and producing...
CNCs of 20-30%. Since CNCs are a good alternative fiber in concrete, physicochemical processes are needed to break hydrogen bonds. Table 1 shows several types of fibers with chemical treatment and flexural strength produced.

Table 1 Effect of fiber treatment on flexural strength from cement paste

| Composite                   | Fiber treatment | Fiber concentration (%) | Fiber length | Increased flexural strength (%) | Reference |
|-----------------------------|-----------------|-------------------------|-------------|---------------------------------|-----------|
| Hemp/Cement Paste           | Non-treated     | 16                      | 1-10 mm     | +40                             | [25]      |
| Cellulose 6 wt% NaOH AICl3 |                 |                         |             |                                 |           |
| Hemp/Lime paste             | Non-treated     | 10                      | 1-10 mm     | Control                         | [26]      |
| Cellulose 17%, pectin 14%, hemicelulose 14%, lignin 6% | NaOH 1.6M | | | +35 | |
| Cane/Cement Paste           | Non-treated     | 2                       | 10 mm       | +100                            | [27]      |
| H2SO4 Ca(OH)2 Pyrolysis     |                 |                         |             |                                 |           |
| Banana/Cement Paste         | Non-treated     | 2                       | 10 mm       | +3,2                            | [27]      |
| H2SO4 Ca(OH)2 Pyrolysis     |                 |                         |             |                                 |           |
| Cotton stalk                | NaOH            | 1%                      | 1 mm        | +10                             | [28]      |
| Cellulose 43,66%, hemicelulose 28%, lignin 23,92% | | | | |

Fiber addition has also been carried out in geopolymers by physicochemical treatment. In Table 2, it can be seen that the addition of fiber with a concentration of 1 to 3% lead to changes in compressive and flexural strength of geopolymers.

Table 2 Experiment related to the mechanical properties of geopolymers with various fiber variations

| Natural Fiber | Geopolymers type | Fiber Concentration (wt%) | Compressive Strength (MPa) | Flexural Strength (MPa) | Reference |
|---------------|-------------------|---------------------------|---------------------------|------------------------|-----------|
| Sisal         | Metakaolin        | 3                         | 6.9                       | 1.4                    | 2.8       | [29] |
| Pineapple leaf| Metakaolin        | 3                         | 6.9                       | 3.1                    | 1.4       | 2       | [29] |
| Sweet Sorghum | Fly Ash (Class F) | 2                         | 27.7                      | 22.9                   | 3.6       | 5       | [30] |
| Bamboo       | Metakaolin        | 5                         | 55.7                      | 29.7                   | 4.5       | 24.95   | [31] |
| Cotton       | Fly Ash (Class F) | 1                         | 24.78                     | 28.42                  | 5.55      | 5.85    | [32] |
| Sisal        | Fly Ash (Class F) | 1                         | 24.78                     | 2516                   | 5.55      | 5.90    | [32] |
| Raffia       | Fly Ash (Class F) | 1                         | 24.78                     | 13.66                  | 5.55      | 3.05    | [32] |
| Coconut fiber| Fly Ash (Class F) | 1                         | 24.78                     | 31.36                  | 5.55      | 5.25    | [32] |

4. Cellulose Nanocrystals (CNCs)

Cellulose with the general formula \((C_6H_{10}O_5)_n\) is an organic compound with a linear chain of many linked D-glucose units. Cellulose is the main ingredient in forming CNCs. It is a white solid, insoluble in water and other solvents. CNCs are a type of renewable nanomaterial that is generally produced by the acid hydrolysis of cellulose fibers in their original form. CNCs are usually in the shape of short rods which are several hundred nanometers long and less than 100 nm wide [33].

The characteristics of cellulose chains are linear with high crystallinity and high intramolecular hydrogen bonds. The chemical structure is in the form of unbranched chains. The cellulose extraction
process chemically removes the lignin, pectin, wax, and glucose. The cellulose content is > 95%, and a small amount of hemicellulose is <5% [34]. Cellulose nanocrystals have a crystal structure that is isolated from rigid rod-like cellulose on the nanometer scale.

Figure 4 shows cellulose can be extracted from plants and formed into nanocrystalline. The first process to do is reducing plant particles through a physical process obtain lumen fiber. Alkalization process generates the lumen fiber into pulp (pulp). In general, wood pulp is made of large amounts of cellulose macrofibrils. The structure of the cellulose macrofibrils wall consists of tight bundles of cellulose microfibrils. Microfibrils contain lots of cellulose. Cellulose is coated with hemicellulose to form an open network filled with lignin. The process of alkalization and acid hydrolysis can remove the amorphous part of the cellulose chain by not removing its crystal part.

![Cellulose structure scheme](image)

**Figure 4.** Cellulose structure scheme

Cellulose in crystalline form benefits composite materials, namely:
1. Increasing the bonding between particles due to its adhesive property, the OH groups bonded to cellulose gives polar properties and will bind Si$^{2+}$
2. Having better strength
3. Being able to form a network
4. Having the capacity to form a strong binding

The use of nanomaterials in construction materials serves as a filler as well as a binding material that can increase the Interfacial Transition Zone (ITZ) between cement paste and other material.

**Synthesis Process**

There are many methods for obtaining CNCs, including alkalization, bleaching, acid hydrolysis, mechanical treatment and enzymatic treatment. Changing cellulose to nanocrystalline cellulose by alkalization and acid hydrolysis has more advantages compared to other methods. These methods could reduce energy consumption and produce a rigid nanocrystalline form with a high degree of crystallinity [35]. The types of acid that are often used in the hydrolysis process are HCl and H$_2$SO$_4$. These acids are used because it is effective in hydrolyzing glucose bonds in cellulose.
5. Conclusion

This review study focuses on the development of nanosilica and CNCs in geopolymer cement. This study shows that the modification of nanosilica and CNCs in geopolymer cement has a high potential in increasing property index, compressive and flexural strength. Most of the authors concluded that the modification of nanosilica and cellulose into cement enhances the mechanical properties of hardened cement. Besides, nanosilica particles promote cement hydration which in turn decreases the setting time and increases the rate of compressive strength development. Based on the review made, future studies should address the following issues;

1. The optimum nanosilica content to be added into cement needs to be determined, depending on the type and average size of nanomaterials. There is no specific formula for determining the optimum value of nanosilica and CNCs; all process must undergone laboratory experiments.
2. Research on the influence of nanoparticles to modify the properties of geopolymer cement, combining two or more types of nanoparticles, needs to be further investigated.
3. Modifications of nanosilica and CNCs need to be further investigated in the resistance to aggressive environments.
4. To date, many of the geopolymer cement researches and publications are findings of the laboratory experiments. Thus, more field trials are suggested for further development of nanotechnology in the construction industry.
5. This study shows that nanosilica and CNCs are very useful but can also cause potential problems if not used properly. Therefore, the results of further research are needed to clarify the health effects associated with nanosilica, CNCs, and other nanomaterials.

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