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Modelling of cement-based systems—the alchemy of cement chemistry

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Abstract

The history and present role of modelling in the field of cement chemistry are described. The complexity of modelling cement-based systems is emphasized and the specific features of models for hardening and hardened cement pastes are briefly described. The potential of models for supporting research and the engineering practice are discussed, particularly in view of multiscale modelling.

Keywords: Hydration products; Microstructure; Modelling; Mercury porosimetry; Backscattered electron imaging

1. Introduction

The search for a technology to transfer base metals into gold has a long history. According to the chronicler Suidas, Caesar Diocletianus ordered to burn all the books of the Egyptian alchemists after he had won the fight with the Egyptians. This was in the year 296. Among the people who have been searching for the philosopher's stone we find the names of the great scientist Tycho Brahé. From the 16th until the 19th century, numerous fortune hunters have spent most of their life to find the key to the world of gold. Although all these efforts finally appeared to be in vain, we could say that what the alchemists actually did find is now much more valuable than the transformation of a base metal into gold could ever have been. For example, in his search for gold, the alchemist Böttger invented the white porcelain in 1709. A large number of products still used in medicine are the fruit of the work of alchemists. In fact, modern chemistry is unimaginable without the tedious work of the alchemists. This holds for both the organic and inorganic chemistry, like the cement chemistry.

The story, or history, of the alchemists may serve as a metaphor for the activity of the modellers in the field of cement chemistry and cement-based materials. Alchemists have tried to "create" real gold out of substance that was not gold at all. To a certain extent, modellers do the same when they try to mimic the real world. They try to represent the real microstructure of a cement paste by a virtual microstructure with properties and features similar to the microstructure to be represented. The increasing amount of experimental data, the increasing knowledge of fundamental laws, and, last but not least, the increasing power of modern computers, constitute an increasingly strong starting point for the design of virtual materials that resemble the materials they are supposed to represent as well as possible. Maybe with a good deal of self-irony, modellers sometime say that they "go for gold." Obviously, modellers believe in the power of models and know, either by intuition or based on clear and well-documented information, that the potential of material models is much greater than has been assumed until now. This holds in general and certainly also for models of cement-based systems.

If all these hold for the modelling of cement-based materials, the following questions may rise: Where we are with this modelling work? What is our goal? What has been achieved so far and what are the challenges for the short term and the prospects on the long term? Moreover, are there any by-products already that justify many years of tedious modelling work in recent decades?

2. Cement-based systems—different from anything else

Of the 850 pages of *Materials Science and Engineering—An Introduction* [1], a standard work on materials science, less than one page has been spent on cement-based materials. This probably illustrates the complexity of these

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materials. This complexity, from both the chemical and physical point of view, may be the reason why materials scientists have spent relatively low attention to it. Today, cement chemistry is a special discipline, which has brought forward scientists who once became fascinated by the complexity of the material without getting lost in it. Unfortunately, due to these materials' complexity and the material scientist's inability to characterize and describe these materials comprehensively, these have been awarded with the qualification "low-technology." With this qualification, the fascinating features and potential of cement-based materials are strongly underestimated. However, the multimineral and multisize characteristics of an ordinary Portland cement cause so many complications when it comes to a description of the material that many scientists give up after a short time. This complexity has brought Wittmann [2] to the statement that there is no hope that it would ever be possible to describe the properties of cement-based materials realistically, i.e., in the same way as this can be done for, for example, with metals and other well-structured materials. The fact that the quality and durability of concrete and concrete structures largely depend on the quality of the crew that is responsible for pouring of the concrete on the site makes it very difficult to believe that the performance of concrete and concrete structures will ever be predictable. At the same time, it can be said that a precondition for reliable modelling of the performance of concrete and concrete structures is the availability of advanced materials models with which the dominant influencing factors are addressed in a reasonable way.

