New Developments with Respect to Concrete

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ABSTRACT

The present paper addresses several topics in regard to the sustainable design and use of concrete based on the binders cement, quicklime and/or gypsum. 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, sustainable building.*

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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. One outcome 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 & Construct (D&C), Build, Operate & Transfer (BOT) and variants from these. So far, 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:

1. the awareness of life-time performance and costs of materials and structures, including aspects such as durability and sustainability;
2. 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].

Ad 1) 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 important. Other -more green- building materials, such as wood, may score more favourably from an energy/CO_2 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

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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 (Cembureau (2005)).

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.

Aspects 2 to 4 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% m/m), may turn waste into a building material, i.e. bringing waste materials (back) in the building life cycle.

Ad 2) 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, crushed concrete can substitute primary stones, and contaminated soil and sludge can be used as filler and aggregate.
- 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 (discussed below in more detail).

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/m^3 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 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 (N/mm^2) 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, 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 five research topics will be addressed that are motivated by the considerations given above:

- Cement hydration;
- Self-Compacting Concrete;
- Earth-moist concrete;
- Gypsum concrete;
- Dredging sludge and soil.

In order to reach the set goals, the *leitmotiv* in 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 quicklime 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 and immobilisates. 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, in concrete mixes. Key parameters upon the application are their reactivity, the prevailing reactions and the microstructure that develops.
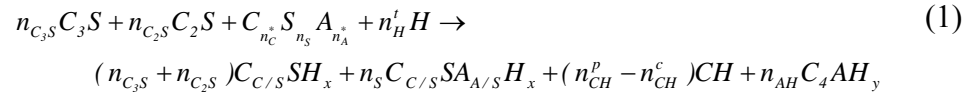
The first step in this hydration research concerned the reactions and numerical simulation of ordinary Portland cement (OPC). Based on the water retention data provided by Powers and Brownyard (1948), the hydration reactions of the five major clinker phases (C_3S, C_2S, C_3A, C_4AF and $C\bar{S}$)[3] and their hydration products were quantified (Brouwers (2003, 2004a, 2004b, 2005a). 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 (Van Eijk (2001), Brouwers and Van Eijk (2003)). The next step in the research is the inclusion of slags in the hydration model.

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

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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, $\bar{S}$ = SO_3.

well (Chen and Brouwers (2007a, 2007b)). 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:

$$n_{C_3S}C_3S + n_{C_2S}C_2S + C_{n_C^*}S_{n_S}A_{n_A^*} + n_H^t H \rightarrow \qquad (1)$$

$$(n_{C_3S} + n_{C_2S})C_{C/S}SH_x + n_S C_{C/S}SA_{A/S}H_x + (n_{CH}^p - n_{CH}^c)CH + n_{AH}C_4AH_y$$

in which n is the number of moles of the respective substances, n_{CH}^p is the amount of CH produced by calcium silicates hydration and n_{CH}^c 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 amount of CH entering slag reaction is related with a factor p to the total amount of CH produced by the clinker hydration as:

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

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 $\overline{S}$ 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 (Figure 1).
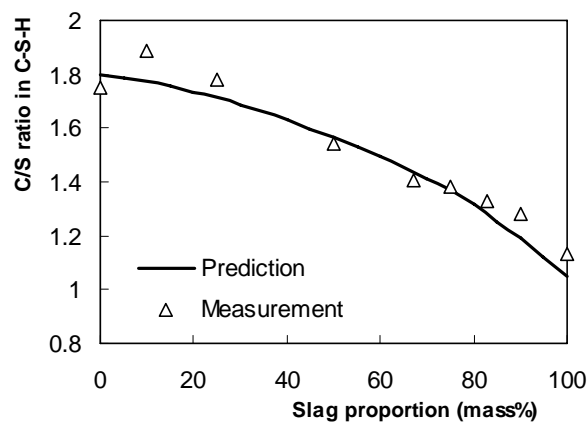

Figure 1. Predicted and measured C/S ratio in C-S-H versus slag proportions in blended cement (experimental data from Richardson and Groves (1992), ratio of the slag/clinker hydration degrees is 0.7, w/b = 0.4).

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 1 year hydration with different slag proportions are presented in Figure 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.
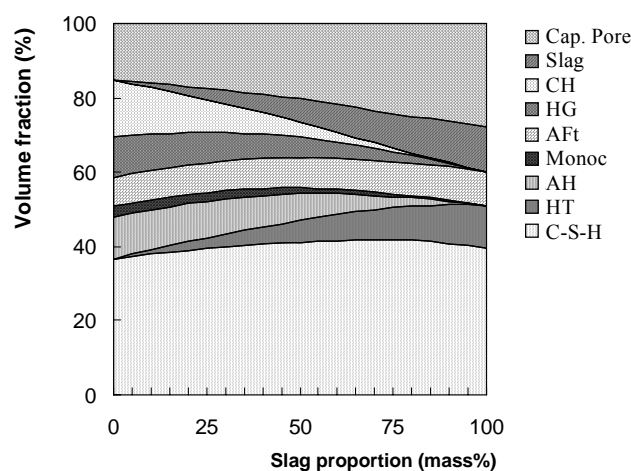

Figure 2. Volume fraction of products in hydrating slag cement paste versus slag proportions (w/b = 0.4, assuming all clinker and 70 percent of slag has reacted).

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 (Chen (2007)). 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 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 (Figure 3). It can be seen that the simulated hydrated layer thickness is very close to that calculated from the experimental measurements.
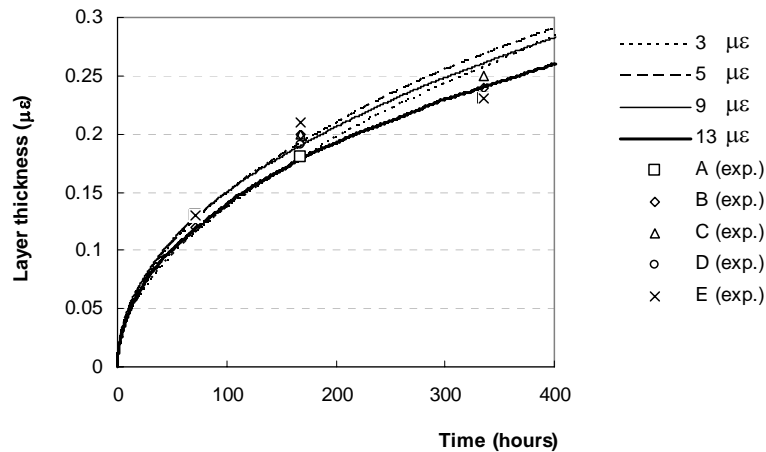
Figure 3. Effect of particle size on the hydrated layer thickness of slag particles (experimental data from Sato et al. (1986)).

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.

