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Wioleta ISKRA-KOZAK[1]
Janusz KONKOL[2]

CONCRETE NANOMODIFICATION WITH SELECTED NANOPARTICLES

The aim of the paper is to present the state of the art and technology in the field of concrete nanomodification. This new approach to the design and manufacture of materials by modifying their microstructure at the nanometric level is increasingly used also in the case of concrete. Owing to C-S-H phase changes concrete porosity and permeability can be reduced, which increases concrete durability. The improvement of concrete properties and the possibility of the manufacture of new building materials are the most important benefits of the impact of nanotechnology on construction. The paper describes the most commonly used nanoparticles in concrete technology, including nano-SiO_2, nano-TiO_2, nano-Fe_2O_3, Fe_3O_4.

Keywords: nanotechnology, nanomaterials, nanoconrete, nanopowders, nanopowders

1. Introduction

Nanotechnology is a new research area in building materials engineering. It is based mainly on physics, chemistry, engineering and biology. Owing to its intensive development the early 21st century is called the beginning of the era of nanotechnology. Nanometre (originating from the Greek word *nanos* meaning dwarf) is a length unit equal to one billionth of the metre 10^{-9}. Nanotechnology covers activities on elements smaller than 100 nm [1,2]. Nanotechnology is targeted at the use of properties of materials to obtain their improved physical, chemical and biological properties. One of the fields applying the achievements of this modern technology is construction. The use of nanomaterials and nanomodification has become highly popular in recent years. New materials (carbon nanotubes, among others) have been invented, however, also traditional materials such as concrete are being modified [3]. The strength and durability of concrete structures should be significantly improved compared with the traditional materials. Nanocement has a larger specific surface area. The very active

[1] Corresponding author: Wioleta Iskra-Kozak, Politechnika Rzeszowska, Katedra Inżynierii Materiałowej i Technologii Budownictwa, al. Powstańców Warszawy 12 35-959 Rzeszów, tel. 178651701, w_iskra@prz.edu.pl
[2] Janusz Konkol, Politechnika Rzeszowska, Katedra Inżynierii Materiałowej i Technologii Budownictwa, al. Powstańców Warszawy 12 35-959 Rzeszów, tel. 178651701, jk7@prz.edu.pl

nanoparticles are distributed evenly, which accelerates the cement hydration process with no detrimental impact on the material's final strength. Moreover, nanoparticles fill in the pores, which increases intermolecular forces, which, consequently, improves the cement microstructure and cement paste – aggregate interaction in concrete [4,5].

2. Mechanism of nanoparticles operation

Cement paste is composed of small grains of hydrated calcium silicate gel and large crystals of hydrated products of hydration. Between these there are nanopores and capillary pores which are the potential space for nanoparticles improving the properties of cement paste to deposit. However, high surface energy makes nanoparticles readily combine into aggregates, which hinders their uniform dispersion (especially in the case of significant amounts). In such conditions the formation of nanoparticles aggregates leads to the formation of voids, which has a negative impact on the mechanical properties of cement paste [6,7]. The mechanism responsible for the improvement of microstructure and strength of cement composites can be explained as follows. When a small number of nanoparticles is evenly dispersed in the cement paste, the cement hydration products begin to deposit on the nanaoparticles due to their high surface energy. During the hydration reaction they form conglomerates with nanoparticles as nuclei. Owing to their high reactivity the nanoparticles located in the cement paste will additionally support and accelerate cement hydration. Nanoparticles' uniform dispersion results in a suitable microstructure of the cement paste with uniformly distributed conglomerate [6,8].

3. Nanomodification of concrete

A large number of papers on the application of materials with nanoparticles in concrete and concrete modification has been published. Nanoparticles operate as heterogeneous hydrate nuclei accelerating the hydration reaction, as nanoreinforcement and as a nanofiller consolidating concrete microstructure, which reduces its porosity.

3.1. Modification of concrete with nano-SiO_2

From among materials in nanotechnology silicon dioxide (SiO_2) is by far the most popular (Fig. 1). Its wide application results from its general availability and specific properties of great utility for both industry and scientific research. It is stable in water and in elevated temperatures. The chemically inert silica reacts only with boiling concentrated aqueous solutions of KOH and NaOH, fused to K_2CO_3 and Na_2CO_3 and hydrogen fluoride or its aqueous solutions [9]. The atoms of nanoparticles can be arranged both at random (amorphous structure) or orderly (crystalline structure). They may be found in another material, for instance in metal alloys. In nanotechnologic applications silica is

