Supplementary cementitious materials in concrete and associated structural and environmental benefits: A review

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Abstract: Supplementary cementitious materials (SCMs) are the materials which can replace certain amount of cement in concrete. In this way, they not only enhance the properties of concrete but also assist in reducing several environment-related issues. This review article presents the various SCMs that have proven beneficial in replacing cement in concrete. In this regard, the various SCMs discussed are fly ash (FA), silica fume (SF), metakaolin (MK), limestone filler, granulated blast furnace slag (GBFS) and nanoparticles (NPs). Further, among the various NPs, nano-TiO₂ (NT) and its addition in concrete and benefits were explained briefly. This article also highlights the NT-based photocatalytic degradation of the various contaminants of the environmental media i.e., water and air. Subsequently, the emphasis was also given on the discussion of its practical usage and then the various structures, comprising NT, built all around the world were also presented. This article concluded that more comprehensive review articles need to be published to encourage the developing nations also adopt the NT-based concrete structures. In this way, impacts associated with the various air pollution sources i.e., stubble burning, vehicular pollution etc., can be mitigated.

Keywords: Supplementary cementitious materials, nano-TiO₂, air pollution, sustainable development goals, concrete.

1. Introduction

In the race of development, most of the countries of the world are investing significant amount of their profits in the innovation of new construction materials. Among the various construction materials available around the world, cement is the most prominent one. Cement is history's important invention
that has assisted in the betterment of mankind in several ways such as, minimizing the impact of natural hazards, breakthrough development of transportation, infrastructure development in the form of health-care, academic institutes. In order to fulfill the timely needs, since, its first invention and use, cement has gone through several modifications. Earlier form of cement mainly consisted of gypsum and limestone, however, later other materials such as, sand and gravel also started getting added. In this way, present form of mortar or concrete is invented which set the basis for the building of large structures [1–3].

The major constituents of concrete are, fine aggregates, coarse aggregates, cement and water. Further, as per the required characteristics of the final structure, the proportion of these constituents can be varied. Moreover, with the various technological interventions, certain mineral admixtures can be added along with the conventional constituents of the concrete which may improve certain properties of the final structure. Another issue associated with the generation of cement are their non-renewability and generation of large amount of greenhouse gases i.e., CO\(_2\). The average global warming potential of cement production is 981 kg CO\(_2\) eq. Therefore, continuing the infrastructural development while depending on the cement, as a major construction material, may stall the progress made in case of the various United Nation’s sustainable development goals (SDGs) i.e., SDG 3, SDG 8, SDG 12 and SDG 13 (HCWH 2020). The condition may even get worse in developing nations such as, India, where the current obsolescence rate of the construction materials is comparatively higher [4].

Therefore, scientific community, comprising inter-disciplinary researchers, has identified that certain amount of cement can be replaced with supplementary cementitious materials (SCMs) which, not only reduce the usage of cement but also add to the properties of the final products. Some of the proposed SCMs are sludge, limestone powder, silica fume, slag, nano-TiO\(_2\) (NT) etc. and they have proven promising in improving the hardened as well as durability properties of concrete (Panesar and Zhang 2020). Addition of NT in the concrete may also provide self-cleaning properties to the buildings and in this way issue of ambient air pollution can be tackled. However, there is still an ambiguity existing among the civil engineers w.r.t. the replacement of cement with NT. Therefore, this paper will provide a comprehensive review of the various international studies conducted to estimate the various impacts of replacing the cement with NT in different types of concrete.

2. **Supplementary cementitious materials**

Supplementary cementitious materials (SCMs) are replacements of cement, in the production of concrete, that have different chemical compositions and characteristics. Owing to variations in the chemical structure and properties [5,6], these SCMs cause significant changes in the properties of final product i.e.,
Concrete. Replacement of SCMs may improve mechanical, durability and fresh properties (...). Some of the SCMs that have proven promising in improving the various characteristics and usability of concrete are, as follows:

a. Limestone filler (LF);
b. Granulated blast furnace slag (GBFS);
c. Silica fume (SF);
d. Fly ash (FA);
e. Metakaolin (MK);
f. Nano-particles (NPs)

The various SCMs, enlisted above, vary from each other in their physical structure and chemical composition. The average chemical compositions of these SCMs, adopted from different studies, are compared in Table 1. The chemical composition of the NPs is not included in this comparison because its chemical composition may vary from one type of NP to another. Further explanation about the NPs will be made in the coming sections. Table 1 is followed by Table 2 which compares the physical properties of the SCMs and then each SCMs is explained one by one.
Table 1. Chemical composition of different SCMs