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 Figure 5.
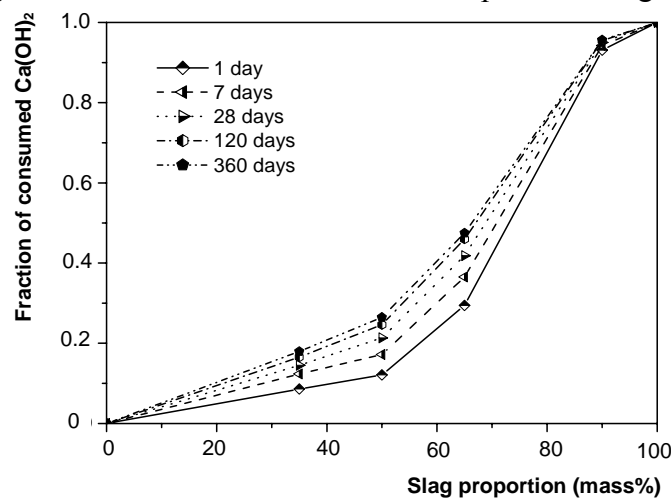

Figure 4. Fraction of consumed CH versus the slag proportions in cement.

The length change of the samples containing various amounts of this admixture measured is presented in Figure 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.
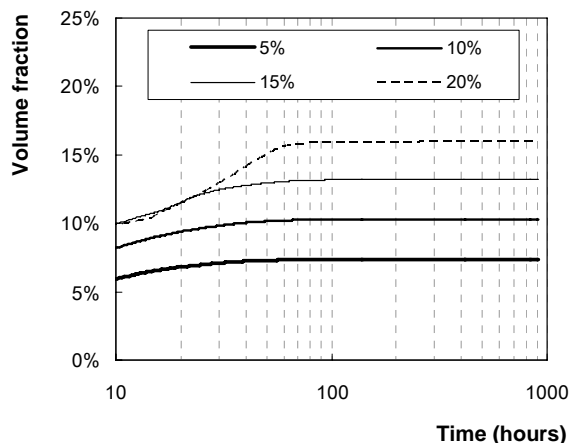

Figure 5. Simulated volume fraction of ettringite with CEMHYD3D in hydrating cement paste containing various amounts of MSC admixture (water/binder ratio = 0.5, at 20 °C, sealed curing).

2.4 Conclusions

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.
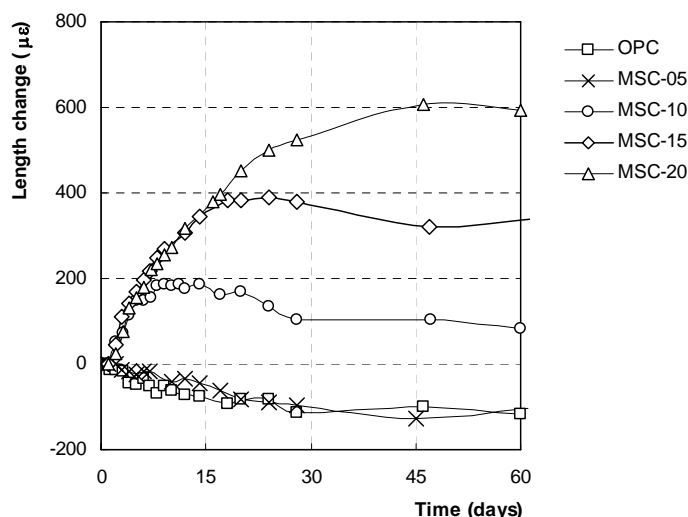

Figure 6. Measured length changes of sealed mortar samples containing various amounts of MSC admixture.

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 and chlorides in the microstructure.

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 (Nagataki (1998)).

Ever since the pioneering work by Féret (1892) 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 (Brouwers and Radix (2005)). Brouwers and Radix (2005) subsequently applied the packing theories by Andreasen and Andersen (1930) and Funk and Dinger (1994) to *all solids*, i.e. aggregates and powders (cement and filler), in the concrete. This is an approach that was actually recommended already by Fuller and Thompson (1907, pp. 242-244). 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 N/mm^2 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 N/mm^2 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 (De Larrard and Sedran (1994)). 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 (2005) 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 (1994). The cumulative finer fraction reads as follows:

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

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 (2005b, 2006) it is proven mathematically that, depending on the sieve width ratios employed (e.g. 2 or $\sqrt{2}$), 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).

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.

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.
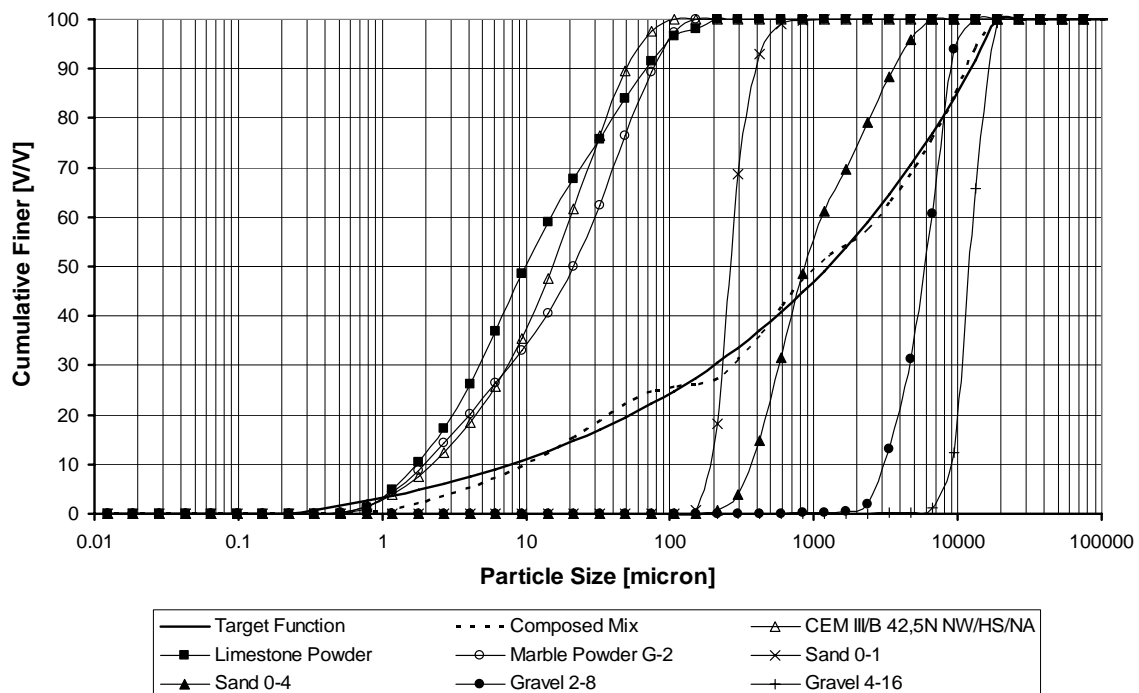
Figure 7. PSD of a mix (dashed line) composed with the help of the new design concept. The target function (solid line) as well as the PSDs of all applied materials are given too (measured with Malvern 2000 and a √2 sieve set).

