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# Recent advances in modeling for cementitious materials

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ABSTRACT

Since the 12th International Congress on the Chemistry of Cement (Montreal, 2007) there has been an intensive research activity devoted to describe the cementitious materials by computational means. This review aims to summarize the collective effort performed on this topic during the last 4 years, and highlights the most relevant results.

**Contents**

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## 1. Introduction

Throughout the history of science models have played an important role. Nevertheless, even the most advanced models of cement based systems are still (crude) simplifications of reality. But fully aware of the fact that model and reality are two different things, we can still observe an increasing demand for models, both in science and engineering. First of all, models are helpful vehicles for understanding and describing the engineering properties of cement based systems, for which purpose these models require knowledge from lower levels [1,2]. Models are also indispensible for performing long-term performance and service life predictions [3] and for generating quantitative data as input for sustainability considerations [4,5]. Models, as part of curing control systems on the building site, support decision making processes that may lead to time savings in the building process and enable the simulation of complex coupled problems, for example degradation processes occurring in concrete while under stress [6]. For developing new materials and material modifications, models can help to reduce the number of trial-and-error cycles that are needed when we actually don't know where we are going and what our material is actually all about. An interesting and challenging example is the role to models for developing self healing materials [7]. Gerard [8] emphasized the industry's need of reliable tools, *i.e.* models, for risk management, decision making, dealing with uncertainties and for teaching and training people. These even more the more complex the systems, *i.e.* concrete mixtures, and/or the exposure conditions are.

This brief and incomplete survey shows a variety of reasons why models are considered increasingly important. Thereby the evolution of models and modeling activities has received much stimulus from the parallel fast evolution of computation power. The availability of strong computers and parallel computing systems has disclosed new horizons. Promising results of *ab-initio* calculations have been published, whereas multi-scale modeling has enabled us to span multiple orders of magnitude, from the atomic scale to the macro-scale of high rise building and huge concrete dams.

A comprehensive review of models used in the research of cement based systems would bring us far beyond the scope of this contribution. Here we have to concentrate on recent advances in models and modeling. However, we have to refer briefly to the preceding period in order to get a picture of the state-of-art in 2006. This review should provide us with a reference for evaluating the new information that has been presented in the past four years and to outline a perspective for further developments in the future.

## 2. Models

### 2.1. On the nature of models

The word “model” is increasingly used and runs the risk of losing its original meaning and becoming an inappropriate term for clear discussions. After “InvestorWords.com” a model is a representation of a system that allows investigating the properties of the system and, in some cases, prediction of future outcomes. Another and more comprehensive definition defines a model as “a graphical, mathematical (symbolic), physical, or verbal representation or simplified version of a concept, phenomenon, relationship, structure, system, or an aspect of the real world. Since most objects and phenomena are very complicated, do consist of numerous parts and are much too complex to be comprehended in their entirety, a model contains only those features that are of primary importance to the model maker's purpose” [9].

Given the fact that we are used to speak about models for cement paste, mortar and concrete, and that, at the same time, a model is, by definition, a representation of a *system*, the logic conclusion could be that cement paste, mortar and concrete should be considered as systems. Looking at these materials as systems is really a step forward, without claiming that from now on we should speak about “system properties” instead of “materials properties”. Looking at cement paste, mortar and concrete as systems, however, puts our mindset in the right direction for investigating cement-based materials at different scales and in all subsequent stages of their lifetime [10].

The fact that even the most advanced models are, by definition, simplifications of reality and generally developed for (only) one specific purpose, should prevent us judging models against inappropriate criteria. This risk is bigger the less accurate we are in defining the purpose individual models are supposed to be used for.

### 2.2. Categorization of models

Models can be categorized, or classified, in different ways. We prefer the word ‘categorize’ instead of ‘classify’, in order to avoid any unjustified value judgment of models. Models for *hydration* of cement-based systems have been categorized in four groups, *i.e.* overall kinetics, particle kinetics, hybrid kinetics and integrated kinetics.

#### 2.2.1. Overall kinetics

With ‘overall kinetics’ of cement-based systems, concepts and formulae are denoted which describe the hydration process in the time domain *without explicit* allowance for the effect of the formation of physical contacts between reacting cement grains on the reaction rate. The effect of the particle size distribution, the poly-mineral character of the cement, and spatial constraints that might occur during the hardening are allowed for *implicitly*.

### 2.2.2. Particle kinetics

Particle kinetic models focus on the dissolution of reacting grains and formation of a shell of reaction products around these grains. Different shells with different shell properties have been distinguished, or at least proposed, *i.e.* shells consisting of inner product, outer product and a dissolving intermediate shell. The diffusion properties of the individual shells determine the reaction rate in the stage that diffusion is the rate controlling step. The development of particle kinetic models dates back to the thirties, whereas more sophisticated ones were proposed in the sixties and seventies. Most of these models are typically analytical models and form the basis of hybrid and integrated kinetic models mentioned hereafter. Models that disregard the formation of interparticle contacts will fail, by definition, to describe the formation of a microstructure and the associated pore structure and microstructure-related materials properties in a direct way.

### 2.2.3. Hybrid kinetics

With hybrid kinetics, models are denoted which explicitly allow for the effects of particle kinetics, the particle size distribution of the cement, and, additionally, for one or more other relevant rate influencing factors, such as the chemical composition of the cement and the pore solution and the moisture state in the hydrating mass. The formation of interparticle contacts, however, and their effect on the rate of reaction are not modeled explicitly.

### 2.2.4. Integrated kinetics

The term “integrated kinetics” has been introduced for models which describe the formation of interparticle contacts and their effect on the rate of reaction *explicitly* [11,12]. These models, mostly computer-based simulation models, can be considered as *operators*, which generate, or have the potential to generate, microstructural data in a *direct* way. Such an operator may consist of a set of mathematical formulae or computational procedures for describing (changes in) the state of the spatial distribution of the anhydrous cement, the reaction products, the moisture state, and, if possible, the state of stresses which develop during hydration.

Another way to categorize models was used by Garboczi [13], who differentiated between *fundamental* and *non-fundamental* models. A fundamental model is defined as a model that deals directly with the microstructural elements that determine the properties of interest of the system. Models which do not directly represent the microstructure at the cement particle level are considered non-fundamental. Integrated models, at least some of them, can be considered as fundamental models. It depends on the extent to which the integrated kinetic model is able to generate a ‘realistic’ virtual microstructure and how this is achieved. Particle kinetic models are typically non-fundamental, since they do not explicitly describe the formation of interparticle contacts and of the resulting microstructure.

Wittmann [14] distinguishes between two levels of sophistication of materials models. Physical models as defined as *first order models,* which allow us to get insight into essential aspects of reality. For characterization of materials properties, *i.e.* of complex systems, we need *second order models*. These models are simplifications of the complex reality they claim to represent. Wittmann furthermore distinguishes between *analytical* and *numerical* models. Analytical models are mathematical description of observed phenomena, for example of crack formation and crack propagation in porous media. Also most of the aforementioned overall kinetic models are analytical models. Numerical models are typical for researching, simulating and predicting the performance of complex heterogeneous material, which can deal with volume concentrations, properties of aggregates and matrix and of the interface properties between matrix and aggregates and/or fibers. In this paper both analytical and numerical models will be considered as they are used at different scales of observation and for different purposes.

## 2.3. Models and scales

Another way to categorize models is by their characteristic length scale. Wittmann proposed three independent simulation levels covering, at the time, the whole range of multi-scale systems [15], *viz.* the micro-, meso- and macro-level.

### 2.3.1. Macro level

When considering the macro-level (Fig. 1a) with respect to the behavior of cementitious materials, continuum model-based calculation, like finite element methods or mesh free particle methods, have been profusely employed for structural calculations, with more than a proved success. The main postulate of these continuum models is that the state of concrete can be monitored by parameters which homogenize the behavior of concrete at this level. All the internal structure is smeared out by average parameters.

### 2.3.2. Meso-level

The next modeling level is the so called meso-level (Fig. 1b), where the aggregates and the cement paste are explicitly differentiated.

