Role of Nanotechnology for Development of Sustainable Concrete

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Abstract **- The present paper addresses several topics in regard to the sustainable design and use of concrete and the role of nanotechnology. First, major features concerning the sustainable aspects of the material concrete are summarized. Then the major constituent, from an environmental point of view, cement is discussed in detail, particularly the hydration and application of slag cement. The intelligent combining of mineral oxides, which are found in clinker, slag, fly ashes etc., is designated as mineral oxide engineering. It results among others in environmentally friendly binders, recipes for soil stabilization (new building products), and impermeable/durable concretes. Subsequently, the mix design of concrete is treated, whereby distinction is made between self-compacting concrete and earth-moist concrete. By combining the particle sizes of all components, so including the powders (cement, fillers), optimum mixes in regard to workability/compatibility and hardened state properties are obtained. This so-called particle size engineering results in concretes that meet all technical requirements, but that also make optimum use of the cement it is containing. This paper concludes with summarizing the opportunities and challenges involved with the introduction of both approaches, viz. mineral oxide engineering and particle size engineering, in the construction industry**.

Index Terms - cement, concrete, mineral oxide engineering, particle size engineering, Nanotechnology

I. INTRODUCTION

This paper is an illustration of how Nanotechnology has changed and will continue to change our vision, expectations and abilities to control the material world. These developments will definitely affect construction and also the field of construction materials. The major achievements in this domain include: the ability to observe the structure at its atomic level and measure the strength and hardness of micro and nano-scopic phases of composite materials; discovery of a highly ordered crystal nanostructure of "amorphous" C-S-H gel; development of paints and finishing materials with self-cleaning properties, discoloration resistance, anti-graffiti protection, high scratch and wear resistance; self-cleaning materials based on photo catalyst technology; nanometer thin coatings protecting carbon steel against corrosion and enhancing thermal insulation of window glass; smart stress-sensing composites; and others.

2. NOVELTY OF TECHNOLOGY

Among new nano-engineered polymers are highly efficient super plasticizers for concrete and high strength fibers with exceptional energy absorbing capacity. Nano particles, such as silicon dioxide, were found to be a very effective additive to polymers and also concrete, a development recently realized in high performance and self-compacting concrete with improved workability and strength. Portland cement, one of the largest commodities consumed by mankind, is obviously the product with great - but at the same time – not completely explored potential. Better understanding and precise engineering of an extremely complex structure of cement based materials at the nanolevel will apparently result in a new generation of concrete, stronger and more durable, with desired stress-strain behavior and possibly possessing the range of newly introduced "smart" properties such as electrical conductivity, temperature-, moisture-, stress sensing abilities. At the same time this new concrete should be sustainable, cost and energy effective – in essence exhibiting the qualities modern society demands. Nano-binders or nanoengineered cement based materials with nanosized cementitious component or other nanosized particles are the next ground-breaking development.

2.1. *The awareness of life-time Performance and costs*

It is known that structures made of well designed and well cast concrete are cheap and durable. Other – more green building materials, such as wood, may score more favorably from an energy, CO2 emissions and renewable point of view. But considering the entire building lifecycle, a more balanced picture of its sustainability will arise. For instance: Though cement and concrete are produced from non-renewable mineral resources, these are some of the world's most abundant ones. Concrete is relatively maintenance-free. Possibly poisonous coatings, which may leach to the environment, need not be applied, nor do their regular removal (using hazardous and dangerous materials) and reapplication. Concrete constructions possess a long lifetime. So they remain relatively long in the building life cycle, which can even be lengthened by building adaptable and/or transportable and/or easily dismantled objects. When this functional reuse of structure or structural parts is not possible anymore, then after demolition and crushing, the broken material may enter another building life cycle. Applied in (non-)residential structures, the thermal capacity of concrete contributes to a reduction of the in-use heating/cooling energy and an increase of energy efficiency and thermal comfort. Cement, lime and gypsum are useful binders to render contaminated sludge/soil and industrial and nuclear wastes less harmful to the environment. This enables safe storage or landfill; in some case even a useful building material is obtained. The second and fourth points also support its sustainability and low life-cycle costs. The last aspect illustrates that the most energy intensive component of concrete, the cement, in relatively low dosages (10%), may turn waste into a building material, i.e. bringing waste materials (back) in the building life cycle.

