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Recipes for porous building materials, More with less

Abstract

The building sector, comprising both buildings and infrastructure, is the largest consumer of energy and materials. As well as the huge amount of raw materials involved, enormous amounts of energy are also used for the production and transport of raw materials, building materials and products. Among all building materials, concrete is chemically and physically the most complex, scientifically the most interesting, and its worldwide production is larger than all other man-made materials combined. In this paper methodologies and examples are presented of more environmentally friendly concretes.

Introduction

The building sector, comprising both buildings and infrastructure, is the largest consumer of energy and materials. Table 1 shows the global production of the most important man-made materials in 2008.

Table 1: Global production of materials in million tons (2011).

Timber	4000	Quicklime	130
Plastics and rubber	300	Glass	120
Steel	1600	Cement	3500
Gypsum	250	Concrete	21000

Some of these materials are exclusively used in the building sector; others such as steel and timber are also used in other industries. The numbers illustrate that building materials are globally of the utmost importance, both economically and environmentally, and their production may involve contamination and the depletion of finite resources. Contamination concerns emissions to water, air and soil, and the production of waste, stench, noise, and other forms of nuisances. This takes place during production, but also during the entire life-cycle (and beyond) of a material and object. In contemporary societies the aspect of 'contamination' has largely been solved in the past 40 years. The challenge we are now facing is a more efficient use of resources.

Many of the building materials contain irregularly shaped particles, of various sizes (polydisperse), mostly randomly packed as is the case in concrete. The particles need to be combined in a specific way to obtain the desired properties of the building material. In other words, there is a need for recipes according to which the raw materials are combined and processed into the desired materials or products. These products not only have to fulfill a broad range of technical demands, but must also meet requirements with respect to maintenance, repair, recycling, sensory qualities etc. The raw materials and ingredients need to be available in sufficient quantities of constant quality, and the product should be manageable at the building site. A porous material that often fulfills these requirements is concrete.

Concrete is a spectacular material, not only because of its enormous production volume. A conventional concrete consists of cement, aggregates and water, and comprises grains with a size ranging from 300 nm to 32 mm, in massive constructions (e.g. dams) even to 64 or 128 mm. There is no man-made material in which such a broad range of particle sizes, comprising five decades, are combined. In fresh state it is fluid and enables a high degree of design freedom, while in the hardened state concrete is durable and almost maintenance-free, with a great architectural potential.

Cement is the most energy-intensive and costly ingredient of concrete, and also produced in huge quantities (Table 1). The manufacture of cement clinker in the rotary kiln is an energy-intensive process. In recent decennia the efficiency of these kilns has increased. Thermodynamically about 3.0 GJ/ton cement clinker is needed, the most modern rotary kilns can achieve 3.6 GJ/ton, and a typical average value for the already operating kilns in developed countries is 5.0 GJ/ton. The most modern kilns produce 10,000 tons of clinker per day. Energy efficiency is improved by replacing conventional fossil fuel with waste as a low-cost secondary fuel, e.g. ground car tires, bone meal, sewage sludge, paper sludge etc. When using alternative fuels, sintering temperatures lower than 1450°C can be seen, which is also beneficial for energy saving [3].

Savings and optimization are also possible on the materials side. By-products from other industries can be used as a substitute for the feedstock of the kiln. If these materials have cementitious properties, they can even substitute the end-product, clinker. Blast furnace slag (BFS) is a by-product from the steel industry and a common substitute for clinker. The use of so-called slag cement results in very durable concrete and comprises about half of the Dutch cement market [4]. Powder coal fly ashes have a very similar composition to clay, and class F fly ash is similar to OPC. These fly ashes are produced in huge quantities (Table 2).

Table 2: Global production of by-products in million tons (2008).