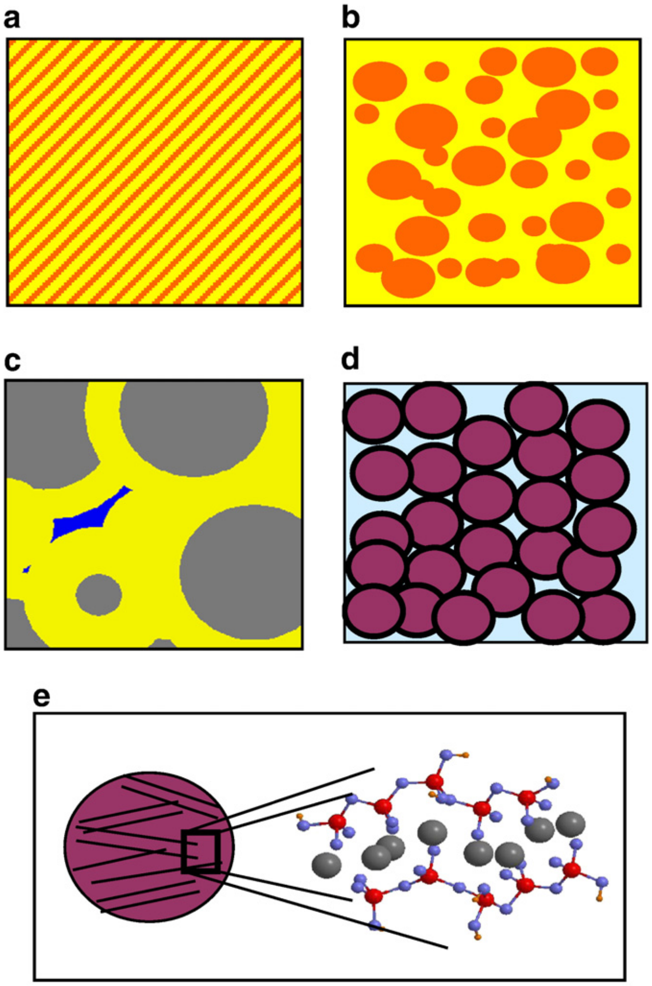

**Fig. 1.** Schematic multi-scale description of concrete; (a) macro, (b) meso, (c) micro, (d) sub-micro and (e) nano.

Here, both finite element programs and lattice-models have turned out to be appropriate for describing and simulating the materials behavior, including the formation of cracks under any type of loading.

### 2.3.3. Micro-level

Finally, the micro-level (Fig. 1c) corresponds to the level where the cement paste is described in terms of their constituents and where chemistry and thermodynamics actually begin to play a role. Over the years, researchers have proposed models that simulate the progress of the hydration process and being a basis for the associated properties. Mature models like CEMHYD3D [16] (part of) DUCOM [17], HYMOSTRUC [11], Navi's model [18], and the more recently proposed μic [19,20] belong to this category of models. In essence they monitor the hydration process by describing simultaneously over time the dissolution of cement grains and, be it in different ways, the microstructure development (integrated kinetics).

Today it is clear that the aforementioned multi-scale computational description should shrink down to smaller modeling levels. Much of this new perspective must be attributed to researchers like Kalinichev, Kirkpatrick, Scrivener, van Damme, Pellenq, etc. who recognized that it is the nano-scale structure of cementitious materials that is responsible for cohesion and durability. In this sense it is worth reminding the seminar lecture of Prof. van Damme during ICCC 2007 [21] foreseeing that the next source of improvement of cement-based materials would lie in the fine-tuning of the nano-scale hydrates and colloidal porosity along with the crucial role of molecular modeling in this important endeavor. This enriching lecture grasped what actually happened along these last four years; namely that the miniaturization of our description of cementitious materials is currently one the most fresh trends in modeling.

Unfortunately the distance between the micro-level and the nano-level is currently too large so as to be bridged by atomistic simulations only. While the improvement of computers is expected to overcome this problem in the near future, current attempts propose an intermediate level (the sub-micro level) to facilitate the handshake between scales.

### 2.3.4. Sub-micro-level

This is the level where the colloidal and gel-like properties of C–S–H are accounted for (Fig. 1d). Computationally speaking this scale is usually tackled by coarse grained simulations which assume the existence of C–S–H particles and study their aggregation.

### 2.3.5. Nano-level

Finally simulations at the nano-level (Fig. 1e) atomistic simulations are employed to get insight in the short-ordering of cementitious structure, being the discussion usually established in terms of tobermorite and jennite crystals (two known C–S–H analogs). Current computational capacities limit the employment of these sorts of simulations to small pieces of material (typically $<10$ nm).

The remaining of this paper aims to summarize the latest achievements in each of the levels discussed in Fig. 1. Methods proposed to jump from one scale to another will be dealt with briefly. However, one comment should be made in advance. The modeling works dealing with pure kinetic aspects will not be covered in detail. To know more about these aspects we remit the reader to a recent review by Thomas et al. [22], where the state of the art on this issue is thoroughly discussed.

## 3. Nano scale modeling

When our description of cement-based materials shrinks down to the nanoscale, the only reliable computational methods are those which pay implicit attention to the atomic nature of concrete at this scale; namely atomistic simulations. The employment of atomistic simulations to describe cement-based materials is a quite new field. However, thanks to several pioneering works [23–28] there is currently a steady impetus in the application of fundamental methods like *ab-initio*, Monte Carlo (MC) or Molecular Dynamic (MD) simulations for the description of cement-based materials. A summary of the most relevant findings is provided below.

### 3.1. Kinetic aspects

Molecular modeling studies done to date have primarily focused on the structural properties of the cementitious phases, rather than the intrinsic kinetic aspects of cement hydration. However, the accurate structural information gained from these atomistic modeling studies may serve as valuable input for the kinetic models. One interesting possibility is the one proposed by researchers at Labein and the CFM [29,30], where quantum simulations based on the Frontier Orbital Theory [31] were employed to determine the reactive sites of $C_3A$ (see Fig. 2). This novel study enabled to map the electrophilic and nucleophilic areas of a cubic tricalcium aluminate unit cell. According to their simulations all the oxygen atoms across the unit cell are reactive under electrophilic attack of species like $Ca^{+2}$ ions and water molecules (Fig. 2a and b). It certainly implies a high number of reactive sites per unit cell, and a small resistance of the aluminum rings to the attack. This could be one of the reasons of the high hydraulic activity of $C_3A$. On the other hand, the simulations demonstrated that some areas are especially reactive in the case of nucleophilic attack ($OH^-$ and $SO_4^{-2}$) (Fig. 2c and d). The presence of specific sites for the reaction with sulfate ions might point to a blockage mechanism for the retardation, something which was already proposed in the literature [32,33]. It is worth noting that the same computational scheme can be easily extended to other cement phases, something which might serve in the near future to design new clinker phases.

### 3.2. Structural aspects

Atomistic simulations are especially well equipped for application to crystalline structures. Several works have been lately carried out on the crystalline phases of cementitious materials; *e.g.* $C_3S$ [34], $\beta$-$C_2S$ [34], $C_3A$ [30,34], Portlandite [23,34–36] etringitte [23,35], etc. These simulations have shown an overall good predictive capacity to reproduce the unit cell parameters, with discrepancies with respect to the experimental parameters of the unit cell typically below 5%.

The real challenge of atomistic simulations has been nevertheless on the description of C–S–H gel. The computational description of C–S–H gel is much more difficult than the one needed for the aforementioned crystalline phases. On the one hand, the molecular organization of C–S–H is still unsettled, so atomistic simulations cannot benefit from a well-defined starting atomic structure. Though C–S–H gel does not show a long-range crystalline order it is widely accepted that its short-ordering is related to the organization found in crystalline C–S–H structures like tobermorite and jennite (see Fig. 1e). Moreover, different experimental techniques like neutron scattering [37,38] or synchrotron X-ray measurements [39] suggest that the lamella structures (C–S–H sheets) stack together to form ~4 nm-sized C–S–H features (particles?) from which the whole C–S–H structure is built (see Fig. 1d and e). How and why these basic building blocks are formed have been largely puzzling, though important steps have been recently given that might provide new clues at this respect.

The atomic structure of C–S–H gel being not completely known, most of the atomistic attempts to computationally describe C–S–H gel have been based on simulations over its mineral analogs (tobermorite and jennite) or have exploited different morphological features present in both layered models [23,24,40–43]. Important conclusions can be reported: On the one hand, the simulations [26] stubbornly demonstrate that contrary to what happens in smectite clays, the calcium ions present in the interlayer spaces are not exchangeable

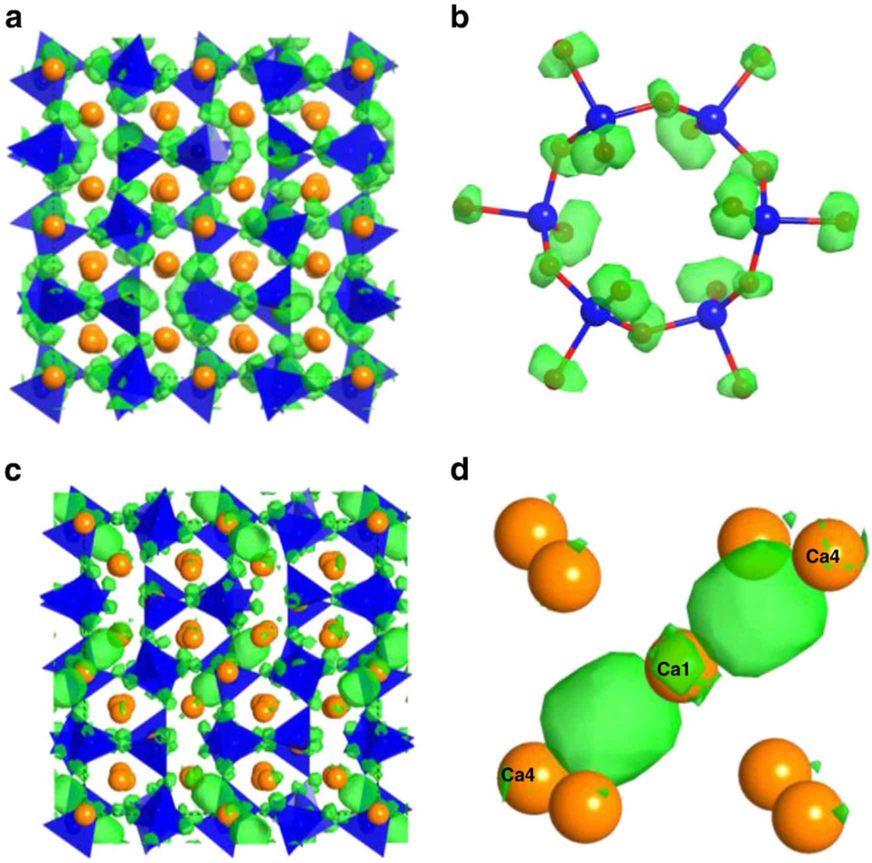

**Fig. 2.** (a) General view of the electrophilic areas (represented by the green clouds) of the unit cell. (b) Detailed view of an $Al_6O_{18}^{-6}$ ring. (c) General view of the nucleophilic areas (represented by the green clouds) of unit cell. (b) Detailed view, where the special reactive areas around Ca1 and Ca4 ions are clearly visible.
From [29].

