

Nano-1: part 2

Nanotechnologie:

Anwendungen in Architektur und Bauwesen:



Materials Science & Technology

Feasibility report for *cemsuisse* project Nano-1

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The mottos:

“I can't see exactly what would happen, but I can hardly doubt that when we have some control of the arrangement of things on a small scale we will get an enormously greater range of possible properties that substances can have, and of different things that we can do.”

“Furthermore, a point that is most important is that it would have an enormous number of technical applications.”

Two quotes from Richard Feynman's talk “There is a plenty of room at the bottom” at the annual meeting of the American Physical Society at the CalTech on December 29th, 1959.

...

...

“Nanotechnology is a multi-faceted field. It cannot be approached as a coherent field at all.”

Rachel Grange (OECD, Switzerland) at 1st year meeting of EU-funded project observatoryNANO. (Düsseldorf, spring 2009)

“It might not even be nanotechnology, but it is surely very interesting topic”.

According to the subjective assessment of Dr Pavel Trtik, one of the most frequently used sentences at the 1st year meeting of EU-funded project observatoryNANO. (Düsseldorf, spring 2009).

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1. Introduction

1.1. The definitions of nanotechnology

As stated in one of the mottos, nanotechnology is a multi-faceted field. It cannot be approached as a coherent field at all. The breadth of the possible definition of nanotechnology is underlined by the fact that, thirteen experts that were asked for the definition of the term provided thirteen rather distinct answers for the first issue of the Nature Nanotechnology journal^[1].

There is no single, ‘universally-respected’ definition of nanotechnology. In its very broad sense, nanotechnology can be viewed as the study and control of phenomena and materials at length scales below 100 nm.

Based on such definition, the term nanotechnology can (and usually does) refer to a broad collection of mostly disconnected fields. As a result, anything sufficiently small and interesting can be (and often is) called nanotechnology.

This fact intrinsically leads to diversity of opinions on what is and what is not nanotechnology, and hence on the utilisation and the impact of nanotechnologies. Even when the attention is focussed on applications of nanotechnology in the field of building materials and of cement and concrete, in particular, the prospects/potentials of nanotechnology are being estimated differently by different people.

The opinions range from very high expectations (“*Vast progress in concrete science is to be expected in coming years by the adaptation of new knowledge generated by a quickly growing field of nanotechnology*” Prof. Konstantin Sobolev ^[2]); to reserved (“*...the potential of nanotechnology in strict sense of the term,..., is less clear.* Prof. Karen Scrivener ^[3]).

In the reality, the prefix ‘nano’ seems to be rather trendy nowadays. Industrial entities “(mis-)use” this prefix for marketing purposes (e.g. Tata Nano, four-passenger, low-cost car built by Tata Motors mainly for Indian market being probably one of the most blatant examples).

Also in the field of fundamental research, the ‘nano-‘ and ‘nanotechnologies’ are trendy. The research funding agencies direct resources towards ‘nanotechnology’. As a result, some fields or terms are being “renamed” to include the ‘nano-prefix’ (e.g. colloidal particles vs. nanoparticles).

1.2. Literature/field survey of relevant publications on nanotechnology in building construction materials

The idea of utilisation of nanotechnologies for the purpose of building construction materials is not completely new. The efforts of combining nanotechnology for building construction materials can be dated to 1990s. There are number of reports already published on the topic(s) of nanotechnology in constructions materials. One of the first reports on the use of nanotechnology in construction domain was prepared by Zhu et al. [4]. The report attempts to summarise the impact of nanotechnology on entire construction domain. The conclusion of this desk study (summarised in [5]) has been that “the nanotechnology R&D in the built environment lags behind other industrial sectors”. The report has predicted “huge potential for nanotechnology application in construction as even minor improvements in materials and processes could bring large accumulated benefits.” Similar report has been published by Institute of Nanotechnology, UK [6]. In Germany, several relevant reports have been published recently [7, 8, 9]. It should be noted that only very few of these reports actually attempt to draw a roadmap of possible future developments in the field [10]. In EU, the development of nanotechnology in number of fields (including construction sector) are currently being analysed within the framework of FP7 funded project observatoryNANO [11].

Number of conferences on the topic of nanotechnology in construction [12, 13, 14, 15] and scientific meetings were organised in last decade producing more output on nanotechnology in construction. More scientific meetings on the topic of nanotechnology in construction are planned in the future. [16]

Last but not the least, Nanocem [17] - a consortium of European academic and industrial partners - should be mentioned here in the review of activities relevant in the domain of nanotechnology in construction materials. The consortium focuses on nanoscale research for cement and concrete.

1.3. Aims of the project

The aim of the project is to identify areas of nanotechnology that are promising for the building construction materials sector (for cement and concrete industries, in particular). Consequently, the further objective of the project is to provide as much objective and critical estimation of possible future impact of nanotechnologies (both positive and negative) in the field of building materials with the focus being directed towards domains of cement and concrete.

The authors feel obliged to highlight here once again the rather broad and unclear definition of nanotechnology. Only in Germany itself, there are 1232 entities (research centers, University institutes, SMEs, etc.) that are included in Nanomap [18]. Intrinsically, there are clearly potential applications stemming from the ability to understand processes and even more from the ability to modify and control materials and their properties on sub-100nm scale. However, the authors observe that the term ‘nanotechnology’ itself is overly used. Therefore, this report includes parts that in the opinion of the authors should not be subsumed under the term nanotechnology, but are generally included (for various reasons) under this currently trendy, many-things-encompassing term.

The major outcome of this project is the report of feasibility investigation focussed on the uses of nanotechnology in the fields of cement and concrete. The estimate of the possible future development in the fields mentioned above is provided in some especially promising examples. The impact assessment of the mentioned applications is carried out with respect to their potential for incremental development only or major breakthrough in the field of cement and concrete. For the most advanced and promising topics, the roadmaps of the estimated development are drafted.

After this concise introduction, the report is divided into the following chapters. Two chapters on applications are presented - first, a chapter on nanomodified bulk materials, and, further, a chapter on nanomodified large surfaces. Further on, the chapter on “nanotoolbox” is presented in which

the advances in (nanotech-based) characterisation techniques are reviewed and their potential for the cement and concrete science is discussed. In the next chapter, the potential health and safety aspects of nanotechnologies are presented. In the last two chapters, the authors propose the directions for possible further research and present conclusions.

2. Applications – nanomodified bulk materials

2.1. Introduction

In this chapter, we put focus on nanomodified bulk materials. Nanoparticles play key role in nanomodified bulk materials, therefore the nanoparticle production methods are reviewed in the beginning of this chapter.

2.1.1. Definition of a nanoparticle

A nano-particle in the common definition of the word is referred to as a particle in the 1 to 100nm size range. The upper and lower bounds are somewhat flexible and depend on the publishing source. Contrary to the term nanotechnology, it is not necessary for a nanoparticle to take advantage of size and related quantum effects at the single digit nanometer level to qualify as such.

Bottom up versus top down:

Generally scientists differentiate between bottom-up and top-down synthetic approaches. In the former, nanoparticles are obtained by chemical reaction and condensation of a molecular precursor which acts as the source of the nanomaterial. In a top-down synthesis, a bulk material is decomposed into small particles or fragments of nanometer dimensions, commonly by the use of high energy beams of fields (lasers, plasma, high temperature, electric discharge etc.). Generally, bottom-up methods afford higher versatility and better control of particle characteristics such as size, morphology and size distribution.

2.2. Review of production processes of nanoparticles

There exists a wide variety of nanoparticle syntheses with many new techniques being added each year driven by the nanoscience as a field of research. Traditionally, nanoparticles have existed for thousands of years: colloidal gold particles (metallic gold nanoparticles) for example were used as a stain for ruby red glass in ancient Chinese art. Noble metal nanoparticles, in general, had been carefully studied at the turn of the century. At that time described by the collective term “colloidal chemistry”, the same chemical synthetic methods and more recent ones have experienced a tremendous revival with the advent of nanotechnology. Given the great diversity of particle systems and chemistries (most chemical compounds can be obtained in a nanoparticulate form), a sheer unlimited number of experimental methods and techniques for the synthesis of such materials is available today. Various parameters can be used to classify synthetic methods and hence facilitate a general overview to then non-expert in the field.

In this chapter, we shall briefly discuss the four most common methods currently used for the synthesis of nanoparticles. This is a rather general description with emphasis on describing various classes of methodologies and their most typical applications.

Simple solution phase chemistry

Perhaps one of the most widely used and most versatile methods, used to synthesize (noble) metal nanoparticles and metal oxide particles; originated from classical colloid chemistry. Typically one or several precursors are dissolved in a suitable solvent. A chemical reaction then leads to the decomposition or activation of the precursor species to yield an activated form of the material – typically individual molecules or small molecular clusters - which condensates to form smaller so called seed nanoparticles. Such a seed particle consists of a few tens to a few hundred atoms. Once formed, seed particles can catalyze the reaction of additional precursor material at the interface between particle and the liquid solution. This is why usually seed formation (nucleation) is followed by particle growth which means that additional precursor molecules will selectively add to already existing particles and foster their growth rather than lead to additional nucleation. Solution phase nanoparticle synthesis is best known for the synthesis of noble metal nanoparticles (Au, Ag, Pt, FePt, Ru etc.) [¹⁹] and metal oxide colloidal sols (SiO₂, Al₂O₃, TiO₂, etc.) [²⁰]. In the

case of metal nanoparticles, the metallic precursor salt usually typically contains the metal in a higher oxidation state which means that the metal needs to be reduced. Typical reducing media used for the synthesis of noble metal nanoparticles are organic salts or solvents (sodium citrate, polyalcohols “polyols” such as ethylene glycol) as well as polymers, inorganic reducing agents (hydrogen, hydrides, boranes) and alternative methods such as light or direct electrochemical reduction. In the case of oxide nanoparticles, sol chemistry typically involves the hydrolysis of a precursor such as an alkoxide to yield the reactive metal hydroxide species which yields the nanoparticles. For a more detailed description of sol-gel chemical methods the reader is referred to section in the Chapter 2.3.

Template based solution synthesis

This methodology employs a template such as a reverse micelle or a well-defined polymer (a so called dendrimer) as a reactive moiety [²¹] which can be charged with a well defined amount of precursor material prior to the reaction. By controlling the amount of available precursor loading in each (identical) template, precise control over particle size and stability can be achieved. Dendrimer and reverse micelle syntheses are particularly well suited for hosting metal nanoparticles due to the strong binding effect (chelation) of the functional groups inside the moiety and are typically used for manufacturing thin film and multilayer structures.

Vapor-phase synthesis

In analogy to the solution phase case, the fabrication of nanoparticles in the vapour phase requires entering a condition (for example by rapid cooling) in which a vapour of a precursor material is thermodynamically less stable when compared with the formation of the corresponding solid [²²]. If the degree of supersaturation in the vapour phase is sufficient, nucleation will take place. In analogy to the liquid phase, a once nucleated system will then respond by condensation of additional material from the vapour phase onto existing seed particles (or nuclei). In comparison to the liquid phase, where growing particles can be protected by so-called capping agents, the unprotected surfaces of vapour phase synthetic conditions allow less control of deposition selectivity. This means that vapour phase methods allow generally less control over particle size and morphology when compared to solution based methods.

Core-shell nanoparticles

For a number of materials combinations, it is possible to coat an already existing nanoparticle with a layer of a second material of a different chemical composition. Such core-shell nanoparticles can then exhibit properties different from the original core particle. Perhaps the most well-known type of core-shell nanomaterials are the so-called quantum dots [²³]. A typical quantum dot is a semiconductor core-shell particle made from CdS/ZnS. Depending on the size of the particle, it emits a luminescence band which varies with particle size from blue all the way to red, covering the entire visible spectrum. The role of the ZnS coating in this system is to improve the luminescence yield of the quantum dot. Core-shell nanoparticles of other classes of materials such as noble metals (e.g. Au/Ag) or transition metal oxides (e.g. TiO/MoO) [²⁴] are readily accessible as well. The number of possible core-shell combinations is nearly unlimited.

2.2.1. Size and shape control of nanoparticles

Because of the nature of the growth mechanism in liquid solution, solution based methods are perfect model systems to study size and shape control effects in nanoparticle synthesis: In solution, a growing particle is constantly protected by a coordinating solvent or stabilizer molecule. By selecting a proper stabilizing environment for particles, their surface can be protected partially protected so that the growth (condensation of additional precursor material) is slowed down significantly and hence is better controlled. In many cases, the nature of the coordinating environment will lead to selective coordination effects. This means that for example one face of a crystalline nanoparticle will grow more rapidly than a second, more strongly coordinated one. In this case, specific particle shapes (cubes, prisms, odd shapes, rods etc.) can be obtained [²⁵]. This area of nanoscience represents a very popular playground for many research teams worldwide. However, in many cases there are some doubts as to the reproducibility of such highly fine-tuned particle preparations.

2.2.2. Synoptic view

Table 2.1 below shows a simplified overview over four classes of fabrication methods as they were described in the previous section. Note that each class contains itself a large number of various techniques. This section describes general trends rather than individual preparations.

Solution phase synthesis is by far the most versatile technology for the fabrication of monodisperse particles with exactly tunable size and shape. Its great versatility comes at the cost of reduced ease of scalability. Generally, methods which allow better control over size and shape are increasingly more difficult to use in large scale manufacturing. Template based methods afford great size control but are limited to surface applications. They have great potential for large area high-density particle arrays used in future microelectronics, display and sensing applications. In general, vapour phase methods are the least versatile when it comes to precisely controlling size and shape of materials. Chemical vapour synthesis methods such as flame spray synthesis are used commercially to fabricate millions of tons of carbon black or oxide materials such as fumed silica.

	Solution phase	Template based	Vapor phase	Core-shell
Size control	+++	++++	+	+++
Shape control	++++	++	+	+++
Versatility	+++	+	++	+++
Scalability	++	++(+)	++++	++
Top down (T) / Bottom up (B)	(B)	(B)	(T) and (B)	(B/B) and (T/B)
Preferred applications	Academic research / sol-gel chemistry	Academic research, surface array and multilayer formation	Industrial manufacture, ceramics, sputtering and coating	Quantum dots, academics

Table 2.1 - Overview over nanoparticle synthesis methods illustrating specific trends

2.2.3. Quality versus quantity: the issue of scalability

Nanotechnology is a field of great promise for the development of new technologies which can eventually come to fruition in the form of new products. Choosing an appropriate synthesis method for the problem at hand is of central importance. Innovation in this field will depend on properly defining and selecting nanomaterials (nanoparticles) with an optimum ‘properties to cost’ ratio. In other words, the preferred method of choice depends on the amount of required material.

For electronics, thin film and coating applications small amounts of particles of more or less well defined size and shape with a narrow particle size distribution are ideal. Such “academic” (solution and template based) systems are limited in their scalability towards large scale manufacture. Many state-of-the-art synthetic methods can produce particle batches with excellent size and shape control at small scales but do not perform as desired when the larger volumes are produced. Bulk applications which could be used for example in the building, food and plastics industry require large amounts of cost-effective material. In this case, the particle properties, such as dispersity and shape are of secondary importance. Vapour phase methods are inexpensive in comparison and can be implemented on a kilogram or metric ton scale; hence they are an ideal candidate for those types of large volume applications.