|                | Limestone filler | Fly ash | GBFS     | Silica fume | Metakaolin |
|----------------|------------------|---------|----------|-------------|------------|
| CaO            | >41.4            | 0.6 - 18.2 | 27 – 43.1 | 0 – 0.9     | 0 – 3.1    |
| SiO₂           | 0.3-14.38        | 31 - 60.2 | 32.9 – 43.1 | >81         | 51.1- 73.2 |
| Al₂O₃          | 0.31-2.23        | 14.1 - 34.3 | 6.7 – 17.12 | 0 – 1.23    | 18.3 – 47.3 |
| Fe₂O₃          | 0.4-1.5          | 2.1 - 22.6 | 0.25 – 2.1 | 0 – 1.9     | 0.6 – 1.3  |
| MgO            | 0.4-2.9          | 0 – 4.9  | 0 – 16.5  | 0 – 4.1     | 0.18 – 0.32 |
| K₂O            | 0.04-0.75        | 0.2 – 7.1 | 0.29 – 0.41 | 0 – 1.1    | 0.19 – 1.23 |
| Na₂O           | 0.02-0.05        | 0.2 – 7.2 | 0 – 1.1   | 0 – 1.7     | 0.12 – 0.25 |
| SO₃            | 0.11-0.4         | 0 – 4.5  | 1.4 – 3.4  | 0 – 1.2     | 0 – 0.02   |
| LoI            | 33.5-41.3        | 0.19 – 30.3 | 0.11 – 1.4 | 0 – 2.4     | 0.9 – 2.2  |
Table 2. Physical properties of different SCMs

|                  | Limestone filler | Fly ash | GBFS    | Silica fume         | Metakaolin |
|------------------|------------------|---------|---------|---------------------|------------|
| Surface area     | 414-1098         | 298-498 | 341-688 | 12,898-29,987       | -          |
| Mean size        | 3.2 – 12.55      | 6 – 72.1 | 13.7 – 23.11 | 0.11 – 0.28 | 1.32 - 19 |
| Shape            | Angular          | Spherical | Angular | Spherical          | Angular    |
| Specific gravity | 2.4-2.8          | 1.12-2.87 | 2.78 – 2.89 | 2.18 – 2.25 | 2.17 – 2.56 |

2.1. Fly ash

On combustion of coal at approximately temperature of 1600°C, small particles of ash are generated which is called as fly ash (FA) [7,8]. These ash particles which can also be delineated as waste materials of coal combustion process, are generally extracted during the air purification process i.e., water sprinkling. In this way, FA mixes with water which is then evaporated and FA is extracted. Therefore, it can be implied that the characteristics of the FA will depend on the several factors such as, constituents of coal, pulverization of coal, availability of O₂ during combustion, collection, handling and storage (ACI 232).

2.2. Granulated blast furnace slag

Granulated blast furnace slag (GBFS) is an another SCMs that is a waste product of one of the industrial processes. During the iron manufacturing process, iron is heated at 1500°C and then quenched using high pressure water jet [9,10]. In this way, GBFS is generated which is dried and grinded. As the GBFS is generated during iron manufacturing, its strength is also higher however, its properties also depend on the efficiency of grinding process.

2.3. Silica fume

Silica fume (SF) is a by-product of several industrial processes wherever, the elements of silicon or its alloys are used and combusted. For an example, when quartz is passed through electric arc furnace, with temperature of ~2000°C, it gets oxidized and silicon dioxide is generated. This oxidized form of silicon is then condensed at low temperature which converts it into solid form which is known as the SF [11,12]. The particle size of the SFs depends on the efficiency of the combustion processes and hence, its size may vary from 0.1 – 100 mm. Due to low particle size, the SFs may improve the properties of concrete by filling the pores and cracks. They may also act as a nucleation site for performing the hydration and pozzolanic processes.

2.4. Metakaolin (MK)
As the name suggests, the metakaolin (MK) is generated during the combustion of kaolinitic clay minerals at high temperature i.e., ~900°C. In this way, the MK majorly consists of alumino-silicates however, its composition is highly dependent on the source of kaolin used during the process of its generation [13].

2.5. Limestone filler

Limestone (LS) is a sedimentary rock that is mainly composed of carbonates of calcium. Two main types of carbonate of calcium that are found in LS are, calcite and aragonite. As being a naturally occurring SCM and being available in abundance, the use of LS, as a SCM, is most popular among the civil engineers. In case of other SCMs, i.e., FA and MK, their availability is highly dependent on the respective industrial processes being taking place in the region. Therefore, civil engineers could not rely wholeheartedly, on FA and MK, as a replacement of cement. Moreover, several countries have also reduced their dependence on coal, as a source of energy. In this way, the generation of FA may vary substantially with respect to the policies and regulations of any nation. Consequently, their popularity is less as compared to the LS [14,15].

2.6. Nanoparticles

Nanoparticles (NPs) are the particles with size ranging from 0.5 nm to 100 nm and hence, their size is comparatively smaller than other SCMs. Due to their smaller size, the NPs can reach deeper into the cracks and pores and improve the porosity of concrete (Sobolev and Gutierrez 2005). Similarly, these NPs may also act nuclei for other constituents of concrete and assist in hydration-based densification of the final structures. Further, on the basis of the particles' size and specific properties, there are various types of the NPs and these are, nano-silica, nano-CaCO$_3$, nano-Fe$_2$O$_3$, nano-TiO$_2$ etc (Shi et al. 2015). Among these types of the NPs, the latter-most SCM is of utmost interest as, while improving the various characteristics of the concrete they also provide them with self-cleaning and oxidizing properties. In this way, in context of the sustainable development, use of nano-TiO$_2$ (NT) in civil engineering structures is crucial to be studied further [16–18].

