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The range values for the design parameters of nano-engineered concrete components. Characteristics, properties, amounts and effects on the concrete behaviour.

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Abstract. The nanometric scale researches results can be found, in present, in every industry domains, due to the effects of the new products, obtained on the basis of this researches. In the concrete industry, the research goal at this level is to obtain, finally, a material with new features, whose structural behavior to be considerably better than of the current one. Basically, it aims to achieve, using nanotechnologies, a new structural material for constructions, starting from the current concrete advantages (good compressive strength, durability, etc.), eliminating the disadvantages (low tensile resistance, cracks, etc.), and controlling, in the same time, the costs. Thus, in this paper are presented the required parameters in order to obtain this kind of material, by highlighting the nanocomponents characteristics and the quantities that are used to achieve the expected quality requirements. The real time influence of these nanocomponents on the quality of the studied material can be observed using a dedicated software, specially developed for this purpose.

Introduction

Concrete, the most used construction material for infrastructure and buildings, is a compound of granular materials, having particles with sizes that cover wide intervals, from ~0.3μm to ~30mm. Both the initial fresh concrete and final hardened concrete properties depend by the mixture grading [1]. In the first case, the distribution of the particle size governs the flow properties and workability of the fresh concrete. In the second case, properties as strength and durability depend on the mix grading and the final particles packing. The actual development of the concrete researches is focused on the micro and nano-levels in order to control the mechanisms that affect the final characteristics that are used for structural design in constructions domain. Another aproach in the concrete development at nano-scale refers to the cement production, in order to develope low temperature sintering of clinker minerals in mechano-chemical reactors. These researches are related, also, to the actual concerns regarding the environment protection.

The grain sizes limits of the nano-particles, considered for nano-engineered concretes, are in the range between 1 to 100nm. In general, small quantities (~1%) of nano-sized materials are sufficient to improve the behaviour of nano-composites [17]. A method to increase the properties of the hardened concrete is the use of particles with sizes below 0.3μm.

Materials with particles sizes in the nano-metric range, proper to be used in concrete mixture in order to improve its properties, are the followings [2]: nano-silica, nano-fly-ash, nano-TiO_2, nano-Fe_2O_3, nano-Al_2O_3, carbon nano-tubes.

Micro and Nano-silica in concrete mixture

In order to improve the characteristics or to reduce the cement quantity in concrete mixtures, silica fines are used. Micro-silica is a very fine pozzolanic material, composed of amorphous silica, obtained as a byproduct of the silicon or ferro silicon alloys (Fe_5Si_2) industry, that can be used in a variety of cementitious based products, such as concrete and mortars.

Nano-silica has, also, a high potential to be used in the concrete mixture:

- as cement substitute,
- to reduce the concrete permeability,
- to improve the resistance to corrosion.

Depending by the synthesis method used (sol-gel process [3], vaporization and condensation [2], biological [4], olivine dissolution [5]), the characteristics of nano-silica vary (Table 1).

Table 1. Production methods and characteristics of nano-silica.

Method	Phase	Diameter size [nm]	Specific surface area [m^2/g]
sol-gell process	concentrated dispersion (20-40%)	-	-
vaporization and condensation of silica	very fine powder	~150	~15…25
biological	biological waste material (~22% SiO_2)	<1000	-
olivine dissolution	precipitated silica with an extreme fineness in an agglomerate form	6…30	-

The effects of nano-silica in the concrete mixture appear at two levels: chemical and physical. In the first case, silica reacts with calcium hydroxide and result more C-S-H gel, and in the second case, silica particles, 100 times smaller than cement particles, fill the voids in the cement paste, increasing its density [6]. The main aspects regarding the micro and nano-silica effects in the concrete mixture refer to the following facts:

- four mass parts of cement could be replaced by one part of micro-silica, maintaining the same characteristics of concrete [7,8],
- the optimization of the particles sizes distribution leads to the increasing of the concrete strengths (Table 2) [17] and durability,

Table 2. The effect on compressive strengths of cements mortars due to the presence of nano-SiO_2. Adapted from [17]

