THE ROLE OF NANOTECHNOLOGY FOR THE 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/compactability 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.

Keywords: cement, concrete, mineral oxide engineering, particle size engineering, nanotechnology

1. INTRODUCTION

In recent decades, the construction sector has faced many changes. One of these changes is the shift in the role of national government from one-sided practices in which the government was solely responsible for strategic and long-term spatial planning to a multi-actor and multi-level arena.

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One outcome related to such change was a rearrangement of the balance between public and private responsibilities. This has led to new procurement routes and contracts such as Private Finance Initiative (PFI) and Public Private Partnerships (PPP), as well as to a more performance-oriented client (both public and private). At the same time, construction firms changed their strategic focus from cost efficiency to adding value for money for the client, resulting in new contract forms such as Design and Construct (D&C), Build, Operate and Transfer (BOT) and variants of these. So far, the governments of most European countries have their own restrictive specifications for the use of building materials.

A positive development, associated with the aforementioned procurement shift, is that all members of the E.U. are developing a CE[1] mark for the building industry. The idea behind this CE mark is that trading across the borders will be facilitated. Within the building industry this implies that buildings and infrastructure facilities will more be judged on functional demands and less on product specifications, the so-called "defined performance design". This creates competition and hence an enormous demand for innovation by the construction industry. This positive attitude towards innovations will work as a catalyst for the development and marketing of new type of production processes and products. Important consequences of all the afore-mentioned incentives are:

- the awareness of life-time performance and costs of materials and structures, including aspects such as durability and sustainability;
- the offered new opportunities for innovations in building materials and their production processes, including the possibilities offered e.g. by nanotechnology.

In the following, these points will be discussed in more detail for cement-based materials, most importantly concrete, as they are by far the mostly produced man-made materials[2].

1.1. 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. Recently, also the aspect "sustainability" has been recognized as being

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[1] European Community conformity marking

[2] World cement production in 2004: 2.1 billion tons, of which almost 50% in China [1]

important. Other – more green building materials, such as wood, may score more favourably from an energy, CO_2 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 their regular removal (using hazardous and dangerous materials) and re-application.
- 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 re-use 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.

1.2. 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, aggregates) by by-products. 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 206-1 clause 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 slags 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/m^3 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/m^3 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/m^3 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/m^3).

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 aluminium industry would prescribe the content of their material in planes. In this context, it is interesting to note that the development of fibre metal laminates (ARALL, GLARE), a combination of aluminium and a fibres layers/epoxy composite, ultimately leads to higher aluminium 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).

2. 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 (C_3S, C_2S, C_3A, C_4AF and $C\check{S}$)[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].

2.1. 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 unhydrated 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:

$$\begin{aligned} & n_{C_3S}C_3S + n_{C_2S}C_2S + C_{n_C^*}S_{n_S}A_{n_A^*} + n_H^t H \rightarrow \\ & \qquad (n_{C_3S} + n_{C_2S})C_{C/S}SH_x + n_S C_{C/S}SA_{A/S}H_x + (n_{CH}^p - n_{CH}^c)CH + n_{AH}C_4AH_y \end{aligned} \tag{1}$$

in which n is the number of moles of the respective substances, $n^p{}_{CH}$ is the amount of CH produced by calcium silicates hydration and $n^c{}_{CH}$ is that entering slag reaction, x and y are the water contents in C-S-H and C_4AH_{13}, depending on the hydration states. The

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[3] Cement chemistry notation is used for mineral oxides: S = SiO_2, C = CaO, A = Al_2O_3, F = Fe_2O_3, Š= SO_3.

amount of CH entering slag reaction is related with a factor p to the total amount of CH produced by the clinker hydration as:

$$n^{c}_{CH} = p \cdot n^{p}_{CH} = \frac{\gamma\lambda(1.8y_{S,sl} - y^{*}_{C})}{(1-\lambda)(1.2y_{C_3S} + 0.2y_{C_2S}) + \gamma\lambda(1.8y_{S,sl} - y^{*}_{C})} \cdot n^{p}_{CH} \qquad (2)$$

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.

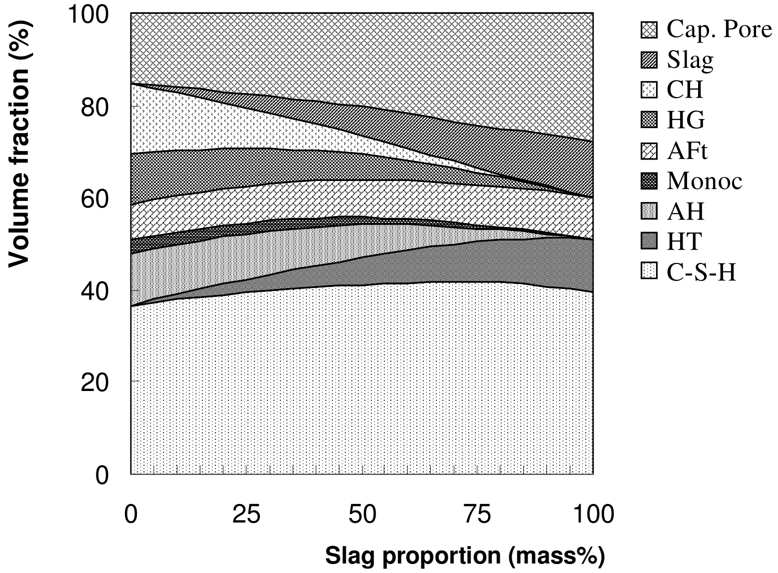

Fig. 1. Predicted and measured C/S ratio in C-S-H versus slag proportions in blended cement *(experimental data from [12], ratio of the slag/clinker hydration degrees is 0.7, w/b = 0.4)*