2.3. Sol-gel technology

The chemical synthesis of colloidal suspensions of nanometer sized particles or sols by wet-chemical (solution based) methods, most commonly by hydrolysis of a metal alkoxide precursor, gives access to virtually any metal oxide in nanoparticulate form (see Overview over nanoparticle synthesis methods). By controlling the interaction of individual particles in solution, their condensation can be triggered at will, creating a gel. A gel is the resulting three-dimensional random network of particles in a solvent matrix. Typically the solvent is then removed in a drying step, which significantly determines pore and microstructure of the final material. There exist a number of technological sol-gel applications: The three main classes are given below:

- **Thin film applications:** For this type of application, the sol is applied to surfaces prior to (or during) the gelation process either by applying from a nebulous spray or by dipping the sample into the corresponding sol solution [26]. Such spray or dip coating techniques can provide large area low-cost coatings for many technological applications such as but not limited to: Windows, protective coatings and paints, electronic and semiconductor industry, display technology.
- **Aerogels:** An aerogel is a sol-gel network from which the solvent was removed without causing considerable shrinkage [27]. This means that the original structure in the gel is mostly maintained giving rise to the low density (<15% of bulk density) and high porosity (>90%) characteristic for aerogels. The choice of the drying method either in a supercritical fluid (such as

CO₂ or halogenated hydrocarbons) or from a normal solvent under ambient conditions has a significant impact on the final aerogel properties.

- **Ceramics:** Ceramics are typically polycrystalline materials which can be obtained either from a metal oxide melt directly, from powders or by a sol gel process [28] and a subsequent sintering and compacting step. An inherent advantage of sol-gel chemistry in this case is a homogeneous mixing of multiple metal oxide precursors which is ensured by the “bottom-up” nature of the sol formation.

Thin film and coatings such as for facades or glazings on one hand and aerogels on the other hand, primarily for (translucent) thermal superinsulation, are the two main fields of interest in sol-gel science for the building and construction industry. The types of ceramics which are used in the building and construction industry are usually derived from oxide melts or compressed from powders. Sol-gel based ceramics find use in high-performance ceramics or for ceramic coating systems. In the following we shall limit our discussion to thin film / coating and aerogels applications based on their greater significance and potential for future cement, concrete as well as building and construction applications.

In coating and thin film science, sol-gel technology has attracted tremendous interest in the past years as an alternative to vapour deposition techniques (PVD and CVD) for the deposition of thin film materials. It has the advantage of combining non-vacuum solution based chemistry with low process temperatures and simple processing steps, making it a very economical choice for large area coating and bulk applications. Typically it is easily scalable towards large-area industrial production. Depending on a particular materials system at hand, vapour deposited thin films are often superior to sol-gel derived analogues. This is attributed mostly to the improved crystallinity of PVD and CVD deposited layers. However, the importance of “amorphous porous mixed oxides” as a promising class of inorganic oxides was recently pointed out by Frenzer and Maier who realized the potential of high-throughput synthesis methods and rapid screening for the development of new materials “by design”. Such systematic parameter investigations allow fast optimization of process parameters and with it a rapid achievement of both, a fundamental scientific understanding and optimized product properties. This opens up a great number of new thin film applications and products based on sol-gel methods, a trend which we expect to become more distinct in the near future.

When dried without considerable shrinkage, wet gels become aerogels, a class of materials with astonishing properties. Invented in 1932 by Kistler, aerogels were first produced by the Monsanto

chemical corporation. Even though commercialized only in the 1980s by Airglass in Sweden, a first commercial was relatively short lived, mostly due to the high price and cheap oil. During the last decade, the synthesis techniques have been masterfully refined and large scale commercialization implemented. Today's worlds largest manufacturers Aspen Aerogels and Cabot ("Nanogel") produce aerogels for thermal insulation in the space / aviation industry, for pipeline insulation and for the building and construction sector which in comparison is still a small market. A great number of aerogel composite products are being developed worldwide: Ratke [²⁹] recently showed excellent thermal insulation and fire protection properties of a light-weight aerogel concrete. Aerogel-filled glazings and aerogel plaster products are or will soon be available on the worlds markets. Aerogels also find use in consumer products such as coats and fashion, foot warmers and even refrigerator prototypes (Samsung). Due to cost reasons (the current market price of 1m³ of silica aerogel is roughly 3000US\$, summer 2009) the number of applications is still limited, however the growth of this class of products in the last decade has been astonishing.

To conclude, sol-gel based methods are among the more cost-competitive ways to fabricate large amounts of nanomaterials or nano-modified bulk materials. From the time of product development, a good decade may pass. Care must be taken to correctly judge the market's readiness (and volume) for new "high-performance" niche products early on.

2.3.1. Impact assessment of sol-gel method for the field of cement and concrete

A proper impact estimation of a fabrication technology or a class of materials requires not only a detailed knowledge of the field but more importantly the ability to differentiate "real" from "wannabe", "hot stuff" from "hot air". At times, when navigating in a field of great popularity, as for example nanotechnology is one right now, the secret is to keep straight course and hold clear of the sirens in the Aegean sea. Our assessment of the impact of sol-gel technology relevant for the concrete and construction industry is based on three criteria which are a) a scientific literature survey, b) an estimation of ease of development of novel sol-gel products and c) a case study of aerogels as a sol-gel model example showing tremendous growth in recent years.

a) Literature: Number of publications containing the following keywords:

In the following a literature study is presented which was conducted using the Web of Science database as a source. First, the following keywords were chosen as the relevant query parameters:

“nano”	“sol-gel”	“colloid”	“concrete”	“cement”
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Pairwise combinations of keywords were entered into the search engine and the number of references found in this way sorted by year. Only the recent literature (2000 – 2008) was considered in this study. The results are summarized in Table 2.2.

Keyword 1	Nano	sol-gel	colloid	nano	nano	sol-gel	colloid	sol-gel	colloid
Keyword 2				concrete	cement	concrete	cement	cement	concrete
Year									
2000	1237	2291	854	1	2	1	5	1	1
2001	1802	2422	807	1	3		1	1	
2002	2358	2607	846	1	3			7	
2003	3464	3144	879	6	9	1	2	8	
2004	4630	3497	1025	11	14	3	6	8	1
2005	5607	3755	1055	8	13	1	2	5	1
2006	6678	3987	1019	12	25		1	16	1
2007	7956	4694	1022	18	37	3	2	13	2
2008	8102	4764	1100	27	33	3	5	13	1

Table 2.2 - Literature search results for “cement” and “concrete” combined with “Nano”, “sol-gel” and “colloid”

First off, a comparison of reference search terms is necessary to describe the general public interest in the various areas of research. Our interest is primarily in nanotechnology and sol-gel applications in the cement and construction domains. The reference keyword “nano” clearly illustrates the popularity of nanotechnology: In the past eight years “nano” has seen a seven fold increase in annual publications, whereas the term “colloid” (colloids, colloidal etc.) has seen only a 30% increase in annual publications. Clearly, the term “nano” is widely used, at the same time people working in the field of colloidal science are much more likely to publish their research under the keyword “nanoparticle” rather than “colloids” these days. In other words colloidal chemistry as a keyword has lost its popularity. Another effect which cannot be denied completely is that older generations, growing up with colloidal chemistry, may still be familiar with the term and even use it still. More recent university graduates however may only be familiar with the modern terms nanoparticles and nanocrystals but not colloids. “Nano” sells, it has become a marketing instrument, also in the academic world. “sol-gel” has experienced great popularity over the past 8 years as well; the number of annually published articles has more than doubled since

2000. Clearly we see that the sol-gel field is in part fueled by nanoscience, in particular sol-gel derived thin films and coatings have attracted great attention as mentioned previously.

nano & concrete	nano & cement	sol-gel & concrete	colloid & cement	sol-gel & cement	colloid & concrete
"cement" >70% DNA, Bio fabrics	"cement" >70% ceramics "glueing / bonding" glasses bio-cements (dental, bone)	"cement" >50% ceramics electrical	"cement" >50% radioactive waste electrical colloidal particle flow	"cement" <50% silica bio-applications "glueing / bonding" castables spinel compounds	"cement" <50% radioactive waste bio-applications

Table 2.3 - Importance of the choice of two-keyword combinations for literature searches (an example)

Two keyword searching can be a great tool to look at the impact of a new field such as nanotechnology for example concrete or cement. Caution is required when interpreting the number of hits: Many search keywords can have several different meanings or they can occur in a number of dissimilar application- or field-specific technical terms. In our case for example, “cement” can have an auxiliary meaning of glue or adhesive. Depending on the second keyword, this meaning is more or less abundant in the respective search results list: “Nano” and “cement” as keywords yield over 70% satisfactory results addressing concrete as the construction material plus “Nano”. A combined search for “sol-gel” and “cement” on the other hand brings less than 50% of useful hits, this combination of search words seems preferentially used in glueing “cement” type applications, perhaps describing a larger number sol-gel based glue and castable systems. The importance of the choice of keyword is shown in Table 2.3. The “Nano/concrete” and “Nano/cement” combinations yield >70%, “sol-gel/concrete” and “colloid/ cement” >50% of useful search hits and hence are reasonable search parameters. With less than 50% of returns, “sol-gel/cement” and “colloid/concrete” are the clearly inferior search term combinations. If a literature survey is to serve as the basis for an impact assessment, care must be taken to thoroughly analyze the results and classify individual hits into two categories (appropriate / inappropriate). This general method of results filtering does not only provide information about other possible applications or uses of the word as a technical term in a perhaps very remote field of research, it also allows one to find out what keywords combinations are currently being used. It must be pointed out again, that the proper reference keyword searches must be preformed as well, as they are crucial to determine trends in a general field. In a second step must one argue about the relevance of a second criterion on that field (for example the abundance of “concrete” in “nano”-technology).

Now let us take a look at the direct impact of nanotechnology and sol-gel science on cement and concrete. Both “Nano/concrete” and “Nano/cement” searches clearly reveal a rapid recent development and a strong emphasis on Nanotechnology applications. Up to 2002, there was virtually no interest in Nanotechnology for cement and concrete applications. The great boom of nanotechnology on the other hand had already began a while ago and was in full bloom in the academic / fundamental science research fields. Even though the absolute number of annual publications are still small, an enormous interest in nanotechnology over the past 5 years is apparent. The nanofascination has clearly reached the cement and concrete field. The sol-gel impact on cement and concrete seems quite small and more or less constant over the past ten years with just a few annual hits for the “sol-gel / concrete” and “colloid / cement” queries. This, by the way, is not surprising at all: For a traditionally less academic and more manufacture oriented field such as cement and concrete, it makes sense to see only a measurable correlation between a new hot field such as nanotechnology but not with well-established chemical technology. It is the nano-hype which propels activities in far remote fields such as cement, concrete and building materials. Sol-gel is not attractive enough to do the same.

The literature survey is a powerful tool to assess current activity, which can in turns be a measure for impact assessment. In our case we can show a strong interest in nanotechnology for cement and concrete applications in recent years based on the number of academic manuscripts published. The same does not hold for sol-gel chemistry.

b) Risk / benefit / cost estimation of new product developments

A second way to look at the (possible) impact of sol-gel technology on cement and concrete industries is based on the (risk / benefit / cost) analysis of new product development possibilities. This is a generally valid method to predict the potential of a given technology for developing future products for a particular trade or business. This analysis requires precise knowledge of current technology and the new technology which is to be implemented into a new process or production scheme. Given the necessary knowledge this method allows to play through a number of alternative and to make a selection of possible candidate systems which are to be pursued in the form of R&D projects. The main advantage is the strongly product / application specific nature of this approach. Figure 2.1 shows the “Gedanken experiment” in its 5 steps.

Let us begin with a global system or problem (1). By defining current technology and its limitations, a next generation product and its improved properties is designed on paper. In a

second step, various sol-gel chemistries / recipes (2) can be considered as new carrier technology. Of central importance is compatibility of each fabrication step with the type of chemistry used. This must entail mastery of the sol-gel chemistry and a good understanding of specific reaction conditions and of course compatibility with materials and further processing steps. Processing of the sol (3) resulting in the formation of a thin film gel coating is the next step. For coating applications, the film composition, viscosity and the solvent are crucial parameters to obtain homogeneous crack-free layers.

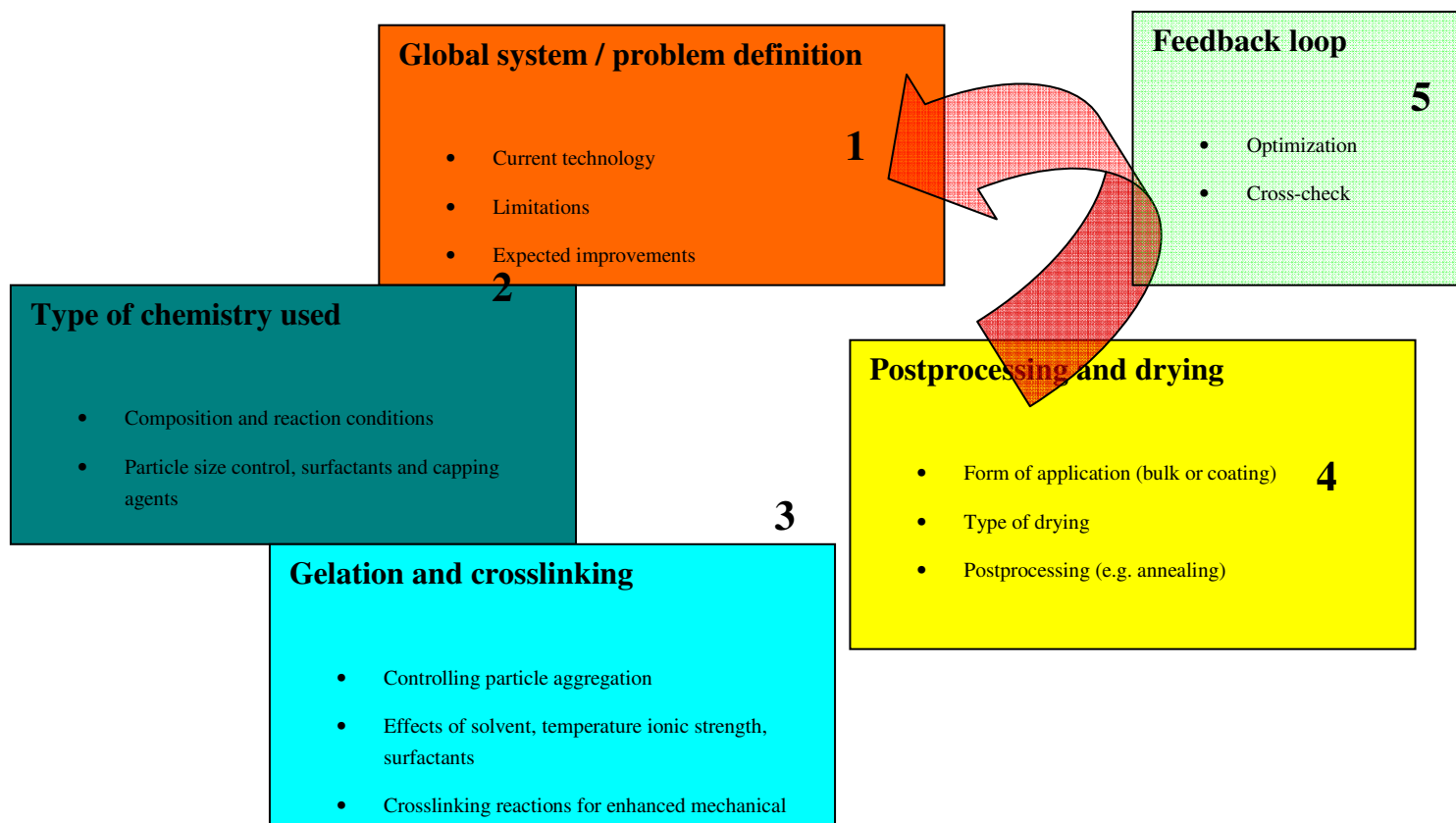


Figure 2.1 - Scheme for the systematic assessment of new product impact and performance based on fundamental scientific estimations

Once deposited, films and coating require a suitable post-treatment in order to become mechanically and structurally stable. Such a post-processing (4) includes solvent removal / drying but also annealing at various temperatures and/or in various reactive gas environments. The final process can be compared with various other possible candidates. A factual comparison must be carried out on the basis of economic, ease of processing and final product properties aspects. The relative weight of each aspect is a matter of the marketing policy and the already existing range of products on the market as well as the readiness of the market for a new generation of products. A correct assessment of the development potential and risks must be able to disclose both advantages

and problems or drawbacks associated with such a new method. Some of those problems may require rethinking. For this reason, a direct feedback (5) with the initial conditions / existing product can help working out one or several optimized solution approaches. Cross-checking with each completed revision / optimization loop can help achieving optimal solutions with minimal effort and time-commitment.