2.2. New opportunities for innovations in building materials

The engineering and environmental properties of concrete still deserve improvements and innovation. Examples are: The substitution of primary raw materials (limestone, fillers, and aggregates) by byproducts. For instance slag and fly ash can substitute clinker, stone sludge waste can substitute limestone filler, and crushed concrete can substitute primary stones.· The cement content can be lowered while improving at the same time the fresh and hardened properties. New mix design methods based on particle packing theory have become available recently. In this context it is however a pity that for a part of the concrete industry the building regulations limit the possible and desired innovation (though standard EN 206-1clause 5.2.5.3 contains the *Equal Concrete Performance Concept*). A most significant example is the definition of “cement” in the mix, and the required minimum cement content. It is an anomaly that slag and fly ashes that replace cement clinker (as is the case in CEM II, III and V) are counted as “cement”, whereas when a concrete producer adds the same by products, they are not or only partly counted as “cement” (not in kg/m3 nor in the w/c), unless an expensive and cumbersome concrete attest route is followed. A second anomaly is the cement content as such. It is possible to make better concrete with 200 kg/m3 of higher quality cement than with 300 kg/m3 of lower quality cement. As will be shown further on, with an intelligent mix design, e.g. by deploying nanoparticles, it is even possible to make the same good concrete with 200 kg/m3 of low to medium quality cement. In this regard, the property *cement efficiency* will be introduced, defined as compressive strength (MPa) per unit of cement content in a concrete mix (kg/m3). These present regulations have a few drawbacks. Obviously, they often result in too high cement contents, so the concrete is too expensive and the environmental image of concrete is – unnecessarily – negatively

Influenced. Furthermore, the regulations hamper the innovation and competitiveness of the concrete industry, and finally, in turn, also the cement industry. Imagine that steel producers would prescribe the content of steel in a car, then lighter and safer cars as we know them now would not be possible. Or imagine that the aluminum industry would prescribe the content of their material in planes. In this context, it is interesting to note that the development of fiber metal laminates (ARALL, GLARE), a combination of aluminum and fibers Layers/epoxy composite, ultimately leads to higher aluminum sales for it enabled the construction of the Airbus A380. The cement and concrete industry can learn from this the following: introduce standards that are more performance driven and that enable innovation. Even if it seems that –in the short term- it will result in “less yearly tons”, in the long run it will lead to more applications and to products with more added value (e.g. nanocement), a better image, and hence, to a higher sales revenue. In this context it is interesting to note that some concrete production sectors, e.g. of earth moist concrete products, enjoy already more freedom in mix design. In this industry one can observe more dynamics in regard to development of new materials and production processes. In what follows three research topics will be addressed that are motivated by the considerations given above:

· Cement hydration;

· Self-Compacting Concrete;

· Earth-moist concrete.

In order to reach the set goals, the leitmotiv of all researches (the so-called “research approach”) comprises mineral oxide engineering and particle size engineering. Next these topics are discussed in more detail. Furthermore, though the main focus lies on cement, also other calcium oxide binders are subject of research, such as lime and calcium sulphates (gypsum, anhydrite).