Coal ashes	1000	Blast furnace slag	120
Steel slag	140	Flue gas desulfurization (FGD) gypsum	50

Fly ash can also substitute clinker, and a substitution rate of 30% is already common. A recent study presented a substitution level of 50% [5]. Both slags and fly ash contain non-crystalline (amorphous) mineral oxides which, in contrast to their crystalline pendants, are reactive.

It has been seen that the cement industry is reducing the environmental impact of cement, for example by fuel and material substitution. The building industry, and the concrete industry in particular, is also interested in a further reduction of cement clinker and even cement, for example by adding inert powders (i.e. fine aggregate) and reactive powders to the concrete mix. One of the performance criteria that is gaining importance is the environmental footprint of the building material used. For concrete, these developments imply smart use of cement, which is the most energy- and cost-intensive component of concrete. A second, equally important motivation is cost reduction, as cement is the most expensive component in a concrete mix. For a sound concrete recipe, all the ingredients need to fit both physically and chemically: this is achieved by ‘particle size engineering’ and ‘mineral oxide engineering’.

Particle size engineering

Particles of various sizes are combined to produce the concrete mix. The combination of all individual particle distributions results in an overall particle size distribution of the mix. This overall grading of the mix, containing particles from 300 nm to 32 mm, determines the mix properties in fresh state: the flow properties and workability. But the properties of the hardened concrete, such as strength and durability, are also determined by the overall particle size distribution. A mix design tool has been developed based on the insight that superior properties of a granular mix are achieved when a so-called geometric particle size distribution is obtained considering *all solids in the mix* (so not aggregates only), an idea already put forward in 1950 [6]. Geometric particle arrangements had been proposed much earlier [7], in their study of *aggregate packing* more than 100 years ago.

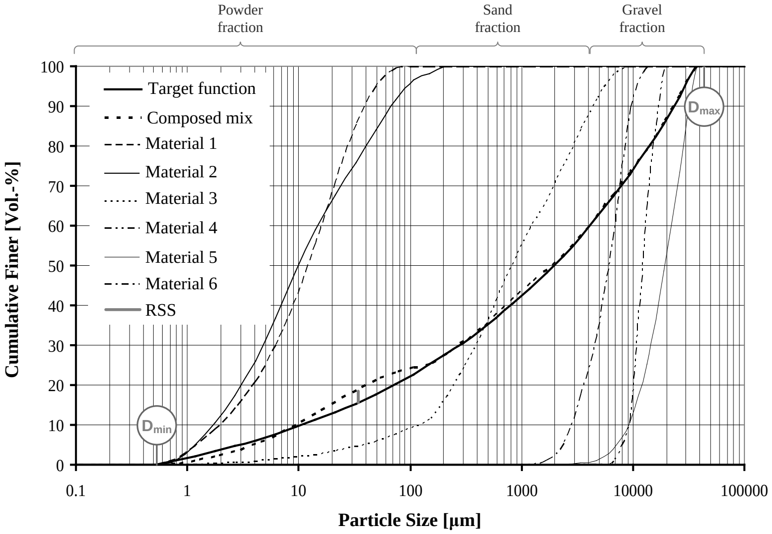

Figure 1: The cumulative particle size distribution (PSD) of all ingredients in a mix (measured with a laser granulometry and sieves), and the PSD of the mix (dashed line) composed with the help of the mix design tool. The target function (solid line) is also shown [8].

Using linear optimization, a fit of a granular blend containing all the solids used, is made according to the defined distribution function [8-10]. Figure 1 shows the cumulative particle size distribution or PSD (close to lognormal distribution) of a number of ingredients (micro-powder, cement, sands, gravel etc.), which are combined in a way that their mix best approaches the geometric packing represented by the ‘target function’. The logarithmic scale in Figure 1 again illustrates the enormous particle size range in this typical concrete mix, namely five decades.