since they are trapped by strong iono-covalent forces; *i.e*. the interlayer Ca ions are chemically similar to those bound into the main calcium oxide layers. On the other hand, the simulations also teach us that the interlayer water behaves much differently from bulk water. In fact, the computed self-diffusion coefficient for the water molecules turn to be about $3.4\times10^{-12}$ $m^2/s$ [26], a figure ~1000 times smaller than the experimental value of bulk water ($2.3\times10^{-9}$ $m^2/s$). This result is clearly consistent with the known fact that the dynamic of water molecules is deeply affected by the nanoconfinement [44–46] and the presence of surfaces [24,46].

The pivotal role of water on C–S–H gel has been clearly addressed in a recent work of Pellenq et al. [47]. Guided by NMR measurements [48], the authors shortened the chains of a dried 11 Å tobermorite so as to reach a C/S ratio of 1.65. Afterwards, they performed Grand Canonical Monte Carlo simulations of water adsorption, coupling the defected dried 11 Å tobermorite sample to an external reservoir at a chemical potential corresponding to liquid water at 300 K. Interestingly, their structural analysis demonstrated that water molecules could be adsorbed not only in the interlayer space but also in the small holes present in the defected structure. That being so, the adsorption of water enabled a plausible explanation for the existing mismatch between the densities of 14 Å tobermorite ($\rho=2.18$ g/cm$^3$) and jennite ($\rho=2.27$ g/cm$^3$) and the experimental values found in C–S–H gel ($\rho=2.6$ g/cm$^3$) [37].

A different but complementary approach to the above mentioned simulations based on tobermorite and jennite minerals is the one proposed by Dolado et al. [49]. In essence the authors simulated the formation of C–S–H gel by analyzing the polymerization of silicic acid, $Si(OH)_4$, in the presence of hydrated Portlandite molecules ($Ca(OH)_2$ $4H_2O$). Though no structural constrain was imposed, the simulations succeeded in capturing the presence of tobermorite-like and jennite-like environments and predicted that at low Ca/Si ratios the simulated C–S–H systems can be seen as mixtures of long polymerized (pentamers and longer chains) 11 Å tobermorite, 14 Å tobermorite, and jennite structures, whereas at high Ca/Si ratios they seem to be composed of short (dimeric) 14 Å tobermorite and jennite pieces.

This Molecular Dynamic scheme has been recently extended to accomplish the difficult task of describing the formation of the 4 nm-sized C–S–H basic units [50]. In fact, to ensure that several 4-nm C–S–H features could be observed in the simulations, the authors studied the formation of C–S–H clusters by placing roughly 60.000 atoms in a square box of 8.8 nm dimension. The atomistic simulations predicted the appearance of a branched three-dimensional C–S–H nanostructure with segments 3×3×6 nm sized (see Fig. 3) which provided a satisfactory comparison with the SANS and water sorption/desorption measurements, while concurrently accounting well for the microstructural information gained from NMR, XRD and INS experiments. It is worth observing that no separate C–S–H bricks were identified at the scale under study, supporting the picture suggested in [26] that the contacts between the segments are governed by the same strong cohesive forces as those binding the layers together.

### *3.3. Performance and engineering properties*

As atomistic simulations are well suited to determine the elastic tensor coefficients of crystalline structures, several atomistic studies have analyzed the elastic response of the crystalline phases of cement-based materials [29,30,34–36,43]. The predicted values for the elastic properties of the clinker phases are given in Table 1 together with their experimental counterparts (when available). As

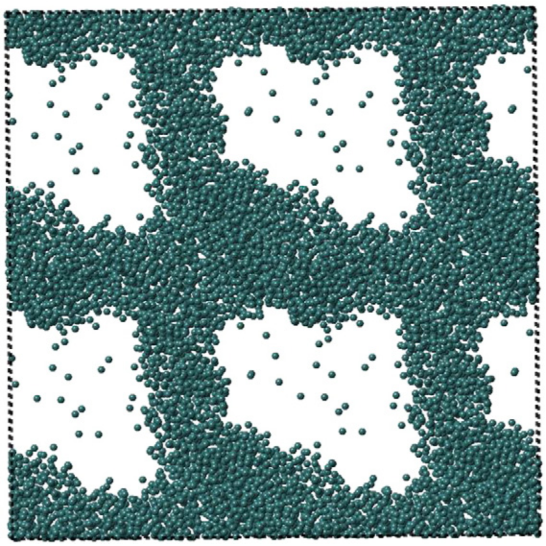

**Fig. 3.** The nano-branched structure obtained in [50]. Only Ca and Si atoms are shown in green for clarity.

can be seen, the predicted anisotropic Young modulus (E) of $C_3S$ and $C_2S$ [34,35] is in excellent agreement with the experimental values. In fact the computed figures are within the range between nanoindentation and resonance frequency measurements [51,52]. In the case of $C_3A$ there is also a quite good agreement between the predictions and the experimental values. While the Young modulus given by the force field simulations (165.5 GPa) [35] is a bit higher than the experimental data (145–160 GPa), the one given by *ab-initio* simulations (138.7 GPa) [30] slightly underestimates the experimental range. However, the calculated E for ferrite (238.2 GPa) [35] is almost twice the value measured by nanoindentation (125 GPa) [51,52]. The reason of such disagreement is not clear, so this is an interesting subject for further analysis.

The results found for crystalline hydrates like Portlandite and ettringite are also shown in Table 1. Numerous experimental studies [51–58] have determined the elastic properties of Portlandite (35–48 GPa). In general the atomistic simulations reproduce well the experimental values. Moreover, they also account well for the strong mechanical anisotropy between the perpendicular and coplanar $Ca(OH)_2$ layers; the Young modulus is ~3 times higher along the coplanar direction. The mechanical properties of ettringite have been fully determined by Brillouin spectroscopy at ambient conditions [59]. Though of the same order of magnitude, the force field simulations employed in [35] seem to underestimate the experimental figures. It seems clear that the complex structure of ettringite calls for quantum *ab-initio* simulations.

The case of C–S–H gel is again different and requires a special treatment. Up to now all atomistic works have been carried out over crystalline minerals related to C–S–H families [34,35,43,60,61]. Nanoindentation studies [53] have determined by inverse analysis that the elastic modulus of the solid C–S–H phase is about 60 GPa. The modulus values found in the literature for 14 Å tobermorite and jennite [34,35,43,60] agree with this value (see Table 1), something which supports the hypothesis that they are good C–S–H analogs. It is worth noting, nevertheless, that the moduli for 11 Å and 9 Å tobermorites are higher, in the range of 75–95 GPa [35,43,60], presumably due to their smaller interlayer spacing, which leads to greater cohesion.

Few works have dared to go beyond the elastic properties. It is worth remarking in this sense that the simulations of Ref. [47] have shown for the first time the lubricating action of the water molecules to response to shear loads in C–S–H gel. This finding is very relevant as it is reasonable to think that this lubricating behavior of water will be a necessary ingredient when describing engineering properties like “creep”. Finally we would like to highlight the recent work of S. J. Murray et al. [62] since they have performed MD simulations over C–S–H units based on 11 Å tobermorite to derive tensile and compressive strengths. While the simulations gave strengths about three orders of magnitude higher than those experimentally observed at the macroscale, they enabled to infer that bond breakage at the atomic level might be the reason for the low tensile strength in cement pastes. As the same authors claim, it is clear that further work is needed to determine how the bond breakage at the atomic level affects tensile strength in cement pastes at the meso- and macroscopic levels.