3. Modelling of hydration kinetics and microstructural development

Since the beginning of modern cement chemistry, a number of formulae have been proposed with which the evolution of the hydration process with time and of the associated materials properties could be predicted. These kinetic formulae can be subdivided in at least four categories, viz. overall kinetics, particle kinetics, hybrid kinetics, and integrated kinetics [3]. With *overall kinetics*, the evolution of the hydration process and of the materials properties is described as a function of time without addressing the mechanisms and processes at the particle level explicitly. The reaction rate may be a function of the chemical composition of the cement, the water/cement (w/c) ratio, and the reaction temperature. *Particle kinetics*, on the contrary, take the reactions at the particle level as the starting point, but without taking into account the effect of any physical interaction between hydrating cement particles. More advanced are the *hybrid kinetic models*, in which the particle size distribution of the cement is considered explicitly, as well as one or more additional factors, like the w/c ratio and the chemical composition of the cement.

In all the aforementioned models, the formation of the microstructure and its effect on the rate of hydration is not considered explicitly. This is otherwise with *integrated kinetic models*. In these models, the formation of the microstructure is modelled explicitly, as well as its effect on the rate of hydration. Since it is the microstructure of cement-based materials that determines their mechanical and physical properties, as well as their transport properties and related durability, integrated kinetic models are considered to provide us with the most promising basis for modern computational research of cement-based systems.

4. Integrated kinetic models for cement-based materials

The microstructure of cement-based materials is far from crystalline. This complicates the (numerical) modelling of the microstructure significantly. For crystalline materials, conceptual models have been proposed in the beginning of the 20th century [4]. Fig. 1 shows subsequent stages in the solidification of a polycrystalline material. The crystals are considered to be composed of square unit cells. Solidification of the material goes along with the formation of contacts between the growing crystals, whereas fracturing of the materials will occur at the contact points of the crystals.

The concept is interesting because of its similarity, at least at first sight, with the most advanced and most well-known integrated model that has been proposed in the 1990s, i.e., the NIST model launched by Garboczi and Bentz [5]. The similarity, however, only concerns one particular modelling aspect, viz. the gradual growth of grains, either a crystal or a noncrystalline grain, through continuous precipitation of reaction products in the form of unit cells, or pixels. In the NIST model, the size of 1 pixel is 1 μm^3 (Fig. 2). For a representative volume of cement paste,

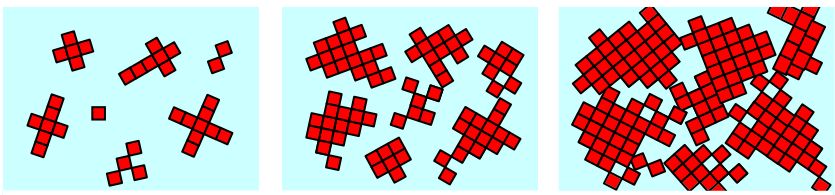

Fig. 1. Schematic representation of solidification of crystalline material (modified after Rosenhain [4]).

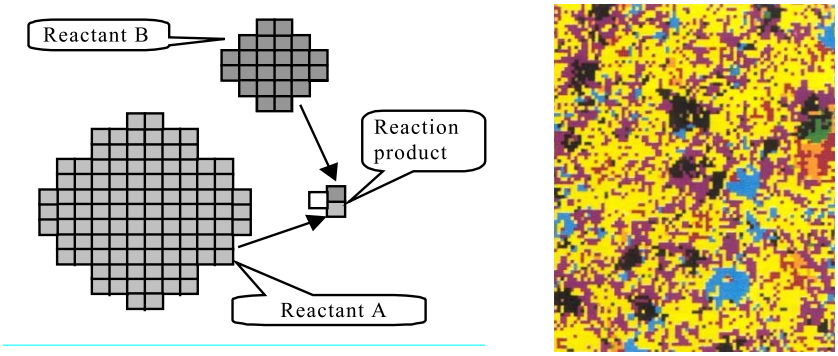

Fig. 2. Typical result of the NIST model. Microstructure composed of 1 μm^3 pixels (after Ref. [5]).

a volume of about 200^3 μm^3 is needed. Adopting smaller pixels would result in a substantial increase of the computation time, which might be undesirable. It has been shown that, with the NIST model, the evolution of the hydration process and of the porosity can be predicted quite accurately. The degree of hydration is defined straightforwardly as the fraction of the cement that has hydrated. This definition has been proposed by, among others, Taylor [6], and is, particularly for modelling purposes, the most convenient one. Either the degree of hydration or the porosity can subsequently be used for predicting the evolution of the mechanical properties. More complicated is the prediction of the permeability, since the latter quantity strongly depends on the connectivity of the pores. This connectivity depends on the adopted pixel size.