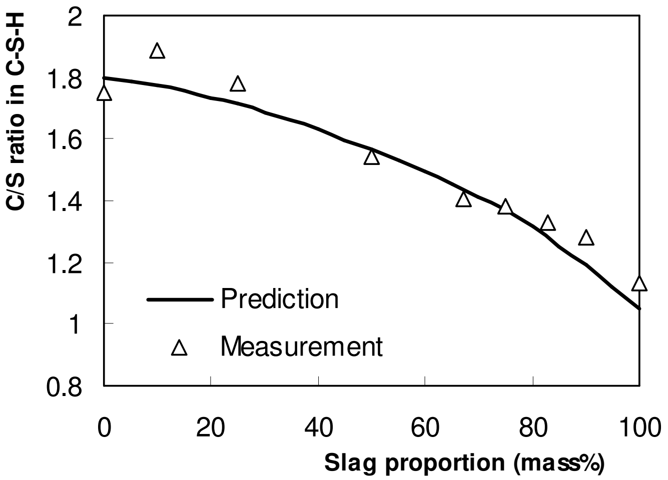

Fig. 2. Volume fraction of products in hydrating slag cement paste vs. slag proportions
(w/b = 0.4, assuming all clinker and 70 percent of slag has reacted)

2.2. Three-Dimensional Computer Modelling of Cement Hydration

The reaction model for slag-blended cement reaction is incorporated into the 3-D computer model [9]. The types of reaction products, their quantities and properties can be computed for the conditions that govern their hydration state (such as relative humidity and temperature). Factors influencing the microstructure development are investigated with the computer model, including: (1) the composition and particle size distribution (PSD) of Portland cement and gypsum (if present), (2) the composition and PSD of slag (3) proportion of slag in the paste, (4) water/binder ratio, (5) curing condition and (6) the slag reactivity. Some properties of the microstructure, such as porosity, CH content and the composition of the main hydration product (C-S-H) are predicted.

The influence of particle size distribution of slag on its hydration rate is investigated with the new computer model and the results are compared with the observations in experiments as well (Fig. 3). It can be seen that the simulated hydrated layer thickness is very close to that calculated from the experimental measurements. It furthermore follows that increase fineness enhances the degree of hydration substantially.

The fraction of CH consumed by the slag reaction at different ages is plotted in Figure 4. For slag proportions smaller than 50 percent, the fraction of CH consumed by the slag reaction is quite limited. For proportions higher than that, a sharp increase is observed, indicating a decline of the CH content in the paste. The fractions of consumed CH increase with age as well.

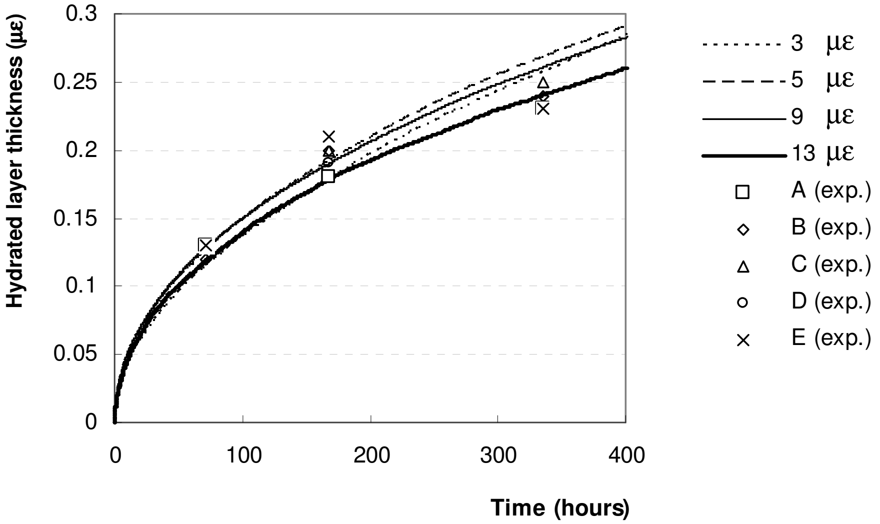

Fig. 3 Effect of particle size on the hydrated layer thickness of slag particles
(experimental data from [13])

2.3. Model Applications

The 3-D computer model is employed for the design of a mineral shrinkage-compensating (MSC) admixture. The reactions of the principal components in the shrinkage-compensating admixture (gypsum, fly ash and slag) are simulated with the computer model, and the recipe is adjusted for maximum performance of the admixture, i.e. controlling the formation time of ettringite, its amount and the stability of the shrinkage-compensating effect. The volume fraction of ettringite in the simulated microstructure is plotted in Fig. 5. The length change of the samples containing various amounts of this admixture measured is presented in Fig. 6. All the mortar prism samples are sealed with plastic foil and cured at 20±1 °C.

It can be seen that this shrinkage-compensating admixture can successfully compensate the autogenous shrinkage. For dosages higher than 10%, slight expansion is generated, which will compact the microstructure if properly restrained.

The theoretical and computer models for the slag cement hydration can successfully simulate the hydration process and predict various properties, for example, hydration degrees of reactants, the microstructure development and the effect of curing conditions. Particularly for the reaction of slag in cement, the amount of CH consumed by the slag reaction is clarified. The effect of slag content, reactivity and particle size (fineness), which are the topics of numerous researches, can be investigated with the models.

The three-dimensional computer model also enables the design of new mineral admixtures for cement. Here as an example the design of mineral shrinkage-compensating admixture is demonstrated. A 10% m/m addition of this type of admixture to CEM I can successfully compensate the autogenous shrinkage.

Future research will comprise, among others, a further quantification of the kinetics, cement/filler packing simulations, and the diffusion and binding of chlorides in the microstructure.