## 4. Sub-micro level simulations

As said in Section 2, the distance between the micro-level and the nano-level is still too large so as to be bridged by atomistic simulations only. Current multi-scale attempts employ an intermediate level, the sub-micro level [63,64] as a practical approach to computationally describe C–S–H gel in the scale that goes from tens to hundreds of nanometers. At this scale our knowledge of C–S–H [65–69] has been mainly centered in the recognition of the colloidal and gel-like properties of C–S–H gel. Current viewpoint is the Jenning's model (JM) [1,69]. In essence, JM incorporates the insights gained from the neutron and X-ray scattering measurements [37,39] which reveal the existence of ~4 nm-sized C–S–H features to propose that C–S–H gel is made up of the aggregation of 4-nm sized C–S–H bricks. According to

**Table 1**
Elastic properties of different cementitious phases. The bulk (K), shear (G), and Young modulus (E) are in GPa. The Poisson's ratio ($\nu$) is dimensionless.

| | *K (GPa)* | | *G (GPa)* | | *E (GPa)* | | $\nu$ | |
|---|---|---|---|---|---|---|---|---|
| | Exp | Comp | Exp | Comp | Exp | Comp | Exp | Comp |
| $C_3S$ | – | 103.0 [34,35] | – | 54.5 [34,35] | 147–135 [51,52] | 138.9 [34,35] | 0.30 [51,52] | 0.28 [34,35] |
| β-$C^2S$ | – | 111.0 [34,35] | – | 53.1 [34,35] | 140–130 [51,52] | 137.9 [34,35] | 0.30 [51,52] | 0.30 [34,35] |
| $C_3A$ | – | 133.26 [35] | – | 63.9 [35] | 145–160 [51,52] | 165.1 [35] | 0.30 [51,52] | 0.29 [35] |
| | | 102.9 [30] | | 54.4 [30] | | 138.7 [30] | | 0.28 [30] |
| $C_4AF$ | – | 175.6 [35] | – | 93.5 [35] | 125 [51,52] | 238.2 [35] | 0.30 [51,52] | 0.27 [35] |
| Portlandite | 39.5 [56] | 31.5 [34,35] | 16.36 [56] | 13.4 [34,35] | 35–48 [53,56] | 31.5 [34,35] | 0.3–0.325 [56] | 0.31 [34] |
| Ettringite | 27.3 [56] | 20.03 [35] | 9.5 [56] | 7.36 [35] | 25.0 [56] | 19.65 [35] | 0.34 [56] | 0.34 [35] |
| 14 Å tobermorite | – | 44.8 [34] | – | 19 [34] | – | 49.94 [34] | – | 0.31 [34] |
| | | 35.91 [43] | | 20.61 [43] | | 51.90 [43] | | |
| 11 Å tobermorite | – | 73.57 [29] | – | 29.19 [29] | – | 77.34 [29] | – | 0.32 [29] |
| | | 66.65 [43] | | 32.03 [43] | | 82.82 [43] | | |
| 9 Å tobermorite | – | 68.95 [26] | – | 37.44 [26] | – | 95.11 [26] | – | 0.27 [29] |
| | | 71.42 [43] | | 37.18 [43] | | 95.06 [43] | | |
| Jennite | | 40.2 [34] | – | 22.1 [34] | – | 56.06 [34] | – | 0.31 [34] |
| | | 31.83 [44] | | 21.96 [43] | | 53.55 [43] | | |

this picture, these C–S–H bricks can aggregate to form High-density (HD) C–S–H or Low-density (LD) C–S–H depending on a packing factor [1,69].

Computationally speaking, the description of the colloidal/gel-like properties of C–S–H is highly testing. Though the results of Dolado et al. [50] give for the first time some information about the sizes and shapes of the smallest C–S–H bricks, to know how and why these C–S–H pieces can eventually produce LD or HD arrangements is certainly beyond any atomistic possibility. Thus, other possibilities must be envisaged. One promising practical approach is the employment of coarse-grained simulations, in which it is assumed that C–S–H gel structure can be represented as an assembly of fictitious interacting C–S–H particles. It is worth noting that *a priori* the method is flexible enough to describe a granular or continuum C–S–H networks just by forbidding or permitting the overlap between the C–S–H particles. Although these coarse-grained simulations have been barely applied, to deal with C–S–H gel, some progress has been made so far.

Through a simple computational implementation González-Teresa et al. [70] proposed a MC scheme which reproduced the colloidal packing of nano-spherical tobermorite-like particles. By tuning the size of the initial C–S–H particles and the packing factors they constructed C–S–H globules, LD C–S–H particles and HD C–S–H particles with the same densities as those reported in the JM [69]. Afterwards the authors analyzed the so formed structures in terms of their sizes, surface areas and mechanical properties. Though the simulations gave sizes for the LD and HD arrangements much smaller than those suggested in the JM, the predicted surface areas remained close to the experimental values when realistic numerical $N_2$-physisorption experiments were carried out. This fact clearly points out that if the sizes and surface areas of JM are correct, other morphologies for the basic C–S–H particles must be sought after. This is actually what Morales-Flórez and Brunet proposed in Ref. [71]. With a packing scheme similar to this of Refs. [70,72], but employing cuboids ($3 \times 2 \times 1.4\ \text{nm}^3$) instead of spheres (see Fig. 4) the authors achieved to provide textural parameters consistent with the $N_2$-physisorption data, while predicting a globule diameter of around 45 nm, something which is in agreement with the values proposed by Bentz et al. [73].

Surely the most striking application of these coarse-grained simulations is the one recently proposed by M. Q. Chandler et al. [74]. These authors employed a discrete element method (DEM) to simulate three different specimens of C–S–H gel in which the arrangements of the particles were random packing with packing ratios of 0.56, 0.64 and 0.74 (*i.e.* those ascribed to the Loose Packed (LP), LD and HD C–S–H gels respectively [1,69]). The interparticle forces consisted of friction and contact forces together with van der Waals and double-layer forces. Afterwards, the authors performed a virtual nanoindentation experiment over the different virtual C–S–H specimens by constructing a rigid Berkovich indenter and displacing the indenter into the specimens at 1 nm/ns up to a penetration depth of 25 nm. Interestingly, by comparing the virtual nanoindentation simulations with the experimental data, relevant information about the nature of the interparticle forces was obtained. In fact, the results pointed to the importance of including rolling resistances to include the effects of nonspherical shapes by using spherical particles. In fact, these virtual nanoindentation experiments provided further evidence that C–S–H bricks are not spherical and showed that HD assemblies are more brittle than the LD and LP structures.

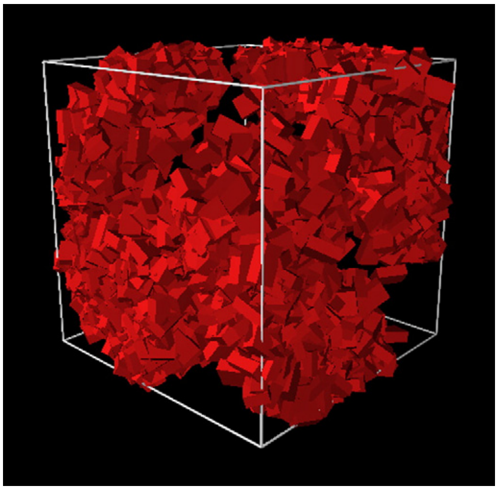

**Fig. 4.** A C–S–H structure made by aggregation of cuboids. Image by courtesy of V. Morales-Florez.

## 5. Micro level models

### 5.1. Integrated kinetic models

In Section 2.3 a few of the most frequently used micro-models for simulating the hydration process and microstructure development of cement-based systems have been mentioned. Models which deal with both hydration and microstructure development were defined there as integrated kinetic models. These models have the potential to produce a virtual microstructure and capillary pore structure as functions of the initial paste composition, including the particle size distribution of the cement, the w/c ratio, the temperature and the chemical properties of the cement and of other powders. In this section this category of models will be used as the reference for further discussion of micro-models.

The virtual microstructure is meant to be the basis for the description of the materials properties, like mechanical and transport properties. All these models have in common that the rate of reaction and the evolution of the microstructure are simulated simultaneously and are mutually interdependent. The rate of dissolution of individual cement grains does not only depend on the chemistry of the systems and on changes thereof, but also on the formation of contacts between particles, at which points the rate of the prevailing reactions is hampered in one way or another. So, both chemical and physical phenomena determine the rate of reaction and hence the rate at which the microstructure and the associated properties of the hardening system develop.

Examples of integrated kinetic models are the CEMHYD3D [16,75], (part of) DUCOM [17], HYMOSTRUC [11], Navi's model [18], the more recently proposed µic (pronounced Mike) [19,20,76,77], the model proposed by Nothnagel [78] and Wang [79,80]. Typical for the CEMHYD3D is its pixel-based architecture, from which the models receive its flexibility to cope with irregular shapes of the cement grains (see Fig. 5). In most other models the cement grains are considered spherical, which is a concession to the granulometric and geometric complexities. Most of these models are inspired by the pioneering modeling work of Jennings [81]. µic is based on the modeling work of Navi [18] and is meant to become a modeling platform that allows customization of simulations by the user. Very nice simulation results with µic were published regarding the rate of heat evolution of alite and cement-based systems [82]. Wang's model is based on a work of Tomosawa [83,84], who has proposed a model for hydration of a single particle, while the formation of interparticle contacts was considered according to Navi's model. A model recently proposed by Park et al. [85,86] shows many similarities with Wang's model. For determination of some model coefficients Park made use of neural network techniques. Nothnagel's model [87] is a finite element-based model and incorporates features found in HYMOSTRUC, SPACE [88] and partially CEMHYD3D. Fig. 6a shows a scheme of the basic model processes and phases considered in Nothnagel's model, whereas Fig. 6b shows a typical example of a virtual microstructure generated with an integrated kinetic model.