The concretes designed with the presented approach show excellent properties in both fresh and hardened states. SCCs have been designed and produced with a D_{max} of 32 mm, with recycled aggregates, with microencapsulated phase changing materials (PCMs), with photocatalytic TiO_2, with dimension stone ‘waste’ etc. Concretes with a specific density of 1100 kg/m^3, a thermal conductivity of 0.27 W/mK and a 28-day compressive strength of

37 N/mm^2 have also been developed using lightweight aggregates [8, 10]. A spin-off project, with the province of Overijssel, the municipality of Hengelo and Struyk Verwo Groep, concerns a street paved with 1000 m^2 TiO_2-containing photocatalytic concrete, a patented technique [11]. This street is monitored and modeled using CFD, and so far the NO_x concentration, on average, was 19% (considering the whole day) and 28% (considering only afternoons) lower than the obtained values in the control street. The pertaining standard deviations (σ) amounts 18% and 20%, respectively. Under ideal weather conditions (high radiation and low relative humidity), a concentration decrease of 45% could be observed.

Compressive CVC and SCC strengths of 30 to 60 N/mm^2 have been achieved with a total binder (cement clinker and cementitious by-products) content of 200-270 kg/m^3 [8]. EMC with a compressive strength of 100 N/mm^2 has been produced with 325 kg/m^3 OPC as sole binder. More importantly, it was seen that the flexural strength hardly decreased when the OPC content was reduced to 175 kg/m^3 [10]. Much better workability and higher strength were obtained compared with concretes with the same cement contents. In this regard, the property *cement efficiency* was introduced, defined as compressive strength (N/mm^2) per unit of cement content in a concrete mix (kg/m^3). Equivalently, it has become possible to design equally performing concretes with less superplasticizer (and without viscosity modifying admixtures) and high cement efficiencies.

For the design of concrete, traditional methods and prescriptions concern for instance the cement content, the total content of particles smaller than 250 μm and the water-cement ratio. The developed design method allows for a more performance-based mix design. Many mixes of members of the sponsor group (see Acknowledgements) have been optimized with regard to efficient cement and admixture use. In many cases this has resulted in the incorporation of alternative ingredients, such as aggregates, inert powders (fine aggregate) and cementitious by-products. For use as binder in mortar, concrete or stabilized waste, insight into the hardening reactions of cement clinker, cementitious by-products and contaminants (if present) is required, which is the rationale for mineral oxide engineering.

Mineral oxide engineering

The hydration of the mineral oxides appearing in OPC, the most abundant binder, was first studied. Based on the water retention data provided by Powers and Brownyard [12], the hydration reactions of the four major clinker phases (C_3S, C_2S, C_3A, C_4AF) and their hydration products, such as C-S-H and CH etc., were quantified [13, 14]. Next, reaction models for alkali-activated slag and slag-blended cement were established based on stoichiometric calculations [4]. The models correlate the mineral compositions of slag and Portland cement clinker, and their blending proportions, with the quantities and compositions of the hydration products formed, including their rate (reaction speed) of formation.

Blast furnace slags typically possess C/S ratios of about unity, and part of the CH produced by the hydration of C_3S and C_2S in the clinker is available to increase the C/S ratio of C-S-H formed from the slag. Chen [4] proposed that the fraction of consumed CH is proportional to the difference in C/S ratio of the slag and the C/S ratio of C-S-H produced by the clinker, namely 1.7, a concept that is compatible with reality (Figure 2).

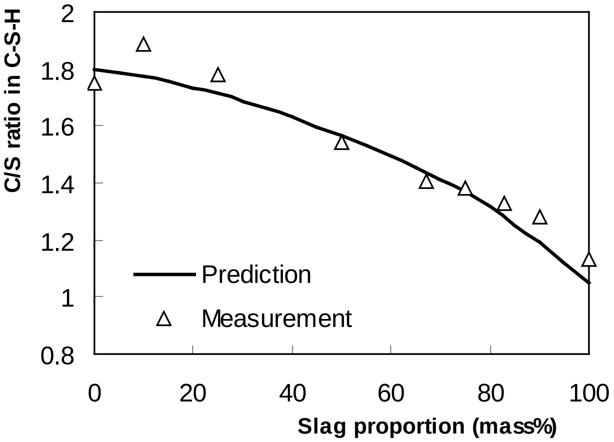

Figure 2: Predicted and measured C/S ratio in C-S-H versus slag proportions in blended cement [4]. C-S-H is the most abundant hydration product.