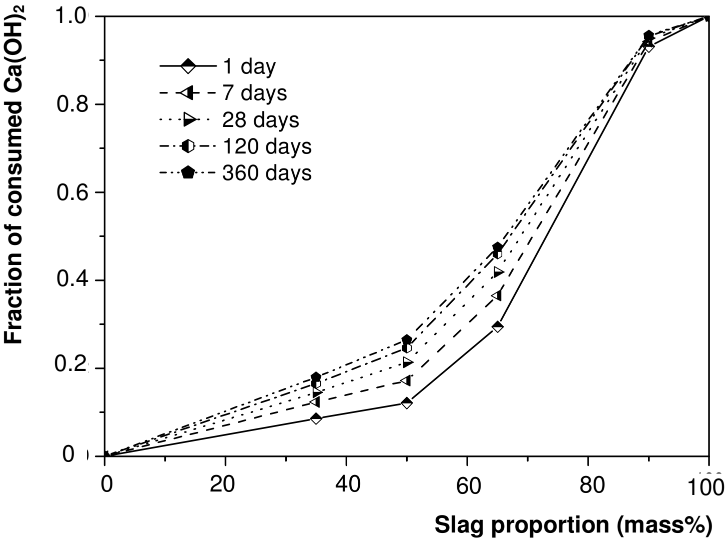

Fig. 4. Fraction of consumed CH vs. slag proportions in cement

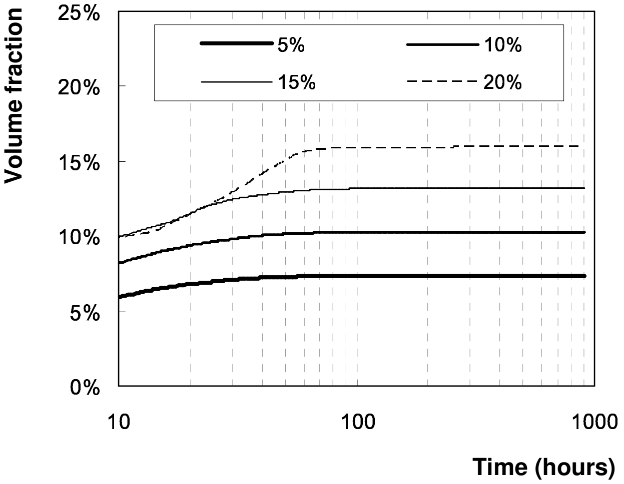

Fig. 5. Volume fraction of ettringite in hydrating cement paste containing various amounts of MSC admixture as simulated with CEMHYD3D *(water/binder ratio = 0.5, at 20 °C, sealed curing)*

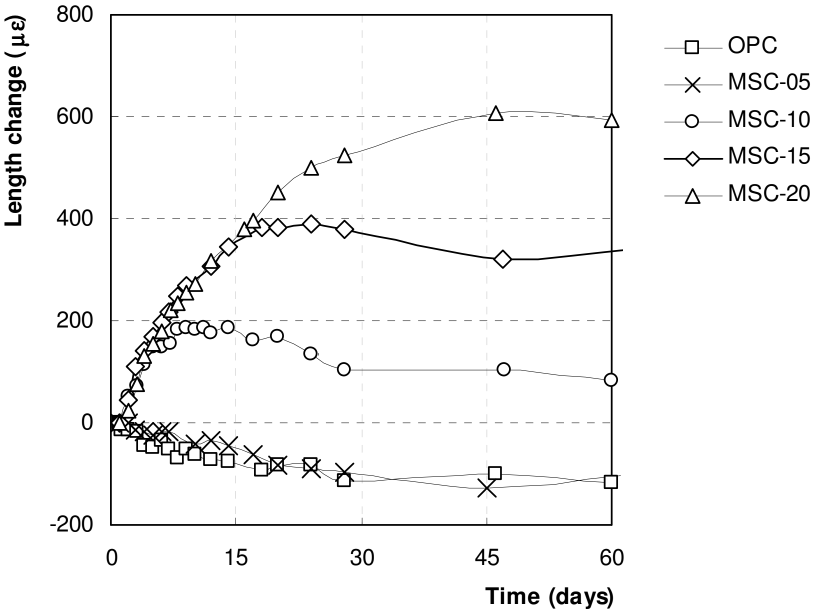

Fig. 6. Measured length changes of sealed mortar samples containing various amounts of MSC admixture

3. SELF-COMPACTING CONCRETE

The development of Self-Compacting Concrete (SCC), also referred to as "Self-Consolidating Concrete", has recently been one of the most important developments in the building industry. The incentive for the first development of this concrete in Japan came from high-fluidity anti-washout underwater concretes developed in Germany during the 1970's [14].

Ever since the pioneering work by Féret [15] it is known that the particle size distribution of the aggregates governs the workability and hardened properties of concrete mixes. The so-called Japanese Method makes use of the packed densities of gravel and sand individually, whereas in the Chinese Method the packing of these aggregates is considered integrally [16]. Brouwers and Radix [16] subsequently applied the packing theories by Andreasen and Andersen [17] and Funk and Dinger [18] to *all solids*, i.e. aggregates and powders (cement and filler), in the concrete. This approach also enables the optimum use of nanoparticles in the mix design. This integral particle packing approach was actually recommended already by Fuller and Thompson [19]. This has resulted in self-compacting concretes with low cement contents that met all technical requirements. The *cement efficiency* was found to be 0.14 MPa per kg/m^3.

The research focuses on the environmental performance (e.g. of waste fillers), as well as on the widening of the size range of the solids -the upper particle size is increased from

16 to 32 mm- and the water demand of the powders. Increasing the size range of the mix and designing mixes that follow the modified Andreasen and Andersen grading line will result in further improvements. It will be seen that the design method allows the reduction of the cement content, and with 32 mm aggregate a cement efficiency of 0.22 MPa per kg/m^3 is already achieved.

3.1. A New Design Concept for SCC

The consideration of the aggregate grading is a fundamental factor for the development of concrete mix designs. So-called standard sieve lines were essential elements in most of the concrete design regulations so far. But within these standards only the coarser aggregates have been considered concerning their aggregate size. Starting from a minimum aggregate size of 0.25 mm different proportions of aggregate fractions were specified up to the maximum particle size. The whole range of grading curves was cut into areas for favourable, useable and unfavourable mixes. However, smaller particles were not taken into account. With the acceptance of the standard EN 206 in the year 2000 these grading curves have been omitted.