Provided sufficient knowledge about a specific product market and the chemistry of the production process can be gathered, a systematic impact assessment for a specific problem at hand can be easily found. With this phenomenological development approach, both R&D cost, pilot scale and large scale commercial manufacturing cost for a range of new products can be rapidly estimated and evaluated by a responsible board. The risk/benefit/cost estimation scheme is equally valid for any other class of materials development process. The sol-gel case was substantiated here as an example.

Given the great versatility of sol-gel science and the great potential of high throughput rapid screening methods, which have not found significant use in industrial R&D laboratories yet, there is a good probability for a significant increase in the number of sol-gel products by design in the years to come. The major concerns are cost performance compared with alternative methods and the processing steps which tend to be the tricky part. Nevertheless we expect to see a significant increase in sol-gel based coating and thin-film products over the years to come.

c) Aerogels as a model example for innovative sol-gel technology

In the introduction we had mentioned the history and recent development in the field of aerogels. A material developed in the 1930ies and since then used mainly for space-applications and in small volumes, the last decade has clearly brought the introduction to public markets. By far the most abundant class of application for aerogels is superinsulation. Given their small pore structure and low density, aerogels are excellent thermal insulators with a thermal conductivity 2-3 times lower than a conventional insulation material such as mineral wool or styrofoam products. The great market success of aerogels in recent years was clearly fuelled by the enormous energy cost in the pre-subprime area. High energy prices hence were the justification for a still extremely expensive niche-product such as aerogels to find a niche in the market.

Today, silica aerogels are commercialized by many companies. The most prominent manufacturers are Aspen Aerogels in Massachusetts, USA, Cabot Corporations aerogels division,

the American Aerogel Corp., TAASI Inc., Airglass Corporation. Some companies such the Birdair Company which sells aerogel-filled membrane products for lightweight suspended roofing solutions specialize entirely on post-processing and implementing commercial aerogels into new products. More recently we have seen a tremendous interest in aerogels on the Asian continent: Within the last four years Nanuo Inc. in China and EM Power in Korea have taken up production of silica aerogel products. We expect that this trend will prevail in the near future and that more and more companies will join this rapidly growing market as it represents a tremendous opportunity for many a businessman. Figure 2.2 shows the global market volume and its projected development for the year 2013. The graph is taken from a market analysis study by BCC Research, a US-based technology market research company.

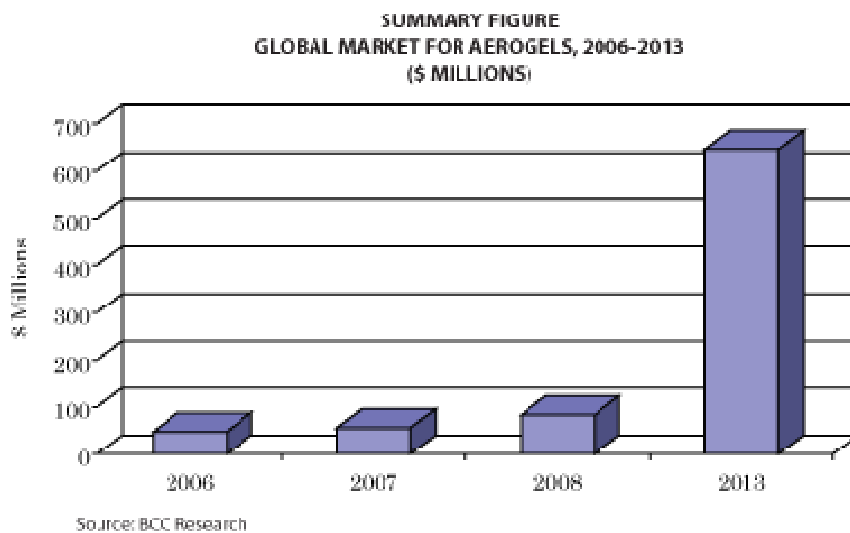


Figure 2.2 - Global Aerogel markets

The aerogels market volume between 2006 and 2008 grew from 62.2M \$ to 82.9M \$. This corresponds to an annual growth rate of approximately 15%. In 2006, insulation held a 58% share of the whole whereas in 2008 the insulation sector accounted for 70% of all aerogel products sold. The study further predicts that over the next five years there will be a tremendous growth of global aerogels markets. For 2013 a global market volume of more than 600M \$ is predicted, corresponding to an annual growth rate of about 50% . This is consistent with the emergence of a number of new aerogel producers worldwide. Also, with the fading of the global financial crisis, energy prices are likely to reach 2008 levels again. This will become a strong driving force for aerogel-based superinsulation products.

We have shown that the development of the Aerogels market in recent years can be viewed as a model example of applied sol-gel technology. A key prerequisite for such a picture-book like evolution of this field on the commercial scale is market-readiness. In this case, global markets were clearly ready for aerogels. Not every product which is developed (for example according to our proposed scheme in part b) of this chapter, will have the same chance of success. Perhaps the aerogels story can be viewed simply as a perfect example of market-readiness.

Potential of sol gel technology for the cement & coatings industry:

Future development in the sol-gel field is likely to target the following three main application sectors:

Various coatings (optical, tribology, anti-wear, anti-graffiti, photocatalysis etc.)

Promising “nano”-modified bulk materials: solution or spray coating of macroparticles (cm – μm size regime) with a functional sol-gel coating in a flow reactor system

Aerogels for thermal insulation (blanket products, high performance Aerogel concrete, insulating plasters and bricks on aerogel basis etc.)

The authors expect to see an increase in activity in those fields of research and hopefully number of new products.

2.4. Nanoparticles for high-performance concretes

After the review of nanoparticle production processes, let us have a look at the uses of nanoparticles in cement and concretes. The notion of using particles of smaller and smaller sizes in cementitious materials is not new. The typical example of this approach is the use of silica fume in concrete mix design. Silica fume, also known as microsilica, is a by-product of the reduction of high-purity quartz with coal in electric furnaces in the production of silicon and ferrosilicon alloys. It may have particles as small as 100 nm and could therefore be called a nanomaterial.

As a results, going “beyond” silica fume and therefore incorporating (for example silica) nanoparticles into cementitious materials for enhancement of properties of final cementitious

products seems to be a logical step of extending the concept of particle packing and particle size distribution.

Some concepts of simple additions of nanoparticles into the concrete mixtures are well summarised in report on Nanotechnology in Bauwesen [8].

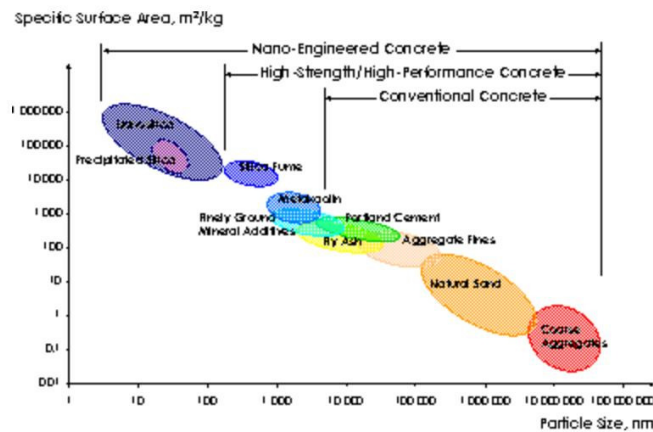


Figure 2.3 – The relationship between specific surface area and particle size for ‘aggregates’ used concretes (image courtesy of Sobolev et al. <http://nano-cement.50webs.com/>)

However, with decreasing size of the particles, the relative surface area increases tremendously (see Figure 2.3). In order to disperse the nanoparticles thoroughly and simultaneously ensure the fluidity/workability of the fresh concrete, a significant amount of superplasticizer has to be added into the mixtures.

It should be highlighted here that not only the improved particle packing but also other factors might be of importance. It is suggested the nanoparticles may act as nucleation sites for the formation of hydration products, consequently having positive effect on the resulting cementitious matrix. (denser pore structure of the mortar matrix, enhanced mechanical properties, lower permeability and hence enhanced durability).

Another issue that should be intrinsically addressed when nanoparticles are to become the integral part of the mix designs is the compatibility of nanoparticles with admixtures.

Last but not the least, the health and safety aspects of nanoparticles have to be addressed (please see Chapter 5). To summarize this sub-chapter, it is the opinion of the authors of this report that this direction of research and development has rather little to do with nanotechnology. In opinion

of the authors of this report, the incorporation of nanoparticles in concrete mix design, fits rather well with “definition” of nanotechnology as presented in Chapter 1.1, paragraph 3.

However, there seem to be another (possibly smarter) way of incorporation of (non)-functionalised nanoparticles into the concrete than just simple addition into the mix design. One of such applications has been reported already some time ago by Cardenas and Struble [³⁰]. It was demonstrated that electrokinetic nanoparticle treatments (using 20 nm silica particles) resulted in reduction of permeability of hardened cement pastes by 1-3 orders of magnitude. Colloidal nanoparticles electrokinetically transported into hardened cement paste pores undergo chemical reactions resulting in reduced permeability. It is interesting to note that despite the not so recent publication date (2006), the paper has not been quoted by any other publication so far and therefore the technique seems to have rather low impact. The penetration depths of the particles were also later simulated to be in order to tens of micrometres [³¹]. Consequently, it is the author’s opinion that the technique might have a potential for some of the applications described in Chapter 3.

2.5. (Nano-)coated (core-shell) cement particles

Cement is a powder material with particles size distribution ranging from the submicrometre to tens of micrometre domains. Since the material is in one of its final production steps processed by grinding, the particle size distribution can be somewhat tuned, but it is hardly possible to engineer particle shapes and composition of individual particles.

Unlike in the approach already described in the above chapter, let us here have a look into the question, if it is possible and feasible to produce cements whose particle size, shapes and composition of individual particles would be defined and tailored. In particular, let us explore the question if a core-shell cement particles of given composition can be possibly (and if yes then how) produced. It should be mentioned here that it is the authors opinion should each micrometre-range cement particle be ‘tailored’ regarding the size shape and composition, such cement could be likely called nanotechnology-based cement.

In other words, can cement particles be produced in such a way that their ‘shells’ would have ,for example, ‘Portland cement-like’ composition, while its ‘core’ would be composed of other (in this moment unspecified) material?

Raisons d’être for the core-shell cementitious particles

Let us here summarise some of the reasons why core-shell cementitious particles would be preferred. The images in Figure 2.4 are shows a “typical microstructure” of hardened cement paste based on ordinary Portland cement.

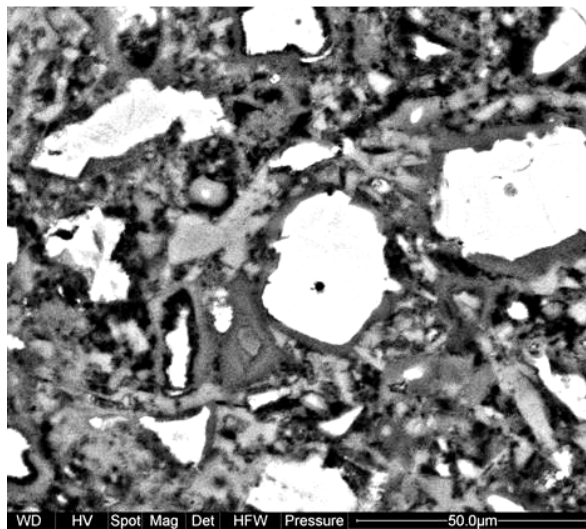


Figure 2.4 - Microstructure observed in hardened cement paste of wcr of 0.3.

By their material properties that are superior to those of hydration products, the unhydrated particles clearly contribute to the overall mechanical properties of the composite material. However, from the point of view of the energy consumption necessary for production of such particles, the standard cement production is highly demanding process with equivalent CO₂ emissions. When lowering the water to cement ratios (as is increasing trend in high-performance concretes and cementitious composites), the volumetric part of the unhydrated residues of cement particles in the material increases.

One of the logical steps how to avoid the use of energy demanding material in the cores would therefore be production of cement particles of ‘nano-engineered’ material structure. Such particles (with the cores made of less energy demanding material) would be (nano-)coated with a shell made of hydraulic binder (Portland cement like material).

Literature survey of relevant core-shell particles

There is currently no such cement available on the market, neither seems to be the above question addressed from point of view of fundamental research. This can be concluded from the survey of the literature presented in Chapter 2. Also, further search has been undertaken using Web of Knowledge search engine for ‘core-shell’ and cement provided limited number of hits (5) in the field of cement-based material used in biomedical applications.

On the other hand, the further Web of Knowledge search for keyword ‘core-shell nanoparticles’, provides 480 hits (July 2009). As already mentioned above, the majority of applications however is currently in the biomedical domain of controlled drug delivery, molecular imaging etc. Frequent are also the applications exploring nanomagnetic properties of core-shell nanoparticles. Regarding the relevant patents, two US patents that mentions production of nanoparticles together with cements were identified in the performed patent search [^{32,33}].

Production of nanoparticles of Portland cement-like composition

A very interesting development has been recently reported by Halim et al. [³⁴] in the Nanotechnology journal. Group of chemists from ETH Zürich were able to prepare calcium silicate-based nanoparticles of a typical Portland cement composition prepared by a new, one-step preparation using **flame spray synthesis**.

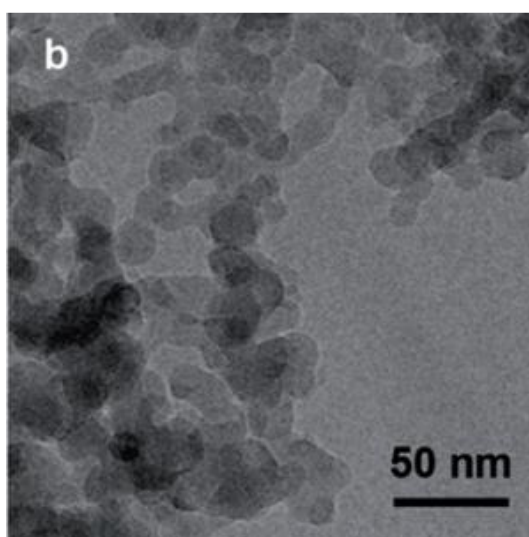


Image courtesy of Halim et al., Nanotechnology, 2007

Figure 2.5 – Image of calcium silicate-based nanoparticles as produced by flame spray synthesis and reported in Halim et al Nanotechnology, 2007.

The typical size of the calcium silicate-based nanoparticles was reported to be about 40 nm. The image of the nanoparticles is shown in the Figure 2.5 The larger particle size distributions (about 300 nm) were reported to be formed when the nanoparticles were sintered after the production. It is interesting to note one point about the publication of Halim et al. By the time of the submission of this report, the publication of Halim [³⁴] has been available already for more than two years. Still, this relevant (from nanotechnology in cement and concrete standpoint) publication is yet to be quoted or referenced by other researchers in a peer-reviewed journals. It can be concluded that therefore the outcome of this publication does not seem to have much impact on the cement community until now.