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 govern 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 (2006). 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 D_{min} and D_{max} 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.

3.3 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 N/mm^2 per kg/m^3 was obtained.

Table 1. Mix proportions of the mix from Figure 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

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 Figure 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).
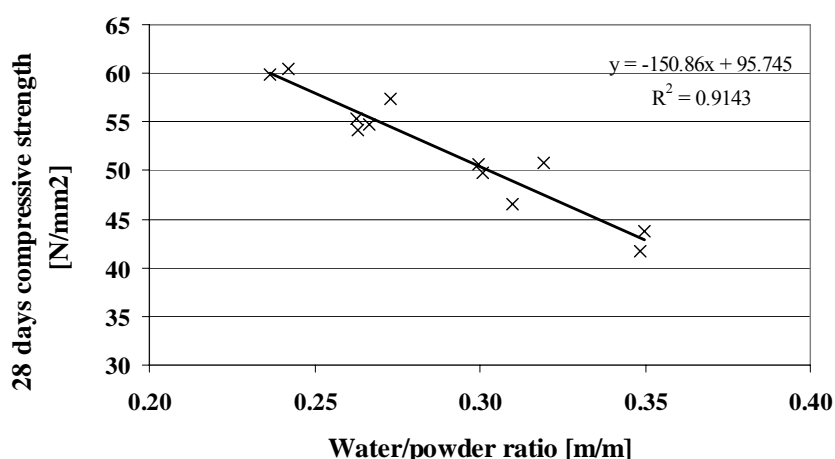

Figure 8. Relation between the compressive strength and the w/p ratio.

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 N/mm^2 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 Figure 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.
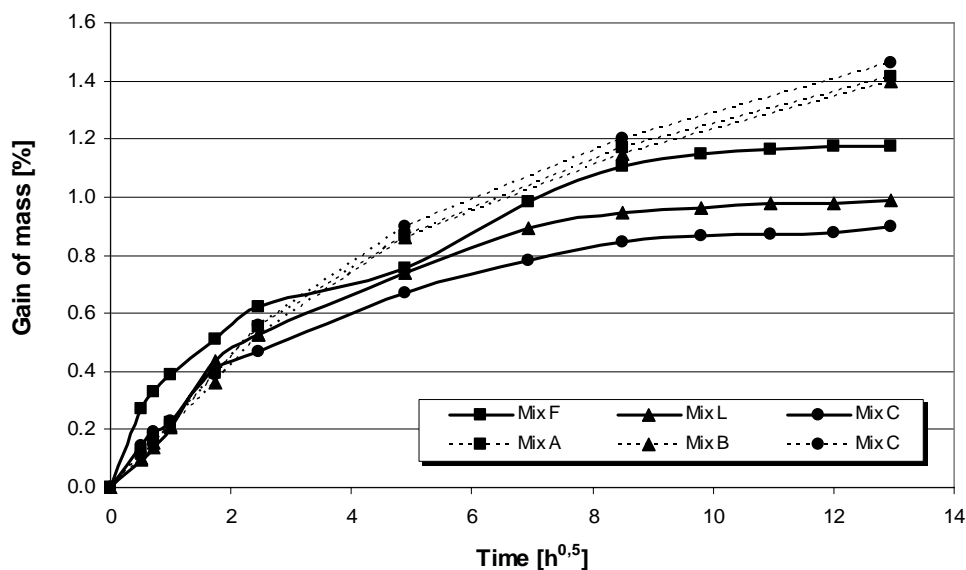
Figure 9. Capillary water absorption of three different mixes (F = fly ash, L = limestone, C = only cement as powder) composed using D_{max} = 32 mm, compared with 3 SCC mixes with D_{max} = 16 mm (A, B and C from Brouwers and Radix (2005)).

3.4 Conclusions

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 cast 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 (2005).

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.

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 (Häring (2002)) which renders the products durable. 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, 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 (1892) and Fuller and Thompson (1907).

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) and natural gravel (sizes 2/8, 4/16, 8/16) as well as broken granite (size 2/8) are 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 are applied as binder. Figure 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 for some selected samples.

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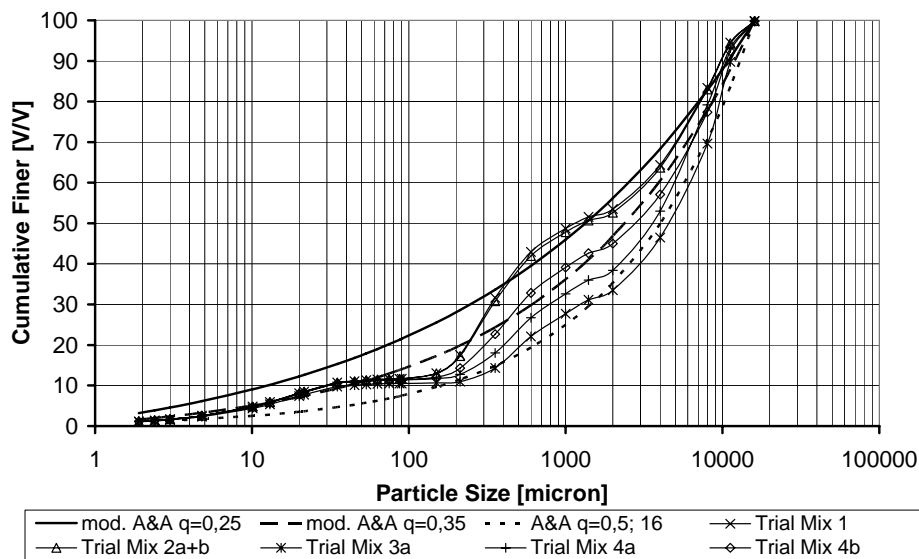

Figure 10. PSDs of tested earth-moist concrete mixes (cumulative finer volume fraction).