In the field of Self-Compacting and High-Performance Concrete a lot of research has been performed with the focus on grading and particle packing. The Linear Packing Density Model (LPDM), the Solid Suspension Model (SSM) and the Compressive Packing Model (CPM) as a representative of the so-called third generation of packing models are well known examples for packing models [20]. For the most part the amount of solids was even cut into coarse and fine sections and optimized separately concerning their packing. A couple of research projects were focused on dense packing of cement pastes. An integral approach based on the particle size distribution of all contained compounds, however, cannot be found that often. This led to the development of a mix design based on an alternative approach of particle packing.

3.2. Development of a Theoretical Model

Based on the work of Brouwers and Radix [16] the particle size distribution of all solids is believed to have the strongest influence on the particle packing beside the particle shape when looking for continuously graded granular blends. Like above mentioned there are different ways of modelling particle size distributions. A reliable solution for the reproduction of natural continuously graded grains is represented by the distribution function from Funk and Dinger [18]. The cumulative finer fraction reads as follows:

$$P(D) = \frac{D^q - D_{min}^q}{D_{max}^q - D_{min}^q} \qquad (3)$$

where D is the particle size of the considered fraction, D_{min} is the minimum particle size and D_{max} is the maximum particle size in the mix. The exponent q is referred to as distribution modulus and allows controlling the amount of fines for a generated mix in a certain range. While higher values of q (typically from 0.4 to 0.7) lead to coarser blends, a lower q will produce mixes with high amounts of fines. A further advantage of this distribution function is the introduction of a minimum particle size. Common functions like the Fuller parabola (where q is set to 0.5) only considers the maximum particle size and the grading of aggregates only, that leading to amounts of fines that in fact do not necessarily exist in the actual mix. Then again, the Funk and Dinger function starts first with quantities of fines, which are effectively present, and thus giving in total more fines. By Brouwers [21, 22] it is proven mathematically that, depending on the sieve width ratios employed (e.g. 2 or √2), a q of about 0.28 results in optimum packing. Furthermore, an analytical expression was derived for the void fraction of a packing that follows Eq. (3). Though the D_{max} is limited, e.g. by rebar spacing, the mix and its packing can be optimized by reducing D_{min} in the mix, e.g. by deploying nanoparticles.

Based on various dry packing tests with tailored grading curves, indeed values in the range from 0.25 up to 0.35 were found for best packing. High amounts of fines, compared to standard concrete, are characteristic for the Japanese Design Method for SCC. These fines are required to ensure sufficient flowability of the fresh concrete. Most of the time this high fineness of SCC mixes was realized with cement, which led to higher material costs and a stronger environmental impact.

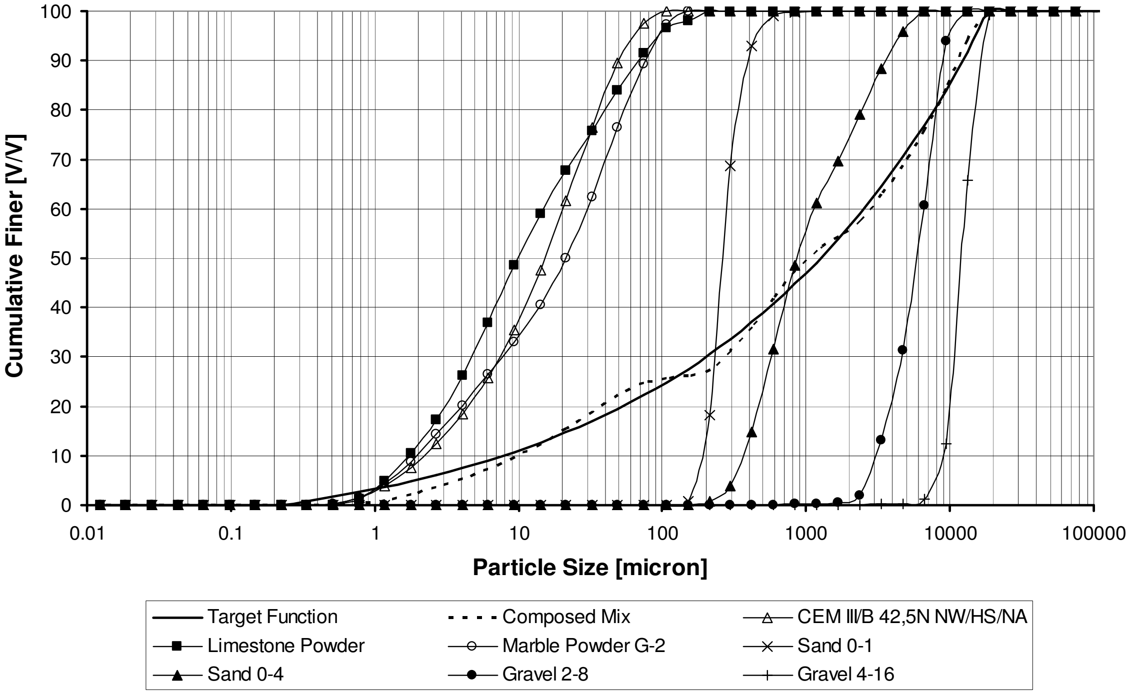

Fig. 7. PSD of a mix (dashed line) composed with the help of the new design concept

Considering the ideas of the new mix design model, a high percentage of these fines can be substituted by other powder materials. Using for this purpose industrial waste products like ashes or process residues like natural stone wastes will have a beneficial effect on the environmental performance of concrete, whereby at the same time material costs will be lowered.

Assuming that optimum packing is obtained the void fraction becomes minimized. This means less voids have to be filled with paste (reduction of required paste amount) and on a smaller scale less void volume has to be filled with water. Conversely, it can be concluded that more water is available for lubrication. However, not only the packing fraction plays a role, also the total specific surface of all solids governs the fluidity of a mix. Having these considerations in mind, a design model based on the above mentioned packing model was established. With the help of linear optimization a fit of a granular blend, containing all solids going to be used, is made according to the defined distribution function.