In the authors' opinion, the flame spray synthesised nanoparticles could possibly be used as the shell material in the core-shell cement particles in the future. Even though only minute amounts of the mentioned calcium silicate nanoparticles were produced so far on laboratory scale (tens of grams per hour), the flame spray synthesis is upscalable.

Flame spray pyrolysis

Flame spray pyrolysis is a chemical process, in which, a combustible precursor is fed into a flame spray reactor. As a results, the composition of the nanoparticles produced by flame spray synthesis can be tailored. The composition of the precursor determines the composition of the resulting nanoparticles. It has been shown that flame spray pyrolysis process may lead to production of nanoparticles of various types (e.g. mixed phase NPs, with segregated phase in one NP, coated NPs, etc.) [³⁵]. The most interesting type (from the standpoint of this report) is naturally the fully coated type of the nanoparticles. TiO₂ nanoparticles fully coated with amorphous SiO₂ were reported to be synthesized recently by flame spray synthesis [³⁶]. The particles were produced as titanium and silicon precursors had been co-introduced into a diffusion flame reactor. The image of such particle is shown in Figure 2.6. Very recently, it was shown [³⁷] that Fe₂O₃ particles can be hermetically coated with nanoscale layer of SiO₂.

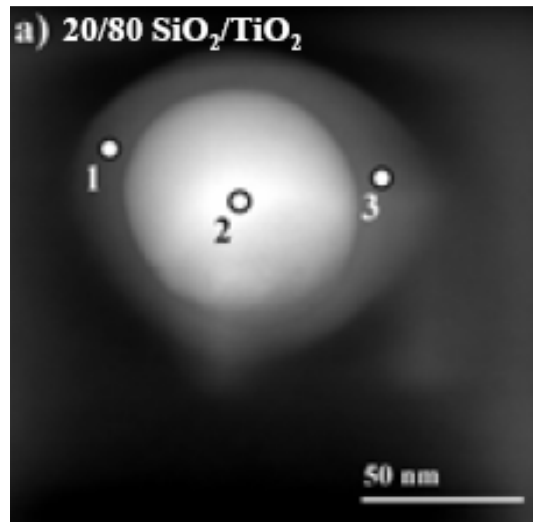


Image courtesy of Teleki et al., ETH Zürich

Figure 2.6 – Image of silica-coated titania nanoparticle produced by flame spray pyrolysis process. Image courtesy of Teleki et al. ETH Zurich.

Even though the size of the coatings (shells) remains only in nanometre regime, the proof-of-the-concept of possibility of production of (nano-)coated particles with hard cores is provided.

It is foreseen that the combination of two techniques mentioned in this Chapter (i.e. flame spray techniques and sol-gel technology) can possibly lead to production of core-shell cement particles of clearly defined sizes, compositions, and shapes in the future.

To the best of the author's knowledge, there has been no attempt reported in the literature so far for production of such core-shell cementitious particles with hard or soft cores. It should be mentioned that nano-tool techniques (as summarised in the chapter No. 4) should play key role in the characterisation of the (nano-)coated particles.

Hollow nano/microparticles

Hollow nano/microparticles can be perceived as special case of core-shell particles, in which the core does not contain any material. One of the examples of hollow microparticles is the use of fly-ash hollow particles generated from coal power plants as partial replacement for Portland cement, thus leading to production of concrete with enhanced strength and durability.

The review of synthesis and application of hollow micro/nanoparticles was recently published by Lou et al. [38]. From this review, it is worth noting that capability of production of silica hollow microparticles of different sizes is reported [39] (see Figure 2.7)

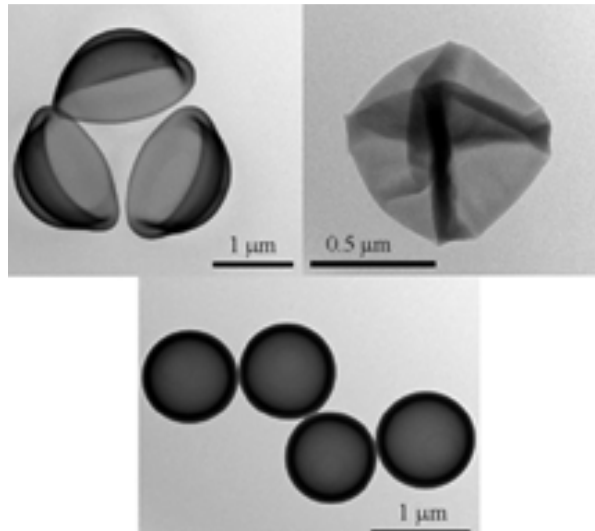


Image courtesy of Zoldesi et al., Advanced Materials (2005)

Figure 2.7 – Image of SiO₂ hollow microparticles of different shapes. Image courtesy of Zoldesi et al., Advanced Materials (2005)

2.5.1. Possible utilisation domains and impact of (nano-)coated particles in cementitious materials

As the core-shell cement particles are so far in the stage of theoretical consideration. It is naturally difficult to foresee all the possible applications and impacts on the cement industry. However, some application can already be foreseen. The (nano-)coated cementitious particles would lead to higher clinker efficiency.

The particles with soft cores (with a special case of hollow core) may find the earliest application in production of ‘light-weight cements’ and also for encapsulation of various additives in (hollow) microparticles.

2.5.2. Estimate of possible reductions in CO₂ emissions due to the use of nano-coated particles

Cement production processes are major sources of CO₂ emissions, accounting for 1.8 Gt CO₂ in 2005 [⁴⁰]. It seems to be the case that the drive for reduction of CO₂ emissions will not fade away in the foreseeable future [⁴¹]

There is likely no singular panacea solution that would do away with CO₂ emissions in cement production. As a result, a number of measures that would reduce CO₂ emissions of the final products will likely have to be employed.

In principle, the use of nano-coated cementitious particles (as envisaged above) has a potential to save CO₂ emissions. How much of the emissions can be possibly saved depends on many factors.

However, the upper bound of the savings is in this case clearly defined by the amount of unhydrated cement particles that remain in the microstructure of cementitious materials. This amount differs from mix design to mix design and thus from application to application.

2.6. Use of carbon nanotubes in cement-based materials

Any feasibility report on nanotechnology in construction materials would be incomplete without a chapter on use of carbon nanotubes (CNTs) in cementitious materials. CNTs are cylindrical carbon molecules that can be manufactured with length to diameter ratio of more than 10⁷:1. There are two main groups of CNTs – (i) single-walled nanotubes (SWCNTs) and multi-walled nanotubes (MWCNTs). The images of both types are shown in *Figure 2.8*.

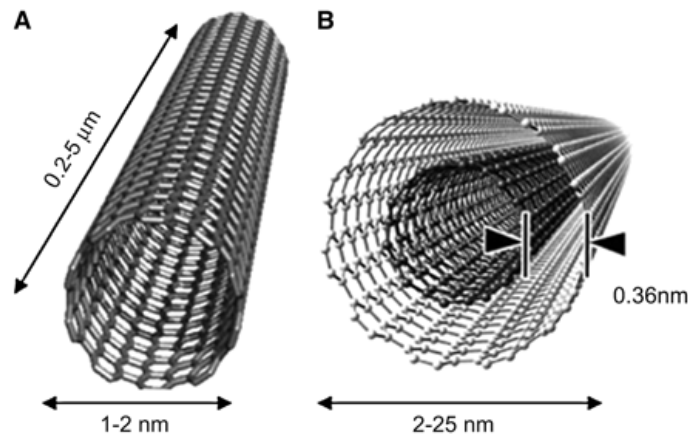


Figure 2.8 – Conceptual diagrams of single-walled (left) and multi-walled (right) carbon nanotubes. The length of the CNTs can be as much as several millimetres. Image courtesy of Society of Nuclear Medicine from Reilly RM, Journal of Nuclear Medicine Vol. 48 No. 7 pp.103.

Carbon nanotubes possess a combination of rather unique properties. From the mechanical point of view CNTs seem to be the strongest material so far discovered. Despite the natural difficulty in measuring the mechanical properties, carbon nanotubes are reported to have modulus of elasticity of over 1 TPa and estimated yield strength as high as 100 GPa [⁴²].

Naturally, such properties (when CNTs used in a composite as a “nanoreinforcement”) seem to have a great potential to enhance the properties of the composite material. The potentials of CNTs as nanoreinforcing materials have been drafted – together with other potential applications - by Makar et al.[⁴³].

In the last decade, several rather unsuccessful attempts [⁴⁴, ⁴⁵] have been performed to enhance the properties of cementitious materials by incorporation of CNTs into the microstructure of cementitious materials. In these attempts, considerable volumes of CNTs (in order of per cents of weight of cement) were added into the cementitious matrix. Not only was the improvement in mechanical properties in these attempts rather low (usually single digit per cents enhancements), but such applications were clearly uneconomical with respect to the volume of CNTs utilised. The price of CNTs is in order of approximately 1\$ per gram, hence additional price of many 1000s of \$ per 1 cubic metre of concrete was required for the mediocre increase in mechanical properties of the cementitious composite reinforced in this way by CNTs. Not only these reports made some other researches to conclude that “At present, however, such materials are not practical as an addition to concrete”. [⁴⁶, ⁴⁷]

However, there has been a reported apparent breakthrough in the use of the CNTs in the domain of cementitious materials. Cwiren et al [48] reported recently an increase in the compressive strength of nearly 50% even with only a relatively small addition of the MWCNTs into the cement paste. The addition of MWCNTs was reported to be in the domain of several hundredths of per cents of the cement weight. Similar enhancement of elastic properties by addition of similar amounts (about 0.05% of CNTs), as well as reduction in shrinkage of such cement paste/CNTs composite material, was recently reported by Shah et al. [49].

Naturally, if the enhancement of the properties due to addition of this rather low dosage of CNTs also translates in the corresponding improvement of properties in the case of concretes (and not only cement pastes as hitherto reported) remains to be investigated.

However, the experimentally obtained increase in elastic properties of such cement paste “nanoreinforced” with several hundredths of weight percent of CNTs is much higher than the prediction provided by simple models for composite elastic properties. Based on this fact, it can be therefore derived that the addition of CNTs has an influence on properties of hydrates in cementitious composites. It remains not fully understood, what physical mechanisms are behind the enhancement of the hydrates/binder properties. Future research will surely be directed into this area.

Of crucial importance in the use of CNTs in cementitious systems is naturally their uniform dispersion throughout the microstructure of the cementitious composite. Homogeneous dispersions of CNTs in mixing water can be achieved by sonification of CNTs in water with addition of a surfactant.

In order to even further utilise the superiour properties of CNTs, bonding properties of CNTs with the cementitious matrix will have to be tailored. The bonding of CNTs with the matrix can possibly be achieved by a surface functionalisation of CNTs. Attempts of such surface functionalisation were already performed [48] and further studies are expected in the future.

Last but not the least, it should be mentioned that papers reporting on nanotubes produced from other types of materials (such as silica) were published recently [50]. Even though there is

currently no true mass producer of silica nanotubes available, SiO₂ nanotubes might be potentially interesting for utilisation in cementitious systems.

2.6.1. Impact assessment of CNTs on the domain of cement and concrete

The facts presented above show an example how complex it might be to make an assessment of possible future impact of any application/material on any field. Especially challenging is to predict future surprising breakthroughs. Before the mentioned apparent breakthrough [⁴⁸], the impact of CNTs on the cement and concrete would be assessed as low to moderate in medium term with possible larger impact in longterm future.

With the price of one gram of CNTs already mentioned above (approximately 1\$ per gram), the CNT addition of the 0.05wt% of cement into the material (i.e. of approximately 200 grams of CNTs per 1 m³ of concrete), the cost of addition of CNTs into cementitious materials and into concrete is not completely prohibitive any more.

Above that, one manufacturer (Bayer AG) currently operates a plant that produces 60 tonnes of CNTs annually. It has been reported [⁵¹] that further upscaling (200 tonnes per year) is planned in the near future.

Consequently, it is possible to foresee (providing the health and safety issues can be successfully addressed) that CNTs might be used in cementitious materials in the medium term future. However, it is necessary to note here, that further research should be directed into the questions, such as, what mechanism is behind the enhancement of properties of cementitious materials due to addition of CNTs and hence, if the same or similar positive effect on properties of cementitious composites can be achieved in some other (more economical) manner.

Last, but not the least, if the addition of small amounts of CNTs (about 100g /1m³ concrete) can be called as ‘utilisation of nanotechnology’ is rather questionable, however, the cementitious material thus produced can likely be considered as an appropriate example of nanomodified bulk material.

2.6.2. Health and safety aspects of CNTs

Health risks and environmental hazards have to be mentioned also in the case of CNTs. Carbon nanotubes can be produced in a variety of sizes (both in various diameters and in various lengths), their surfaces can be functionalised. In principle, the entire life cycle assessment of each different CNTs must be performed before mass production is started.

There is, to the best of the knowledge of the author of this chapter, no report that would cover the health and safety aspects of the utilisation of CNTs in cementitious materials throughout the entire life cycle. The toxicity of CNTs has been however investigated and pulmonary toxicity in mammals is reported [⁵²]. Health and safety issues connected with nanotechnology are also presented in Chapter 5.

3. Applications – surfaces of concrete structures

3.1. TiO_2 Photocatalysis

a) TiO_2 Photooxidation chemistry: the basics

Photocatalysis is catalysis by a photochemical reaction typically occurring at a solid/gas interface. Such a catalyst absorbs the energy of a photon (“light particle”) and uses this energy to produce highly reactive radicals (e.g. hydroxyl radicals ($\text{OH}\bullet$)) from water. These radicals are then reacting in a number of possible ways to cause oxidation and reduction of various compounds adsorbed on the active surface. Like in any redox chemical process, at least two reactions must occur simultaneously, the first involving oxidation, from photogenerated hole states of the TiO_2 , and the second involving reduction, from photogenerated electrons. Oxidation usually affects organic (carbon based) species whereas reduced species are for example nitrous oxides or molecular oxygen. Both, oxidation and reduction processes must be balanced precisely in order for the photocatalyst itself not to undergo an irreversible change, at which point it would stop to be a catalyst. The types of reactions occurring, their extent and their rates depend upon a host of factors that are being unravelled through many academic research studies. Many efforts have been devoted to clarifying the oxidizing species generated at the irradiated TiO_2 surface, which is essential for understanding the mechanism of photocatalysis and for designing photocatalyst systems for environmental cleanup applications. Still, the exact mechanism is not yet known and depends on many factors such as temperature and the substances in contact with the photocatalyst. Ideally, the reaction products are water and less harmful compounds such as CO_2 (in the case of VOCs) or nitrate (in the case of NO_2). Theoretically most metal oxides could act as photocatalyst. But the - by far - most common photocatalytic nanomaterial is titanium dioxide (TiO_2). Besides titanium dioxide only zinc oxide (ZnO) is sometimes used in laboratory studies. Other

photocatalysts (e.g. a complex with manganese) are being developed, but they are too expensive for mass production. This article will thus focus only on nTiO₂.

Titanium dioxide (TiO₂) is one of the most popular nanomaterials. This is due to its outstanding, versatile properties (semiconductor, super hydrophilic, photocatalyst), its abundance and chemical stability, which make it inexpensive and “non-toxic”. There are three naturally occurring crystal structures of TiO₂: anatase (used for for example in photocatalytic applications), rutile (used in pigments) and brookite (only small amounts available). Titanium dioxide nanoparticles are available in particulate form or as suspensions – usually with a particle size around 30-50 nm. It is produced commercially by several companies in Europe. Main application areas of nano-TiO₂ include: UV-protection (e.g. in sunscreens, textiles), antimicrobial materials (e.g. tiles, water purification systems), self-cleaning surfaces (e.g. glass), non-fogging materials (e.g. car mirrors), air purification (e.g. paints, air filter systems, concrete/pavements) and solar cells.