Besides the NIST model, at least three other integrated models have been developed. These models have in common that cement particles are considered as spherical grains. In Japan, the DUCOM model has been developed (extensively discussed in Ref. [7]). In the model, the cement is considered as a monosized powder. Pure Portland cements, as well as blended cements, can be dealt with. Like the NIST model, the DUCOM model is able to predict the degree of hydration quite accurately. The evolution of the materials properties is linked to the degree of hydration. Although a monosized cement is in fact a questionable starting point for numerical simulation of the microstructure and the pore structure, the researchers have been able also to predict the evolution of permeability and diffusion coefficients by relating these properties to the degree of hydration. The changing materials properties, including the transport properties, can be used in FE calculations for durability predictions.

In Navi and Pignat's model, launched in the early 1980s, cement particles are also considered as spherical grains [8]. The hydrating grains grow in outward direction and build up a 3D network of hydration products and anhydrous cement cores. The reaction products are either CSH gel or calcium hydroxide. To limit the computation time, the small particle fractions are not considered explicitly in the calculations.

The last integrated model that will be mentioned here is the HYMOSTRUC model, developed at Delft University of Technology. The main features of the model have been presented extensively elsewhere [3,9,10]. On reaction with water, the cement particles grow in outward direction, while making contact with adjacent particles. The adjacent particles, which might still be hydrating themselves, will gradually become embedded in the outer shell of the growing particles. The resulting growth process is described with a mathematical series. Fig. 3 shows a microstructure, simulated with the latest version of the HYMOSTRUC program. From this microstructure, the pore structure has been deduced by removing the solid phase, i.e., the still anhydrous cement cores and the gel. The resulting pore structure exhibits typical features, of which its irregularity is the most obvious one.

5. Experimental verification of simulated pore structure

The numerically simulated microstructure and pore structure, as shown in Fig. 3, is the basis for the determination of

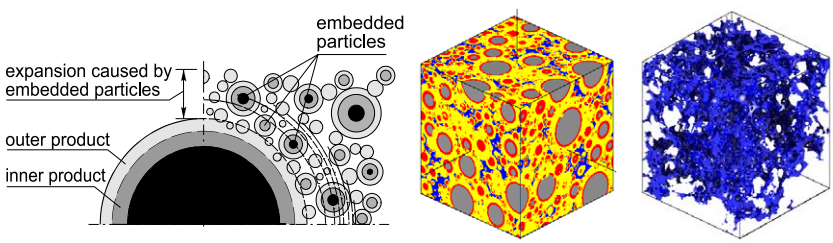

Fig. 3. Simulated microstructure of cement paste. Left: Growth process and embedding of cement particles. Right: Cube with 200 μm rib size (w/c = 0.3; degree of hydration $\alpha = 0.75$ [3,10]).