Figure 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 Figure 11 extrapolate to compressive strengths of 118 and 183 N/mm^2 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 N/mm^2 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. From Figure 11 one can see that at a packing fraction of 85%,

actual *cement efficiencies* of 0.20 (310 kg) to 0.30 (325 kg) N/mm² per kg/m³ 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 m³, the design method also allows reducing the cement content further. The achieved compressive strength of about 100 N/mm² 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 m³ is with 4.9 N/mm² to 5.0 N/mm² 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 N/mm² and an individual value higher than 2.9 N/mm² 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 substituent 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 substituent could 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.
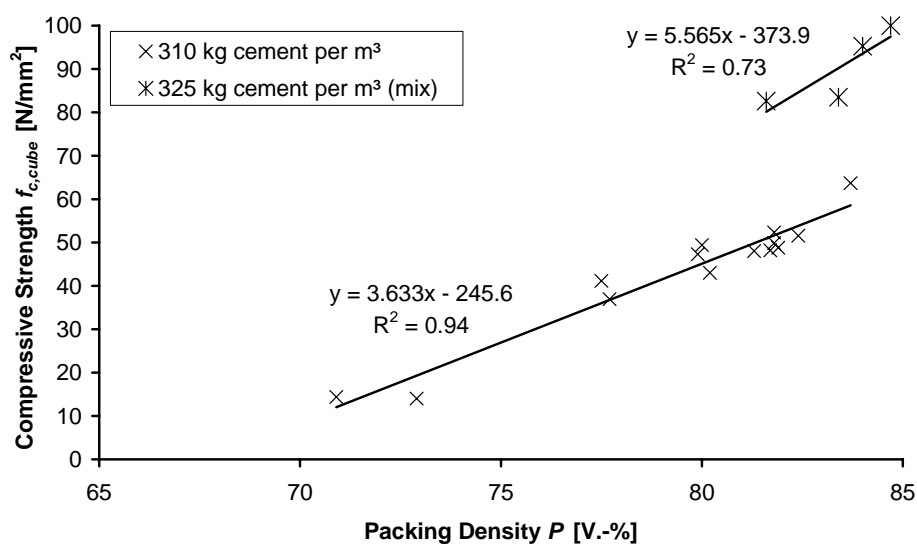

Figure 11. Compressive strength versus packing density for tested preliminary mixes with cement content of 310 kg and 325 kg per m3 concrete, respectively.

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 m³ per m³ concrete
Water/powder ratio (w/p):	0.30 – 0.39
Water/cement ratio:	0.35 – 0.40 (used according to the classical definition of concrete)

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 (see Figure 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.
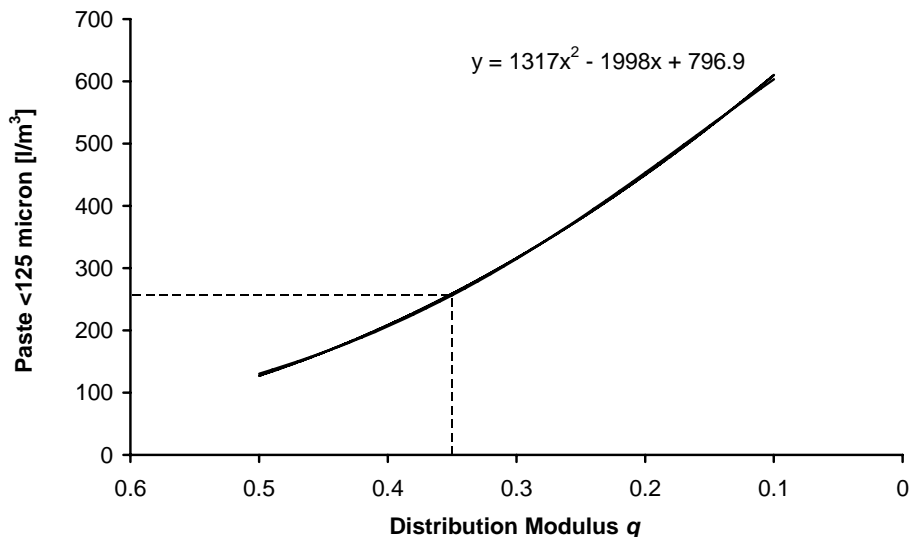

Figure 12. Computed paste content (particles < 125 μm plus water) per m³ concrete for a given water/powder ratio (w/p) of 0.35; D_{max} = 18.9 mm, D_{min} = 12.3 nm.

4.2 Conclusions

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.

5. GYPSUM CONCRETE

Both hemi-hydrate and anhydrite are tested as calcium sulphate binders for structural mortar and concrete. The advantage of using calcium sulphates instead of cement as a binder is the fact that the production of calcium sulphate is more environmental friendly than that of cement. In addition, calcium sulphate based concrete could still have an economic and environmental advantage since gypsum is a by-product of the flue gas desulphurization process. It is also a by-product with the phosphate fertilizer refining process, but because of the low radioactive levels this gypsum is not allowed on the commercial market at this moment yet.

5.1 Theory

When the water content of a concrete mix is reduced, the capillary pores formed by the excess in water will also be reduced. Optimising the particle packing of the mix as described above has a positive influence on the water content needed in the concrete mix. A second method to

reduce the free water in hardened gypsum concrete is obtained by chemical binding. By enabling ettringite formation during the hydration process water molecules will be fixed chemically into the crystal structure of ettringite. The chemical reaction for the formation of ettringite is as follows:

$$3C\bar{S}H_2 + 3C + A + 26H \rightarrow C_6A\bar{S}_3H_{32} \tag{4}$$
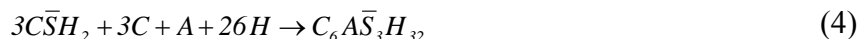
This should lead to a situation where the ettringite will fill up the pores caused by water while crystallizing the water. Trass and fly ash can be sources of A and C and are believed to have chemical properties that should enable the formation of ettringite during hydration. As an extra source for calcium oxide quicklime can be used.

5.2 Experiments

Since this study has the aim of evaluating the possibilities of gypsum concrete, the main focus was on the workability of the fresh concrete and the compressive strength of the hardened concrete. The workability will be measured with the standard cement concrete slump flow test. These parameters are considered to be the most important for initial evaluation and can also be relatively easily measured. The influence of retarding admixtures and plasticizers is also tested. The compressive strength and the tensile splitting strength of the hardened concrete are measured according to the norms, EN 12390-3:2001 and EN 12390-6:2000 which hold for standard cement concrete.
Concretes were designed with activated (premixed) anhydrite as binder. Anhydrite was firstly selected (instead of hemi-hydrate) because it is already used in practice for screed floors.

Table 2. Concrete mixes with premixed anhydrite as binder.

Material	Mix 1 mass (g)	Mix 1 volume (cm³)	Mix 2 mass (g)	Mix 2 volume (cm³)
anhydrite (premix)	575.0	197.2	552.3	189.4
sand 0-1	104.6	39.7	87.4	33.1
sand 0-2	0.0	0.0	0.0	0.0
sand 0-4	611.0	231.3	638.1	241.5
gravel 2-8	280.8	107.2	297.5	113.5
gravel 4-16	473.8	181.8	518.5	199.1
Water	212.8	212.8	193.3	193.4
air	0.0	30.0	0.0	30.0
total	2258.0	1000.0	2287.1	1000.0

The composition of two designed concrete mixes are given in Table 2. The results of tests with these concrete mixes are given in Table 3 and described in more detail below.

Table 3. Experimental results of gypsum concrete.