Titanium dioxide must absorb photons with an energy of $h\nu \geq 3.2\text{eV}$ or $\lambda \leq 385\text{nm}$ (which corresponds to UV-light) in order to exert its photocatalytic activity. This limits its applicability to outdoor use. Alternatively the titanium dioxide must be irradiated with artificial UV-light for indoors applications. Research is now being carried out to develop materials which can also absorb blue visible light to power the catalytic reaction. The most promising class of materials are n-doped TiO₂ where n-dopants (negative) are for example nitrogen, phosphorus, boron, anthocyanines or carbon. One major challenge which limits the field of operation of nTiO₂ is that titanium dioxide bound in an organic matrix degrades its own binder because its photocatalytic activity targets all organic materials. Coatings/materials containing nTiO₂ must thus be inorganic such as cement. Additionally the following points should be respected when working with nTiO₂: No silicone rubbers should be used in sealants next to photocatalytic materials as this may inhibit the photocatalytic activity of nTiO₂.

The nTiO₂-containing material may not be covered with any kind of coatings or film-forming detergents which impedes the contact between the photocatalyst and the target compounds.

The surface of the photocatalytic material should possibly be moist. Water is necessary for the radical formation. (The water vapour present in the ambient air should normally be sufficient.)

b) Typical applications of TiO₂ photocatalysts

As previously mentioned, nTiO₂ is not only a photocatalyst which decomposes certain substances, it also exhibits superhydrophilic properties. Water on the surface of nTiO₂-containing materials

forms a continuous film instead of droplets. Materials with nTiO₂ are thus not only able to degrade pollutants (depolluting) but the products are even washed off by the water film (“desoiling”). The superhydrophilic property can be inhibited by the oil in silicon-based seals and sealants or other hydrophobic materials (e.g. oils or detergents). So far nTiO₂ has been studied for the degradation of three main classes of substances/organisms namely NO_x, VOC and microorganisms.

The disinfection potential of nTiO₂ was shown in diverse studies and field tests. Different antimicrobial products with nTiO₂ are on the market and are already widespread in Japan. The disinfection aspect is closely linked to the self-cleaning aspect. By killing microorganisms nTiO₂-containing façades and roof tiles prevent microorganisms such as algae from growing on such surfaces. The degradation of NO_x has been intensely studied in the frame of a EU-project named Picada. Degradation rates for NO₂ of up to 80% were found depending on factors such as wind direction, humidity, irradiation (incident solar flux and shading effects). Derneestere et al. [⁵³] studied the removal of toluene from air using photocatalytic TiO₂ in building materials. Toluene removal efficiencies up to 78% were observed depending on factors such as the gas residence time, temperature, and the relative humidity. The results revealed lower toluene removal efficiencies at higher relative humidity.

c) Use of TiO₂ into cement, building and construction materials

According to the Verband Deutscher Zementwerke, there are two major cement factories in Germany working with nTiO₂: HeidelbergCement and Dyckerhoff. HeidelbergCement has licenced a product called TioCem which was developed by Italcementi who is one of the leaders in this field of business [^{54,55}]. The product which guarantees long lasting depolluting effects (TX-active standard) is produced in Leimen and Ennigerloh. It has been applied to various places and is sold commercially. More information regarding these projects and the cement can be found on the Heidelberg cement company website. Dyckerhoff currently has no information available on its photocatalysis activities. In Switzerland Holcim (Schweiz) AG is observing the activities in the field of nanoscale additives, but has no projects in this area at this time. There are also several products for façade coating and paints on the market. These products have the advantage that they are applied on the surface and thus less of the nanoenabled material is needed compared to the integration of nTiO₂ in cement. Experts suggest using products like TioCem only in the exposed layer of the material. Also, thin walled products such as glass fibre reinforced panels for claddings

are intrinsically potential candidates for use of TioCem [⁵⁶]. This reduces material costs while still developing the full catalytic potential. One example for a nTiO₂-containing paint is StoPhotosan.

In densely populated countries (e.g. Japan) and big cities which face serious air quality problems (e.g. Rome) authorities are eager to test new ways to address air pollutants. In Japan the Sumitomo Osaka Cement is working since 1991 with nano-enabled products (Luxreport 2008). Different products are evaluated on larger scales in Osaka and Tokyo. Concrete pavement blocks on the “Leien” (main road) also have been specially treated in Antwerp: TiO₂ was added to a cement mortar to diminish the air polluting effect by exhaust gas. In particular, the conversion of NO_x to nitrate was targeted. The total surface area covered with photocatalytic material is 48’000m². The Jubilee Church, la Chiesa del Dio Padre Misericordioso, was built from high-density concrete enriched with white carrara marble and TiO₂ to achieve a bright white color. Through the self-cleaning and depolluting properties of photocatalytic TiO₂ the building will preserve its white colour despite the air pollution in the city. Some general information on the application of photocatalytic nanoparticles in construction materials can be found on www.observatoryNano.eu.

Applications of photocatalytic materials field have experienced quite a boost in popularity with many new products available in the building and construction markets today. Environmental issues play a central role in the applications of titania fillers. These include taking advantage of the photocatalytic behaviour in the development of self-cleaning surfaces for buildings, i.e. anti-soiling and antifungal growth as well as VOC (volatile organic compounds) and NO_x (nitrous oxides) emissions reduction [⁵⁷]. The latter can cause lung damage while in combination with VOCs it produces smog & ground level ozone and contributes to acid rain causing long-term damage to buildings. From a commercial point-of-view such benefits have an enormous impact on society. Japanese scientists [⁵⁸] have been actively exploiting the development of a variety of materials and products. Shortly thereafter, a number of European ventures have followed, most notably the ones in Italy by Global engineering and Millennium Chemicals. Also worth mentioning is the European PICADA Consortium [⁵⁹]. Here again, the focus is on self-cleaning and depolluting surfaces and facades based on TiO₂ nanoparticle activated coatings and cementitious materials. These applications include, anti-soiling, de-pollution of VOCs and NO_x airborne contaminants at the city level as well as antifungal/microbial activities. Numerous reports have appeared in newspapers and magazine articles highlighting such applications, i.e. self-cleaning paving and building blocks and facades that can also de-pollute the surrounding atmosphere [⁶⁰]. TiO₂ photocatalytic cements are normally loaded up to 5% by weight for

optimum activation and cost / performance efficiency. The relative catalytic activity of nanoparticles and pigments should be judged in the first instance by cross comparing positive effects with the durability of the product. In the case of paints and organic thin film coatings for example, this is a crucial point, because TiO_2 is likely to degrade also the paint matrix together with the targeted contaminants. For coatings and cementitious coated materials this would imply a surface which under light activation would have the ability to continuously destroy or burn off the surface dirt layers whether they be, carbonaceous, oil or soil by oxidation, but also deteriorate the integrity of the coating itself, if organic (such as resin-based) matrix materials are used. This can be seen visually in some of the commercial trials by Millennium Chemicals in tunnels in Italy: the photocatalytic cement remains clean after a period of use compared to that for un-doped cement. For paints and coatings the idea is to limit the oxidation and chalking of the paint film to the very near surface layers such that over time with weathering rain water will wash the top layer leaving an underlying clean fresh surface. In the cementitious case, the surface deposits are oxidised or “burnt off” leaving the surface layer clean. The photocatalytic activity of such coatings can be measured by for example, determining the fading rate of an impregnated dye such as Methylene Blue, a commonly used model substance to study oxidative degradation reactions. A siloxane coating with photocatalyst exhibits a rapid dye fade when exposed over a given period to sunlight; in comparison, the un-doped coating does show virtually no color fade.

d) Indoor and outdoor products, outlook

In general one can distinguish two classes of application of photocatalytic nTiO_2 : indoor and outdoor. Outdoor applications aim at clean façades (mainly private interest) and at reducing air pollution from traffic (public interest). Materials containing nTiO_2 for outdoor application are available and as it is fairly inexpensive, we expect the application of nTiO_2 to expand/increase significantly. It may be assumed that TiO_2 will be the only photocatalyst for market application also in the near and midterm future. Nanoscale titanium dioxide for indoor application targets indoor air pollution (e.g. VOC from organic solvents, paints/varnish etc.) and odours (e.g. cigarette smoke). As mentioned in a previously, nTiO_2 itself does not work efficiently with light in the visible range of the optical spectrum. However, it can be doped with different materials so that it is able to absorb also photons with less energy (visible light). Doped nTiO_2 is not yet commercially available though.

Photocatalytic nanomaterials for indoor application will enter the market possibly in less than 10 years. Indoor and outdoor application of nTiO_2 is assumed to increase considerably if air quality

standards are introduced. Governments are yet thinking about indoor air quality regulations for public buildings. It is also likely that cities with air quality problems will advance the use of photocatalytic building materials and pavements. It is yet a challenge to know the exact reactions that will take place on photocatalytic surfaces and to give binding efficiencies for the products. The reason is that laboratory studies can not perfectly simulate the environmental conditions while field tests face outside influences that cannot be controlled such as for example weather conditions and air pollutants present in the ambient air.

To conclude, photocatalytic coatings have gained significant attraction in the past years and will further strengthen their position in the building and construction industry. Even though initial expectations on product performance were partly exaggerated, there is a sizeable market for depolluting or “easy-to-clean” coating or façade systems. Used widely in large metropolitan areas, second generation improved products could bring about a significant depollution. Water purification is another main area of application for TiO_2 photocatalysts which has great potential for the future. TiO_2 photocatalysts being a nanoparticulate material, a thorough risk analysis for all relevant applications is essential (see Chapter 5).

4. Nano-characterisation toolbox for the investigation of properties and nanoscale processes in cement and concrete

The nano-characterisation toolbox is surely not a new thing. Many characterisation techniques that will be discussed hereinafter existed even before the term ‘nanotechnology’ was coined [61]. However, we will focus on the recent advances in the toolbox capabilities, especially those ones (i) where nanotechnology proved to be the enabling technology for nanoscience and (ii) potentially useful for investigations of cement and concrete.

With the expected development in nanomodified bulk materials, the techniques included in the toolbox will become even more important than it has been until nowadays.

4.1. Electron microscopy techniques

In the famous already quoted lecture, Richard Feynman appealed on physicists to make electron microscope 100 times better. Nanotechnology is not about electron microscopy, but electron microscopy is an important part of the toolbox for nanoscience.

Electron microscopy has been utilised for the imaging of cementitious materials shortly after the onset of electron microscopes. We will not go into the detail of electron microscopy techniques here. Neither shall we provide exhaustive survey of the use of electron microscopy. Both of these are provided in detail in Chapter 6 of [62].

However, we will concentrate on three techniques that recently led to breakthrough in electron microscopy techniques and in which nanotechnology played a key role as the enabling technology for nanoscience.

4.1.1. Electron microscopy of saturated samples - WETSEM technology

One of the principal disadvantages of standard electron microscopy is the fact that sample needs to be exposed to the high-vacuum environment. In environmental scanning electron microscope (ESEM), the sample can be kept in high range of relative humidities, however the imaging at close to hydrated conditions is difficult and the sample has to be placed on Peltier stage and cooled down.

The WETSEM technology avoids these difficulties and enables the back-scattered electron imaging and EDX chemical analysis of saturated samples at atmospheric pressure. The technology is based on a tailored capsule that can be located on the sample stage of a standard SEM. The principal point of the capsule is a nanoengineered membrane that is electron transparent and that withstands the pressure difference between the inside of the capsule and occurring within the used SEM chamber. Such test arrangement allows electrons to enter and exit the capsule, while the sample is maintained in its natural state at atmospheric pressure. The Figure 4.1 shows the test arrangement of the WETSEM capsule in electron microscope chamber.

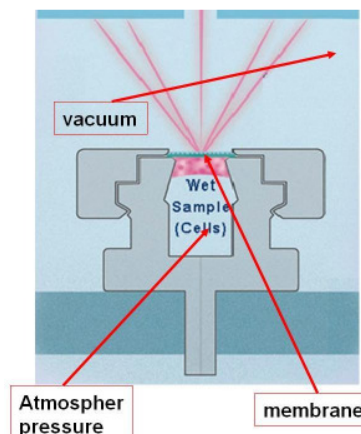


Figure 4.1 – Schematic diagram of the air-tight electron-transparent WETSEM capsule (image courtesy of Quantomix Ltd)

The possible applications of this technology are manifold ranging from observation of biological materials in their ambient environment, to assessment of foams and volatile materials. Samples that are very hard or impossible to be observed by electron microscopy (emulsions, suspensions,

gels etc.) can be thus observed and characterised. Another principal advantage is that observation of quasi-dynamic processes (such as cement hydration) is possible.

In the field of cement and concrete, the technology seems to provide a tool for observation of hydration products in the early phases of hydration. Very early phase of hydration from time $t = 0$ s to approximately 10 minutes cannot be observed as the SEM chamber has to be evacuated. Some initial investigations using this technology were already performed by Katz et al.^[63] and by Gallucci et al. ^[64]. In these investigations, continuous in-situ observation of early hydration process was performed. The disadvantages of this method are (i) intrinsic 2D observation (like any SEM), (ii) the view blocked after major hydration product, such as large calcium hydroxide crystals appear in the vicinity of the membrane (see ref. [64]), (iii) unrepresentative particle distribution in vicinity of the membrane and (iv) electron beam damage.

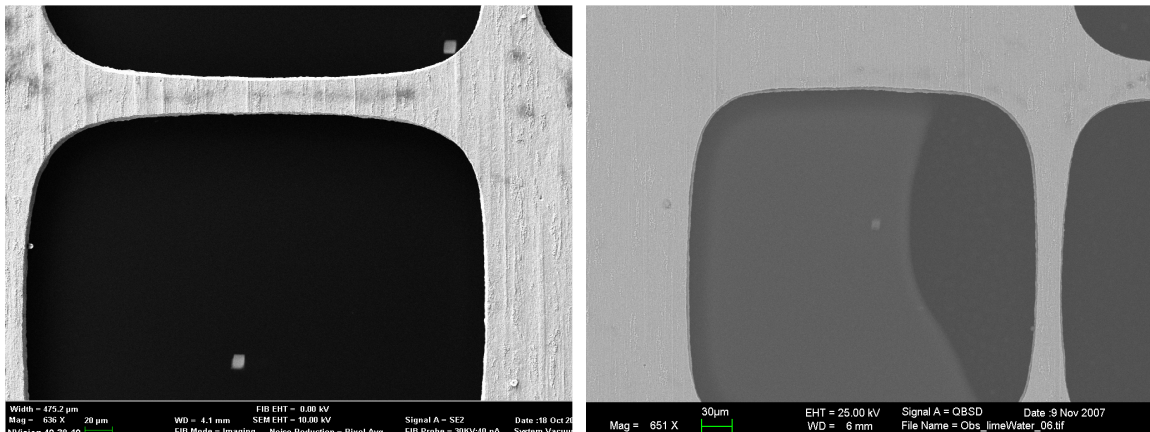


Figure 4.2 – (left) SiO₂ ‘particles’ deposited on the inside of the membrane of WETSEM capsule – imaged in air, (right) detail of one of the particles imaged in aqueous environment.