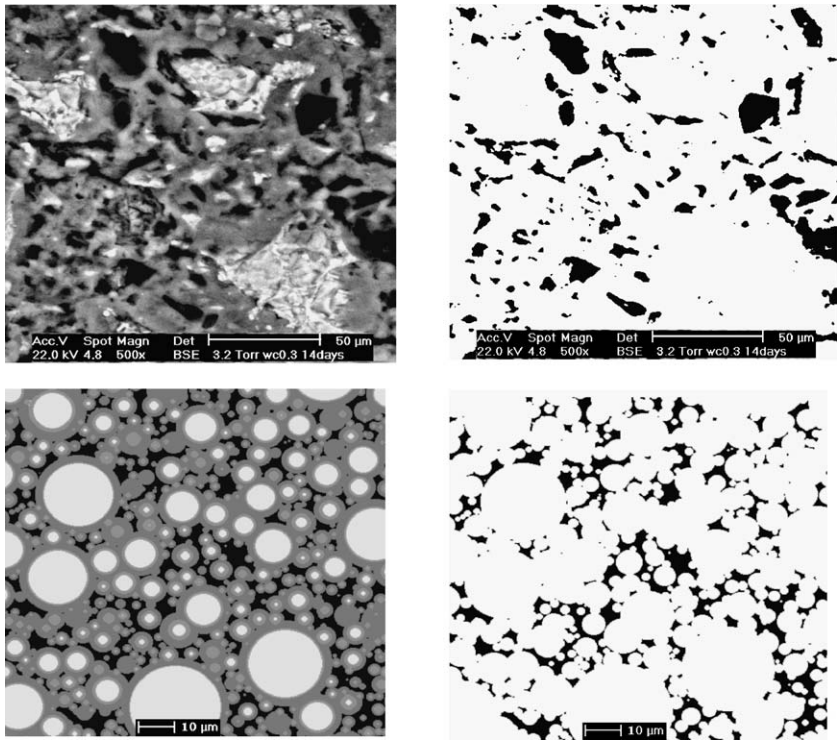

Fig. 4. Upper part: Backscattered electron image of cement paste and pore structure (w/c = 0.3; age = 14 days; degree of hydration $\alpha = 0.63$). Bottom part: Microstructure, simulated with HYMOSTRUC. Note: Scales differ by a factor of about 1.5 (after Ref. [19]).

the transport properties. For transport properties, i.e., mass flow, the capillary pore structure is of major importance. For checking the reliability of the simulated virtual microstructure, its pore structure has been compared with the results of MIP tests and SEM observations. Fig. 4 shows a SEM picture of a cement paste (top, left) and a black-and-white presentation of the same picture (top, right). For the same paste, a microstructure simulated with HYMOSTRUC is shown in the left-bottom corner of Fig. 4, with the corresponding black-and-white representation in the right-bottom corner. From these pictures, a similarity of the two pore structures can be observed.

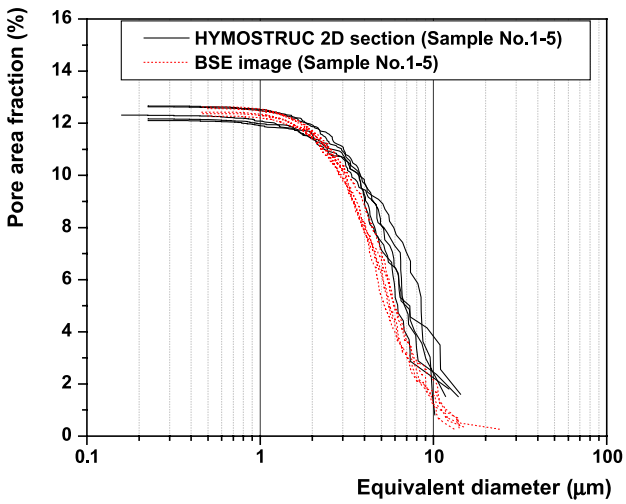

Fig. 5. 2D pore size distribution of simulated cement paste and backscattered electron image analysis (five samples) (w/c = 0.3; age = 14 days; $\alpha = 0.63$ [19]).

From the 2D pictures of Fig. 4, which have been taken from a 3D paste volume, the pore size distribution has been determined. The results are shown in Fig. 5. To get a good average of the microscopic observations, five specimens were used. The good correlation between microscopic observations and the simulated pore size distribution makes us prepared to accept the simulated microstructure as a reliable starting point for the determination of the transport properties of cement paste and concrete.

For a good correlation between the simulated pore size distribution of the capillary pores and MIP results, it is important that the smaller cement particles are taken into consideration. However, according to Ye Guang et al. [11], it is not easy to get a very good correlation, particularly because of the overestimation of the smaller pores in the MIP tests due to the well-known ink bottle effect.