That means that the proportions of the selected materials are changed as long as the least deviation from the target curve is obtained. This deviation is determined using a least squares method, which is described in detail by Hüsken and Brouwers [23]. In Figure 7 an example of a composed mix (dashed line) in comparison with the target function (solid line) is given. For the design of the target function the model automatically will take the Dmin and Dmax over from the selected materials. The used distribution modulus amounts to 0.23. For the purpose of comparison the PSDs of all contained materials are given too.

Table 1. Mix proportions of the mix from Fig. 7.

Material	Volume (dm^3)	Mass (kg)
CEM III/B 42,5N NW/HS/NA	103.8	300.0
Limestone Powder	35.0	91.5
Marble Powder	63.5	174.1
Sand 0-1	38.4	101.3
Sand 0-4	259.7	686.2
Gravel 2-8	122.9	321.9
Gravel 4-16	214.7	559.2
Water	150.0	150.0
Air	12.0	-
Total	1,000.0	2,384.3

3.3. Experimental Results

Using both the new design concept based on the particle grading and the information given by the determination of the water demands, various SCC mixes have been produced and tested for their fresh and hardened concrete properties. The analysis of this information shows a promising way of designing new kinds of SCC with improved qualities in regard to their workability, mechanical properties and durability. A profound further increase of the cement efficiency to values of 0.19 - 0.22 MPa per kg/m^3 was obtained.

Another basic observation concerns the application of the water/cement ratio. Up to now the strength was given as a function of the water/cement ratio, the cement content and type of cement (it must be understood that there are also other influences). In applying the new design tool, unconventionally low cement contents (250 to 280 kg/m^3) were selected, the water/cement ratio therefore sometimes considerably exceeded the mark of 0.60. Considering the limits given for different exposure classes in the standards, this might be a handicap. Note that with these high water/cement ratios, no high total water contents are obtained. In evaluating the data gathered in the framework of these test series no distinct correlation between water/cement ratio and strength properties could be derived. Creating different states of packing with equal water/cement ratios, a broad margin of strength values was obtained and contrary equal strength was achieved with different water/cement ratios. Relating, however, strength to water/powder ratios (w/p) a clear linear correlation could be found (all particles smaller than 125 µm are counted as powder). The data in Fig. 8 show that for a certain amount of powder in a mix, the lowest possible water content should be found by means of grading optimization (with compliance of requested workability).

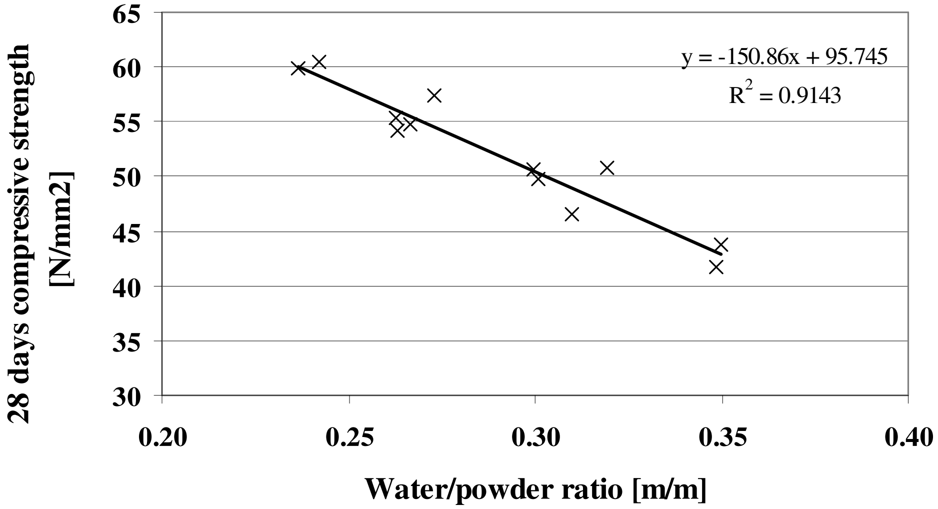

Fig. 8. Relation between the compressive strength and the w/p ratio

Focusing on the achieved compressive strength data, it can be noticed that the general level is high, knowing that a SCC was produced using a cement type CEM III/B 42,5N and aggregate sizes up to 32 mm (for most of the mixes). As filler material limestone powder, fly ash and stone waste powders (granite) were employed. The majority of strength measurements amounted to values in the range of 50 up to 60 MPa (7000-8400 psi) which is remarkable considering the fact that for most mixes only 270 kg of cement or even less was used.

Another interesting aspect is the application of these bigger aggregates in SCC. Normally, maximum aggregate sizes of 16 mm or sometimes 22 mm are applied for SCC. Given that with increasing aggregate size especially the durability properties are affected, a loss of durability qualities was expected for these kinds of concrete. But the packing influence by the *"particle size engineering"* showed a much stronger effect. Finally, SCC mixes have been produced with $q = 0.22$ having a better durability performance than SCCs designed with D_{max}= 16 mm. As an example in Fig. 9 the capillary water absorption as a simple indirect durability parameter of these SCCs is given compared with the improved mixes containing 32 mm aggregates.

Concretes with D_{max}= 32 mm and with good workability, durability and medium strength seem to be feasible with cement contents of only 150 kg/m^3 or even less. The used method is based on the particle packing and internal specific surface of all solids in the mix. It offers an enormous potential for cement reduction and is one emphasis of ongoing research. Future research will among others concern the widening of the particle size ratio by lowering the smallest particle size from 400 nm down to 10 nm, adding natural stone aggregate and filler (to produce aesthetic SCC), and developing inorganic coatings that will bond photo-catalytic powders to the concrete surface (so that the surface becomes self-cleaning and degrades NO_x).