3. CEMENT HYDRATION

Knowledge of cement hydration is necessary for the development of cement recipes (“mineral oxide engineering”) and assessing the macroscopic properties of concrete. A major technical and environmental improvement has been the introduction of ground granulated blast-furnace slag and of powder coal fly ash in cement. One can also see the trend to introduce these pozzolanic by products, from a more diverse range of Sources and sometime in the nano-size range, in concrete mixes. Key parameters upon the application are their reactivity, the prevailing reactions and the microstructure that develops. The first step in this hydration research concerned the reactions and numerical simulation of ordinary portland cement (OPC). Based on the water retention data provided by Powers and Brownyard [2], the hydration reactions of the five major clinker phases (C3S, C2S, C3A, C4AF and CŠ)3 and their hydration products were quantified [3-6]. For the numerical simulation of the hydration reactions and the pore water composition, a 3-D simulation model (CEMHYD3D) from NIST was adopted and extended [7-8]. The next step in the research is the inclusion of slag in the hydration model [9].

3.1. Theoretical Model for Slag-Blended Cement Hydration

Recently, reaction model for blended cement containing various amounts of slag is established based on stoichiometric calculations, which are valid for alkali activated slag as well [10-11]. The model correlates the compositions of the anhydrate slag-blended cement, i.e. the mineral compositions of the slag and Portland cement clinker, and their blending proportions, with the quantities and compositions of the hydration products. Mutual influence between the hydration of the reactants (slag and calcium silicates in clinker) is investigated. The most prominent features of the interaction include the product equilibrium, i.e. the C-S-H from the clinker and slag hydrations has the same composition, and the amount of CH entering the slag reaction. The reaction equation of slag together with those of calcium silicates is written as:

n C S + n C S + C S A + nt H ®

n*A H

C3S 3 C2S 2 n*C nS

(1)

AH 4 y

c

CH

pC

(nC3S + nC2S)CC/SSHx + nSCC/SSAA/SHx + (n H -
n

)CH + n C AH

in which n is the number of moles of the respective substances, np CH is the amount of CH produced by calcium silicates hydration and nc CH is that entering slag reaction, x and yare the water contents in C-S-H and C4AH13, depending on the hydration states. The 3 Cement chemistry notation is used for mineral oxides: S = SiO2, C = CaO, A = Al2O3, F = Fe2O3, Š= SO3. amount of CH entering slag reaction is related with a factor p to the total amount of CH produced by the clinker hydration as:

pC

* H

C3S C2S S,sl C

*

C sl , S pC

H

c

CH n

(1)(1.2y 0.2y) (1.8y y)

(1.8y y)

n p n ×

- l + + gl -

gl -

= × =

(2)

It was found with the reaction model that blending slag with portland cement clearly lowers the C/S ratio in C-S-H and increases the A/S ratio. Furthermore, the A content in slag was first combined with M to form the hydrotalcite and with Š to form the ettringite. The remaining A then enters C-S-H to substitute for S. The theoretical model is validated with measurements in a series of experiments investigating slag-blended cements with various ingredients. The predicted Composition of the main hydration product, C-S-H is compared with the measured values in experiments, and good agreement is observed (Fig. 1). The microstructure development of the hydrating slag cement paste is also simulated with the theoretical model. The volume fractions of products in the paste after one year hydration with different slag proportions are presented in Fig. 2. C-S-H can be seen to be the dominant phase in the paste in volume for all slag proportions. Its fraction is approximately constant, about 40 percent of the paste. The volume fraction of ettringite (AFt) is approximately constant as well. A remarkable reduction of the CH fraction is observed with increasing slag proportions.

0

20

40

60

80

100

0 25 50 75 100

Slag proportion (mass%)

Volume fraction (%)

Pore
Slag
CH
HG
AFt
Monoc
AH
HT
C-S-H
Slag proportion (mass%)
Volume fraction (%)
Cap. Pore
H
Slag proportion (mass%)
Volume fraction (%)
1. Predicted and measured C/S ratio in
C-S-H versus slag proportions
In blended cement *(experimental data from*
[12],
Ratio of the slag/clinker hydration degrees is
0.7, w/b = 0.4)
0.8
1
1.2
1.4
1.6
1.8
2
0 20 40 60 80 100
Slag proportion (mass%)
C/S ratio in C-S-H
Prediction
Measurement
2. Volume fraction of products in
hydrating slag cement paste vs. slag
proportions
(w/b = 0.4, assuming all clinker and 70
Percent of slag has reacted)