6. Connectivity

Besides the pore size distribution, the transport properties in cement-based systems depend, to a large extent, on the connectivity of the pores. Fig. 6 (left) shows a simulated microstructure of a cement paste, w/c= 0.4, at a degree of hydration $\alpha = 0.9$. In the image, three narrow pores can be

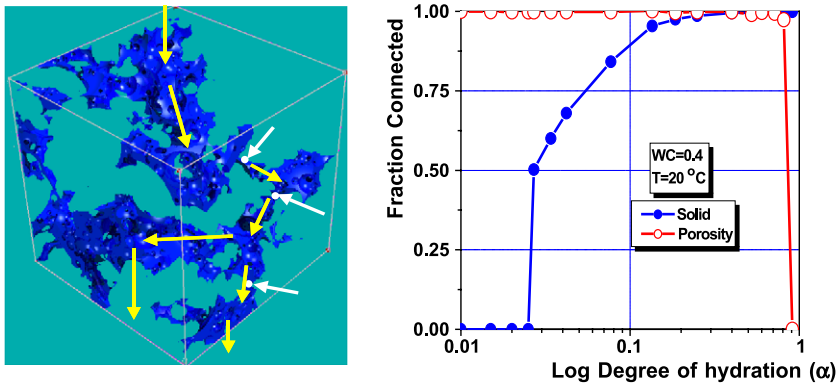

Fig. 6. Connectivity of pores in a cement paste (w/c = 0.4; degree of hydration in left picture $\alpha = 0.9$; after Ref. [19]).

identified. These narrow pores govern the resulting permeability of the paste to a large extent. A small increase of the degree of hydration would disconnect the pore system completely and will stop any transport through the cement paste. In the graph of Fig. 6, the degree of hydration at which a certain fraction of the particles becomes connected and the pores become disconnected are shown for a paste with w/c ratio 0.4. Fig. 6 shows that the percolation thresholds for the solid and for the pore system are very narrow. The degree of hydration at which these thresholds are (mathematically) reached strongly depends on the resolution with which the analyses are performed.

7. Modelling of small capillary pores

The behaviour of a cement paste strongly depends on the interaction between the xerogel and the water in the pore system. This holds in general and more in particular for the volume changes associated with changes in the moisture content and moisture distribution in the cement paste [12,13]. The fine pores are of particular importance, certainly at low relative humidity. Quantitative modelling of this interaction presupposes that a microstructural model can represent the fine pores accurately. Fine pores are those smaller than 0.5–1.0 μm. With the various numerical models mentioned in the foregoing, quantification of the fine pores is a problem. With a pixel-like model, the size of the fine pores is determined by the size of the pixels. In models in which the cement grains are represented as spheres, the pores are made up of the space that is left between growing spheres. Schematically, this is shown in Fig. 7. Mathematically, the distance between expanding spheres can be made arbitrary small. In this way, it is possible to find, mathematically, very fine pores. However, in reality, the pore structure of the small pores can hardly be considered as distances between expanding spheres. The growing spheres are made up of CH crystals and CSH chains, of which the size is of the same order of magnitude as, or larger than, the pore size to be modelled. In other words, the pore size of the narrow pores is determined by the average size of the hydration products. An accurate description of these narrow pores requires modelling of the microstructure on the scale of hydration products, i.e., a scale about two orders of magnitude lower than the average size of cement particles. This illustrated the need for multiscale modelling.

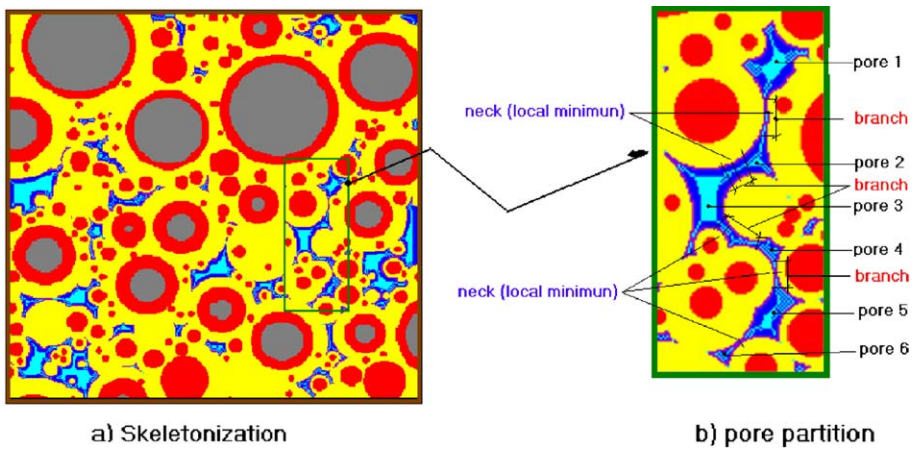

Fig. 7. The "narrow pore problem." Right: 2D blow-up of a simulated pore structure. The smaller the distance between expanding spheres, the more the local simulated microstructure will deviate from the "real" microstructure (after Ref. [19]).