	Mix 1	Mix 2
7 days compressive strength (N/mm^2)	21.65	37.2
7 days tensile strength (N/mm^2)	no data	3.02
28 days compressive strength (N/mm^2)	29.41	no data
slump flow (mm)	638	280

5.3 Results

The mechanical properties of the gypsum concrete depend, as might be expected, strongly on the binder content. The first tests with a binder content of 400 kg/m^3 were unsuccessful since they resulted in a 28 days compressive strength lower than 10 N/mm^2. Concrete mixes with a higher content, about 550-575 kg/m^3 were more successful. A decrease of 30% in the binder content resulted in a 70% drop in the compressive strength of both mortar and concrete. The 7-days compressive strength of 37.2 N/mm^2 found for Mix 2 gives reason to believe that for the 28-days compressive strength a value of more than 40 N/mm^2 can be achieved easily.

From the results of the compressive strength tests on the gypsum concrete it becomes once more clear that the water content in the mix also has a large influence on the final compressive strength. In Figure 13 therefore the compressive strengths are set out against the water/powder ratios.
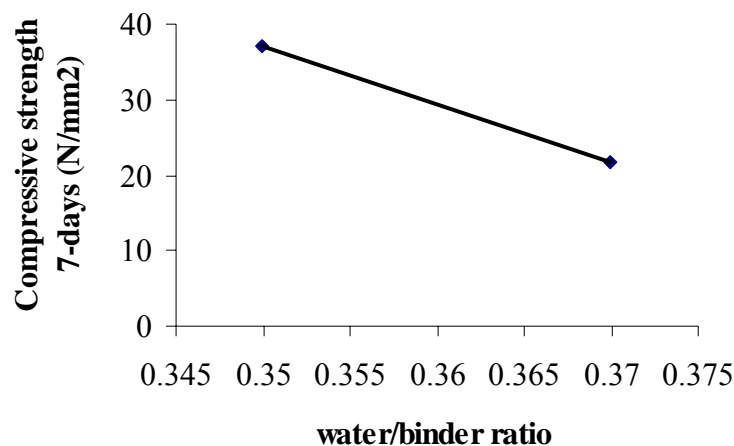

Figure 13. Compressive strength (Mixes 1 and 2) versus w/b ratio, for anhydrite based concrete.

From the tests on the anhydrite mortars it can be concluded that an optimised PSD curve with addition of for instance fly ash is beneficial for the strength development in mortars. A mortar without filler was found to have a 28 days compressive strength of 5.0 N/mm^2. A mortar with the same water/binder ratio and the same binder content, but with fly ash as filler, was found to have a 28 days compressive strength of 7.8 N/mm^2. In Figure 4 it can be seen that the mortar mix containing fly ash has a PSD curve much closer to the target curve than the mix with sand 0-1 mm. It is expected that this is also true for concrete.
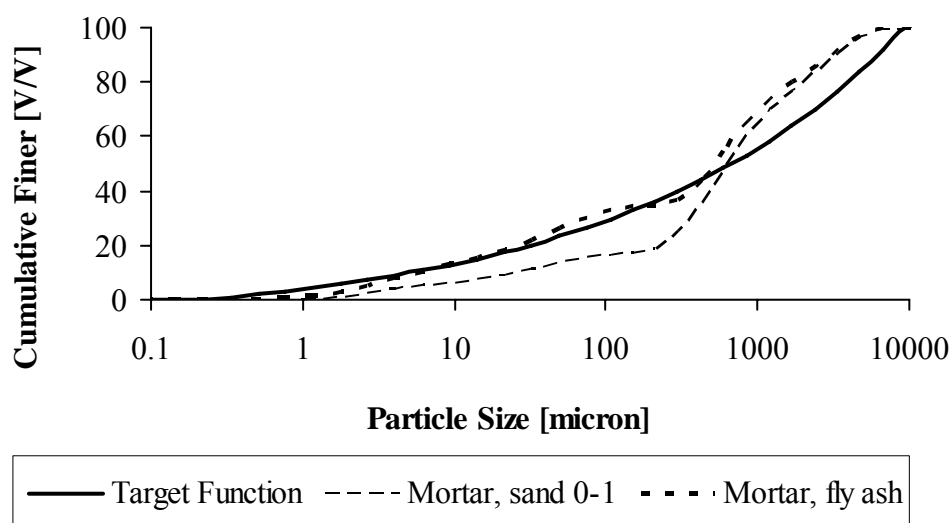
Figure 14. PSD curves of mortar mixes with (boldly dashed) and without fly ash as filler.

With anhydrite based concrete a value for the tensile strength of 3.02 N/mm^2 was found. This value is in line with the formula used for calculating the tensile strength from the compressive strength for cement based concrete (Reinhardt (1998)):

$$f_t = 0.27 f_c^{2/3} \tag{5}$$

For a compressive strength of 37.2 N/mm^2, this equation yields a tensile strength of 3.01 N/mm^2, which is very close to the measured one. This implies that eq. (5), derived for cement based concrete, also seems to hold for gypsum concrete.

Concrete with a binder content of 400 kg/m^3, does not have a good workability either. This is due to the fact that the designed mixes should contain more powder materials if one wishes to follow the Andreasen & Andersen curve (eq. (3)). Since the only powder material in these mixes is the gypsum, which is restricted by the binder content, the amount of fine powders is too low in these mixes. It was found that the water/binder ratio should be in the range of 0.35 to 0.40 for a 'good' workability. This is based on a binder content of 550 – 575 kg/m^3. Since the water/binder ratio is dependent on the binder content it is hard to establish one suitable range for every mix. For this reason one should give more attention to the water/powder ratio of a mix, which enables the replacement of binder by powders. The w/p of the anhydrite mixes, with powders being defined all particles <125 μm, were in the range of 0.34 to 0.37 (Figure 5). Figure 15 shows that a slight decrease in the water/powder ratio has a major effect on the slump flow of the fresh concrete.

Some hardness tests were performed on the surface of 7-days old cubes. These tests showed that the surface of the calcium sulphate based concrete cubes is quite soft. With an iron rod one could easily scratch the cube surface. Also the impact of the Schmidt hammer caused some noticeable damage on the surface.
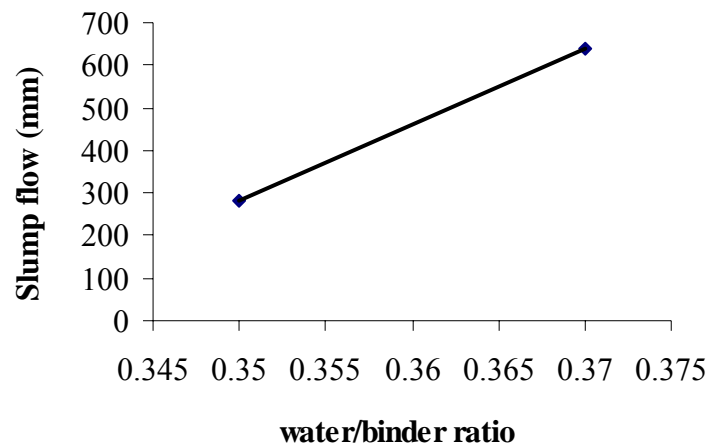
Figure 15. Slump flow Mixes 1 and 2 versus w/b ratio.