3. Photocatalysis and nano-TiO$_2$

Photocatalysis is an oxidation process in which oxidation reaction takes place at the surface of a catalyst. These catalysts generate free electrons and holes in the presence of sunlight and water which further acts as a trigger to start the oxidation reaction, as shown in Figure 1.
Applications of NT-based photocatalysis have vastly been studied by several researchers in case of degradation of different water pollutants such as, xenobiotic compounds, organic pollutants etc. Currently, its applications have also been reported in microbial decontamination of health-care units. Subsequently, scientific community is now inclined towards exploring the uses of the NT-based photocatalysis in purification of air. In this way, it can be proposed that incorporation of NT as a construction material may provide a solution of several air pollution-related issues such as, smog, vehicular pollution, biomass burning etc.

### 4. Air pollution and NT-based photocatalysis

The major gaseous pollutants that are of major concern include carbon dioxide, carbon monoxide, Sulphur dioxide, nitrogen monoxide, nitrogen dioxide, lead and volatile organic compounds. Various studies have tried to estimate the degradation of these pollutants using NT-incorporated concrete and some of their findings are compiled in Table 3.

**Table 3. NT-based photo-catalysis of different air pollutants**

| S.No. | Pollutant(s)                        | Reaction involved                                                                 |
|-------|-------------------------------------|----------------------------------------------------------------------------------|
| 1     | Carbon monoxide                     | \( CO + O^* \rightarrow CO_2 \)                                                 |
| 2     | Nitrogen dioxide and nitrous oxide  | \( NO_2 + OH^* \rightarrow NO_3^- + H^+ \)                                        |
|       |                                     | \( NO + 2OH^* \rightarrow NO_2 + H_2O \)                                        |
| 3     | Sulphur dioxide                     | \( SO_2 + OH^* \rightarrow HOSO_2 \)                                             |
|       |                                     | \( HOSO_2 + O^* \rightarrow OH^* + SO_3 \)                                       |
| 4     | Lead                                | \( R^* + Pb(II) \rightarrow R_{OX} + Pb(I) \)                                   |
| 5     | Volatile organic compounds          | Multiple reactions involved                                                     |
From Table 3, it is evident that addition of NT is concrete can help in reducing the ambient air pollution and therefore, various NT-comprising civil engineering structure were built in different parts of the world. A list of some of the structures, with NT, built around the world, is given in Table 4.

Table 4. Various international civil engineering structures with NT

| S.No. | City                  | Country  | Structure type   | % reduction in NO\textsubscript{x} |
|-------|-----------------------|----------|------------------|-------------------------------------|
| 1     | Antwerp               | Belgium  | Parking lanes    | 22                                  |
| 2     | Via Morandi - Segrate | Italy    | Urban road       | 55                                  |
| 3     | Calusco d'Adda, Bergamo | Italy    | Industrial road  | 42                                  |
| 4     | Porpora street, Milan | Italy    | Tunnel-road      | 25                                  |
| 5     | Borgo Palazzo, Bergamo | Italy    | Urban road       | 45                                  |
| 6     | Rue Jean, BleuZen, Vanves | France  | Urban road       | 24                                  |
| 7     | Vanves               | France   | Urban road       | 45                                  |
| 8     | St-Denis              | France   | Urban road       | 26                                  |

As seen in Table 4, the NT-based structures can efficiently degrade the NO\textsubscript{x} levels in ambient air, which is emitted mainly by the vehicles. Further, most of the NT-based structures are built in developed nations and developing nations are yet lagging behind in using them for improving their environmental conditions. Therefore, in India, where traffic jams are frequent and where, open burning is a prominent practice adopted to get rid of the crop stubble, the need of innovative techniques for purification of ambient air is a crucial issue. Hence, it can be speculated that the deteriorating atmospheric conditions of India, demands an innovative approach for decontaminating the environment.
5. Conclusions

From the presented literature-review, it can be illustrated that the replacement of cement with the SCMs may prove beneficial in several ways such as, decontamination of pollutants in different environmental media i.e., water and air, reducing the carbon footprints associated with production of cement, reduction in generation of construction and demolition waste, and enhanced properties of the civil engineering structures. Owing to the photocatalytic activity of NT, its applicability has been observed in several building structures around the world. However, major NT-based structures were reported in developed nations and developing nations are yet to adopt such changes. Therefore, more review articles, presenting the comprehensive insights of NT-comprising concrete and its applicability in decontamination of air pollutants, are still required to be published. In this way, developing nations may also be inspired to incorporate NT-based structure in their infrastructural development.

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