8. Multiscale modelling—vehicle for transfer of basic knowledge to the practice

In the engineering practice, structural design models are used for predicting the crack width in reinforced concrete structures with an accuracy of tenth of millimeters. Deformations caused by cracking of the concrete can be related to the overall deformations of a complete concrete structure tens of meters in height. For the determination of the crack width and of the deformations of the entire structure, models that span length scales from tenth of millimeters to tens of meters are used, altogether about six orders of magnitude. Starting from a scale of tens of millimeters and extrapolating to smaller scales, six orders of magnitude will bring us even beyond the nanometer scale. If it is possible to model the behaviour of concrete structures with models spanning six orders of magnitude, would it not then be possible to model the performance of cement-based materials with nano- and microstructural models, together spanning length scales from the nanometers to millimeters? In fact, much of the research work of cement physicists, like the work of Powers [12], and even more that of cement chemists, like the work of Taylor, refers to processes, mechanisms, and concepts on the nanostructural level. It is through models and multiscale modelling that this fundamental knowledge can be transferred from the nanolevel to the millimeter level, i.e., the mesolevel. Schematically, this is shown in Fig. 8.

Suggesting that this multiscale modelling is a realistic option for the future does not mean that this is an easy job. It took designers many decades to develop a consistent set of models that spans length scales from tens of millimeters to tens of meters. The development of microstructural models, like the NIST model, DUCOM, HYMOSTRUC, and Navi's model took researchers two decades and these models are still in a stage of development. Although these models do contain a lot of recent information gathered from different fields, there is still scope for further extension and maturing of them. Maturing will require the joint effort of all disciplines involved, i.e., chemistry, physics, colloid chemistry, stereology, rheology, thermodynamics, mechanics, and mathematics. Moreover, experimental research will remain indispensable for validating the models. Microscopic observations may open our eyes for self-