5.4 Conclusions

Based on the results of this study it seems possible to compose a calcium sulphate based structural concrete. With a 28 days compressive strength of 35 to 40 N/mm^2 this material is suitable to have a structural function indoors (and outdoors with a protection against water). However, there are still some points of attention. The required binder content of 550 kg/m^3 is about twice as high as is needed for cement based concrete with the same compressive strength. Despite this, calcium sulphate based concrete could still have an economic and environmental advantage.

Concerning the ettringite formation a more extensive research and analysis is needed. First results with fly ash and trass as powders indicate that reaction (1) does not (or hardly) take place. It is believed that actually the reaction of trass and fly ash is too slow to act as source for aluminium oxide. A better option would be to use pure aluminium oxide, which is available on the market.

In future research the present experience will used as a starting point for further improvement of the mix, e.g. the reduction of binder by the introduction of powders and the addition of more reactive aluminium oxide (to promote water binding by ettringite formation).

6. DREDGING SLUDGE/SOIL

From a mineral oxides point of view, dredging sludge, soil and cement are very similar. Besides minerals, sludge and soil contain water and organic matter. They mainly differ in water content (sludge has a lower amount of dry matter) and fineness (sludge particles are usually finer). In what follows, a project on treatment of dredging sludge with cement is presented; more detailed information can be found in Brouwers et al. (2005). The numerical simulation background can be found in Van Eijk and Brouwers (1999) and Van Eijk (2001).

It is allowed to spread clean or slightly contaminated sludge over land or surface water. This is done with only 30% of the total amount of fresh water dredging sludge, the remaining part cannot be spread because of high contamination levels or limited space along the waterways. The most common technique employed at this moment is ripening. Ripening of sludge is the natural process where the sludge is transformed by drying and oxidation from a wet substance into a soil-like material. In this technique, after dredging the sludge is transported to an open-air depot. The dredging sludge arrives at the depot with a dry matter content of 20-25% and is

stored in layers of 1 m thickness. This material has no mechanical bearing capacity and is as such not applicable. When the sludge reaches a dry matter content of 35-40% the aerobic conditions for biological activity are reached, initiating the oxidation process. To enhance the oxidation process and evaporation the dredging sludge is turned over two to three times a year. Only when a dry matter content of 50-55% is reached the product can be deployed as a building material in civil structures (e.g. as road base material). In current practice this ripening process could take one and a half to two years. This points out the need for alternative treatment methods that reduce the handling time.
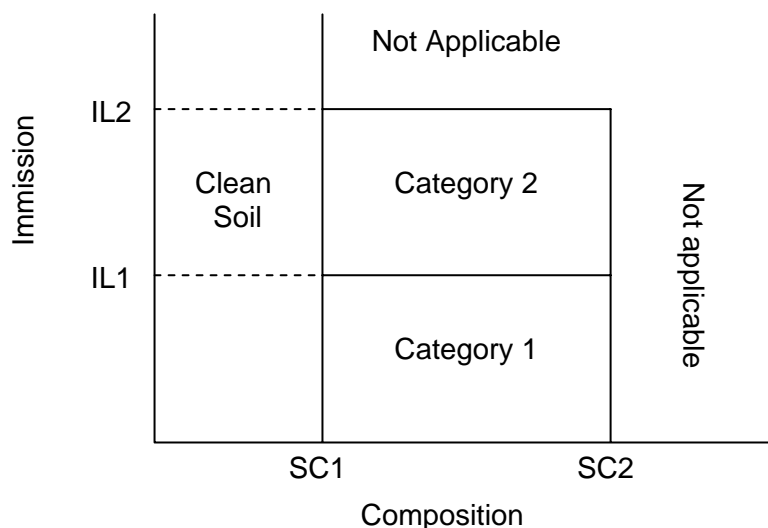

Figure 16. Classification of soil for the applicability as building material (SC = standard composition, IL = immission level).

Another problem with the reuse of dredging sludge is the level of contamination. Before the dredging sludge can be applied it needs to fulfil stringent requirements. In the Netherlands four categories for soil as building material are distinguished (Ministry of VROM, 1995): Clean Soil, Category 1 or 2, and Not Applicable (see Figure 16), based on the leaching and composition.

Objective of this research is to reduce the treatment time for contaminated dredging sludge by ripening and to reduce leaching (immobilisation), such that a stable product is obtained that can be applied as a building material, by mixing the sludge with cement and unslaked lime. In the Netherlands the contamination level of dredging sludge is divided into five classes, Class 0 being the cleanest, Class 4 being the most contaminated. In this study Class 4 dredging sludge from urban waters was used to assess the effect of both binders on the different contaminants. The studied dredging sludge contains 13.6% organic matter, determined by loss on ignition at 550°C. The loss on ignition at 1200°C was 18.9%. A significant portion of the minerals is crystalline (58% quartz, 12% calcite), whereas the remaining part most likely contains amorphous material. Analyses revealed that some constituents exceed SC1, but none SC2. This means that the used dredging sludge can be classified as Category 1, Category 2 or as Not Applicable (see introduction and Figure 16). The final classification depends on the leaching, which is discussed later on.

6.1 Experimental set-up

Cylindrical containers with a diameter of 40 cm were filled with 10 cm of sand and 20 cm dredging sludge on top of it. Prior, during and after the experiment several parameters were monitored such as mass, dry matter content, temperature and humidity. The relative humidity was regulated with a plastic cover (with opening flaps) and maintained at a value of around 70%. The temperature in the laboratory was 23-24 °C. The conditions thus created are therefore representative for summer conditions.

The sludge in the containers was mixed with different amounts of additives: no additives (reference), 7% cement and 0.5% lime, 14% cement and 1% lime, and 15% cement only. Except for the last one, each combination was carried out with and without regular mixing. All experiments were carried out in duplicate. The initial dry matter content (dm) of the original sludge was 39%. This was lowered to 35% by adding water. In Table 4 the composition of the samples is given. The first number of the code of the sample gives the percentage of cement, the second the percentage of lime and the third indicates whether the sample was regularly mixed manually (1) or not (0).

Table 4. Composition of the samples (mass in kg).

	additive	Mixed	sludge	water	Cement	lime	dm
0/0/0	None	No	27	3	0	0	35.0%
0/0/1		Yes	27	3	0	0	35.0%
7/½/0	7%cement	No	27	3	2.1	0.15	39.6%
7/½/1	0.5% lime	Yes	27	3	2.1	0.15	39.6%
14/1/0	14% cement	No	27	3	4.2	0.3	43.5%
14/1/1	1% lime	Yes	27	3	4.2	0.3	43.5%
15/0/0	15% cement	No	27	3	4.5	0	43.5%

6.2 Drying and water binding

The evaporation of water was determined by measuring the weight of the samples biweekly. The difference between the measured mass and the mass at $t = 0$ equals the mass lost by evaporation. Based on the original dry mass content and the mass loss due to evaporation an apparent dry matter content could be calculated, set out in Figure 17. The initial values at $t = 0$ correspond to the last column of Table 4. It can be seen that the mixed samples have a larger increase in dry matter content than the samples that are not mixed. After 20 weeks the mixed samples have a dry matter content that is about 3 to 4% higher. Regular mixing improves the aeration and enhances the evaporation of water and as such has a positive effect on the dry matter content of the sludge.