4. CONCRETE WITH NANOPARTICLES

Mechanical properties of cement based materials with nano-SiO2; TiO2 and Fe2O3 were recently studied. Experimental results demonstrated an increase in compressive and flexural strength of mortars containing nano-particles. Based on the available data, the beneficial action of the nanoparticles on the microstructure and performance of cement based materials can be explained by the following factors:

- Well-dispersed nano-particles increase the viscosity of the liquid phase helping to suspend the cement grains and aggregates, improving the segregation resistance and workability of the system;
- Nano-particles fill the voids between cement grains, resulting in the immobilization of "free" water ("filler" effect);
- Well-dispersed nano-particles act as centers of crystallization of cement hydrates, therefore accelerating the hydration;
- Nano-particles favor the formation of small sized crystals (such as Ca(OH)2 and AFm) and small-sized uniform clusters of C-S-H;
- Nano-SiO2 participates in the pozzolanic reactions, resulting in the consumption of Ca(OH)2 and formation of extra C-S-H;
- Nano-particles improve the structure of the aggregates' contact zone, resulting in a better bond between aggregates and cement paste;
- Crack arrest and interlocking effects between the slip planes provided by nanoparticles improve the toughness, shear, tensile and flexural strength of cement based materials. Compressive strength of concrete with Gaia [1]

The application of Gaia, super plasticizer containing nano-SiO2 particles, at a dosage of 1.3% provides nearly two-fold increase in concrete compressive strength at the age of 7 and 28 days. The early strength of the concrete with Gaia was 68.2 MPa, which is approximately three times higher than that of reference concrete. The 28-day compressive strength of the concrete made with Gaia had demonstrated the dependence on W/C.

5. EXPECTED DEVELOPMENTS

Vast progress in concrete science is to be expected in coming years by the adaptation of new knowledge generated by a quickly growing field of nanotechnology. The development of the following concrete-related nanoproducts can be anticipated:

- Catalysts for the low-temperature synthesis of clinker and accelerated hydration of conventional cements;
- Grinding aids for superfine grinding and mechano-chemical activation of cements;
- Binders reinforced with nano-particles, nano-rods, nano-tubes (including SWNTs), nano-dampers, nano-nets, or nano-springs;
- Binders with enhanced/nano-engineered internal bond between the hydration products;
- Binders modified by nano-sized polymer particles, their emulsions or polymeric nanofilms;

- Bio-materials (including those imitating the structure and behavior of mollusk shells);
- Cement based composites reinforced with new fibers containing nano-tubes, as well as with fibers covered by nano-layers (to enhance the bond, corrosion resistance, or introducing the new properties, like electrical conductivity etc.);
- Next generation of super plasticizers for "total workability control" and supreme water reduction;
- Cement based materials with supreme tensile and flexural strength, ductility and toughness;
- Binders with controlled internal moisture supply to avoid/reduce micro-cracking;
- Cement based materials with engineered nano- and micro- structures exhibiting supreme durability;
- Eco-binders modified by nanoparticles and produced with substantially reduced volume of portland cement component (down to 10- 15%) or binders based on the alternative systems (MgO, phosphate, geopolymers, gypsum);
- Self-healing materials and repair technologies utilizing nano-tubes and chemical admixtures;
- Materials with self-cleaning/air-purifying features based on photo catalyst technology;
- Materials with controlled electrical conductivity, deformative properties, nonshrinking and low thermal expansion;
- Smart materials, such as temperature-, moisture-, stress- sensing or responding materials.