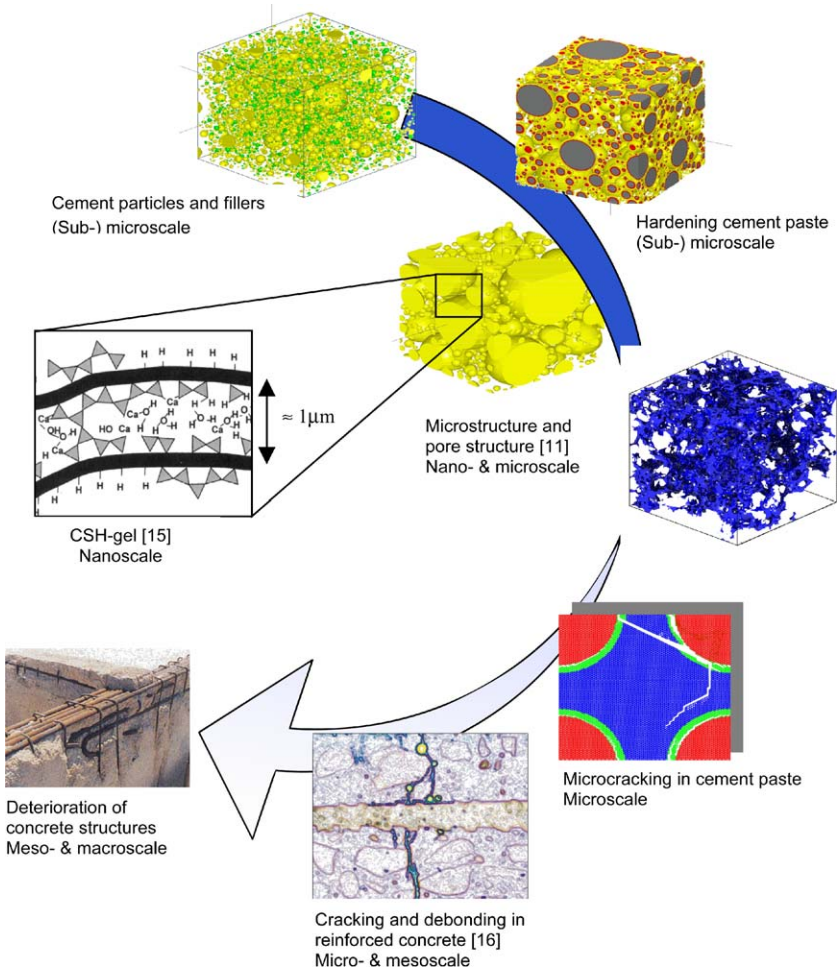

Fig. 8. Multiscale modelling of cement-based system: from micro- to macrostructure (compilation picture with input from Refs. [13,15,16] and *Concrete International*).

Fig. 9. Shrinkage-induced cracking in gel generated by alkali–silica reaction (microscale) [14] and in clay (macroscale).

similarity on different levels of observation and that can help us to identify the mechanisms behind the observed phenomena. As an example of this, Fig. 9 shows a microscopic picture of a dried ASR gel in the pore of a cement paste that contains expanded glass particles. The drying process has caused a crack pattern in the gel similar to that observed in the clay of a drying riverbed. Apart from the fact that the two pictures illustrate the similarity in the result of drying processes that occur at different scales, this example can also be seen as a metaphor illustrating the potential of multidisciplinary research in this complicated field. Similar phenomena studied at different levels of observation go back to universal physical laws. This should stimulate researchers to benefit from the knowledge and expertise developed in adjacent fields and to strive at cross-fertilization wherever and whenever possible.

9. Tailor-made materials

Since the 1980s, there is an enormous evolution in the field of cement-based materials. It started with the development of high-strength concretes. Today, self-compacting fibre-reinforced concretes are made with water/powder ratios as low as 0.2. The trend is now to try to design tailor-made concrete mixtures with a predefined set of properties concerning workability, strength and stiffness, and transport properties (in view of durability predictions). This is only achievable when all available knowledge about particle size distributions and particle packing of the different granular materials is used, a substantial amount of admixtures is used, and the compatibility between cement and admixtures is guaranteed. It has to be admitted that the development of new and advanced concrete mixtures has been strongly driven by the building industry. To find the right combination of cement, fillers, and admixtures was too often a tedious process of trial and error. For a more rational approach, instead of the trial and error process, the knowledge of cement chemistry should be on a high level. It goes without saying that, in this respect, Taylor's work has been, and still is, extremely important. It is almost inconceivable that modern tailor-made materials can be designed without being, in a way, also Taylor-made!

10. Conclusion

For many centuries, alchemists have been searching for something they have never found: a process to make gold from base metals. However, the relevance of the spin-off of their tedious research work has far exceeded their original aim. Their work has contributed to a large extent to the development of the modern chemistry. With this modern chemistry, it is even possible to make materials that can hardly be distinguished from real gold. Modellers also try to mimic the real world as reliably as possible, although they know in advance that a model will never transform in the substance to be represented. With the knowledge of today, we still have to admit that cement-based systems are still too complicated to describe them realistically. In spite of this, however, it has also to be admitted that even models that do exhibit shortcomings can support both fundamental research and the engineering practice. Parts of the DUCOM system, for example, have been used for supporting a study on radon transport in concrete [17]. Most probably, the researchers who developed the DUCOM system have never thought about the use of their model for that purpose. This example stands for the many "fruits" of modelling work and reminds us of Michaelangelo's provocative statement that "A builder's most blessed expense is the money spent on models" [18]. The quality of these models, however, will never exceed the quality of the input. It is the specialists who have to provide us with this input, and it is the joint responsibility of these specialists and the modellers to implement this input in the correct way. The contribution of Taylor to this interdisciplinary process can hardly be overestimated.

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