Interestingly, the electron transparent membrane also withstands deposition of solids using focus ion beam deposition. Preliminary test using deposition of SiO₂ on the membrane were carried out by Trtik ^[65]. The image of deposited SiO₂ “particle” on the membrane is shown in Figure 4.2. As mentioned above, it is currently not possible to observe the first approximately 10 minutes of the dynamic process. Should the WETSEM capsule be connected with a microinjector, a small amount of liquid/gas could be injected into the capsule in-situ (i.e. in-situ wet-capsule microinjection). We foresee that such enhancement might prove useful for the observation of very early hydration process.

4.1.2. (Cryo-) transmission electron microscopy/tomography

Transmission electron microscopy (TEM) is the original electron microscopy technique that has been long used for analysis of nanostructure of hydration products of cementitious materials [66].

The problematic side of TEM is twofold. First very thin samples (that are electron transparent) have to be prepared for this microscopy technique. Second, as is the case with high resolution SEM imaging, the electron beam damage might be very high. For example, the ettringite phase is known to be rather unstable in the electron beam.

Recently, the cryo-TEM technique has been developed and was used for microscopic investigation of C-S-H filaments in their close-to-natural state by Roessler et al. [67]. By limiting the dose of absorbed electrons in the sample Roessler et al. showed that (i) C-S-H possess crystalline structure (ii) the granular structure of C-S-H ‘observed’ by Gatty et al. [68] can be interpreted as the bubbles occurring in the C-S-H filament due to the electron beam damage.

With its cryo-, low-electron dose version, the transmission electron microscopy promises to be a tool for true nanostructural analysis of hydrated materials in their close-to-native state. However, it needs to be highlighted that the preparation of electron transparent samples will remain a demanding exercise.

It is envisaged that 3D imaging of nano-structure of the hydration products will be possible using low-dose cryo-TEM tomography. This technique proves to be helpful for the analysis of nanostructure of biological cells that exhibit certain amount of symmetry [69]. The resolution of TEM tomography is about 3-5 nm and is strongly limited by ‘missing wedge’ of projections, which cannot be taken on thin, 2D samples due to the geometrical constraints.

The very recent development of sample stages and sample production procedures for TEM tomography of cylindrical (nano)microsamples gives hope for true 3D observation of nanostructure of samples without symmetry (such as hydration products of cementitious materials) in the future.

4.1.3. Focussed ion beam nanotomography

The intrinsic disadvantage of scanning electron microscopy is its 2D nature of observation. Even though some 3D information can be obtained from SEM images taken from two ‘stereological

angles' and despite attempts of simulation of 3D images from 2D templates [70], the information obtained from SEM is two dimensional. When properties (e.g. connectivity of porosity) of complex materials such as those based on hydraulic cements are to be characterised, 3D techniques are required and some type of tomography has to be employed. As tomography based on X-ray imaging will be discussed in further chapters, we will just note here that 3D images of resolution below 1 μm based on X-ray tomography are still rather rare.

If higher resolutions are required, such as in the case of characterisation of the pore volumes in hardened cement pastes, one currently needs to employ a locally destructive method of focussed ion beam nanotomography (FIB-nt). This rather novel technique [71,72] utilises dual (electron & ion beam instrument) for procurement of a three-dimensional stack of electron microscopy images. The spacing between the images in Z-direction is achieved by milling the material away using focussed ion beam. The use of FIB-nt for assessment of cementitious materials was pioneered by Holzer et al. [73]. However, in these investigations only porosity and matter could be segmented from these images.

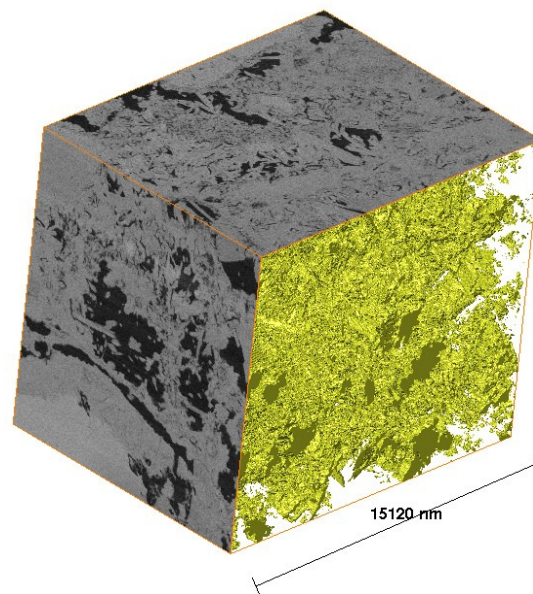


Figure 4.3 – 3D image based on FIB-nt dataset (using dedicated BSE detector) of hardened cement paste (OPC, 0.3 wcr). Other phases apart from the porosity can be also segmented from the dataset.

By utilising a dedicated backscattered detector, images of much higher signal to noise ratio were captured by Trtik et al. [74] within the *cemsuisse* supported project on Relationship between porosity and permeability of hardened cement pastes. The nanostructure of various hydration

products can be segmented in 3D from such datasets. An example of 3D rendering of one of these datasets is shown in Figure 4.3.

Such datasets provide a plethora of information and even though the question of representativity and sample preparation of the FIB-nt volumes to be further addressed in the future, the 3D images can be very well used for simulation of various experiments (i.e. virtual experiments), from which physical and mechanical properties of the imaged materials can be derived. A short summary of such virtual experiments is presented in Chapter 4.3.

The major disadvantage of the classical FIB-nt is the fact that the sample has to be exposed to high vacuum. The utilisation of cryo-FIB [75,76] is envisaged in the near future for 3D observation of cryo-prepared hydrated samples. However, it must be pointed out that the technique can be used only for the saturated samples.

4.2. X-ray microscopy techniques

X-ray techniques are complementary to the electron microscopy techniques. The resolving power of X-ray microscopy lies between that of the optical microscopy and the electron microscopy, however, it possesses a clear advantage over conventional electron microscopy that hydrated samples can be observed in their natural state.

It should be however mentioned here that exposure of hydrated samples to X-rays is not damage-free. The radiation damage is an issue that has to be taken into account seriously in all X-ray experiments and in those that utilise the intense X-ray sources (such as synchrotrons) in particular. The author suggests that the radiation damage experiment [77] should be performed as preliminary experiment for every experiment utilising intense sources of X-rays for imaging [78]. We acknowledge the fact that such practice is only seldom applied (or seldom reported in publications).

4.2.1. 3D Synchrotron X-ray imaging techniques

Synchrotron-based X-ray microtomography (SR μ CT)

The combination of X-ray microscopy with tomographic techniques as well as the exceptional properties of third-generation synchrotron radiation sources (such as Swiss Light Source, PSI, Villigen) allow to obtain volumetric information of a specimen with resolution of about 1 μm^3 . The method is apparently non-invasive and requires minimal sample preparation. Over the recent decades, the synchrotron-based X-ray microtomography established itself as an important tool for non-invasive 3D imaging of broad range of samples (from materials science to biological materials). X-ray tomography provides a clear advantage possibility of multiple observation of an identical sample. This fact can be well utilised for observation of changes in the material microstructure. In the particular case of materials cement-based materials, the changes in time (hydration), due to changes in moisture (shrinkage), due to loading (fracture) can be observed.

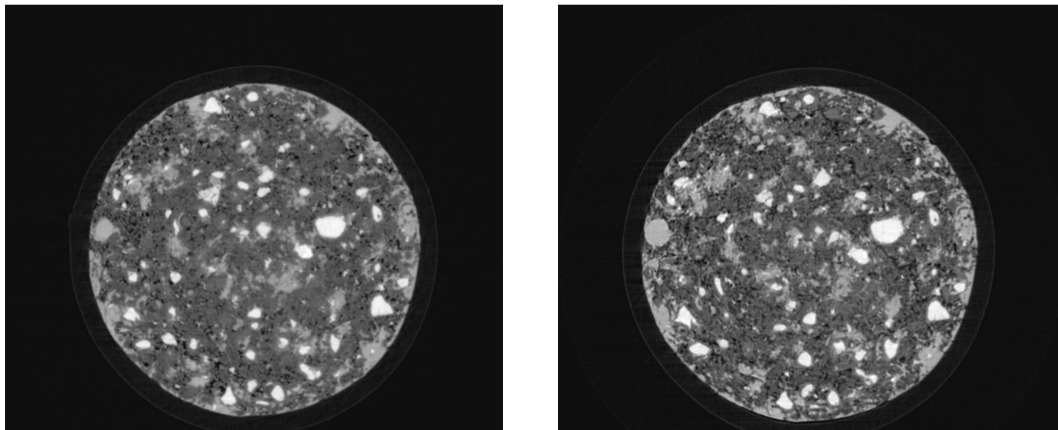


Figure 4.4 – Corresponding axial cross-sections (2D images) based on 3D SR μ CT images of cylindrical sample of hardened cement paste (left) fully saturated before drying, (right) after exposure drying.

SR μ CT is not per se nanotechnological testing technique. Its resolution is not in the nm-range, it is limited to the micron range. However, it has been shown recently that sub-voxel deformations in 3D disordered materials such as hardened cement pastes can be resolved using volumetric digital image correlation [79] down to approximately 2 per cent of the voxel size (i.e. corresponding to better than 15 nm) [80]. It is envisaged that such resolution is sufficient for nanoscale assessment of shrinkage in cementitious materials. Figure 4.4 shows results of a preliminary experiment exhibiting clear microstructural changes in sample of saturated hardened cement paste that was exposed to drying.

Synchrotron-based X-ray nanotomography (SRnCT)

As mentioned above, thanks to the brilliance of modern third generation synchrotron sources, voxel sizes in the micrometer range are routinely achieved by X-ray microtomography. However, the challenge of trespassing the 1 micron and 100 nm barriers is realised only by few instruments.

In the soft X-ray regime, the 2D observation of cement hydration with resolution down to 25 nm has been realized already several years ago using ALS bending magnet test set-up. However, the soft X-ray regime does not allow observing samples of realistic water-to-cement ratio and thus wcr of 100-500 were employed [81]. Also, the low temporal resolution of the mentioned particular test set-up hinders the 3D/4D imaging capabilities.

The very recent development in nanotechnology based focussing elements (e.g. beamshapers and Fresnel zone plates, Zernike phase contrast elements), however, show promise in X-ray tomographic imaging of sub-100nm resolution. One of these few instruments, namely the full-field nanoscope at TOMCAT beamline [82], SLS, PSI Villigen, was recently developed and commissioned in Switzerland. This instrument operates at hard X-rays regime (about 10 keV). Relatively high temporal resolution (order of several minutes per one tomography experiment) of this 3D nanoimaging instrument is expected, thus providing capability of following time-dependant processes (such as cement hydration) in 4D.

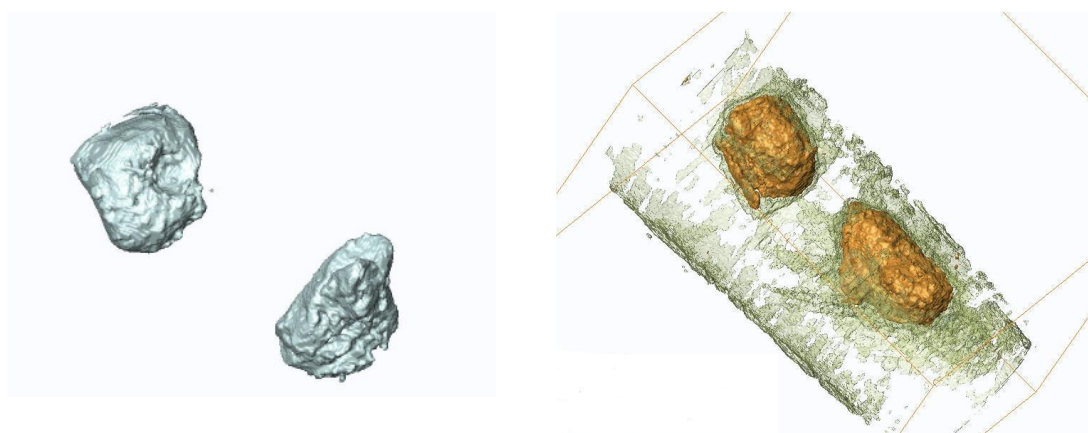


Figure 4.5 – (left) 3D rendering of two particles(approximately 8 μm in size) of pure tetracalcium aluminoferrite (C_4AF) as imaged using full-field nanoscopic tomography at TOMCAT beamline with approximately 100 nm resolution. (right) 3D rendering of the same sample after several hours of hydration. Please note the hydrate assemblage with AFm phases (likely C_4AH_{13})

Pilot experiments revealing hydration of a limited number of particles of pure tetracalcium aluminoferrite ($C_4AF = 4 \text{ CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$) enclosed in capillary of approximately 15 micrometres in diameter were performed recently by Trtik et al [⁸³]. The hard X-ray regime utilised at this test set-up will enable the observation of the samples of realistic water-to-cement-ratios. The partially absorbing samples can be observed using phase-contrast modality of the nanotomography test set-up⁸⁴. In general, the direct observation of processes occurring in cement paste in 4D has a potential to bring much better understanding of durability-related issues in cementitious materials [⁸⁵].

4.3. Characterization of material properties based on 3D images

3D nanoscale imaging (as described above) can be considered quickly developing field of science. In this chapter, we shortly focus on the equally important and equally challenging step of scientific investigations - processing and data analysis of the outcoming 3D images. In other words, a short paragraph of techniques, which take the 3D imaging beyond the acquisition of ‘pretty pictures’ is reviewed hereinafter.

The very first step in understanding the properties of a specimen is to provide a three-dimensional visualisation of the specimen. 3D surface renderings of segmented images provide a clear 3D view of the image. High-quality, artefact-free [⁸⁶] images are required for successful material phase segmentation. Even though the visualisation is only the first step in the characterisation of 3D images, it can bring the understanding of complexity of materials phases that would not be obtainable from 2D imaging.

On successful 3D segmentation of the dataset into material phases (e.g. porosity, hydration products, unhydrated residues of cement particles, etc.), morphological and geometrical analysis of the individual phases can be commenced. As for the granular materials, such as cement particles, size distributions can be revealed after application of successful particle splitting procedures. Object recognition from densely packed microstructures requires specific algorithms for splitting of agglomerated particles [⁸⁷]. At this stage, the surface topography can be also assessed using a virtual topographical experiment.

When the 3D image is representative of the material and its resolution is adequate, numerical analysis might be successfully applied in a virtual experiment and thus the material properties can be calculated purely on 3D image. Mechanical properties such as **elasticity** of multiphase materials can be calculated using a finite element method. The crux of the method lie in (i) superimposition of a 3D FE mesh onto the original 3D digital image and (ii) in the provision and assignment of the correct mechanical properties of individual phases in the model [88]. **Stress-strain curves** and hence material strength can be also assessed by application of beam-lattice models that are based on the 3D images of the material (micro-)structure [89].

Apart from the mechanical properties, transport properties as **permeability** can be virtually assessed on tomograms using lattice Boltzmann method [90]. Steady-state **diffusive transport** caused by e.g. chemical potential gradient can be modelled by random walk algorithms [91]. Also, thermal conductivity and electric resistance of the multiphase materials can be assessed by such virtual experiments performed on realistic 3D images of material (micro-)structure.

Last but not the least, processes occurring in the complex pore space of porous media (e.g. **drying**, **vapour condensation** [92] in nanoscale porosity of hardened cement paste, or **intrusion** processes [93]) can be modelled and virtually assessed based on the segmented 3D images of the complex 3D pore space.

It should be highlighted that all the numerical methods described above require significant computational efforts that can be assured only by parallel computing.