Cement type	Compressive strength [MPa]	
	7-days	28-days
normal cement	17.60 (reference)	28.90 (reference)
silica fume (15%)	18.90 (+7.38%)	31.80 (+10.03%)
nano-SiO_2 (3%)	18.60 (+5.68%)	32.90 (+13.84%)
nano-SiO_2 (5%)	21.30 (+21.02%)	33.80 (+16.95%)
nano-SiO_2 (10%)	21.30 (+21.02%)	36.40 (+25.95%)

- the accelerating effect in cement paste - more rapid hydration of cement in the presence of nano-silica due to its chemical reactivity resulting from their important surface activity [9],
- the tendency for supplementary water adsortion – the mixture needs more water in order to maintain a constant workability [10] ,
- a stronger tendency to agglomerate – to prevent this, dispersing additive (superplasticizers) must be used,
- a smaller water permeability of hardened concrete – for the same workability, using 10 to 20nm nano-silica particles with a specific surface area of 160m^2/g [11],

- nano-silica increase the interfacial transition zone between aggregates and cement paste due to the reaction with the crystals of $Ca(OH)_2$ and fills the voids in the C-S-H gel structure [7] increasing the concrete durability,
- the nano-silica reduces the calcium leaching rate of cement pastes [14],
- in order to obtain these effects the nano-silica, its concentration must be limited to a maximum amount of ~5…10% by weight of cement [12, 13]. High concentration of nano-silica leads to the increasing of the cracking potential risk due to autogenous shrinkage.
- the addition of 0.25% of nano-silica increases the flexural strength of cement mortars with 25% [19].

Nano-fly-ash in concrete mixture

The result of the burning process of harder, older anthracite and bituminous coal generallly produces class F fly-ash with a less than 20% lime (CaO) content. The usual proportions of compounds varies in the following limits: SiO_2 – 20...60%, Al_2O_3 – 5...35%, Fe_2O_3 – 10...40%, CaO – 1...12%. This fly-ash with pozzolanic characteristics (due to the content of silica and alumina) mixed with a cementing agent (ex. Portland cement) in the presence of water produces cementitious compounds.

The utilization of fly-ash in concrete is based on their unique properties: fineness, specific surface area, particle shape, that increases the concrete hardness and freezethaw resistance.

In order to reach the nano-size dimensions of the fly-ash particles, the high energy ball mill can be used. The high impact collisions that reduce the microcrystalline materials down to nanocrystalline structure, don't affect chemically the composition of the fly-ash [15].

As result of replacing a certain amount of coarse aggregate (10%, 20% and 30%) with nano-fly-ash in the concrete mixture, two important aspects can be observed (Table 3): both the workability of fresh concrete and the compressive strength of hardened concrete increase [16].

Table 3. Effects on concrete workability and compressive strength when different percents of the coarse aggregates are replaced with nano-fly-ash in the concrete mixture.

Concrete Mixture	Slump test [mm]				Compressive strength on cube, 28-days [MPa]			
	0%	10%	20%	30%	0%	10%	20%	30%
Mix. I	25	48	51	58	25	38	40	41
Mix. II	28	52	58	66	30	40	45	47
Mix. III	30	56	64	72	44	53	55	56
Mix. IV	34	58	72	79	49	57	59	60

Nano-TiO_2 in concrete

The concretes containing nano-TiO_2 degrade the pollutants from vehicles and industrial emissions (NOx, carbon monoxide, chlorophenols, aldehydes) due to a photocatalytic mechanism [20]. The carbonation aging affects the catalytic efficiency [23]. In addition to these self-cleaning characteristics, nano-TiO_2 particles present the following effects in the concrete mixture:

- accelerate the early-age hydration of Portland Cement [21],
- improve concrete compressive and flexural strengths [22],
- enhance the concrete abrasion resistance [24].