4. EARTH-MOIST CONCRETE

As stated in the introduction, in the precast concrete products industry (such as pavement stones, kerbstones and concrete pipes), earth-moist (or "zero-slump") concrete is applied for the mass production of these products. These concrete mixes are dry with a very stiff consistency, so they are rammed in the rigid mould, and after dense compaction, demoulding can take place almost immediately so that short processing times with high quantities can be achieved. In the past, relatively little attention has been paid to these concretes; a recent thorough study was made by Bornemann [24].

Capillary forces between the finer particles combined with the inner friction of the mix then provide the required so-called green strength. In soil mechanics this phenomenon is also called apparent cohesion, which can only be activated in partially saturated sands or sandy soils. Here, the content of fines as well as the fineness of the smaller particles and the degree of saturation influences the capillary forces.

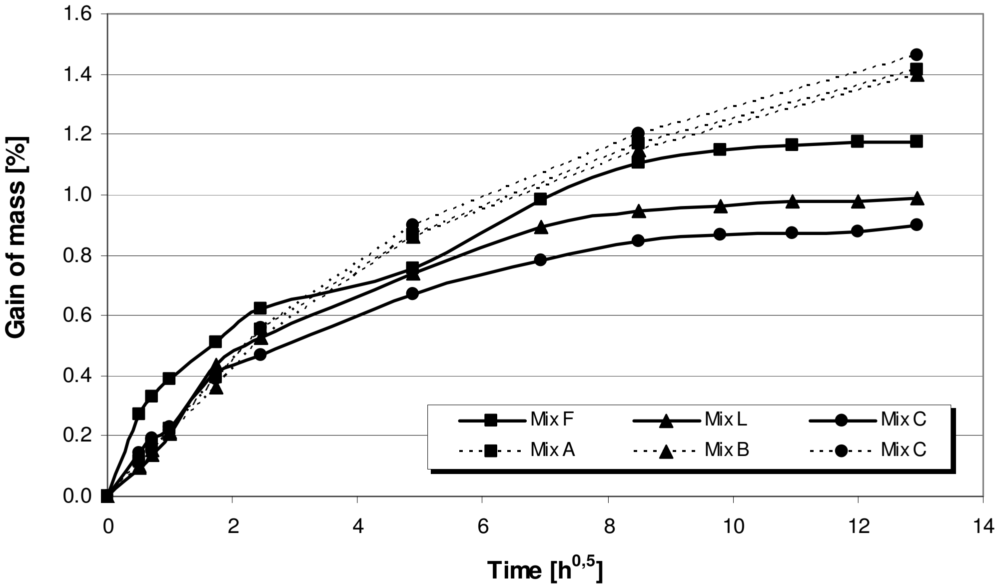

Fig. 9. Capillary water absorption of three different mixes
composed using D_{max} = 32 mm and compared with 3 SCC mixes with D_{max} = 16 mm
(F = fly ash, L = limestone, C = only cement as powder; A, B and C from [16])

Caused by their dry consistency associated with low water content, earth moist concrete mixes show a low degree of hydration after production and a high potential for reactions afterwards during weathering which renders the products durable [25]. For that reason, and caused by the short processing times, earth-moist concrete mixes are the ideal starting substance for the mass production of concrete products.

Although earth-moist concrete mixes are used on a big scale for the mass production of the aforementioned earth-moist concrete products, the applied methods for designing mixes are strongly geared to procedures and standards for standard concrete. Nevertheless, the regulations that apply to these products allow innovations such as cement reduction, introduction of nanoparticles, application of stone sludge waste, a higher and tailor-made aggregate content etc. In particular, the reduction and substitution of expensive primary filler materials (cement) by secondary stone waste materials is of vital importance for the cost reduction. Here, this will be demonstrated by the results of first preliminary tests on earth-moist concrete.

4.1. Preliminary Tests on Earth-Moist Concrete

First tests on earth-moist concrete were executed in order to confirm the fundamental idea of the newly developed mix design which was already applied for the mix proportioning of self-compacting concrete mixes (see above). Improved densest possible packing is the philosophy of this new approach. With an improved and optimised packing of all aggregates, considering all particles from the coarsest to the finest particle size, the properties of concrete in hardened as well as fresh state can be affected in a positive way. This was already observed and recommended by Féret [15] and Fuller and Thompson [19].

To determine the usability of the newly developed mix design tool for earth-moist concrete, several mixtures with different mix proportioning were investigated. Based on the distribution function for continuously graded particle mixtures based on Eq. (3), different distribution moduli q were examined. The range of investigated distribution moduli ranged from 0.25 to 0.40 in combination with different w/c ratios. For the mix proportioning different kinds of Rhine sands (sizes 0/1, 0/2, 0/4), natural gravel (sizes 2/8, 4/16, 8/16), as well as crushed granite (size 2/8) were used. A CEM III/B 42.5N LH/HS or a mix of CEM III/B 42.5N LH/HS and CEM I 52.5N were applied as binder. Fig. 10 shows the PSDs for some of the tested earth-moist concrete mixes. These designed mixes were evaluated regarding:

- Degree of compactibility using defined and constant compaction effort;
- Packing density;
- Density of fresh concrete according to DIN-EN 12350-6:2000;
- Density of hardened concrete according to DIN-EN 12390-7:2001;
- Compressive strength according to DIN-EN 12390-3:2002;
- Tensile splitting strength according to DIN-EN 12390-6:2001.