4.4. X-ray Scattering techniques

Various techniques have been developed to determine the structure and size of particles with sizes down to the single nanometer range. Among the most commonly used methods for the nanoparticle characterization are electron microscopy, X-ray diffraction (XRD), small-angle X-ray scattering (SAXS) as well as light scattering, particularly dynamic light scattering (DLS). SAXS and XRD are both indirect methods, which means that the size is derived from a model which is used to fit the scattering data. Such models normally assume mono-or polydisperse distributions of particles of a given shape (e.g. spheres) and then can predict the main components of a particulate specimen. SAXS and XRD provide more reliable information from a statistical point of view

because the measurements are based on macroscopic sampled volumes containing huge numbers of individual particles which are averaged and give rise to the total signal. In transmission electron microscopy often only a few particles are characterized, sized and counted.

Uncertainties in the determination of particle sizes are a well-known and frequently encountered problem in the nanoworld. A good example reflecting those uncertainties is the establishment of so-called “sizing curves” for semiconductor nanocrystals (quantum dots) where the band gap determined by optical spectroscopy is plotted against the particle size [⁹⁴]. Despite all efforts reported in the literature, there is still a need to compare results from different methods in order to check their applicability to nanoparticles, especially in the size range below 10 nm where quantization effects crucially depend on the particle dimensions. Recent progress in colloidal chemistry makes it possible to synthesize nanocrystals of high quality, that is, nearly monodisperse, highly crystalline nanoparticles with controllable size and shape. Such particle preparations are ideal model systems for the establishing the cross-correlation of the different analysis methods. In this case, the comparison of different methods produces more precise and meaningful results.

XRD:

Diffraction occurs as waves interact with a regular structure whose repeat distance is about the same as the wavelength of the electromagnetic radiation used to irradiate. The phenomenon is common in the natural world, and occurs across a broad range of wavelengths, from IR over the visible spectral range all the way to high energy (hard) X-rays. Visible light for example can be diffracted by a grating having arrays of regular lines spaced by dimensions of hundreds of nanometers, about the wavelength of light. This phenomenon is used in a grating monochromator in optical spectrometers.

X-rays, having wavelengths on the order of a few angstroms, which is also the lengthscale of typical interatomic distances in crystalline solids, are ideal to study diffraction of such materials. In other words, X-rays diffract off minerals which are by definition crystalline and have regularly repeating atomic structures. If an X-ray diffraction (XRD) pattern is recorded, various crystal lattice planes give rise to dissimilar diffraction signals depending on the angle of observation and the crystals chemical composition and geometry [⁹⁵]. Therefore, the most common use of powder (polycrystalline) XRD is chemical analysis. This can include phase identification (search/match), investigation of various phases including the presence of various thermodynamically stable and or

unstable phases, solid solutions and determinations of unit cell parameters of materials under investigation. In addition, X-ray diffraction provides an intriguingly simple possibility for estimating the particle size from the broadening of the XRD reflections by means of the so-called Scherrer formula.

$$d = \frac{K \cdot \lambda}{\omega \cdot \cos(\theta)}$$

where d is the particle size, λ is the wavelength of the radiation, θ is the angle of the considered Bragg reflection, ω is the width on a 2θ angular scale, and K is a constant close to unity. Values for the coefficient “ K ” depend on factors such as the geometry of the crystallites and are, unfortunately, not always consistently used in the literature. Moreover, powder X-ray diffraction is sensitive to the size of coherent scattering domains which can significantly differ from the particle size in the case of eventually present lattice defects or amorphous surface layers.

SAXS:

Small angle X-ray scattering (SAXS) is a technique for studying structural features of colloidal particle ensembles or complex porous materials with regular structural features in the nanometer size^[96]. Examples include polymers, liquid crystals, oils, colloidal (nanoparticle) suspensions, aerogels and biological samples like fibres or protein molecules in solution. It is performed by focusing a monochromatic low divergence X-ray beam onto a sample and observing the coherent scattering pattern that arises from electron density inhomogeneities within the sample. Because the dimensions typically analyzed are much larger than the wavelength of the X-ray wave used ($\lambda = 1.54 \text{ \AA}$ for a Cu source), dimensions from tens to thousands of angstroms can be analyzed within a narrow angular range, the so-called small angle scattering range. Small-angle X-ray scattering (SAXS) covers a range between 2-200 nm and scattering angles from 1° to 10° whilst wide-angle X-ray scattering (WAXS) typically covers an angular range between 5° and 60° . The scattering pattern is analyzed using the inverse relationship between particle size and the scattering angle to distinguish characteristic shape and size features within a given sample.

The technique is used beneficially when applied simultaneously with methods that influence and/or change the samples' structural characteristics (e.g. during temperature changes, under shear forces or upon the application of electric/magnetic field stimuli). The high flux of synchrotron X-rays allows us to follow these changes in a time-resolved manner.

The high intensity of X-rays produced from synchrotron radiation sources enables dynamic X-ray scattering experiments to be performed on materials contained within sample environments that mimic processing conditions and mechanical function. For example in polymers it can provide information on crystallite size, unit cell size, thickness of the interface between microphases, or between the crystalline and amorphous regions. For proteins in solution it provides information regarding size in terms of the radius of gyration, insights into the distance distribution function of the sample (its maximum size envelope), shape and an a priori shape reconstruction or a low resolution, model-independent molecular envelope structure.

4.5. Nanomechanical testing

No tool-box of nanotechnology-based techniques would be complete without at least a short paragraph on nanomechanical testing. One of the most popular nanoscale testing techniques for assessment of mechanical properties on nanoscale is nanoindentation. Nanoindentation is an experimental technique that provides access to elastic properties of materials. The technique can in principle be used at any lengthscale; the development in measuring techniques over the recent decades allows for standard indentation testing in the sub-nanometre resolution. The use of nanoindentation for the characterisation of the elastic properties of materials at the nanoscale is ample; this can be deduced from the number of citations of the early pioneering work on nanoindentation [⁹⁷]. Also, there is a very large number of publications (e.g. [⁹⁸]) that utilise the statistical (grid) indentation for assessment of material properties of individual phases in hardened cement pastes. Based on the results of nanomechanical testing, the nanogranular nature of calcium-silicate-hydrates [⁹⁹] is deduced. Recently, publications that shed some doubt on the applicability of statistical nanoindentation testing appeared in the peer-reviewed literature [¹⁰⁰] and a critical examination of the technique has been called for [¹⁰¹].

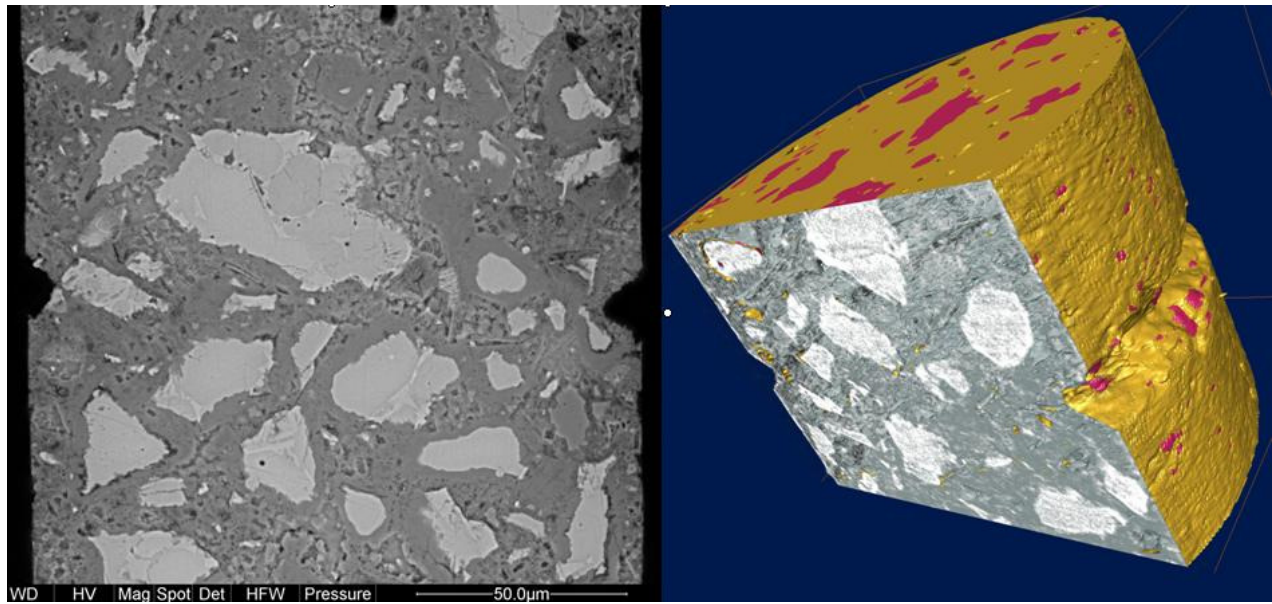


Figure 4.6 – (left) SEM image showing a cross-section of a cylindrical microspecimen of hardened Portland cement paste. Note the laser ablation sites on the sides of the specimen, (right) 3D rendering of the microspecimen shown left based on synchrotron microtomography SRμCT experiment. The size of the specimen is 150 μm in diameter (both images from [104])

Alternative approaches towards testing of mechanical properties on nanoscale include a large dynamic range nanomechanical mapping using tapping-mode atomic force microscopy [¹⁰²]. Another approach is to downscale by several orders of magnitude the standard mechanical testing applied on the macroscale.

The mechanical testing on such lengthscales [¹⁰³] poses some challenges (e.g., sample preparation [¹⁰⁴], etc.). However, it may provide interesting information about particle-particle interactions [¹⁰⁵].

4.6. Conclusions

- Characterisation techniques are necessary tools for understanding the structure-property relationships of any material. Nanotechnology proves useful as an enabling technology for the assessment of moisture sensitive materials, such as cement-based materials.
- As shown in previous chapters, the use of nanomaterials (such as engineered nanoparticles) is envisaged in the future for the cementitious materials and therefore the

characterisation techniques of relevant resolution will be required for assessment of the influence of their utilisation on the properties of the resulting material.

- Novel nanotechnology-based WETSEM technology is foreseen to prove useful for the in-situ electron microscopy observation of very early hydration process.
- Cryo-TEM techniques are foreseen to provide information on the mesostructure of calcium silicate hydrates.
- Porosity plays an important role in durability of cement-based materials. 3D imaging of relevant resolution is necessary for assessment of connectivity of material porosity of cement based materials.
- Focussed ion beam techniques (FIB-nt) provide high resolution tools for 3D imaging of porosity (and other materials phases) of cementitious materials. The disadvantage of the technique is that it is a locally destructive technique that therefore does not permit the observation of dynamic processes.
- The direct observation of processes occurring in cement paste in 4D with high enough resolution (such as in synchrotron-based nanotomography) has a potential to bring much better understanding of durability-related issues in cementitious materials.

5. Environmental, health, safety/sustainability (EHS) and regulatory issues of engineered nanoparticles in the cement industry

The increasing use of engineered nanoparticles (ENP) in products has raised certain concerns over their safety to human health and the environment [¹⁰⁶, ¹⁰⁷, ¹⁰⁸, ¹⁰⁹, ¹¹⁰, ¹¹¹]. In the preceding chapters the potential benefits of engineered nanoparticles in the cement industry are well illustrated.

Nanoparticles	Function	Morphology	Examples of applications
Silver (Ag)	<ul style="list-style-type: none"> Antimicrobial (Silver ions (Ag⁺)) 	<ul style="list-style-type: none"> Spherical nanoparticles (different shapes, polyhedral) Coatings 	Textiles
Zinc oxide (ZnO)	<ul style="list-style-type: none"> UV-protection, antimicrobial (photocatalytic), Self-cleaning/water- and dirt-repellent (nanoscale surface structure), Abrasion resistance 	<ul style="list-style-type: none"> Spherical nanoparticles* Nanorods and nanowires (nanorings, (c) nanospirals, and (d) nanohelices (Wang 2004), Single-crystalline, polyhedral cages and shells of ZnO.(Wang 2004) 	Façade coatings,
Silicium oxide (SiO ₂)	<ul style="list-style-type: none"> Self-cleaning/water- and dirt-repellent (nanoscale surface structure), Abrasion resistance Carrier of agents, 	<ul style="list-style-type: none"> spherical nanoparticles* Xero-Gel- coatings (different porosities) amorphous crystalline (for electronics only) 	Nanosilica additive in concrete,
Titaniumdioxide (TiO ₂)	<ul style="list-style-type: none"> photocatalytic (antimicrobial, self-cleaning) UV-protection (UV-Absorption) (photocatalytic), water- and dirt-repellent (nanoscale surface structure), Abrasion resistance 	<ul style="list-style-type: none"> spherical nanoparticles* nanorods Xero-Gel_coating (different porosities), amorphous crystalline (anatase or rutile) 	TiO ₂ - anatase in façade coatings TioCem
Layered silica („nanoclays“, e.g. montmorillonite) Al ₂ [(OH) ₂ /Si ₄ O ₁₀]•nH ₂ O	<ul style="list-style-type: none"> Flame retardancy, Abrasion resistance Carrier of agents 	Nanoplates	Flame retarding glass coatings
Carbonnanotubes (CNT)	<ul style="list-style-type: none"> Crack Hindrance (Lee et al. 2009) partly flame retardant (thermal conductivity), abrasions resistance Electric conductivity 	<ul style="list-style-type: none"> Single wall, multi wall , flexible, stiff, entangled purified/containing impurities such as catalysators 	Nanoreinforcement of cement and concrete

Table 5.1 : Engineered nanoparticles (ENP) may have different functions and morphologies for cement, concrete, façade coating and other applications [¹¹², ¹¹³]. The authors make no claim to be complete.

In this chapter we aim to give an overview of the state of knowledge and the knowledge gaps regarding the risks of engineered nanoparticles for the environment, human health, safety and sustainability (EHS). The focus lays on engineered nanoparticles that are of interest for cement, concrete applications and coating systems: silver (Ag), zinc oxide (ZnO), silicium dioxide (SiO₂), titanium dioxide (TiO₂), layered silica (“nanoclays”) and carbon nanotubes (CNT) (Table 5.1 or in the chapter 2.6.). Ultrafine particles, that origin unintendedly from combustion or abrasion processes, are not part of this chapter.

The risk is determined by the potential hazard of a material and by the exposure to the material.

$\text{Risk} = \text{Hazard} \times \text{Exposure}$
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Hazard identification

Engineered nanoparticles (ENP)¹ are defined to have one, two or three external dimensions in the nanoscale (approximately 1 nm to 100 nm). But physicochemical properties of particles may also change below 1 nm or above 100 nm. Biological nanospecific effects were observed also with particles sizes in the scale of 100 to 500 nm and below 1 nm. Thus, the Federal Office for Public Health (FOEN) proposes an upper limit of 500 nm for the identification of nanospecific risks in handling engineered nanoparticles in the industry [¹¹⁴].

The new and fascinating properties of ENP base on the relatively high surface area to volume ratio compared to bulk materials and on the quantum size effects [¹¹⁵]. The large specific surface causes the high reactivity of ENP compared to bulk materials. These new properties mean on one hand a high potential of ENP for innovation. On the other hand, they cause different interactions of ENP with biological organisms and different behaviour of ENP in environmental compartments (water, soil, air) and technical systems (e.g. waste water treatment facilities) compared to bulk materials.

¹ Caused by the novelty and the high interdisciplinarity of the field of nanotechnologies the term “engineered nanoparticles (ENP)” is not used in a uniform manner. The International Organization for Standardization (ISO 2008) proposes the collective term „nano-objects“ instead of the term “nanoparticles” for discrete entities with one (“nanoplate”), two (“nanofibre”) or three (“nanoparticle”) external dimensions in the nanoscale (approximately 1 nm to 100 nm). Thus, according to ISO the term “nanoparticle” is valid for discrete entities with all three similar external dimensions in the nanoscale only. Consequently according to the ISO Definition “nanoplates” and “nanofibres” are “nano-objects” and not “nanoparticles”. Nevertheless, we will use the term “nanoparticle (ENP)” as collective term for all forms of discrete entities in this chapter because the term “nano-object” is not widely recognised.