For the numerical simulation of the hydration reactions and the pore water composition, in the author's group a 3-D simulation model (CEMHYD3D) from NIST [15] was adopted and extended [4, 16]. Performing cellular-automata like rules on the matrix of voxels simulates the hydration (Figure 3).

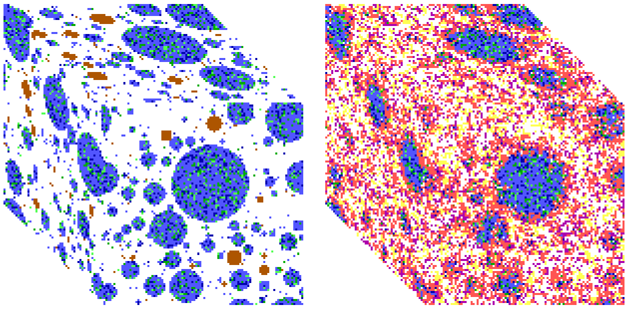

Figure 3: Development of OPC microstructure by CEMHYD3D in a 100 µm box, at the left the initial OPC/water system, and at the right the partly hydrated system [16].

Van Eijk [16] and Chen [4] modeled the pore water composition (e.g. pH), and incorporated the reactions of fly ash and slag. As well as the chemical extensions, the kinetics of the model has also been modified. In the original model the system resolution had considerable effect on the simulation results. The simulations performed with different system resolutions (from 0.5 to 2 µm) demonstrated the robustness of the improved model [4]. Currently, CEMHYD3D has been extended with several additional possibilities which enable the hydration of particles as small as 0.2 µm, designated as 'multi-scale' feature [17].

Furthermore, several secondary binders have been designed and tested for members of the sponsor group. Motivated by clause 5.2.5.3 of the EN 206-1 standard, these companies dose cementitious by-products to the mix themselves, and follow the relevant attestation route. This development has increased utilization of cementitious by-products from different sources, so not only the traditional blast furnace slag and powder coal fly ash.

Both suppliers and appliers (concrete companies) of these by-products are assisted by investigating their suitability as binder. For their application as binder in concrete, three technical criteria are important as well as price (sometimes negative if it relates to 'waste'), constant composition and availability in sufficiently large quantities:

i) The workability, hardening and related strength development.
ii) The durability of the product.
iii) The presence of contaminants.

A first indication for the suitability of a material as cement substitute is obtained by preparing standard mortars and studying the fresh workability, and the subsequent strength development during 28 days. For this purpose also CEMHYD3D is used. For these cementitious by-products, it can also be opportune to blend them to obtain a composition of particle sizes and mineral oxides with optimum reactive characteristics.

Durability, for instance, can be assessed by measuring water absorption, water intrusion and freeze-thaw resistance, and by accelerated chloride migration tests. An emerging test is the rapid chloride migration (RCM) test [18]. The apparent diffusion coefficient determined by this method follows from assuming Cl^- concentration profiles in the specimen as shown in Figure 4 (left).