In Figure 18 the change in dry matter content determined by drying at 105°C is given. Like in Figure 17 the dry matter content increases faster for samples including additives. Since cement reacts with water, part of the water will become chemically bound. This water will not evaporate at 105°C, consequently the dry matter content observed in Figure 17 is higher than the apparent dry matter content based on mass loss given in Figure 16.
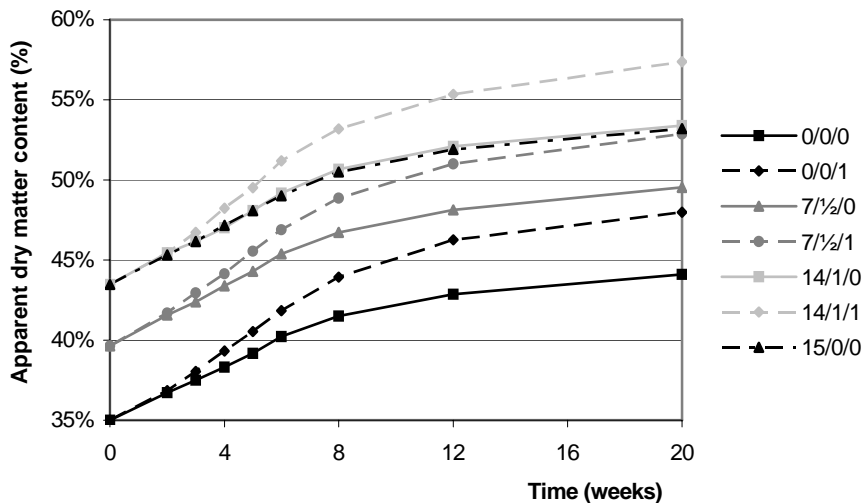
Figure 17. Apparent dry matter content (%) versus time (weeks) based on mass loss due to evaporation.
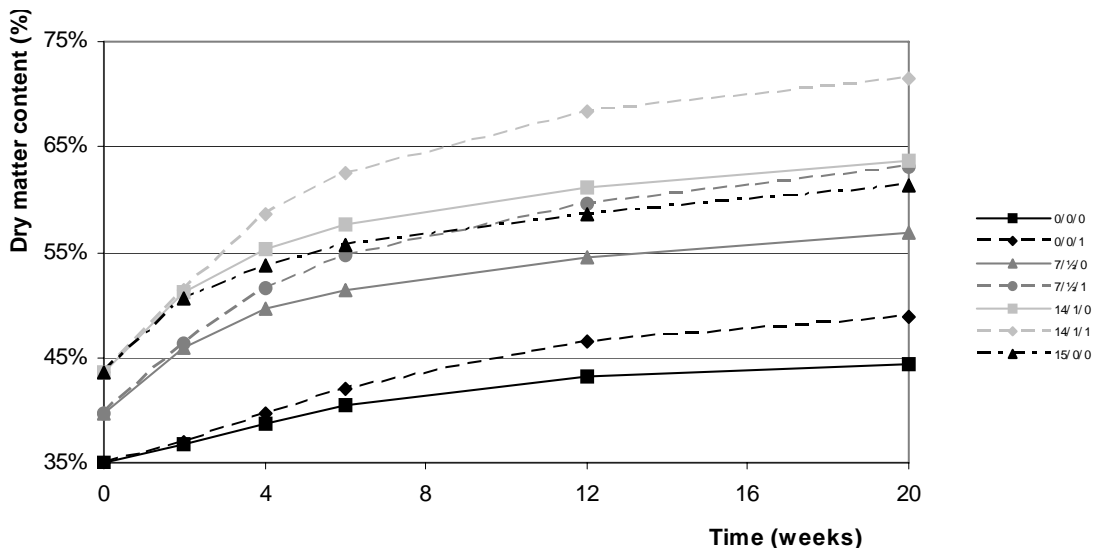

Figure 18. Actual dry matter content (%) versus time (weeks) based on drying at 105 °C.

The trends in Figures 16 and 17 are the same, only the effects of cement and lime are more pronounced in the latter. Besides the advantage of accelerated drying and an additional increase in dry matter content due to chemically bound water the samples with additives already start with a higher dry matter content. Samples with 7½% additives have a time advantage of about 4 weeks compared to samples without additive. The samples with 15% additive gain 8 weeks. Moreover, in the first four weeks the dry matter content of the samples with additives increases faster than that of the samples without additive. This is mainly caused by the reactions of cement and lime with water. After four weeks this reaction is more or less completed and the dry matter content increases at a similar rate as the samples without additive.

As said, the dry matter content of the dredging sludge should be at least 50-55% before it is applicable as a building material. Based on extrapolation, the samples without additive reach a dry matter content of 50% after approximately 26 (mixed) or 60 (not mixed) weeks. For the

mixed sample with 7½% additives this is already reached within 4 weeks. This includes the time benefit gained by mixing in the additives. When it is assumed that 8 weeks are required to obtain a dry matter content of 35% after the dredging sludge is stored in the depots and the additives can be mixed in, this means that the treatment time in the depots is reduced by about 65%. For the samples with 14 and 15% additives the treatment time is even reduced by about 70%. The acceleration of the ripening process by mixing additives with the dredging sludge means that in the same time span, three times as much dredging sludge can be treated compared to current practice, and consequently the process appears to be economical.

From Figures 16 and 17 it is apparent that the reaction of cement and lime with water resulted in an increase of the dry matter content. The cement reacts with water and retains this water even after drying at 105 °C. It is known that after complete reaction with water cement is able to retain 40% of its own weight, of which 15% is evaporable water (evaporates after drying at 105°C) and 25% of the water is non-evaporable water (Powers and Brownyard (1948), Brouwers (2004a, 2004b)). This was verified in a limited number of additional basic experiments (Brouwers et al. (2005)).

Table 5. Chemically bound water expressed as % of added mass of cement as a function of time (weeks), w/c is based on water in sludge on mixed.

Code	w/c	t=2	t=4	t=12	t=20
7/½/0	9.3	60.7%	82.4%	74.0%	82.6%
7/½/1	9.3	62.8%	96.1%	94.4%	107.6%
14/1/0	4.6	41.4%	57.4%	56.4%	62.6%
14/1/1	4.6	42.9%	71.7%	78.8%	82.3%
15/0/0	4.3	38.8%	46.1%	43.6%	51.5%

The derived observed amounts of chemically bound water are much larger than the expected 25% for cement (and maximal 32% for lime) alone. The presence of the dredging sludge enhances the formation of chemically bound water. This is because some minerals in the dredging sludge form new compounds with water, cement, and lime forming more and probably new reaction products that contain a higher amount of chemically bound water.