The nanoscale size allows the ENP to overcome biological barriers such as cell membranes and the blood-brain barrier [¹¹⁶]. Pristine (i.e. not functionalized) ENP tend to agglomerate to larger particles - so called secondary particles. These secondary particles may not overcome these barriers anymore. However, the agglomeration of ENP may not be persistent in some biological or environmental compartments and the secondary particles may de-agglomerate. Functionalized or deagglomerated ENP in particular may stay at nanoscale for long time and thus overcome biological barriers. Additionally, nanoscale particles may interact with biological structures of similar size (e.g. DNA, proteins) [¹¹⁷].

The solubility of ENPs (especially metal or metal oxide such as ZnO and Ag) under environmental or physiological conditions is another important property and is not systematically investigated yet. ENPs may be taken up by cells, whereas dissolved ENPs (i.e. ions) are repelled by plasma membranes. Thus, one could argue that soluble ENPs are not a problem. However, “since dissolution kinetics is frequently proportional to the surface area, nanomaterials are likely to dissolve much more rapidly than larger sized materials” (from [¹¹⁸]). Therefore, soluble ENPs may dissolve in locally high concentration of ions and thus may cause hazard.

Due to the high reactivity of ENP they may change their physicochemical properties as soon as they get in contact with organisms, environmental compartments or technical systems. Biological and chemical processes in environmental compartments may change the ENP surface and therefore influence the agglomeration/disagglomeration behaviour of the ENP and the uptake pathways in organisms. Furthermore, ENP may interact with materials in the product matrix and change their properties unexpectedly (e.g. ageing processes).

As was pointed out in the Chapter 2.2.1, it is expensive to produce uniform ENP of high purity. Therefore, we assume that in many products ENP of a wide size distribution and with impurities (e.g. crystallization nuclei) are used. In the chapter 2.2.3, it is assumed that for applications in cement and concrete, cost-effective material may be sufficient. In these applications particle properties such as uniform size, uniform shapes and purities seem to be of secondary importance. The size of ENP and the impurities are relevant factors for the risk assessment. These factors may determine the potential uptake pathways in organisms, the interaction with biological structures and the behaviour of the ENP in environmental compartments.

The fascinating physicochemical properties of ENP cannot be transferred to a product of high quality and functionality by simply embedding them into the product material. It is a challenge to integrate the ENP homogeneously and stably regarding their position into the product matrix [^{113,119}]. Thus, the functionalization of ENP, i.e. the modification on the surface of nanoparticles,

is a key. It is expected that the majority of ENP applied in high quality products will be functionalized. The variety of functionalization is not limited (see e.g. chapter “Core-shell nanoparticles”). Functionalized ENP display different physicochemical properties and thus may behave differently in organisms or in environmental compartments compared to pristine (i.e. not functionalized) ENP. Probably, the functionalized surface of ENP is more relevant than the ENP itself regarding the effects of ENP on EHS issues.

To summarize, ENP such as Ag, ZnO, SiO₂, TiO₂, “nanoclays” and CNT are not uniform groups of particles but rather differ in size, morphology, functionalization, purity and additionally in their crystallinity and porosity [¹²⁰, ¹²¹, ¹²²]. ZnO and CNT enfold especially heterogeneous groups of ENP (see Table 5.1).

In the majority of the toxicological, ecotoxicological and environmental fate studies only pristine ENP are investigated. Acute toxic effects have been observed often only with unrealistic high concentration of ENP. Chronic toxic effects have not been investigated in many studies. The methods to investigate the potential hazards are not standardized yet and thus the quality of the studies is variable. BMU [¹²³] defined minimal criteria for toxicological studies in order to produce valuable results. The following rough assessment on the ENP is mainly based on studies that comply with most of these criteria and on today’s state of knowledge and has to become adjusted to upcoming knowledge (for more detailed information please see report on www.empa.ch/nanosafetextiles):

- **Health:** Based on studies of acute toxicological effects, nanoscale pristine Ag, TiO₂ and amorphous SiO₂ seem to be rather harmless. This assessment is supported by experiences with bulk TiO₂ and SiO₂ as additives in the food sector. However, there is uncertainty concerning chronic effects of nanoscale Ag, TiO₂ and amorphous SiO₂ and health effects of their functionalized derivatives. For montmorillonite no studies are available. CNT are difficult to assess based on their high variability and impurities. Poland et al. [¹²⁴] demonstrated that CNT’s asbestos-like pathogenic behaviour “conforms to a structure-activity relationship based on length, to which asbestos and other pathogenic fibres conform”. Thus, stiff and long multiwalled CNT may cause similar effects as asbestos. Nanoscale ZnO seem to have an effect on biological systems; they may penetrate tissue barriers and there is some evidence for DNA damage. Nevertheless, these effects occur only in relatively high concentrations and nanoscale ZnO seems harmless compared to nanoscale particles of cigarette smoke.

- **Environment:** Nanoscale SiO₂ , montmorillonite, CNT seem to be rather harmless, whereas Ag and ZnO might be comparatively harmful based on their solubility and the negative effects on organisms of their ions. In several studies about TiO₂, effects were observed in relatively low concentration, whereas these effects are relatively weak compared to approved pesticides in Switzerland.

To sum up, the high variety of ENP regarding their physicochemical properties and the high reactivity of ENP complicate the hazard assessment. Thus, the current risk assessment report of SCENHIR [118] concludes: “As there is not yet a generally applicable paradigm for nanomaterial hazard identification, a case by case approach for the risk assessment of nanomaterials is warranted.” Consequently, for hazard assessment, each specific size, morphology and functionalization of ENP must be investigated.

Exposure Assessment

The hazard assessments in the antecedent chapter have to be adjusted not only to upcoming knowledge of environmental and health effects of ENP, but also to the amount of applied ENP for future nanoproducts and their specific life cycle. Mueller and Nowack [125] modelled the quantities of nanoscale Ag, TiO₂ and CNT released into the environment. The life-cycle of the nanoproducts formed the basis for assessing the mass flows of the ENP based on the present estimated worldwide production volume of the respective ENP. The results of this study suggest further detailed studies of nanoscale TiO₂.

The life cycle of a product defines exposure scenarios, i.e. during what life stages of a product ENP may be unintendedly released, in what forms, in what amount and in what compartments (air, water, soil). The ENP may be handled and added to the production process and integrated in the products as nanopowders, suspended in air (aerosols), suspended in liquid (colloids) and embedded in solids or generated in situ. Depending on exterior impacts during the life cycle the ENPs may get released from nanoproducts as:

- free ENP;
- agglomerated ENP;
- ENP partially or totally embedded in nanoscale or micro-sized matrix material.

Currently, it is assumed that the uptake of ENP by the respiratory tract is the most critical one. Healthy skin seems to be a good barrier for nanoscale TiO₂ [126]. Little is known for the uptake behaviour and fate of ENP in the gastrointestinal tract [127].

Up to now, experimental data on the unintended release of ENP during production, use or disposal of nanoproducts are very scarce and there are no standardized methods. First measurements done at companies producing ENP indicate that worker exposure may occur, during production and handling of dry powders mainly [128, 129, 130, 131, 132]. However, compared to the occurrence of ambient ultrafine particles (< 100 nm) at workplaces [133], total particle number concentrations of ENP seem to be significantly lower. Vorbau et al. [134], in an initial study, did not detect significant release of ENP during abrasion of ZnO-containing coatings and most of the ENP were still embedded in larger particles. Nguyen et al. [135] showed that epoxy matrix containing CNT undergoes photo-degradation resulting in a concentration increase of CNT on the nanocomposite surface. Ag released in ionic form was considered to be the major process of its release from plastics and textiles [136]. However, Benn and Westerhoff [137] found that nanoscale Ag can also be released from textiles containing nanoscale Ag during washing. Kaegi et al. [138] observed engineered nanoscale TiO₂ in surface water and traced the origin of the particles to leaching from façades that had been treated with nanoscale TiO₂ containing paint. Electron microscopy of the façades and the released particles showed that they were still partially embedded in the organic binder but that also many single particles were observed from aged façades. It is probable that an appropriate design of the nanoproduct may minimize the unintended release of ENP [113], e.g. by fixing ENP to the matrix material.

Safety

For safety reasons it is recommended to avoid the exposure to nanopowders and aerosols for workers and for consumers or to take appropriate measures for protection during the production process [139]. One relevant property of ENP is the dustiness (i.e. respirable fraction). The dustiness of ENP does rather depend on their size, morphology and their functionalization than on the class of ENP. From the view of consumer safety, it is of advantage to provide products with a minimal unintended release of ENP. In most cases the prevention of unintended release of ENP, by an appropriate product design, implies a high product quality and a long lasting functionality of the product. Thus, safety equals high product quality.

Sustainability

The “S” in “EHS” could also stand for “Sustainability”. Apart from improved performance and new functionalities nanotechnologies may offer a reduction in the use of hazardous chemical substances, in the consumption of energy and materials, and in the generation of waste. There is also some scepticism over whether these benefits can actually be achieved [¹⁴⁰]. However, the application of life cycle concepts such as the life cycle assessment (LCA) may help to understand the potential risks and benefits of the use of ENP in the respective product. Additionally, aspects such as recyclability, potential cross-product contamination and disposal problems may be revealed and handled at an early stage of the innovation process and thus companies can avoid misguided investments and gain a competitive advantage in the marketplace.

Regulation

Although there is no nanospecific regulation yet, ENP are included in the protection targets of many laws in Switzerland (chemical law, environmental protection law, food law). Future nanospecific regulation will probably orientate towards to the European legislation (complemented REACH, European cosmetic and food directives). In case a product is merchandized in Switzerland as antimicrobial, the use of nanoscale Ag is managed by the “„Verordnung über das in Verkehrbringen von und den Umgang mit Biozidprodukten“ (VBP, SR 813.12). Also in the USA these products have to be registered to the Environmental Protection Agency (EPA). The EPA also has announced that companies which import and use CNT are obliged to apply for an approval by the EPA in future [¹⁴¹]. CNT are already classified as new substance under the Toxic Substance Control Act (TCSA) since July 2007. More nanospecific actions are announced under <http://www.nanolawreport.com/tags/alumina/>. In Switzerland the uncertainties of risk assessment and regulation should be mitigated by the precautionary matrix for synthetic nanomaterials. This matrix was elaborated by the Federal Office for Public Health (FOPH) and the Federal Office for the Environment (FOEN) in co-operation with Swiss industry and science. The precautionary matrix enables trade and industry to adopt a structured approach to recognising the possible risks in dealing with synthetic nanomaterials [¹¹⁴].

6. Proposals for future work and conclusions

Based on the reasoning provided in the above chapters, we would like to propose the following directions for future research work and of application domains.

The following nano-research domains were identified as the ones worth following up in the future.

(i) Core-shell cement particles

As was shown in Chapter 2, cementitious materials based on Portland cement (and in particular those materials that utilise low water cement ratios), partially derive their superior properties from the fact that a relatively large portion of the original volume of the cement particles remains unhydrated. These residues of unhydrated cementitious materials represent material that had undergone the very energy-demanding process of cement production. As the energy demanding process can be easily translated into production of CO₂ emissions, there is a scope for savings in them.

The principal idea therefore is to attempt to produce cement particles whose shell is produced from Portland cement, while its core is produced from material whose production is far less energy-demanding.

Clearly, the choice of the materials for both the core and the shell offers manifold combinations for design of such (micro/nano-)engineered particles. Flame spray and sol-gel techniques were identified as possible methods for production of such cement core-shell particles.

The core-shell cement particles produced with hard cores may first find the application domains in high-performance (high strength) concretes and cementitious materials, in which rather low water-to-cement-ratios are utilised and therefore currently exhibit relatively low degree of hydration.

The particles with soft cores (with a special case of hollow core) may find the earliest application in production of ‘light-weight cements’ these might be used for light-weight applications, such as in thin-walled claddings panels, or in other types of thin walled structures).

From the perspective of cement producers, production of cements made of engineered core-shell particles (not necessarily only nanoscale in size) was identified as one of future promising domains, with applications ranging from light-weight cements for light-weight concrete applications, cements of tailored properties, etc. However, it should be also mentioned here that regarding the light-weight concretes, also the properties of other constituents (LWAs, fillers) should be tailored in parallel.

Sol-gel techniques and flame spray synthesis techniques were identified as possible methods for production such cements. The authors suggest to attempt for a production of core-shell cement particles as a proof-of-the-concept investigation in the future.

(ii) 3D-characterisation techniques

High-resolution imaging is a truly important technique for understanding the properties of the materials of complex micro/nano-structure. Material properties (such as mechanical and transport ones) can be derived from 3D images by means of ‘virtual experimental techniques’.

3D imaging of materials is particularly necessary in the case of the disordered materials of complex microstructures (in particular with non-periodic, non convex and asymmetric microstructures) are to be investigated and characterised. Such material microstructures can appear significantly different in 2D than in three dimensions and therefore incorrect conclusions might be reached. Microstructures appearing in materials based on hydraulic cements fit into this category. Above that, non-invasive testing techniques for temporal observation of hydration/degradation processes are necessary. We are currently experiencing an onset of availability of such experimental techniques with lengthscale and timescale resolution relevant for materials based on hydraulic cements. One of the major issues connected with the high-resolution imaging, and hence with the properties derived from the virtual testing, is the question of representativity of the image volume with respect to the material properties of the material on macroscale. We suggest that this question should be addressed by the future research work.

From the materials point of view, the authors identified that the admixing of nanoobjects (such as nanosilica, nanotitania, nanoalumina, carbon nanotubes) and admixing them into concrete is likely to be of increasing trend in the future, even though such applications should not – in the opinion of

authors of this report – be called ‘nanotechnology’. Cementitious materials, such as hardened cement pastes, mortars and concretes are disordered materials with porosity and other (micro)-structural features spanning several lengthscales. For understanding the structure-properties relationships of such materials, the characterisation techniques (FIB-nt, SRnCT) that provide high-resolution 3D information about the nature of such materials are required. Such techniques can provide valuable information about properties (for example about connectivity the nanoscale porosity – please refer to *cemsuisse* project on Porosity/Permeability) of the cementitious materials and are hence very relevant for understanding the durability of these materials.

(iii) Other possible routes and technologies

Nanotechnology applications aside from the use in advanced cementitious materials cannot be neglected altogether. Even though the likelihood of nanotechnology to revolutionize all of building materials and cement products form just part of the building materials scope, there are a few fields of activity which deserve special attention. In the authors opinion, those fields will continue to be of growing importance to certain industry branches. Current and future research projects on the following topics are likely to bear fruit in the near future:

- TiO₂ photocatalytic materials: A number of products are currently available. Over time there will be an increasing product variety with more and more specialized applications (indoor, outdoor, pavement, façade, window coatings etc.).
- Smart window and façade coatings: The next leap in building and construction is going to be the implementation of smart functional coatings and multilayer systems for facades and glazing surfaces. The use of thin film nanotechnology for this purpose will enable the development of an almost infinite number of new products with tailored properties: Such are for example anti-graffiti, anti-fouling, non-wetting (superhydrophobic), superhydrophilic, coloured and colour changing, light absorbing (for photovoltaics, and hydrogen generation via water splitting), light emitting, and other optical properties. Sol-gel technology as a platform for coating preparation offers a variety of advantages over alternative methods. The fraction of products based on sol-gel based technologies is expected to increase over the coming years

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