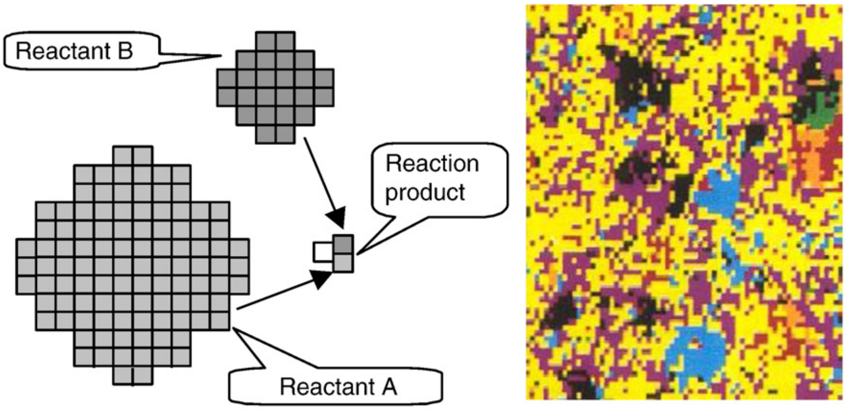

**Fig. 5.** Schematic representation of the pixel-based system (left and middle) and a sphere-based model (right).

Apart from difference in architecture, most of these models differ in focus. For specific features and the strong points of the individual models reference is made to original papers. In the following emphasis is on some common features and constraints of this type of models.

One of the common things in all these models is the possibility to simulate the evolution of the degree of hydration of the reactant. Since Portland cement is a poly-mineral material and the individual components do not react at the same rate, the use of the term degree of hydration is debatable, and the term degree of materials conversion might be more appropriate. For a given cement paste the degree of materials conversion determines the corresponding microstructure and pore structure of the system, provided that the algorithms for the formation of reaction products are correct and adequate. From the engineering point of view the degree of hydration – in the following we stick to that term – is a most interesting parameter since it can be used for quantifying the evolution of the materials properties like strength, stiffness and, be it at higher computation effort, permeability. In this way the degree of hydration can be the connecting parameter between micro-models and both meso- and macro-models. Even though some macro-models used for simulating the hydration process in hardening concrete structures have adopted the degree of hydration as the backbone for quantitative modeling of the evolution of the materials properties, there are still a number of tedious constraints that micro-models have to cope with. A few of them will be addressed in the following.

### 5.1.1. Particle shape

Cement grains and other powders that went through a grinding process are not spherical. For a given particle size distribution the real specific surface differs substantially from the calculated specific surface in which spherical particles were considered. This means that in hydration models correction factors are needed to 'repair' this discrepancy between reality and model. Besides an effect of the particle shape on the reaction kinetics there is also an effect of the particle shape on the moment at which hydrating particles will become connected. This determines, in absolute sense, the rheology of the system, the moment of setting and details of the pore structure. Pixel-based models are more flexible in this respect than sphere-based models, since they can adopt any particle shape without impact on the simulation algorithms.

### 5.1.2. Particle size distribution

In a poly-size powder the number of small particles (below 1 μm) can be very high. If mixtures are used which contain silica fume or other fine powders, the number of very small particles can become extremely high, even if only a few percent of these powders are used. In order to follow the reaction process of each individual particle, including that of the very small ones, a huge computation time is required. To reduce the computation time the smaller fractions are sometimes ignored. The small particles, however, because of their high reactive surface area, have a large effect on the early rate of hydration and also on the rheological properties of the mixture. At this point a balance between reliability, accuracy and computation effort has to be found. Another way to solve the fine particle problem could be the step to multiscale modeling or to consider the solution with the very fine particles as a 'liquid' with particular properties that are determined by the properties of the very fine particles.

### 5.1.3. Pore size distribution

The starting point for a numerical simulation of the microstructure of cement paste is a random spatial distribution of the cement grains

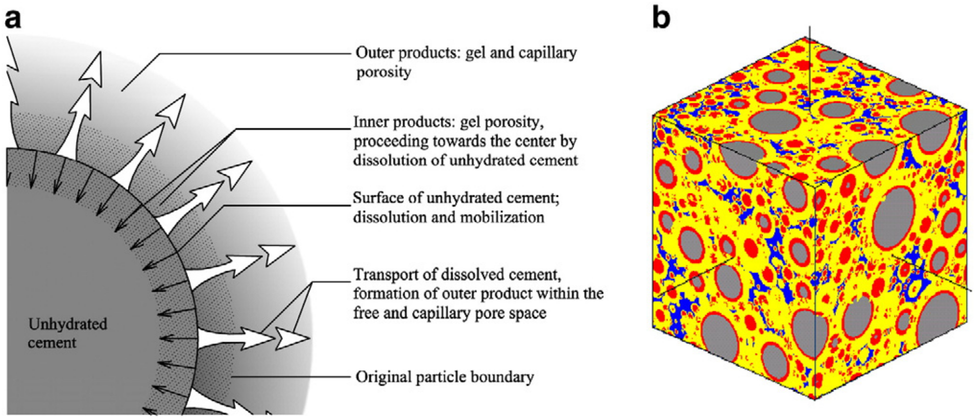

**Fig. 6.** (a) Example of sphere-based model after Nothnagel [78] and (b) virtual microstructures obtained from HYMOSTRUC [11].

in the paste. This random special distribution of the particles results in a pore structure that looks like anything but a system of connected cylindrical tubes (Fig. 7). Crucial for the permeability and diffusion coefficient of the paste is the size of the smaller pores and their connectivity [89]. In a virtual microstructure, however, it is very difficult to produce a realistic picture of the small pores and their connectivity. In a pixel-based model the size of the smallest pores is determined by the size of the voxels. In sphere-based models growing spheres can mathematically reach each other at any desired small distance. This does not mean, however, that the thus calculated narrow pores represent the reality. The outer surface of a hydrating and 'growing' spherical cement grain is anything but a smooth surface. Its irregular texture is determined by average the size of reaction products. Literature from past decades reports ettringite crystals up to even 120 μm long and 2 to 3 μm thick. The typical size of calcium silicate hydrates is between 0.1 and 2.0 μm, whereas calcium hydroxide crystals can reach a size up to 100 μm and even much bigger [11]. Given these sizes, it is clear that sophisticated calculations of distances between growing spherical particles and suggesting that these distances represent real pore sizes must be considered with care. The constraints encountered with capturing the small pore sizes from a virtual microstructure are schematically shown in Fig. 8.

In pixel-based models adoption of smaller voxels will result in smaller pores. However, also then one has to consider the question as to whether the thus created small pores are an unavoidable artifact of the simulation model rather than a realistic representation of the real pore sizes. For reliable predictions of the small pores in the range of smaller pores multi-scale modeling could offer solace. What is basically needed for capturing the small features of the microstructure is a clear understanding and modeling of the real mechanisms and processes that determine the formation of the (sub)microstructure, for which purpose modeling at the nanoscale is required.

#### 5.1.4. Rheology

The formation of interparticle contacts in the very early stage of hydration has been investigated experimentally by USPV-measurements. These measurements exhibit a sharp increase in the response of a hydrating fresh paste at the moment of setting of the paste starts [90]. The sharp increase in wave velocity reflects the start of the formation of interparticle contacts. It was found that the experimentally found setting times correlated well with the numerically determined moment that a solid percolation path was formed by the hydrating cement particles [91,92]. This positive result opens the way for parameter studies about the effect of the particle size distribution on, for example, the length of the dormant period and rheology of fresh systems [93].

### 5.2. Hybrid kinetic models

Hybrid models were defined as models which allow for physic-chemical processes and particle properties and particle size distribution of the reaction, but with which the formation of the microstructure is not modeled explicitly. This type of models can be strong in predicting the evolution of the hydration process and the degree of hydration, but doesn't yield a virtual microstructure as basis for estimating the evolution of materials properties. Materials properties are estimated as function of the degree of hydration. Guillon's model [94] for hydration of OPC-pastes is an example of a hybrid model. The authors denoted their model as a semi-analytical model for predicting the evolution of the cement paste composition, porosity and degree of hydration with time and the pore solution composition as a function of the mineralogy and particle size distribution of the cement. Hydration kinetics were based on Tomosawa's single particle model [83,84]. This mathematical model operates with a differential equation which relates the hydration rate of an isolated spherical particle to the current hydration degree, to the thickness and diffusion coefficient of the surrounding porous hydrate layer, and finally to the dissolution constant of the anhydrous phase. To allow for particle interaction a global kinetic reduction factor is adopted. The effect of internal desiccation with progress of the hydration process was worked out according to earlier work of Parrot [95], whereas the reduction of reactive surface of the cement grains was accounted for in a way as proposed by Navi [18].

Tomosawa's model was also the basis for the modeling work of Maruyama et al. [96]. In Maruyama's model allowance is made for the clinker composition and particle size distribution of the cement. Total degree of hydration is the result of the hydration degree of individual components. The main aim was to predict adiabatic hydration curves and the associated materials properties, for which reason he called his model Computational Cement-Based Materials Model (CCBM). Effect of interaction between particles was not modeled explicitly.