The samples that were regularly turned over had higher percentages of chemically bound water. Mixing the samples improves the dispersion of the additives and consequently provides more optimal conditions for reaction of the cement and lime with water and minerals.

Table 6. Emission values (mg/kg) for the original (E_i) and treated samples.

	Symbol	E_i	$E_{0/0/1}$	$E_{7/½/1}$	$E_{14/1/0}$	$E_{15/0/0}$	E_{max}[1]
Acidity	pH		11.7	9.8	8.4	8.3	
Fluoride	F	3.7	1.9	1.8	2.2	3.6	3.0
Chloride	Cl	-	570	520	90	40	51
Bromide	Br	0.5	2.1	0.5	1.3	1.5	2.6
Sulphate	SO_4	2200	1200	2400	5500	7100	354
Arsenic	As	0.17	0.12	0.14	0.20	0.075	0.7
Mercury	Hg	0.0003	0.0003	0.0003	0.0003	0.0003	0.016
Cadmium	Cd	0.001	0.001	0.001	0.001	0.001	0.021
Chromium	Cr	0.02	0.02	0.02	0.02	0.02	0.09
Copper	Cu	0.02	0.90	0.38	0.37	0.02	0.25
Nickel	Ni	0.05	2.50	1.80	0.45	0.05	0.63
Lead	Pb	0.05	0.05	0.06	0.05	0.05	0.8
Zinc	Zn	0.21	0.025	0.035	0.10	2.50	2
Molybdenum	Mo	80	950	1000	1100	330	0.45
Antimony	Sb	5	200	200	300	200	0.06
Selenium	Se	10	500	500	500	500	0.09
Vanadium	V	70	900	3000	2900	170	1.2

[1] E_{max} = maximum permissible emission

6.3 Leaching

To analyse the effect of ripening on immobilisation, leaching tests were performed on the original dredging sludge, and after the ripening experiments (Table 6).

E_i is the emission value of the original, untreated dredging sludge, for the others the codes are as used before. In the last column the maximum permissible emission according to the Building Materials Decree (Ministry of VROM (1995)) is given. With shades the values exceeding this maximum value are marked. For the untreated sludge the emission of fluoride, sulphate, and four exotics (molybdenum, antimony, selenium and vanadium) are exceeded. The measurement for chloride was not successful.

The emission values of the untreated dredging sludge are relatively low, but during ripening organic matter is oxidized, releasing some compounds more. Looking at the emission of the sample 0/0/1 without additives after ripening reveals that the emission of some elements has increased significantly. Besides the values of sulphate and the exotics, also the values of copper and nickel exceed the maximum permissible emission. On the other hand, the value for fluoride has dropped below E_{max}. The values for the other constituents are all below E_{max}.

By mixing cement and lime a few changes can be observed in the leached concentrations. The values of chloride, copper and nickel decrease with increasing amount of cement. The values for the samples with 15% cement even drop below the maximum emission level. However, there are also constituents, like fluoride and zinc, for which the emission increases when cement is added. The emission of these constituents even exceeds the maximum value. For both constituents, the combination with lime shows a smaller increase, and the emission remains below E_{max}.

The Building Materials Decree has been adapted (relaxed) at several points in the past years. The limitations for fluoride, bromide, and sulphate have been cancelled, taking away some constraints for the applicability (Table 6). Also for the four exotics (molybdenum, antimony, selenium and vanadium) a new regulation has been formulated. When the concentration of

these constituents is below a certain maximum concentration (c_{max}) they do not have to be tested on their emission.

Table 7. Maximal concentrations for the exotic constituents (c_{max} in mg/l) according to the Building Materials decree.

Eluate	Symbol	c_0	c_{max}
Molybdenium	Mo	3.3	101.5
Antimony	Sb	4.2	9
Selenium	Se	0.03	50.35
Vanadium	V	90	146

In Table 7 these maximum concentrations are given, as well as the concentration of these constituents in the dredging sludge. The concentrations of all exotics are below $c_{max.}$ The last two columns of Table 6 indicate that the treated dredging sludge can be considered a Category 1 building material with a maximum height of 3 m, as the zinc and copper concentrations are still slightly exceeded (Brouwers et al. (2005)).

6.4 Conclusions

The binding of water enhances the increase in dry matter content and accelerates the ripening process such that the material has reached the preferred consistency in a much shorter time. By adding 7% cement and ½% lime the ripening process is accelerated by a factor 3. Larger amounts of additive do not accelerate the ripening process proportionally, so for lightly contaminated sludges this is a feasible treatment route. By decreasing the handling time the depots can be used much more efficiently.

In regard to binding, for the considered heavily contaminated sludge (Class 4), it is recommended to add 14% cement and 1% lime. With this addition ripening is speeded up, and the sludge is rendered into a Category 1 building material. In contrast to Category 2, this is a building material that can be used freely in civil works, so without additional measures (such as an envelope) to reduce the emission to the environment. In a more recent project, contaminated soil has been treated with cement, lime and gypsum, and transformed into concrete blocks, a shaped building material (De Korte and Brouwers (2008)).

7.   CONCLUSIONS

New European regulations allow more and more the performance design of materials and structures. 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 and immobilisates 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 slags, 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 (SCC) to 0.30 (earth-moist concrete) N/mm^2 per kg/m^3. For the reader's reference: considering a steel density of 7900 kg/m^3, this material would need a compressive strength of 1738 N/mm^2 to 2370 N/mm^2 to match these cement efficiencies. Though the comparison is not completely fair, as full hydration of 1 g of the cement requires about 0.4 g of water, the required steel strength is not so easy to achieve.

Based on *mineral oxide engineering*, slag reactivity and hydration can be simulated, and shrinkage-compensating additions developed. Another result is recipes that speed up the ripening process of dredging sludge, and that render highly contaminated dredging sludge into a building material. 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 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).

Some of the properties that have to deal with the durability of materials and/or a structure are more difficult to assess (than for instance the 28 days compressive strength) and to fit in a performance-based design. For concrete, one can think of freeze-thaw resistance, susceptibility to chloride ingress and rebar corrosion, aggregate reactivity (ASR) etc; though for this purpose accelerated tests have been developed. In case of immobilisates, one can think of the long-term immobilisation effect and actual leaching behaviour. As an alternative or in addition to the employed accelerated tests, one could also involve the designer and contractor in the lifetime performance of the object. Recent developments in procurement routes and contracts, which were addressed in the beginning of this paper, enable this approach.

Summarizing, the recent "functional demand" approach, the new contract forms and alternative procurement routes, as well as the combined particle size engineering and mineral oxide engineering presented here, enable a cost effective and sustainable development of civil and residential structures.

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