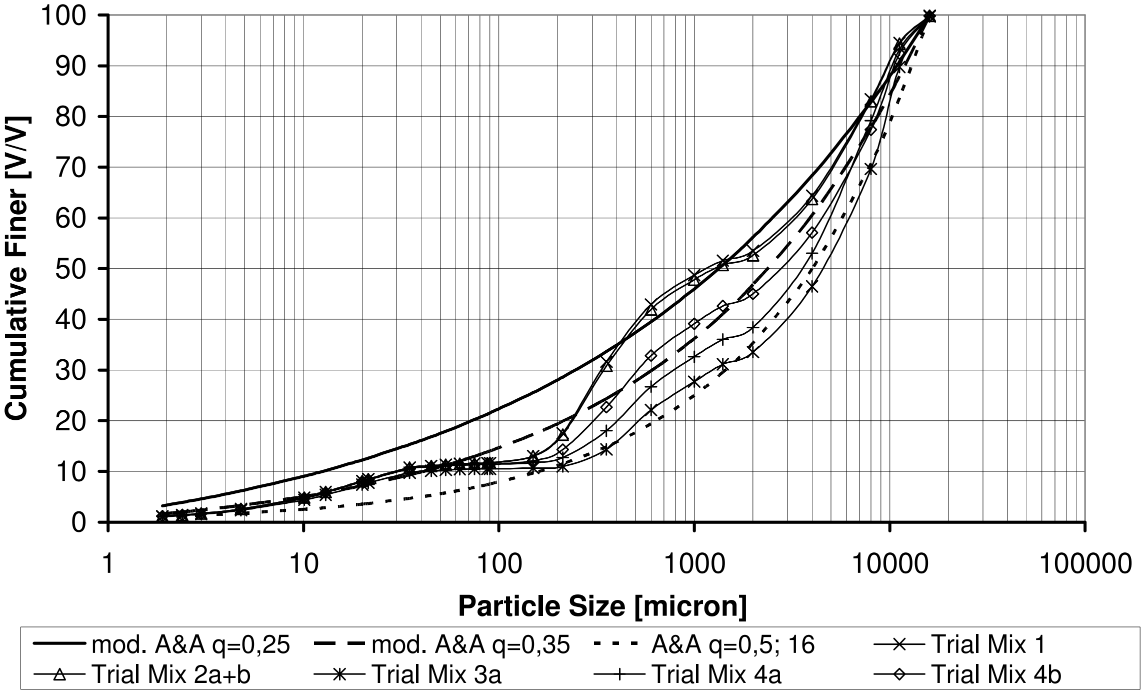

Fig. 10. PSDs of tested earth-moist concrete mixes
(cumulative finer volume fraction)

Furthermore, the water demand of the used powders was determined according to the applied test procedures described for SCC.

Fig. 11 depicts the improvement of the mechanical properties of hardened concrete considering the relation between packing density and compressive strength. The line pertaining to 310 kg cement per m^3 concerned CEM III/B 42.5N LH/HS, the line pertaining to 325 kg cement per m^3 concerned a mix of CEM III/B 42.5N LH/HS and CEM I 52.5N. Both lines clarify that an improved packing with higher packing density results in a stronger concrete while maintaining constant cement content. The applied cement contents of 310 kg and 325 kg per m^3 concrete are necessary to follow the given target function for the grading as close as possible. Cement contents between 350 kg and 375 kg per m^3 concrete are usually used in current line productions. But this amount can be reduced by selecting the right distribution modulus q for the target function. In doing so, the reduction of cement content from 375 kg to 325 kg per m^3 leads to a cost reduction of 13.3%, considering the actual prices for aggregates and cement in the Netherlands. Note that the fitted trend lines in Fig. 11 extrapolate to compressive strengths of 118 and 183 MPa for 310 kg and 325 kg cement per m^3, respectively, if 100% would be achieved, implying maximum theoretical cement efficiencies of 0.38 and even 0.56 MPa per kg/m^3. The latter value reveals that adding a finer cement (CEM I 52.5N to CEM III/B 42.5N LH/HS) substantially improves the cement efficiency, most likely by the improved packing and the larger specific surface.

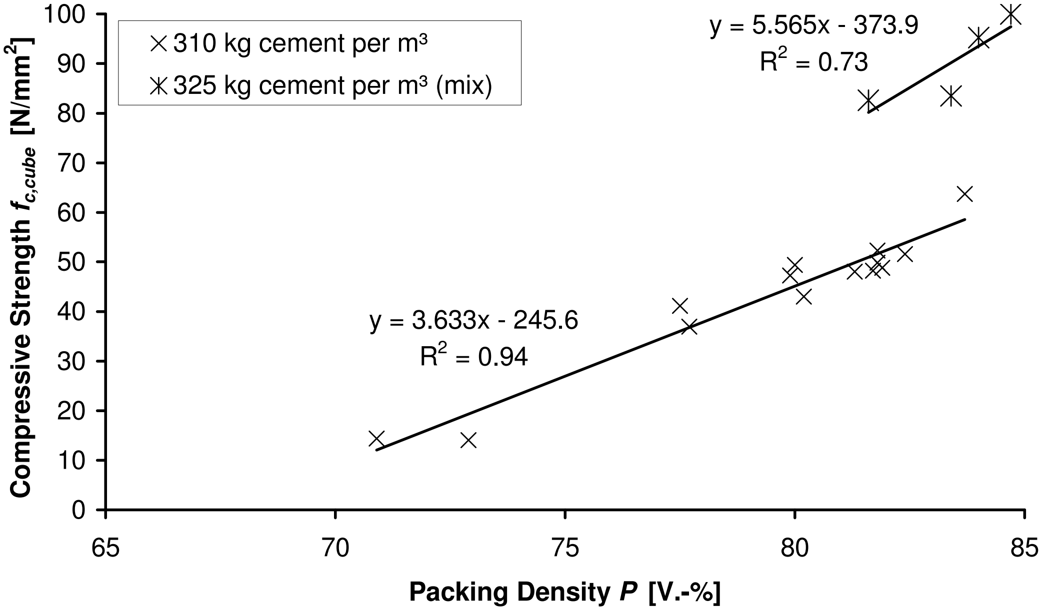

Fig. 11. Compressive strength versus packing density for tested mixes with cement content of 310 kg and 325 kg per m^3 concrete, respectively

From Fig. 11 one can see that at a packing fraction of 85%, actual cement efficiencies of 0.20 (310 kg) to 0.30 (325 kg) MPa per kg/m^3 are achieved, which can be further enhanced by improved packing, e.g. by applying nanometre particles.