Sugiyama [97] proposed a mathematical model for cement hydration and microstructure formation starting from the hydration of a single cement particle. The rate of hydration was estimated by a second order reaction theory, by which it was assumed that the rate of hydration is proportional to both the concentration of water and the concentration of cement components. For predicting the evolution of materials properties an index $\chi_{\text{CELL}}$ was introduced, by which the volume ratio of the hydration product in a cement paste cell is determined (comparable with gel-space ratio).

### 5.3. Kinetics

In integrated kinetic models the rate of reaction is assumed to be affected by physical constraints associated with the formation of

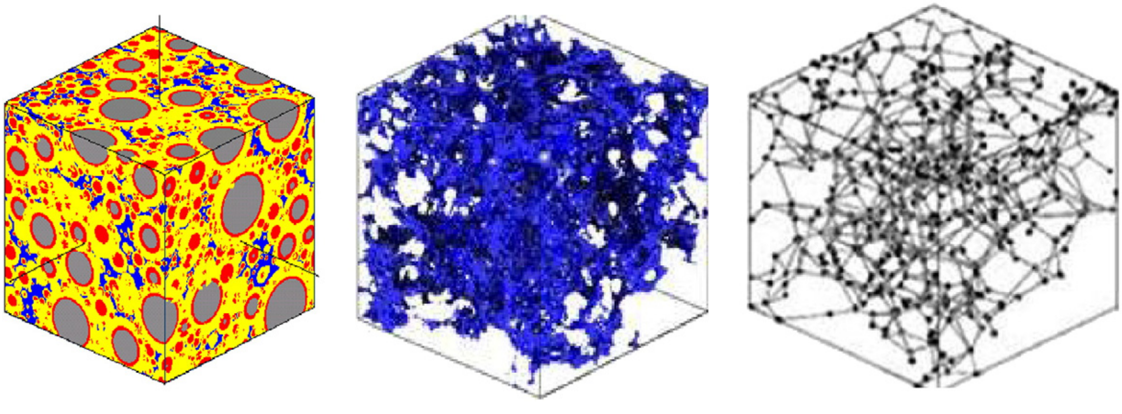

**Fig. 7.** Example of a virtual microstructure (left) and pore structure (right), generated by a sphere-based micro-model. After [92].

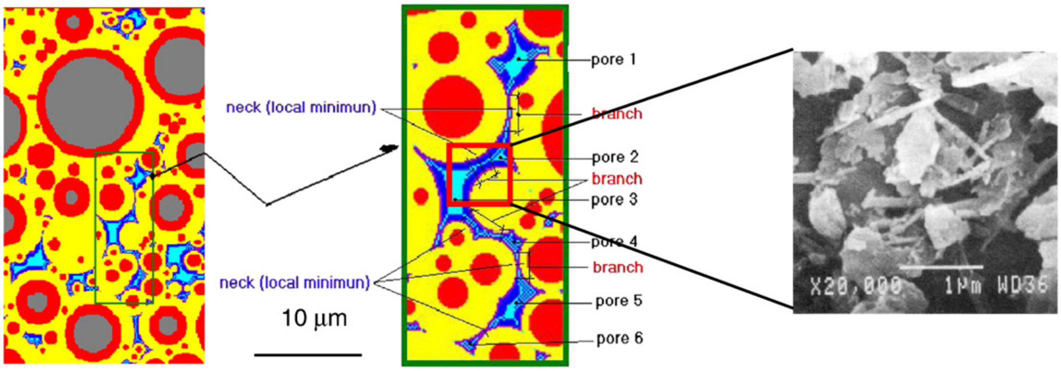

**Fig. 8.** Capturing small pore sizes from virtual microstructure — Constraints. Texture of growing spheres is determined by size and shape of reaction products.

interparticle contacts. However, the driving force that initially determines the rate of reaction has not been addressed yet. Decisive in this respect is the chemistry of the system, as well as the temperature and pressure during the reaction, *i.e.* the thermodynamics.

### *5.3.1. Early reactions*

A first and rapid reaction after the first contact of cement and water is followed by the so called dormant period. What actually causes the start and end of the period has been discussed many times. Garrault [98] assumed growth of clusters of C–S–H horizontally and vertically in a dissolution–precipitation process. Although the authors reported good correlations between (different) models and observations, they stated that the limiting steps controlling the dormant period, the acceleration and the deceleration phase are still controversial. According to Gallucci [99] a thin shell of C–S–H nuclei is formed at the surface of alite grains. As a result of intensive numerical simulations with the newly developed code HydratiCa [100–103] Bullard demonstrated that a thin, passivating layer of CSH on $C_3S$ surfaces could not only explain the unusually slow dissolution rate of $C_3S$ during the dormant period, but also the evolution in pore solution composition, the nucleation of a more stable form of CSH and its effect on destabilizing the semi-permeable layer and subsequent acceleration of $C_3S$ dissolution [104]. More recently, HydratiCa have explored a newer “slow dissolution step” hypothesis [105] which assumes that no layer forms on the $C_3S$ surface, but that active dissolution sites at surface defects are deactivated. Interestingly these simulations also agreed well with experimental data without having to assume markedly different diffusivities for the C–S–H phases. The HydratiCa code concentrates on the pore solution and changes thereof, aspects that are less strongly addressed in the aforementioned integrated kinetic models. The code addresses four individual chemical reactions in parallel: 1) dissolution and growth, 2) diffusion of mobile species in solution, 3) complexation reactions among species in solution or at solid surfaces, and 4) nucleation of new phases. In this way HydratiCa has made a very important step in upscaling information from the molecular scale to the microscale.

### *5.3.2. Temperature*

Even though a huge amount of date about the effect of temperature on the rate of hydration is available, there still appears a demand for further studies on this rate-controlling parameter. The increasing use of blended cements [96,106,107] and the need for higher accuracy of the available data are among the most important reasons for continuing interest in temperature effects.

Lothenbach [108,109] modeled the effect of temperatures in the range from 0 to 60 °C on the hydration of Portland cement. Thermodynamic modeling was carried out using the Gibbs free energy minimization program GEMS, a broad purpose geochemical modeling code. Chemical interactions involving solids, solid solutions and aqueous electrolytes are considered simultaneously. The effect on temperature on the porosity, *i.e.* denser reaction products and hence a higher capillary porosity, was considered as well. Acceleration of the reaction was accounted for using the Arrhenius equation.

Kishi [110] proposed a universal model for heat (and strength) development, based on a multi-component system. The rate of hydration of a cement–water system was calculated as the results of the hydration rate of each component. In his model allowance was made for the effect of temperature on the properties of the reaction products.

### *5.3.3. Activation energy*

The activation energy E [kJ/mol] of hydrating systems determines the temperature sensitivity of the reaction processes and is generally analyzed with the Arrhenius concept. From discussions on the applicability of this concept for analyzing temperature effects in poly-size and poly-mineral systems, in which different reactions proceed simultaneously, it is clear that we should speak about the *apparent activation energy* $E_A$ [kJ/mol]. The $E_A$-values are important parameters in maturity-concepts used in the engineering practice.

Several procedures have been tried to get accurate values for $E_A$. Poole et al. studied the activation energy for Portland cement systems and found the model of Kada-Benameur [111] the most practical one. Zhang [112] studied the temperature sensitivity of different materials properties and found $E_A$-values not to be constant throughout the hydration process. Kaman [113] found that for ultra high performance fiber reinforced concretes the Arrhenius concept did apply with an activation energy $E_A = 33$ kJ/mol, a value also used for conventional concretes. Other values, however, were found as well. Garcia [114] studied the temperature effect and magnitude of the activation energy on the setting time of concrete mixtures.

### *5.3.4. Pressure*

Even though in most, if not all, simulation models reaction products are supposed to form in a stress free state, it is well known that the reactions are sensitive to applied pressure during the reaction [115]. Scherer [116] found that both temperature and pressure change the rate of reaction, but not the nature of the process, at least as long as the temperature was below 60 °C.

## *5.4. Microstructure and materials properties*

For macro-level engineering applications it often suffices that micro-models can provide engineers with a reliable value of the degree of hydration. The evolution of the degree of hydration can then be used as the parameter to which the evolution of materials properties can be related in a phenomenological way. This approach, however, leaves us with the question what really causes the strength and stiffness of cement paste. A similar question has been addressed already when discussing the strength and stiffness of materials at the nano-scale. At that scale the focus is on the nature and magnitude of bonds between and within reaction products. At the microscale the focus is on the nature and size of contacts, or contact areas, between cement grains and other powders. The assumption is that the strength increases with increasing intensity of interparticle contacts. This means that an increase in strength can be expected in systems with a lower water/cement ratio and a higher degree of hydration. This will lead to a lower porosity, or higher degree of space filling [108]. Sun [117] found a strong correlation between the summarized interparticle contact area of a virtual microstructure and the compressive strength of cement paste (Fig. 9) and the shear modulus. The correlation appeared to hold irrespective of the water/cement ratio, which ranged from 0.35 to 0.6.