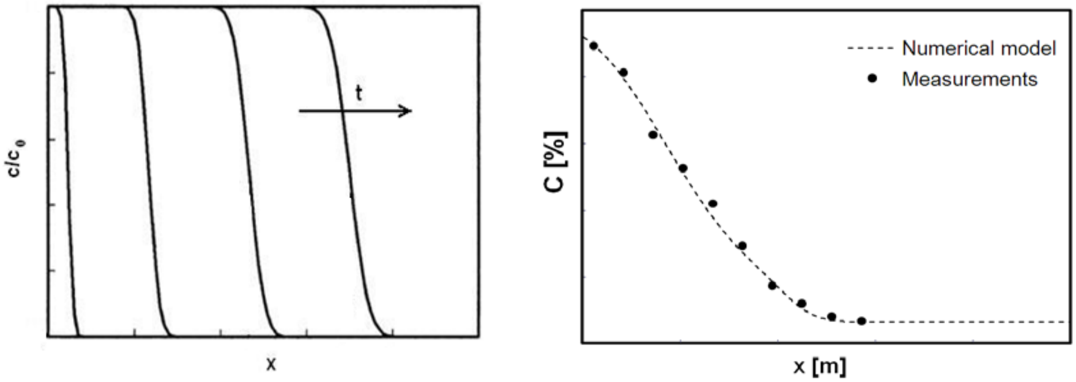

Figure 4: Chloride profiles in a concrete during RCM test: at the left the assumed profile, and at the right a measured profile and the model prediction [19].

A typical example of a true measured profile, however, can be seen in Figure 4 (right). A new diffusion model based on non-linear (Freundlich) Cl^- absorption by the concrete and non-equilibrium with the pore water, yielded excellent agreement (Figure 4). This new model yields a more realistic diffusion coefficient together with the mass transfer coefficient.

As well as strength and durability, the purity and maximum level of contamination, both in composition and in leaching, are also relevant. In the Netherlands, the Soil Quality Decree sets limits for the composition and leaching of granular materials, designated as 'non-shaped', with respect to chloride, mercury, molybdenum and strontium, for example. If these requirements are not met, the granular material is considered as 'waste', and landfill of these materials is a remaining option. The composition and leaching are also leading in selecting the type of applicable landfill, namely for mineral or hazardous waste, and the relevant safety measures as laid down by the Landfill Decree.

By stabilization, e.g. combining different materials and adding primary binders (quicklime/hemi-hydrate/cement), a granular ('non-shaped') or a shaped product can be obtained for non-hazardous landfill, and sometimes it is even possible that the treated material meets the Soil Quality Decree requirements of a building material.

Contaminated soil and dredged soil material are interesting 'wastes' that can be combined with primary binders and cementitious by-products (whether or not contaminated). By treatment of these 'wastes', cheaper landfill or even the application as building material becomes feasible. This saves the production of primary building materials, as well as the space and costs associated with landfill. A few stabilization projects have been carried out in which contaminated soil and dredged spoils have been made into acceptable building materials [17, 20]. Non-shaped stabilized wastes can be used as road base material, traffic noise barriers, etc. Shaped stabilized wastes may be used as plain (unreinforced) concrete products such as slabs and blocks.

Hydration models are also used to relate (Freundlich) binding and transport of anions (chloride) and cations (heavy metals) and microstructure. This is related to binder recipe and hardening conditions [21]. Fixation of heavy metals is important for the stabilization of waste, binding of chloride for stabilization *and* the durability of concrete structures, as seen before.

Conclusions

Changing environmental regulations and technical standards enable performance-based recipes rather than prescriptive-based recipes of cement-based construction materials, driving product innovation. The scientifically and technically driven design and production methodology will be continued to obtain more sustainable, durable and functional concrete. There are still plenty of practical problems to be solved, scientific questions to be answered, new raw materials that enter the market, and conceivable product innovations. Furthermore, the present approach is used to develop architectural building products/components such as cladding materials. The sensory properties are then of special interest, and this is an endless source of new ideas for our research. The air purifying and self-cleaning concrete just referred to is already of interest to architects. This type of concrete has been applied in the Dives in Misericordia church in Rome (architect Richard Meier), and the George Harrison Memorial Garden in London. And the lightweight SCC mentioned above is suitable for monolithic concrete buildings.

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[1] Each member contributes € 5000 (excluding VAT) per year.

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