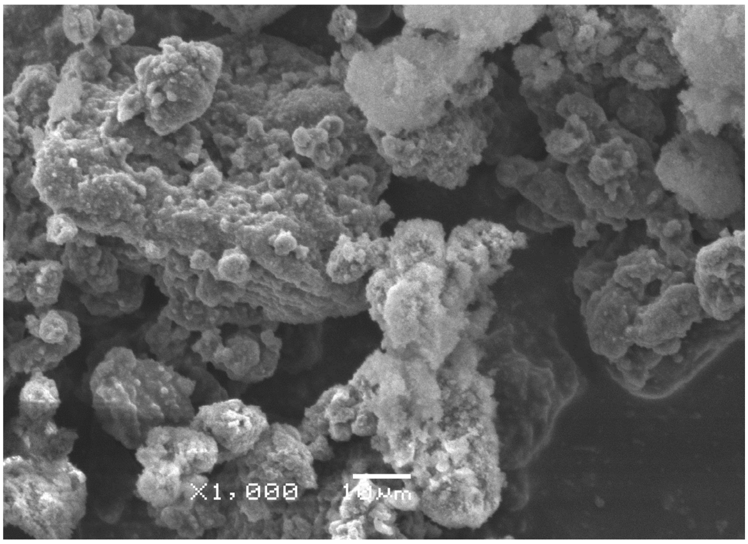

Fig. 1. SEM of SiO_2 nanoparticles

used for the production of various types of silica and hybrid nanostructures. The diameter of the most frequently obtained silica nanoparticles ranges from 5 to 1000 nm, and their specific surface area from 545 to 2.73 m^2/g. Silica nanoparticles are mainly found as precipitated amorphous silica, gels, sols, colloids and flame silica [4, 10–12].

The use of SiO_2 nanoparticles reduces porosity and permeability, which improves concrete durability. The properties fresh concrete to a large extent depend on the particle-size distribution (PSD*)* [14]. The effect of SiO_2 nanoparticles on the properties of concrete during the hydration reaction is shown in figure 2.

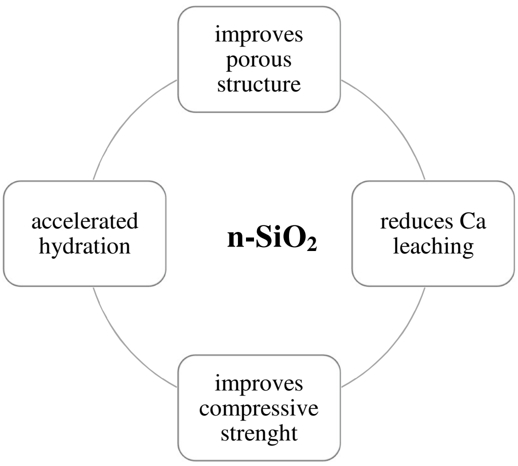

Fig. 2. Effect of nano-SiO_2[15] on concrete properties during hydration reaction

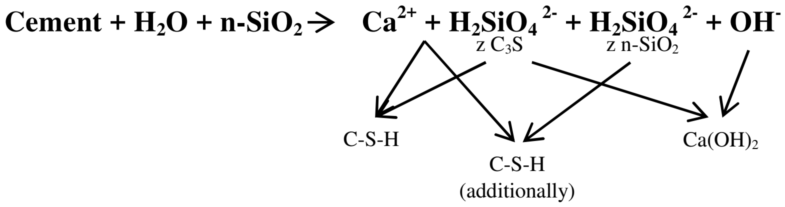

Fig. 3. Processes in cement paste after the introduction of nanosilica [15]

Micro- and nanoparticles of silica fill in the voids between cement grains. Nanosilica has much higher pozzolanic reactivity than silica fume. When cząstki nano-SiO_2 particles are added to cement grains, H_2SiO_4 in reaction with Ca^{2+} ions produces an additional amount of hydrated calcium silicates (Fig. 3). By filling in the pores, nanoparticles increase the intermolecular forces, which, consequently, improves cement microstructure and cement paste – aggregate interaction in concrete.

The use of nanosilica primarily improves concrete compressive strength. The admixture of nanosilica instead of silica fume to cement makes the paste denser and the hydration reaction faster. The investigations have proved that the hydration of cement with a high fly ash or slag content is faster with the admixture of only 1% nanosilica. On the other hand, However, the use of 2% shortens the beginning and end of the bonding on the one hand, but, on the other hand, increases concrete compressive strength after three to seven day curing. In combination with nanoferrite, nanosilica improves also concrete compressive, bending and tensile strengths, as well as modulus of elasticity [12,15–16].

3.2. Modification of concrete with nano-TiO_2

Titanium oxide IV (TiO_2) was discovered by William Gregor in Cornwall in 1791. It is composed of a titanium atom and two atoms of oxygen. It is an odourless, white and grey solid body. In nature TiO_2 is found in three different crystalline structures: as rutile, anatase and brookite. On industrial scale TiO_2 is produced from titanium ores or ilmenite ($FeTiO_3$). TiO_2 is commonly known as titanium white or titania [17, 18].

Titanium nanooxide is mainly used in the production of photocatalytic cement Owing to its photocatalytic properties, under the influence of UV radiation and in precipitation water environment on the surface of concrete, TiO_2 accelerates decomposition of hazardous substances. Cement with titanium oxide nanocrystalline content also has superhydrophilic properties, which means that a surface containing this binding agent in its composition has self-cleaning properties. An important aspect is that when used as a catalyst, titanium oxide is not worn during the processes, consequently, air purification phenomenon is continuously renewable and long-term. One of the best known objects built with the use of TiO_2 nanoparticles is the Jubilee Church in Rome (Fig.4) [10,17].