Pichler [118] proposed a micro-mechanical model for strength prediction of Portland cement pastes with $w/c = 0.35$ to 0.60. He concluded that the morphology of hydrates significantly influences the micromechanical elastic stiffness of cement paste only at very early ages, whereas elastic properties of mature cement paste can be estimated reliably on the basis of either spherical or acicular shaped hydrates. The development of a reliable *strength* model, however, would require consideration of hydrates as non-spherical particle, no matter what age of cement paste is considered. Sanahuja [119] performed predictions of the elasticity of cement paste by homogenization of the heterogeneous cement paste. A scheme of inner and outer hydrates and unhydrated cores was considered. Inner or high density hydrates were considered as a porous poly-crystal with dimensions of $60 \times 30 \times 5$ nm. He stated that the distinction between high and low density hydrated is not sufficient. For simulating real cement pastes also various hydration products which differ not only in density but also with respect to their chemistry should be considered. Incorporating Portlandite would allow, for example, to simulate the mechanical effect of calcium leaching, where Portlandite progressively dissolves.

Qian [120,121] studied the fracture properties of a virtual microstructure when subjected to an external tensile loading. For that purpose the virtual microstructure was represented by a lattice model, in which each lattice represented particular phases of the microstructure. Lattice models have successfully been used for investigating the cracking properties in mortar and concrete (mesoscale). Qian found this approach to be also feasible for investigating the fracture properties of cement paste (microscale). Fig. 10 shows an example of a virtual microstructure loaded in tension and the resulting cracking pattern in the paste. The paste was represented by a spatial lattice system. Each of the elements of the lattice system represents a specific phase of the virtual microstructure. Crucial for the outcome of these types of numerical analyses are the mechanical properties that are assigned to the individual phases. For that purpose the increasingly used nano-indentation tests can be most instrumental [53,122]. From the perspective of modeling, the results of nano-level modeling offer interesting and promising prospects as discussed earlier in this paper.

### 5.5. Volume changes

Cracking in cement paste may result from external loads, as discussed in the foregoing, or from volume changes of the matrix. The latter may be hydration-induced or caused by drying out of the porous matrix. Grondin [123,124] studied the deformations of solidifying cementitious systems. Volume changes caused by both chemical and autogenous shrinkage were considered. They related autogenous shrinkage to negative capillary pressure in the pore system calculated with the Kelvin equation. Studies focused on the period up to 48 h, for which period good predictions were yielded. Although not considered in the model, cracks were observed and improvements of predictions were expected from coupling their model with a damage model. Also Aly [125], Meddah [126], and Lin [115] correlated autogenous shrinkage to the capillary tensile stresses ($\sigma_{cap} = -(2\gamma/r)$). Aly further concluded that early-age shrinkage during drying in concretes is governed by capillary tensile forces and not necessarily correlated to the amount of moisture loss.

Grasley [127] studied the correlation between the coefficient of thermal dilation (CTD) and the internal relative humidity. The internal RH was coupled to the capillary pressure calculated with the help of the Laplace equation. In their study they observed a discrepancy between the measured internal RH changes and those predicted by the Kelvin equation. From that observation it was suggested that the pore structure of the material is an important factor controlling the additional dilation. Even below $RV = 45\%$ mechanisms other than capillary pressure influence the CTD. Disjoining pressure and solid surface tension are likely active at low RH.

Volume changes due to capillary pore pressure were also studied by Benboudjama [128]. Shrinkage was considered as being the elastic *and* creep response of the material under drying-generated pore pressures. Shrinkage strains were studied in the RH range from 50 to 100%, where both the capillary and disjoining pressures are the driving forces of shrinkage. For quantifying the volume changes a numerical viscoelastic model was used. It was suggested that their model could be used in combination with a damage model in order to investigate the structural part of shrinkage strains. The importance of disjoining pressure, up to high RH-values, for explaining and modeling drying-induced volume changes has also been emphasized by Wittmann and collaborators [14,129]. For $RH > 50\%$: water held in nanopores creates a disjoining pressure on the surfaces of the surrounding particles which leads to swelling of the system.

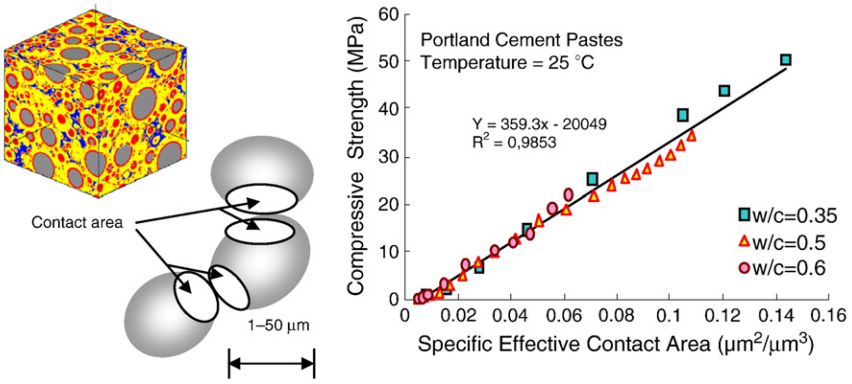

**Fig. 9.** Concept of interparticle contact area (middle) and relationship between calculated contact area of a virtual microstructure (left) and compressive strength of cement paste (right) (after [117]). Strength in contact areas is determined by nano-scale phenomena.

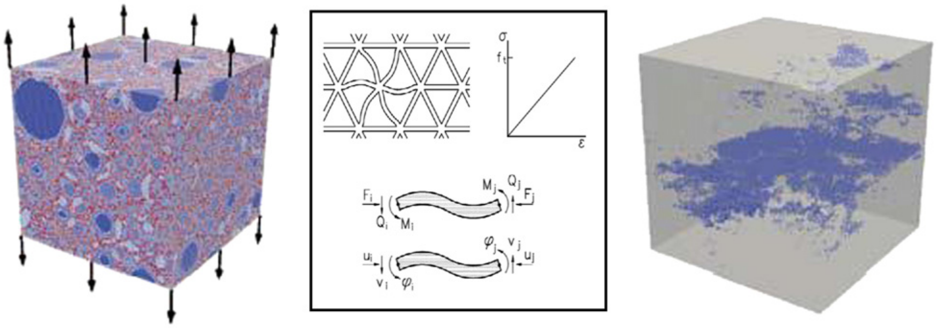

**Fig. 10.** Virtual 3D microstructure, externally loaded in tension (left) for investigating the propagation of cracking in a cement past sample hydrated to a degree of hydration of 69%. Sample $100 \times 100 \times 100$ μm$^3$, w/c = 0.4 [120,121].

### 5.5.1. Internal curing

The importance of the relative humidity for resulting volume changes being known, internal curing in order to manipulate the internal RH in a direction yielding less autogenous volume changes has become an important issue for both research and practical application. Cusson [130] found that internal curing of mixtures with LWA particles of mixtures with w/c from 0.28 to 0.34, $(w/c)_{ic} = 0.06$, was sufficient to prevent autogenous shrinkage. According to Meddah [126] a 30% porous ceramic coarse aggregate was sufficient to produce a non-shrinking high performance concrete up to 7 days, accompanied by a significant increase of the compressive strength. Bentz [131] studied the internal curing of high performance concretes made with SF, GGBFS and FA with LWA as water containers. Autogenous shrinkage related to capillary stress in pores was calculated with the Kelvin equation. According to that model a coarser pore structure leads to lower capillary stresses and less shrinkage. With reference to work of Jensen and Hansen in 1996, Bentz warned that part of autogenous shrinkage in systems with pozzolans could be due to decalcification shrinkage.

### 5.6. Time dependent behavior

In most models for describing creep and relaxation of cement based materials the hydrates and changes thereof are supposed to be the only material phase causing time dependent deformations. As a consequence of these models for predicting volume changes and deformations on the macro-scale are supposed to bridge several length scales, from the (sub)micro-level of hydrates to the macro-level. Scheiner [132] proposed a continuum microviscoelastic model for cementitious materials for time dependent relaxation of cementitious materials as a function of the viscoelastic properties of hydrates, the elastic properties of cement, of water and of aggregates, and of the aging-dependent volume fractions of these material phases within the composite material. In their model a distinction was made between low density and high density C–S–H, Portlandite and aluminate. In the model a representative volume element was defined which contains hydration products, unhydrated cement grains, liquid (capillary) pores and air pores. Asamoto [133] proposed a multi-scale time dependent deformation model of solidifying cementitious materials. This model is one of the modules of DUCOM [17], a multi-scale model used for engineering purposes. Also long-term creep of concretes under both sealed and drying conditions could be simulated reasonably well. For low w/c concretes, however, improvements are reported necessary. Kamen [113] studied early-age tensile creep of UHPFRC. In composite structures the non-linearity due to the high induced tensile stresses susceptible to develop at the young age under restrained conditions is a relevant problem. For modeling the creep behavior a Maxwell chain model was used. Above 35% of the tensile strength at the loading age the material exhibited viscoplastic behavior. Gawin [134] proposed a new model with direct coupling of the degree of hydration and material creep, described by means of the modified microprestress solidification theory (as originally presented by Bazant and Prasannan [135,136]). Van der Ham [137] proposed a numerical model for creep and relaxation of early-age concrete based of the assumption that transport of water through shells of hydration products could explain the time-dependent deformations of hardening cement pastes. His model presupposes the existence of hollow shells in hydrating cement pastes. Even though the precondition of the presence of hollow shells cannot always be fulfilled, this model forces researchers to consider the water transport within a hydrating cement paste.