Nano-Fe_2O_3 in concrete

The concretes containing nano-Fe_2O_3 present self-sensing capabilities. In the cement mortar volume that contains nano-Fe_2O_3 the electric resistance varies by the applied loads. The main effects of this nano-particles on concretes are the followings:

- due to self-sensing capabilities is possible to monitor, in real time, the structural response of the buildings to the applied loads,
- improve the concrete compressive strength (Table 4) [17],
- enhance the concrete flexural strength [25]

Table 4. The effect on compressive strengths of cements mortars due to the presence of nano-Fe_2O_3. Adapted from [17]

Cement type	Compressive strength [MPa]	
	7-days	28-days
normal cement	17.60 (reference)	28.90 (reference)
nano-Fe_2O_3 (3%)	21.40 (+21.59%)	36.40 (+25.95%)
nano-Fe_2O_3 (5%)	20.60 (+17.04%)	33.10 (+14.53%)
nano-Fe_2O_3 (10%)	21.10 (+19.88%)	30.00 (+3.80%)

Nano-Al_2O_3 in concrete

The main effects of nano-alumina particles on the concrete behaviour are related to:

- the increasing of its modulus of elasticity up to 143% at a dosage of 5% [26],
- small variations of the concrete compressive strength.

Nano-cement particles

In order to increase the cement behaviour by decreasing the size of its particles down to nano-scaled dimensions, several approaches are possible [27, 28]:

- top-down method that consists in a high energy milling of Portland cement particles,
- bottom-up method that is a chemical synthesis of nano-particles,
- the nano-binder method that involves an inter-grinding of cement with dry mineral additives in the ball mill [29],
- the use as admixtures to cement of nano-clay particles (~1nm size), obtained by exfoliating the base structure of clays that is formed by crystalline layers of aluminium phyllosilicates [30]. In this method, natural clays (non-calcined) are intended to be used and, in order to obtain a reduction in the water amount, the addition of organic cations replace sodium and calcium in the interlayer [31]. Furthermore, polyvinyl alcohol is added to link the exfoliated clay particles and to form chains [32].

The main effects of the use of cement with nanosized particles compared with the conventional Portland cement refer to the following aspects:

- faster setting times,
- increasing in early compressive strength,
- as result of mechano-chemical modification when high volume of blast furnace was used, the compressive strength increase up to 65% [29],
- the chains of linked clay nano-particles improve the post-failure properties of the cement,

Nano-reinforcements – carbon nano-tubes

The main disavantage of cement-based materials is their small tensile strength, about ten times smaller than compressive strength. The development of micro-cracks converts to bigger cracks, leading to fracture. An aproach to increase the tensile strength and to reduce the cracks propagation is the use of nano-reinforcements in the cement-based materials.

An important type of nano-sized materials, proper to be used in the cement and concrete mixture are carbon nano-tubes. In what follow, theirs main characteristics are presented:

- highly structured graphene ring-based materials,
- great tensile strength (GPa order),
- great modulus of elasticity (TPa order) [33],
- uniques properties as electomagnetic field shielding and self-sensing capabilities [34],
- three main types: as single-wall or multi-wall nano-tubes, or as nano-fibers,
- very large aspect ratio, greater than 1000 (the proportional relationship between their lengths and their diameters) [35],
- very high surface areas,
- carbon nano-fibers present exposed edge planes on their surfaces that have the potential to interact physical or chemical,
- one main disadvantage results from the difficulty to assure a proper dispersion into cement paste, both for carbon nano-tubes and nano-fibers, due to their hydrophobicity and strong self-attraction [18],
- good interaction between carbon nano-tubes and nano-fibers and cement phases [34],
- a dispersing agent (ex. gum Arabic) is required to be used in order to obtain a proper dispersion of carbon nano-tubes,
- the absence of dispersing agent in cement mixture containing carbon nano-tubes (ex. multi-wall nano-tubes 0.006-0.042 wt.%) leads to a the decreasing of mechanical properties, in comparison with the standard cement mixtures, without nano-tubes [36],
- the bonding between multi-wall nano-tubes and cement matrix is weak under tension [36],
- carbon nano-tubes increase the quantity of high stifness C-S-H, thus the cement paste matrix is reinforced and its porosity is decreased [37],
- the surface treatment of carbon nano-tubes with nitric acid in Portland cement pastes facilitates the dispersion [38],
- the pre-dispersion in acetone (0.5 wt.% carbon nano-tubes), facilitates also the dispersion [39],
- the addition of silica fume, for carbon nano-tubes content in the range 0.002-2 wt.%, improve theirs dispersion in cement paste [40],
- the pre-treatement of carbon nano-tubes with nitric and sulfuric acid leads to an increase up to 19% in compressive strength and up to 25% of flexural strength of cement mortars [41],
- using a grown in-situ method to incorporate carbon nano-tubes on the cement particles, a composite cement was obtained with a content of carbon nano-tubes up to 20%. In this case the change in the flexibility strength was insignifiant [42].