Fig. 4. Jubilee Church in Rome [13]

Titanium oxide nanoparticles are used in self-compacting concrete. The results of research done by Nazari and Riahi confirm that the admixture of TiO_2 nanoparticles improves the compressive strength of self-compacting concrete, as a result of accelerated hydration of cement and reduces concrete porosity [18–19].

3.3. Modification of concrete with nano-Fe_3O_4 and nano-Fe_2O_3

The most promising nanomaterials include nano-Fe_3O_4 (nanomagnetite) (Fig. 5). The research on the application of iron oxides (Fe_2O_3, hematite in particular) in cement composite materials has proved that these materials favourably affect their mechanical properties and microstructure. They improve compressive and bending strengths and reduce their overall porosity. Moreover, the use of nano-Fe_2O_3 very favourably affects the properties of self-compacting concrete [11]. Researchers confirm that the use of iron oxides in the dispersed phase can be important in the future production of high performance concrete. The research on the effect of Fe_3O_4 on the protective properties of concrete has indicated satisfactory results. However, due to high surface energy of iron oxides, these particles tend to agglomerate. When a large number of these is used, they may lead to the reduction of concrete strength [15]. Some researchers claim that the use of nano-Fe_3O_4 in small amounts (up to 0.3% by weight in relation to cement) may improve the mechanical properties of composites and pores structure. Some other researchers maintain that the admixture of 1.5% nano-Fe_3O_4 by weight improves concrete compressive strength, reduces chlorides penetration and water absorption in the cement matrix. Also, the research on the impact of iron oxides on the properties of cement paste in elevated temperatures has indicated promising results [20].

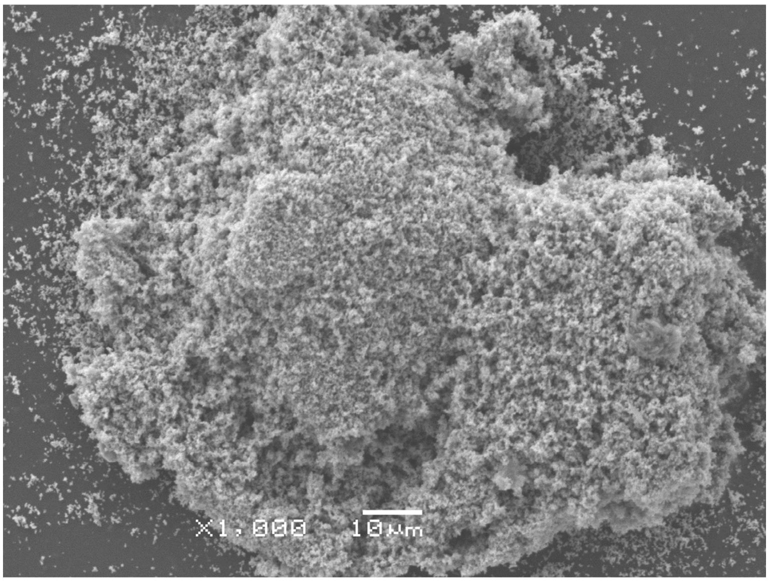

Fig. 5. SEM of nano-Fe_3O_4

Research has shown that Fe_3O_4 [20]:

- does not significantly affect fresh mixture consistency provided the nanoparticles content does not exceed 5% of cement by weight,
- operates as a filler of the microstructure by reducing the overall porosity, thus increasing the composite's density,
- does not affect the cement hydration rate,
- the use of too large amount of Fe_3O_4 nanoparticles results in local agglomerations, which, in consequence, has an unfavourable effect on the mechanical properties of cement composite materials,
- the admixture of 3% by weight of Fe_3O_4 most favourably affects the properties of cement composite materials.

4. Conclusions

In spite of being by far one of the newest areas of science, nanotechnology is becoming more and more widely spread. The majority of phenomena used to be investigated at the macroscopic level, but the progress in science has enabled nanoresearch. In construction industry nanotechnology is used on a large scale. The materials that are nanomodified include a commonly known material, i.e. concrete. Owing to its wide applicability it is appreciated not only for its mechanical properties, but also as a cutting-edge architectonic material. An enormous emphasis is placed on improving its strength and physical parameters. The admixture of nanoSiO_2, nanoFe_3O_4 and nanoFe_2O_3 greatly improves concrete compressive strength. NanoTiO_2. enjoys a wide range of applications. It is used for bacteria destruction in the environment of low intensity UV radiation, odour elimination from closed spaces and in self-cleaning surfaces. Compared with traditional concrete, nanoconcrete is considered as more durable, of higher strength and with smoother surface. The admixture of nanoparticles to cement paste, mortar or concrete improves their functional characteristics and technological parameters. It should be remembered that research in this field is only beginning to unfold [4,6].

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