Bazant [138] compared several creep and shrinkage prediction models. Five models were considered, of which the RILEM model appeared to perform best, whereas the old 1972 ACI model, reapproved by ACI in 2008, was the worst.

## 6. Meso-level models

### 6.1. Effect of presence of aggregate particles on cement matrix properties

In mortar and concrete the paste properties vary throughout the matrix. Due to a less dense packing of cement particles near the surface of sand and aggregate particles, the microstructure in the paste-aggregate interfacial zone (ITZ) will be different from that in the bulk paste. In principle integrated kinetic models can cope with the effect of the variation in local water/cement ratios in fresh paste on the rate of hydration. The gradient in w/c in the fresh paste results in corresponding gradients in the microstructure and moisture distributions in the hardening paste. Gradients in moisture distribution will cause moisture transport within the paste. This, on its turn, will affect the local rate of hydration in particular zones within the paste. The effect of hydration-induced moisture transport with a mortar or concrete paste has been considered by van der Ham [139]. This phenomenon deserves more attention, particularly in view of the internal curing concepts that have been proposed in view for mitigating autogenous shrinkage in low water/binder ratio mixtures [130,131].

### 6.2. Workability of fresh concrete pastes

Roussel [140] has presented an overview of the current status of models for simulating concrete flow, *i.e.* workability of concrete. The authors noted that this field is a very new research area: the first papers dating back to 1994. The computational modeling techniques reported in literature were divided into three main categories: single fluid simulations, numerical modeling of discrete particle flow and numerical techniques allowing the modeling of particles suspended in a fluid. For single fluid simulations reference was made to work of Mori and Tanigawa [141], who used a Viscoplastic Finite Element Method (VFEM) and the Viscoplastic Divided Element Method (VDEM) to simulate flow of fresh concrete. Both methods assume that concrete can be described as a homogeneous single fluid with given rheological properties. Wallevik [142] performed simulations based on the assumption of a viscoplastic material. He used a combination of several different techniques which he combined in his own software. Roussel [140] proposed a model based on the Bingham model and was able to describe the thixotropy of fresh concrete characterized by two intrinsic parameters: the yield stress $\tau$ [Pa] and a so-called re-structuration rate $\partial\lambda/\partial t$, in which $\lambda$ is the structuration rate that evolves through the flow history. The model developed by Shyshko [143,144], although not mentioned in Roussel's overview, can be considered as an example of a discrete particle (element) model. Their Particle Flow Code, based on Bingham's model, contains simple constitutive relations for particle interaction in shear and normal. They were successful in modeling the classical slump test. However the simulation of the rheological behavior of fresh concrete was not completely satisfactory yet. In their modeling approach there is a clear need for detailed information about the pore water properties and surface properties of the powders used because these properties determine the attractive and repulsive forces between particles [145].

### 6.3. Mechanical properties of hardened concrete

The mechanical properties of hardened cement paste are determined by the stereological parameters (the packing of the aggregate particles), the properties of the (bulk) cement paste and of the interfacial transition zone (ITZ). Apart from its influence on the mechanical properties, the ITZ also affects the transport properties of the concrete. Interfaces are found around the aggregates, but also around fibers, if present [146]. Against foregoing considerations it is reasonable that at the meso-level uncracked hardened concrete is considered as a three-phase material. Li [147] applied a three phase model for predicting the elastic modulus of concrete with a particular focus on the effect of the elastic modulus of the aggregate and of the water/cement ratio of the cement paste. Barbosa [148] determined the elastic modulus of the ITZ by micromechanical modeling. Ke [149] studied the evolution of the Young's modulus both experimentally and by numerical simulation. Even though LWA-concretes are known not to have a pronounced porous ITZ, also for these concretes a three-phase model did apply well and better than a two-phase model. Gruber [150] proposed a model for dealing with debonding interfaces between matrix and fibers. For this purpose he used a so-called linear softening interface concept, based on a cohesive model introduced earlier by Camacho [151]. The properties at the fiber interface are determined by the paste properties, and that's where the cement chemistry comes in.

## 7. Macro-level models

Al least two models, or better analytical expressions, are frequently used in the engineering practice which in fact strongly rely on accurate information about the hydration process and the microstructure, and the pore structure. The first one is the hydration model, *i.e.* hydration input curve, used in concrete curing control systems, whereas the second model is used in service life predictions.

### 7.1. Concrete curing control systems

The key-component of concrete curing control systems is the differential equation of Fourier for determination of the temperature distribution in hardening concrete elements:

$$\frac{\partial T}{\partial t} = a_c\left[\frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2} + \frac{\partial^2 T}{\partial z^2}\right] + \frac{C}{\rho_c c_c} + \text{source term} \quad (1)$$

in which the source term deserves our attention. In the past an estimated heat production curve was generally adopted which was assumed valid for all locations in the hardening structure and for the total duration of the hydration process. This, however, is not correct (see also [152]). The rate of hydration depends on the local temperature which varies throughout the cross section of a structure. What these macro-level models do need as input is an adiabatic, isothermal or semi-adiabatic hydration curve for the concrete mixture in view, as well as information about the apparent activation energy in order to correct the rate of heat production for the prevailing temperatures. Studies on modeling and prediction of hydration curves and the temperature sensitivity of the hydration process are, therefore, still very important, aware of the variety of new and modified concrete mixtures that enter the marked today [153–156]. The source term and its quantification can be seen as the link between the micro-level to the macro-level. Output of a temperature calculation is the temperature distribution in the concrete as well as the degree of hydration. The degree of hydration, on its turn, serves as the basis for quantification of development of the materials properties.

### 7.2. Service life predictions — Chloride induced corrosion

Most of the analytical formulae for estimating the onset of chloride-induced corrosion in reinforces and prestressed concrete are based on Fick's second law of diffusion. The chloride content is calculated with the formula:

$$C(x,t) = C_s - (C_s - C_i)\, erf\left[\frac{x}{\sqrt{\{4kD(t)t\}}}\right] \quad (2)$$

where C(x,t) is the chloride content at depth x at time t, $C_s$ is the surface chloride content, $C_i$ the initial chloride content in the concrete, k a correction factor and D(t) the apparent diffusion coefficient as a function of time. The apparent diffusion coefficient D(t) is multiplied by a correction factor k to obtain the chloride diffusivity of the concrete in a real structure. This correction factor depends on the binder type, the environment and the curing. The correct value of the diffusion coefficient is extremely important for the outcome of service life predictions. It is of utmost importance, therefore, to study the long-term evolution of this coefficient. This includes the long-term evolution of the pore structure as well as the chloride binding capacity of the reaction products. For this purpose in-depth thermodynamic modeling is badly needed. The modeling activities of Bullard [102] and the long-term goals of his thermodynamic modeling approach is worth to be mentioned.

## 8. Conclusions

Increased knowledge about cement-based systems, the availability of huge computation power and the increased awareness of the practical applicability of models in research and the engineering practice has paved the way for growing interest in numerical modeling of cement-based materials. On its turn modeling activities have revealed, and continue to reveal the complexity of cementitious systems. The complexity increases when going down to smaller scales of observation, *i.e.* to the nano-, molecular and atomic scale. But also when we make the step to larger scales, where practical boundary conditions do apply, complexity increases. To say it differently, a journey through scales implies a journey through disciplines. This makes modeling a tedious job, but not less fascinating.

Most of the currently used advanced simulation models, of which the origin dates back to the eighties of the last century, meanwhile underwent serious revisions — first of all because of increased knowledge about cementitious systems and secondly because of the spectacular increase in computation power. Over the last few decades the computation speed increased by a factor of 1.5 to 2 every year. A calculation that lasted for 24 h in the beginning of the eighties will now last only 2 to 5 min. This evolution makes it realistic to expect further developments as well as a wider use of models in both research and engineering in the coming decades. In both research works engineering multi-scale modeling is considered the most suitable vehicle to transfer knowledge from one scale to another and to cross borders between different disciplines [157–160]. The need of length scale- and border-crossing modeling activities requires an open mind, preparedness to collaborate and, maybe most importantly, clear goals. Today the goals in science and engineering can no longer be considered value-free. The increasing awareness of our responsibility for sustainable development of our society has put our scientific and engineering activities in a new and challenging perspective. Even though the solution of environmental problems is not in the hands of material scientists and engineers alone, we should not underestimate the importance of our contribution to those solutions. With reliable models we are able to demonstrate the potential of cement-based systems, and of all possible modifications and blends that are conceivable today, in view of mitigating the impact of building activities on the environment. These goals justify in-depth research at the atomic, molecular and nano-scale, as well as the efforts to develop multi-scale simulation and predictive models for direct use in the engineering practice [6,8].

The trend to establish open platforms for (multiscale) modeling and for use of simulation models for engineering purposes illustrates both the wish of modelers to be visible, as well as increasing demand for this type of tools for solving real engineering problems. This trend is not without risk and needs careful supervision by experts in the field in order to avoid both over- and underestimations of the significance of models and modeling. Users who are in the need of simulation and predictive models may easily overlook the limitations of these models and the fact that most of them are in a continuous state of development. Aware of these risks, however, there is no doubt that the access of a wider community to these models will stimulate their use, will increase the feedback from users to the modelers and is a promising way to improve and mature these models.

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