6. EMERGING RESEARCH

Incorporation of nano-tubes into the cement matrix would result in a ductile and energy absorbing concrete. The performance of such concrete can be further enhanced by the addition of polymers and nano-structured materials, such as nano-rods, nano-dampers, nano-nets, nanosprings or nano-engineered fibers. Nano-binder can be proposed as a logical extension of the two concepts: Densified System with Ultra Fine Particles (DSP) and Modified Multi- Component Binder (MMCB) extended to the nano-level. In these systems the densification of binder is achieved with the help of ultra-fine particles: silica fume (SF) dispersed with superplasticizer (SP) in DSP and finely ground mineral additives (FGMA) and SF modified by SP in MMCB; these particles fill the gaps between cement grains. In these systems portland cement component is used at its "standard" dispersion to provide the integrity of composition. In contrast to DSP and MMCB, the nano-binder can be designed with a nano dispersed cement component applied to fill the gaps between the particles of mineral additives (including FGMA). In nano-binder, the mineral additives (optionally, finely ground), acting as the main component, would provide the structural stability of the system and the micro- or nanosized cementitious component (which can also contain the nano-sized particles other than portland cement) would act as a glue to bind less reactive particles of mineral additives together. Such nano-sized cementitous component can be obtained by the colloidal milling of a conventional (or especially sintered/high C2S) portland cement clinker (the top-down approach) or by the self-assembly using mechanochemically induced topo-chemical reactions (the bottom-up approach). Development of nanobinders can lead to more than 50% reduction of the cement consumption, capable to offset the demands for future development and, at the same time, combat global warming. In addition to nano-binders, the mechanochemistry and nano-catalysts could change the face of modern cement and concrete industry by the great reduction of clinkering temperature and even realizing the possibility of cold sintering of clinker minerals in mechano-chemical reactors.

7. CONCLUSION

Incorporation of nano-tubes into the cement matrix would result in a ductile and energy absorbing concrete. The performance of such concrete can be further enhanced by the addition of polymers and nano-structured materials, such as nano-rods, nano dampers, nano-nets, nanosprings or nano-engineered fibers. Nano-binder can be proposed as a logical extension of the two concepts: Densified System with Ultra Fine Particles (DSP) and Modified Multi- Component Binder (MMCB) extended to the nano-level. In these systems the densification of binder is achieved with the help of ultra-fine particles: silica fume (SF) dispersed with super plasticizer (SP) in DSP and finely ground mineral additives (FGMA) and SF modified by SP in MMCB; these particles fill the gaps between cement grains. In these systems Portland cement component is used at its "standard" dispersion to provide the integrity of composition. In contrast to DSP and MMCB, the nano-binder can be designed with a nano- dispersed cement component applied to fill the gaps between the particles of mineral additives (including FGMA). Based on *mineral oxide engineering*, slag reactivity and hydration can be simulated, allowing the optimum substitution of clinker by granulated slag. The model also permits the development of new binders/additions, such as shrinkage-compensating cement. These additions add to the size stability and to the tightness (durability) of concrete. Another result is recipes that speed up the ripening process of dredging sludge, and that render highly contaminated dredging sludge into an applicable building material4 [26]. Furthermore, the 3-D simulation of the prevailing cement packing and subsequent chemical reactions has proven to be a useful design tool. The results show that by combining coarser and finer (nano-) cements, the cement efficiency can be improved, i.e. this offers opportunities for increasing the added value of cement. From this study it also appears that the water/powder ratio (w/p, whereby powders are defined as all particles in the mix < 125 mm) is an important design parameter. The w/p is perhaps a better parameter for assessing the mechanical and physical properties of concrete than the conventional w/c. In this respect it could also be recommended to use the w/p as reference for the maximum water content of a concrete mix, or alternatively, to simply maximize the water content as such, e.g. 150 l/m3, as is also the case already with the air content in concrete (commonly maximized to 30 l/m3). Summarizing, the recent "functional demand" approach, as well as the combined particle size engineering and mineral oxide engineering presented here, enable a cost effective and more sustainable development of civil and residential concrete structures. Applied in a smart way, using advanced mix design tools, nanoparticles can play an important role in this development.

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