Principles and parameters of a dedicated computational research tool

In the last decade, the progress of nano-technologies and nano-materials fields as result of a multi-disciplinary researches have produced many results and valuable observations, reported and published in the scientific literature wold-wide. The main problem is to find a method to use the current knowledges in a way that can produce practical applications for a specific domain.

In order to develop a proper tool to synthetize the available data as result of current researches in the nano-technologies domain of concrete and to be able to provide a behaviour description of nano-sized concretes, we work to a software apllication based on the following facts (Figure 1):

- the selection of the nano-materials that can be used in the concrete mixture to increase its properties,
- the main parameters taked into account refer both to fresh and hardened concrete,
- the cement at nano-scale is considered both in the case when its content include partially or totally particles with nano-sized dimensions,
- at the start, the software will include the current stage results concerning each concrete components, as derives from the significant scientific literature,
- the software is intended to be an „web-free-access” one, that means that every researcher that will contribute to the platform will be able to access freely and to use the obtained results from the web-platform,

- in the first stage, the software will be able to predict the properties of a virtual concrete based on its micro- and nano-components of its mixture, and on the closest available informations from the databases.
- in the second stage, the concrete behaviour prediction take into account specific algorithms developed also on the known specific informations from the databases.
- the possibility to modify and actualize the databases and algorithms each time when a relevant information appears, will lead to a more and more accurate scientific tool,
- the researchers from many fields will be able to interact with this tool, to improve it and to use valuable informations from it.

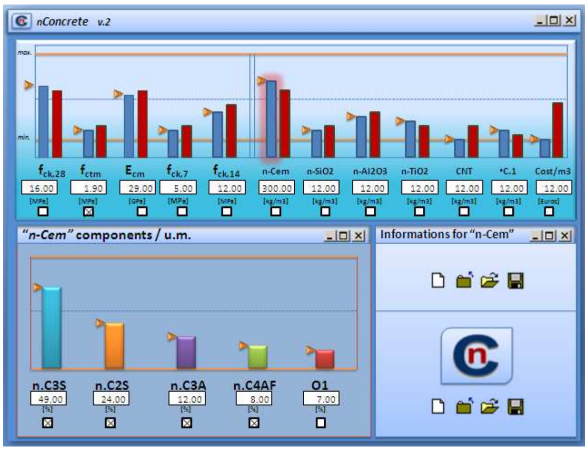

Figure 1. *nConcrete* software interface

Conclusions

The multitude of available data in the concrete nano-techology domain research are difficult to be properly used without a powerful specific scientific tool. In this paper was revealed that many researches lead to results that sometimes can't be explained totally based on current nano-scale knowledge, or it is difficult to predict an expected characteristic of concrete when the nano-materials are used. For example, the expectation regarding the tensile strength of the concrete when carbon nano-tubes are used, it was not yet fulfilled.

The present work represent the base to a better understanding of the nano-sized materials effects in the concrete mixture. A great advantage of this software concept is the logical structure and the „self-learning" ability, all this presented in a simple but precise manner.

Another advantage is the „web-free-acces" posibility, that offers the oportunity to bring togheter researchers from the concrete domain, materials science, chemistry, physics and other researches domains with interest in the nano-materials field.

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