Considering the high compressive strength, as well as tensile splitting values for mixes with 325 kg per m^3, the design method also allows reducing the cement content further. The achieved compressive strength of about 100 MPa at 85% packing is namely far in excess of the requirements given by the Dutch standards. Also, the tensile splitting strength for mixes with 325 kg cement per m^3 is with 4.9 MPa to 5.0 MPa higher than required by the Dutch standard NEN-EN 1338. For tensile splitting strength, the NEN-EN 1338 prescribes a characteristic value higher than 3.6 MPa and an individual value higher than 2.9 MPa for pavement stones.

A further reduction of the cement content is therefore possible if a suitable material for replacement is available. For this purpose, the grading of the mineral additive should follow the grading of the replaceable part of cement as close as possible or should have even a higher fineness (lower mean particle diameter). A suitable mineral additive can be found in stone waste powders generated during the processing of natural stone. These powders will be applied in future tests on earth-moist concrete regarding their positive effects on mechanical as well as durability properties.

Based on the results obtained from tests on concrete in fresh as well as hardened state, the following standard values for the proportioning of earth-moist concrete are advisable.

Distribution modulus q:	0.325 – 0.375 (mean 0.35)
Paste content (< 125 μm):	0.225 – 0.25 m^3 per m^3 concrete
Water/powder ratio (w/p):	0.30 – 0.39
Water/cement ratio:	0.35 – 0.40 *(used according to the classical definition)*

The use of lower distribution moduli than 0.30 is not advisable for earth-moist concrete mixes as the content of fines is strongly increasing with distribution moduli smaller than 0.30 (Fig. 12) and the mixes are not workable without using high compaction efforts or big amounts of admixtures. The use of distribution moduli higher than 0.40 is also not suitable for earth moist concrete mixes as the better workability/compactibility of these mixes without plasticizers is resulting in a worse packing caused by a missing content of powders (particles smaller than 125 μm). The best results regarding packing density and compressive strength could be achieved for the preliminary mixes using the above mentioned values.

Based on the first results presented here, future research will focus on the role of basic parameters such as the internal specific surface, packing density, water/air content (saturation) etc on compactability, green strength, production speed and properties in hardened state. The objective is to design mixes that are cheaper and environmentally friendly, and that also meet all practical requirements.

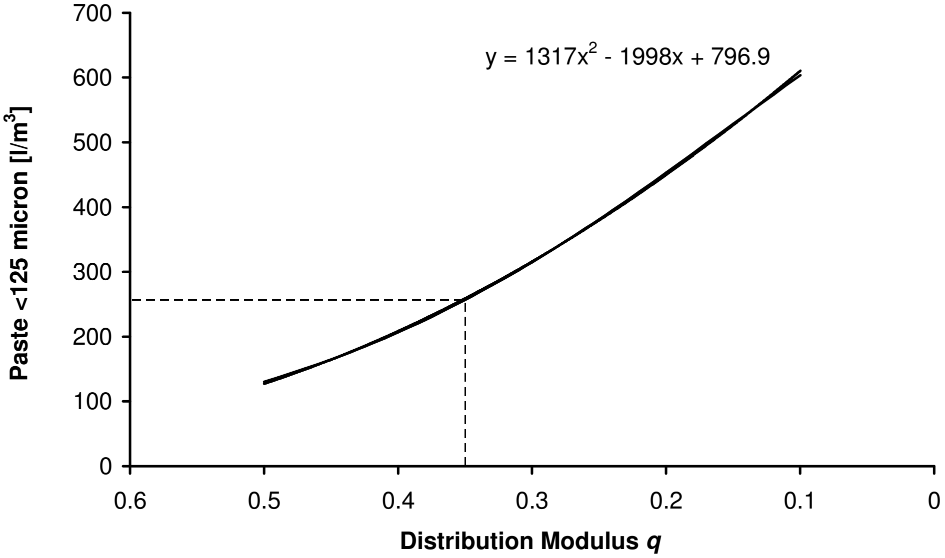

Fig. 12. Computed paste content (particles < 125 μm plus water) per m^3 concrete for a given water/powder ratio (w/p) of 0.35; D_{max}= 18.9 mm, D_{min} = 12.3 nm

5. SUMMARY AND CONCLUSIONS

New European regulations allow more and more the performance design of materials and structures, which offers opportunities to introduce nanoparticles in a cost effective way in concrete mixes. For properties that can relatively easily be evaluated, such as mechanical (compressive strength etc), it enables cost effective solutions, also in regard to the materials choice. In this paper, which focuses on calcium oxide-based products (cement, lime, sulphates), examples are given of concrete that outperform in regard to technical properties, sustainability and costs. These products are obtained by the consequent and systematic use of *mineral oxide engineering* and *particle size engineering*.

This *particle size engineering* approach is based on the packing and internal specific surface area of all solids in a concrete mix. Up to now, already 13 binders (cements, lime, calcium sulphates), 11 fillers (natural stone waste, fly ashes, granulated slag, TiO_2 powders etc), 7 sands and 6 gravels (primary, recycled) have been characterized in regard to their PSD (from 10 nm to 32 mm) and specific surface area, and this number is steadily growing. They can all be combined in the newly developed mix design software tool. This mix design method renders the common material cement a high-tech material when the obtained specific strength (*cement efficiency*) is considered: from 0.22 MPa (SCC) to 0.30 MPa (earth-moist concrete) per kg/m^3 (14-19 psi/lb). For example, considering a steel density of 7900 kg/m^3, this material would need a compressive strength of 1738 MPa to 2370 MPa to match these cement efficiencies. Though the comparison is not completely fair, as full hydration of 1 kg of the cement requires about 0.4 kg of water, the required steel strength is not so easy to achieve.

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 material[4] [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 μm) 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/m^3, as is also the case already with the air content in concrete (commonly maximized to 30 l/m^3).

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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[4] The fruitful application of *mineral oxide engineering* for the development of recipes for soil and dredging sludge, that both also mainly consist of mineral oxides, has not been discussed in the present paper.

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